Application of the hydroxyapatite crystallization-filtration process to recover phosphorus from wastewater effluents

Hyangyoun Chang, Nari Park, Yeoju Jang, Hyunman Lim and Weonjae Kim

ABSTRACT

Phosphorus crystallization-filtration (PCF) was devised as a novel tertiary process for phosphorus removal from domestic wastewater. The results obtained showed that during the PCF process, high pH and excessive calcium dosage conditions were required to obtain effluents with total phosphorus (T-P) and suspended solid (SS) concentrations below 0.2 and 10 mg/L, respectively, within 2 h of operation. Phosphorus was precipitated during the pre-treatment step, and thereafter it crystallized on the surface of the fixed seed material in the PCF reactor. Furthermore, the addition of Ca^{2+} resulted in phosphorus removal efficiencies >95%, and pH, residual Ca^{2+}, filtration depth, and linear velocity were identified as the main design and operation parameters of the PCF process. Following the pilot-scale PCF process, the average concentrations of T-P, PO_4-P, and SS in the effluent were 0.05, 0.04, and 1.1 mg/L, respectively, corresponding to removal efficiencies of 90.9, 86.5, and 79.7%, respectively. The investigation of the backwashing sludge characteristics of the PCF process using scanning electron microscopy (SEM), Fourier transform-infrared vacuum spectrometry (FT-IR), energy dispersive X-ray spectroscopy (EDS), and X-ray diffraction (XRD) analyses showed that owing to its high contents in calcite and hydrated phosphorus compounds, PCF sludge could be used as an alternative soil amendment resource.

Key words | calcite, crystallization-filtration, hydroxyapatite, phosphorus, soil amendment, wastewater

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HIGHLIGHTS

- Phosphorus crystallization-filtration (PCF) was devised as a novel tertiary process for phosphorus removal from domestic wastewater.
- The investigation of the backwashing sludge characteristics showed high contents in calcite and hydrated phosphorus compounds.
- PCF sludge could be used as an alternative soil amendment resource.

INTRODUCTION

In Korea, cyanobacterial algal blooms represent one of the major issues associated with lakes and rivers during all summer seasons. The primary substance responsible for this excessive growth of aquatic organisms is phosphorus, originating from wastewater treatment plants (WWTPs) and croplands. Kim *et al.* (2007) demonstrated that with respect to algal growth, phosphorus is a more important nutrient than nitrogen. They also stated that in Korean lakes and rivers, algal growth was controlled by phosphorus loads. To prevent eutrophication and algal bloom, the management of the phosphorus content of domestic wastewater is essential before its discharge (Bashan & Bashan 2004; Bal Krishna *et al.* 2016). Thus, in Korea, the total phosphorus (T-P) content of domestic wastewater effluent has been regulated under 0.2 mg/L in water resource conservation areas.

In domestic WWTPs, after the preliminary biological treatment followed by the secondary sedimentation process, the tertiary phosphorus removal process is performed. The most extensively used tertiary phosphorus removal process is coagulation, which is performed alongside sedimentation, filtration, or flotation. However, owing to relatively high variations in pollutant loads and flow rates, such tertiary phosphorus removal processes cannot be integrated into most small-scale WWTPs that are used to treat less than 500 m^3 of influent per day (Lee *et al.* 2004). Owing to the unstable water quality as well as the varying quantity of influents that is characteristic of WWTPs in small agricultural villages, controlling the dosage of the coagulant required remains challenging. Additionally, coagulation-based processes generate large amounts of sludge, and their phosphorus recovery performance is very poor.

Therefore, to overcome the limitations associated with coagulation-based processes, new phosphorus removal processes are required. Deliyanni *et al.* (2007), Berg *et al.* (2006), Kim *et al.* (2006), and Joko (1985) reported that hydroxyapatite (HAP, Ca$_5$(PO$_4$)$_3$OH) crystallization is a plausible alternative for the removal and recovery of phosphorus from wastewater. HAP crystallization involves the removal of phosphorus from wastewater in the form of HAP; that is, HAP is grown and recovered on the surface of seed crystals via the crystallization of phosphate, calcium, and hydroxyl ions under relatively high pH conditions. HAP growth as well as the associated phosphorus removal efficiency are affected by several reaction conditions, including pH, temperature, and the concentrations of phosphate, calcium, and bicarbonate ions. The quality of the recovered sludge, including purity, morphology, and particle distribution, is also affected by the Ca/P ratio, temperature, pH, ion concentrations, mixing conditions, as well as the sedimentation time of the crystallization process (Al-Harahsheh *et al.* 2014; Cichy *et al.* 2019). The equation for reaction that brings about HAP growth is as follows (Nancollas 1968):

$$3PO_4^{3-} + 5Ca^{2+} + OH^- \rightarrow Ca_5(PO_4)_3OH \qquad (1)$$
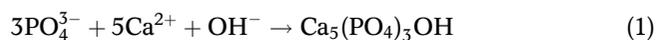
Furthermore, calcite (Song *et al.* 2001), sand (Momberg & Oellermann 1992), cow bone (Jang & Kang 2002), tobermorite (Moriyama *et al.* 2001, 2003), xonotlite (Chen *et al.* 2009), and porous calcium silicate hydrate (PCSH) (Guan *et al.* 2014) have been suggested as seed crystals for the crystallization process. Usually, seed crystals for HAP crystallization are calcium-based materials that are characterized by high surface areas. Based on laboratory-scale experiments, several studies have reported the use of calcite in phosphorus removal; thus, it is considered one of the most promising materials for use as HAP seed crystals (Ishikawa & Ichikuni 1981; Song *et al.* 2001, 2006; Liu *et al.* 2012).

To achieve high phosphorus removal efficiency within a short operation time, high pH conditions and excessive Ca^{2+} dosage are required (Momberg & Oellermann 1992; Chen *et al.* 2009; Menglin *et al.* 2016; Cichy *et al.* 2019). Most laboratory-scale phosphorus removal experiments with artificial wastewater using HAP crystallization have shown that phosphorus removal to concentrations below 1.0 mg/L (PO$_4$-P) could not be achieved. In a study conducted by Momberg & Oellermann (1992), under high pH conditions, an effluent phosphate concentration below 1.0 mg/L was achieved; however, the phosphate concentration did not remain below this threshold owing to the use of a fluidized sand media as seed crystals. Conversely, Donnert & Salecker (1999) reported that calcite can be used as seed material to achieve a stable phosphorus removal efficiency in both pilot- and full-scale industrial WWTPs without replacement for several years. They found that the average PO$_4$-P concentrations in the effluent from the pilot- and full-scale industrial WWTPs were 1.3 and 1.1 mg/L, respectively. Based on regulatory standards, to apply calcite as seed crystal in the tertiary removal of phosphorus from Korean domestic wastewater, it is required that phosphorus should be removed within a short operation time such that its concentration in the effluent is below 0.2 mg/L. Additionally, the removal of suspended solids (SS) is also necessary.

The phosphorus crystallization-filtration (PCF) process could generate sludge containing calcite and phosphorus compounds under conditions of high Ca^{2+} and dissolved carbonate concentrations. Calcite and limestone powder are commonly used as soil amendment to neutralize acidic soils (Tozsin *et al.* 2014). Additionally, it has been estimated that in 100 years, phosphate resources will be depleted given that phosphorus is greatly consumed in the form of agricultural fertilizers (Woods *et al.* 1999). However, studies on phosphorus recovery technologies utilizing Ca-P crystallization in secondary treated effluents are scarce owing to their low recovery potential (Cordell *et al.* 2011; Egle *et al.* 2015).

In this study, the PCF process is presented as a novel tertiary process for the removal of phosphorus from domestic wastewater. The PCF process was designed to achieve an effluent T-P concentration less than 0.2 mg/L and also remove SS to concentrations below 10 mg/L within 2 h of operation. In the PCF reactor, Ca^{2+} and pH conditions were controlled during the pre-treatment step, and subsequently, HAP crystals were precipitated and crystallized

on the surface of fixed seed calcite sands, while allowing for sufficient contact time. The discharged sludge from the PCF reactor containing calcite and phosphorus compounds could then be recycled or upcycled as a valuable resource.

Thus, to simulate the PCF process, cylindrical column tests were performed with operation parameters, including pH, additional Ca^{2+} dosage, and linear velocity. The design and operational parameters of PCF are suggested from the results of column tests. Finally, the pilot-scale PCF process was conducted. Furthermore, the sludge characteristics of PCF were evaluated for application as an alternative soil amendment resource for acidic soil neutralization.

MATERIALS AND METHODS

Laboratory-scale cylindrical column tests

To simulate the PCF process, cylindrical column tests (Figure 1) were performed using the effluents from a secondary sedimentation basin. The column had a diameter of 5 cm, a filtration depth of 1.4 m, and a volume of 2 L. Samples were collected from the column at 0.2 m intervals for analysis. The average diameter of the limestone sand, which was packed into two serial columns, was 2.0–3.0 mm. The influent water had the following characteristics: pH, 6.4–7.2; Ca^{2+}, 25.7–32.4 mg/L; T-P, 0.6–2.4 mg/L; and PO_4-P, 0.3–1.5 mg. Table 1 shows the experimental conditions of the column tests. To supply Ca^{2+} and OH^- and obtain pH values between 10 and 11, the effluent of the secondary sedimentation basin was pre-treated using 20% of $Ca(OH)_2$. After the addition of 50 mg/L of Ca^{2+} using a 25% $CaCl_2$ solution, the secondary sedimentation

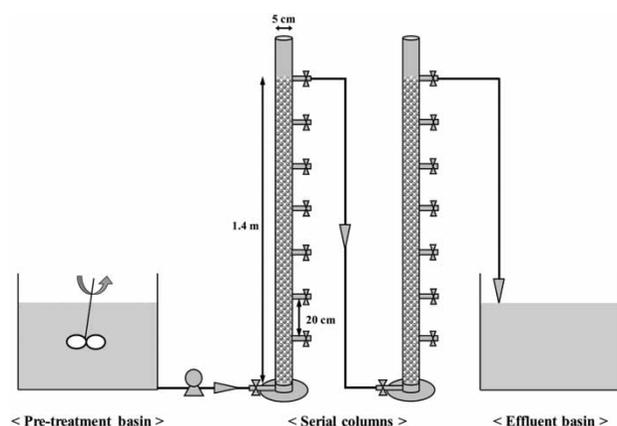**Table 1** | Experimental conditions of column experiments

| Test no. | Condition | | |
	pH	Ca²⁺ addition (mg/L)	Linear velocity (m/hr)
1	10.0	0	2.0
2	10.0	50	2.0
3	11.0		2.0
4	10.0		5.0
5	10.0		10.0

basin effluent was filtered through a 2.8 m depth of two serial columns under 2.0, 5.0, and 10.0 m/h linear velocity conditions.

Pilot-scale operation

A pilot PCF process plant was constructed at Ilsan Wastewater Treatment Center as shown in Figure 2. The plant consisted of a pre-treatment basin (A), a PCF reactor (B), and a post-treatment basin (C). The pre-treatment and post-treatment basins both had volumes of 1.0 m³, and the PCF reactor had the following specifications: diameter, 1.2 m; depth, 3.0 m; volume, 3.5 m³; moreover, it was filled with limestone (2.0–3.0 mm diameter) as seed material.

The operating conditions of the pilot PCF plant from June 2018 to September 2018 are shown in Table 2. The pre-treatment pH was adjusted to 10.5 ± 0.3 using 20% $Ca(OH)_2$. More Ca^{2+} was added to reach a residual value >80 mg/L using 25% $CaCl_2$ solution. The operating linear velocity of the reactor was 1.9 m/h (i.e. a flow rate of 50.4 m³/day). The quality of the raw water that was fed into the reactor was as shown in Table 3.

Characterization of PCF sludge

To evaluate the performance of the recycling process, the precipitated and filtered sludge samples obtained after the PCF process were analyzed. The pH was controlled in the range 10.5–10.8, and more Ca^{2+} (100 mg/L) was added. The initial PO_4-P concentrations in the experiments were 0.16, 2.0, 10.0, and 50.0 mg/L. Using a centrifugal separator, the sludge samples were separated from the effluent and dried at 50 °C.

Thereafter, scanning electron microscopy (SEM, S-4800, HITACHI), energy dispersive X-ray spectroscopy (EDS, EDX S-10, Oxford), X-ray diffraction (XRD, MiniFlex600, Rigaku), and Fourier transform-infrared vacuum spectrometry (FT-IR, VERTEX 80 V, Bruker) were employed to
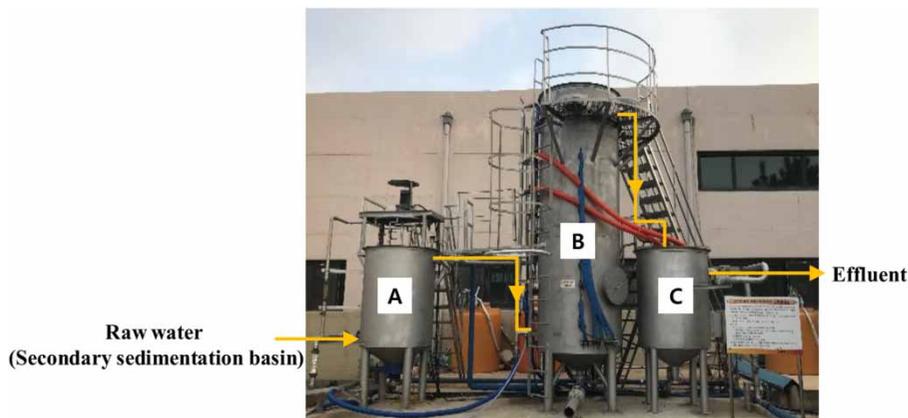

Figure 1 | Schematic diagram of column experiments for the PCF process.

Figure 2 │ Pilot PCF process plant in the Il-san Wastewater Treatment Center (50.4 m³/day).

Table 2 │ Operating conditions of PCF pilot plant

Operating condition	Specification/value
Filtration depth	2.5 m
Media	Limestone sand (2.0–3.0 mm)
Flow rate	50.4 m³/day (L.V. 1.9 m/h)
pH	10.6 ± 0.3 (20% $Ca(OH)_2$)
Residual Ca^{2+}	>80 mg/L (25% $CaCl_2$)

Table 3 │ Raw water quality of PCF pilot plant

Water quality parameter	Value (average)
Water temperature (°C)	25.2–33.5 (29.4)
pH	6.4–7.0 (6.8)
T-alkalinity (mg/L as $CaCO_3$)	43.9–127.7 (84.0)
T-P (mg/L)	0.23–1.09 (0.61)
PO_4-P (mg/L)	0.07–1.04 (0.43)
Ca^{2+} (mg/L)	21.9–34.2 (26.0)
Conductivity (μS/cm)	363–607 (543)
SS (mg/L)	0–77 (13.2)

determine the chemical composition of the PCF sludge samples.

RESULTS AND DISCUSSION

Laboratory-scale cylindrical column experiments

During the pre-treatment step, $Ca(OH)_2$ released Ca^{2+} and OH^- ions. As shown in Figure 3, pH values increased from 7.0 to 10.0, and then to 11.0. Owing to $Ca(OH)_2$ supplementation, Ca^{2+} concentration increased to ~30 mg/L at a pH of 10.0 and 50 mg/L at a pH of 11.0, as shown in Figure 4. For
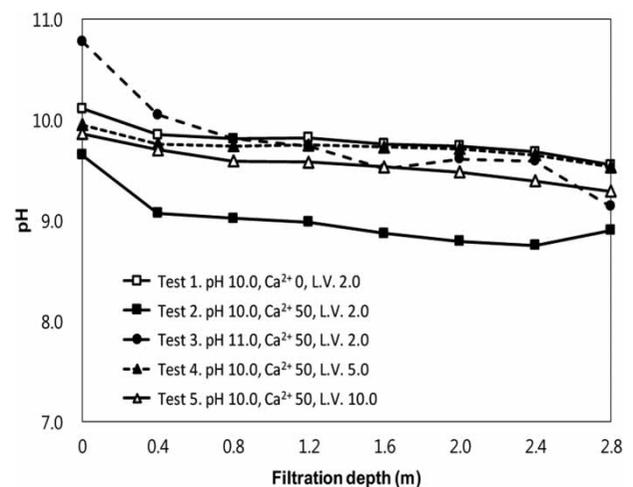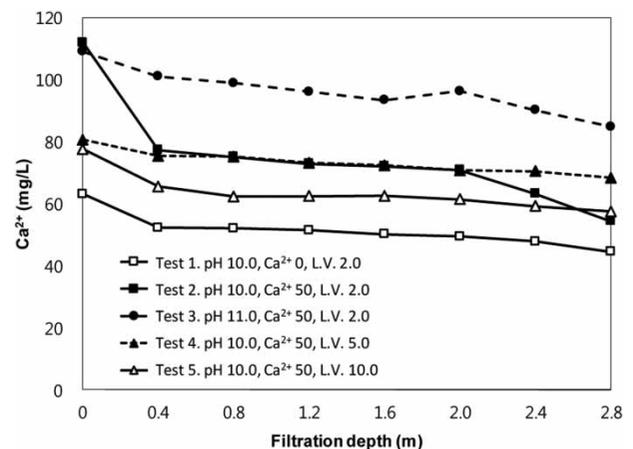

Figure 3 │ pH variation with filtration depth.

Figure 4 │ Ca^{2+} variation with filtration depth.

tests 2–5, Ca^{2+} concentration was increased to ~50 mg/L via the addition of more $CaCl_2$. Within a filtration depth of 0.4 m, there was a rapid decrease in both pH and Ca^{2+} concentration. Beyond 0.4 m, both quantities decreased generally, depending on the conditions associated with the different filtration depths. Under high pH conditions and low linear velocity, the decrease in pH was higher than that observed under lower pH or higher linear velocity conditions. This implied that a higher pH and a lower linear velocity favored the rapid consumption of OH^- and CO_3^{2-}. Additionally, higher phosphorus removal and calcite regeneration were expected under these conditions than under low pH and high linear velocity conditions.

The variations of T-P and PO_4-P with depth are shown in Figures 5 and 6, respectively. There were two steps for phosphorus removal. Firstly, approximately 30–60% of T-P and PO_4-P removal efficiencies were achieved via precipitation under the high pH condition of the pre-treatment step. In the case of test 2, in which the initial Ca^{2+} dosage was higher than in the other tests, more phosphorus was removed during the pretreatment step than under other conditions.

Secondly, phosphorus was gradually removed via crystallization and filtration as the filtration depth increased under all conditions. Without additional Ca^{2+} dosage, phosphorus removal efficiencies were approximately 75% at the end of the column. However, both T-P and PO_4-P removal efficiencies remarkably increased and reached >95% under all pH conditions when the linear velocity ranged between 2.0 and 10.0 m/h owing to Ca^{2+} supplementation. In particular, phosphorus was rapidly removed within 0.8 m of filtration depth under supplemental Ca^{2+} conditions. The removal efficiency of phosphorus at a pH of 11.0 was not higher than that at a pH of 10.0. The highest T-P and PO_4-P removal efficiencies (98.1 and 100.0%, respectively) were realized when the supplemental Ca^{2+} ion concentration was 50 mg/L, under a linear velocity of 2.0 m/h. In principle, under pH values above 10, coupled with additional calcium adjustment and a filtration depth above 2.0 m, phosphorus removal efficiency was stable.
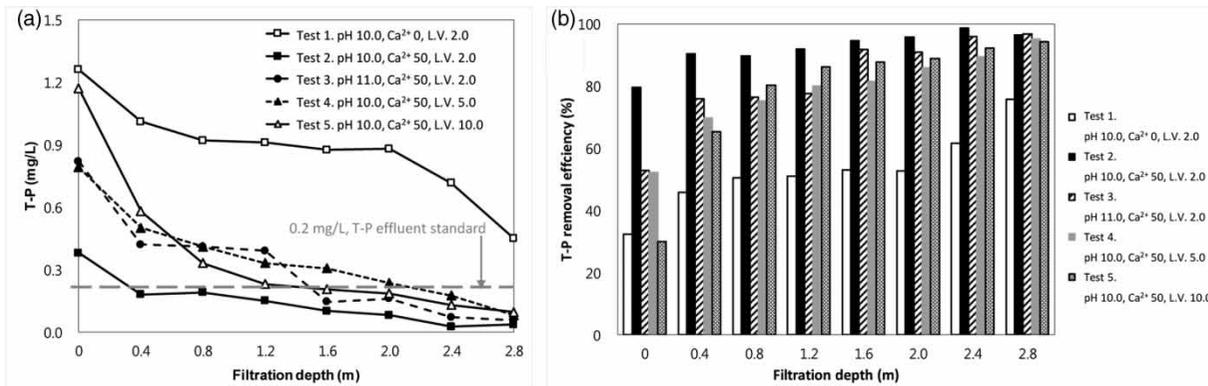

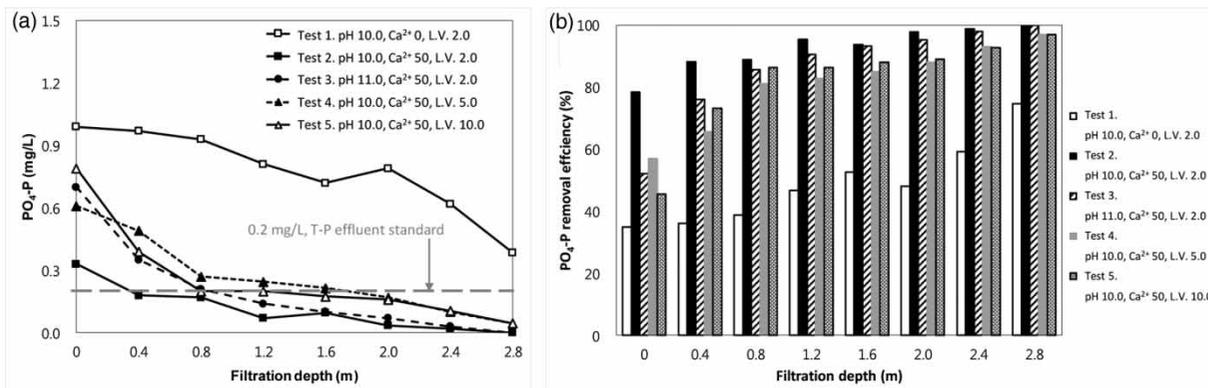**Figure 5** │ Variation of (a) T-P and (b) phosphorus removal efficiencies with filtration depth.

Figure 6 │ Variation of (a) PO_4-P and (b) phosphorus removal efficiencies with filtration depth.

A stable effluent phosphorus concentration below 0.2 mg/L was realized compared with the value that was obtained by Momberg & Oellermann (1992). The estimated total operation time of the PCF process was 1–2 h (40 min for pre-treatment and 20–80 min for crystallization-filtration), which was significantly shorter than those reported by Chen *et al.* (2009) (>24 h) and Momberg & Oellermann (1992) (>4 h).

Design and operating parameters for the PCF process

The schematic illustration, design parameters, and operational conditions of the PCF process for 50.0–100.0 m³/day of treatment capacity are shown in Figure 7 and Table 4.

The T-P concentration in the influent was 1.0–3.0 mg/L, and it was expected that after the PCF process, it would be less than 0.2 mg/L in the resulting effluent. Based on the results of column experiments, T-P removal efficiencies were expected to reach >95%, and be stable at a 2.4 m filtration depth with a linear velocity of 2 m/h, accompanied

with the supplementation of Ca^{2+}. When the influent T-P concentration was less than 2.0 mg/L, a linear velocity in the range 2–10 m/h or a filtration depth <2.4 m allowed the removal of T-P to values below 0.2 mg/L. Thus, depending on the T-P content of the influent and linear velocity, the reactor could be designed to have a filtration depth in the range of 2.0–3.0 m. A linear velocity between 1.0 and 5.0 m/h, which represents an empty bed contact time (EBCT) in the range 40–180 min (20–90 minutes of hydraulic retention time (HRT) in 0.5 filter media porosity) in a cylindrical basin with a diameter of 1.2 m is recommended. Additionally, the PCF reactor should be filled with limestone sand (diameter, 2.0–3.0 mm).

To retain a sufficient contact time with the seed crystals and ensure stable phosphorus removal, fixed bed filtration was preferred over fluidized bed filtration. However, backwashing is necessary for fixed bed filtration when the filter bed becomes blocked.

The pressure in the PCF reactor could be measured and used as an operating index for the determination of the
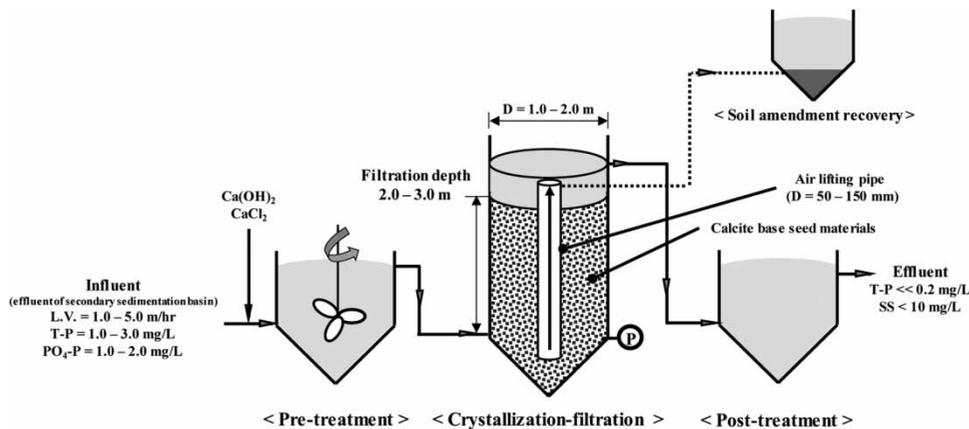

Figure 7 │ Schematic representation of the PCF process.

Table 4 │ PCF design parameters and operational conditions

Parameter	Design parameter	Specification/value
Pre-treatment	pH	>pH 10.0
	Residual Ca^{2+}	>80 mg/L
	OH^- supplier	$Ca(OH)_2$
	Ca^{2+} supplier	$Ca(OH)_2$, $CaCl_2$
PCF reactor	Filtration media	2.0–3.0 mm limestone sand
	Filtration direction	Up-stream
	Filter depth	2.0–3.0 m (depending on T-P load and linear velocity)
	Backwashing method	Air lifting (intermittently operated according to pressure of PCF reactor)
	Linear velocity	1.0–5.0 m/h
	EBCT	40–180 minutes

backwashing phase. The backwashing sludge containing phosphorus compounds, and calcite should be separated from the PCF reactor for recycling. The air lifting method can also be recommended for the backwashing of the media. This method probably resulted in the effective removal of the filtered sludge in the lower part of the reactor, leading to a recovery of the PCF reactor pressure.

Pilot-scale operation

The operation of the pilot-scale PCF process (June, 2018–September, 2018) was monitored, and different parameters were measured. The influent and operational pH values were in the ranges 6.4–7.0 (mean = 6.8) and 10.2–10.8 (mean = 10.5), respectively, as shown in Figure 8.

The T-P and PO_4-P concentrations in the influent were in the range 0.23–1.09 (mean = 0.62) and 0.07–1.04 (mean = 0.43) mg/L, respectively, as shown in Figure 9. Despite the variation of the T-P concentration in the influent, the

T-P in the effluent was in the range 0.03–0.11 (mean = 0.05) mg/L, indicating a 90.0% removal efficiency. Additionally, in the effluent, PO_4-P concentration ranged between 0 and 0.06 (mean = 0.04 mg/L), indicating an average removal efficiency of 86.5%. During the monitoring period, it was observed that T-P and PO_4-P concentrations were stably maintained below 0.2 mg/L.

Moreover, SS removal was also monitored, and the results are shown in Figure 10. The standard for effluent SS content is <10.0 mg/L. The influent SS content fluctuated between 0 and 77 mg/L. However, in the effluent, it was averagely 1.1 mg/L, indicating a 79.7% removal efficiency.

Interestingly, the influent PO_4-P proportion of T-P varied in the range 23.6–100% (mean = 67.9%), suggesting the presence of both PO_4-P (soluble) and particulate phosphorus (T-P – PO_4-P) in the influent. The fractions of soluble and particulate phosphorus in real domestic wastewater could vary greatly. Regarding the lowest influent
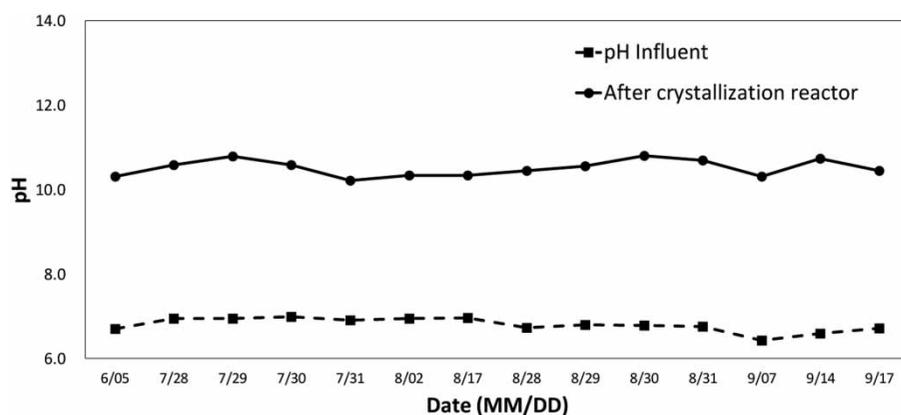

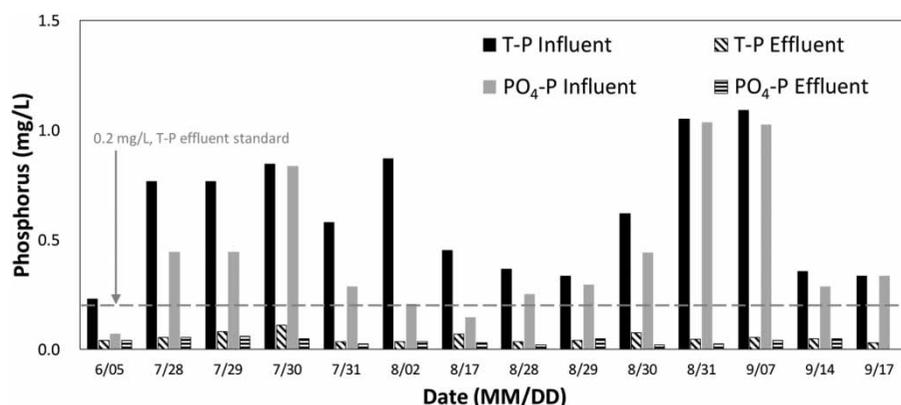**Figure 8** | pH variation during the pilot-scale PCF process.

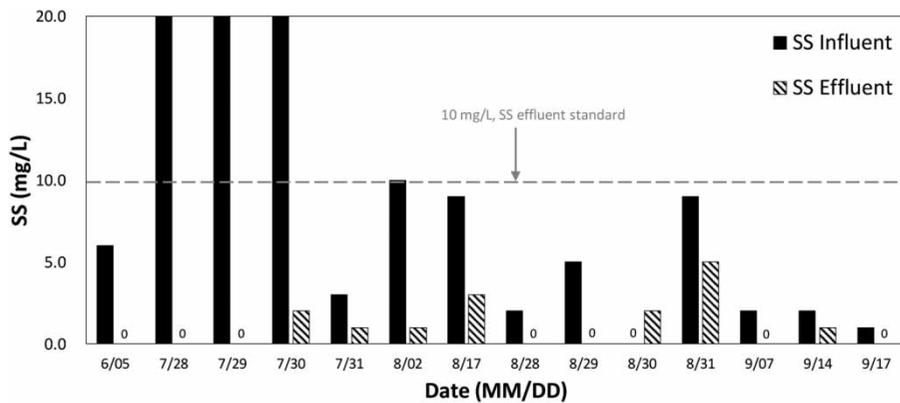**Figure 9** | Phosphorus removal during the pilot-scale PCF process.

Figure 10 │ Suspended solids removal during the pilot-scale PCF process.

PO$_4$-P ratio of T-P (8/02), crystallization-filtration resulted in successful T-P (PO$_4$-P and particulate phosphorus) removal (96%). Thus, it was demonstrated that the PCF process can be adapted to suit a wide variety of soluble and particulate phosphorus fractions in domestic wastewater. Compared with the results reported by Donnert & Salecker (1999) based on pilot-scale experiments using calcite, the PCF process in this study resulted in a lower and relatively stable effluent PO$_4$-P content.

Characterization of the PCF sludge

The sludge obtained after the PCF process was analyzed and evaluated as an alternative soil amendment. Figure 11 shows the SEM images of the PCF sludge obtained from influent with adjusted PO$_4$-P concentrations in the range 0.16–50.0 mg/L. The sludge resulting from the influent with initial PO$_4$-P content <0.2 mg/L was characterized by an amorphous layer without any particles (Figure 11(a)). However,

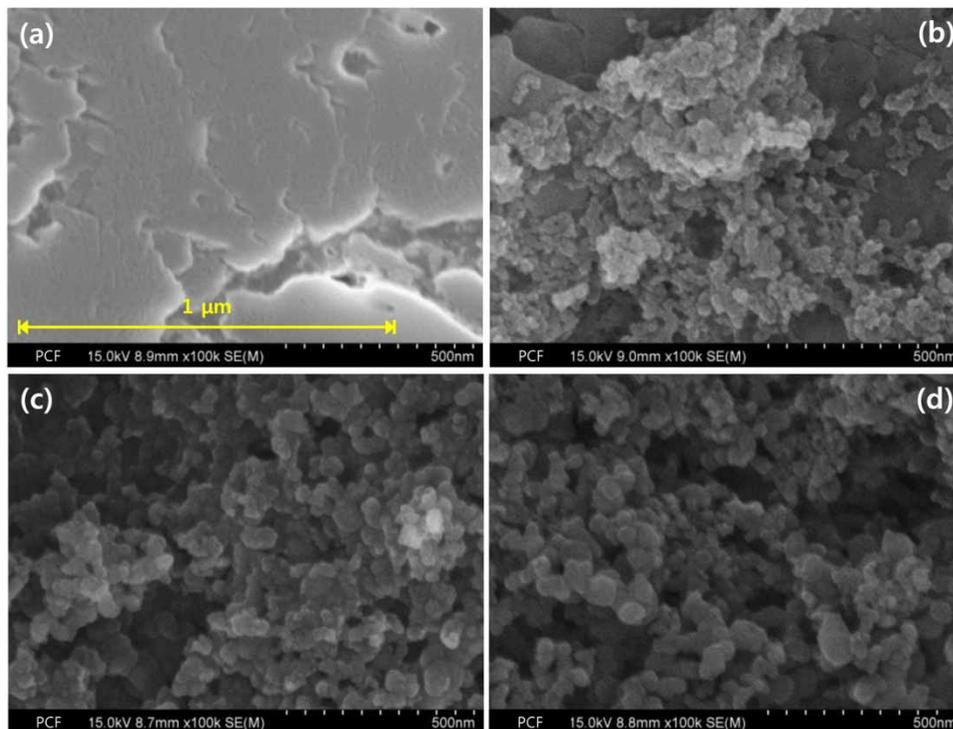**Figure 11** │ SEM images of PCF sludge obtained from influents with initial PO$_4$-P concentrations of (a) 0.16, (b) 2.0, (c) 10.0, and (d) 50.0 mg/L.

particles with diameter ~30 nm or less appeared on the surface of the amorphous layer of the sludge obtained from the influent with an initial PO_4-P concentration of 2.0 mg/L (Figure 11(b)). Additionally, the diameter of sludge particles resulting from influents with initial PO_4-P concentrations of 10.0 and 50.0 mg/L were greater (Figure 11(c) and 11(d)) relative to the particles shown in Figure 11(b). Notably, the sludge resulting from the influents with higher initial PO_4-P concentrations did not show any amorphous layers. They consisted of accumulated particles with diameters of 50 nm or larger.

Calcite and phosphorus enrichment in the PCF sludge was interpreted based on FT-IR peaks. Figure 12 shows the FT-IR diagrams of the sludge samples based on the initial PO_4-P values. Typical wave numbers that indicate the presence of PO_4^{3-} include 560–600 and 1,000–1,100 /cm. Additionally, a wave number of 875 /cm indicates the presence of HPO_4^{2-}, while a wave number of 873 /cm and ~1,420 /cm indicates the presence of CO_3^{2-}. Wave numbers in the range 2,600–3,600 /cm indicate the presence of H_2O (adsorbed water). The absorbance of the sludge samples obtained from influents with lower initial PO_4-P conditions presented larger peaks at wave numbers corresponding to CO_3^{2-}, possibly implying that in the sludge, calcite $(CaCO_3)$ fractions were higher than phosphorus compound fractions. On the other hand, the absorbance of the sludge samples obtained from influents with higher initial PO_4-P contents showed larger peaks at wave numbers corresponding to PO_4^{3-} and H_2O, implying that the sludge compounds

were hydrated under conditions of higher initial PO_4-P content.

Additionally, based on EDS analysis, the average atomic ratios of the phosphorus particles obtained from influents with initial PO_4-P concentrations in the range 0.16, 2.0, 10.0, and 50.0 mg/L were 0, 1.3, 2.7, and 9.5%, respectively. FT-IR and EDS results also confirmed that sludge from influents with higher initial PO_4-P concentrations contained more hydrated phosphorus compounds than calcite.

The main crystal composition of the PCF sludge was determined using XRD analyses (Figure 13). Peaks corresponding to calcite were the most predominant, while peaks corresponding to HAP crystal were insignificant. Synthetic carbonate-hydroxylapatite $(Ca_{10}(PO_4)_3(CO_3)_3 \cdot (OH)_2)$ and phosphoric acid (H_3PO_4) were also detected; however, their peaks were also insignificant. EDS analysis showed an increase in phosphorus atomic ratios, and FT-IR showed significant absorbance peaks corresponding to phosphorus compounds depending on the initial PO_4-P concentration. However, a few minor peaks corresponding to HAP crystal peaks were detected. The phosphorus removed during the PCF process was assumed to be formed as a major portion of amorphous hydrated phosphorus compounds and a minor portion of the HAP crystal.

Overall, the results of this study showed that calcite and hydrated phosphorus compounds are the main components of backwashing sludge. This conclusion was inferred from FT-IR and XRD data. Additionally, the fact that the
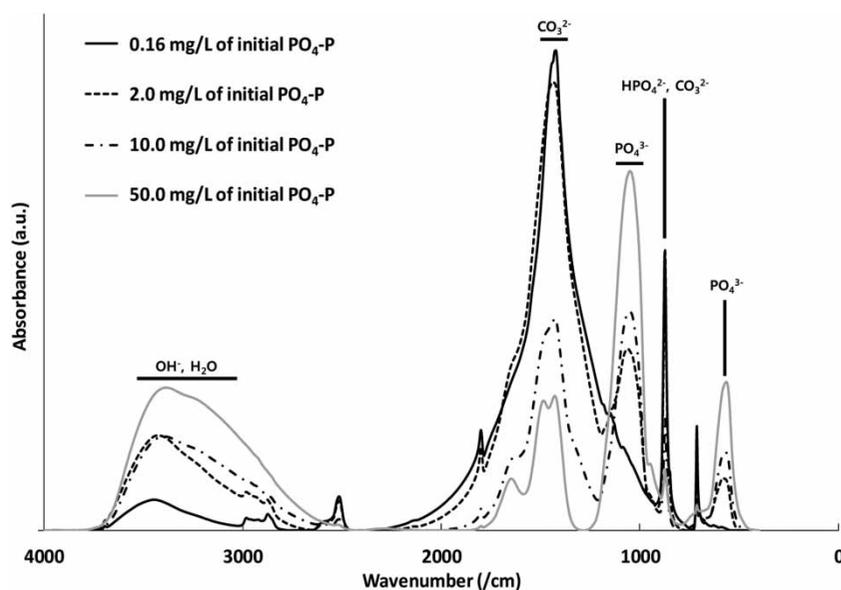

Figure 12 │ FT-IR diagrams for PCF sludge obtained from influents with initial PO_4-P concentrations of 0.16, 2.0, 10.0, and 50.0 mg/L.
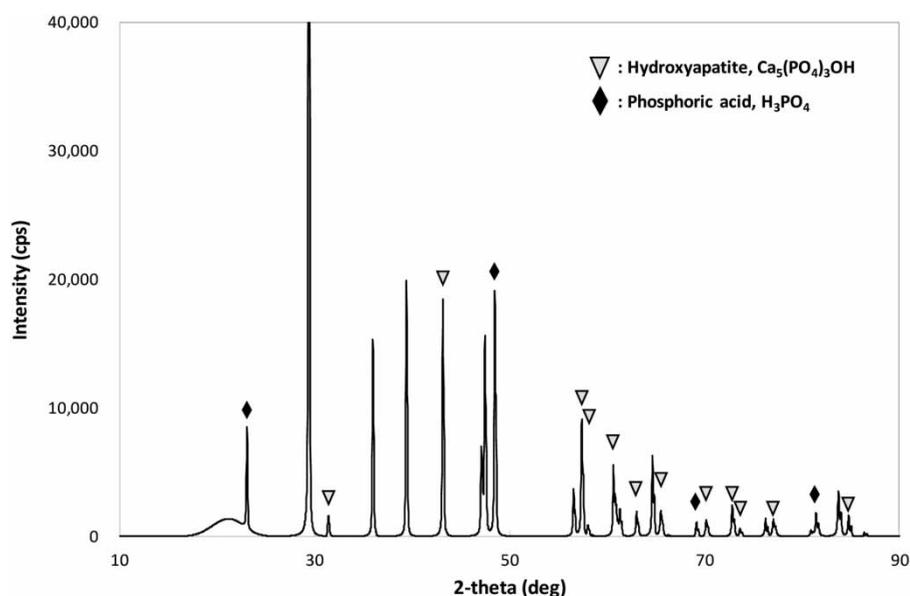
Figure 13 | XRD analysis results of the PCF sludge.

phosphorus portion of the recycled sludge could be larger with higher initial PO_4-P concentrations was confirmed by FT-IR and EDS data. Thus, when attempting to recycle the backwashing sludge of PCF as an alternative soil amendment or fertilizer, it should be noted that the phosphorus content and composition would vary depending on the initial influent PO_4-P concentration.

CONCLUSIONS

A phosphorus crystallization-filtration (PCF) process was designed and operated as an alternative process for the removal of phosphorus from domestic wastewater as hydroxyapatite (HAP). During laboratory-scale column tests, Ca^{2+} dosage supplementation greatly enhanced phosphorus removal efficiency, and under a residual Ca^{2+} condition >80 mg/L, T-P and PO_4-P, removal efficiencies above 95% were realized in several tests regardless of the pH condition or the linear velocity. Based on the results of the laboratory experiments, pre-treatment conditions (pH, residual Ca^{2+}), filter depth, and linear velocity (EBCT and flow rate) are suggested as the major design and operating parameters of the PCF process. A successful pilot-scale operation showed that PCF is a promising process for phosphorus removal from domestic wastewater. After the PCF process, the average effluent concentrations of T-P, PO_4-P, and SS were 0.05, 0.04, and 1.1 mg/L, respectively, corresponding to removal efficiencies of 90.0, 86.5, and 79.7%, respectively. Finally, the effluent

T-P contents <0.2 mg/L and SS contents <10 mg/L obtained from the pilot-scale process satisfied Korean regulation regarding water resource conservation. Furthermore, the characteristics of the sludge obtained after the PCF process using influents with various initial PO_4-P contents were investigated using SEM, FT-IR, EDS, and XRD analyses. Considering the high content of calcite and hydrated phosphorus compounds in the sludge recovered from the PCF process, the sludge can be used as an alternative soil amendment or fertilizer for the neutralization of acidic soils.

ACKNOWLEDGEMENTS

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