

Hydroxyapatite crystallization from a highly concentrated phosphate solution using powdered converter slag as a seed material

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Abstract

A system for recovering phosphorus from membrane-filtrate from a sludge reduction process containing high phosphorus concentrations was developed. In this system, referred to as the completely mixed phosphorus crystallization reactor, powdered converter slag was used as a seed material. In a preliminary experiment, the optimal pH range for metastable crystallization of phosphorus from membrane-filtrate containing about 100 mg/L PO₄-P was found to be 6.6–7.0. The laboratory scale completely mixed phosphorus crystallization reactor, actually operated in pH range of 6.8–7.6 for influent 72.9 mg/L PO₄-P, achieved an average efficiency of phosphorus removal from the membrane-filtrate of 52.4% during a 30-day experiment. Mixed-liquor suspended solids (MLSS) measurements revealed that, out of 0.24 kg PO₄-P in the original membrane-filtrate fed into the reactor, 0.12 kg PO₄-P was recovered on the seed particles after 30 days. X-ray diffraction (XRD) pattern and Fourier transform infrared (FT-IR) spectra of the crystalline material deposited on the seed particles showed peaks consistent with hydroxyapatite. Scanning electron micrograph (SEM) images exhibited that finely distributed crystalline material was formed on the surfaces of seed particles. Energy dispersive X-ray spectroscopy (EDS) mapping analysis revealed that the molar composition ratio of Ca/P of the crystalline material was 1.84. The Ca/P molar ratio > 1.67 for crystalline substance might result from the presence of CaCO₃ on the crystalline surfaces. A particle size distribution analysis showed that the average particle size increased from 22 μm for the original converter slag seed particles, to 94 μm after 30 days of phosphorus crystallization. Collectively, the present results suggest that the proposed phosphorus crystallization recovery system is an effective tool for recycling phosphorus from phosphate solution.

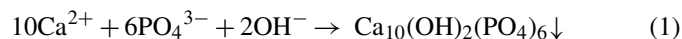
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Keywords: Completely mixed phosphorus crystallization process; Converter slag; Phosphorus recovery; Seed particles; Hydroxyapatite

1. Introduction

The widespread and rapidly increasing consumption of phosphorus-containing materials has substantially depleted phosphorus reserves such as phosphate rock and caused great concern that natural phosphorus reserves may be exhausted in the near future [1,2]. In the search for alternative solutions that would ensure a constant supply of phosphorus, many studies have been carried out on methods for recovering and recycling phosphorus from phosphorus-containing sources such as wastewater. To date, however, no reliable technique has emerged. One recent method that has drawn widespread interest is the phosphorus crystallization process, which has been shown

to be very effective in removing phosphorus from wastewater [3–7]. In this process, crystals of hydroxyapatite (HAP; Ca₁₀(OH)₂(PO₄)₆) are formed on the surfaces of seed particles by the following reaction [8]:



As shown in Eq. (1), the PO₄-P in the aqueous solution phase can be continuously removed from the solution by the crystallization of HAP in the presence of appropriate concentrations of Ca²⁺ and OH⁻, and the crystallized HAP can then be recovered from the surfaces of the seed particles. Hence, this phosphorus crystallization process could potentially be used as the basis for recovering phosphorus from wastewater. In the phosphorus crystallization process, the seed particles can be withdrawn from the crystallization reactor system when they grow to above a certain size, and the removed particles can

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be replaced with new seed material. The recovered material can then be reused as a phosphoric resource of high value. In fact, this principle has already been used in several studies to recover and utilize phosphorus from wastewater [9–11]. Seckler et al. [9,10] performed fundamental research on the removal and recovery of phosphorus using sand as the seed material in a fluidized bed reactor to enhance the phosphorus crystallization reaction. Donnert and Salecker [11] showed that successful removal and recovery of phosphorus could be attained using calcite as the seed material in a concentrated phosphorus solution (>20 mg/L).

Recently, converter slag has been shown to be an efficient seed material for the phosphorus crystallization process. Several studies have shown that relatively low concentrated phosphorus (<5 mg/L) in wastewater can be efficiently retrieved if converter slag is used as the seed material for the phosphorus crystallization process [7,12]. In terms of technical and cost factors, converter slag was found to be a better seed material than similar materials such as sand, phosphate rock, and bone charcoal [7]. Kim et al. [12] demonstrated that phosphorus crystallization process using converter slag as seed material achieved a stable and high phosphorus recovery in relatively low concen-

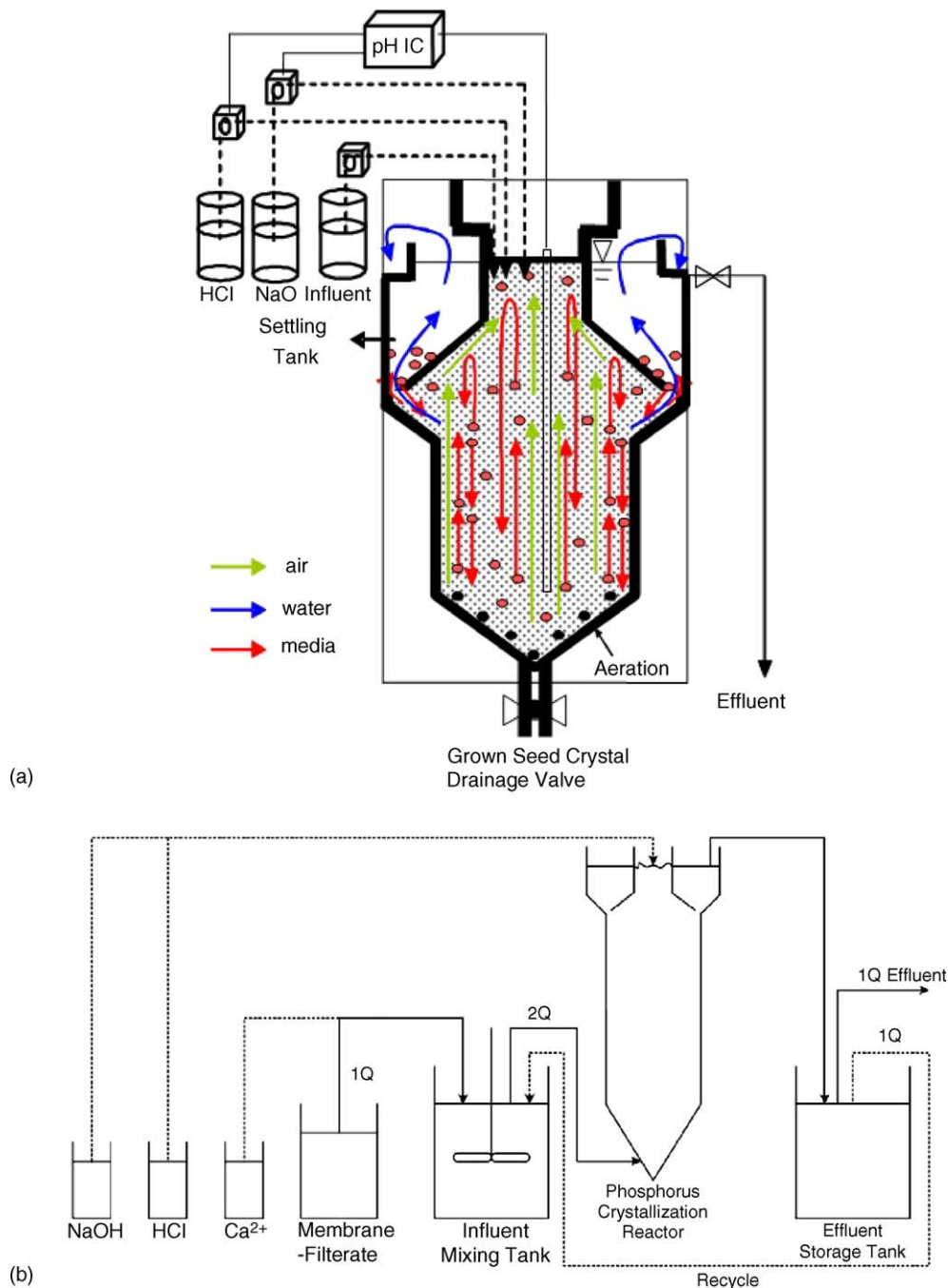


Fig. 1. Schematic diagrams of (a) a completely mixed phosphorus crystallization reactor and (b) a laboratory scale phosphorus crystallization system.

trated phosphate solution (<5 mg/L). Hence, converter slag has the potential to be a highly efficient and cost-effective seed material for phosphorus recovery by the phosphorus crystallization process. To date, however, little research has been conducted on the utilization of converter slag as seed material in phosphorus crystallization process for phosphorus recovery in highly concentrated phosphate solution (>100 mg/L).

In the present study, we sought to develop a new phosphorus recovery system to recycle highly concentrated phosphorus in membrane-filtrate from a sludge reduction process. A completely mixed reactor and converter slag were used in the proposed phosphorus crystallization process for phosphorus recovery, which is referred to as the completely mixed phosphorus crystallization process. The specific objectives of this study were to evaluate the applicability of the new process as a phosphorus recovery system, to investigate the factors influencing the viability of the system, and to qualitatively elucidate the phosphorus crystallization phenomenon in the phosphorus recovery system through microscopic analyses. In addition, preliminary experiments on the solubility and supersolubility curves of calcium phosphates including HAP in highly concentrated phosphorus solution were conducted to find the optimal pH for phosphorus crystallization in the phosphorus recovery system.

2. Materials and methods

2.1. Experimental apparatus

Fig. 1a and b shows schematic diagrams of the completely mixed phosphorus crystallization reactor and phosphorus crystallization recovery system used in the present work, respectively. The reactor is made up of three main parts: the reaction, storage, and upflow settling parts. In the reaction part, powdered converter slag is thoroughly mixed with the membrane-filtrate and HAP crystallization takes place. In the storage part, which is situated in the bottom of reactor, sufficiently grown particles covered in crystalline HAP are separated from the solution. The upflow settling part is included so that minute crystalline particles, which flow upward, are separated in settling compartment and added back into the mixing reactor. Air from the aeration apparatus was used to completely mix the seed particles and membrane-filtrate. Through a valve at the bottom of the reactor, seed particles that have grown to a specified size are discharged before new seed material is added into the reaction part. The pH of the reactor is controlled to be within the optimal range using a pH indicator and controller (pHIC) in order to achieve efficient crystallization. The overall process of the phosphorus recovery system is shown in Fig. 1b. The membrane-filtrate is mixed with a solution of constant Ca^{2+} concentration in the influent mixing tank and then flowed into the phosphorus crystallization reactor. Because the $\text{PO}_4\text{-P}$ concentration in the membrane-filtrate flowed into the reactor is high (>100 mg/L), 1Q of effluent in the effluent storage tank that passed through the phosphorus crystallization reactor is recycled into the influent mixing tank for the purpose of dilution.

Table 1
Water quality of membrane-filtrate

Item	Range	Average
pH	6.8–9.3	8.5
DO (mg/L)	0.3–5.8	3.4
Temperature (°C)	21–29	23.2
COD_{cr} (mg/L)	118–982	850
T-N (mg/L)	68–214	102
$\text{PO}_4\text{-P}$ (mg/L)	82–210	146
Alkalinity (mg/L)	870–2310	1523
Ca^{2+}	13.4–87.5	42.5

2.2. Materials

The converter slag used in this study was obtained from Pohang Iron and Steel Co. Ltd., Pohang, Korea. The converter slag used in the experiments was a powder obtained by sieving through a 200 ASTM mesh sieve (0.015 mm). In this study, membrane-filtered effluent from a membrane bioreactor in a sludge treatment process was used as the highly phosphorus concentrated influent. The water quality of the wastewater is shown in Table 1. The average $\text{PO}_4\text{-P}$ concentration was very high (146 mg/L). The average alkalinity was also very high (1523 mg/L), resulting from the fact that this wastewater was subjected to a sludge treatment process in alkaline solution.

2.3. Experimental methods

Preliminary batch experiments were performed to determine the solubility and supersolubility curves of calcium phosphates including HAP, which were used to find the optimal pH for HAP crystallization in a highly concentrated phosphorus solution. In the experiments to determine the supersolubility curves, the solutions containing supersaturated calcium phosphates were prepared in 500 mL volumetric flasks by using highly concentrated $\text{PO}_4\text{-P}$ and Ca^{2+} with a constant P:Ca concentration ratio of 1:2. The spontaneous precipitation of supersaturated calcium phosphates was observed for pH values in the range of 2–10. The supernatant in the batch reactor was filtered to measure the variation of $\text{PO}_4\text{-P}$ concentrations before and after pH control in the solution with supersaturated calcium phosphates. In the preliminary experiments to determine the solubility curves for calcium phosphates, solutions with saturated calcium phosphates in the metastable zone were prepared and mixed with 1% (w/v) of leached converter slag under various pH conditions to induce the crystallization of calcium phosphates on the surface of the seed material. The solubility curves of calcium phosphates were determined from measurements of the concentration $\text{PO}_4\text{-P}$ remaining in the solution after the crystallization reaction.

Continuous flow experiments were conducted in the completely mixed phosphorus crystallization reactor for 30 days, during which time membrane-filtrate with high phosphorus concentrations was continually fed into the reactor and phosphorus was removed in the form of HAP. Since alkaline conditions can inhibit the phosphorus crystallization reaction, the highly

alkaline membrane-filtrate was passed through a decarbonation process whereby it was aerated in acidic conditions ($\text{pH} \sim 4.5$) before it was flowed into the reactor. In the 30-day experiment, the pH was automatically controlled by pHIC to remain within the metastable zone and Ca^{2+} was continually added into the reactor to maintain a constant Ca^{2+} concentration in the reactor. The Ca^{2+} concentration of the solution added into the reactor was set so that the Ca^{2+} concentration was roughly twice the $\text{PO}_4\text{-P}$ concentration in the reactor, based on the mole ratio of Ca^{2+} to $\text{PO}_4\text{-P}$ in HAP (Eq. (1)). As mentioned above, the amount of converter slag added into the completely mixed phosphorus crystallization reactor was set at 1% w/v. Hydroxide and Ca ions were leached out of the converter slag before it was added into the reactor. The hydraulic reaction time (HRT) of the reactor was 2 h, and water quality was assessed by analyzing pH, Ca^{2+} , $\text{PO}_4\text{-P}$, and mixed-liquor suspended solids (MLSS). The physicochemical properties of the crystallized particles were determined by scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared (FT-IR), and energy dispersive X-ray spectroscopy (EDS). Particle size distribution (PSD) analysis was also conducted to examine the change in size of the crystallized particles.

2.4. Analytical methods

A UV spectrophotometer (Helios α , Unicam, UK) was used to determine the phosphorus concentrations in solutions using the ascorbic acid standard method [13]. The calcium and alkalinity concentrations were measured by the chelate standard method and titration method, respectively [13]. X-ray and FT-IR measurements were conducted using a Rigaku D/Max X-ray diffractometer (Japan) and a Thermo Nicolet Nexus 670 spectrometer (USA), respectively. The microstructures of the seed particles were examined by SEM using a Voyager microscope (USA) equipped with EDS (Hitach Co., S-2500C, Japan). The change in the size of the seed particles was analyzed by PSD using a Coulter LS230 particle size analyzer (USA).

3. Results and discussion

3.1. Preliminary experiment

This study examined the solubility and supersolubility curves of calcium phosphates including HAP to identify the pH condition that was optimal for phosphorus crystallization in solutions containing high phosphorus concentrations. The metastable zone for calcium phosphate crystallization, which was attained in the batch experiments, is shown in Fig. 2. As shown in Fig. 2, the supersolubility curve dividing the unstable and metastable zones tends toward lower pH as the phosphorus concentration is increased. Given that the average $\text{PO}_4\text{-P}$ content of the membrane-filtrate used in the present study was 72.9 mg/L, the optimal pH range for the HAP crystallization was pH 6.6–7.0. This pH range is very different from the optimal pH range of 8.0–9.5 for HAP crystallization at low phosphorus concentrations (<5 mg/L).

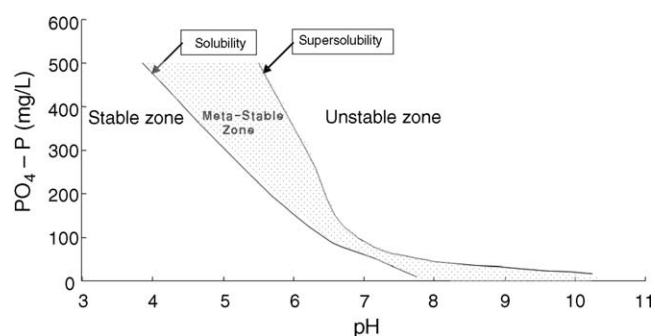


Fig. 2. Metastable zone for calcium phosphate crystallization according to pH and phosphorus concentration.

3.2. Removal and recovery of $\text{PO}_4\text{-P}$ by phosphorus crystallization

3.2.1. Variation of pH and Ca^{2+} concentration

The operational influent pH range in the phosphorus crystallization reactor was set to 6.6–7.0, which corresponds to the metastable zone for HAP crystallization in the system studied. Fig. 3a shows the variation over time of the pH of the wastewater flowing into and out of the phosphorus crystallization reactor.

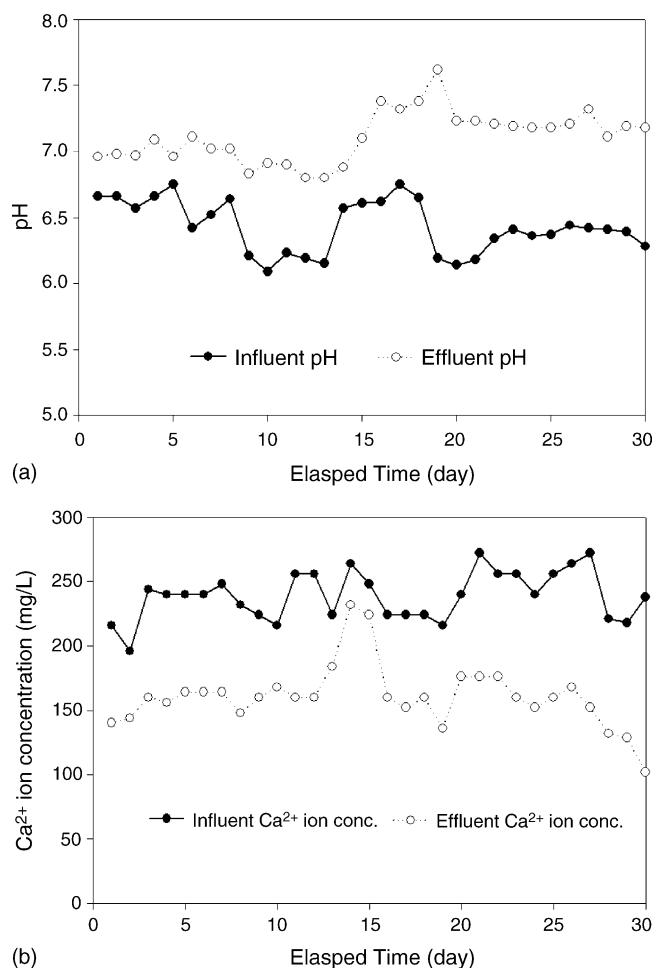


Fig. 3. Variation of (a) pH and (b) Ca^{2+} as a function of time.

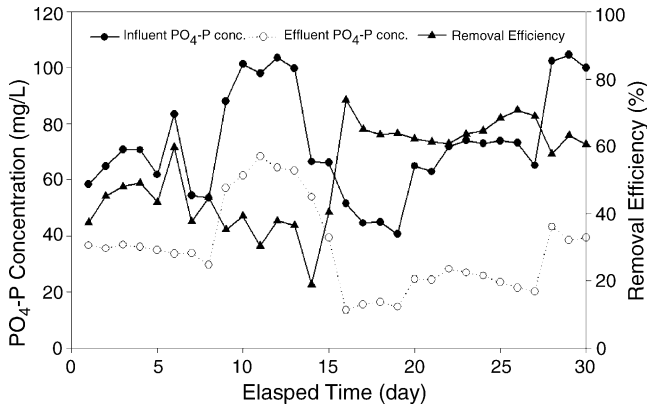


Fig. 4. Variation of PO₄-P and phosphorus removal efficiency as a function of time.

The pH of the effluent ranged from 6.8 to 7.6, indicating that the actual operational pH range in the phosphorus crystallization reactor was slightly higher than influent pH range. The difference between influent and effluent pH ranges might result from hydroxide leached from converter slag. Fig. 3b shows the time evolution of the concentration of Ca²⁺ during the 30-day run. The concentration of Ca²⁺ in the effluent flowing out of the

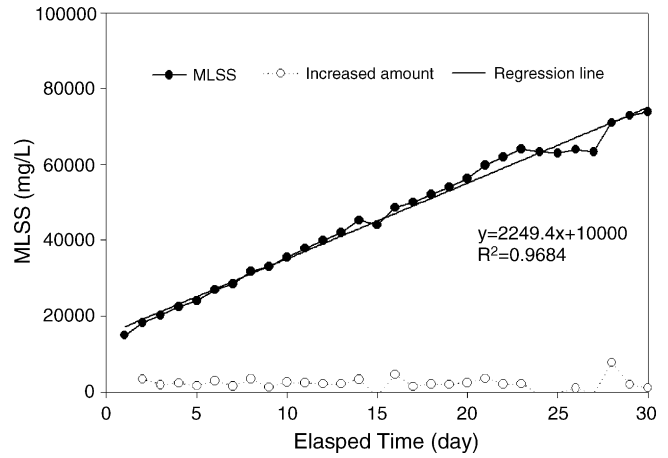


Fig. 5. Variation of MLSS as a function of time.

reactor remained almost constant over time, similar to the case of pH.

3.2.2. Efficiencies and characteristics of PO₄-P removal

Fig. 4 shows the variation over time of the PO₄-P concentrations in the influent and effluent of the reactor, as well as the time

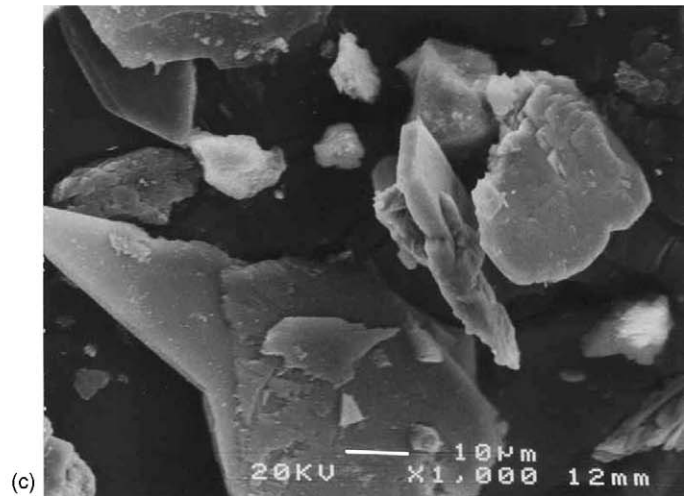
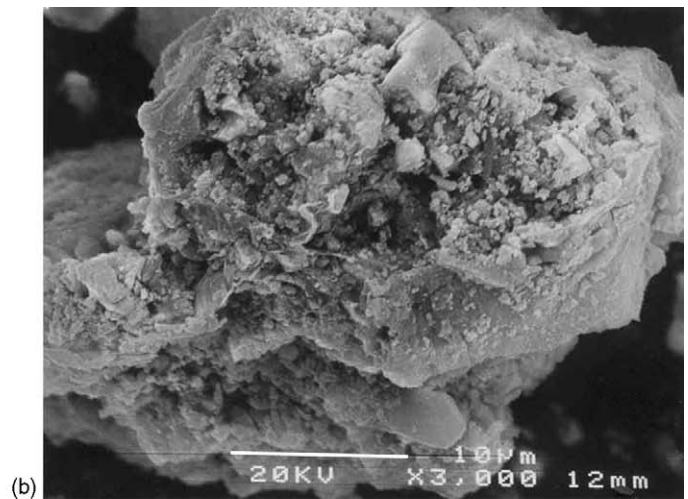
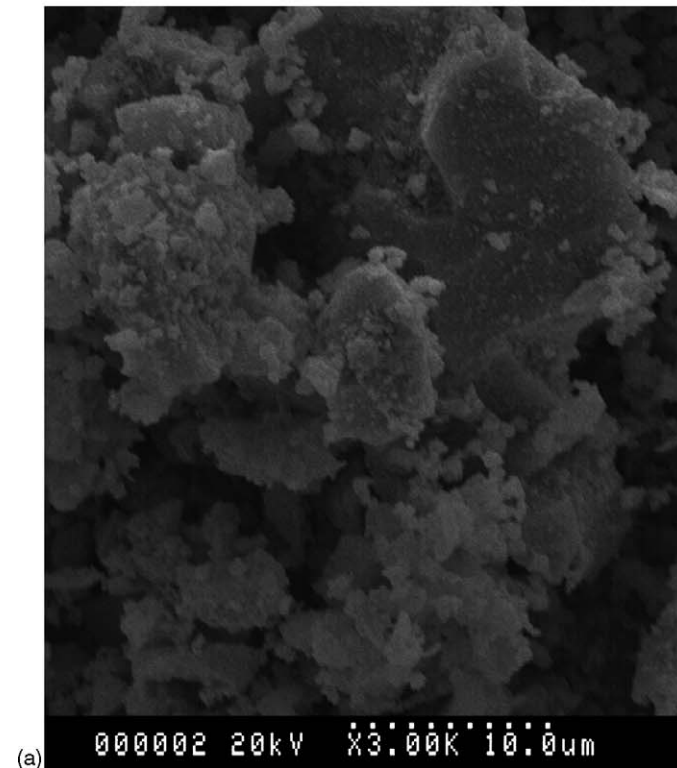


Fig. 6. SEM photographs of powdered converter slag (a) before and (b) after leaching, and (c) after 30 days of phosphorus crystallization.

evolution of the $\text{PO}_4\text{-P}$ removal efficiency. The average $\text{PO}_4\text{-P}$ concentrations of the solutions flowing into and out of the reactor were 72.9 and 35.4 mg/L, respectively, corresponding to an average $\text{PO}_4\text{-P}$ removal efficiency of 52.4% at temperature range of 19–22 °C during the 30-day experimental period. On days 8 and 15, the phosphorus removal efficiency was lower than the average, ranging from 30% to 45%. This result might be due to the fact that, on these days, the reactor influent pH was 6.1–6.4, which lies slightly lower than the optimal pH range of 6.6–7.0, while the concentration of $\text{PO}_4\text{-P}$ flowing into the reactor was high. When the pH was between 6.4 and 6.8, the $\text{PO}_4\text{-P}$ removal efficiency increased to 70.1%, indicating that the pH range of 6.4–6.8 was more appropriate for the concentration of $\text{PO}_4\text{-P}$ flowing into the reactor. This result emphasizes the important role played by pH at the adjacent region to supersolubility curve of HAP in the phosphorus crystallization reaction in a phosphorus recovery system.

3.2.3. Variation of MLSS concentration

To analyze the amount of phosphorus recovered in the form of HAP deposited on the surfaces of the seed particles, we measured the MLSS concentration of the seed particles in the reactor as a function of time. There was no withdrawal of seed particles from the reactor during the 30-day experimental period. Fig. 5 shows the time evolution of the MLSS concentration in the reactor. Since the converter slag was added at a concentration of 1% (w/v) to the reactor at the beginning of the run, the MLSS started at 10,000 mg/L. By the end of the 30-day run, it had increased to 73,940 mg/L; thus, the MLSS concentration of seed particles in the reactor increased by 2033 mg/L per day on average. During the 30-day experimental period, a total of 0.24 kg of $\text{PO}_4\text{-P}$ was fed into the system in the membrane-filtrate, and a total of 0.12 kg of $\text{PO}_4\text{-P}$ was removed in the form of HAP on the seed particles.

3.3. Microscopic analyses

SEM, XRD, FT-IR, and EDS analyses were conducted to investigate the physicochemical properties of the seed particles before and after HAP crystallization in the completely mixed phosphorus crystallization reactor. Additionally, the change over time in the size of the seed particles was analyzed using a PSD analyzer.

3.3.1. SEM analysis

The surfaces of the seed particles before and after HAP crystallization were examined by SEM. Fig. 6a and b shows SEM micrographs of the converter slag before and after leaching in aqueous solution. Comparison of these micrographs indicates that leaching caused the surface of the converter slag to become rougher. This can be attributed to the Ca^{2+} and OH^- ions erupting from the surface during leaching. Fig. 6c shows a SEM micrograph of the converter slag after 30 days in the completely mixed phosphorus crystallization reactor. The micrograph shows that the converter slag is covered with a finely distributed crystalline substance. The results of the XRD, FT-IR, and EDS analyses, presented

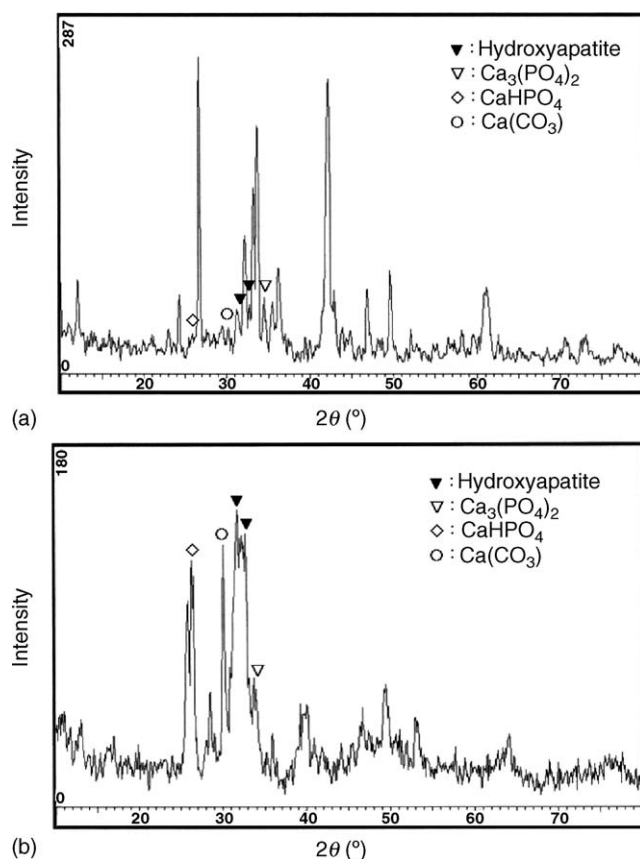


Fig. 7. X-Ray diffraction diagrams for the seed particles (a) before and (b) after 30 days of phosphorus crystallization.

below, indicate that a principal ingredient of this substance is HAP.

3.3.2. XRD analysis

XRD analysis was conducted to investigate the variation in the crystal structure of the material deposited on the converter slag during the phosphorus crystallization reaction. The XRD analysis was performed over a 2θ range of 0–80°, which encompasses the angles of 31.7° and 32.9° at which features are observed for crystalline HAP. Fig. 7a and b shows the XRD

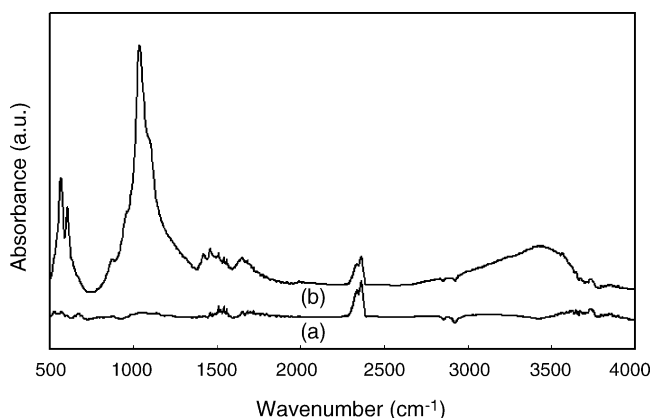


Fig. 8. FT-IR spectra of seed particles (a) before and (b) after 30 days of phosphorus crystallization.

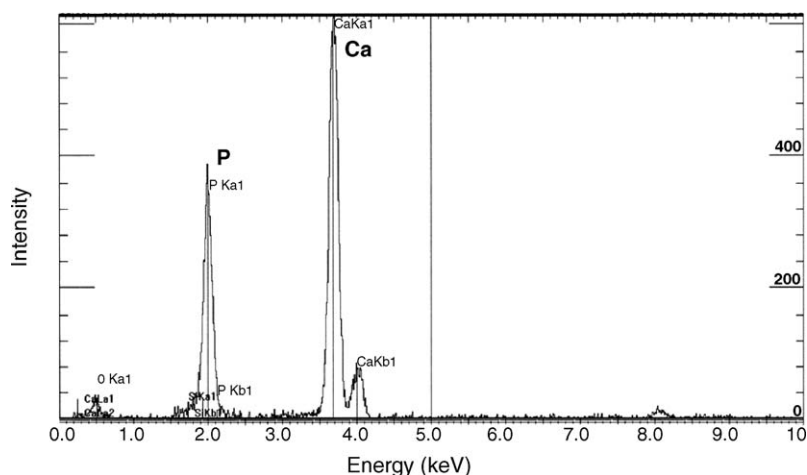


Fig. 9. EDS mapping analysis graph of seed particles after 30 days of phosphorus crystallization.

patterns for the seed particles before and after 30 days of the phosphorus crystallization reaction, respectively. Comparison of Fig. 7a and b shows the appearance of two sharp and intense peaks characteristic of HAP ($2\theta = 31.7^\circ$ and 32.9°) after HAP crystallization. This XRD result suggests that growth of crystalline HAP on the seed particles causes the amount of order in the particles to increase as the phosphorus crystallization reaction progresses.

In addition to HAP, the presence of calcium phosphate compounds such as tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$) and calcium hydrogen phosphate (CaHPO_4) was observed at the angles of 30.7° and 26.5° in the XRD patterns of Fig. 7b. The formation of $\text{Ca}_3(\text{PO}_4)_2$ and CaHPO_4 on crystalline surfaces in HAP crystallization reaction could be explained by the Oswald step rule, which postulates that the precipitate with the highest solubility will form first in a consecutive precipitation reaction [14]. In other words, the HAP crystallization make progress via precursors or intermediates such as $\text{Ca}_3(\text{PO}_4)_2$ and CaHPO_4 , which have more soluble phase than HAP. Zoltek [8] demonstrated that the HAP crystallization could be attained through intermediate phase by conforming to the Ostwald step rule. Meanwhile, calcium carbonate (CaCO_3) was also detected at the angle of 30.0° in Fig. 7b. The appearance of CaCO_3 in the XRD patterns might be attributed to co-crystallization of calcium carbonate due to the carbonate alkalinity in membrane-filtrate wastewater.

3.3.3. FT-IR analysis

The FT-IR spectra of the seed particles before and after 30 days of phosphorus crystallization are depicted in Fig. 8a and b, respectively. For the seed particles after phosphorus crystallization reaction, the FT-IR spectra in Fig. 8b exhibited sharp peaks at 565 , 604 , and 1036 cm^{-1} (corresponding to the PO_4^{3-} vibrations) and a shoulder of the broad band at 3442 cm^{-1} (corresponding to the OH^- vibration), which correspond to the characteristic bands of HAP. However, the presence of calcium phosphate compounds such as tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$) and calcium hydrogen phosphate (CaHPO_4) was not distinctly observed in the FT-IR spectra of Fig. 8b while they were detected in the XRD patterns of Fig. 7b. Hence, the

results of FT-IR and XRD analyses suggest that the phosphorus in membrane-filtrate wastewater might be eliminated mainly by HAP crystallization although the phosphorus on the surfaces of seed particles can be crystallized partly as several types of calcium phosphates. In addition, the CO_3^{2-} bands were observed around 1421 and 1458 cm^{-1} in Fig. 8b.

3.3.4. EDS mapping analysis

An EDS mapping analysis was performed to determine the chemical composition of the crystalline substance formed on the surface of seed particles. Fig. 9 shows the result of the EDS mapping analysis on the surface of the particles after phosphorus crystallization. The EDS mapping analysis revealed that the crystalline surface consisted predominantly of Ca and P, with a molar ratio of Ca to P (Ca/P) of 1.84, which is slightly higher than a theoretical Ca/P molar ratio of 1.67 for HAP. The Ca/P molar ratio > 1.67 found in the present work might result from the presence of CaCO_3 on the surfaces of seed particles, which was confirmed in XRD and FT-IR analyses. The increment of Ca^{2+} composition due to presence of CaCO_3^{2-} , which substitutes the sites for the HAP crystallization, can lead to the Ca/P molar ratio > 1.67 . These similar phenomena were observed in the experiments for production of HAP powder performed by several researchers. Donadel et al. [15] reported that the Ca/P molar ratio could increase up to 1.85 due to the transform of CO_3^{2-} to CaCO_3 in the production procedure of HAP powder using wet-chemical methods. Ning et al. [16] and Ślósarczyk et al. [17] also demonstrated the Ca/P > 1.67 could be obtained because of carbonate alkalinity in production of HAP substance.

3.3.5. PSD analysis

The converter slag seed particles are expected to increase in size as the phosphorus crystallization reaction proceeds. PSD analysis was conducted to investigate the change in size of the particles as a function of time. As illustrated in Fig. 10, the average initial particle size (corresponding to 50% cumulative finer mass percent) of the powdered converter slag, which had been passed through a 200 ASTM mesh sieve, was $22\ \mu\text{m}$. After 16 and 30 days in the phosphorus crystallization reactor, the aver-

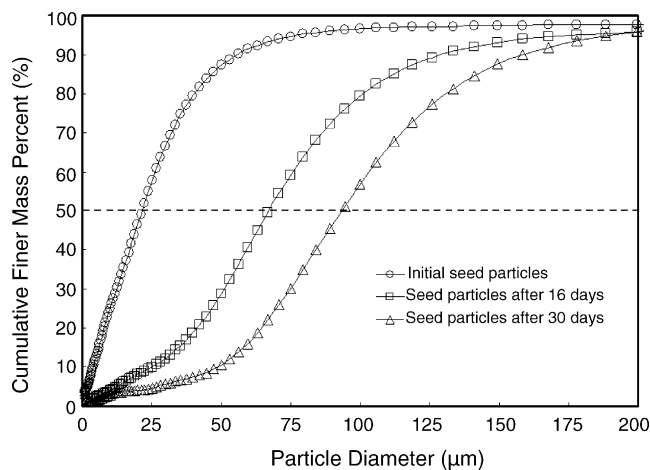


Fig. 10. Variation of particle size distribution of seed particles before and after 16 and 30 days of phosphorus crystallization.

age particle size had increased to 67 and 94 μm , respectively. In addition, 87.3% of the initial converter slag particles were under 50 μm in size, whereas only 28.8% and 10.6% of particles were in this size range after 16 and 30 days, respectively. The increase in the size of the original seed particles during the experimental period indicates that the highly concentrated phosphorus in the completely mixed phosphorus crystallization reactor is recovered in the form of HAP deposited on the surfaces of seed particles.

4. Conclusion

A phosphorus recovery system, referred to as the completely mixed phosphorus crystallization process, was developed to remove and recover the highly concentrated phosphates in membrane-filtrate from a sludge reduction process by using a powdered converter slag as the seed material. By using solubility and supersolubility curves for calcium phosphates including HAP, the optimal metastable zone of pH for the membrane-filtrate wastewater, which contained 72.9 mg/L $\text{PO}_4\text{-P}$ on the average, was found to be 6.6–7.0. The average $\text{PO}_4\text{-P}$ removal efficiency of the phosphorus recovery system for this membrane-filtrate wastewater was 52.4% over 30 days. The MLSS concentration of seed particles in the completely mixed reactor increased by 2033 mg/L a day on average, indicating that 0.12 kg out of the total of 0.24 kg phosphorus flowing into the reactor was recovered on the surface of seed particles in the form of HAP. A SEM study showed that the surfaces of the converter slag particles were coated with a large amount of crystalline material, which was conjectured to be HAP. An XRD and FT-IR analysis supported this conjecture. The Ca/P molar ratio > 1.67 found in the EDS mapping analysis might be attributed to the presence of CaCO_3 on the surfaces of seed particles. PSD analysis showed that the seed particles increased in size from an average particle size of 22 μm for the raw converter slag powder, to 67

and 94 μm after 16 and 30 days in the phosphorus crystallization reactor, respectively. The results of this study suggest that the completely mixed phosphorus crystallization process with converter slag as seed material is a very promising technique for efficiently removing and recovering phosphorus from highly concentrated phosphorus solutions.

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