



## Nutrients removal and recovery from anaerobically digested swine wastewater by struvite crystallization without chemical additions

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### ABSTRACT

Anaerobically digested swine wastewater contains high concentrations of phosphorus (P) and nitrogen (N). A pilot-scale experiment was carried out for nutrients removal and recovery from anaerobically digested swine wastewater by struvite crystallization. In the pilot plant, a sequencing batch reactor (SBR) and a continuous-flow reactor with struvite accumulation devices were designed and employed. The wastewater pH value was increased by CO<sub>2</sub> stripping, and the struvite crystallization process was performed without alkali and Mg<sup>2+</sup> additions. Results of the long-term operation of the system showed that, both reactors provided up to 85% P removal and recovery over wide ranges of aeration times (1.0–4.0 h), hydraulic retention times (HRT) (6.0–15.0 h) and temperatures (0–29.5 °C) for an extended period of 247 d, in which approximate 30% of P was recovered by the struvite accumulation devices. However, 40–90% of NH<sub>4</sub><sup>+</sup>-N removed was through air stripping instead of being immobilized in the recovered solids. The recovered products were detected and analyzed by scanning electron microscope (SEM), X-ray diffraction (XRD) and chemical methods, which were proved to be struvite with purity of more than 90%. This work demonstrated the feasibility and effects of nutrients removal and recovery from anaerobically digested swine wastewater by struvite crystallization without chemical additions.

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### 1. Introduction

Extensive swine breeding is an effective way to increase meat production efficiency. However, a large quantity of swine wastewater will be generated. Since the swine wastewater contains high concentrations of phosphorus (P) and nitrogen (N), it has previously been considered as one of the major pollution sources around livestock farms, and has an increasing contribution to eutrophication of water bodies. Therefore, feasible and effective swine wastewater treatment technologies are required for nutrient pollution control. Furthermore, P is a valuable and limited resource, while the known reserves of phosphate rocks will be depleted at the turn of this century if the increase rate of demand is unchanged [1]. P recovery from wastes has become an inevitable process.

Struvite (MgNH<sub>4</sub>PO<sub>4</sub>·6H<sub>2</sub>O) was identified in wastewater treatment plants as early as 1939 [2]. The crystallization of struvite

occurred naturally, which had caused substantial operational problems in wastewater treatment works [3]. However, such properties also provided the pathway for P and N removal and recovery [4]. Previous studies focused on the optimization of solution conditions [5] as well as the characterization of nucleation and crystal growth [6]. Thermodynamic studies [7,8] and kinetic studies [9] were also conducted to describe the process of struvite crystallization. In particular, the use of computer models (such as PHREEQC and MINTEQA2) provided good investigation approaches for understanding the behavior of phosphate crystallization. All these studies have laid good foundation for process control of struvite crystallization, which made struvite crystallization process more and more widely be used in a variety of wastewaters [4,10,11].

Studies have also been conducted to examine struvite formation in swine and livestock wastewaters. Depending on the composition of the wastewater, struvite precipitation can be used to remove ammonia [4,12], phosphate [13] or both of them [14]. Regardless of the compound that was targeted for removal, almost all the studies up to date have utilized the addition of chemicals at least Mg<sup>2+</sup> ion.

In struvite crystallization processes, increasing the operational pH values and adjusting the molar ratios of magnesium, ammonium and phosphate are the most important process parameters [15]. Celen et al. [16] used a chemical equilibrium model to predict

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## Nomenclature

$P_{ortho,in}$	the average concentration of influent dissolved $PO_4^{3-}$ -P (mg/L)
$P_{ortho,ef}$	the average concentration of effluent dissolved $PO_4^{3-}$ -P (mg/L)
$P_{TIP,ef}$	the average concentration of effluent total inorganic phosphorus (TIP) (mg/L)
$P_{total,in}$	the average concentration of influent TP (mg/L)
$P_{total,ef}$	the average concentration of effluent TP (mg/L)
$\eta_{cry}$	the crystallization efficiency (%)
$\eta_{ret,cry}$	the crystal retaining efficiency (%)
$\eta_{rec}$	the overall phosphorus recovery efficiency (%)
$\eta_{lost}$	the crystal lost rate (%)
$[NH_3]$	the free ammonia concentration (mol/L)
$[NH_4^+]$	the ammonium concentration (mol/L)
$[H^+]$	the hydrogen ion concentration (mol/L)
$K_a$	the acid ionization constant of ammonium ion (mol/L)
$K_b$	the ionization constant of aqueous ammonia (mol/L)
$K_w$	the ionization constant of water (mol/L)

amendments required to precipitate phosphate as struvite in liquid swine manure. By adding magnesium, additional phosphate can be removed. However, the small increase in P recovery would not justify the additional magnesium cost. Zeng and Li [14] also found that the required Mg/P molar ratio was more than 5 times higher than the stoichiometric values in the anaerobically digested and centrifuged manure effluents by struvite precipitation. Reasons for additional magnesium sources requirement are: (i) For many swine wastewaters, there is a lack of  $Mg^{2+}$  for struvite formation [15,16]. (ii) NaOH is generally used for pH adjustment. The addition of NaOH will produce a quick elevation of solution pH value and cause sharp increase of saturations of other magnesium precipitations besides struvite [14]. Thus, much of  $Mg^{2+}$  will be consumed in the formation of other magnesium precipitations (i.e. bobierrite and magnesite). Then, the actually required  $Mg^{2+}$  will be higher than the theoretical values. Alternatively, when anaerobically processed wastewaters were treated, another method could be employed for pH adjustment. Williams [17] showed the wastewater pH values could be increased by simple  $CO_2$  stripping. This method provides much gentler pH increase. Thus, the excessive growth of solution saturations will be prevented, then the formation potential of other magnesium precipitates will be reduced and well struvite crystallization will be insured. Therefore, the utilization of  $CO_2$  stripping for pH adjustment will not only save NaOH addition, but also reduce  $Mg^{2+}$  addition or even save all of them.

In practical application, both precipitation of struvite and the separation of struvite crystals should be considered. For these purposes, several reactors for removing and recovering phosphorous from swine wastewater have been designed [18–20]. However, the separation of struvite particles for the total phosphorus (TP) removed was still an outstanding issue [21]. To enhance the separation or collection of struvite particles, attempts have also been made by seeding the reaction or by developing crystal accumulating devices. Burns et al. [22] showed that seeding the struvite crystallization reaction did not significantly enhance the recovery efficiency. Perera et al. [23] proved that the use of an accumulating device was a promising way to recover pure struvite, and it was also recommended that pilot-scale and long-term studies should be conducted for further demonstration.

Now, full-scale reactors have been incorporated into a few municipal and industrial wastewater treatment systems all over the world but their implementation was not common practice in

livestock production facilities [22], only seldom studies in pilot-scale have been reported [20]. The demonstration of struvite crystallization process applied to swine wastewater treatment and the development of new, economical and efficient reactors for P removal and recovery from swine wastewaters was urgently needed.

In this study, a sequencing batch reactor (SBR) and a continuous-flow reactor was developed with stainless steel struvite accumulation devices installed in the reactors. The wastewater pH values were elevated by  $CO_2$  stripping, and the struvite crystallization process was performed without  $Mg^{2+}$  addition. The objective of this study was to test the long-term performance of the newly developed pilot-scale system for nutrients removal and recovery without chemical additions.

## 2. Materials and methods

### 2.1. Pilot plant design and operational parameters

The experiments were carried out at a deep-pit pig farm (10,000 head/a) at the suburban area of Beijing, where dry collection systems for manure and wastes were used in the pig farm.

The struvite crystallization process unit was installed between the anaerobic biological process unit and the aerobic biological process unit. Through anaerobic digestion, more than 90% of organic P and N in swine wastewater were transformed into phosphate and ammonia. Then most of the phosphate and part of the ammonia were expected to be removed and recovered by struvite crystallization process. The schematic diagram of the pilot scale SBR and continuous-flow reactors built up for real swine wastewater treatment is shown in Fig. 1.

The SBR was a barrel with a conical bottom. The effective volume of the reactor was  $1.0\text{ m}^3$ . A stainless steel crystal collector (1.0 m diameter  $\times$  1.5 m height) made of four layers (layer distance 0.125 m) of concentric cylindrical stainless steel meshes were installed in the reactor. The mesh was woven with a 1.0 mm steel wire forming 5 mm holes. The total surface area of the accumulating faces was  $14.8\text{ m}^2$ . Three coarse air bubble diffusers were mounted at the bottom of the reactor to provide diffused aeration for mixing and  $CO_2$  stripping. The reactor was operated in the sequencing batch mode with four phases: loading (0.5 h),  $CO_2$  stripping by aeration (1.0–4.0 h), sedimentation (0.5 h), and drainage (0.5 h). Four aeration times of 1.0 h, 2.0 h, 3.0 h and 4.0 h (lab-scale tests showed that the wastewater pH values could increased from about 7.0 to about 8.5 by  $CO_2$  stripping of 1.0 h, and the pH value become stable at about 9.0 after 4.0 h aeration) were used to study the effects of aeration time on struvite crystallization and P removal and recovery efficiency. Furthermore, nutrients removal and recovery efficiencies of the reactor at low temperature ( $<10^\circ\text{C}$ ) were studied with the aeration time of 1.0 h.

The continuous-flow reactor was a cubic column with a pyramid bottom, and had a volume of  $4.0\text{ m}^3$  (Fig. 1) consisting of a reacting zone of  $1.3\text{ m}^3$  and a settling zone of  $2.6\text{ m}^3$ . The same crystal collector as used in SBR was installed in the reacting zone. Four coarse air bubble diffusers were mounted at the bottom of the reacting zone. The reactor was operated at the continuous-flow mode. Four hydraulic retention time (HRT) of 6.0 h, 9.0 h, 12.0 h and 15.0 h were used to check the effects of HRT on struvite crystallization and P removal and recovery efficiencies (The selection of HRTs was based on the lab-scale tests. Suzuki et al. [20] had also demonstrated that, at HRTs of 16.8 h and 22.3 h, promising results were obtained by using a similar reactor treating swine wastewater. The present study attempted to try some shorter HRTs.) Equally, the nutrients removal and recovery efficiencies of the reactor at low temperature ( $<10^\circ\text{C}$ ) were studied under the HRT of 15.0 h.

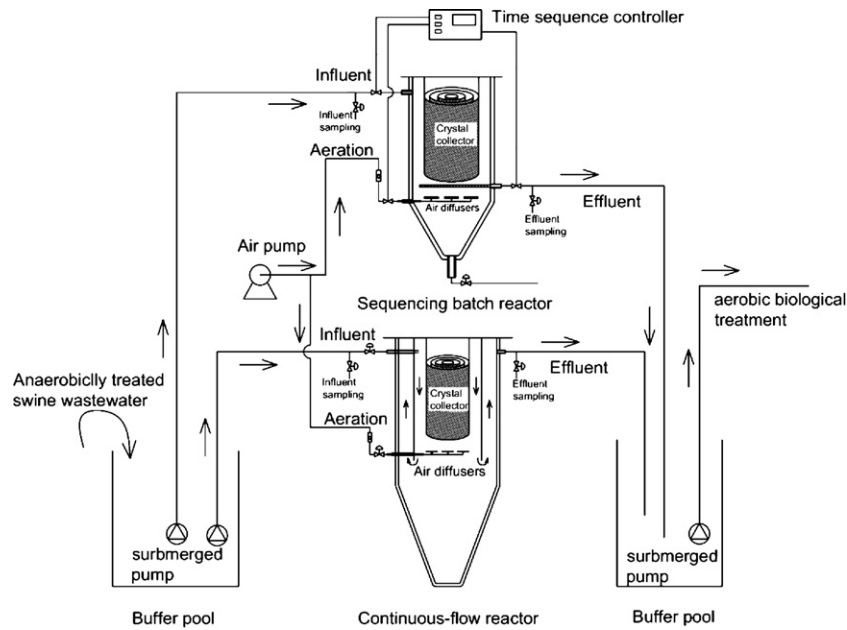


Fig. 1. Struvite crystallization pilot plant.

The crystal collectors were taken out of the SBR and the continuous-flow reactors at the end of each stage, and the recovered solids were scraped off the collectors.

The operational parameters of the two reactors were summarized in Table 1. The supernatant from an upflow anaerobic sludge blanket reactor for swine wastewater treatment was fed into two reactors. Table 2 shows the range, arithmetic average and standard deviation of daily sampling of the influent during the whole pilot-scale experiment. Significantly high concentrations of  $\text{NH}_4^+$ -N,  $\text{PO}_4^{3-}$ -P,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  were observed.

## 2.2. Analytical methods

The concentrations of  $\text{NH}_4^+$ -N,  $\text{PO}_4^{3-}$ -P, and TP in influent and effluent of each reactor were measured by using a spectrophotometer (752N, China) with standard methods [24].  $\text{NH}_4^+$ -N was determined with Nessler's reagent colorimetric method.  $\text{PO}_4^{3-}$ -P was measured with molybdate–ascorbic acid colorimetric method. TP was measured with persulfate digestion molybdate–ascorbic acid colorimetric method. The total inorganic phosphorus (TIP) in the effluent was determined by adjusting the effluent pH value to 1.0 with concentrated hydrochloric acid, then measuring  $\text{PO}_4^{3-}$ -P.  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were measured with an atomic adsorption photometer (Shimadzu AA-6800, Japan). The wastewater was filtrated with 0.45  $\mu\text{m}$  membranes, and the filtrate was diluted with 0.2 M  $\text{HNO}_3$  to the specified volume to prepare samples for atomic adsorption analyses. Other parameters, including alkalinity, pH value and temperature were monitored at regular intervals. Alkalinity was analyzed by using titration method. pH value and temperature were measured with a pH meter (WTW Model 3300I with SenTix 41 pH electrode, Germany).

The morphology of the captured solids on the collector of the continuous-flow reactor was observed by using scanning electron spectroscopy (SEM, KYKY-2800, China), and the composition of the crystals were analyzed with X-ray diffraction (XRD, Rigaku DMAX-RB, Japan).

All the analyses were performed in triplicate and the average figures were calculated. Statistical analysis of experimental data was performed by using the analytical software SPSS 11.0 (SPSS Inc., USA).

## 2.3. P removal and recovery assessment in the struvite crystallization process

The P removal and recovery capacity of the reactor was assessed by taking into account three types of efficiencies: the crystallization efficiency  $\eta_{\text{cry}}$  (Eq. (1)), the crystal retaining efficiency  $\eta_{\text{ret,cry}}$  (Eq. (2)) and the overall P recovery efficiency  $\eta_{\text{rec}}$  (Eq. (3)), as well as the crystal lost rate  $\eta_{\text{lost}}$  (Eq. (4)). The crystallization efficiency  $\eta_{\text{cry}}$  represents the process efficiency transforming  $\text{PO}_4^{3-}$ -P into struvite crystals, which is equal to the  $\text{PO}_4^{3-}$ -P removal efficiency. The crystal retaining efficiency  $\eta_{\text{ret,cry}}$  represents the process efficiency retaining crystals (since the struvite crystals in the influent are negligible,  $P_{\text{TIP,in}}$  is equal to  $P_{\text{ortho,in}}$ ). The overall P recovery efficiency represents the reactor efficiency retaining P in all forms, which is equal to the TP removal efficiency. The crystal lost rate represents the percentage of crystal lost with the effluent, which can be obtained by  $\eta_{\text{cry}}$  minus  $\eta_{\text{ret,cry}}$ .

$$\eta_{\text{cry}} = \frac{P_{\text{ortho,in}} - P_{\text{ortho,ef}}}{P_{\text{ortho,in}}} \quad (1)$$

$$\eta_{\text{ret,cry}} = \frac{P_{\text{ortho,in}} - P_{\text{TIP,ef}}}{P_{\text{ortho,in}}} \quad (2)$$

$$\eta_{\text{rec}} = \frac{P_{\text{total,in}} - P_{\text{total,ef}}}{P_{\text{total,in}}} \quad (3)$$

$$\eta_{\text{lost}} = \frac{P_{\text{TIP,ef}} - P_{\text{ortho,ef}}}{P_{\text{ortho,in}}} = \eta_{\text{cry}} - \eta_{\text{ret,cry}} \quad (4)$$

## 3. Results and discussion

### 3.1. Phosphorus removal and recovery in SBR

The influence of aeration time on struvite crystallization and P removal and recovery, as well as the effects of low temperature ( $<10^\circ\text{C}$ ) were studied in SBR. The results were shown in Figs. 2 and 3. It was clear that the removal rates of  $\text{PO}_4^{3-}$ -P kept at a high level (85–95%) in all the aeration times (Fig. 2). In addition, it seemed that the decrease of the aeration time had no distinct effect on  $\text{PO}_4^{3-}$ -P removal.

**Table 1**  
Operational parameters and P removal and recovery efficiencies of the SBR and the continuous-flow reactors.

Parameter	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5
Time (d)	1–44	45–90	91–150	150–190	190–247
Temperature (°C)	13.0–25.5	19.0–29.5	14.0–29.0	10.0–20.0	0.0–10.0
SBR					
Aeration time (h)	4.0	3.0	2.0	1.0	1.0
Sedimentation time (h)	0.5	0.5	0.5	0.5	0.5
Aeration intensity (m <sup>3</sup> /h)	15.0	15.0	15.0	15.0	15.0
Cycles completed (cycle)	176	188	144	160	96
$\eta_{cry}$ (%)	90.5 ± 4.0	94.8 ± 3.1	91.4 ± 2.6	89.6 ± 2.8	88.4 ± 2.6
$\eta_{ret,cry}$ (%)	79.1 ± 5.7	84.3 ± 5.8	87.2 ± 7.2	81.5 ± 6.7	79.4 ± 6.6
$\eta_{rec}$ (%)	88.4 ± 6.1	89.1 ± 4.0	89.1 ± 2.6	87.9 ± 4.2	85.8 ± 4.0
$\eta_{lost}$ (%)	11.4 ± 5.2	10.5 ± 6.5	4.2 ± 6.3	8.1 ± 7.2	9.0 ± 6.1
Continuous-flow reactor					
HRT (h)	6.0	9.0	12.0	15.0	15.0
Aeration intensity (m <sup>3</sup> /h)	25.0	25.0	25.0	25.0	25.0
$\eta_{cry}$ (%)	85.4 ± 5.6	86.1 ± 7.9	93.9 ± 2.7	88.6 ± 3.2	87.8 ± 4.1
$\eta_{ret,cry}$ (%)	71.2 ± 8.6	77.5 ± 5.5	85.7 ± 11.1	79.7 ± 5.0	79.1 ± 6.9
$\eta_{rec}$ (%)	84.1 ± 8.8	86.9 ± 5.0	88.3 ± 4.1	87.4 ± 3.5	84.3 ± 4.5
$\eta_{lost}$ (%)	14.2 ± 6.4	8.6 ± 7.1	8.2 ± 10.5	8.9 ± 5.3	8.7 ± 6.8

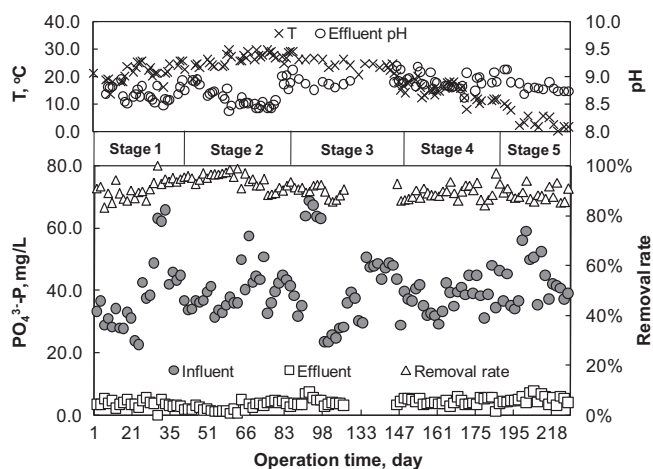
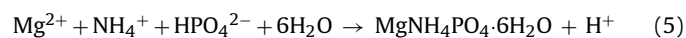
$\eta_{cry}$ , the crystallization efficiency (%);  $\eta_{ret,cry}$ , the crystal retaining efficiency (%);  $\eta_{rec}$ , the overall phosphorus recovery efficiency (%);  $\eta_{lost}$ , the crystal lost rate (%). The  $\eta_{cry}$ ,  $\eta_{ret,cry}$ ,  $\eta_{rec}$ , and  $\eta_{lost}$  values showed the arithmetic average and standard deviation of all dairy samplings within each stage.

**Table 2**  
Influent quality of the pilot-scale struvite crystallization system (the range, arithmetic average and standard deviation of daily sampling of the influent during the whole pilot-scale experiment).

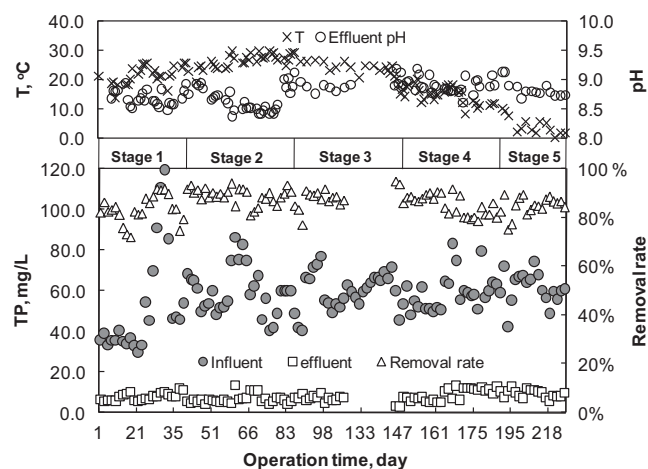
Parameters	Range	Arithmetic average	Standard deviation
pH	6.95–7.81	7.18	0.18
COD (mg/L)	1123–3286	2108	479
NH <sub>4</sub> <sup>+</sup> -N (mg/L)	410–1379	706	216
PO <sub>4</sub> <sup>3-</sup> -P (mg/L)	22.2–68.7	40.3	9.5
Ca <sup>2+</sup> (mg/L)	102.0–167.7	123.6	16.7
Mg <sup>2+</sup> (mg/L)	53.7–69.0	60.0	4.3
Alkalinity (as CaCO <sub>3</sub> ) (mg/L)	5210–6840	5920	570
Mg/P molar ratios	1.31–2.42	1.79	0.3

Solution pH value is an important parameter for struvite crystallization. The formation of struvite normally occurred in slightly alkaline environment, and the optimal pH value for struvite crystallization was considered to be 8.0–10.0 [25]. Suzuki et al. [20] further found the feasibility for reaching pH values around 8.5–8.6 only by CO<sub>2</sub> stripping. In the whole process of the present study, the pH value fluctuated between 8.5 and 9.0, which was consistent with the pH value at which the solubility of struvite was the lowest in solution. Generally, stripping of dissolved CO<sub>2</sub> would be inten-

sified with the increase of aeration time, thus the pH value of the wastewater would increase as aeration time increased. However, the solution pH in stage 2 was a little lower than that in stages 3, 4 and 5. Maybe it was because struvite crystallization process could produce protons (Eq. (5), [26]). From Fig. 2, the highest phosphate removal occurred in stage 2, and more proton production under this condition lowered the pH values.



**Fig. 2.** PO<sub>4</sub><sup>3-</sup>-P removal in the SBR (stage 1: 1–44 d, aeration time 4.0 h, 13.0–25.5 °C; stage 2: 45–90 d, aeration time 3.0 h, 19.0–29.5 °C; stage 3: 91–150 d, aeration time 2.0 h, 14.0–29.0 °C; stage 4: 150–190 d, aeration time 1.0 h, 10.0–20.0 °C; stage 5: 190–247 d, aeration time 1.0 h, 0.0–10.0 °C).



**Fig. 3.** TP removal in the SBR (stage 1: 1–44 d, aeration time 4.0 h, 13.0–25.5 °C; stage 2: 45–90 d, aeration time 3.0 h, 19.0–29.5 °C; stage 3: 91–150 d, aeration time 2.0 h, 14.0–29.0 °C; stage 4: 150–190 d, aeration time 1.0 h, 10.0–20.0 °C; stage 5: 190–247 d, aeration time 1.0 h, 0.0–10.0 °C).

Temperature may also affect the struvite crystallization. It was clear that lower temperature benefited struvite crystallization for thermodynamic reasons [7]. However, low temperature also led to the decrease of the reaction rate of crystallization. Zeng and Li [14] found that the phosphate removal efficiency was increased from 63% to 78%, when the reaction temperature increased from 5 to 50 °C. However, there was also a number of contradicting experimental results in the literature regarding the effect of temperature on struvite formation [27]. In the present experiment, high removal of  $\text{PO}_4^{3-}\text{-P}$  could be obtained even under low temperature (<10 °C).

The removal of TP was shown in Fig. 3, the effluent TP kept low concentrations despite the aeration time reduced from 4.0 h to 1.0 h and the average concentration of TP in the effluent was lower than 8.0 mg/L, which met the pollutant discharge standards of livestock and poultry breeding industry of China [28].

Moreover, the P removal and recovery capacity of the reactor was evaluated, the  $\eta_{cry}$ , the  $\eta_{ret,cry}$ , the  $\eta_{rec}$ , and the  $\eta_{lost}$  in five runs were shown in Table 1. The highest  $\eta_{cry}$  was obtained at the aeration time of 3.0 h, but the highest  $\eta_{ret,cry}$  and the lowest  $\eta_{lost}$  were observed at the aeration time of 2.0 h.

Theoretically, the crystallization rate is mainly determined by thermodynamic conditions. While the crystal recovery rate and the crystal lost rate are closely related to the characteristics of the struvite crystals formed, it must take into account both the dynamic and the hydraulic factors. From a dynamic point of view, the formation of crystals usually occurs homogeneously or heterogeneously, depending on the degree of solution super-saturation which can be described by the saturation index (SI) value. Studies indicated that a clear change from heterogeneous to homogenous nucleation happened when the SI value increased [29]. Long aeration time would naturally increase the SI value. Although the higher crystallization rate would be obtained, the higher SI value would possibly result in additional formation of fine struvite crystals homogeneously in the bulk solution. Even more unfavorably, at long aeration time, higher hydraulic shear forces would further break fine struvite crystal into much smaller particles, and then higher crystal lost rate was observed.

Additionally, in the formation process of the crystals, the nucleation was figured to be much more difficult than the crystal growth [30], as the formation of a new phase had to overcome a bigger potential energy barrier of phase transition. At the beginning of operation, the crystal-free crystal collector was not conducive for the attachment of struvite crystals. Therefore, higher  $\eta_{lost}$  was observed in the initial run (aeration time = 4.0 h) of the reactor.

Considering from the economic costs, the application of long aeration time should be avoided. And for the purpose of P removal and recovery an aeration time of 1.0 h would be favorable.

### 3.2. Phosphorus removal and recovery in the continuous-flow reactor

The influence of HRT on struvite crystallization and P removal in the continuous-flow reactor was shown in Figs. 4 and 5.

The P removal efficiency of the reactor kept stable and was almost not affected by the water temperature (0–29.5 °C, the actual temperature range of the swine wastewater around a year) and the influent P concentration (29.52–119.26 mg/L) during the pilot-scale experiment. The effluent TP concentration could meet the pollutant discharge standards of livestock and poultry breeding industry of China [28].

Comparatively, the removal rates of TP and  $\text{PO}_4^{3-}\text{-P}$  in the continuous-flow reactor were a little lower than that in the SBR. That was mostly due to the flow regime difference in two reactors. And under the continuous-flow condition, P rich particles had a higher tendency to escape from the reactor.

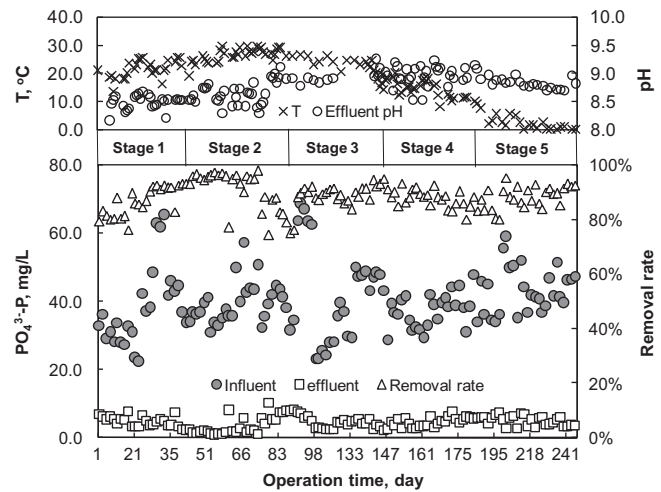


Fig. 4.  $\text{PO}_4^{3-}\text{-P}$  removal in the continuous-flow reactor (stage 1: 1–44 d, HRT 6.0 h, 13.0–25.5 °C; stage 2: 45–90 d, HRT 9.0 h, 19.0–29.5 °C; stage 3: 91–150 d, HRT 12.0 h, 14.0–29.0 °C; stage 4: 150–190 d, HRT 15.0 h, 10.0–20.0 °C; stage 5: 190–247 d, HRT 15.0 h, 0.0–10.0 °C).

The P removal and recovery capacity was assessed in the continuous-flow reactor. The  $\eta_{cry}$  (which was equal to the average removal rate of  $\text{PO}_4^{3-}\text{-P}$ ), the  $\eta_{rec}$  (which was equal to the TP removal rate) and the  $\eta_{lost}$  were shown in Table 1. Almost the same  $\eta_{lost}$  was observed under all the stages except for the HRT of 6.0 h. Short HRT would certainly shorten the sedimentation time of the struvite crystals. Pastor et al. [31] also observed an increase of the proportion of small particles (10 and 100  $\mu\text{m}$ ) when short HRT was employed. It revealed that, the decrease of HRT would not only change the hydraulics of the reactor, but also cause a decrease of the crystal size. All of these would contribute to the increase of  $\eta_{lost}$  at short HRT conditions. In this experiment, for the purpose of P removal and recovery an HRT of 9.0 h would be favorable. The continuous-flow reactor could also achieve good effects of P removal and recovery.

Several reactors for P removal and recovery from swine wastewaters have been designed. Bowers and Westerman [32] developed a cone-shaped fluidized bed reactor for swine wastewater treatment. In the fluidized bed struvite was used as seed to promote the growth of struvite crystals. Modeling and test results indicated that the conical reactor created plug-flow conditions for liquid and

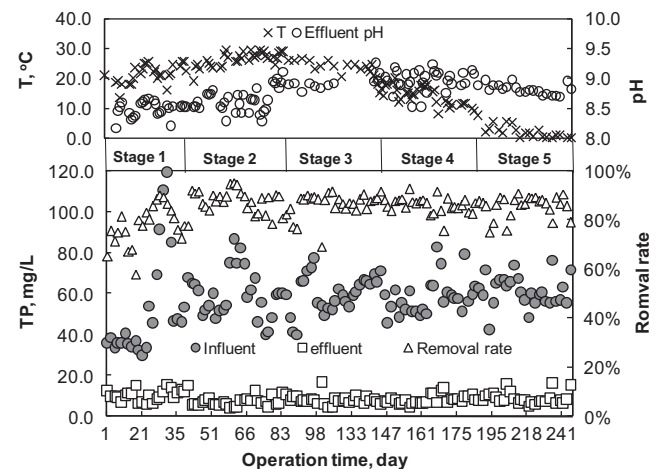


Fig. 5. TP removal in the continuous-flow reactor (stage 1: 1–44 d, HRT 6.0 h, 13.0–25.5 °C; stage 2: 45–90 d, HRT 9.0 h, 19.0–29.5 °C; stage 3: 91–150 d, HRT 12.0 h, 14.0–29.0 °C; stage 4: 150–190 d, HRT 15.0 h, 10.0–20.0 °C; stage 5: 190–247 d, HRT 15.0 h, 0.0–10.0 °C).

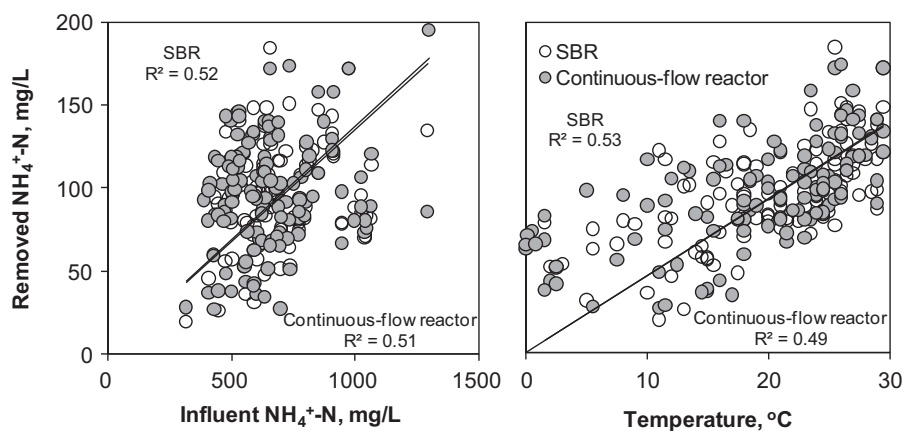


Fig. 6. Relationships between the influent  $\text{NH}_4^+\text{-N}$ , temperature and removed  $\text{NH}_4^+\text{-N}$  for both reactors during the whole operation time (247 d).

provided complete mixing in the reactor. Field tests demonstrated that P removal rates ranged from 36% to 74%, and TP reductions ranged from 24% to 58% at HRT of 72–74 s. Shepherd et al. [21] used a bench-scale continuous flow tank reactor for swine manure slurries treatment and struvite was precipitated. This system took air sparging for pH adjustment and for mixing, and  $\text{MgCl}_2$  injection for struvite precipitation. It provided phosphate reduction of up to 93%. However, the separation of struvite particles for TP reduction was not achieved with an up-flow clarifier operated in continuous flow mode at an HRT of 10 min. Suzuki et al. [20] developed a dual function continuous-flow reactor, i.e., to realize crystallization of struvite through  $\text{CO}_2$  stripping, and to separate the formed struvite by settling; the HRT for the aeration column was 3.6 and 22.3 h for the total reactor; with 30%  $\text{MgCl}_2$  addition, 72.8% phosphate and 79% TP removals were obtained. Compared with above studies, in our present system, both reactors provided up to 85% P removal and recovery over a wide aeration time range of 1.0–4.0 h, a wide HRT of 6.0–15.0 h and a temperature range of 0–29.5 °C. The crystal collectors installed in the reactors had trapping effect on the suspended struvite crystals [23]. Additionally, in our SBR, the sequencing batch operation mode provided an isolated and undisturbed sedimentation period in each cycle, and the sedimentation height was 1.2 m; while struvite had a specific gravity of 1.7, according to the Stokes law, all struvite particles larger than 55  $\mu\text{m}$  would be removed by sedimentation within 30 min. In our continuous-flow reactor, all struvite particles larger than 65  $\mu\text{m}$  would be removed at the HRT of 6.0 h. In all, the two reactors were efficient for P removal and recovery. Especially they could capture small struvite particles due to their good retention effects.

Additionally, throughout the experiment, no chemicals were added.  $\text{CO}_2$  stripping could realize pH adjustment instead of NaOH addition. As for magnesium requirements for struvite crystallization, Burns et al. [22] determined that an Mg/P molar ratio of 1.6 would be effective for phosphate removal from swine manure slurries. Jordaan et al. [13] also pointed out that with an Mg/P ratio of 1.6 the maximum P removal of 80% could be achieved at pH value 9.0 for struvite precipitation from anaerobically digested swine manure. In our experiments, without magnesium addition the wastewater possessed an Mg/P molar ratio of 1.31–2.42 with an average value of 1.79 (Table 1), so sufficient magnesium in wastewater insured high P removal and recovery.

In this study, both the SBR and the continuous-flow reactor could achieve long term, stable and high phosphate and TP removal and recovery under wide ranges of aeration time, HRT and temperature conditions, and this demonstrated these kinds of reactors were suitable for practical phosphate removal and recovery from swine wastewaters.

### 3.3. Nitrogen removal and recovery in two reactors

The relationships of the influent  $\text{NH}_4^+\text{-N}$ , removed  $\text{NH}_4^+\text{-N}$  and temperature were shown in Fig. 6. Ammonia can be combined together with Mg and phosphate ions to form struvite, so it can be removed and recovered with struvite crystals. During the operation period, the average removal of  $\text{PO}_4^{3-}\text{-P}$  was 38.1 mg/L for SBR and 36.6 mg/L for continuous-flow reactor. According to the stoichiometric relationship, the  $\text{NH}_4^+\text{-N}$  recovered in the struvite crystal would be about 15 mg/L. However, the average removal of  $\text{NH}_4^+\text{-N}$  was 69.0 mg/L for SBR and 64.8 mg/L for the continuous-flow reactor. It was proposed that in the  $\text{CO}_2$  stripping process, the air agitation could also strip some free ammonia. Then, a large amount of  $\text{NH}_4^+\text{-N}$  would be removed with the free ammonia form.

Furthermore, the concentration of free ammonia in solution was a function of  $\text{NH}_4^+\text{-N}$  concentration, pH value and temperature [33], which was shown in Eq. (6). Using this formula, it could be calculated that at pH value of 8.5, when the temperature was 0 °C, only about 2.5% of the  $\text{NH}_4^+\text{-N}$  was in the form of free ammonia. However, when the temperature rose to 30 °C it reached 20.3%. Therefore, it could be seen from Fig. 6 that the removal amount of  $\text{NH}_4^+\text{-N}$  increased along with the increase of influent  $\text{NH}_4^+\text{-N}$  (the correlation coefficients was 0.52 for SBR and 0.51 for the continuous-flow reactor) and temperature (the correlation coefficients was 0.63 for SBR and 0.59 for the continuous-flow reactor).

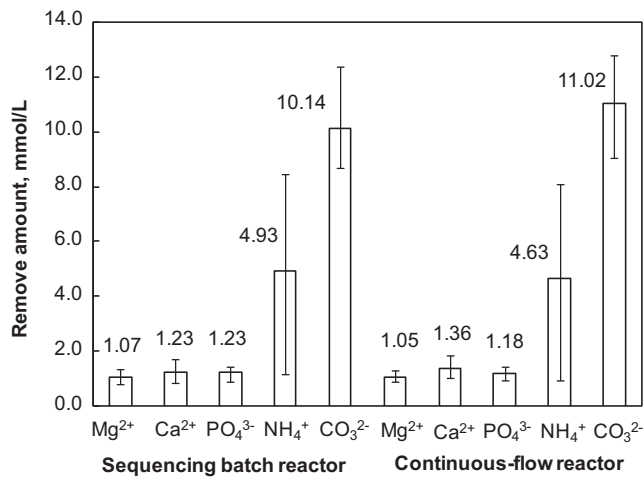
$$[\text{NH}_3] = \frac{[\text{NH}_3] + [\text{NH}_4^+]}{(1 + [\text{H}^+])/K_a} \quad (6)$$

$$K_a = \frac{K_w}{K_b} = e^{-(6344/(273/T))} \quad (7)$$

In all runs (Table 1), the removal rate of  $\text{NH}_4^+\text{-N}$  in two reactors was from 7.5% to 35%. Just assessing the value calculated from the stoichiometric relationship, there were about 40–90%  $\text{NH}_4^+\text{-N}$  removed was through air stripping.

### 3.4. Relationship among removals of dissolved $\text{PO}_4^{3-}$ , $\text{NH}_4^+$ , $\text{Mg}^{2+}$ , $\text{Ca}^{2+}$ and $\text{CO}_3^{2-}$

The relationships among removals of dissolved  $\text{PO}_4^{3-}$ ,  $\text{NH}_4^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  were shown in Fig. 7.  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  were also removed remarkably in both reactors besides the removal of  $\text{Mg}^{2+}$ ,  $\text{PO}_4^{3-}$  and  $\text{NH}_4^+$ . From a thermodynamics point of view, in anaerobically digested swine wastewater where  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{PO}_4^{3-}$ ,  $\text{NH}_4^+$  and  $\text{CO}_3^{2-}$  coexisted. When the pH value was about 8.5, struvite and magnesium phosphate were the only two magnesium precipitates that most likely to be formed [34]. While  $\text{Ca}^{2+}$



**Fig. 7.** Removal amounts of dissolved PO<sub>4</sub><sup>3-</sup>, NH<sub>4</sub><sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, and CO<sub>3</sub><sup>2-</sup> in two reactors during the whole pilot-scale experiment (calculated from daily sampling results of 247 d operation, the error bar represent for the standard deviation).

could form calcium phosphate and calcium carbonate by combining with PO<sub>4</sub><sup>3-</sup> and CO<sub>3</sub><sup>2-</sup>, respectively. The formation of other minerals like newberyite and dolomite is normally negligible due to inappropriate pH value or low precipitation rates [31]. Since there was high concentration of CO<sub>3</sub><sup>2-</sup> in the anaerobically digested swine wastewater which could strongly inhibit the combination of Ca<sup>2+</sup> and PO<sub>4</sub><sup>3-</sup> [35], and the presence of strong NH<sub>4</sub><sup>+</sup> would promote the formation of struvite, the removed Mg<sup>2+</sup> could be used to evaluate the percentage of PO<sub>4</sub><sup>3-</sup> precipitated as struvite [34].

During the experiment, the average molar ratios of removed Mg<sup>2+</sup> and PO<sub>4</sub><sup>3-</sup> was 0.80–0.88, which indicated that at least 12–20% of dissolved PO<sub>4</sub><sup>3-</sup> was removed by other ways such as being combined with Ca<sup>2+</sup>. Other Ca<sup>2+</sup> might combine with CO<sub>3</sub><sup>2-</sup> to form calcium carbonate. CO<sub>3</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup> could be transformed into carbon dioxide and free ammonia, so they could be degasified from wastewater. In order to find the final fates of the five ions, the recovered solids were analyzed.

### 3.5. Analysis of recovered solids

The recovered solids were scraped off the collectors at the end of each stage. In all stages, the solids was easily recoverable by gentle scraping, the recovered solids were crystal particles with a mean diameter of 3.41 ± 0.85 mm. The crystal particles was strong, non-shattering and was resistant to moderate shaking and hitting. The amount of solids varied among stages. However, the recovery rates were all about 30%, e.g. the amount of solids for the SBR at aeration time of 1.0 h and the continuous-flow reactor at HRT of 6.0 h could be found in Table 4. As no mechanical elevation equipment was installed, the collector was lifted out the reactors manually. Because the crystal-covered collectors were heavy, they were somewhat

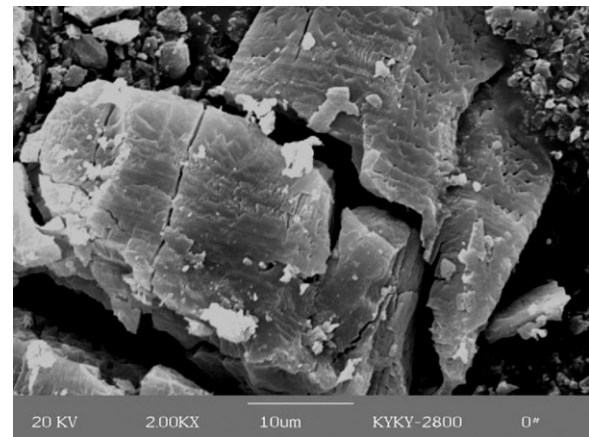
**Table 3**  
Element contents of the recovered solids and the sediments (the arithmetic average and standard deviation of 5 samplings in both the SBR and the continuous-flow reactors compared to the theoretical contents of pure struvite).

Elements	Phosphorus	Magnesium	Nitrogen	Calcium
<b>SBR</b>				
Solids deposited on the collector (mg/g)	118.7 ± 4.3	88.9 ± 5.2	51.0 ± 3.1	13.1 ± 3.0
Sediments settled at the bottom (mg/g)	92.2 ± 3.7	72.4 ± 3.5	36.5 ± 5.2	37.4 ± 4.9
<b>Continuous-flow reactor</b>				
Solids deposited on the collector (mg/g)	117.5 ± 6.8	88.7 ± 4.1	51.7 ± 3.1	15.2 ± 2.2
Sediments settled at the bottom (mg/g)	89.7 ± 5.1	69.2 ± 3.9	38.1 ± 4.2	35.5 ± 6.2
Theoretical element contents of struvite (mg/g)	126.5	98.0	57.1	–

**Table 4**

Mass balance of phosphorus within the SBR and the continuous-flow reactor (estimated material flow of phosphorus during 160-cycle operation of the SBR at aeration time of 1.0 h and 44-d operation of the continuous-flow reactor at HRT of 6.0 h).

Mass balance	SBR	Continuous-flow reactor
Operation period (d)/completed cycles (cycle)	160	44
Influent P (kg)	6.06	26.82
Effluent P (kg)	0.72	3.35
Solids deposited on the collector		
Solids (kg)	15.7	67.3
P content (%)	12.1	11.9
P accumulated on the collector (kg)	1.90	8.01
Proportion in influent P (%)	31.4	29.9
Sediments settled at the bottom		
Sediments (kg)	28.9	126.5
P content (%)	9.4	8.9
P in bottom sediments (kg)	2.72	11.3
Proportion in influent P (%)	44.9	42.1



**Fig. 8.** The SEM photo of recovered solids (scraped off the collector in the continuous-flow reactor at the very end of the pilot-scale experiment, magnification 2000 times).

difficult to handle, that was a problem to be solved in further operations.

The solids were dried naturally at room temperature, the morphology was observed by SEM, and the structure of the solids was detected with XRD. Figs. 8 and 9 show the results of recovered solids in the continuous-flow reactor at the very end of the pilot-scale experiment, the results of the solids collected at other stages both in the SBR and the continuous-flow reactors were all similar to these results. Furthermore, the solids from each stage were dissolved by using 0.10 M HCl, and the element contents of N, P, Mg and Ca were analyzed repeatedly for three times to check the reproducibility of the results. Table 3 shows the arithmetic average and standard deviation of the 5 samplings of both SBR and the continuous-flow reactors.

The XRD diffractogram was shown in Fig. 9. The patterns of the recovered solids matched well with the struvite patterns. How-

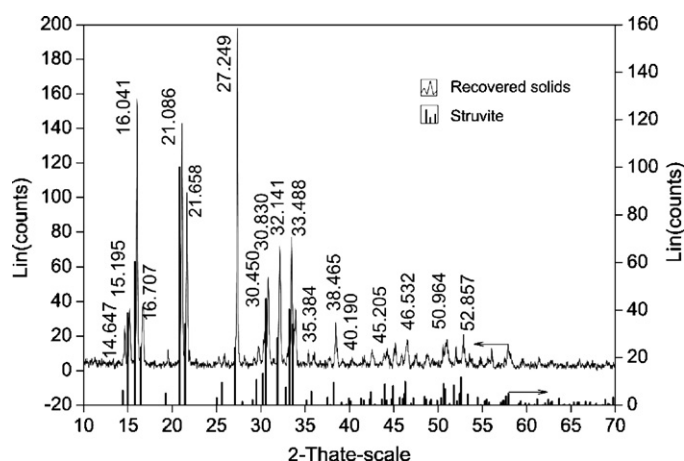


Fig. 9. XRD diffractogram of recovered solids (scraped off the collector in the continuous-flow reactor at the very end of the pilot-scale experiment).

ever, offsets of solids peaks to big diffraction angles were observed. According to Bragg's equation, it indicated the lattice expansion of the recovered solids. That was probably because in the struvite crystallization process, some of the  $Mg^{2+}$  in the crystal lattice might be replaced by the same second main group element, Ca. Since the ionic radius of  $Ca^{2+}$  was bigger than that of  $Mg^{2+}$ , the doping of  $Ca^{2+}$  would result in lattice expansion of the crystals. Furthermore, the distribution of the peak abundance for recovered solids was inconsistent with struvite patterns, which indicated the transformation of crystal orientation and the formation of secondary structures in the recovered solids. That was due to the complicated crystallization condition in anaerobically digested swine wastewater as well as the continuous and repeated crystallization and re-crystallization of recovered solids during the experiment.

From the SEM photo shown in Fig. 8, the shape of the recovered crystals was different from the familiar needle-like ones [36], which validated the transformation of crystal orientation shown in the XRD diffractogram. However, the recovered solids had the same surface characteristics with pure struvite crystals. Both of them had flake-like structure and triangular cavity on the surface, which revealed the same lattice arrangement.

As mentioned in Section 3.4, calcium phosphate and calcium carbonate might form in the process, but none of these substances were observed either in the XRD or SEM analysis. That might be because two amorphous calcium precipitates tended to be lost with the effluent or accumulated in the sediments instead of attaching on the collectors in the reactors.

To determine the chemical composition of the recovered solids, the element contents were analyzed, and the results were shown in Table 3. The element contents of N, P, and Mg in the recovered solids were all slightly lower than those theoretical values in pure struvite. Additionally, a certain amount of Ca was detected in recovered solids which confirmed the deduction that  $Ca^{2+}$  might participate in the struvite crystallization process. The sum of N, P, Mg and Ca was around 270 mg/g. Most of the remainder of the mass (730 mg/g) could be attributed to the  $H_4$  in  $NH_4$ ,  $O_4$  in  $PO_4$  and the  $6(H_2O)$  in struvite. The purity of recovered solids was more than 90% by checking the elements content of N, P, and Mg, which was not affected by  $Ca^{2+}$  precipitation so much.

The element content of the sediments accumulated at the bottom of both reactors was also shown in Table 3. Because N could only come from struvite, by checking the elements content of N, P, and Mg, about 70% of the sediments should be struvite. Other 30% might be some Ca precipitation like calcium carbonate and other insoluble solids came from the influent.

Studies indicated that  $Ca^{2+}$  could affect struvite crystallization by competitively integrating phosphate. Le-Corre et al. [37] reported that, at Ca/Mg molar ratios of higher than 1.0, no crystalline compound was formed but an amorphous calcium phosphate substance was identified. Our previous research also showed that, at Ca/Mg molar ratios  $> 0.5$ ,  $Ca^{2+}$  could inhibit the crystallization reaction of struvite and significantly affect the purity of struvite crystals [38]. In the present study, the Ca/Mg molar ratios ranged from 1.13 to 1.45, and a satisfying recovery rate of struvite was obtained with crystals of high purity and ordered structure. Possible explanations might be that the solution pH value of this study was about 8.5, while the optimal pH for calcium phosphate precipitation was between 9 and 11 [39]. Furthermore, high concentration of ammonia might make the crystallization of struvite be prior to the formation of amorphous calcium phosphate. Since the anaerobically digested swine wastewater was a complexly composed system, further investigations should be carried out.

### 3.6. Mass balance of phosphorus within the systems

The mass balance of P within the systems was studied. The amount of solids varied among stages. However, the recovery rates were approximately the same. Estimated material flow of P during 160-cycle operation of the SBR at aeration time of 1.0 h and 44-d operation of the continuous-flow reactor at HRT of 6.0 h was shown in Table 4.

In the SBR, 31.4% and 44.9% P in the influent was recovered as struvite and settled to the bottom of the reactor, 11.9% P was lost with the effluent. In the continuous-flow reactor, 29.9% and 42.1% of the P in the influent was recovered as struvite and settled to the bottom of the reactor, 12.5% P was lost with the effluent. The rest 11.8% P in the SBR and 15.5% P in the continuous-flow reactor might accumulate on the inside surfaces of the reactors or other devices installed in the reactors.

### 3.7. Economic evaluation

Economic analysis of the continuous-flow reactor and the SBR were carried out. In this assessment, direct and indirect cost items, as well as the market values of the struvite recovered by the collectors were taken into account. The operating cost for the SBR reactor at aeration time of 1.0 h and the continuous-flow reactor at the HRT of 6.0 h were given in Table 5. It could be calculated that the total operating cost of the continuous-flow reactor was  $\$0.682/m^3$ , and for the SBR it was  $\$0.447/m^3$ , and  $0.095 kg/m^3$  and  $0.098 kg/m^3$  struvite could be recovered by the collectors in continuous-flow reactor and the SBR, respectively. If struvite product could be sold at a favorable price ( $\$0.620/kg$  [40]), then the net operating cost for the continuous-flow reactor and the SBR were  $\$0.623/m^3$  and  $\$0.386/m^3$ , respectively. Comparatively, if NaOH addition was used for pH adjustment, the added amount of NaOH would be  $4.2 kg/m^3$  wastewater, and the chemical cost of NaOH would be  $\$1.344/m^3$  wastewater. Simultaneously, mechanical stirring was need for mixing, the electricity cost of which was basically equal to air pumping. Then, about 66% and 75% of the total operation cost could be reduced in the continuous-flow reactor and the SBR by using  $CO_2$  stripping instead of NaOH addition, respectively.

In the study of Ozturk et al. [41], only the chemical cost of NaOH was  $\$5.44/m^3$ . Ryu et al. [42] also calculated that, when swine wastewater was treated by struvite precipitation, the added amount of NaOH was  $6.0 kg/m^3$  wastewater, and the chemical cost of NaOH would be  $\$1.92/m^3$ . Shepherd et al. [43] reported that the total operation cost was  $\$35.3/m^3$  for the system using  $MgCl_2$  injection for P removal and recovery, in which the energy cost for the system was estimated to be only  $\$0.045/m^3$ , chemical



**Table 5**  
Economic analysis of the SBR and the continuous-flow reactor (the operating cost for the SBR reactor at aeration time of 1.0 h and the continuous-flow reactor at the HRT of 6.0 h).

Operating cost items	SBR (\$/m <sup>3</sup> )	Proportion in total operating cost (%)	Continuous-flow reactor (\$/m <sup>3</sup> )	Proportion in total operating cost (%)
Electricity	0.184	41	0.469	69
Water pumping	0.026	6	0.078	11
Air pumping	0.158	35	0.391	57
Labor	0.208	47	0.156	23
Maintenance	0.017	4	0.026	4
Analytical monitoring	0.020	4	0.018	3
Depreciation	0.018	4	0.013	2
Total operating cost	0.447		0.682	
Value of struvite	-0.061		-0.059	
Net operating cost	0.386		0.623	

cost accounted for most of the cost of operation. In this study, all chemical addition was saved, and then the operation cost could be significantly reduced. The struvite crystallization process described in this study was economically viable for P removal and recovery from swine wastewater, and the SBR system was more economical.

#### 4. Conclusions

A pilot-scale system for nutrients removal and recovery from anaerobically digested swine wastewater was designed consisting of a SBR and a continuous-flow reactor. The wastewater pH values were elevated by CO<sub>2</sub> stripping, and the struvite crystallization process was performed without Mg<sup>2+</sup> additions. The long-term performance of the newly developed pilot-scale system was tested at various aeration time, HRT and temperature. Good elevation effects of pH value by CO<sub>2</sub> stripping, sufficient magnesium in the wastewater and high retention ability on small struvite particles made the system be operated for an extended period of time (247 d) without chemical additions and provided high P removal and recovery over a wide range of aeration time (1.0–4.0 h), HRT (6.0–15.0 h) and temperature (0–30 °C). The SBR provided 90.5% phosphate removal and 88.4% overall P recovery (31.4% P was recovered by the collector) at the minimum aeration times of 1.0 h, and 85.4% phosphate removal and 84.1% overall P recovery (29.9% P was recovered by the collector) were achieved in the continuous-flow reactor at the minimum HRT of 6.0 h. Ammonia could also be removed and recovered by struvite crystallization. However, 40–90% of NH<sub>4</sub><sup>+</sup>-N was removed by air stripping instead of being immobilized in recovered solids. The solids recovered during the experiment were proved to be struvite adulterated with a small amount of Ca, and the purity was more than 90%. The presence of high concentration of Ca<sup>2+</sup> showed little impact on the formation of struvite and the purity of crystals. This work demonstrated the feasibility and effects of nutrients removal and recovery from anaerobically digested swine wastewater by struvite crystallization without chemical additions.

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