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FERRIMAGNETIC COAGULATION PROCESS FOR PHOSPHATE ION REMOVAL USING HIGH-GRADIENT MAGNETIC SEPARATION

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ABSTRACT

An efficient magnetic separation system for phosphate ion removal has been studied for developing a practical environmental protection technology for water purification in rivers, lakes, etc. using ferrimagnetic fine particles (FMFPs), which can be prepared from $FeCl_2$ and $FeCl_3$ aqueous solutions. With 15 mg/L of $FeCl_3$ solution, without the addition of FMFP, phosphate ion recovery increased from 20 to 80% with increasing magnetic field from 0.8 to 8 T. By the addition of 5 mg/L of FMFP with 15 mg/L

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of $FeCl_3$ solution, above 95% recovery was achieved in a wide range of magnetic field ($H = 0.8-8\,T$). A high magnetic field gradient generated in the vicinity of steel wool caused the enhancement of the magnetic coagulation of the complex with phosphate ion and Fe(III) ion, and the paramagnetic iron–phosphate complexes were attracted to FMFP in the reactor, which resulted in high (95%) recovery in a wide range of magnetic fields.

Key Words: Ferrimagnetic fine particles; Magnetic coagulation; Magnetic separation; Phosphate ion removal; Water purification; Superconducting magnet

INTRODUCTION

The nutritive salts such as phosphate and nitrogen, which are contained in synthetic fertilizers and phosphate detergents, remain behind in living sewage and drainage of plains such as rice field and farm, and are discharged into rivers, landlocked bodies of water such as lakes and ponds; these nutritive salts cause an eutrophication problem in environmental water, and the eutrophication enhances the growth of algae and the evolution of poisonous chemicals. In landlocked body of water, the problem is extremely serious, and phosphate removal from the environmental water is an essential process to protect water resources from pollution. However, the phosphate concentration in the environmental water is very low (in general, below 0.1 mg/L), and the amount of water to be treated is very large; therefore, we cannot apply an effective process for the complete removal of phosphate.

The removal of phosphate from water can be accomplished by some biological and chemical processes. The chemical processes of phosphate removal, such as coagulation and adsorption treatment using $AlCl_3$, $Al(OH)_3$, and poly-$AlCl_3$,[1,2] precipitation of calcium phosphate induced by seeding crystals,[3] adsorption on slags obtained from coal gasification plants,[4] method of precipitation using $Ti(SO_4)_2$ as precipitant and crystallization with granular magnesia clinker,[5,6] adsorption of orthophosphate on activated carbon,[7] and adsorption and desorption by lepidocrocite [γ-FeO(OH)] and hematite (α-Fe_2O_3),[8] have been studied. Recently, electrochemical elution of iron as applied to phosphorus removal,[9,10] adsorption on alumina/precipitation of calcium phosphate,[11] application of precipitation processes in activated sludge,[12] and precipitation on goethite [α-FeO(OH)][13] have been reported.

However, these studies are not appropriate to remove phosphate from the dilute environmental water in which the concentration is below 0.1 mg/L, and a rapid treatment and large amount of water purification requires further experimental and theoretical knowledge.

High-gradient magnetic separation (HGMS) has been developed to apply for the purification and recycling of suspended water.[14–16] Using this technique, a large amount of polluted water can be treated under the limited atmosphere, such as high and low temperatures, acid and alkali solutions, and the load of environment can be reduced because the waste generated from water purification process is decreased. In these ways, HGMS is suitable for the purification of environmental water. Phosphate removal system using electromagnet[17,18] requires large consumption of power to purify small amount of water. However, superconducting magnet, which has an excellent operability and an advantage of less consumption of electric power, can generate a higher magnetic field than the electromagnet. Therefore, HGMS using superconducting magnet is useful for rapid and large amount of environmental water treatment.

For magnetic separation in an aqueous suspended solution, pretreatment technology for imparting magnetic seeding to soluble pollutants, such as phosphate and heavy metal ions is necessary. Iron oxide is an economical, safe, and stable chemical in an environment, and magnetic seeding process using ferrimagnetic substances (e.g., magnetite) is suited for the pretreatment of magnetic separation.

Based on the above, the aim of the present study is to examine the efficiency of phosphate ion removal, using ferrimagnetic substance, from the environmental water by magnetic separation using superconducting magnet.

EXPERIMENTAL PROCEDURE

Preparation of Ferrimagnetic Substance

All chemicals ($FeCl_2 \cdot 4H_2O$, $FeCl_3 \cdot 6H_2O$, $Na_2HPO_4 \cdot 2H_2O$, NaCl, Fe_3O_4) used were of analytical grade (Wako Pure Chemicals, Inc., Tokyo, Japan). Distilled water (below 5 μg/L of impurities) was used for the preparation of $FeCl_2$ solution [1 g/L of Fe(II) ions], $FeCl_3$ solution [2.5 g/L of Fe(III) ions], and phosphate–NaCl solution [1.25 g/L of PO_4(III) ions, 125 g/L of NaCl]. To prepare $FeCl_2$ solution, distilled water was degassed by passing nitrogen gas through it. Nitrogen gas was continuously passed through the $FeCl_2$ solution, to prevent the oxidation of the solution, throughout the experiment.

$FeCl_2$ and $FeCl_3$ solutions [Fe(II) ion/Fe(III) ion = 1/2] were added to the degassing alkaline solution (pH = 12) without magnetic field. After reaction at room temperature, iron ion coprecipitates were produced, which were recovered by magnetic separation and washed with distilled water for the removal of byproducts. Magnetic separation is the process in which the suspended solution is stirred for 2 min under high magnetic fields ($H = 8\,\mathrm{T}$), and the solid product attracted to the magnetic field is recovered. Chemical analyses on the Fe(II) and Fe(III) ions were done with α,α'-bipyridyl absorption spectrophotometry. A part of the recovered product was dried at room temperature for the sample of x-ray diffractometry (XRD). The crystal size of the product was determined from the XRD peak by the following equation:

$$L = 0.94\lambda/\Delta(2\theta)\cos\theta \qquad (1)$$

where L, λ, and $\Delta(2\theta)$ are the magnitude of crystal size, the wavelength of Fe Kα line (0.1936 nm), and the diffracted beam half-width at 45° (2θ), respectively.

Phosphate Ion Removal by Magnetic Separation

The experimental set-up used in the present study is schematically given in Fig. 1. As shown in Fig. 1, ferromagnetic filament (steel wool) was placed in the reaction suspension as the origin of the high magnetic field gradient. Nitrogen gas was continuously passed through the reaction vessel to stir the suspension during

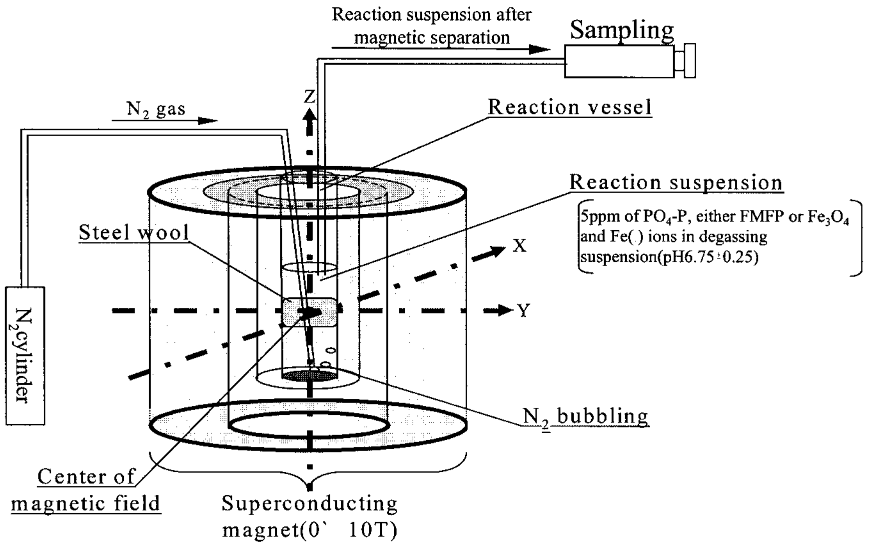

Figure 1. Experimental set-up for phosphate ion removal by magnetic separation in a high magnetic field.

reaction at room temperature. The reaction suspension [PO_4(III) = 5 mg/L, NaCl = 100 mg/L] was prepared by adding a given amount of phosphate–NaCl solution (1.25 g/L of PO_4-P, 125 g/L of NaCl) in degassed distilled water (100 mL). The $FeCl_3$ solution was added to the reaction suspension. The pH of the reaction suspension was gradually raised to pH 6.75 ± 0.25 by adding NaOH solution, and kept constant during reaction. After allowing the suspension to stand for 5 min to the reaction, the commercial magnetite, Fe_3O_4 was added to the suspension. After the solid products attracted with steel wool in the reactor were recovered by magnetic separation for 5 min, the concentration of phosphate remaining in reaction solution was determined by molybdenum blue absorption spectrophotometry.

A 10 T cryocooler-cooled superconducting magnet (National Institute for Materials Science, Tsukuba, Japan) was used for magnetic separation. The x-ray diffractometer with Fe Kα radiation (RINT 2000 Rigaku Corp., Tokyo, Japan) was used for the determination of crystal size of the product. The pH of the solution during the reaction was measured using digital pH meter (HG-30G, DKK-TOA Corp., Tokyo, Japan). An absorption spectrophotometer (Model 124, Hitachi Corp., Tokyo, Japan) was used for colorimetry to measure the phosphate ion (α,α'-bipyridyl absorption spectrophotometry and molybdenum blue absorption spectrophotometry).

RESULTS AND DISCUSSION

XRD and Colorimetry Analyses of Ferrimagnetic Substance (Ferrimagnetic Fine Particles)

The identification of the iron ion coprecipitates produced from the reaction suspension was done using XRD. Figure 2 shows XRD patterns of the iron ion coprecipitates prepared by aqueous reaction (A), and the commercial magnetite powder (B) purchased from Wako Pure Chemicals Inc. The peaks in the pattern (A) were very weak compared to that of commercial magnetite, and the main peaks were similar to that of Fe_3O_4 with spinel structure. This result indicates that the iron ion coprecipitates are the magnetite fine particles, which are termed ferrimagnetic fine particles (FMFPs). According to the XRD patterns shown in Fig. 2(A) and (B), the crystal sizes of FMFP and commercial magnetite were determined to be 8 and 63 nm, respectively. The concentration of Fe(II) and Fe(III) ions in FMFP was measured by α,α'-bipyridyl absorption spectrophotometry. This analysis resulted in the Fe(III)/Fe(II) molar ratio of 4/1, and excess Fe(III) ion compared with the ratio of 2/1, which is the stoichiometric composition of magnetite (Fe_3O_4).

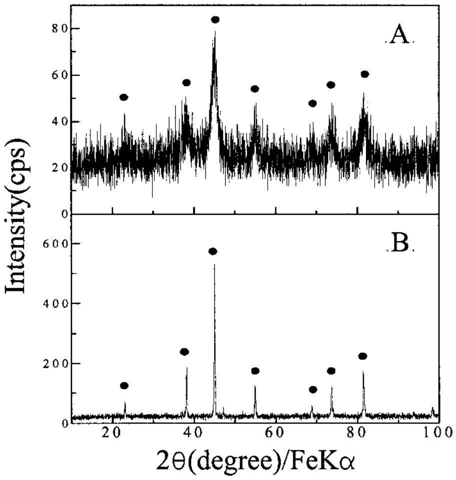

Figure 2. XRD patterns of (A) the iron ion coprecipitates prepared by aqueous reaction (FMFP) and (B) a commercial magnetite.

Phosphate Ion Removal by Magnetic Separation

Figure 3 shows adsorption capacity of FMFP and commercial magnetite for phosphate ion in a high magnetic field ($H = 8\,\mathrm{T}$). The numbers on the abscissa indicate the iron ion concentration in the solution after adding FMFP or magnetite. By the addition of commercial magnetite, the phosphate ion recovery increased with increase in iron ion concentration in the solution. The phosphate ion recovery was greater and was enhanced 5–10 times in the case of FMFP addition when compared to the addition of commercial magnetite. Hence, compared with commercial magnetite, this result shows that FMFP has a high adsorption capacity for phosphate ion. The result shown in Fig. 2, the ratio of Fe(III) ion in FMFP [molar ratio of Fe(III)/Fe(II) = 4/1] was more than that in commercial magnetite (2/1); the result was consistent with the presence of a large amount of Fe(III) ion on the surface of FMFP compared to that of commercial magnetite. The Fe(III) ions on the surface of FMFP and commercial magnetite reacted with phosphate ions. The paramagnetic iron–phosphate complexes formed, which are iron–phosphate hydroxides [$Fe_4(PO_4)_n(OH)_3$, etc.] and phosphosiderite ($FePO_4{\cdot}2H_2O$),[19,20] were recovered with FMFP and commercial magnetite by the magnetic separation. Thus, adsorption capacity of phosphate ion for FMFP addition would be higher than that for commercial magnetite. In addition, the difference in crystal size between the FMFP and the commercial magnetite can affect the phosphate ion recovery. With increasing

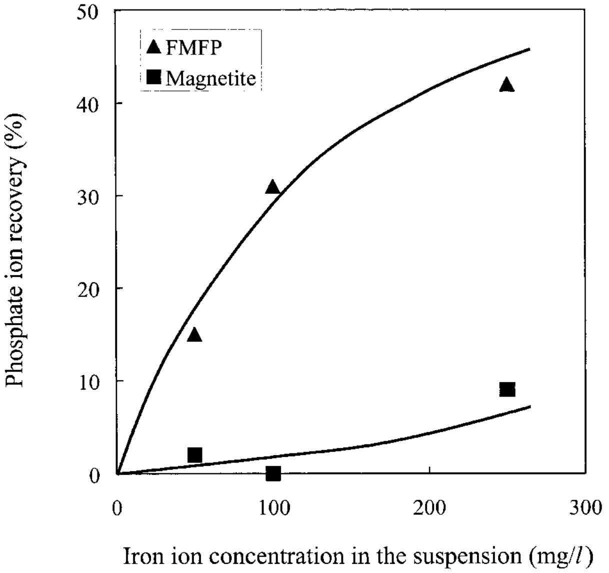

Figure 3. Adsorption capacity of phosphate ion by adding FMFP and commercial magnetite at 8 T.

iron ion concentration in the solution, the surface area of FMFP is larger than that of commercial magnetite: the adsorption site of phosphate ion on the surface of FMFP is larger than that of commercial magnetite. Therefore, the adsorption of phosphorus ion increased with the addition of FMFP, and adsorption capacity of phosphate ion for FMFP was higher than that for commercial magnetite.

Figure 4 shows the adsorption capacity of phosphate ion for FMFP addition (the concentration of FMFP in solution = 100 mg/L) in high magnetic fields ($H = 2{-}8$ T). Phosphate ion recovery increased from 20 to 30% with increase in magnetic field. The phosphate ion recovery achieved in the magnetic field of 8 T was about 1.5 times higher than that in the magnetic field of 2 T, although magnetic field gradient induced by the steel wool might saturate at 2 T. This result would be considered as due to the enhancement of FMFP–FMFP coagulation in the suspension in high magnetic fields, and the FMFPs attracted phosphate ions in the suspension in a high magnetic field (the paramagnetic iron–phosphate complex), which resulted in the higher recovery of phosphate ions that are to be attracted to the steel wool.

Figure 5 shows phosphate ion recovery (%) by the addition of Fe(III) ion in high magnetic fields. With 15 or 20 mg/L of Fe(III) ion, without the addition of FMFP, the phosphate ion recovery increased from 20 to 80% with increasing magnetic field from 0.8 to 8 T (curves C and D). This result indicates that higher

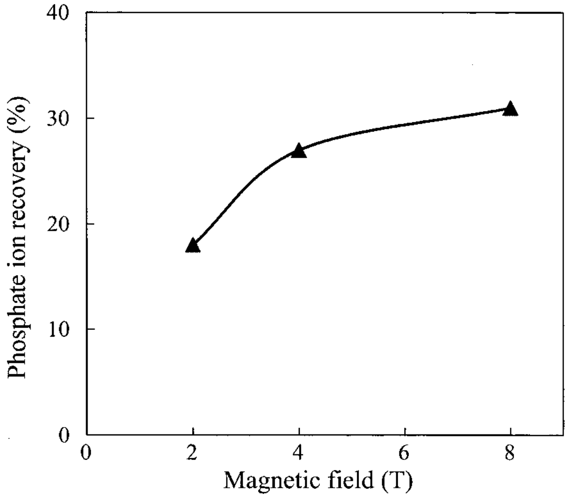

Figure 4. Adsorption capacity of phosphate ion for the addition of FMFP. (FMFP = 100 mg/L).

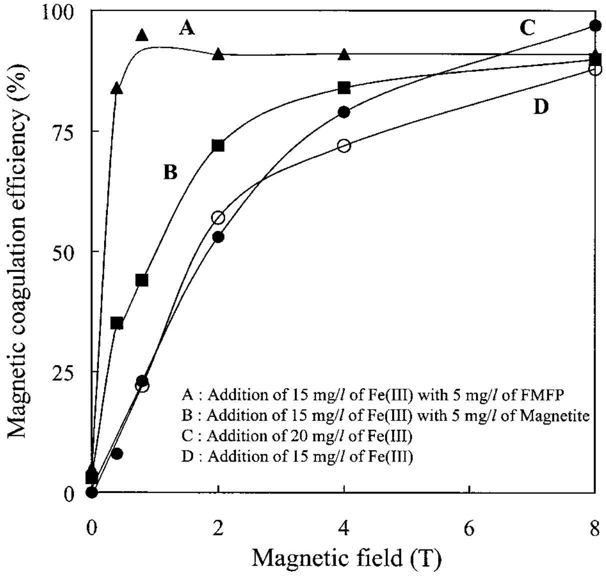

Figure 5. Phosphate ion recovery by the addition of FMFP, commercial magnetite, and Fe(III) ion.

Fe(III) ion concentration causes higher recovery of phosphate ion due to the formation of paramagnetic $FePO_4$ in the reaction suspension. In the case of adding 5 mg/L of commercial magnetite (Fe_3O_4) with 15 mg/L of Fe(III) ion, phosphate ion recovery was higher than that of adding 15 or 20 mg/L of Fe(III) ion without the addition of FMFP (curves B, C, and D). However, by the addition of 5 mg/L of FMFP with 15 mg/L of Fe(III) ion, above 95% recovery was achieved in a wide range of magnetic field from 0.8 to 8 T (curve A). It shows that FMFP has higher efficiency of magnetic separation than commercial magnetite.

The phosphate ion recovery was around 0% without magnetic field under the present conditions (curves A–D), the recovery was proved to be a magnetic coagulation reaction induced in a high magnetic field, and the magnetic coagulation reaction could be estimated to an FMFP–FMFP (magnetite–magnetite) coagulation, which attracted the phosphate–iron complex and the phosphate–iron complexes coagulation. With Fe(III) ion, without the addition of FMFP or magnetite, the phosphate–iron complex that is a paramagnetic substrate was formed. In a high magnetic field at 8 T, the complex with phosphate ion and Fe(III) ion could be sufficiently used by HGMS (curves C and D). On the other hand, when the magnetic field decreased to 4 T or less, the magnetic coagulation efficiency of the phosphate–iron complex was not large enough to obtain the high recovery of phosphate ion. By the addition of FMFP with Fe(III) ion, the recovery of phosphate ion could keep up high recovery in a low magnetic field (curve A). This result came from a high magnetic field gradient generated in the vicinity of steel wool, and furthermore phosphate ions were attracted to FMFP in high magnetic fields (the formation of paramagnetic iron–phosphate complexes). The magnetic force, which worked on the paramagnetic complex with phosphate ion and Fe(III) ion, was enhanced due to the high magnetic field; the reaction of magnetic coagulation of the complexes occurred in reaction suspension, so high recovery was obtained in low magnetic fields (<4 T).

CONCLUSIONS

An efficient magnetic separation system for phosphate ion removal has been studied for developing a practical environmental protection technology for water purification using FMFP, which can be prepared from $FeCl_2$ and $FeCl_3$ aqueous solutions.

The Fe(III)/Fe(II) molar ratio of 4/1 was an excess of Fe(III) ions compared to the ratio of 2/1, which is the formula of magnetite (Fe_3O_4). The phosphate ion recovery by the addition of FMFP in high magnetic field (8 T) was 5–10 times higher than the addition of commercial magnetite. With the addition of 100 mg/L of FMFP in high magnetic fields from 2 to 8 T, phosphate ion recovery increased from 20 to 30% with increasing magnetic fields, although magnetic field gradient induced by the steel wool might saturate at 2 T. In the case of 5 mg/L of FMFP addition with 15 mg/L of Fe(III) ion, above 95% recovery was obtained in a low magnetic field of 0.8 T. The addition of FMFP enhances the magnetic coagulation efficiency and adsorption capacity of phosphate ion. It is considered that magnetic separation efficiency of phosphate ion, attracted to FMFP, is improved by adding Fe(III) ions because the magnetic coagulation occurs sufficiently in a low magnetic field due to the generation of high magnetic field gradient in the vicinity of steel wool, and the paramagnetic iron–phosphate complexes were formed by adding Fe(III) ions.

In future, an efficient magnetic separation system using FMFP could be expected to develop as a practical environmental protection technology for rapid purification of large amount of wastewater.

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