

## Phosphorus removal and recovery from wastewater by highly efficient struvite crystallization in an improved fluidized bed reactor

Bin Lu, Jingcheng Xu, Ming Zhang<sup>†</sup>, Weihai Pang, and Li Xie

State Key Laboratory of Pollution Control and Resources Reuse, College of Environmental Science and Engineering,  
Tongji University, No. 1239 Siping Road, Shanghai 200092, P. R. China

(Received 6 March 2017 • accepted 24 July 2017)

**Abstract**—Phosphorus is the crucial factor causing eutrophication in the aquatic ecology. The high phosphorus loading in water bodies may result from the direct disposal of untreated wastewater. In this study, a fluidized bed reactor (FBR) was specially developed to remove and recover phosphorus effectively and efficiently via struvite crystallization. Different physiochemical and hydraulic conditions, including hydraulic retention time (HRT), pH, and molar ratios of Mg : P, N : P and Ca : Mg, were explored to optimize the performance of this improved FBR. For the continuous operating trials, promising removal and recovery efficiencies were achieved at the phosphorus concentration of 25.0 mg/L: >90% of phosphorus could be removed under the optimum condition (pH=9, HRT=12 h, Mg : P=1.25 and N : P=7.5). Increasing the recycle flow rate and prolonging the contact time could also enhance the FBR efficiency. The crystal products obtained in FBR were analyzed in terms of composition and structure. Results indicated that almost pure struvite (>99%) was achieved at low calcium concentrations, which could be considered as a high quality fertilizer.

**Keywords:** Phosphorus Removal and Recovery, Fluidized Bed Reactor, Struvite Crystallization, Wastewater

### INTRODUCTION

Phosphorus, a non-renewable, non-interchangeable finite resource, is an essential nutrient for living organisms (animals, microbes, plants and algae) [1]. The release of large amounts of primarily phosphorus (limiting factor for aquatic organism) can stimulate the excessive growth of algae. The municipal wastewater contains high concentrations of phosphorus; once being discharged into the aquatic environment, it may enrich the nutrient level of the water bodies. Current studies show that many developed and developing countries have suffered from the acute effects of eutrophication in major water bodies; for instance, the eutrophication linked to phosphorus pollution has been documented in the United States (Chesapeake Bay and Lake Okeechobee) [2,3], Australia (Gippsland Lakes and Murray-Darling river system) [4,5], European [6] and Asian countries [7, 8]. In China, the Taihu Lake has successively reported a major nutrient linked algal growth since 2008 [9]. Obviously, there is a great demand for resolving phosphorus pollution problems. On the other hand, simultaneously removing and recovering phosphorus is greatly recommended since phosphorus is also a globally depleting element [10,11]. The diminution of available natural resources requires the recovery of phosphorus from water or wastewater; as an alternative source, the recovered phosphorus can then be reused in related industries.

Municipal wastewater is a potential candidate for sustainable phosphorus recovery. Phosphorus from wastewater can be recovered as struvite, which is currently an attractive fashion in many countries

[12]. Previous studies showed that struvite ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ) is considered as the most promising crystallization product of phosphorous in wastewater treatment plants [13,14]. It is well understood that phosphorus reacts with nitrogen and magnesium to produce struvite under alkaline condition. Struvite ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ) formation occurs either spontaneously or intentionally when the Mg :  $\text{NH}_4$  :  $\text{PO}_4$  molar ratio  $\geq 1 : 1 : 1$  [15]. The struvite crystallization can be a either spontaneous or controlled process. Spontaneous struvite crystallization and its negative impact in wastewater treatment plants have been widely documented [16]. Struvite is an orthophosphate, containing magnesium, ammonium, and phosphate in equal molar concentrations. The general formula for struvite ( $\text{MgNH}_4 \cdot 6\text{H}_2\text{O}$ ) precipitation is given by Eq. (1) (with  $n=0, 1$ , and  $2$ ) [12]:



Although struvite crystallization is attractive in phosphorus precipitation and recovery method from wastewater, it has not been widely adopted. The development of full scale struvite plants is limited by the difficulty in controlling the conditions of precipitation and crystal growth, including supersaturation, pH, temperature, foreign ions, and so forth. Moreover, it is significant to improve the reactor as well [11], for example, to improve the design of fluidized bed reactor (FBR) which is among the most extensively used reactors and therefore to enhance its performance in the removal and recovery of phosphorus [17].

Our aim here was to place the phosphorus-involved environmental issue in a sustainable development context by recovering phosphorus in the form of struvite. Accordingly, the objective was to effectively and efficiently remove and recover phosphorus from wastewater using struvite crystallization in a newly designed FBR. Different experiments were carried out at various conditions which

<sup>†</sup>To whom correspondence should be addressed.

E-mail: mzhang@tongji.edu.cn, freda1102@163.com

Copyright by The Korean Institute of Chemical Engineers.

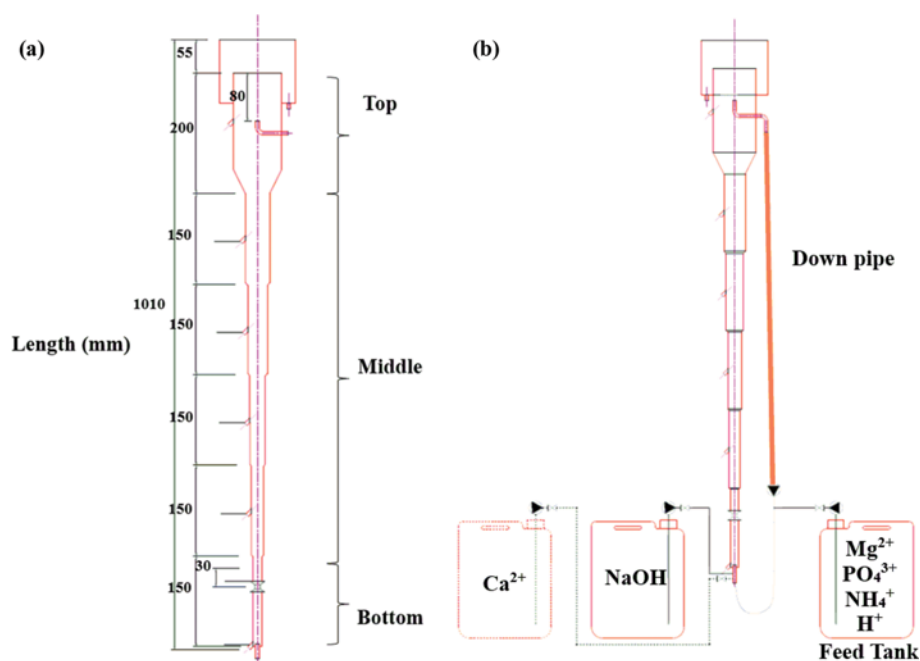


Fig. 1. (a) Schematic graph (unit: mm) and (b) setup of the fluidized bed reactor.

affected the struvite recovery in the FBR system, including intermittent aeration cycle, hydraulic retention time (HRT), initial pH of influent and molar ratios (Mg : P, N : P and Ca : Mg). The performance of the improved FBR was evaluated via standard procedures and appropriate instruments; meanwhile, the relevant mechanisms of efficient struvite crystallization and phosphorus removal were analyzed.

## MATERIALS AND METHODS

### 1. Reactor Design and Operation

Being designed following the basic principle of fluidized bed, the reactor in the present work was divided into three parts: bottom, middle and top (Fig. 1(a)). The total volume and height of the reactor were about 9.5 L and 1.1 m, respectively, but those three parts were of different cross-sectional areas, heights and volumes (Table 1). Different parts of the FBR were connected by a cone-shape structure at an angle of 45° (Fig. 1(a)), which aimed at reducing unwanted crystal loss at each junction. As shown in Table, the cross-sectional area of the reactor  $A$  and the upflow velocity of the fluid differed in these three parts, which could be figured out by using Eq. (2) and (3) [13]:

$$A = \pi r^2 \quad (2)$$

Table 1. The dimensions and working condition of FBR

Parts	Length (mm)	Diameter (mm)	Volume (mL)	Area (mm <sup>2</sup> )	Upflow velocity (m·s <sup>-1</sup> )
Top	200	40-80	1005	1256-5024	0.00011-0.00045
Middle	600	15-40	430	176.6-1256	0.0044-0.031
Bottom	150	6-15	27	28.3-176.6	0.0316-0.197

$$\text{Upflow velocity} = \frac{Q}{A} \quad (3)$$

where  $r$  and  $A$  represent the radius and area of the cross-section, individually;  $Q$  is the flow rate of synthetic wastewater (influent) and fixed as 20 L/h in this case. Obviously, the upflow velocity decreased as moving from the bottom part to the top part of the FBR. The real upflow rate  $v_r$  could be obtained by Eq. (4):

$$v_r = \frac{Q + Q_{\text{recycle}}}{A} \quad (4)$$

where  $Q_{\text{recycle}}$  was the flow rate resulting from the recycling liquid. By controlling the external recycle ratio, the flow rate running through the FBR changed accordingly.

During the experimental operation, the influent and the alkaline solutions (i.e., NaOH solution) were continuously pumped into the FBR reactor from the bottom inlet as depicted in Fig. 1(b). The phosphorus-containing liquid was fluidized-up when crossing the various areas; meanwhile, the nucleation and crystal growth took place at the middle part of the reactor. As the liquid flowed upward, its flow velocity decreased leading to the segregation of precipitates or crystals. The large crystals settled down and accumulated at the bottom center of the FBR, being collected when the quantity of stored crystals reached a certain level. The liquid with fine precipitates flowed out of the FBR from the top to an external recycler. The treated effluent was collected in a supernatant tank while the rest returned to the FBR.

### 2. Feed Preparation and Experimental Procedures

#### 2-1. Feed Preparation

Synthetic wastewater with the struvite constituent ions was used as influent. Synthetic wastewater was employed in the present study to optimize the working conditions of the newly designed FBR.

Commercial-grade magnesium chloride hexahydrate ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ), potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ) and ammonium chloride ( $\text{NH}_4\text{Cl}$ ), purchased from the Sinopharm Chemical Reagent Company in China, were used as salts to prepare the influent feed. Depending on the designed experimental conditions, different concentrations of  $\text{KH}_2\text{PO}_4$  (0.40 and 3.87 mmol/L),  $\text{NH}_4\text{Cl}$  (2.99–34.59 mmol/L) and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  (0.74–6.74 mmol/L) solutions were prepared in a 60 L influent holding tank and fed to the reactor every 1 to 2 days. To investigate the effect of foreign ions, a series of calcium chloride solutions ranging from 0–9.65 mol/L were added as the source of calcium.

## 2-2. Experimental Procedures

To assess the struvite recovery performance in the FBR system and understand related mechanisms, different trials were performed at a fixed initial phosphorus concentration of 25.0 mg/L, but different other conditions, including external recycle ratio (0, 0.50, 0.75, 1.00, 1.25 and 1.50), HRT (2, 4, 6, 8, 10, 12, 24 and 48 h), pH (7.0, 7.5, 8.0, 8.5, 9.0, 9.5 and 10.0),  $\text{Mg}:\text{P}$  (0, 0.75, 1.00, 1.25, 1.50 and 1.75),  $\text{N}:\text{P}$  (1.0, 2.5, 5, 7.5 and 10.0) and  $\text{Ca}:\text{Mg}$  (0, 0.5, 1.0 and 2.0) molar ratios. Those conditions were well controlled by monitoring the concentration of synthetic wastewater constituents and/or the pump flow rates. When one factor was varied, the others were kept constant. All experiments were at room temperature. A summary of the initial operating conditions is given in Table 2.

Since struvite formation is highly dependent on the pH of the FBR influent [13,18], the commercial grade sodium hydroxide ( $\text{NaOH}$ , Sinopharm Chemical Reagent Company, China) was prepared as pH-adjuster and fed to the FBR. By using the low (0.0125 mol/L) and high concentrations of  $\text{NaOH}$  solutions (0.1 and 0.2 mol/L  $\text{NaOH}$ ), the pH could be easily controlled to the required range. The pH values of samples taken at each part of the reactor zone were measured using pH meter. The pH value of wastewater in FBR was adjusted by controlling the pump which injected the  $\text{NaOH}$  solution into the reactor.

## 2-3. Sampling, Crystal Harvest, Crystallization Performance and Product Analyses

The crystals resulting from the nucleation in the liquid phase and the abrasion of the grains in the FBR left the reactor with effluent together with the remaining phosphorus in solution. Thus, the per-

formance of the FBR was defined in terms of the phosphorus removal efficiency  $\eta_p$ , which was calculated by considering the amount of orthophosphate transformation [19]:

$$\eta_p = (C_{P, \text{inf}} - C_{P, \text{eff}}) / C_{P, \text{inf}} \times 100\% \quad (5)$$

where  $C_{P, \text{inf}}$  is the phosphorus concentration of influent (mg/L);  $C_{P, \text{eff}}$  is the total phosphorus concentration of FBR effluent (mg/L), which was rapidly filtered by 0.45- $\mu\text{m}$  membranes (Millipore HAWP01300, USA) after sampling.

Influent and effluent samples were collected daily for chemical analyses at different sites of the treatment layout:  $\text{NH}_4^+\text{-N}$  and  $\text{PO}_4^{3-}\text{-P}$  were analyzed using UV-visible spectrophotometer (UV 1700, Shimadzu), magnesium was analyzed using flame atomic absorption spectrophotometry (PE-AA400, Perkin Elmer, USA). The concentration of calcium was measured using an inductively coupled plasma-optical emission spectrophotometer (ICP-OES) (ICP-720ES, Agilent, USA).

At the end of experiment, the crystal products were harvested and then air-dried at room temperature before analysis. The quality of the crystals was determined by their composition and crystal structure. For chemical composition tests, 30 mg of crystal sample was dissolved in 50 mL of 0.5% nitric acid solution [20]. The suspension was stirred and kept overnight before analyses. Then, the solution was analyzed for  $\text{PO}_4^{3-}\text{-P}$ ,  $\text{NH}_4^+\text{-N}$ , Mg and Ca concentrations.

The structure of the harvested crystals was examined using Bruker D8 Advance X-ray diffractometer with  $\text{Cu K}\alpha$  radiation (Optik GmbH, Ettlingen, Germany). The XRD patterns were recorded in the scanning range of 2-theta from  $10^\circ$ – $90^\circ$ . Data were collected and processed using MDI Jade 5.0 software. The phase peaks were identified by comparing the observed XRD patterns to that of standard struvite compiled by the Joint Committee on Powder Diffraction and Standards (JCPDS, 1980).

## RESULTS AND DISCUSSION

### 1. Effect of Operating Conditions on FBR Performance

Struvite crystallization efficiency is always decided by a combination of operating conditions and physiochemical parameters, including recycle ratio, HRT, pH, initial concentration of ionic species in solution, mixing speed and the presence of foreign ions [15]. Hence, to evaluate the performance of the improved FBR in the current study, those factors were examined.

The phosphorus removal efficiencies with and without external recycle were first investigated in the range of 0–1.50:1, and meanwhile, HRT, initial pH,  $\text{Mg}:\text{P}$  and  $\text{N}:\text{P}$  in influent were set to be 12 h, 9.0, 1.25:1 and 2.5:1, respectively. Results in Fig. 2 show that the phosphorus removal improved from 83% to 94% when the external recycle ratio increased from 0 to 1.50:1. The precipitation potential of the FBR reactor was enhanced when the external recycler was employed in the system. By means of entering in the recycler, those fine particles which might have been lost from the top of FBR got a chance to return to the reactor. However, when the recycle ratio was greater than 1.00:1, the visible precipitates were reduced and the increase in removal efficiency turned out to be less important. This might have been caused by the dilution

**Table 2. Initial operating conditions at the fixed phosphorus concentration**

Initial conditions	Phosphorus concentrations
$\text{PO}_4^{3-}\text{-P}$ (mg/L)	25.0
$\text{NH}_4^+\text{-N}$ (mg/L)	11.3–112.9
Mg (mg/L)	14.7–34.3
$\text{Mg}:\text{P}$	0.75–1.75
$\text{N}:\text{P}$	1.0–10.0
$\text{Ca}:\text{Mg}$	0–2.0
pH	7.0–10.0
HRT (h)	2–48
External recycle ratio	0–1.50
Recycle flow rate (mL/min)	30
Temperature ( $^\circ\text{C}$ )	20–26

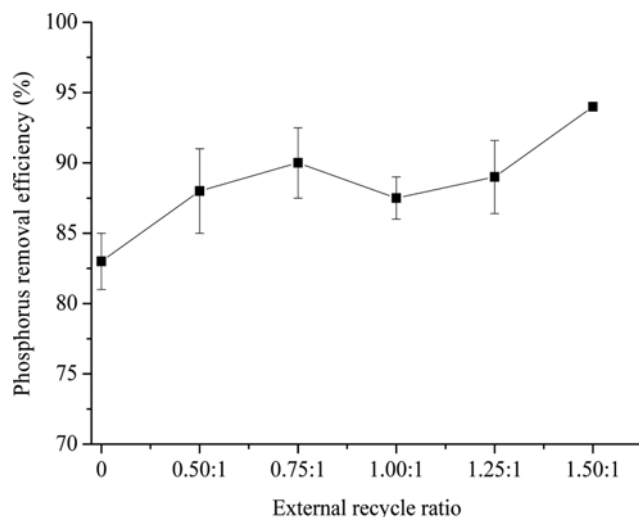


Fig. 2. Effect of external recycle ratio on phosphorus removal.

effect, which inhibited the growth of crystals. The favorable precipitates observed when the amount of influent and recycling liquid were the same (Recycle ratio=1.00:1). Compared to other parameters, the recycle ratio might not be an essential factor since as much as 83% of phosphorus could be removed even if no liquid was recycled.

Note that different cross-section areas of the FBR were particularly designed, and accordingly, the upflow velocities varied so that the washout of the tiny crystals could be avoided from the effluent. Crystals in the bottom part of FBR were of comparatively high upflow velocity, and the velocity gradually decreased during the process of flowing up. Larger crystals were able to overcome the higher upflow velocities and move towards the lower section. Studies have noted that a higher upflow velocity at the bottom section may enhance the growth of crystals because of stronger turbulence. The reinforced turbulence of the suspension could not only promote the solid-liquid mass transfer, but also enhance the wear effect between crystals leading to the overall small particle size and low settling

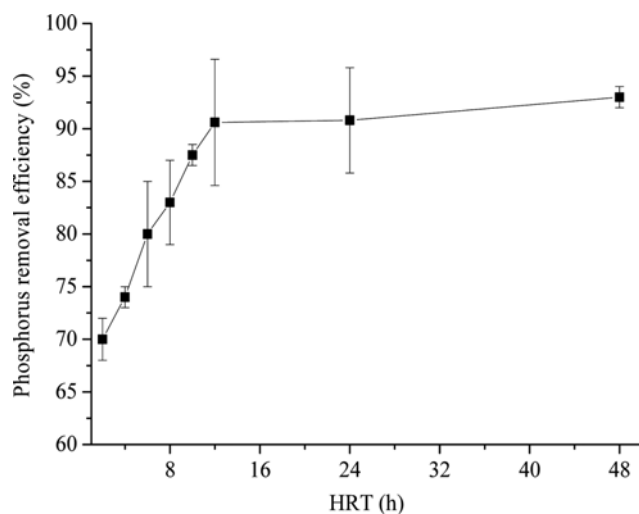


Fig. 3. Effect of HRT on phosphorus removal.

rate [17,21].

Samples were taken and analyzed at different time intervals to explore the influence of HRT on the phosphorus removal. The HRT of 2, 4, 6, 8, 10, 12, 24 and 48 h was investigated at constant pH, Mg:P, and N:P (9.0, 1.25 and 2.5, respectively). The results showed more than 70% of phosphorus was removed in the first 2 h (Fig. 3). When the HRT increased from 2 h to 10 h, the phosphorus removal grew from 70.0% to 87.5% for the high concentration of phosphorus in influent. To keep the removal higher than 90%, the HRT had to be  $\geq 12$  h. As for the HRT longer than 48 h, the bed volume of crystals grew greatly, though the removal efficiency of phosphorus did not increase significantly. Herein, the HRT of 12 h was used to ensure the sound removal efficiency of phosphorus and favorable crystal growth [16].

## 2. Effect of Physiochemical Conditions on FBR Performance

### 2-1. Initial pH of Influent

In this study, the effects of initial pH from 7.0 to 10.0 were investigated. Experiments without and with pH adjustment were carried out (Fig. 4). The pH values of the FBR influent were adjusted by controlling the flow rates of NaOH solution with pump, and the constant HRT, Mg:P, and N:P (12 h, 1.25 and 2.5, respectively) were kept throughout this part of the experiments. The phosphorus removal efficiencies increased from 55.0% to 96.0% when the reactor pH rose from 7.0 to 10.0. When the reactor was working at  $\text{pH} \geq 9$ , more than 90% of phosphorus could be removed. Lower phosphorus removal efficiencies were achieved at  $\text{pH} < 7.0$ ; according to the precipitation chemistry, struvite should be soluble under acidic condition, which hindered the precipitation process [12].

Many studies have stated that the operating range of pH for struvite formation is between 8 and 10 [22,23]. The results in the present work were consistent with phosphorus removal efficiencies reported by Britton et al. [24] (30-90% at  $\text{pH}$  7.6-8.8), Pastor et al. [25] (40-80% at  $\text{pH}$  8.2-9.5) and Le Corre et al. [15] (75-80% at  $\text{pH}$  8.5-10). As has been reported herein, all those studies also exhibited the increase of the phosphorus removal along with the increase of pH. Also, struvite was soluble at the acidic pH conditions but turned out to be highly insoluble at alkaline pH. In the

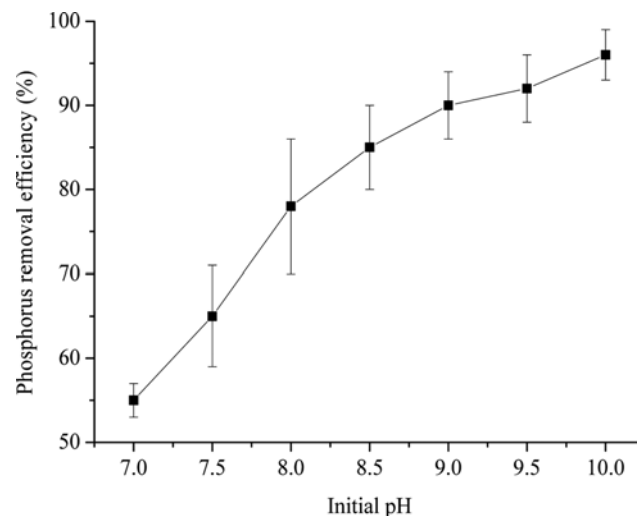


Fig. 4. Effect of initial pH on phosphorus removal.

pH range of 8-10, crystallization was known to be metastable [26].

#### 2-2. Mg : P Molar Ratio

An efficient struvite crystallization demanded at least 1 : 1 molar ratio of Mg : P [27]. It has been reported that increasing Mg : P molar ratio could facilitate both struvite recovery and phosphorus removal [28]. Therefore, the concentration of magnesium ion should meet the basically stoichiometric requirement so that the magnesium content would not be a limitation of the process. Also, an Mg : P molar ratio of 1 : 1 was not the unique condition ensuring the struvite crystallization and the phosphorus removal.

As shown in Fig. 5, a range of Mg : P molar ratios (0.75-1.75) was evaluated at the constant HRT, N : P, and pH (12 h, 2.5 and 9.0, respectively, in this study. At lower Mg : P molar ratio (0.75), the removal efficiency was low (68%). When the Mg : P molar ratio for the struvite formation was adjusted to the theoretical value (Mg : P = 1 : 1), the phosphorus removal efficiency was found to be higher than 80%. The Mg : P molar ratio growing from 0.75 to 1.75, the phosphorus removal improved from 78% to 93%; however,

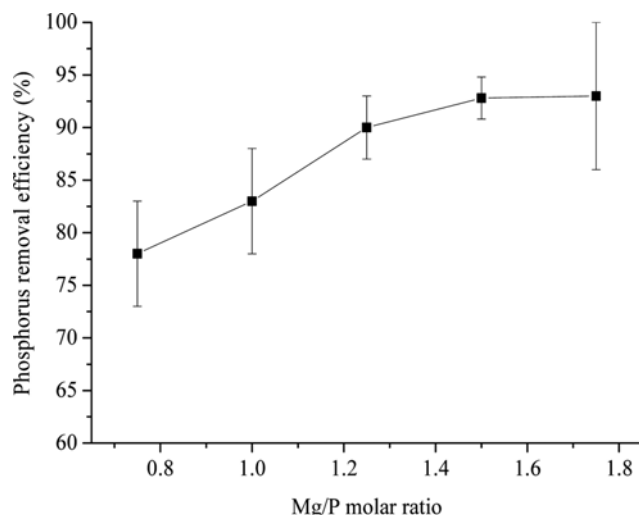


Fig. 5. Effect of Mg : P molar ratio on phosphorus removal.

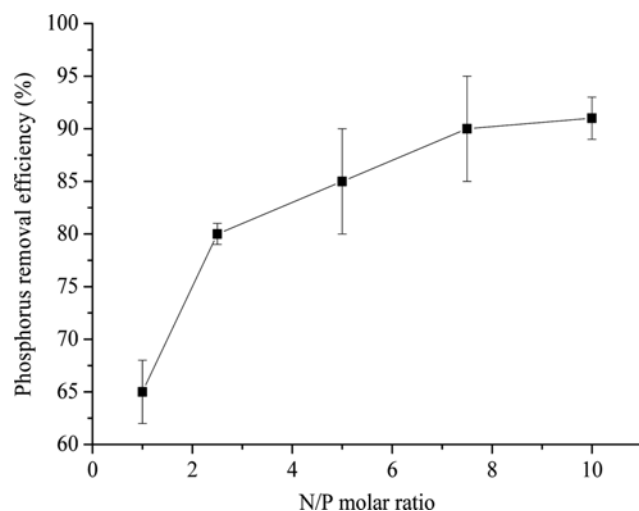


Fig. 6. Effect of N : P molar ratio on phosphorus removal.

the increase was insignificant when Mg : P molar ratios increased from 1.25 to 1.75 (Fig. 5). In the struvite crystallization process, the Mg : P molar ratio of 1.25 was chosen instead of higher values by considering the cost of magnesium salt.

#### 2-3. N : P Molar Ratio

The effect of N : P molar ratio was also investigated at the constant HRT, Mg : P, and pH (2 h, 1.25 and 9, respectively). When the N : P molar ratios increased from 1.0 to 10.0, ranges of phosphorus removal efficiencies (65-90%) were observed (Fig. 6). When the N : P molar ratios increased from 1 to 7.5, the phosphorus removal efficiencies were increased gradually from 65 to 90%. For N : P molar ratios above 7.5, the phosphorus removal efficiencies did not show any significant changes. The positive effects of increasing N : P molar ratios for phosphorus and nitrogen removals were consistent with other studies [22,25]. When the N : P molar ratio increased from 1 to 6, the phosphorus removal efficiency of 50% and 80% was observed, respectively.

#### 2-4. Ca : Mg Molar Ratio

Calcium has been reported to greatly impact the struvite crystallization efficiency [29]; hence, the influence of Ca : Mg molar

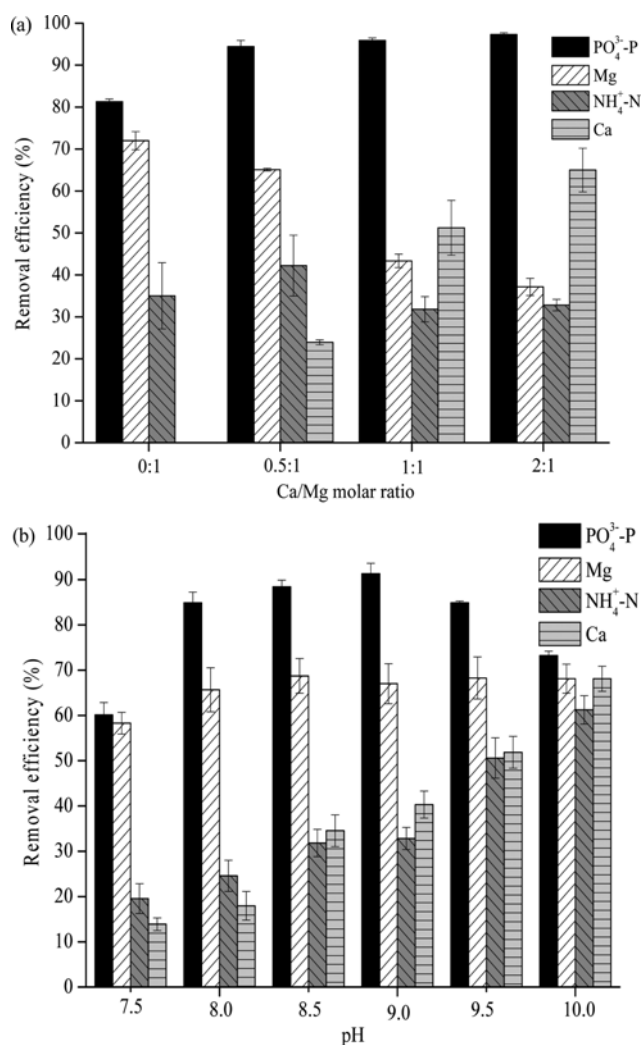
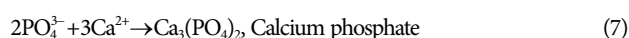


Fig. 7. Phosphorus removal varying with (a) Ca : Mg molar ratios and (b) pH values of influent.

**Table 3. Composition analysis of struvite**

Elements	Composition (mg/L)		Composition (%)	
	Measured	Theoretical	Measured	Theoretical
Mg	24.7±1.2	24.5	9.9±0.5	9.9
N	14.3±0.8	14.3	5.7±0.3	5.7
P	31.6±0.3	31.6	12.6±0.1	12.6
Struvite (estimated)			100	100

ratio on the struvite formation in the improved FBR was also studied in this work. Under the constant HRT (12 h), pH (9.0), Mg:P (1.25) and N:P (7.5) molar ratios, the phosphorus and calcium removal efficiencies progressively increased with increasing Ca:Mg molar ratios (Fig. 7(a)). Phosphorus removal efficiencies were 81% without calcium and 98% for the maximum calcium added (Ca:Mg=2). This high phosphorus removal efficiency might not be totally associated with struvite formation but rather from reaction of phosphorus with calcium (Eqs. (5) and (6)) [30]:



The lower  $\text{NH}_4^+$ -N removal efficiencies observed at higher Ca:Mg molar ratios also confirmed the effect of calcium on struvite formation. The  $\text{NH}_4^+$ -N removal efficiencies were found to be 42% for Ca:Mg molar ratio of 0.5:1 and 33% for Ca:Mg molar ratio of 2:1, which likely indicated less reaction of nitrogen with phosphorus at higher Ca:Mg molar ratios.

An investigation was also performed at the initial solution of influent varying from 7.5 to 10.0 under fixed conditions of Ca:Mg molar ratio=1:1, HRT=12 h, Mg:P molar ratio=1.25, N:P molar ratio=2.5 and pH=9.0. Results in Fig. 7(b) show that the phosphorus removal efficiencies grew from 60 to 91% when pH increased from 7.5 to 9.0, whereas decreased at pH higher than pH of 9.0. Meanwhile, throughout the investigated pH range, the magnesium removal kept almost stable while both of the nitrogen and calcium removals progressively increased. The reduction of nitrogen could be attributed to the loss of  $\text{NH}_3$ ; the increase of calcium removal was probably caused by the reaction between calcium and other substances present in the solution (e.g., carbonate) in addition to phosphorus. Le Corre et al. [15] and Pastor et al. [31] have found that, in the solutions containing calcium, magnesium, ammonia, phosphate and carbonate, the possible precipitates could be struvite, hydroxyapatite, calcium phosphate, calcite ( $\text{CaCO}_3$ ) and dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ).

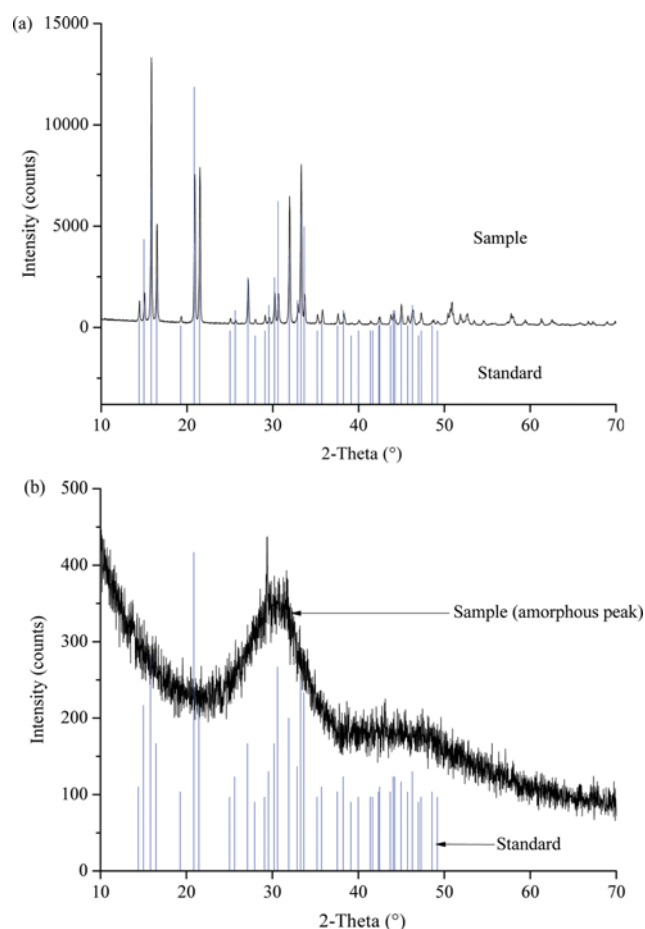
### 3. Struvite Crystal Characterization

The main advantages of removing and recovering phosphorus from wastewater are solving the environmental issue of eutrophication as well as the global problem of struvite stock depletion. Hence, the performance of FBR not only on the phosphorus removal but also the quantity and quality (composition and morphology) of the final product recovered.

The products were collected at the end of each experiment every two or three days. The height of sediment bed was measured from the bottom section of FBR before the product was drawn. The height

was found to vary from 6.3 cm to 15.0 cm depending on the physiochemical conditions adopted. The minimum bed height was obtained when the system ran without the external recycler and at the lower pH and the smaller Mg:P molar ratio.

To verify the composition of the crystals grown in this study, samples were dissolved in the nitric acid solution and analyzed for the content of struvite elements. The crystal composition results in Table 3 confirmed the product to be pure struvite (>99%) and the FBR in this study was able to produce high-grade crystals. Impurities (such as aluminum, calcium, iron, etc.) in the analyzed sample were almost negligible, implying that the product could be used safely for agricultural purposes. Moreover, the quantity of struvite reacting species in the crystal was more than the theoretical value.



**Fig. 8. XRD spectra of sample and standard struvite (a) without calcium and (b) with calcium (Ca:Mg=1).**

The deviation of the results could be the errors of analysis but did not indicate the bad struvite.

Struvite is a white orthorhombic crystalline substance composed of magnesium, nitrogen and phosphorus in the same molar concentration. The white crystals produced in this study were further confirmed as struvite by XRD. As shown in Fig. 8(a), the XRD pattern of most samples in this study agreed well with that of the standard struvite pattern in the absence of calcium, indicating a typical orthorhombic shape as observed in other studies [30,32]. However, a broad amorphous peak was observed from the XRD pattern of struvite in the presence of calcium (Fig. 8(b)), which was obviously different from the standard crystal. A similar result was also found by Pastor et al. [25] and Le Corre et al. [29], respectively: the growth of struvite was inhibited at the Ca:Mg molar ratio greater than 0.5 and 1.6, respectively. It indicated the bad quality of struvite.

## CONCLUSIONS

FBR was improved and constructed to effectively remove and recover phosphorus from synthetic wastewater. The enhanced struvite recovery rate was achieved by using a novel cone-inserted fluidized bed reactor. Under continuous operating conditions, the reactor showed promising removal and recovery efficiencies at a comparatively low phosphorus concentration of 25.0 mg/L. More than 90% of phosphorus was removed under the optimal operating conditions (pH=9, HRT=2 h, Mg:P=1.25 and N:P=7.5). The reactor efficiency was also enhanced when higher recycle flow rates and longer HRT were adopted in the FBR. The chemical composition results showed that the harvested crystals were the characteristic struvites with high quality. In the absence of calcium, the analyses of chemical composition and XRD confirmed that the recovery products were almost pure struvites. In sum, with the improved FBR in the present work, phosphorous could be successfully removed and recovered in the form of struvite from wastewater by monitoring recycle ratio, HRT, pH and molar ratios of Mg:P, N:P and Ca:Mg.

## ACKNOWLEDGEMENTS

This research was supported by the National Science Foundation (No. 51378373 and No. 51608373) and the 59th China Postdoctoral Science Foundation (No. 2016M591713).

## REFERENCES

1. P. J. A. Withers, J. J. Elser, J. Hilton, H. Ohtake, W. J. Schipper and K. C. van Dijk, *Green Chem.*, **17**, 2087 (2015).
2. W. M. Kemp, W. R. Boynton, J. E. Adolf, D. F. Boesch, W. C. Boicourt, G. Brush, J. C. Cornwell, T. R. Fisher, P. M. Glibert, J. D. Hagy, L. W. Harding, E. D. Houde, D. G. Kimmel, W. D. Miller, R. I. E. Newell, M. R. Roman, E. M. Smith and J. C. Stevenson, *Mar. Ecol. Prog. Ser.*, **303**, 1 (2005).
3. K. E. Havens and R. T. James, *Lake Reserv. Manage.*, **21**, 139 (2005).
4. P. I. Boon, P. Cook and R. Woodland, *Mar. Freshw. Res.*, **67**, 721 (2016).
5. J. R. Davis and K. Koop, *Hydrobiologia*, **559**, 23 (2006).
6. M. Karydis and D. Kitsiou, *Environ. Monit. Assess.*, **184**, 4931 (2012).
7. J. Zhao, X. Feng, X. Shi, Y. Bai, X. Yu, X. Shi, W. Zhang and R. Zhang, *Mar. Pollut. Bull.*, **99**, 76 (2015).
8. N. K. Tsugeki, T. Agusa, S. Ueda, M. Kuwae, H. Oda, S. Tanabe, Y. Tani, K. Toyoda, W. Wang and J. Urabe, *Ecol. Res.*, **27**, 1041 (2012).
9. Y. Zhang, X. Yao and B. Qin, *Environ. Sci. Pollut. Res.*, **23**, 12811 (2016).
10. P. Balmer, Phosphorous Recovery, an Overview of Potentials and Possibilities, Norwegian Univ. Sci. Technol., Trondheim (2003).
11. L. Birnhack, O. Nir, M. Telzhenski and O. Lahav, *Environ. Technol.*, **36**, 1892 (2015).
12. K. S. Le Corre, E. Valsami-Jones, P. Hobbs and S. A. Parsons, *Crit. Rev. Environ. Sci. Technol.*, **39**, 433 (2009).
13. X. Ye, Z.-L. Ye, Y. Lou, S. Pan, X. Wang, M. K. Wang and S. Chen, *Powder Technol.*, **295**, 16 (2016).
14. H. Hiroyuki and S. Toru, in 2003 3<sup>rd</sup> Int. Symp. Environ. Conscious Des. Inverse Manuf. 2003 EcoDesign 03, 422 (2003).
15. K. S. Le Corre, E. Valsami-Jones, P. Hobbs and S. A. Parsons, *Environ. Technol.*, **28**, 1245 (2007).
16. C. M. Mehta and D. J. Batstone, *Water Res.*, **47**, 2890 (2013).
17. Z. Liu, Q. Zhao, D.-J. Lee and N. Yang, *Bioresour. Technol.*, **99**, 6488 (2008).
18. D.-Y. Kang, J.-H. Lim, T.-Y. Lee and J.-K. Lee, *Korean J. Chem. Eng.*, **32**, 2342 (2015).
19. H. Dai, X. Lu, Y. Peng, H. Zou and J. Shi, *Chemosphere*, **165**, 211 (2016).
20. M. I. H. Bhuiyan, D. S. Mavinic and F. A. Koch, *Water Sci. Technol.*, **57**, 175 (2008).
21. C. Fang, T. Zhang, R. Jiang and H. Ohtake, *Sci. Rep.*, **6**, 32215 (2016).
22. K. P. Fattah, D. S. Mavinic, F. A. Koch and C. Jacob, *J. Environ. Sci. Health Part -Toxic/Hazardous Subst. Environ. Eng.*, **43**, 756 (2008).
23. M. P. Huchzermeier and W. Tao, *Water Environ. Res.*, **84**, 34 (2012).
24. A. Britton, F. A. Koch, D. S. Mavinic, A. Adnan, W. K. Oldham and B. Udala, *J. Environ. Eng. Sci.*, **4**, 265 (2005).
25. L. Pastor, D. Mangin, R. Barat and A. Seco, *Bioresour. Technol.*, **99**, 6285 (2008).
26. M. I. H. Bhuiyan, D. S. Mavinic and F. A. Koch, *Chemosphere*, **70**, 1347 (2008).
27. L. E. de-Bashan and Y. Bashan, *Water Res.*, **38**, 4222 (2004).
28. H. Huang, D. S. Mavinic, K. V. Lo and F. A. Koch, *Environ. Technol.*, **27**, 233 (2006).
29. K. S. Le Corre, E. Valsami-Jones, P. Hobbs and S. A. Parsons, *J. Cryst. Growth*, **283**, 514 (2005).
30. J. Wang, J. G. Burken, X. Q. Zhang and R. Surampalli, *J. Environ. Eng.-Asce*, **131**, 1433 (2005).
31. L. Pastor, D. Mangin, J. Ferrer and A. Seco, *Bioresour. Technol.*, **101**, 118 (2010).
32. S. Dunn, S. Impey, C. Kimpton, S. A. Parsons, J. Doyle and B. Jefferson, *Water Sci. Technol.*, **49**, 183 (2004).