Characteristics of Granular Boehmite and Its Ability to Adsorb Phosphate from Aqueous Solution

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In this study, we investigated the surface properties of granulated boehmite with vinyl acetate (G-BE20) and measured the amount of phosphate it adsorbed and the effect of contact time and solution pH on the adsorption process. The specific surface area ($144.9\text{ m}^2/\text{g}$) and the number of surface hydroxyl groups (0.88 mmol/g) of G-BE20 were smaller than those of virgin boehmite (BE), which gave a specific surface area and number of surface hydroxyl groups of $297.0\text{ m}^2/\text{g}$ and 1.08 mmol/g , respectively. The amount of phosphate adsorbed increased with the temperature. The isotherm model of Langmuir was used to fit experimental adsorption equilibrium data for phosphate adsorption onto G-BE20. The calculated thermodynamic parameters show the spontaneous and endothermic nature of the adsorption process. The equilibrium adsorption onto G-BE20 was reached within 16 h and the amount of phosphate adsorbed was 8.4 mg/g . The kinetic mechanism of phosphate uptake was evaluated with two different models: the Lagergren pseudo first- and pseudo second-order models. The data obtained showed a better fit to the pseudo second-order model (0.991) than to the pseudo first-order model (0.967), as indicated by the r values. The rate constants for the adsorption of phosphate onto G-BE20 were calculated as 0.481 h and 0.029 g/mg h . The adsorption of phosphate onto G-BE20 was the maximum in the pH range 3.0–4.0.

Key words phosphate; adsorption; boehmite

Phosphorus is an important nutrient involved in several biochemical reactions, and it cannot be substituted by other elements. It is widely used in agriculture and industry.¹⁾ The presence of trace amounts of phosphorus, exceeding about 1 mg/L , in treated wastewater can stimulate algal growth (eutrophication); phosphorus is usually considered a rate-limiting factor for algal growth.²⁾ Algal blooms lead to short- and long-term environmental and aesthetic problems in lakes, coastal areas, and other confined water bodies.³⁾ Moreover, phosphate is an exhaustible resource, and Japan depends solely on imports owing to a lack of native rock phosphate. As a consequence, phosphate removal and recovery from wastewater has been considered an important factor related to environmental sustainability.⁴⁾

Several physicochemical and biological processes have been investigated for the removal of dissolved nutrients in water and wastewaters.^{5–9)} They include adsorption methods, physical processes (settling and filtration), chemical precipitation (with aluminum, iron, and calcium salts), and biological processes that rely on biomass growth (bacteria, algae, and plants) or intracellular bacterial polyphosphate accumulation.¹⁰⁾ Adsorption is one of the most attractive approaches in water treatment, and it has the advantage of having high removal efficiency without producing harmful by-products.¹¹⁾ It is also well known that phosphates have a strong affinity for mineral surfaces.¹²⁾ Its affinity for hydroxide surfaces depends not only on the anion's complexing capacity, which allows phosphates to bind to surface groups through ligand exchange reactions, but also on electrostatic interactions with the charged hydroxide surfaces.¹³⁾

Boehmite (BE), a form of aluminum oxyhydroxide, is a very inexpensive adsorbent and can be recycled using a desorption solution. It also possesses anion exchange ability due to the surface hydroxyl groups.¹⁴⁾ BE, the molecular

formula of $(\text{AlOOH})_n$, is colorless, insoluble in water, and exhibits acid, base, and thermal resistance, which makes it useful as a catalyst, an abrasive, or a filler. However, powdered BE needs to be granulated with a binder for use in fields; it is not useful for removal of phosphate because plugging occurs, which indicates that the particle size of the BE adsorbent is too small. Moreover, the amount of phosphate adsorbed onto BE can be easily desorbed and recovered using sodium hydroxyl solution.¹⁵⁾ This technology can also be used in the field. Although the phosphate adsorption ability of BE is widely known,¹⁴⁾ the phosphate adsorption ability of granular BE has never been reported.

In this study, we produced granular BE with vinyl acetate as an organic binder. The phosphate adsorption ability, effect of contact time and pH, and the adsorption mechanism of phosphate were investigated for examining the use of the BE in the field.

Experimental

Materials For the preparation of boehmite (AD220NS; Tomita Pharmaceutical Co., Ltd., Japan), noncrystalline aluminum hydroxide was placed in an aqueous medium. After heat treatment at $90\text{--}100^\circ\text{C}$ for 1–3 h, the aluminum oxyhydroxide obtained was spray-dried. The main chemical composition of the resultant aluminum oxyhydroxide was AlOOH , less than 0.1% Cl^- , and less than 0.8% SO_4^{2-} . Its loss of mass upon drying and its pH, mean particle size, and pore volume were 7.8%, 8.2, $100\text{ }\mu\text{m}$, and 0.402 mL/g , respectively.

Granular BE was prepared by mixing vinyl acetate with virgin BE and allowing the mixture to dry. Hereafter, we refer to virgin BE containing about 20% vinyl acetate as G-BE20 (Columnar construction: diameter 3 mm × height 5 mm).

Thermogravimetric-differential thermal analysis (TG-DTA) and scanning electron microscopy (SEM) were carried out using a DTG-60AH (Shimadzu, Japan) and a JSM-5500LV (JEOL, Japan), respectively. The specific surface area of each

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Fig. 1. SEM Images of Virgin BE and G-BE20

sample was measured using a Flowsorb II 2300 (Micromeritics, Japan), the number of surface hydroxyl groups was measured by fluoride ion adsorption,¹⁶⁾ and the pH of each solution was measured using a digital pH meter (Mettler-Toledo International Inc., Japan).

Phosphate solution (using distilled water) or environmental water (using water from Lake Biwa) was prepared by $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ (Wako Pure Chemical Industries, Ltd., Osaka, Japan).

Adsorption Isotherms G-BE20 (0.05 g) was added to 50 mL of phosphate solution or environmental water at different concentrations (1–50 mg/L) of pH 5.32–6.00 (ionic strength: 0.1×10^{-4} – 5.2×10^{-4}). The suspension was shaken at 15, 25, and 35°C for 24 h at 100 rpm and then filtrated using a 0.45- μm membrane filter. The concentration of phosphate was measured using DR/890 (HACH, U.S.A.). The amount of phosphate adsorbed onto the adsorbent was calculated as follows by using the concentration before and after adsorption:

$$X = (C_0 - C_e)V / M \quad (1)$$

where X is the amount of phosphate adsorbed (mg/g), C_0 is the concentration before adsorption (mg/L), C_e is the concentration after adsorption (mg/L), V is the solvent volume (L), and M is the mass of the adsorbent (g).

Effect of Contact Time and Solution pH on the Adsorption of Phosphate onto G-BE20 The pH of the solution was adjusted from 2 to 7 by adding suitable volumes of 0.1 mol/L hydrochloric acid or 0.1 mol/L sodium hydroxide solution. G-BE20 (0.05 g) was added to 50 mL of phosphate solution at 50 mg/L. The suspension was shaken at 25°C for 24 h at 100 rpm and then was filtrated using a 0.45- μm membrane filter.

Similarly, G-BE20 (0.05 g) was added to 50 mL of phosphate solution at 50 mg/L, and after 1–24 h, the solution was filtrated using a 0.45- μm membrane filter. The amount of phosphate adsorbed onto G-BE20 was calculated using Eq. 1.

Results and Discussion

Characteristics of G-BE20 SEM images of virgin BE and G-BE20 show that virgin BE can be granulated with vinyl acetate (Fig. 1) and that the particle size of G-BE20 is larger than that of virgin BE. The results of TG-DTA of G-BE20 show that the adhesive water evident in G-BE20 was dehydrated at about 105°C and that the peak for the combustion of the binder (vinyl acetate) occurred at around 462°C (Fig. 2).

The specific surface area (144.9 m²/g) and the number of surface hydroxyl groups (0.88 mmol/g) of G-BE20 were less than those of virgin BE, and these values gave the specific surface area and number of surface hydroxyl groups as 297.0 m²/g and 1.08 mmol/g, respectively.¹⁴⁾ These results

Fig. 2. TG-DTA of G-BE20

indicate that the particle size of G-BE20 increased upon granulation with the binder. However, the binder masked available adsorption sites on the G-BE20 surface. The pH of the G-BE20 solution was 6.37.

Isotherm for Adsorption of Phosphate onto G-BE20

The isotherm for the adsorption of phosphate onto G-BE20 is shown in Fig. 3, and it indicates that the amount of phosphate adsorbed increased with the temperature. The equilibrium adsorption capacities of phosphate at 15, 25, and 35°C were 6.2, 8.7, and 10.3 mg/g, respectively. We previously reported that the amount of phosphate adsorbed onto virgin or calcined BE depends on the specific surface area and the number of hydroxyl groups in the BE. The amount of phosphate adsorbed onto calcined BE increased with the temperature. With G-BE20, a similar tendency was seen in the calcined BE. Further, the solution pH increased from 5.32–6.00 to 5.89–6.72 which indicated that the surface hydroxyl groups of BE was exchanged with phosphate.

The isotherm model of Langmuir was used to fit the experimental adsorption equilibrium data for phosphate adsorption onto G-BE20.¹⁷⁾ These models are represented mathematically as follows:

$$X = aWsC_e / (1 + aWs) \quad (2)$$

where X (mg/g) is the amount of phosphate adsorbed, a (L/mg) is a constant related to the affinity to the binding sites and to the adsorption, Ws (mg/g) is the maximum monolayer adsorption capacity, and C_e (mg/L) is the equilibrium concentration.

Langmuir constants for the adsorption of phosphate onto G-BE20 are listed in Table 1. From the table, the Langmuir constant a at 15, 25, and 35°C is seen to be 0.05, 0.44, and 1.32, respectively. These results indicated an endothermic process. Moreover, this reaction is the spontaneous nature of the adsorption process and the feasibility of the adsorption

Fig. 3. Adsorption Isotherms of Phosphate onto G-BE20 at Different Temperatures

Fig. 4. Adsorption Rate of Phosphate onto G-BE20

of phosphate onto G-BE20. The adsorption of phosphate onto G-BE20 may involve not only chemical adsorption but also physical adsorption. The correlation coefficient at 15, 25, and 35°C is 0.998, 0.996, and 0.994, respectively.

Effect of Contact Time and Solution pH on the Adsorption of Phosphate onto G-BE20 The rate of phosphate adsorption onto G-BE20 is shown in Fig. 4. It can be seen that the equilibrium adsorption onto G-BE20 was reached within about 16 h and the amount of phosphate adsorbed was 8.4 mg/g. Faster reactions have previously been reported for the adsorption of phosphate on iron oxide tailings,¹⁷⁾ bauxite,¹⁸⁾ and alunite.¹⁹⁾ These reports indicated that the adsorption reached equilibrium in 25–60 min. The reaction between phosphate and the adsorbent is of primary importance in the use of adsorbents in wastewater treatment.

The kinetic mechanism of phosphate uptake was evaluated with two different models: the Lagergren pseudo first- and pseudo second-order models.²⁰⁾ The pseudo first-order equation takes the form

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

where q_t is the amount of phosphate adsorbed at time t (mg/g), q_e is the amount of phosphate bound at equilibrium (mg/g), and k_1 is the equilibrium rate constant for pseudo first-order kinetics.

The pseudo second-order equation is expressed as

$$t / q_t = 1 / k_2 q_e^2 + t / q_e \quad (4)$$

Fig. 5. Amount of Phosphate Adsorbed onto G-BE20 at Different pH

where k_2 is the equilibrium rate constant for the pseudo second-order kinetics (g/mg h). The data obtained showed a better fit to the pseudo second-order model (0.991) than to the pseudo first-order model (0.967), as indicated by the r values in Table 2. The rate constants for the adsorption of phosphate on G-BE20 were calculated as 0.481 1/h and 0.029 g/mg h.

The pH of the aqueous solutions containing the adsorbent is an important parameter in the adsorption process. The adsorption of phosphate onto G-BE20 as a function of pH is shown in Fig. 5. It can be seen that the adsorption has strong pH dependence. In the pH range 3.0–4.0, the adsorption reached the maximum. Generally, phosphate exists in three forms in diluted aqueous solutions. In a strongly basic solution,

Table 1. Langmuir Constants for Phosphate Adsorption onto G-BE20

Sample	Temperature (°C)	Langmuir constants		
		W_s (mg/g)	a (L/mg)	r
G-BE20	15	11.47	0.05	0.998
	25	8.38	0.44	0.996
	35	7.69	1.32	0.994

Table 2. Pseudo First- and Second-Order Constants for Phosphate Adsorption onto G-BE20

Sample	Model	q_e (mg/g)	k_1 (h ⁻¹) or k_2 (g/mg h)	r
G-BE20	Pseudo first-order	6.1	0.481	0.967
	Pseudo second-order	9.9	0.029	0.991

Fig. 6. Adsorption Isotherm of Phosphate onto G-BE20 in Environmental Water

PO_4^{3-} predominates. In weakly basic conditions, HPO_4^{2-} predominates; in weakly acidic conditions, H_2PO_4^- predominates; and in strongly acidic conditions, H_3PO_4 predominates. Here, in our case, since the adsorption was found to be the maximum at pH 3.5, it can be said that H_2PO_4^- is predominant. We have previously reported that the phosphate ion (H_2PO_4^-) was exchanged with surface hydroxyl groups on powder BE. Moreover, Sverjensky and Watanabe *et al.* were reported that the surface charge characteristics of aluminum hydroxide must related to the pH dependency of phosphate adsorption on the aluminum hydroxide.^{21,22)}

Amount of Phosphate Adsorbed onto G-BE20 in Environmental Water The adsorption isotherm of phosphate adsorption onto G-BE20 in environmental water is shown in Fig. 6. The adsorption amount in environmental water agreed with that in aqueous solutions. This result implied that the components of environmental water did not affect the adsorption. Sometimes the components of environmental water competed with phosphate for adsorption in aqueous solutions. Therefore, G-BE20 was found to be useful for the adsorption of phosphate in environmental water.

Conclusion

Results from this study indicated that G-BE20 has a high phosphate removal capacity. BE was granulated with vinyl acetate and the properties of the resulting G-GB20 were evaluated. The specific surface area and the number of surface hydroxyl groups of G-BE20 were smaller than those of virgin BE, and the amount of phosphate adsorbed increased with the temperature. The data obtained showed a better fit to the pseudo second-order model (0.991) than to the pseudo first-order model (0.967), as indicated by the *r* values. The rate constants

for the adsorption of phosphate onto G-BE20 were calculated to be 0.481 l/h and 0.029 g/mgh. Moreover, the amount of phosphate adsorbed onto G-BE20 in environmental water agreed with that absorbed onto G-BE20 in aqueous solutions. The results also showed that the components of environmental water did not affect the absorption of phosphate onto G-BE20. These results indicate that G-BE20 will be useful for the removal of phosphate in environmental water.

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References

- 1) Liu Y., Villalba G., Ayres R. U., Schrode H., *J. Ind. Ecol.*, **12**, 229–247 (2008).
- 2) Peleka E. N., Deliyanni E. A., *Desalination*, **245**, 357–371 (2009).
- 3) Oguz E., Gurses A., Yalcin M., *Water Air Soil Pollut.*, **148**, 279–287 (2003).
- 4) Zhang T., Ding L., Ren H., Guo Z., Tan J., *J. Hazard. Mater.*, **176**, 444–450 (2010).
- 5) Jutidamrongphan W., Park K. Y., Dockko S., Choi J. W., Lee S. H., *Environ. Chem. Lett.*, **10**, 21–28 (2012).
- 6) Yue Q., Zhao Y., Li Q., Li W., Gao B., Han S., Qi Y., Yu H., *J. Hazard. Mater.*, **176**, 741–748 (2010).
- 7) Anirudhan T. S., Rauf T. A., Rejeena S. R., *Desalination*, **285**, 277–284 (2012).
- 8) Zach-Maor A., Semiat R., Shemer H., *J. Colloid Interface Sci.*, **363**, 608–614 (2011).
- 9) Kamiyango M. W., Sajidu S. M. I., Masamba W. R. L., *Afr. J. Biotechnol.*, **10**, 11972–11982 (2011).
- 10) Rodrigues L. A., daSilva M. L. C. P., *Desalination*, **263**, 29–35 (2010).
- 11) Zhang S., Li X. Y., Chen J. P., *J. Colloid Interface Sci.*, **343**, 232–238 (2010).
- 12) Torrent J., Schwertmann U., Barron V., *Clay Miner.*, **40**, 14–21 (2005).
- 13) Antelo J., Avena M., Fiol S., López R., Arce F., *J. Colloid Interface Sci.*, **285**, 476–486 (2005).
- 14) Ogata F., Kawasaki N., Nakamura T., Tanada S., *J. Colloid Interface Sci.*, **300**, 88–93 (2006).
- 15) Ogata F., Tominaga H., Yabutani H., Kawasaki N., *J. Oleo Sci.*, **60**, 133–138 (2011).
- 16) Boehm H. P., *Angew. Chemie.*, **78**, 617–628 (1966).
- 17) Zeng L., Li X., Liu J., *Water Res.*, **38**, 1318–1326 (2004).
- 18) Ozacar M., *J. Hazard. Mater. B*, **137**, 218–225 (2006).
- 19) Barrow N. J., *J. Soil Res.*, **37**, 787–829 (1999).
- 20) Huang W., Wang S., Zhu Z., Li L., Yao X., Rudolph V., Haghseresht F., *J. Hazard. Mater. B*, **158**, 35–42 (2008).
- 21) Sverjensky D. A., *Geochim. Cosmochim. Acta*, **69**, 225–257 (2005).
- 22) Watanabe Y., Kasama T., Fukushi K., Ikoma T., Komatsu Y., Tanaka J., Moriyama Y., Yamada H., *Sep. Sci. Technol.*, **46**, 818–824 (2011).