Adsorption/Desorption Characteristics of Phosphate Ion onto Calcined Boehmite Surface

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Boehmite (aluminum oxyhydroxide, BE) selectively adsorbs phosphate ion. Recently, we studied the recovery efficiency of phosphate ion and the adsorption/desorption mechanism by calcining the BE surface in the temperature range of 200~1150°C. As a result, the amount of phosphate ion adsorbed/desorbed by BE at a calcining temperature of 400~700°C exhibited a higher value than the BE at other calcining temperatures, and the recovery efficiency of the phosphate ion was 90% or higher. On the other hand, the amount of phosphate ion adsorbed/desorbed onto BE at a calcining temperature of 1100°C or higher exhibited a lower value than the BE before calcining. Based on the phosphate ion adsorption/desorption behavior results, and the XRD and FT-IR results, it was determined that when the calcined BE is suspended in water, water molecules are dissociated, producing hydroxyl groups on the surface, and these hydroxyl groups exchange ions with the phosphate ion, thus the amount of phosphate adsorbed ion reaches a maximum. The phosphate ion adsorbed by BE was adsorbed by a sodium hydroxide solution, just like the BE before calcination. It became evident that by calcining BE, it is possible to obtain an adsorbent with a high phosphate ion recovery efficiency.

Keywords: Adsorption isotherms; Phosphorus; Aluminum oxide

I. INTRODUCTION

Since 1998, large-scale red tides have occurred in the Ariake Sea, causing color-fading damage to laver. The cause of this is said to be the influx of large volumes of nutritive salts from the rivers [1]. Eutrophication causes the occurrence of the red tides in closed sea areas such as the Seto Inland Sea, and of water blooms in lakes and marshes. The main factors involved in the eutrophication are nitrogen and phosphorus. In particular, it has been reported that algae will grow at a concentration of 0.03 mg/L [2].

On the other hand, there are no phosphorus resources in Japan, and at present, it is being 100% imported. Also, the global reserves of phosphate rock are 14 billion tons, and there is a possibility that these will be depleted by 2035 [3]. In the last few years, the price of phosphate rock has steadily risen, and may be a few times higher in the future.

In this way, Japan is importing expensive phosphate rock, and scattering it in large volumes onto the soil for agricultural purposes. This causes environmental destruction due to eutrophication, and therefore, large amounts of money are spent on treatment to remove the phosphorus. The recovery of phosphorus will prevent resource depletion, and is also important to prevent eutrophication. The coagulating sedimentation method and MAP method have been reported as methods of phosphorus recovery, but these are effective only for the recovery of phosphorus in a high concentration.

It has been previously shown that boehmite (aluminum oxyhydroxide, BE) selectively adsorbs phosphate ion and has a high adsorption ability [4]. Furthermore, when BE, which contains adsorbed phosphate ion is treated with alkali solution, the phosphate ion easily desorbs, and 50 cycles of continuous phosphate ion adsorption/desorption can be achieved with BE [5]. However, it is known that the amount desorbed onto BE is two-thirds the amount adsorbed, and one-third of the phosphate ion remains in the BE [5]. The adsorption ability of phosphate ion by BE has been increased by sulfuric acid treatment of the BE surface [6], but desorption ability has not been studied.

In this study, we used BE, which was calcined at 100~1150°C, and studied the adsorption ability/desorption ability of the phosphate ion. We evaluated the material’s performance as an adsorbent of phosphate ion based on the results of SEM, FT-IR, TG-DTA, saturation adsorption amount, amount desorbed, and specific surface area.

II. EXPERIMENTAL

A. Materials

For the BE, we used AD220NS (Tomita Pharmaceutical, Japan). For the BE, we placed non-crystalline aluminum oxyhydroxide in an aqueous media, and after heat treatment for 1~3 hours at 90~100°C, spray dried the obtained aluminum oxyhydroxide. For the differential thermal analysis, we used the DTG-60AH differential thermal analysis and thermogravimetry simultaneous measuring instrument (Shimazu, Japan). For photography with an electron microscope, we used the JSM-5500LV (JEOL,
**AD220NS**

- $\text{Al}_2\text{O}_3$ : 69.5%
- Loss of Drying: 7.8%
- Chloride : 0.1%
- Sulfate : 0.8%
- Alkalinity : pH8.2
- Specific Area : 297 m$^2$/g
- Chemical Formula: AlOOH 0.3H$_2$O

**B. Calcination of BE**

For the calcination treatment, 20 g of BE was placed in a porcelain crucible, and kept at 200 $\sim$ 1150 $^\circ$C for 2 hours in a muffle furnace.

**C. Phosphate ion adsorption/desorption isotherms**

BE (0.2 g) was added to 20 mL of a Na$_2$HPO$_4$ aqueous solution at a concentration of 1060 $\sim$ 132 mg-PO$_4$/L, and after shaking for 15 hours at 25$^\circ$C, the solution was filtered through a 0.1 $\mu$m membrane filter, and the concentration of phosphate ion was then measured. The concentration of phosphate ion adsorbed by the BE was calculated using $q = V(C_0 - C_e)/W_s$, where $q$ is the amount adsorbed (mg-PO$_4$/g), $W_s$ is the amount of aluminum oxyhydroxide (g), $C_0$ is the initial concentration of phosphate ion (mg-PO$_4$/L), $C_e$ is the equilibrium concentration (mg-PO$_4$/L), and $V$ is the amount of sample fluid (L). In the adsorption experiment, BE was recovered, and after drying for 12 hours at 110$^\circ$C, 0.08 g of BE (weight of adsorbed phosphate ion + weight of BE) was added to 20 mL of a 5 mM NaOH aqueous solution, and after shaking for 15 hours at 25$^\circ$C, it was filtered through a 0.1 $\mu$m membrane filter, and then the phosphate ion concentration was measured. The amount of phosphate ion desorbed was calculated from the equilibrium concentration after desorption.

**D. Recovery efficiency of phosphate ion using BE**

For the saturated amount adsorbed, 1.0 g of BE was added to 100 mL of a Na$_2$HPO$_4$ aqueous solution at a concentration of 4625 mg-PO$_4$/L, and after shaking for 15 hours at 25$^\circ$C, it was filtered through a 0.1 $\mu$m membrane filter, and the phosphate ion concentration was measured. For the amount desorbed, on the other hand, BE was recovered in the adsorption experiment, and after drying for 12 hours at 110$^\circ$C, 0.7 g of BE (weight of adsorbed phosphate ion + weight of BE) was added to 100 mL of a 5 mM NaOH aqueous solution, and after shaking for 15 hours at 25$^\circ$C, it was filtered through a 0.1 $\mu$m membrane filter. The phosphate ion concentration was then measured. We reported that the adsorption of phosphate ions onto BE became the equilibrium adsorption after 2 hours [4]. The recovery rate of phosphate ion was calculated from the value obtained by dividing the amount desorbed by the saturated amount adsorbed.

**III. RESULTS AND DISCUSSION**

**A. Properties of calcined BE**

The properties of BE and the results of the differential thermal analysis are shown in Fig. 1 and Fig. 2, respectively. It was determined from the X-ray diffraction analysis results that almost all the structural water is lost due to dehydration when the calcining temperature is 500$^\circ$C or higher. The XRD results of the calcined BE are shown in Fig. 3. As a result, it was determined that BE with a calcining temperature of 200 or 300$^\circ$C has a boehmite structure, but in BE with a calcining temperature of 400$^\circ$C or higher, the boehmite structure is destroyed and aluminum oxide is...
produced. It was found that, as the calcining temperature increases, the aluminum oxide goes through the following transitions: $\beta$-type $\rightarrow$ $\eta$-type $\rightarrow$ $\gamma$-type $\rightarrow$ $\delta$-type $\rightarrow$ $\Theta$-type and finally becomes the stable $\alpha$-type. These crystal system changes were almost the same as the commonly mentioned results due to the calcining of aluminum oxide [7].

Figure 4 shows an SEM photograph of BE. The results showed no evidence of collapse of the BE particles due to gas produced by the thermal decomposition during calcination. Figure 5 shows the relationship between the calcining temperature and the values for the specific surface area. As a result, it was found that the specific surface area of BE decreases as the calcining temperature increases.

B. Adsorption/desorption isotherms of phosphate ion

Figure 6 shows the results for the adsorption isotherm for phosphate ion adsorbed by the BE. As a result, the adsorption of phosphate ion by the BE at the calcining temperatures of $1000^\circ\text{C}$ or less was greater than the amount
adsorbed by the BE prior to calcination. Despite the fact that the specific surface area of BE drops as the calcining temperature increases, the phosphate ion adsorption amount is higher than that of BE before calcination when the calcining temperature is 1000°C or less. Based on these results, it was determined that the adsorption of phosphate ion does not depend on the specific surface area of the BE.

BE with a calcining temperature of 400∼700°C adsorbs the greatest amount of phosphate ion, and the adsorption of phosphate ion by the BE at a calcining temperature of 1100°C or higher was less than that of the BE before the calcination. In light of the XRD results, this is postulated that the calcination has changed the BE into the stable α-type aluminum oxide.

Figure 7 shows the desorption isotherm of phosphate ion onto the BE. The desorption isotherms were measured from the amount of phosphate ion eluted from the BE after the adsorption of the phosphate ion in a NaOH aqueous solution. The results are almost the same as the adsorption isotherm case. On the other hand, the amount of phosphate ion desorbed from the BE at a calcining temperature of 1000°C or less was greater than that of the BE before calcination. On the other hand, the amount of phosphate ion desorbed by the BE at a calcining temperature of 1100°C or less was less than the amount of desorption of the BE before calcination. This is thought to be due to the fact that adsorbed phosphate ion desorbs more easily if the calcining temperature is 1000°C or less, but if the calcining temperature is 1100°C or higher, it is difficult for the adsorbed phosphate ion to desorb, and this suggested that the state of the phosphate ion adsorption sites differs depending on the calcining temperature.

C. Recovery efficiency of phosphate ion due to BE

The saturated amount adsorbed and the amount of phosphate ion desorbed by the BE were measured, and are shown in Fig. 8. For the saturated amount adsorbed, 1.0 g of BE was added to 100 ml of a Na2HPO4 aqueous solution at a concentration of 4625 mg-PO4/L and the concentration of phosphate ion was then measured. For the amount desorbed, on the other hand, BE was recovered in the adsorption experiment, 0.7 g of BE (weight of adsorbed phosphate ion + weight of BE) was added to 100 mL of a 5 mM NaOH aqueous solution and the concentration of the phosphate ion was measured. The recovery rate of the phosphate ion was calculated from the value obtained by dividing the amount desorbed by the saturated amount adsorbed. As a result, the saturated amount adsorbed by the BE at a calcining temperature of
400~1000°C exhibited a higher value than the BE before calcination. We can infer that this result is due to the fact that BE with a calcining temperature of 400~1000°C is in a transitional state to aluminum oxide, so there was an increase in comparison with the amount adsorbed/desorbed by the BE before calcination. The amount desorbed also exhibited the same tendency. On the other hand, BE at a calcining temperature of 1100°C is the α-type aluminum oxide, and thus it is thought that there was a reduction in comparison with the amount adsorbed/desorbed by the BE before calcination.

Table 1 shows the efficient recovery of phosphate ion using BE. As a result, the recovery efficiency of the phosphate ion is 90% or higher for the BE at a calcining temperature of 400~700°C, and the exhibited value was higher than that for BE at the other calcining temperatures. The recovery efficiency of the phosphate ion is 62~66% for BE before calcining, or for BE at a calcining temperature of 200 or 1150°C. It was determined that about one-third of the phosphate ion adsorbed due to the 5 mM NaOH aqueous solution treatment could not be desorbed.

D. Mechanism of phosphate adsorption onto BE

The FT-IR results of the calcined BE are shown in Fig. 9. The IR results of the BE have been reported by Wickersheim, et al. [8] and Peric, et al. [9]. The FT-IR results of the BE calcined for this study indicate that BE with a calcining temperature of 200 or 300°C has the features of boehmite, while the features of boehmite could not be confirmed in the BE at a calcining temperature of 400°C. Weller [10] and Peri [11] have reported that water molecules dissociate and adsorb into aluminum oxide. In order to clarify the dissociation and adsorption of water molecules into the BE, the calcined BE was suspended in purified water, and after agitating for 3 hours, the BE was naturally dried for 12 hours at room temperature. Fig. 10 shows the FT-IR results on this BE. In these results, the spectrum of boehmite was only evident in BE at a calcining temperature of 1000°C or less. This is thought to be due to fact that the BE at a calcining temperature of 1000°C or less reacts with water molecules, and hydroxyl groups are produced just as with boehmite.

Figure 11 shows the changes in the pH of the aqueous solution during the adsorption of phosphate ion by the calcined BE. As a result, the pH rose after the adsorption compared to the pH of the aqueous solution before adsorption. This result shows that during the phosphate ion adsorption by the calcined BE, hydroxyl groups on the BE surface exchange ions with phosphate, just as in the adsorption by the BE before calcination. The aqueous solution pH values and FT-IR results suggest, as a mechanism of the phosphate ion adsorption by the calcined BE, that hydroxyl groups are first formed due to the reaction between the BE and water molecules, and next the hydroxyl groups exchange ions with the phosphate ion. Furthermore, the phosphate ion adsorbed by the calcined BE is desorbed due to treatment with the NaOH aqueous

| Temperature (°C) | 0   | 200 | 300 | 400 | 500 | 600 | 700 | 800 | 900 | 1000 | 1100 | 1150 |
|-----------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|------|------|------|
| Recovery (%)    | 66.3| 61.6| 85.7| 93.5| 103 | 91.3| 95.9| 77.9| 106.8| 73.5 | 82.5 | 66.2 |

FIG. 9: FT-IR of calcined BE.
solution, just as with the BE before calcining.

The desorption rate of phosphate ion by the BE at a calcining temperature of 400–700°C was 90% or higher, and therefore, it is evident that the affinity between the phosphate ion and the hydroxyl groups produced by the reaction between the calcined BE and water molecules is less than the affinity between the phosphate ion and hydroxyl groups of the BE before calcination. The pH value of the aqueous solution depends on the amount of phosphate ions adsorbed, and BE at a calcining temperature of 400–1000°C, which has a high amount of phosphate ion adsorbed, had a higher aqueous solution pH value. On the other hand, BE at a calcining temperature of 1100 or 1150°C has a reduced amount of adsorbed phosphate ion, and the pH value of the aqueous solution was also lower. For these reasons, it was determined that the adsorption mechanism of the phosphate ion by the BE was based on the ion exchange.

Figure 12 is a schematic diagram of the adsorption/desorption mechanism of phosphate ion by the calcined BE. When BE is calcined, the boehmite structure is destroyed, and it changes to BE having the structure of aluminum oxide. When this BE is suspended in purified water, the water molecules are dissociated, and hydroxyl groups are formed on the BE which has the structure of aluminum oxide. These hydroxyl groups exchange ions with the phosphate ion, and adsorb the phosphate ion. Thereafter, it is thought that the phosphate ion adsorbed by the BE exchange ions with OH due to treatment with the NaOH aqueous solution, and desorbs from the BE surface. BE also has hydroxyl groups on its surface, and thus can be reused as a phosphate ion adsorbent if it is treated with a NaOH aqueous solution. That is, it suggests that it can be repetitively used, just like BE before calcination, and phosphate ions can be recovered with a high efficiency. We have already applied BE to phosphate ions in sea water and the selectivity of the anion onto BE. Mostly anion species in sea water are chloride and sulfate ions. The selectivity of anion adsorption onto BE...
was in the order of chloride, nitrate, hydrogen carbonate, sulfate and phosphate. The selectivity adsorption ratio of nitrate, hydrogen carbonate, sulfate and phosphate to chloride is 1:8, 1:17, 1:28 and 1:7254, respectively [4].

IV. CONCLUSIONS

The specific surface area of BE decreases as the calcining temperature increases, but the phosphate ion amount adsorbed/desorbed does not depend on the specific surface area. When BE is calcined, it passes through the transition states of aluminum oxide, finally becoming the stable $\alpha$-type aluminum oxide. When the calcined BE is suspended in water, the water molecules dissociate and adsorb, and hydroxyl groups are produced on the BE surface. These hydroxyl groups act to adsorb the phosphate ions, and the phosphate ion is desorbed by treating with a NaOH aqueous solution. The recovery efficiency of phosphate ion using calcined BE is the highest for BE at a calcining temperature of 400–700°C, and the transition states of aluminum oxide due to calcination are thought to be ideal as BE for recovering phosphate ion. These results suggest that an adsorbent, which dissociates and adsorbs water molecules, and is suitable for the adsorption/desorption of phosphate ion, can be produced for the first time by the calcined BE.

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