



Phosphorus removal and magnetic separation using magnetic schwertmannite

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ABSTRACT

Phosphorus is an eutrophication agent for aquatic environment. An adsorption method is used for phosphorus removal; however, solid–liquid separation of adsorbent and the limit of adsorption relative to particle size are problematic. This study focused on phosphorus removal using schwertmannite combined with magnetite (magnetic schwertmannite). Magnetite is a ferromagnetic material. The magnetic schwertmannite with more than 33.7 mass% of magnetite content demonstrated good magnetic separation. The optimum adsorption pH was found to be 2.5, and the adsorption amount decreased with increase in solution pH. The maximum adsorption amount for phosphate was observed to be 1.42 mmol/g, and the adsorption isotherm was approximated by the Langmuir equation. The maximum adsorption amount was more than twice that previously reported because the particle size used in the current study was smaller than that used previously.

Keywords: Composite material; Ion-exchange; Magnetic separation; Phosphorus removal; Schwertmannite

1. Introduction

Phosphorus, which causes eutrophication, is an important element in agricultural, chemical, and medical industries. However, the price of phosphate ore has increased with increasing global demand. Phosphorus must be removed and recovered from waste. Phosphorus is discharged to aquatic environments through domestic and industrial wastewaters. Several phosphorus removal technologies for domestic wastewater have been developed and employed, such as chemical precipitation [1, 2], crystallization [3, 4], adsorption, and biological processes [5].

Many type of adsorbents have been used in the removal of phosphate, such as activated aluminum oxide [6], iron oxide [7], dolomite [8], calcite [9], MnO₂ [10], titanium oxide [11], zirconium hydroxide [12], and hydrotalcite-like compounds [13–15].

Schwertmannite is an effective adsorbent of anions, and the targets of schwertmannite are phosphate [16], arsenate [17], fluoride [18], and chromate [19]. Schwertmannite is an iron oxide and low crystallinity material. The chemical formula for schwertmannite is Fe₈O₈(OH)_{8-2X}(SO₄)_X·nH₂O (1 < X < 1.75). The removal mechanism is an ion-exchange reaction, and SO₄²⁻ is replaced by other anions. The regeneration condition has been previously reported [20].

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The adsorption amount of an adsorbent increases with decrease in particle size. However, the separation performance between an adsorbent and a liquid phase decreases with decrease in particle size. Typically, the separation force in the liquid phase is gravity; thus, important factors are specific weight and particle size of the adsorbent. It is difficult to miniaturize an adsorbent; however, relative to particle size, magnetic separation has less influence than gravity separation. A few adsorbents can improve magnetic separation performance to combine magnetic materials [21–23]. This method can combine schwertmannite and magnetite [24]. Magnetic schwertmannite has been synthesized; however, the magnetic content of the synthesized product is too low to separate without a superconducting magnet [18].

In this study, we focused on adsorption and magnetic separation performance of magnetic schwertmannite using permanent magnets. We examined synthesis conditions, adsorption performance on phosphate, and magnetic separation performance of magnetic schwertmannite.

2. Materials and methods

2.1. Schwertmannite

In this study, synthesis of magnetic schwertmannite was performed according to a previously filed patent [24]. Schwertmannite was synthesized from an $\text{Fe}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$ solution and was precipitated by changing the solution pH using NaHCO_3 . Schwertmannite is precipitated at pH 2.5, and decomposed at higher pH than 2.5. The solution pH was increased from 1.8 to 2.5 during precipitation of schwertmannite. Magnetic schwertmannite was prepared by adding commercial magnetite (Fe_3O_4 , particle diameter: 0.2 μm) to the $\text{Fe}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$ solution. Magnetic schwertmannite was collected by a neodymium magnet, and schwertmannite was filtrated using a 0.45 μm membrane filter. The collected adsorbent was washed by 3 mmol/L sulfuric acid solution and dried at 40°C for 24 h. The dried adsorbent was crushed and classified less than 80 μm by sieves. All reagents used in this study were obtained from Nacalai Tesque Inc. (Kyoto, Japan).

The content ratio of magnetite was calculated using the following equation. Here, C_{mag} is the percentage of magnetite content in the adsorbent, W_t is the weight of the adsorbent collected by magnetic separation, and W_m is the weight of the added magnetite.

$$C_{\text{mag}} = \frac{W_m}{W_t} \times 100.$$

2.2. Adsorption experiment

The adsorption properties were examined by batch type adsorption experiments. The phosphate solution was prepared with Na_2HPO_4 . The initial concentrations of phosphate were adjusted to 5 mmol/L. The pH of the solutions was adjusted with 1N HCl and 1N NaOH.

Schwertmannite (0.05 g) was added to the phosphate solution (50 mL), and the adsorption reaction was performed for 24 h at 25°C under rotary shaker or stirrer mixing condition with a PTFE impeller.

2.3. Analytical methods

Phosphate was detected using the molybdenum blue method [25]. The surface morphology was observed by a scanning electron microscope (SEM, JSM-6330F, JEOL). The adsorbent was identified by an X-ray diffractometer (XRD, XRD-6100, Shimadzu). Separation performance using a neodymium magnet was evaluated by turbidity, and turbidity was analyzed by a portable turbidity meter using the scattered light method (HI 93703, HANNA). The analytical cell of the turbidity meter was placed on the neodymium magnet, and the turbidity was analyzed by time-dependent change. The pH of the mixed solution for magnetic separation analysis was approximately 4.

3. Results and discussion

3.1. Precipitation of magnetic schwertmannite

The magnetite content of magnetic schwertmannite is an important factor in this study, and the influence of the magnetite concentration in the synthesis solution on magnetite content is shown in Fig. 1.

The relationship between synthesis yield of magnetic schwertmannite and the magnetite concentration in the synthesis solution is shown in Fig. 2.

Magnetic schwertmannite was not synthesized from the synthesis solution contained 1 g/L of magnetite, the synthesis material was schwertmannite, only. Magnetic schwertmannite with less than 18.8 mass% magnetite content could not be synthesized. The synthesis yield of magnetic schwertmannite was calculated using the following formula, where R_{mag} is the percentage of synthesis yield of the adsorbent, W_t is the weight of the adsorbent collected by magnetic separation, and W_c is the total weight of the synthesized schwertmannite, magnetic schwertmannite and magnetite.

$$R_{\text{mag}} = \frac{W_t}{W_c} \times 100.$$

The color of magnetic schwertmannite collected by the magnet was dark green, and the color of the synthesis

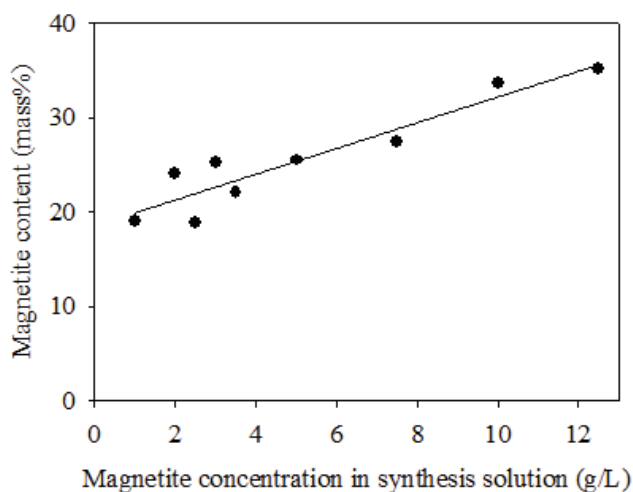


Fig. 1. Influence of magnetite concentration on the magnetite content in the synthesis solution.

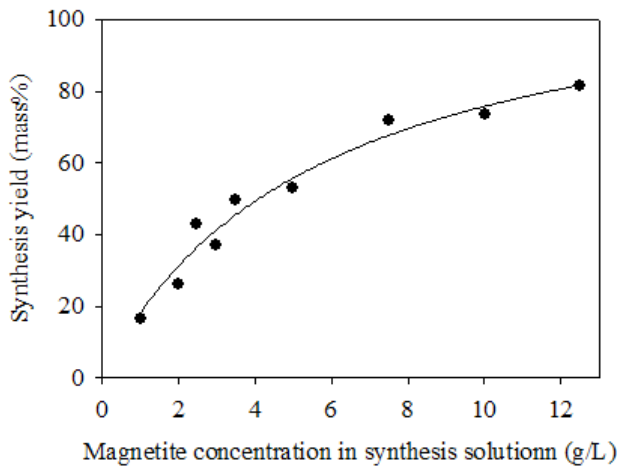


Fig. 2. Influence of magnetite content on synthesis yield.

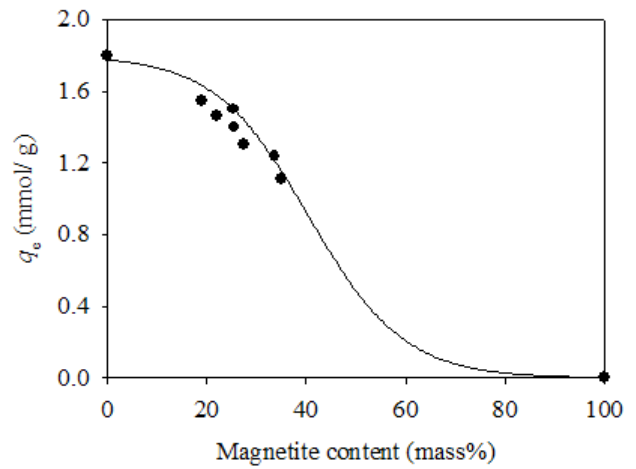


Fig. 3. Influence of magnetite content on adsorption amount.

solution changed from brown to yellow. The total amount of synthesized material was constant in this study. However, the magnetite content of magnetic schwertmannite increased with increase in magnetite concentration in the synthesis solution, and the synthesis yield of magnetic schwertmannite also increased with increase in magnetite concentration. Fig. 3 shows that the adsorption amount (q_e) of magnetic schwertmannite was influenced by the magnetite content of magnetic schwertmannite. The adsorption amount of magnetic schwertmannite decreased when combined with magnetite; the amount of magnetite increased as a quadratic function. As can be seen in Figs. 1–3, magnetic schwertmannite with lower magnetite content shows a thick schwertmannite layer.

The magnetic curve of the adsorbent is shown in Fig. 4 (the number is the magnetite content in magnetic schwertmannite). It can be seen that schwertmannite is a non-magnetic material, and the hysteresis of the magnetic curve shows that magnetic schwertmannite became a ferromagnetic material. The saturated magnetic flux density increased with increase in magnetite content in magnetic schwertmannite.

Fig. 5 shows the temporal change in Suspended solid (SS) concentration of the adsorbent using magnetic separation. The SS concentration was calculated by the turbidity measurement. The SS concentration of magnetic schwertmannite with more than 33.7 mass% of magnetite decreased sharply. The magnetic schwertmannite with less than 27.5 mass% was shown the same behavior as magnetic schwertmannite with 33.7 mass% within 5 min.

After 20 min, the behavior of magnetic schwertmannite with less than 27.5 mass% was similar to schwertmannite. The gravity settling rate of magnetic schwertmannite with 33.7 mass% was lower than that of schwertmannite. The particle size of magnetic schwertmannite in the liquid phase was larger than schwertmannite, and the details are shown in Section 3.3. The separation behavior of magnetic schwertmannite with less than 27.5 mass% of magnetite using magnetic separation was similar to a gravity settling adsorbent. It was observed that magnetic schwertmannite with less than 27.5 mass% was exfoliated the schwertmannite at the surface. These results show that the optimum magnetite content was 33.7 mass%.

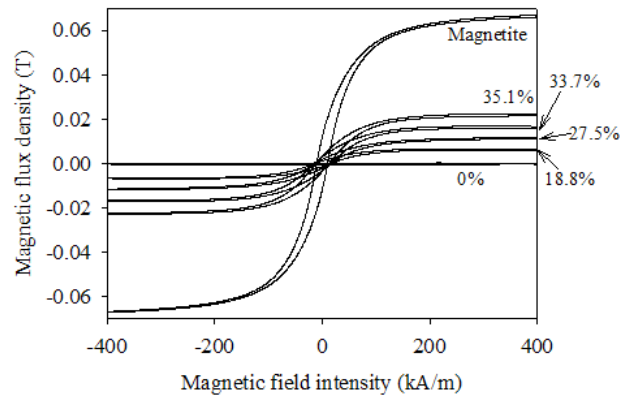


Fig. 4. Magnetic curves of magnetic schwertmannite and schwertmannite.

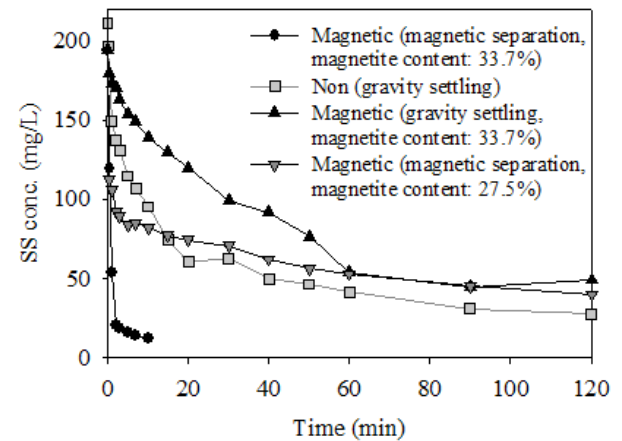


Fig. 5. Influence of magnetic separation performance on magnetic content.

3.2. Characteristics of adsorbent

The SEM image of magnetic schwertmannite with 33.7 mass% of magnetite and schwertmannite is shown in Fig. 6; the XRD pattern is shown in Fig. 7.

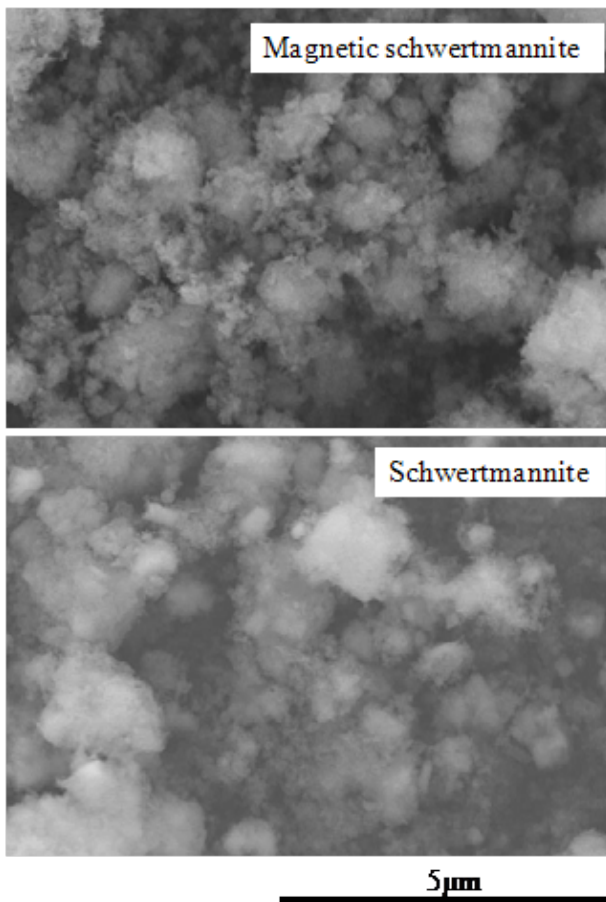


Fig. 6. Scanning electron microscopy (SEM) images of magnetic schwertmannite and schwertmannite.

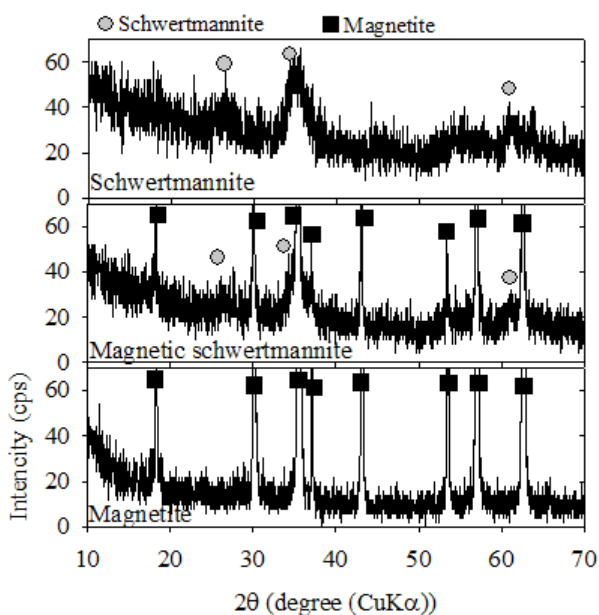


Fig. 7. X-ray diffractometer (XRD) patterns of magnetic schwertmannite and schwertmannite.

Schwertmannite has a unique structure, and many needle-like structures were observed in both the synthetic schwertmannite and magnetic schwertmannite. The crystalline structure of magnetic schwertmannite is similar to that of natural schwertmannite [26]. The structure does not significantly influence combinations of schwertmannite and magnetite.

3.3. Influence of solution pH

pH is the most important factor in water treatment. The influence of the adsorption amount on the solution pH is shown in Fig. 8. The magnetite content of magnetic schwertmannite was 33.7 mass%.

The adsorption amount decreased with increase in solution pH. The adsorption amount of schwertmannite decreased linearly; however, that of magnetic schwertmannite decreased as a quadratic function. The decreasing adsorption amount ratio between schwertmannite and magnetic schwertmannite is similar to the magnetite content ratio of magnetic schwertmannite under acidic conditions. At pH 9, the adsorption amount of magnetic schwertmannite is the same as that of schwertmannite. The influence of the solution pH on the turbidity of the mixed liquid is shown in Fig. 9; the SS concentration is 0.2 g/L in each liquid and adsorbent.

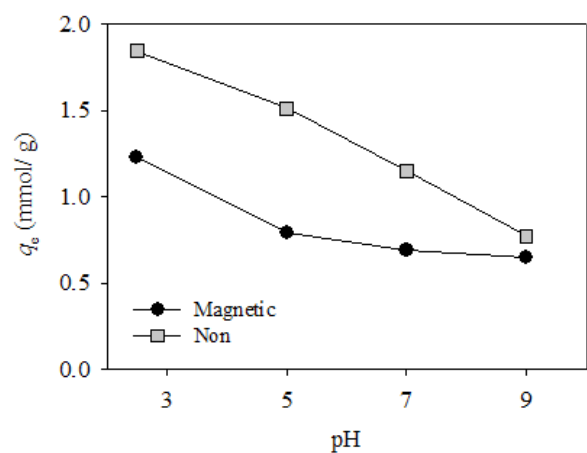


Fig. 8. Influence of pH on adsorption amount of schwertmannite and schwertmannite.

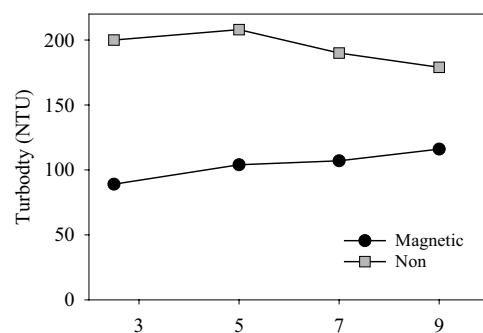


Fig. 9. Influence of pH on turbidity at 0.2 g adsorbent/L.

The turbidity of magnetic schwertmannite is lower than that of schwertmannite. The SEM images (Fig. 6) show that the magnetic schwertmannite particles are of the same size as the schwertmannite particles. It is suggested that magnetic schwertmannite is easier to flocculate than schwertmannite. The turbidity of magnetic schwertmannite increased with the solution pH; however, that of schwertmannite decreased. The increase in turbidity indicates the miniaturization of the particles at the same solid SS concentration. Magnetic schwertmannite particles of the alkaline conditions were finer than that of the acidic condition; however, schwertmannite particles became coarse with increase in solution pH. The increase of particle size leads the increase of surface area. As it has a proportional relationship between surface area of adsorbent and adsorption amount, the adsorption amount is increased with decrease in particle size.

3.4. Adsorption isotherm

The adsorption isotherm at pH 3 is shown in Fig. 10. The magnetite content of magnetic schwertmannite was 33.7 mass%.

The adsorption amount saturated at a high equilibrium concentration. The maximum adsorption capacities of magnetic schwertmannite and schwertmannite were observed to be 1.42 and 1.86 mmol/g, respectively. The adsorption isotherms for both magnetic schwertmannite and schwertmannite were approximated using the Langmuir equation:

$$q_e = \frac{9.12C_e}{1 + 6.41C_e} \text{ for magnetic schwertmannite and}$$

$$q_e = \frac{17.3C_e}{1 + 9.32C_e} \text{ for schwertmannite}$$

In a previous study on phosphorus removal with schwertmannite, the adsorption amount was 26.8 mg/g (0.86 mmol/g), the adsorption amount of this study (1.86 mmol/g) increased from the value found in previous work [16]. The adsorption amount increased as the specific surface area increased, and the specific surface area increased as the adsorbent particle size decreased.

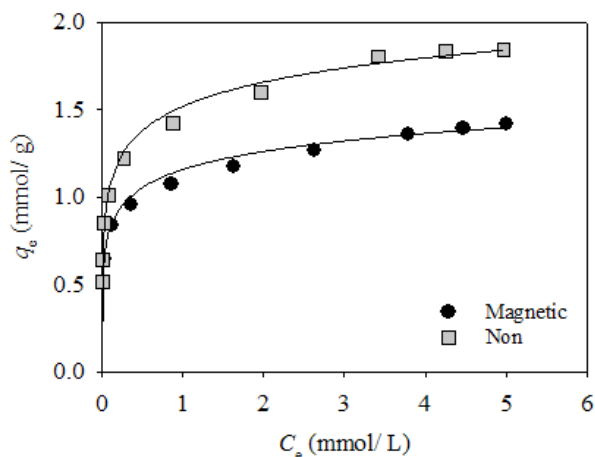


Fig. 10. Adsorption isotherm at pH 3 and 25°C.

The adsorbent particle size was smaller than previous one from SEM image, because the pH adjusted, reagent and addition rate in the synthesis differ between this study and previously reported study. In this study, NaHCO_3 was used to adjust pH. The solution pH increased with dissociation of NaHCO_3 and schwertmannite was synthesized in the upper position. Schwertmannite was not synthesized and grew the upper position of synthesis solution. The addition rate used in this study is faster than that used previously. For these reasons, it is obtained finer schwertmannite. In this study, magnetic schwertmannite and schwertmannite were washed in a 3 mmol/L sulfuric solution for washed impurities. The purity of schwertmannite found in this study is higher than observed previously.

4. Conclusions

The performance of magnetic adsorbent for phosphorus removal has been discussed. The optimum content of the adsorbent and magnetic separation performance of the magnetic adsorbent have been reported. The following conclusions can be drawn from the experimental results.

- (1) The amount of magnetic schwertmannite was the limit of magnetite content. The adsorption amount was decreased with the increase in the magnetite content. The saturated magnetic flux density was dependent on the magnetite content. The optimum magnetite content was 33.7 mass%.
- (2) Retention of a typical crystal structure in magnetic schwertmannite was observed in SEM images. The XRD peak pattern of magnetic schwertmannite indicated the combination of schwertmannite and magnetite.
- (3) Magnetic schwertmannite containing 33.7 mass% of magnetite was swiftly separated by a neodymium magnet.
- (4) The adsorption capacity of magnetic schwertmannite decreased with increasing pH of the solution. The decrease ratio of adsorption amount between schwertmannite and magnetic schwertmannite is similar to the magnetite content ratio of magnetic schwertmannite under acidic conditions.
- (5) The adsorption isotherm was approximated by the Langmuir equation. The maximum adsorption capacity of magnetic schwertmannite was 1.42 mmol/g.

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