Separation Science and Technology
Publication details, including instructions for authors and subscription information:
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To cite this Article Kang, Suck-Ki , Choo, Kwang-Ho and Lim, Kwang-Hee(2003) 'Use of Iron Oxide Particles as Adsorbents to Enhance Phosphorus Removal from Secondary Wastewater Effluent', Separation Science and Technology, 38: 15, 3853 — 3874

To link to this Article: DOI: 10.1081/SS-120024236

URL: http://dx.doi.org/10.1081/SS-120024236

SEPARATION SCIENCE AND TECHNOLOGY
Vol. 38, No. 15, pp. 3853–3874, 2003

Use of Iron Oxide Particles as Adsorbents to Enhance Phosphorus Removal from Secondary Wastewater Effluent

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ABSTRACT

Potential use of iron oxide particles (IOPs) as adsorbents for removal of residual phosphorus from the secondary effluent discharged from activated sludge treatment was investigated under various operating conditions. Substantial phosphorus removal was achieved with IOPs including ferrihydrite, goethite, and hematite, though the adsorption capability for phosphorus depended on the types of IOPs tested. Adsorption isotherm tests and SEM images helped to understand the behavior of the adsorptive properties of phosphorus on different IOPs. Phosphorus removal efficiencies for secondary effluent remained constant or further increased over the wide pH range of below neutral

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DOI: 10.1081/SS-120024236 0149-6395 (Print); 1520-5754 (Online)

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to alkaline values, in contrast to those for a synthetic phosphorus solution. This could be in close association with the interaction of phosphorus with Ca and Mg ions present in secondary effluent leading to chemical precipitation, such as apatite, dolomite, calcite, and brucite. The reactivity of IOPs with phosphorus at neutral pH appeared to be almost independent of the existence of background inorganic species, such as inert salts, alkalinity, and hardness. The phosphorus removal efficiency was compared during regeneration and recovery of used IOPs using centrifugation and microfiltration (MF) methods. MF following IOP adsorption was found to be efficient enough to accomplish significant phosphorus removal during continuous adsorption/regeneration runs, suggesting that the combination of IOP adsorption with MF would be attractive as a tertiary treatment alternative.

Key Words: Iron oxide particle; Phosphorous removal; Adsorption; Secondary effluent; Microfiltration; Advanced treatment.

INTRODUCTION

Phosphorus removal from wastewater before discharge to rivers and lakes is one of the critical issues related to eutrophication problems of the receiving water bodies.[1] In recent years, several treatment techniques based on biological uptake, chemical precipitation, or adsorption have been introduced and developed for enhanced phosphorus removal and recovery, and also their hybrid processes were applied to maximize phosphorus removal.[1–12] Enhanced biological phosphorus removal processes rely on the uptake of phosphorus by microorganisms through cyclic or alternating operations of a biological system under aerobic and anaerobic conditions.[2–8] During biological treatment, both polyphosphate-accumulating organisms (PAOs) and extracellular exopolymers contributed to the removal of phosphorus from municipal wastewater.[13,14] Furthermore, the composition of feed wastewater, such as calcium, magnesium, and carbon, was found to have an effect on biological phosphorus removal and so it was demonstrated that phosphorus removal was improved with the addition of magnesium,[15–17] possibly due to struvite formation. Except for Ca-rich wastewater, however, chemical precipitation was not expected to take place in most cases when treating municipal wastewater.[16] Other researchers pointed out that a decrease in the BOD_5 concentration in the mixture of influent and return sludge reduced phosphorus removal.[18] Biological phosphorus removal is still limited and should be further improved for stable operations because the system performance is sensitive to biological conditions and wastewater composition.

Thus, chemical precipitation by the addition of coagulants to biological systems has been undertaken to improve treatment efficiencies, since the biological treatment efficiency was often not sufficient to get rid of phosphorus to an appropriate level.[8,9,19] Several studies reported that the removal of phosphate from aqueous and wastewater samples was improved by dosing with iron salts.[8,19–21] The effect of pH, iron dosage, and initial phosphate concentration was tested. It was found that optimal phosphorus removal could be achieved with 1:1 molar addition of ferric ions at acidic pH and that excess iron doses were not necessary for complete phosphorus removal.[20] Also, the addition of alum into biological reactors played a significant role in phosphorus removal by chemical precipitation.[8,9,22] However, the addition of chemicals into biological systems causes other serious issues such as biological nitrification inhibition.[22]

Adsorption after biological treatment has been also considered as another alternative to remove phosphorus stably and efficiently. Development and testing of various adsorbents such as sands, slag media, activated alumina, zeolite-iron, polymer hydrogels, and red mud have been investigated for the removal of phosphorus and metals from wastewater.[10–12,23–25] The most important factor determining phosphorus removal capacity by sands was found to be the content of Ca in the sands, because Ca is associated with the precipitation of phosphorus as sparingly soluble calcium phosphates at alkaline conditions.[10] It was also reported that the slag media, obtained from the steel industry, had a substantially high sorption capacity for phosphorus, since the large portion of metals present in the media surface contributed to the sorption of phosphorus.[11] However, little information is available on the recovery and regeneration of used adsorbents in continuous operations, and also, the development of new adsorbents for enhanced phosphorus removal is still needed.

Therefore, the purpose of this work was to apply different types of iron oxide particles synthesized in the laboratory as new adsorbents for phosphorus removal from secondary effluent. The effects of iron oxide particle structures and doses, solution pH, alkalinity, and hardness on phosphorus removal were explored with feed solution with different phosphorus concentrations. Particularly, the regeneration and recovery of used iron oxide particles by their exposure to alkaline solution and subsequent separation by centrifugation or microfiltration (MF) were attempted. The phosphorus removal efficiency by regenerated particles was evaluated during successive runs.

EXPERIMENTAL

Secondary Effluent and Synthetic Phosphate Solution

The secondary effluent used for this study was obtained from the activated sludge process of the Gyeongsan City Wastewater Treatment

Table 1. Quality of secondary effluent.

Parameter	Value (1 SD)
pH	7.0 (0.1)
Suspended solids (mg/L)	2.7 (1.52)
COD_{Cr} (mg/L)	22 (2.83)
DOC (mg/L)	10.5 (0.050)
PO_4^{3-}-P (mg/L)	0.68 (0.05)
NH_4^+-N (mg/L)	1.55 (0.03)
NO_3^--N (mg/L)	7.81 (0.25)
Ca^{2+} (mg/L)	16.1 (0.96)
Mg^{2+} (mg/L)	5.37 (0.16)
Alkalinity (mg/L as $CaCO_3$)	67.5 (0.99)

Plant. The secondary effluent samples were collected from the final clarification step of the treatment plant, moved to the laboratory, and then stored at 4°C before being used for experimental runs. Their composition was analyzed in the laboratory before experiments and average values for specific parameters are given in Table 1. Since the phosphorus concentration in the original secondary effluent was relatively low, more phosphorus was added into the intact secondary effluent using stock phosphate solution with a concentration of 100 mg/L as P. Considering the discharge limit (2 mg/L as P) of total phosphorus in Korea, the phosphorus concentration of the modified secondary effluent for testing was normally adjusted to approximately 2.7 mg/L with additional 2 mg/L from stock solution. To obtain a wide range of equilibrium phosphorus concentration (0 to 6 mg/L as P) in adsorption isotherm tests, feed solution samples containing higher phosphorus concentrations, up to 7 mg/L as P, were prepared by the addition of 4 to 12 mL of stock solution to 200 mL secondary effluent. A synthetic feed solution containing 2.5 mg/L as P only was prepared by diluting stock solution with pure water.

Preparation of Iron Oxide Particles

The three types of iron oxide particles (IOPs) used as adsorbents, ferrihydrite, goethite, and hematite, were prepared in the laboratory using ferric chloride salts as follows.[26,27] A ferrihydrite stock slurry was prepared by neutralizing a ferric chloride solution with an Fe concentration of 10 g/L. Goethite was then synthesized by holding a freshly precipitated ferrihydrite at 70°C for 60 hours under an alkaline condition ($pH > 12$), while hematite production was done by holding the ferrihydrite suspension

Table 2. Characteristics of the IOPs used.

IOP	Formula	Surface area (m^2/g)	Shape*
Ferrihydrite	$Fe_5HO_8 \cdot 4H_2O$	200–300	Amorphous layer/sphere
Goethite	α-FeOOH	20	Rod
Hematite	α-Fe_2O_3	20–25	Hexahedron

*Based on SEM images in Figure 3.

at 90°C for 48 hours under a slightly alkaline condition (pH 8.5). Goethite and hematite are relatively stable in the wide pH range compared to freshly precipitated ferrihydrite. Properties of the IOPs tested are given in Table 2.

Adsorption Tests

To determine the adsorptive removal efficiency of different IOPs for phosphorus present in secondary effluent, adsorption tests were performed at various IOP doses from 0 to 150 mg/L as Fe. For each test, a certain amount (approximately 0 to 6 mL, depending on the concentrations of IOP slurries prepared) of the IOP slurries were placed into each 300-mL Erlenmeyer flask and the solution was then mixed at 200 rpm and 20°C in a shaking incubator (DF-94F, Duri Science, Korea). After 30 min of shaking, the solution was filtered through a 0.45-μm filter (Millipore, USA) and the samples collected from the filtration step were used for analyses. Particularly for adsorption tests using regenerated IOPs, a 50-mL Felcon tube and a 180-mL stirred cell unit (Model 8200, Amicon, USA) were used for adsorption and regeneration purposes. Specific conditions for regeneration are detailed in a later section.

Solutions of 1.0-M NaCl, 0.1-N $NaHCO_3$, 0.1-M $CaCl_2$, and 0.2-N HNO_3 (or 0.2-N NaOH) were used to change the concentration of ionic strength, alkalinity, hardness, and the pH of feedwater samples, respectively. The addition of NaCl, HCO_3^-, Ca^{2+} to secondary effluent was in the ranges of 0 to 50 mM, 0 to 400 mg/L as $CaCO_3$, 0 to 200 mg/L as $CaCO_3$, respectively, while the final pH of the solutions was adjusted in the range of 5.0 to 13.0, depending on specific experiments.

Regeneration Methods

Two regeneration methods using a centrifuge and an MF membrane were employed to recover and reactivate the used IOPs after adsorption experiments. In the former case, secondary effluent was placed in a 50-mL Felcon tube with an IOP dose of 100 mg/L as Fe, then, the 30-min adsorption period began as described previously. The supernatant, after 10-min centrifugation (2260 *g*), was transferred and filtered through a 0.45-μm filter to obtain treated water samples. The IOP pellets collected in the bottom of the tube were exposed to 50-mL 0.2-N NaOH solution for 5 min with vigorous mixing. The suspension was recentrifuged under the same conditions to separate regenerated IOPs. This procedure was repeated one more time and finally, the regenerated IOPs were neutralized and collected by one more centrifugation. The regenerated IOPs were reused in the next batch.

In the latter case of using MF for regeneration, a stirred cell unit with a 0.1-μm polypropylene MF membrane was used for the separation and regeneration of used IOPs. Secondary effluent, 100 mL, with an IOP dose of 100 mg/L as Fe was placed in the stirred cell under the same adsorption conditions and MF of the sample started after a 30-min reacion period to obtain permeate as final effluent. The IOP cakes attached at the membrane after MF were exposed to 50-mL 0.2-N NaOH solution under vigorous mixing for 10 min and another MF was done to remove phosphorus-laden regenerant and, thereby, to collect regenerated IOPs. The regenerated particles were washed for 10 min in the stirred cell with 100 mL of pure water and then separated and captured by MF. One more wash and separation were done in the same manner after neutralizing the particles and finally, the regenerated IOPs were ready for the next test.

Analytical Methods

Feed wastewater (secondary effluent) and treated water samples were analyzed for orthophosphate phosphorus to evaluate the phosphorus removal efficiency by IOPs. The orthophosphate concentration was determined using the ascorbic acid method using Hach reagent powders (PhosVer 3), which is equivalent to USEPA method 365.2 and *Standard Method* 4500-P-E.[28] The DOC concentration was determined using a Shimadzu TOC analyzer (TOC5000A, Japan), whereas the UV absorbance (UV_{254}) was determined at 254 nm using a Hach spectrophotometer (DR4000U, USA). Chemical oxygen demand, NH_4^+-N, and NO_3^--N were determined using the reactor COD digestion (with low range reagents), Nessler, and cadmium reduction methods. Particle size and its distribution of IOPs were measured using a particle size analyzer (Micromeritics, SediGraph5100, USA), while the surface of IOPs was visualized using a field emission scanning electron microscope (S-4300, Hitach, Japan). Other physicochemical determination of the samples was done according to *Standard Methods*.[28]

RESULTS AND DISCUSSION

Effect of IOP Types and Doses

Phosphorus removal efficiencies for treatment of secondary effluent using various IOP types at different dosages are shown in Figure 1. Ferrihydrite removed more than 60% of the initial phosphorus at an IOP dosage of 25 mg/L as Fe, steadily increased with increasing IOP dosages, and reached more than 90% at as high as an IOP dosage of 140 mg/L as Fe. Goethite and hematite removed 47% and 14% of the initial phosphorus at a maximum IOP dosage of 150 mg/L as Fe, respectively. Phosphorus removal by IOPs can be explained by ligand exchange reactions at the IOP surfaces,[29,30] and so the reaction between IOPs and phosphate can be expressed at neutral pH as follows:

$$\equiv F - OH + H_2PO_4^- \rightarrow \equiv F - O - H_2PO_3 +^- OH$$

The difference in phosphorus removal for the three IOPs used should be primarily attributed to the surface area of each IOP, which is related to the size and structure of the particles. First, when the size of IOPs was measured using a particle size analyzer,[31] the three types of IOPs tested

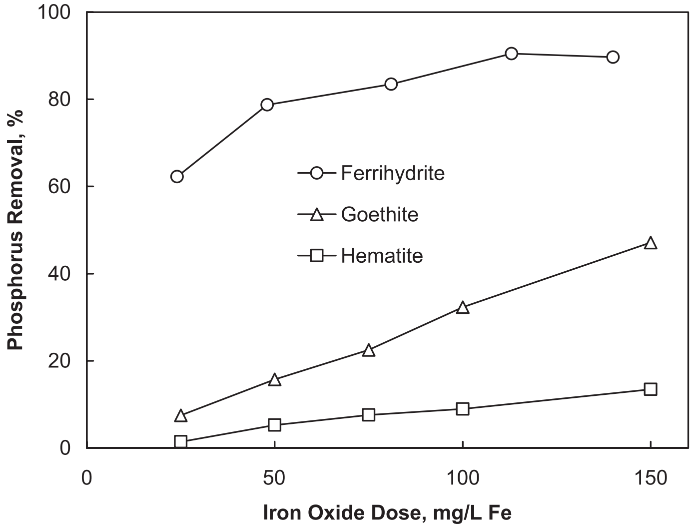

Figure 1. Effect of iron oxide types and dosages on phosphorus removal from secondary effluent.

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had almost the same size distributions, with an average diameter of approximately 3.5 μm (Figure 2). Based on the SEM pictures of Figure 3, however, the structures of the IOPs looked pretty different, though the nominal IOP sizes measured by the laser scattering method were similar. Thus, the IOP surface structure related to its morphology seemed to be more responsible for the discrepancy of phosphorus removal by different IOPs. As shown in Figure 3, there were very amorphous layers on the surface of a spherical form of ferrihydrite, supporting its highest phosphorus removal efficiency.

To further evaluate the sorption properties of different IOPs for phosphorus, isotherm tests were performed, and the results are shown in Figure 4. High equilibrium concentrations were obtained by the addition of an appropriate amount of stock phosphate solution into the original secondary effluent. The Freudlich isotherm equation is useful to assess adsorption data of mineral oxides in aqueous phase:[32,33]

$$q_e = KC_e^n$$

where q_e is the amount of phosphorus adsorbed at equilibrium (normalized to adsorbent mass or area) (mg-P/g-Fe or mg-P/m^2-IOP), C_e is the equilibrium solution phase concentration (mg/L as P), and K and n are empirically determined parameters related to site energy. In Figure 4a, ferrihydrite had an adsorption amount per unit mass 10 times and 20 times larger in the range of phosphorus concentrations tested than goethite and hematite, respectively. When the sorption capacity was expressed based on

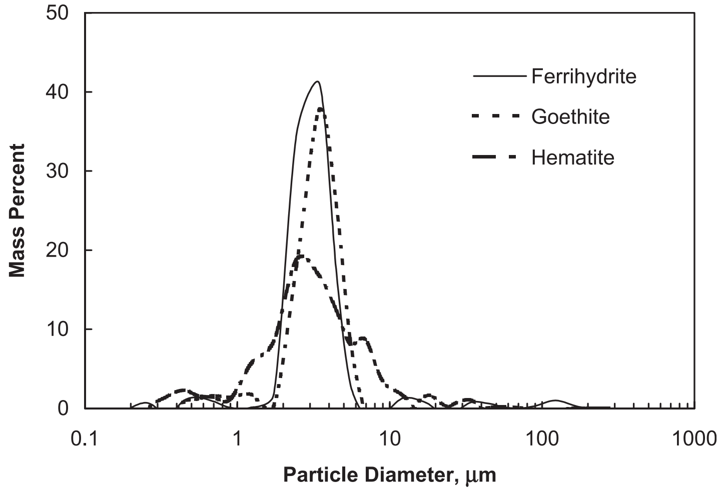

Figure 2. Size distribution of different types of iron oxide particles.

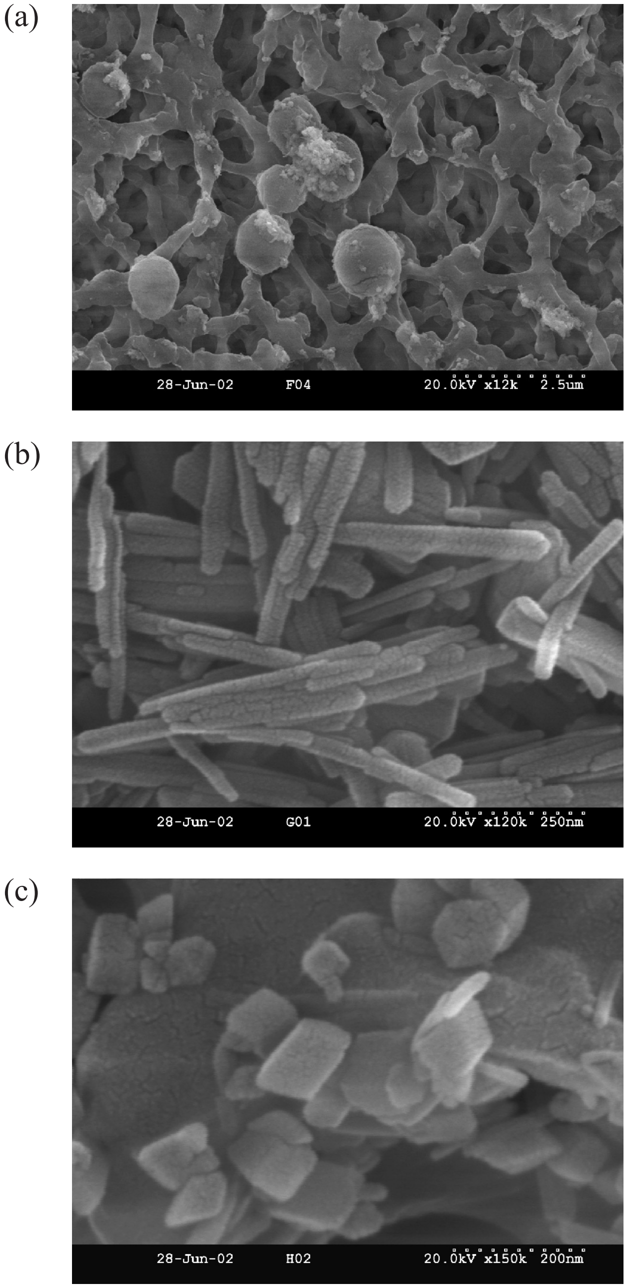

Figure 3. SEM pictures of IOPs used: (a) ferrihydrite; (b) goethite; (c) hematite. All IOPs sit on the MF membrane surface with 0.45-μm pores.

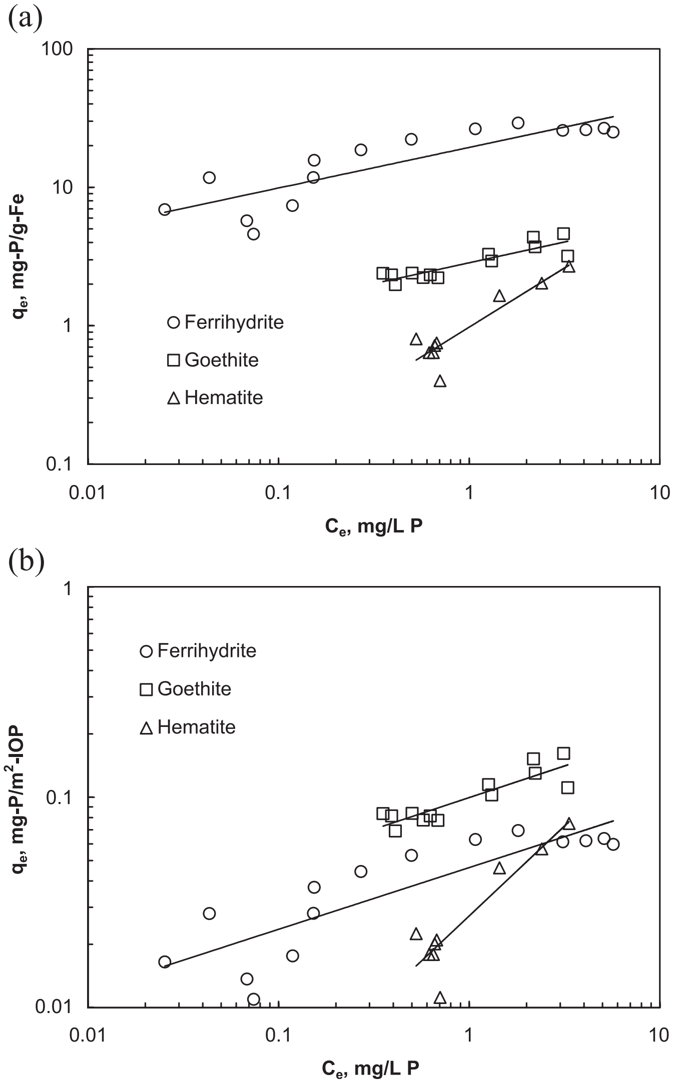

Figure 4. Adsorption isotherms of phosphorus on different iron oxide particles at pH 7. Additional phosphorus was placed into original secondary effluent samples to have higher equilibrium solution phase concentrations: (a) adsorption capacity normalized to adsorbent mass; (b) adsorption capacity normalized to adsorbent surface area.

Table 3. Summary of Freudlich isotherm parameter and R-square values from Figure 4.

IOP	K [(mg-P)/(g-Fe) (mg-P/L)^n]	K [(mg-P)/(m^2-IOP) (mg-P/L)^n]	n	R^2
Ferrihydrite	19.4	0.0463	0.293	0.732
Geothite	2.85	0.0996	0.301	0.791
Hematite	0.977	0.0273	0.855	0.833

unit area of adsorbent dosed (Figure 4b), however, the three IOPs fell to a comparatively similar level, indicating that the surface chemistry would be the same. From the slope (exponent n) of the isotherm fit, it was thought that the adsorption capacity of ferrihydrite and goethite was less sensitive to the change of phosphorus concentration than that of hematite (Table 3). Also, the Freudlich unit capacity parameter, K, revealed that ferrihydrite would be most effective in removing phosphorus to a very low concentration even at low IOP dosages. Accordingly, it was believed that IOPs such as ferrihydrite could act as an effective adsorbent to enhance the removal of residual phosphorus that could be hardly eliminated by biological treatment.

Effect of Feed pH

Figure 5 compares the effect of feed pH on phosphorus removal for secondary effluent and synthetic phosphorus solution. When the pH of the secondary effluent changed from 5 to 12, phosphorus removal was always maintained at a high level of approximately 80% in the pH range of 5 to 10, but interestingly, a further increase in phosphorus removal was observed at pH levels higher than 10. In fact, however, there was some doubt if the high phosphorus removal by IOP adsorption could occur even under alkaline conditions considering the ligand exchange reaction.[26,27,34] In contrast to the results with secondary effluent, phosphorus removal efficiency for synthetic phosphate solution containing 2.5 mg/L as P continuously decreased as the solution pH increased from 5 to 13. Since phosphorus removal by IOPs could be caused by coordinative reactions at the IOP surfaces, a decrease in phosphorus removal at elevated pH levels was expected as it occurred with the synthetic solution, but it did not happen with secondary effluent. Thus, the chemical interaction of phosphates with other components present in the secondary effluent, such as calcium and magnesium ions, should be considered in the unexpected phenomena. The reaction of phosphates with calcium and magnesium ions

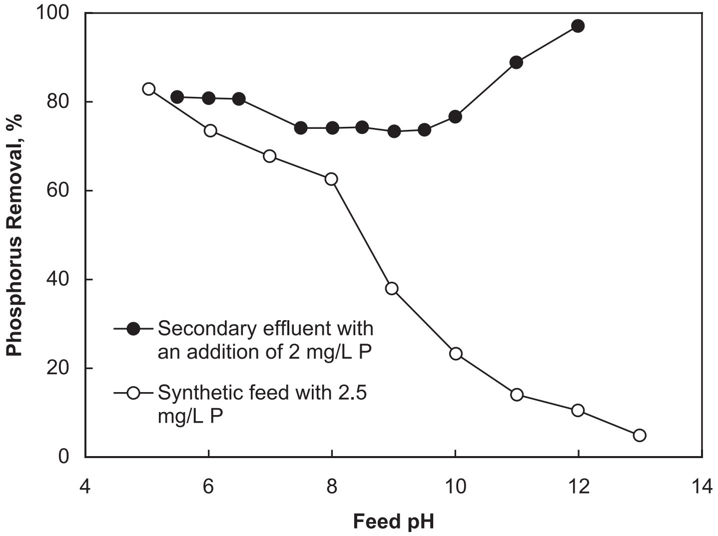

Figure 5. Variation of phosphorus removal for secondary effluent and synthetic solution at different pH levels: ferrihydrite dose, 100 mg/L as Fe.

could be in close association with substantial phosphorus removal at higher pH levels because sparingly soluble phosphorus-based precipitates, such as $Ca_5(PO_4)_3OH(s)$ (apatite) and $MgNH_4PO_4(s)$ (struvite), could be formed at alkaline conditions (Figure 6). Apatite started being generated around pH 6.5 and its formation dramatically increased until the solution pH reached 8, but the formation of struvite and its contribution to phosphorus removal were negligible. Accordingly, significant phosphorus removal by precipitation was occurring mainly due to apatite formation around neutral pH. This result supported the previously discussed hypothesis, though actual removal efficiency in Figure 5 was a little bit low as compared to the value based on theoretical calculations (see Figure 6). The difference in actual and theoretical phosphorus removal efficiencies might be caused by a complex formation between calcium and dissolved organic matter, as reported elsewhere.[35,36]

On the other hand, further phosphorus removal in the alkaline pH range could be primarily attributed to the precipitation of $CaMg(CO_3)_2(s)$ (dolomite) that can begin to form at pH 9, while sorbing the remaining phosphorus (see Figure 6). The formation of $Mg(OH)_2(s)$ (brucite) and $CaCO_3(s)$ (calcite) was minimal below pH 11 because apatite and dolomite precipitation prevailed, but they played a part in precipitating at extreme

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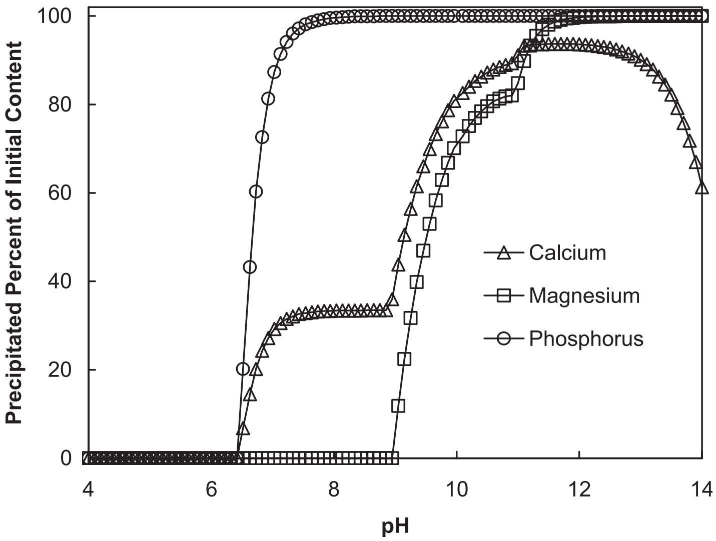

Figure 6. Calculation of the precipitated percentage of initial content of calcium, magnesium, and phosphorus present in the secondary effluent containing additional 2 mg/L P: temperature, 20°C; ionic strength, 0.01 M. It was assumed that calcium, magnesium, phosphate, carbonate, and ammonium could be primarily involved in the formation of precipitates, e.g., apatite, dolomite, calcite, brucite, and struvite.

pH levels ($>$pH 11). To confirm that significant phosphorus removal at high pH levels was obtained by the formation of Ca- and Mg-based precipitates, not by the involvement of iron oxide particles, phosphorus removal at elevated pH was examined without IOP addition. It was found that without IOP, 92% of the initial phosphorus was removed at pH 12. However, other inorganic species, such as Fe and Al, which might form precipitates, had no effect on phosphorus removal at high pH levels during this study when they were included in the equilibrium equations involving chemical precipitation. As a result, it was believed that due to the presence of calcium and magnesium ions in the actual effluent, apatite, dolomite, calcite, and brucite could be produced at increased pH levels leading to significant phosphorus removal.

Effect of Background Species

Since phosphorus removal efficiencies might be affected by inorganic species present in the secondary effluent, the effect of addition of inert

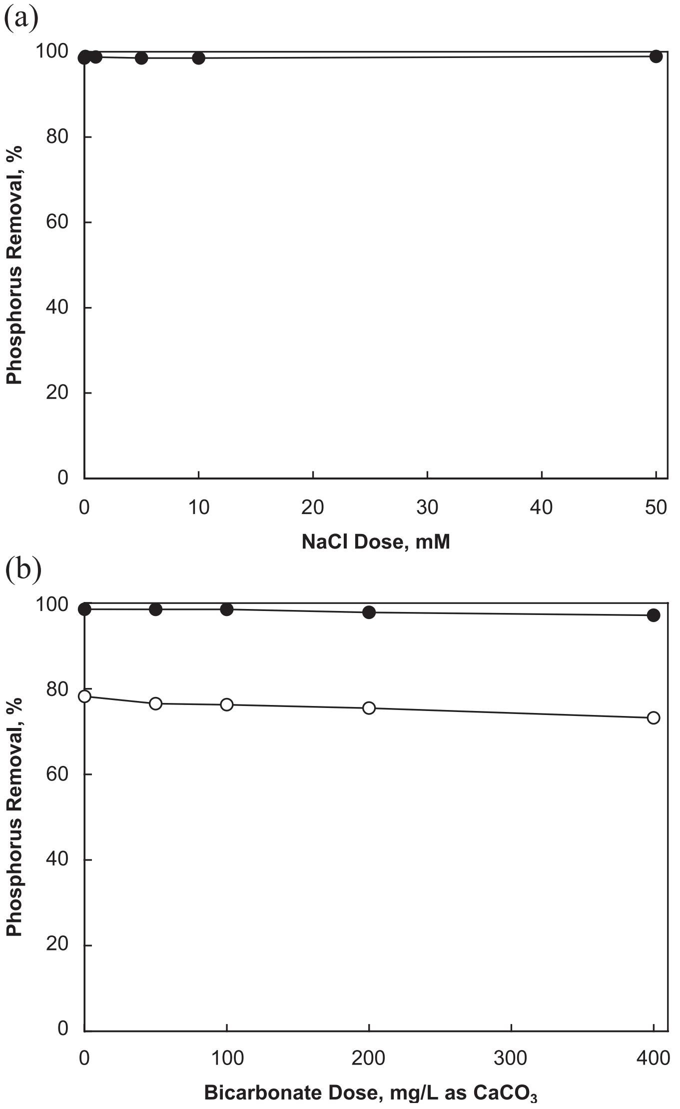

Figure 7. Effect of background inorganic composition on phosphorus removal from secondary effluent (○) with and (●) without additional 2 mg/L P when the experiments were done at neutral pH with a ferryhydrite dose of 100 mg/L. The ionic strength, alkalinity, and hardness of feed solution were changed by the addition of (a) NaCl, (b) $NaHCO_3$, and (c) $CaCl_2$, respectively.

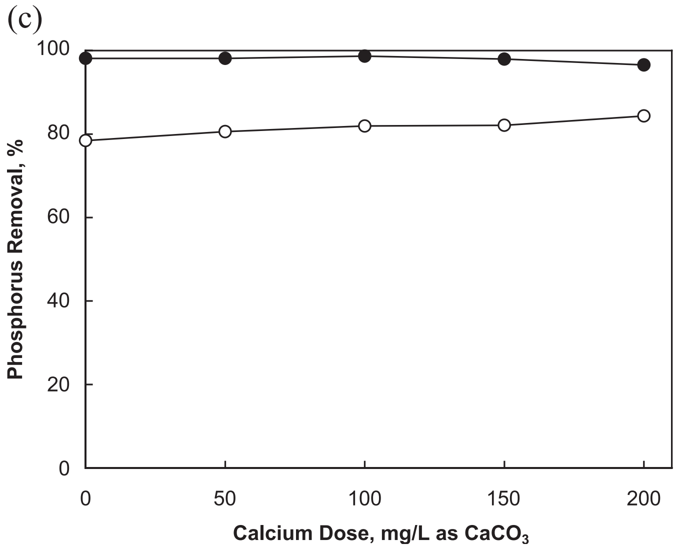

Figure 7. Continued.

salts, alkalinity, and hardness to secondary effluent was examined at neutral pH (Figure 7). When NaCl was added as an inert salt to secondary effluent from 0 to 50 mM (corresponding to 0 to 2292 mg/L), no change in phosphorus removal efficiency was observed, indicating that high ionic strength had no effect on phosphorus removal (see Figure 7a). With the addition of bicarbonate (see Figure 7b) or calcium (see Figure 7c) to secondary effluent, phosphorus removal also remained nearly constant or changed very slightly, without any sign of a significant change in water chemistries. Particularly, however, with the addition of Ca^{2+} further phosphorus removal by chemical precipitation was expected but little additional removal was occurring (see Figure 7c). This could not be clearly explained, but the complex formation of Ca^{2+} with organic matter in secondary effluent might be involved. Further research will be needed on the behavior of Ca^{2+} ions. It could be, thus, found that the change of ionic strength, alkalinity, and hardness in secondary effluent had a minimal effect on phosphorus removal.

Recovery and Regeneration of Used IOPs

Figure 8 shows the adsorptive removal efficiencies of phosphorus using regenerated ferrihydrite and goethite particles recovered by a centrifuge

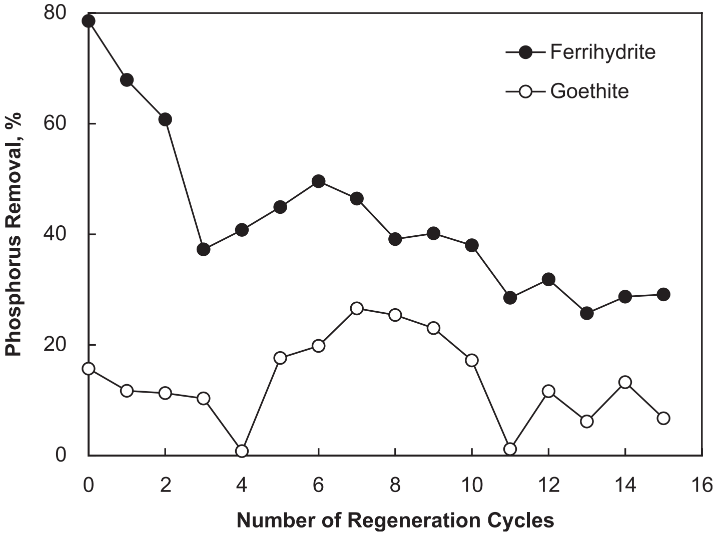

Figure 8. Phosphorus removal efficiencies using new and regenerated IOPs that were recovered by a centrifuge: relative centrifugation force, 2260 *g*; initial IOP dose, 100 mg/L as Fe. Solution pH for IOP adsorption was 7.

during continuous treatment of secondary effluent with additional 2 mg PO_4^{3-}-P/L. Data from the runs using fresh IOPs (which have been regenerated zero times) are shown on the *y* axis. For both IOPs, overall phosphorus removal efficiency appeared to decrease when regenerated particles were used instead of fresh IOPs. In particular, a relatively sharp drop in phosphorus removal was observed with ferrihydrite in the first three regeneration cycles and then a slight, continuous decrease was occurring during the rest of regeneration testing. With goethite, larger fluctuations took place and on occasion, even no phosphorus removal was observed. The concentration of IOPs after finishing ten cycles of regeneration experiments was, on average, about 80% less than the initial concentration. This was probably because of incomplete separation of fine IOPs by centrifugation at alkaline regeneration conditions. In addition, the break-up and resuspension of the IOP pellets obtained after centrifugation might be associated with losses of effective sorption sites of regenerated particles. Based on mass balances of the amount of phosphorus removed and ferrihydrite lost, however, approximately 12.9 mg of phosphorus per g of iron was removed at the last cycle. This could be ascribed to the involvement of other precipitates generated during regeneration, as discussed as follows. Also, the inactivation of regenerated IOPs themselves was not expected.

Another method to separate regenerated IOPs instead of centrifugation needed to be attempted to completely and stably recover the particles that were regenerated at alkaline pH. The recovery of regenerated ferrihydrite was done using an MF membrane and phosphorus removal efficiencies with the regenerated system are shown in Figure 9. The phosphorus removal efficiency increased a bit significantly from 75% to about 100% during the first few regeneration cycles and remained constant at its highest levels during the remainder of the test. This result suggests that there was no inactivation of IOPs during alkaline regeneration. Rather, phosphorus removal was improved in the initial stage of regeneration cycles. This might be attributed to the formation of precipitates, such as dolomite, calcite, and brucite, by the addition of alkaline solution (0.2-N NaOH) during regeneration, which could act as a secondary adsorbent in phosphorus removal. Consequently, IOPs regeneration at alkaline pH and separation by MF membranes can be considered as an efficient method with respect to the recovery and reuse of IOPs. It could be also suggested that the combination of IOP adsorption with MF might be attractive as an alternative for phosphorus removal in advanced treatment.

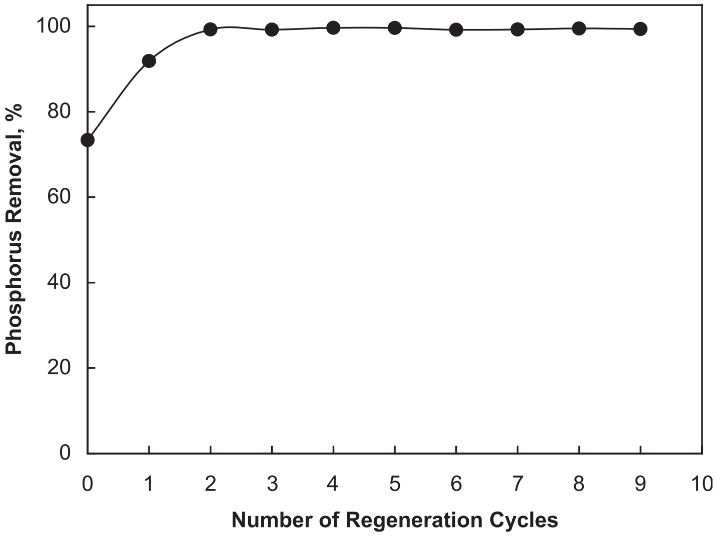

Figure 9. Phosphorus removal efficiencies using new and regenerated ferrihydrite that was recovered by a 0.1-μm MF membrane: initial ferrihydrite dose, 100 mg/L as Fe. Solution pH for IOP adsorption was 7.

Mass balances of the usage of regenerant were performed in the regeneration method using MF. Fifty mL of 0.2-N NaOH was used to regenerate IOPs that had applied for 100 mL of secondary effluent, which corresponds to 4 kg of NaOH applied per 1 m^3 of secondary effluent containing approximately 2.7 g of P. A substantially large amount of NaOH was dosed for rapid regeneration in the laboratory tests and, thereby, the amount of regenerant used per the volume of wastewater treated appears to be large. Since hydroxyl groups in the regenerant should not be exhausted yet, however, the regenerant could be reused and so its usage would be reduced in actual applications, though how much it can be reduced depends on the ligand exchange reaction between hydroxyl groups in the regenerant and adsorbed phosphates.

CONCLUSIONS

Adsorptive removal of phosphorus from secondary wastewater effluent was conducted using different iron oxide particles (IOPs) as new adsorbents under various experimental conditions. The effects of iron oxide types and doses, feed pH, and background species on phosphorus removal were investigated and, particularly, the recovery and regeneration of used IOPs were evaluated using two different regeneration methods. The following conclusions could be drawn:

1. Ferrihydrite played a significant role in phosphorus removal (i.e., $>60\%$ phosphorus was removed even at an IOP dosage of 25 mg/L Fe), showing a relatively large sorption capacity (>5 mg-P/g-Fe) at very low equilibrium phosphorus concentrations as compared to hematite and goethite. This could be attributed to the existence of amorphous layers of a spherical ferrihydrite surface. Thus, ferrihydrite particles can be an effective adsorbent to eliminate residual phosphorus that could not be removed by secondary treatment.
2. For actual secondary effluent, phosphorus removal efficiencies using ferrihydrite were always kept at high levels over the wide pH range of 5 to 12, as opposed to those for synthetic phosphate solution. The unexpected, high phosphorus removal for actual wastewater effluent could be closely associated with the formation of precipitates caused by the interaction of phosphate and carbonate with the calcium and magnesium ions present in the effluent.
3. The reactivity of ferrihydrite with phosphorus at neutral pH seemed not to be affected at all in the presence of a large amount

of inorganic background species, such as inert salts, alkalinity, and even hardness, showing little change in phosphorus removal.

4. The IOPs used for phosphorus removal could be readily regenerated with the exposure of the particles to alkaline solution, and the recovery of regenerated IOPs by MF was more efficient than that by centrifugation, along with the retention of additionally precipitated adsorbing solids. Thus, the combination of IOP adsorption with MF could serve as a potential process to strip away phosphorus in advanced wastewater treatment.

ACKNOWLEDGMENTS

Part of this work was supported by the Daegu University Research Grant (2001). The authors thank Mr. Byung-Chul Choi and Min Lee of the Environmental Management Corporation Gyeongsan District for their help in obtaining wastewater samples. The instrumental analysis assistance provided by the staff of the Center for Laboratory Facilities, Daegu University is appreciated.

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Received August 2002
Revised February 2003

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