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Adsorption behavior of phosphorus on synthetic boehmites

Yujiro Watanabe[1,4], Hirohisa Yamada[2], Takeshi Kasama[3]
Junzo Tanaka[4], Yu Komatsu[5], Yusuke Moriyoshi[1]

[1]Faculty of Engineering, Hosei University, 7-2-3 Kajinocho, Koganeishi, Tokyo 184-8584, Japan.
[2]Ecomaterial Center, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan.
[3]Institut fur Mineralogie Universitat Muenster, Muenster 24-D-48149, Germany.
[4]Biomaterials Center, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan.
[5]Faculty of Engineering, Kanazawa Institute of Technology, 7-1 Ohgigaoka, Nonoichi, Ishikawa, 921-8501, Japan.

Abstract

This study presented the basic research on the use of boehmite for the removal of phosphate from wastewater. Boehmites synthesized at 100, 150 and 200˚C were characterized by XRD, SEM and BET. Amounts of phosphate adsorbed on these boehmites in phosphoric acid solution of 0.1 to 3.0 mmol dm^{-3} were measured using ICP analysis. The boehmite synthesized at 100˚C showed the highest value of phosphate adsorption, which was 1.24 mmol/g. The results showed the phosphate adsorption was clearly dependent on the crystallinity and the surface area of boehmite.

1. Introduction

The increasing of phosphate in wastewater is one of the main factors of eutrophication and level causes increases in BOD (Biochemical Oxygen Demand) and COD (Chemical Oxygen Demand) in rivers and lakes. The amount of phosphate is now being controlled by legislation on discharge limits in many countries. The increase in phosphate Therefore, further processing to reduce the quantity of phosphate in wastewater is demanded.

The behaviors and mechanisms of phosphate sorption on soils and minerals have been investigated extensively by many workers (1-9). Especially, Al-OH bearing minerals such as boehmite and gibbsite have high phosphate capacity due to a small particle size, large surface area and exchange reaction involving surface OH groups. The study of phosphate sorption using the boehmite was reported by Bleam et al. (9). They showed that the maximum phosphate adsorption of boehmite synthesized at 170˚C for 8h was 1.8±0.3 mmol / m^2 in the pH range 4 to 3.

The synthesis and characterizations of boehmites have been carried out by a number of authors (10-11). Tettenhorst et al. (1980) indicated that the crystallinity of boehmite was increased with the increase of synthetic temperature from RT to 300˚C. They also showed that boehmite synthesized at lower temperature has lower crystallinity and a higher surface area than these synthesized at higher temperature. The boehmites with different crystallity and surface area would be expected to show the different adsorption behavior of phosphorus.

In the present study, the synthesis conditions of boehmite for optimum phosphorus adsorption were investigated in order to get better phosphorus absorbent in rivers and lakes.

2. Experimental procedures

Starting materials

Starting material was produced in the following way. 150 ml of 5 N NaOH solution added dropwise into a 300 ml beaker containing 50 ml of $AlCl_3$ solution over a period of 30 min. To remove remaining NaCl, the gelatinous precipitate was diluted immediately with 1500 ml of distilled water and filtered. The obtained gel was freeze-dried and used as starting material.

Synthesis of boehmites

The mixture 1.0 g of starting materials and 50.0 ml of distilled water were placed in 100ml content of Teflon cup fitted into a stainless steal pressure vessel and heated at 100, 150 and 200°C for 1 day. Obtained boehmites were centrifuged and freeze-dried. The products synthesized at 100, 150 and 200°C were expressed as B100, B150, B200, respectively.

All samples were characterized by the powder X-ray diffraction (XRD) apparatus with filtered CuKa radiation (RIGAKU RINT 2200). Undisturbed samples were examined with scanning electron microscope (SEM) (JEOL S-5500). Surface area was calculated by the BET method using N_2 adsorption data obtained by BATE4201 after removal of physical adsorbed water at 150°C for 3 hours.

Phosphate adsorption

Phosphate adsorption experiments were carried out by two experimental systems.

The initial concentration dependency for the adsorption was examined in the following way. 30.0 ml solutions containing different proportions of H_3PO_4 (3-90 ppm) were added to 0.1g of boehmites samples contained in stoppered polyethylene tubes. The tubes were shaken at 25˚C for 24 hours and then the solution were separated by centrifugation and filtration.

The pH dependency for the adsorption was investigated in the following way. 30.0 ml solutions containing different pH values of H_3PO_4 solution (60 ppm) adjusted to be 0.1 N $NaNO_3$ as background electrolyte were added to 0.1 g of boehmites samples contained in stoppered polyethylene tubes. The pH values were adjusted by adding a HNO_3 or NaOH. The tubes were shaken at 25˚C for 24 hours and then the solution were separated by centrifugation and filtration.

P and Al concentration of filtrated solution were determined by ICP analysis (SEIKO-SP4000). Adsorption amounts of P were calculated from the loss of P between separated solution and initial solution. The pH values were measured by pH meters (Toa Dempa Kogyo HM-60V). After the adsorption experiments, boehmites were examined by XRD to reconfirm the unchanged of boehmite structures.

3. Results and discussions

The characterization of boehmites

XRD patterns of boehmite are shown in Figure 1. It is clear that the crystallinity of the boehmite was improved with the increase of synthesis temperature, judging from the decrease of the full width at half maximum intensity (FWHM) of reflections. The FWHMs of (020) reflection were agreed with the literature by Tettenhorst et al (10). The morphology of boehmite was changed dependency on the synthetic temperature from amorphous-like shape (B100) to fine platy crystalline of nanometer in size (B200) (Fig. 2).

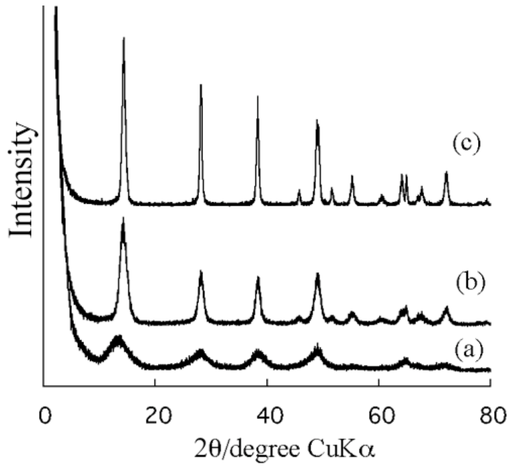

Figure 1. X-ray diffraction pattern of boehmites synthesized at (a) 100°C, (b) 150°C and (c) 200°C.

Surface area for the samples measured by the BET method, are given in Table 1. BET surface were decreased with the increase of crystallinity and synthesis temperature. It is reasonable that the increase of crystallite size, decreases the external surface of beohmite particle. B100 with lower crystallinity showed the highest value of 113.2 m^2 g^{-1}, but B200 with higher crystallinity showed the lowest value of 50.2 m^2 g^{-1}.

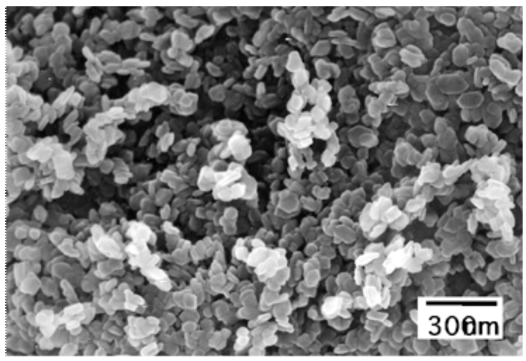
Figure 2. SEM image of boehmite synthesized at 200°C.

Table 1. Surface area of boehmites.

Synthetic temperature (℃)	Surface area (m^2/g)
100	113.2
150	65.2
200	50.2

P adsorption behavior

No change of crystallinity of boehmite and no impurity were observed by XRD method after P adsorption.

The leaching behavior of aluminium from boehmite was confirmed in solutions of different pH (Fig. 3). The leaching amount of aluminium decreased dramatically at around pH 3, and then the negligible amount of aluminum was observed at higher pH regions. The maximum amount of leaching aluminium was less than 1 wt% of the sample investigated. The above results clearly indicated that the following P adsorption behaviors were dependent on boehmite itself. The P adsorption isotherm of boehmites in different concentration of H_3PO_4 solution is shown in Figure 4. The maximum amount of P adsorption on the boehmites were clearly dependent on the synthesis temperature, that is, surface area. B100, which had the highest value of surface area, showed the highest P capacity among the present boehmites.

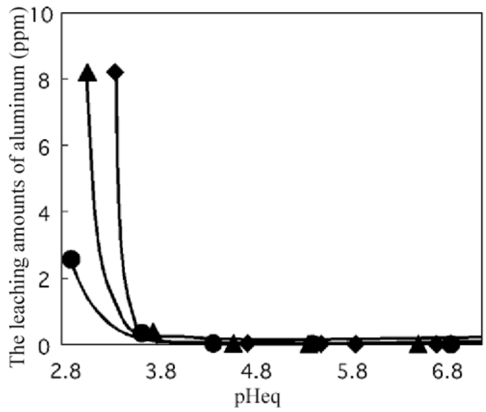

Figure 3. The relationship between equilibrium pH values and the leaching amounts of aluminum in solution from the boehmite synthesized at 100°C (◆), 150°C (▲) and 200°C (●).

The relationship between equilibrium pH values and the percent of P adsorption on boehmites in 60ppm H_3PO_4 solution is shown in Figure 5. P adsorption on boehmites decreased with increasing of the equilibrium pH. This result may be explained by the changing of phosphate ion states from $H_2PO_4^-$ to HPO_4^{2-} in the increase of the equilibrium pH value and OH^- in solution.

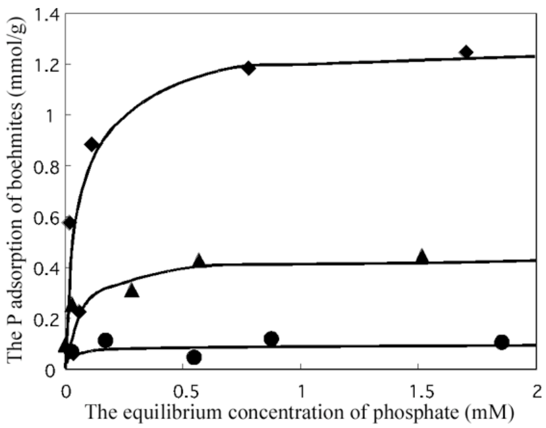

Figure 4. The P adsorption isotherm of boehmites synthesized at 100°C (◆), 150°C (▲) and 200°C (●).

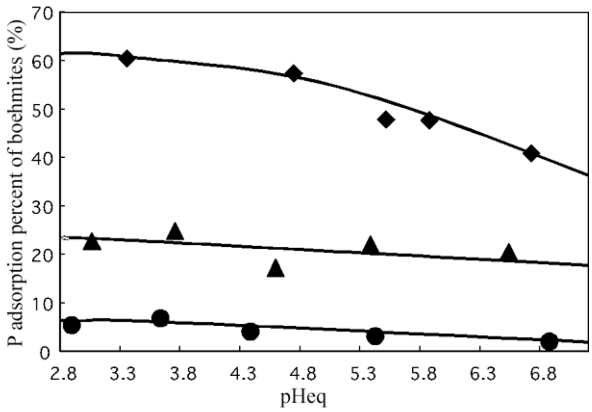

Figure 5. The relationship between equilibrium pH values and the percent of P adsorption of boehmite synthsized at 100°C (◆), 150°C (▲) and 200°C (●).

4. Conclusion

The adsorption behaviors of P were clearly dependent on the crystallinity and surface area of boehmite. B100, which had the lowest crystallinity and the highest surface area among samples, showed the maximum P adsorption. The pH dependency of P adsorption was supported the ion-state change from $H_2PO_4^-$ to HPO_4^{2-}. The present study confirmed that boehmite will be one of candidates for phosphate adsorbent in rivers and lakes.

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