

# Development of phosphorus recovery reactor for enlargement of struvite crystals using seawater as the magnesium source

Pidchaya Wongphudphad and Patiya Kemacheevakul

## ABSTRACT

Struvite crystallization is an interesting method for the recovery of phosphorus (P) from wastewater. However, the struvite crystals obtained are small, which makes them difficult to separate from wastewater. A continuous reactor for enlarging struvite crystals was developed. Batch-scale experiments were conducted to investigate the optimum factors for the enlargement of struvite crystals. The results of pH experiments showed that P recovery efficiency increased with an increase of pH values (7.6 to 10), while the size of struvite crystals decreased. The results of the Mg:P ratios found that the maximum P recovery efficiency occurred at the maximum ratio of Mg:P. The sizes of struvite crystals were not significantly different. For the variation of temperature values, the results showed that P recovery efficiency and crystal sizes decreased when temperature values increased. Therefore, the optimized conditions for P recovery efficiency and enlargement of struvite crystals for the continuous reactor were pH 8.5 and an Mg:P ratio of 1.2:1 at 30 °C (room temperature). The treated swine wastewater and seawater were continuously fed in at the bottom of the reactor. After 30 days, the size of struvite crystals had increased from 125 µm to 0.83 mm (seven times).

**Key words** | phosphorus recovery reactor, seawater, size enlargement of struvite crystal, treated swine wastewater

**Pidchaya Wongphudphad**

**Patiya Kemacheevakul** (corresponding author)  
Department of Environmental Engineering,  
Faculty of Engineering,  
King Mongkut's University of Technology Thonburi,  
126 Pracha-uthit Rd., Bangmod, Tungkrui,  
Bangkok 10140,  
Thailand  
E-mail: [patiya.kem@kmutt.ac.th](mailto:patiya.kem@kmutt.ac.th)

**Patiya Kemacheevakul**

Center of Excellences on Hazardous Substance  
Management (HSM),  
Bangkok 10330,  
Thailand

## INTRODUCTION

Phosphorus (P) is an important nutrient for plants. Large amounts of P are used in agriculture and industry. Recently, P resources (phosphate rock) have dramatically decreased because the world population is increasing very fast. The consumption of phosphate rock is over one million tons per year by both the agricultural and industrial sectors (Rahman *et al.* 2011). Many researchers suggest that the supply of phosphate rocks will be exhausted in 50–100 years (Steen 1998; Smil 2000; Kemacheevakul *et al.* 2014). Moreover, the increase in the world population has increased the amount of wastewater which contains high concentrations of nutrients (Deng *et al.* 2006) and that is discharged into the environment without undergoing any treatment processes. This situation can harm aquatic life and cause environmental problems such as eutrophication because of the P and nitrogen (N) contained in wastewater (Khan & Ansari 2005). Eutrophication, which can reduce light infiltration and dissolved oxygen in the water, is the

excessive growth of aquatic plants or algal blooms. This leads to the dying-off of aquatic life because of the oxygen depletion. So, treatment processes for wastewater are required before discharge to the aquatic environment (Rahman *et al.* 2014).

There are many processes that can be used to remove and recover nutrients from wastewater, including chemical and biological processes. Struvite formation is one of the chemical precipitation processes (Yeoman *et al.* 1988). Recently, the struvite crystallization process has been selected for recovery of nutrients (P and N) from different types of wastewater, such as agricultural wastewater (Muhmood *et al.* 2019a), industrial wastewater (Diwani *et al.* 2007), landfill leachate (Kim *et al.* 2007; Wu *et al.* 2018), human urine (Kemacheevakul *et al.* 2014, 2015), swine wastewater (Suzuki *et al.* 2005; Ichihashi & Hirooka 2012; Huang *et al.* 2017), and pharmaceutical wastewater (Yang *et al.* 2019). The mixture of two kinds of wastewater

(i.e., anaerobic sludge supernatant and human urine) has also been studied (Zeng *et al.* 2018). The recycling of P from wastewater can therefore solve both the depletion of P resources and environmental problems.

Struvite ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ) or MAP is a crystal which consists of magnesium (Mg), ammonium ( $\text{NH}_4^+$ ) and phosphate ( $\text{PO}_4^{3-}$ ) with a molar ratio of 1:1:1 and a molecular weight equal to 245.43 g/mol (Le Corre *et al.* 2009). Pure struvite crystal is a white powder, but it can occur with different morphologies and sizes (Munch & Barr 2001). It can be used as a slow-release fertilizer or bio-soil to improve soil quality. It can be formed as a crystal under alkaline conditions but dissolves as ions in acid conditions. There are two struvite formation processes, which are nucleation and crystal growth (Doyle & Parsons 2002). However, the separation of struvite crystals from wastewater is quite difficult because they are small – in the range of micrometres.

Treated swine wastewater is one of the interesting sources for nutrient recovery because it contains high concentrations of nutrients (N and P). Struvite formation occurs when wastewater contains Mg,  $\text{PO}_4^{3-}$ , and  $\text{NH}_4^+$ , but treated swine wastewater has low concentrations of Mg. So, the addition of Mg to treated swine wastewater is required to complete precipitation (Tunay *et al.* 1997; Moerman *et al.* 2009). This research selected seawater, which contains a high concentration of Mg, as the Mg source. Moreover, seawater is low cost and easy to source.

Many researchers have studied struvite precipitation from swine wastewater. Nelson *et al.* (2003) studied the effect of adjusting the pH and Mg:P ratio on struvite precipitation in anaerobic swine lagoon liquid. Struvite precipitation decreased the concentration of orthophosphate by 85% at pH 9.0 for an initial molar ratio of Mg and P equal to 1.2:1. Liu *et al.* (2011) reported the effect of aeration rate and molar ratio of Mg:P on P recovery by struvite precipitation. Swine wastewater and  $\text{MgCl}_2$  were used in this study. They found that the best Mg:P molar ratio and aeration rate were 0.8–1:1 and 0.73 L/L.min, respectively.

Lahav *et al.* (2013) studied struvite crystallization from the supernatant of sludge dewatering facilities using seawater that had been passed through a nanofiltration membrane as the Mg source. The efficiency of P removal was high. This research found a reduction of cost of around 50% from using additional chemical substances as the Mg source. Desmidt *et al.*'s (2013) result of an experiment on P recovery efficiency with the use of the struvite precipitation process showed that the efficiency of P recovery increases when  $\text{PO}_4$  ion concentration is very high. Tarrago *et al.* (2016) found that up-flow velocity has a

direct effect on the particle size of struvite crystals. Muhmood *et al.* (2019b) reported that in the struvite precipitation process, biochar seeding increased the particle size of struvite crystals. Although the effect of various factors on struvite formation has been studied, few reports have focused on the size of struvite crystals. Therefore, nutrient recovery efficiency and size enlargement of struvite crystals via a continuous reactor were the focus of this research.

## MATERIALS AND METHODS

### Treated swine wastewater

The treated swine wastewater that was used in this research had already been treated by an anaerobic process (upflow anaerobic sludge blanket reactor: UASB). Wastewater was collected from a pig farm in Nakhon Pathom province in Thailand and kept in a clean container at 4 °C before use for all experiments.

### Seawater

Seawater was selected as an alternative Mg source in this research because of the high concentration of Mg in seawater. The seawater used in all experiments was collected from Rayong Province, Thailand. The location for collection of the seawater was far from the beach area. The collected seawater was stored in a clean container at 4 °C. The characteristics of the seawater are shown in Table 1.

### Determination of optimum factors for continuous reactor experiment

There are various factors that affect P recovery efficiency and the size of struvite crystals. pH has a direct effect on the solubility of struvite, i.e. struvite solubility decreases

Table 1 | Characteristics of seawater

Parameter	Value
pH	8.25
Magnesium (mg/L)	1,392
Calcium (mg/L)	433
Sodium (mg/L)	10,805
Orthophosphate (mg/L)	-
Salinity (ppt)	30.9
Conductivity (ms/cm)	47.4

with increasing pH (Ronteltap *et al.* 2007). The molar ratio of Mg:P is also an important factor for P recovery, struvite nucleation, and struvite growth rate (Nelson *et al.* 2003). Temperature is another factor that thermodynamically affects crystal growth (Ronteltap *et al.* 2010). Therefore, these three factors were selected to study for their effect on both P recovery efficiency and size of struvite crystals.

### pH experiments

The batch-scale pH experiments consisted of six different pH values, which were: initial pH of sample (pH = 7.6), 8, 8.5, 9, 9.5, and 10. The pH in each sample was adjusted by 1 N of sodium hydroxide (NaOH). For the Mg source, seawater was added to each beaker at the Mg:P ratio of 1.2:1. The treated swine wastewater (800 mL) and seawater were mixed into 1 L glass beakers for each pH value at room temperature ( $30 \pm 1$  °C). The samples were mixed by a jar-tester with a rapid mixing speed of 120 rpm for 1 min, followed by a slow mixing speed of 30 rpm for 20 min. After the mixing process, the supernatant and precipitates of each sample were separated by using glass fiber filters (GF/C Filtres Fioroni). The phosphate, ammonium, and Mg concentration that remained in the supernatant of each sample were analyzed. Precipitates as solid parts were analyzed according to morphology, composition, and size of crystal.

### Molar ratio experiments

Four different molar ratios of Mg:P were investigated in these batch-scale experiments, which were: initial molar ratio of Mg:P of sample without addition of Mg source (0.66:1), 1:1, 1.2:1, and 2:1. The pH of all samples was adjusted to the optimum pH values with NaOH (as described in the 'pH experiments' section). The additional amounts of Mg (seawater) in treated swine wastewater were calculated by the analysis results of common parameters. The treated swine wastewater (800 mL) and seawater as the Mg source were mixed into 1 L glass beakers at room temperature ( $30 \pm 1$  °C). The samples were mixed by a jar-tester at the rapid and slow mixing speeds as described in the 'pH experiments' section. After the mixing process, the samples in the supernatant and precipitates of molar ratio experiments were similarly analyzed in the same way as the pH experiments.

### Temperature experiments

The batch-scale temperature experiments were separated into three variations, which were:  $30 \pm 2$  °C (room

temperature),  $40 \pm 2$  °C and  $50 \pm 2$  °C. The experiments in this section were conducted for the investigation of the optimum location for the continuous reactor (indoor or outdoor locations). This experiment used the optimum values for pH (8.5) and molar ratio of Mg:P (1.2:1). The treated swine wastewater (500 mL) and seawater as the Mg source were mixed into 1 L glass beakers at various temperature values ( $30 \pm 2$  °C,  $40 \pm 2$  °C, and  $50 \pm 2$  °C). The samples were mixed in a water bath at the rapid mixing speed for 1 min, followed by slow mixing for 20 min. After the mixing process, the supernatant of each sample was separated from the precipitates by glass fiber filters. The samples of the supernatant and precipitates of the temperature experiments were analyzed in the same way as the previous experiments.

### Enlargement of struvite crystals through continuous reactor experiment

The continuous reactor used to enlarge the struvite crystals was designed in two parts (reaction and settling zones) as shown in Figure 1. Struvite formation occurred in the reaction zone and struvite crystals (products) were precipitated in this zone because the continuous reactor was quite tall (70 cm). Only very small struvite crystals could pass to the settling zone. The purpose of the settling zone was to settle and accumulate small struvite crystals at the bottom of the settling zone where a valve could be opened to return the struvite crystals to the reaction zone. The reactor was started up with 4.5 L of treated swine wastewater which was mixed with the Mg source at pH 8.5 at an Mg:P ratio of 1.2:1 at room temperature. The pH in the reactor was adjusted with NaOH. Then the treated swine wastewater and seawater were continuously fed into the reactor and mixed by a paddle. The conditions (pH, Mg:P ratio, and temperature) in the reactor were constant for the month-long experiment. The effluent was collected and analyzed for the remaining concentrations of orthophosphate (PO<sub>4</sub>-P), ammonia nitrogen (NH<sub>4</sub>-N), and Mg. The struvite crystals that occurred in the reactor were collected every day and investigated for size and morphology.

### Crystal morphology and composition

For the batch-scale experiments, struvite crystals (products) obtained after the struvite crystallization process from the pH, molar ratio, and temperature experiments were dried at room temperature. The morphology and composition of

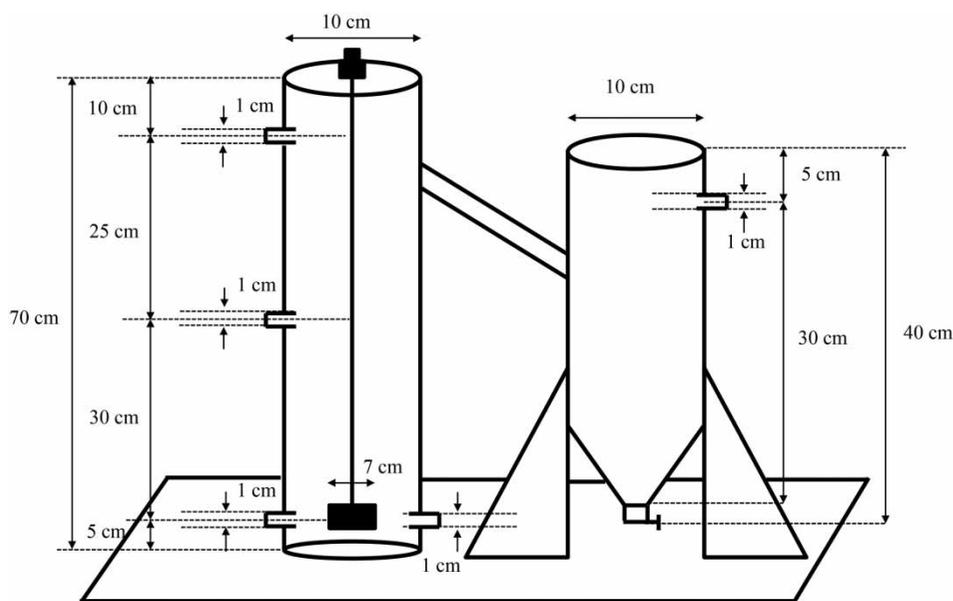


Figure 1 | Continuous reactor for enlargement of struvite crystals.

the products were characterized by a scanning electron microscope (SEM, JEOL JSM-6610LV) operating at an acceleration voltage of 3 kV, and an X-ray diffractometer (XRD, Bruker AXS Model D8 Discover) with a voltage of 40 kV and a super speed detector. In the case of the continuous reactor experiment, struvite crystals in the reactor were investigated by microscope with stage and ocular micro-metre and analyzed for composition by XRD.

### Analytical method

In the case of the common parameters,  $\text{PO}_4\text{-P}$ ,  $\text{NH}_4\text{-N}$ , and Mg that remained in the separated supernatant of each sample were analyzed. The  $\text{PO}_4\text{-P}$  concentration was measured by the stannous chloride method, and the  $\text{NH}_4\text{-N}$  concentration was analyzed by the distillation and titration ammonia method according to *Standard Methods* (APHA 2012). In the case of Mg concentration, it was measured by the inductively coupled plasma method (ICP, optima 2000 DV). All experiments were carried out twice to ensure correct and reliable results.

## RESULTS AND DISCUSSION

### Effect of pH

The experiments at various pH values (initial pH value of wastewater sample (7.6), pH 8, 8.5, 9, 9.5, and 10) for struvite

recovery from treated swine wastewater used seawater as an Mg source at a constant molar ratio of Mg:P (1.2:1).

### Nutrient recovery

The results showed that P recovery efficiencies at the initial pH value of the wastewater sample (7.6), pH 8, 8.5, 9, 9.5, and 10 were 37%, 56%, 81%, 90%, 93%, and 94%, respectively. The amount of dissolved P as  $\text{PO}_4\text{-P}$  that remained in each sample decreased, which meant P recovery efficiency increased when the pH was increased. Moreover, the results of the pH experiments found that high P recovery efficiencies occurred at pH 8.5–10, which were higher than 80%. The highest efficiency was found at pH 10. Hao *et al.* (2008) mentioned that the suitable pH values were between 7.5 and 9. So pH has a significant effect on P recovery from treated swine wastewater. The results of  $\text{NH}_4\text{-N}$  and Mg concentrations also showed the same tendency as P recovery efficiency. The concentrations of  $\text{NH}_4\text{-N}$  and Mg decreased with increasing pH because  $\text{NH}_4$  and Mg were precipitated with phosphate in the form of struvite. In the case of decreasing  $\text{NH}_4\text{-N}$  concentration in the samples, there was another reason, which was the conversion of ammonium ions in the sample at neutral pH to ammonia gas in alkaline conditions (Le Corre *et al.* 2009).

### Morphology and amount of precipitates

For the amount and size of struvite crystals in each pH sample (Table 2), the results showed that the amount of

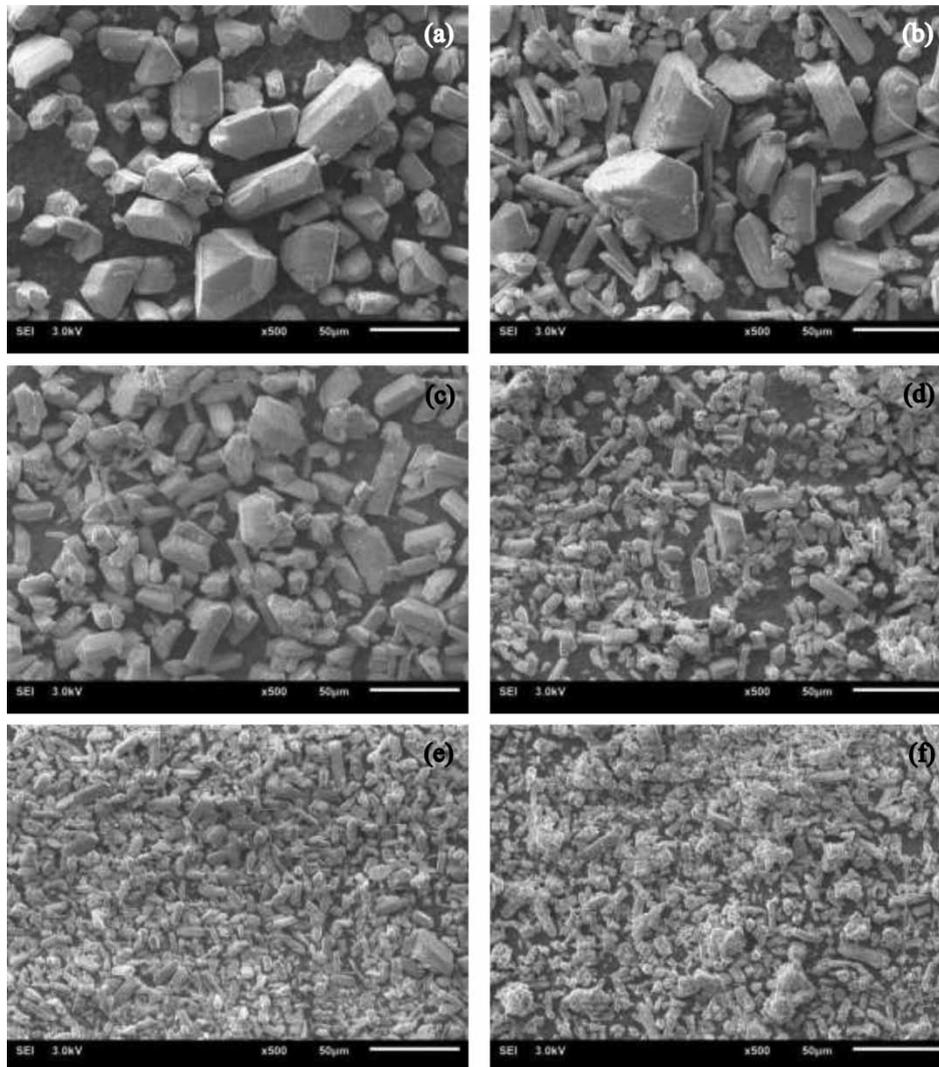
**Table 2** | Range of struvite crystal size and quantity of struvite crystal at different pH conditions

pH	Range of struvite crystal size ( $\mu\text{m}$ )	Quantity of struvite crystals ( $\text{g}^{\text{a}}$ )
7.6	20–64	0.15
8.0	24–70	0.23
8.5	10–78	0.27
9.0	14–26	0.29
9.5	12–26	0.31
10.0	10–22	0.36

<sup>a</sup>Quantity of struvite crystals (g) per 1 L of wastewater sample.

precipitates (mainly struvite crystals) increased when the pH of the samples increased but the size decreased, especially at

high pH conditions (9–10) as shown in Figure 2. Although the efficiency of P recovery at pH 9–10 was higher than 90%, the average size of crystals was only between 10 and 26  $\mu\text{m}$ . As mentioned in the previous section, the size of the struvite crystals is quite important for the separation process. However, the efficiency of nutrient recovery should be of concern as well. Thus, the optimum pH to form struvite crystals of a suitable size for start-up in a continuous reactor as seed was found to be pH 8.5. Moreover, the efficiency of P recovery at pH 8.5 was higher than 80%. For the shape of struvite crystals (Figure 2), the results showed that most of the struvite crystals were a coffin lid shape, which was the possible shape of struvite crystals as reported by McLean *et al.* (1990) and Wierzbicki *et al.* (1997).



**Figure 2** | SEM images (500 $\times$ ) of struvite crystals from treated swine wastewater at different pH values: (a) initial pH (7.6), (b) pH 8, (c) pH 8.5, (d) pH 9, (e) pH 9.5, and (f) pH 10.

## Effect of molar ratio

The batch-scale experiments in this section were conducted at various Mg:P molar ratios (Mg:P = 0.66:1, 1:1, 1.2:1, 2:1). The experiments were conducted at pH 8.5 at room temperature ( $30 \pm 1$  °C).

## Nutrient recovery

The efficiencies of P recovery at Mg:P ratios of 0.66:1 (without the addition of seawater as an Mg source), 1:1, 1.2:1, and 2:1 were 56%, 72%, 80%, and 84%, respectively. The results showed that the increasing Mg concentration (Mg:P ratio) could reduce the remaining concentration

of  $\text{PO}_4\text{-P}$  in each sample. The highest efficiency of P recovery was found at the Mg:P ratio of 2:1, which indicated that Mg:P molar ratio has a significant effect on P recovery efficiency. For the result of the  $\text{NH}_4\text{-N}$  concentration in the supernatant, it was found that the remaining  $\text{NH}_4\text{-N}$  concentrations decreased while the molar ratios of Mg:P increased. The reason for the reduction of  $\text{NH}_4\text{-N}$  concentrations in the sample was that the Mg ions increased at higher Mg:P ratios. Thus, struvite crystals had more chance to form. For Mg concentration, the results showed that the remaining Mg concentration increased when the molar ratio of Mg:P increased. According to the theoretical Mg:P ratio of 1:1, the addition of seawater to the samples at a higher Mg:P ratio ( $>1:1$ ) could lead to the extra Mg ions in the samples.

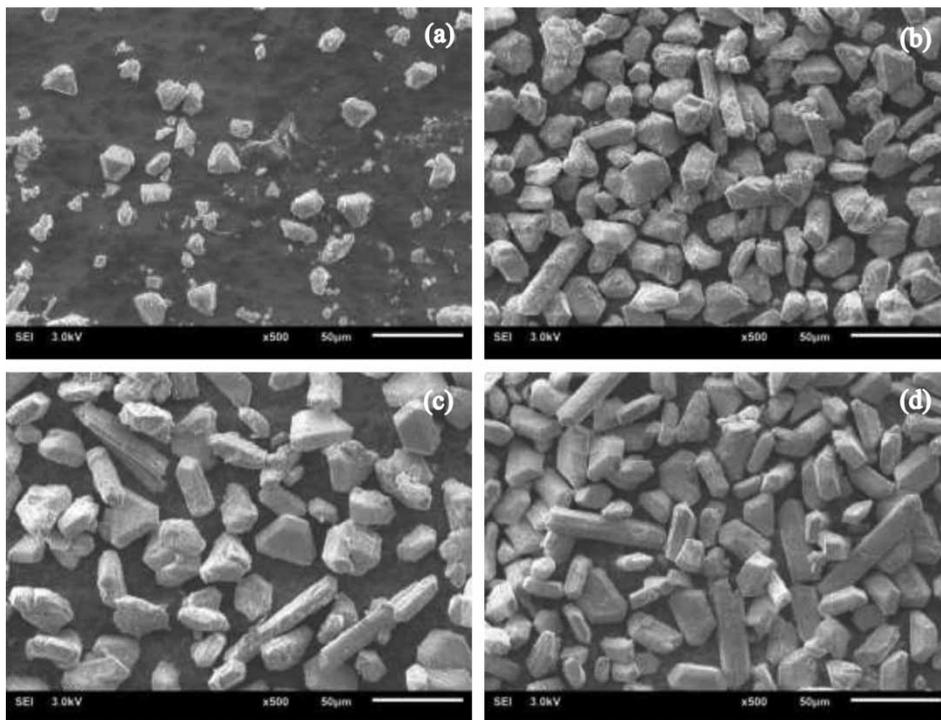
## Morphology and amount of precipitates

The struvite crystal sizes from the molar ratio experiments are shown in Table 3 and Figure 3. The initial molar ratio (0.66:1) led to smaller sizes (14–60  $\mu\text{m}$ ) than other Mg:P ratios. For Mg:P ratios between 1:1 and 2:1, the sizes of the struvite crystals were very similar. These results are in accordance with those obtained in a previous study (Liu *et al.* 2018). They found that there was no significant difference in average crystal size among varying Mg:P ratios (1.1–2:1). For the shape of struvite crystals, the results

**Table 3** | Range of struvite crystal size and quantity of struvite crystal at various Mg:P ratios

Mg:P ratios	Range of struvite crystal size ( $\mu\text{m}$ )	Quantity of struvite crystals ( $\text{g}^{\text{a}}$ )
0.6:1	14–60	0.20
1.0:1	22–72	0.26
1.2:1	22–78	0.28
2.0:1	20–70	0.31

<sup>a</sup>Quantity of struvite crystals (g) per 1 L of wastewater sample.

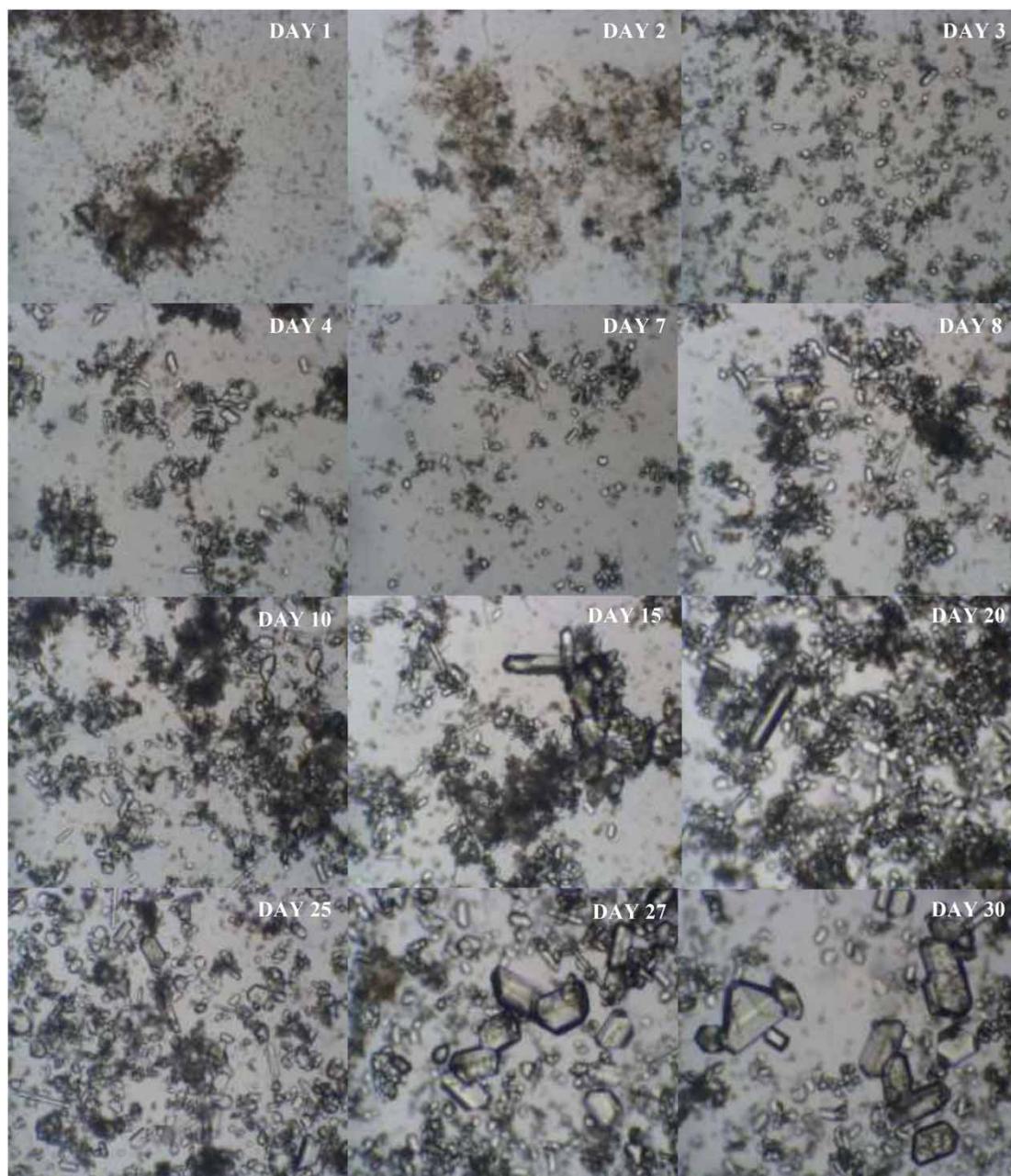


**Figure 3** | SEM images (500 $\times$ ) of struvite crystals from treated swine wastewater at different Mg:P molar ratios: (a) 0.66:1, (b) 1.0:1, (c) 1.2:1, and (d) 2.0:1.

showed similar shapes, as mentioned in the section ‘Morphology and amount of precipitates’, which was a coffin lid shape. In the case of the amount of struvite crystal, it increased when the Mg:P ratio increased. The Mg:P molar ratio of 2:1 gave the highest P recovery efficiency (84%). However, the Mg:P ratio of 1.2:1 was the optimum molar ratio condition for this research because the struvite crystals were slightly larger than at the Mg:P ratio of 2:1. Moreover, the P recovery efficiency was quite high (80%) at the Mg:P ratio of 1.2:1.

### Temperature experiment

The purpose of this experiment was to investigate the optimum location (indoors or outdoors) for the continuous reactor. Experiments were conducted at three temperatures, 30 °C, 40 °C, and 50 °C. The results illustrated that the highest P recovery efficiency was 87% at  $30 \pm 2$  °C (room temperature), while the P recovery efficiencies of the higher temperatures of  $40 \pm 2$  °C and  $50 \pm 2$  °C were 83% and 77%, respectively. Moreover, the size of struvite crystals



**Figure 4** | Microscope images (10 $\times$ ) of struvite crystals in the continuous reactor.

tended to slightly decrease with the increasing temperature. The smallest size was at  $50 \pm 2^\circ\text{C}$  ( $3\text{--}25\ \mu\text{m}$ ). The reason was that solubility increases at the higher temperature. It indicated that the temperature of  $30 \pm 2^\circ\text{C}$  (room temperature or indoor location) was the best for P recovery efficiency and optimum size of struvite crystals.

### Enlargement of struvite crystals in the continuous reactor

The optimum conditions used to operate the continuous reactor were obtained from the batch-scale experiments. The optimum pH, Mg:P ratio, and temperature for P recovery efficiency and large size of struvite crystals were pH 8.5, Mg:P ratio of 1.2:1, and  $30 \pm 2^\circ\text{C}$  (room temperature). Treated swine wastewater and seawater were continuously fed into the reactor (Figure 1) for 30 days. The results showed that P recovery efficiency was almost 70% for the 30 days of the experiment. During struvite crystallization, large amounts of crystals formed and settled in the reaction zone. The morphology, size, and composition of the struvite crystals were analyzed by SEM, microscope, and XRD. The size range of crystals in the first day was around  $50\text{--}125\ \mu\text{m}$ .

After 30 days, the size of crystals was in the range of  $70\text{--}830\ \mu\text{m}$ . The increase in struvite crystal size was around seven times from the first day, as shown in Figure 4. An XRD spectrum of solids in the continuous reactor compared with a struvite standard is shown in Figure 5 and indicated that the main composition of solids in the reactor matched with a struvite standard (position and intensity of the peak) and confirmed that the solids were struvite.

### Discussion

Size enlargement of struvite crystals via a continuous reactor with high nutrient recovery efficiency is aim of this work. There are two main parts to this study. In the first part, batch-scale experiments were conducted to find the optimum conditions for P recovery efficiency and size enlargement of struvite crystals from treated swine wastewater using seawater as the Mg source. The effects of pH, molar ratio of Mg:P, and temperature were investigated. For the pH experiment, it was found that the P recovery efficiency increased with the increase in pH, but that struvite crystal size decreased with increasing pH. The reduction of  $\text{PO}_4\text{-P}$  in each sample (supernatant) came from the combination

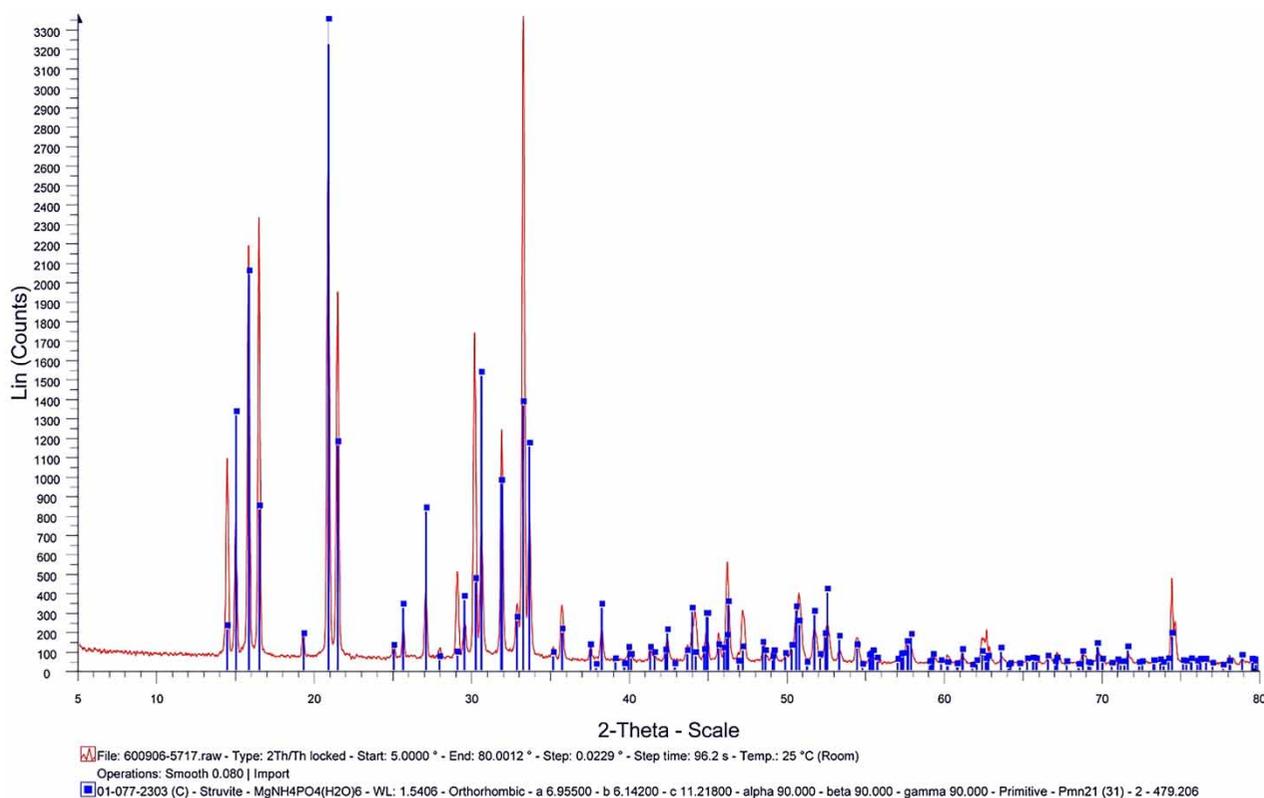


Figure 5 | XRD spectrum of struvite crystals in the continuous reactor (line without any dots) compared with a struvite standard (number 01-077-2303) (line with square dots).

of  $\text{PO}_4\text{-P}$  and other ions in the sample, such as Mg,  $\text{NH}_4\text{-N}$ , and calcium (Ca) and the precipitation process. However, the main product that occurred in the experiment was struvite crystals, because the wastewater sample had a low concentration of Ca and the molar ratio of Mg:Ca was high. Moreover, the solubility of struvite crystals was reduced at a high pH, which was similar to research by [Borgerding \(1972\)](#). [Borgerding \(1972\)](#) reported that the solubility of struvite crystals decreased from 3,000 mg/L at pH 5 to 100 mg/L at pH 7.5. For the decrease of struvite crystal size with the increasing pH, [Matynia et al. \(2006\)](#) also reported that the increase in pH from pH 8 to 11 affected the size of the crystals, i.e. the crystal size was reduced by around five times. Moreover, [Le Corre et al. \(2006\)](#) mentioned that the negative zeta-potential of struvite significantly affected to struvite particle size. The crystals did not agglomerate, because of their negative zeta-potentials. Larger negative zeta-potentials at higher pH values lead to reduction of particle sizes. The most suitable pH for high P recovery efficiency (>80%) and large struvite crystals was 8.5.

In the case of the Mg:P molar ratio experiment, the results showed that the P recovery efficiency increased with increasing Mg:P ratio. The results in this experiment were similar to those reported by [Liu et al. \(2018\)](#). They found that P removal efficiency increased when the Mg:P ratio increased from 1.0 to 2.0. The increase in the degree of saturation with increasing Mg:P ratio might enhance P removal efficiency ([Munch & Barr 2001](#); [Adnan et al. 2003](#)). However, the sizes of struvite crystals for the Mg:P ratios between 1:1 and 2:1 were not significantly different. The optimum Mg:P ratio was 1.2:1 because of high P recovery efficiency and the use of a small amount of seawater. For the temperature experiment, the optimum temperature was 30 °C or room temperature (indoor location) because higher temperatures tended to decrease the P recovery efficiency and size of struvite crystals.

For the second part of this study, the continuous reactor was operated according to the optimum conditions from the previous experiments. The treated swine wastewater and seawater were fed in at the bottom of the reactor in a continuous flow. The size of struvite crystals was successfully enlarged by around seven times with almost 70% P recovery efficiency after the month-long experiment. The larger struvite crystals will be easier to separate out. They will also last longer in soil, which can increase the nutrients available for uptake by plants. Moreover, recovery P from treated swine wastewater can enhance the quality of final effluent discharge and reduce eutrophication problems.

For practical purposes the economic point of view should also be considered. The operating costs are electricity for running the system and chemicals for pH adjustment. In the case of the electricity, solar power, which is a clean technology, can be used for electricity generation (in terms of operating costs, not capital costs). Therefore, the main cost is only the alkaline chemical. In order to decrease the expense, alkaline wastewater can be substituted for the alkaline reagent. In this study, only a small amount of alkaline chemical was used because the initial pH of the treated swine wastewater was close to 8.5. Thus, the cost for chemicals can be set against the obtained product (struvite crystals), which can be sold or reduce the expense of buying fertilizer for the pig farm.

## CONCLUSION

In this research, the effects of pH, molar ratio of Mg:P, and temperature on P recovery efficiency and size of struvite crystals from treated swine wastewater using seawater as the Mg source were investigated. The continuous reactor was operated at the optimum conditions (pH 8.5, Mg:P ratio of 1.2:1, and 30 °C). The size of struvite crystals from the reactor was successfully enlarged (seven times) with high P recovery efficiency (~70%) after a month-long experiment. From this study it can be seen that the continuous reactor designed shows potential for size enlargement of struvite crystals and can be used for practical applications.

## ACKNOWLEDGEMENTS

The authors express gratitude to the Thailand Research Fund and Office of the Higher Education Commission, Thailand (grant no. MRG5980109) for financial support. This research was also supported by Research Strengthening Project of the Faculty of Engineering, King Mongkut's University of Technology Thonburi, the 55th Anniversary Commemorative Fund of King Mongkut's University of Technology Thonburi, and the Austrian Federal Ministry for Science, Research and Economy, Austria and Office of the Higher Education Commission (ASEA-UNINET staff exchange). The authors also wish to express their thanks to Prof. Dr-Ing. Joerg Krampe and Dr Lukas Egle for technical support. The support from the Department of Environmental Engineering, Faculty of Engineering, King Mongkut's University of Technology Thonburi is also gratefully acknowledged.

## REFERENCES

- Anan, A., Mavinic, D. S. & Koch, F. A. 2003 Pilot-scale study of phosphorus recovery through struvite crystallization-examining the process feasibility. *J. Environ. Eng. Sci.* **2**, 315–324.
- APHA 2012 *Standard Methods for the Examination of Water and Wastewater*, 22nd edn. American Public Health Association/American Water Works Association/Water Environment Federation, Washington, DC, USA.
- Borgerding, J. 1972 Phosphate deposits in digestion systems. *J. Water Pollut. Control. Fed.* **44**, 813–819.
- Deng, L. W., Zheng, P. & Chen, Z. A. 2006 Anaerobic digestion and post-treatment of swine wastewater. *Process Biochem.* **41**, 965–969.
- Desmidt, E., Ghyselbrecht, K., Monballiu, A., Rabaey, K. & Meesschaert, B. D. 2013 Factors influencing urease driven struvite precipitation. *Sep. Purif. Technol.* **110**, 150–157.
- Diwani, G. E., Raffie, S. E., Ibiari, N. N. E. & El-Aila, H. I. 2007 Recovery of ammonia nitrogen from industrial wastewater treatment as struvite slow releasing fertilizer. *Desalination* **214**, 200–214.
- Doyle, J. & Parsons, S. A. 2002 Struvite formation, control and recovery. *Water Res.* **36**, 3925–3940.
- Hao, X. D., Wang, C. C., Lan, L. & Von Loosdrecht, M. C. M. 2008 Struvite formation, analytical methods and effects of pH and  $\text{Ca}^{2+}$ . *Water Sci. Technol.* **58**, 1687–1692.
- Huang, H., Zhang, D. D., Li, J., Guo, G. & Tang, S. 2017 Phosphate recovery from swine wastewater using plant ash in chemical crystallization. *J. Clean Prod.* **168**, 338–345.
- Ichihashi, O. & Hirooka, K. 2012 Removal and recovery of phosphorus as struvite from swine wastewater using microbial fuel cell. *Bioresour. Technol.* **114**, 303–307.
- Kemacheevakul, P., Chuangchote, S., Otani, S., Matsuda, T. & Shimizu, Y. 2014 Phosphorus recovery: minimization of amount of pharmaceuticals and improvement of purity in struvite recovered from hydrolysed urine. *Environ. Technol.* **35**, 3011–3019.
- Kemacheevakul, P., Chuangchote, S., Otani, S., Matsuda, T. & Shimizu, Y. 2015 Effect of magnesium dose on amount of pharmaceuticals in struvite recovered from urine. *Water Sci. Technol.* **72**, 1102–1110.
- Khan, F. A. & Ansari, A. A. 2005 Eutrophication: an ecological vision. *Bot. Rev.* **71**, 449–482.
- Kim, D. K., Ryu, H. D., Kim, M. S., Kim, J. & Lee, S. I. 2007 Enhancing struvite precipitation potential for ammonia nitrogen removal in municipal landfill leachate. *J. Hazard. Mater.* **146**, 81–85.
- Lahav, O., Telzhensky, M., Zewuhn, A., Gendel, Y., Gerth, J., Calmano, W. & Birnhack, L. 2013 Struvite recovery from municipal-wastewater sludge centrifuge supernatant using seawater NF concentrate as a cheap Mg(II) source. *Sep. Purif. Technol.* **108**, 103–110.
- Le Corre, K. S., Valsami-Jones, E., Hobbs, P., Jefferson, B. & Parsons, S. A. 2006 Agglomeration of struvite crystals. *Water Res.* **41**, 419–425.
- Le Corre, K. S., Jones, E. V., Hobbs, P. & Parsons, S. A. 2009 Phosphorus recovery from wastewater by struvite crystallization: a review. *Crit. Rev. Environ. Sci. Technol.* **39**, 433–477.
- Liu, Y., Kwag, J. H., Kim, J. H. & Ra, C. 2011 Recovery of nitrogen and phosphorus by struvite crystallization from swine wastewater. *Desalination* **277**, 364–369.
- Liu, X., Wen, G., Hu, Z. & Wang, J. 2018 Coupling effects of pH and Mg/P ratio on P recovery from anaerobic digester supernatant by struvite formation. *J. Clean Prod.* **198**, 633–641.
- Matyenia, A., Koralewska, J., Wierzbowska, B. & Piotrowski, K. 2006 The influence of process parameters on struvite continuous crystallization kinetics. *Chem. Eng. Commun.* **193**, 160–176.
- McLean, R. J. C., Downey, J., Clapham, L. & Nickel, J. C. 1990 A simple technique for studying struvite crystal growth in vitro. *Urol Res.* **18**, 39–45.
- Moerman, W., Carballa, M., Wandekerckhove, A., Derycke, D. & Werstraete, W. 2009 Phosphate removal in agro-industry: pilot- and full-scale operational considerations of struvite crystallization. *Water Res.* **43**, 1887–1892.
- Muhmood, A., Lu, J., Dong, R. & Wu, S. 2019a Formation of struvite from agricultural wastewaters and its reuse on farmlands: status and hindrances to closing the nutrient loop. *J. Environ. Manage.* **230**, 1–13.
- Muhmood, A., Lu, J., Kadam, R., Dong, R., Guo, J. & Wu, S. 2019b Biochar seeding promotes struvite formation, but accelerates heavy metal accumulation. *Sci. Total Environ.* **652**, 623–632.
- Munch, E. V. & Barr, K. 2001 Controlled struvite crystallization for removing phosphorus from anaerobic digester sidestreams. *Water Res.* **35**, 151–159.
- Nelson, N. O., Mikkelsen, R. L. & Hesterberg, D. L. 2003 Struvite precipitation in anaerobic swine lagoon liquid: effect of pH and Mg:P ratio and determination of rate constant. *Biores. Technol.* **89**, 229–236.
- Rahman, Md. M., Liu, Y. H., Kwag, J. H. & Ra, C. 2011 Recovery of struvite from animal wastewater and its nutrient leaching loss in soil. *J. Hazard Mater.* **186**, 2026–2030.
- Rahman, Md. M., Salleh, M. A. M., Rashid, U., Ahsan, A., Hossain, M. M. & Ra, C. S. 2014 Production of slow release crystal fertilizer from wastewaters through struvite crystallization: a review. *Arab. J. Chem.* **7**, 139–155.
- Ronteltap, M., Maurer, M. & Gujer, W. 2007 Struvite precipitation thermodynamics in source-separated urine. *Water Res.* **41**, 977–984.
- Ronteltap, M., Maurer, M., Hausherr, R. & Gujer, W. 2010 Struvite precipitation from urine-influencing factors on particle size. *Water Res.* **44**, 2038–2046.
- Smil, V. 2000 Phosphorus in the environment: natural flows and human interferences. *Annu. Rev. Energy Environ.* **25**, 53–88.
- Steen, I. 1998 Phosphorus availability in the 21st century: management of a non-renewable resource. *Phosphorus Potassium* **217**, 25–31.
- Suzuki, K., Tanaka, Y., Kuroda, K., Hanajima, D. & Fukumoto, Y. 2005 Recovery of phosphorus from swine wastewater through crystallization. *Bioresour. Technol.* **96**, 1544–1550.

- Tarrago, E., Puig, S., Rusalleda, M., Balaguer, D. & Colprim, J. 2016 Controlling struvite particles' size using the up-flow velocity. *Chem. Eng. J.* **302**, 819–827.
- Tunay, O., Kabdasli, I., Orhon, D. & Kolcak, S. 1997 Ammonia removal by magnesium ammonium phosphate precipitation in industrial wastewaters. *Water Sci. Technol.* **36**, 225–228.
- Wierzbicki, A., Sallis, J. D., Stevens, E. D., Smith, M. & Sikes, C. S. 1997 Crystal growth and molecular modeling studies of inhibition of struvite by phosphocitrate. *Calcified Tissue Int.* **61** (3), 216–222.
- Wu, S., Zou, S., Liang, G., Qian, G. & He, Z. 2018 Enhancing recovery of magnesium as struvite from landfill leachate by pretreatment of calcium with simultaneous reduction of liquid volume via forward osmosis. *Sci. Total Environ.* **610–611**, 137–146.
- Yang, M., Shi, J., Xu, Z., Zhu, S. & Cui, Y. 2019 Phosphorus removal and recovery from fosfomycin pharmaceutical wastewater by the induced crystallization process. *J. Environ Manage.* **231**, 207–212.
- Yeoman, S., Stephenson, T., Lester, J. N. & Perry, R. 1988 The removal of phosphorus during wastewater treatment: a review. *Environ. Pollut.* **49**, 183–233.
- Zeng, F., Zhao, Q., Jin, W., Liu, Y., Wang, K. & Lee, D. J. 2018 Struvite precipitation from anaerobic sludge supernatant and mixed fresh/stale human urine. *Chem. Eng. J.* **344**, 254–261.

First received 5 November 2018; accepted in revised form 5 April 2019. Available online 15 April 2019