

Study of struvite crystallization in a semi-batch jet loop fluidized bed reactor

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(Received 29 December 2014 • accepted 8 April 2015)

Abstract—A semi-batch jet loop fluidized bed reactor (JLFBR) was used as a crystallization reactor to remove nitrogen and phosphorus from synthetic wastewater through struvite crystallization. The reactor performance obtained in the JLFBR was compared with that in a same-size jet loop reactor (JLR). The time required to increase the initial pH of the synthetic wastewater from 7.3 to 8.0 by aeration in the JLFBR was shorter than in the JLR. Moreover, the removal rates of ammonium nitrogen (NH₄-N) and total phosphorus (T-P) were faster in the JLFBR. This may be due to the enhanced turbulent intensity that promoted struvite formation, as well by the fluidized particles in the JLFBR.

Keywords: Jet Loop Fluidized Bed Reactor, Struvite Crystallization, Ammonium Nitrogen Removal, Total Phosphorous Removal, Fluidized Particles

INTRODUCTION

The struvite (MgNH₄PO₄·6H₂O) crystallization process is an interesting technique to simultaneously remove nitrogen and phosphorus from sewer and waste water. This can help reduce the nitrogen and phosphorus load in a biological treatment plant and the volume of generated sludge [1]. Furthermore, crystallized struvite can be reused as a slow release fertilizer; some other commercial applications are also expected [2]. In this context, some studies had been performed on the removal of nitrogen and phosphorus using struvite crystallization as a way to remove ammonium and phosphate from sewer and waste water [3].

Most studies related to struvite crystallization have used a fluidized bed reactor (FBR) as the crystallization reactor. When an FBR is used for struvite crystallization, the fluidized particles supplied in the fluidized bed reactor promote heterogeneous nucleation and eventually accelerate struvite crystallization [4]. There is also a report that highly pure struvite crystals can be obtained, if struvite seed is used as the fluidized particles [5].

The crystallization of struvite in liquid solution can require an appropriate pH (8.5-9.5) for operating at a metastable supersaturation zone near to the critical supersaturation curve [6]. Thus, caustic chemicals, such as NaOH and Ca(OH)₂, are usually added to the solution to increase the pH value above 8.5 [7].

To reduce the caustic chemical cost needed to control the pH for the struvite crystallization reaction, Ohlinger et al. [5] and Fattah et al. [8] performed studies to raise pH by installing a CO₂ stripper for aeration into the wastewater. According to these studies, the pH rises because of CO₂ stripping, and the struvite crystal size grows larger than before. Thus, it has been proposed that a CO₂ stripping process should be added to reduce the caustic chemical

cost needed for the struvite crystallization reaction. Their method, however, requires the extra cost of installing a separate reactor outside the crystallization reactor for aeration by CO₂ stripping.

Cha et al. [9] studied struvite crystallization using a jet loop reactor (JLR) to combat these problems. When a JLR is used as the struvite crystallization reactor, two-fluid nozzles installed inside the draft tube of the JLR form micro bubbles, which enlarges the contact surface of the gas-liquid, and provides strong turbulence intensity because of two-fluid flows, resulting in a high mass transfer rate [10]. Additionally, the JLR does not need a separate CO₂ stripper because the struvite crystallization and aeration reactions occur in the same reactor. Thus, using a JLR as a struvite crystallization reactor can reduce the chemical costs associated with adjusting the wastewater's pH, and further achieves excess nitrogen removal through NH₃ stripping [9].

The struvite crystal nucleus is initially created by a homogeneous nucleation and a heterogeneous nucleation process. Literature reports suggest the growth rate of crystal nuclei by heterogeneous nucleation is faster than by homogeneous nucleation [11]. Thus, if a new reactor - the jet loop fluidized bed reactor (JLFBR) having fluidized particles within the JLR - is used, those particles can provide the site needed for heterogeneous nucleation for a struvite crystallization reaction and, accordingly, can accelerate the struvite crystallization rate. In addition, as fluidized particles in the JLFBR enhance turbulence intensity, it should enhance the growth rate of struvite crystallization and the pH increase by CO₂ stripping, compared with the JLR. However, to date, there has been no reported study using a JLFBR as a struvite crystallization reactor.

In this study, we investigated struvite crystallization performance in a semi-batch jet loop fluidized bed reactor (JLFBR), where both the struvite crystallization and aeration can be carried out at the same time. We also compared and reviewed the struvite crystallization performance of a JLR of the same size as the JLFBR. Moreover, we examined the pH change and removal rate of ammonium nitrogen (NH₄-N) and total phosphorus (T-P) with different gas

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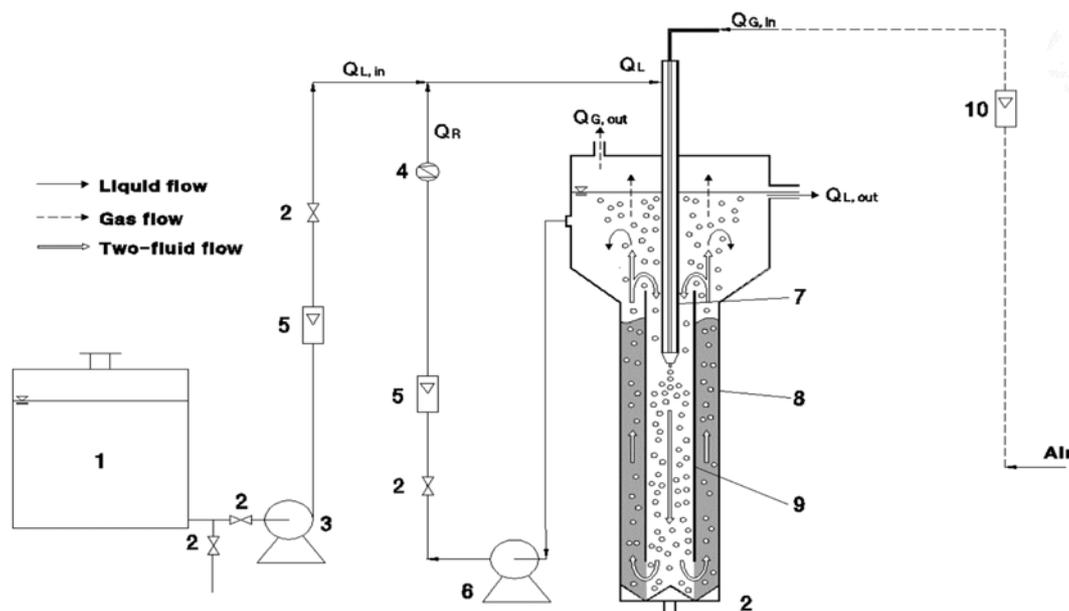


Fig. 1. Schematic of the experimental apparatus used in this study.

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|-----------------|------------------|---------------------|-----------------------------------|-------------------|
| 1. Storage tank | 3. Metering pump | 5. Liquid flowmeter | 7. Two-fluid nozzle | 9. Draft tube |
| 2. Valve | 4. Check valve | 6. Circulation pump | 8. Jet loop fluidized bed reactor | 10. Gas flowmeter |

flow rates and liquid circulation flow rates.

EXPERIMENTAL DETAILS

The lab-scale JLFBR system consisted of a storage tank, JLFBR, metering pump, and circulation pump, as shown in Fig. 1.

The JLFBR has a downstream circular cylinder shape and an interior consisting of a two-fluid nozzle, draft tube, gas-liquid separation tank, and reaction section with fluidized particles. The JLFBR was manufactured with acrylic, with a height of 1 m and effective volume of 18 L. The height and the inner diameter of the reaction tube were 0.75 m and 0.10 m, of the draft tube, 0.60 m and 0.049 m, and of the gas-liquid separation tank, 0.35 m and 0.30 m, respectively. Unlike the gas-liquid separation tank of a conventional JLR [12,13], the JLFBR was sloped, from the reaction tube (inner diameter of 0.10 m) to the gas-liquid separation tank (inner diameter of 0.3 m) so that the inner diameter enlarges gradually. This prevents the fluidized particles from stagnating at the gas-liquid separation tank. The bottom part was changed from a cone shape in a conventional JLR to a cone shape rising at a 45° angle from the center of the bottom (section=W shape). As a result, the bed materials supplied in the reactor are fluidized without segregation.

The liquid induction tube of the two-fluid nozzle was used with a PVC tube with an inner diameter of 16 mm. The interior of the lower part of the nozzle was cone-shaped, and the inner diameter of the nozzle at the point that was 40 mm above the liquid nozzle tip decreased gradually to 5 mm at the liquid nozzle tip. The gas induction tube was a stainless tube with an outer diameter of 3 mm, and was fixed coaxially at the center of the liquid induction tube [12,13].

This section describes the basic operating principle of the system. First, the volumetric pump (Longer Co., China) fills up the

JLFBR with 18 L of synthetic wastewater and the circulation pump (WILO, South Korea) drives the wastewater into the liquid induction tube of the two-fluid nozzle ($Q_{L,in}$). Next, the air blower (GAST, USA) flows air into the gas induction tube of the two-fluid nozzle. The air flowing through the gas induction tube meets the synthetic wastewater (Q_G+Q_L) and the micro bubbles generated from the process are released into the nozzle tip. The fluid released from the nozzle flows downstream through the draft tube and passes the annular space (between the reaction tube and draft tube), where the bed materials are fluidized upstream. Then, part of the gas and liquid that went up along the stream line adjacent to the outer wall of the draft tube is circulated into the draft tube again by the flow released from the nozzle. However, the fluid close to the outer wall of the reaction tube from upstream fluid (that is, fluid far from the draft tube outer wall) does not recirculate, but flows into the gas-liquid separation tank. Finally, the gas is separated from the fluid that entered the gas-liquid separation tank, and is released through the upper gas release valve ($Q_{G,out}$) while treated water is circulated (Q_R) outside the reactor through the circulation pump and released through the two-fluid nozzle again.

Table 1. Compositions of the synthetic wastewater used

Component	Concentration (mg/L)
Glucose	1,000
Poly peptone	1,200
NH ₄ Cl	1,600
CaCl ₂ ·2H ₂ O	140
FeCl ₃ ·6H ₂ O	8
NaHCO ₃	1,500
KH ₂ PO ₄	360

Table 2. Operating conditions of the JLFBR

Operating parameters	Conditions
Method of pH increment	NaOH injection, NaOH injection after aeration
Mg/PO ₄ molar ratio	1.05
Mg source	MgCl ₂
Aeration	With or without aeration after adding Mg source
Gas flow rate(Q _G)	1, 1.5, 2, 2.5, 3 L/min
Liquid circulation flow rate (Q _L)	18 L/min
pH	8.5

The components and concentration of the synthetic wastewater used in this study are listed in Table 1. The experiment was carried out with 18 L of synthetic wastewater filling up the reactor with varying conditions of gas flow rate (Q_G) and liquid circulation flow rate (Q_L), as shown in Table 2.

The bed material applied to the JLFBR was *Jumumjin Sand* with a particle diameter in the range of 2-2.2 mm, having a mass of 700 g (density of 1.78 g/cm³).

The pH, T-P, and NH₄-N concentrations were measured according to reaction time to identify the struvite crystallization properties. The T-P concentration was analyzed with an ascorbic acid method from Standard Methods [14] while NH₄-N concentration was determined with the Nessler method [15,16].

RESULTS AND DISCUSSION

1. pH Change with Respect to Aeration

Fig. 2 shows the pH change of synthetic wastewater in both JLFBR and JLR with respect to aeration time. The pH increased gradually with aeration time in the JLFBR. In addition, pH remained at a certain level after it reached 8.0. This is similar to the pH change in the JLR. Likewise, pH rose due to CO₂ stripping because reaction (1) occurred if synthetic wastewater containing HCO₃⁻ under-

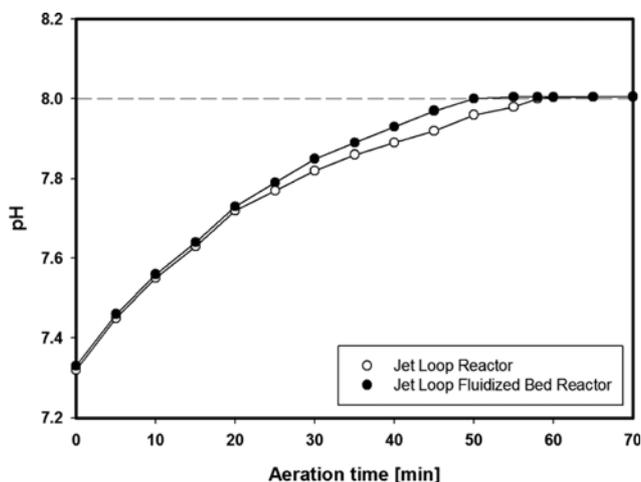


Fig. 2. pH change with respect to the aeration time (Q_L=18 L/min, Q_G=2 L/min).

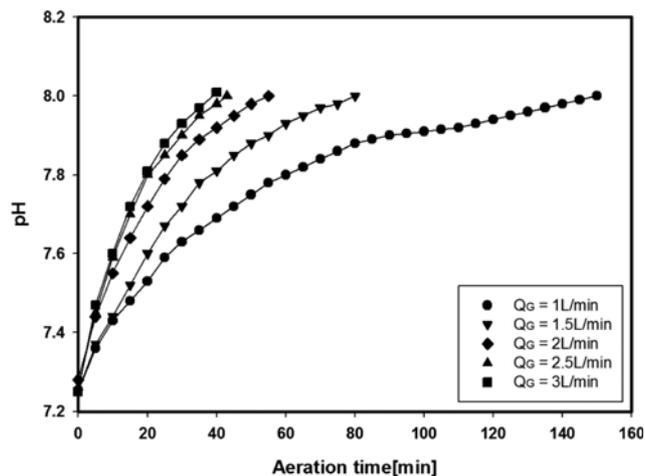


Fig. 3. Effect of the gas flow rate on the pH change.

went aeration [17]. Furthermore, maintaining the same range of pH after reaching pH 8.0 is consistent with previous results [9]. This phenomenon may be due to a possible buffering effect of the many kinds of ions that exist in synthetic wastewater.



As shown in Fig. 2, it took 50 min in the JLFBR and 58 min in the JLR to reach pH 8.0. The turbulence intensity increased in the JLFBR by fluidization of bed material. As a result, pH change due to CO₂ stripping was accelerated.

We observed pH changed with different gas flow rates (Q_G) in the JLFBR. As shown in Fig. 3, synthetic wastewater reached pH 8.0 as aeration time increased under all Q_G conditions. As mentioned above, this is due to HCO₃⁻ removal by CO₂ stripping. Also, the rate of pH change accelerated with increasing gas flow rate (Q_G). This can be explained by the increase in contact area of the gas-liquid interface as the gas flow rate goes up as well as the increasing turbulence intensity, which accelerates the mass transfer rate.

Thus, when aeration is carried out using the JLFBR, increasing turbulence intensity raises the mass transfer rate and, eventually, the rate of pH increase. Furthermore, the rate of pH change can be raised even further if the gas flow rate is increased to an optimum level.

2. T-P and NH₄-N Removal Efficiencies

An equimolar ratio of Mg, NH₄-N, and PO₄-P should exist for struvite crystallization, as shown in reaction (2) [18]. Generally, anaerobic fermentation supernatant and livestock wastewater contain many N and P constituents. However, as Mg is insufficient, its external injection is needed to induce struvite crystallization.



The synthetic wastewater used in this study had fewer moles of Mg than NH₄-N and PO₄-P, as shown in Table 1. Thus, more Mg was injected for the experiment to induce struvite crystallization. We sought to determine the effects of aeration time on struvite crystallization in the JLFBR. Thus, total phosphorus (T-P) and NH₄-N removal efficiencies were investigated in the JLFBR and JLR, depending on operating time under the same conditions (Figs. 4, 5).

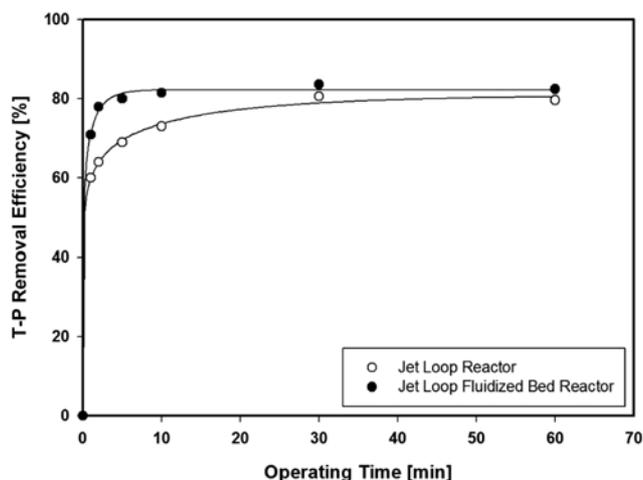


Fig. 4. T-P removal efficiencies with respect to the operating time.

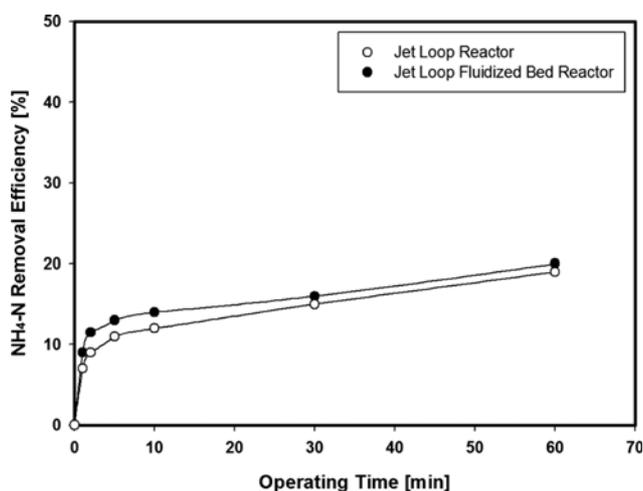


Fig. 5. NH₄-N removal efficiencies with respect to the operating time.

The T-P and NH₄-N removal efficiencies were defined as follows:

$$\text{removal efficiency (\%)} = \frac{C_{i0} - C_i}{C_{i0}} \times 100 \quad (3)$$

where C_{i0} is the initial concentration of component T-P or NH₄-N and C_i the concentration at time t .

To investigate the removal efficiencies, the pH of the synthetic wastewater was raised from 7.3 to 8.0 with CO₂ stripping by air injection through the two-fluid nozzle ($Q_G=2$ L/min). Then, MgCl₂ was injected so that the Mg/PO₄ molar ratio of the synthetic wastewater became 1.05. It was difficult to reach a pH greater than 8.5 with CO₂ stripping (Fig. 2). Thus, NaOH was finally injected to make the pH 8.5 for the experiment.

As shown in Fig. 4, the T-P removal efficiency of synthetic wastewater by struvite crystallization in the JLFBR was 82.4%, slightly higher than the JLR, and the maximum removal efficiency of T-P according to the operating time was reached within the initial 10 min, so it remained constant as the operating time was increased. This result is slightly different from the curve that shows T-P removal

efficiency in the JLR. That is, as shown in the figure, T-P removal efficiency of the JLR was 69.0%, 73.2%, and 80.6% when operating time was 5, 10, and 30 min, respectively. The T-P removal reaction persisted significantly even after the initial 10 min. However, the T-P removal efficiency of the JLFBR was 79.9%, 81.4%, and 83.5%, suggesting that most of the T-P removal reaction was completed within the initial 10 min.

This study assumes that the bed material fluidized in the JLFBR accelerated heterogeneous nucleation, enhancing the struvite formation rate. Moreover, the fluidized particles strengthen the turbulence intensity, resulting in enhancing the struvite crystallization rate.

Fig. 5 demonstrates the variation of NH₄-N removal efficiency depending on operating time. As shown in Fig. 5, the NH₄-N removal rate remained at around 20% when the operating time for both reactors was increased to 60 min. However, the JLFBR showed a slightly greater efficiency. The JLFBR operation also recorded a shorter operating time than the JLR to reach a certain level of removal rate, like T-P removal.

These results suggest that NH₄-N removal efficiency is markedly lower than T-P removal efficiency. This can be attributed to the higher NH₄-N concentration of synthetic wastewater (ten times or more) compared with the T-P concentration. The removed mass of NH₄-N from synthetic wastewater was 2.5 times higher than the T-P concentration because NH₄-N was removed by struvite crystallization; aeration also contributed to its removal. These findings are similar to those of Liao et al. [19] who reported NH₄-N removal by ammonia stripping through aeration of swine manure wastewaters.

CONCLUSIONS

A new type of reactor, referred to as a jet loop fluidized bed reactor (JLFBR), which has fluidized particles within a jet loop reactor (JLR), has been used to investigate reactor performance characteristics during treatment of NH₄-N and T-P in synthetic wastewater through struvite formation. Comparing the reactor performance obtained from the JLFBR with that from the JLR based on the pH increase by CO₂ stripping, as well as NH₄-N and T-P removals under the same conditions, the following conclusions can be made:

1. Application of the JLFBR in the struvite crystallization process can help raise the pH of wastewater, compared with the JLR, thereby reducing operating costs.
2. T-P and NH₄-N removal efficiencies by the struvite crystallization reaction were higher in the JLFBR than in the JLR. The removal efficiencies for the first 10 min in the JLFBR, in particular, were quite high. This is because the fluidized particles filled into the JLFBR accelerated the heterogeneous nucleation and the growth rate of struvite crystallization.

ACKNOWLEDGEMENTS

This work was supported by the Pukyong National University Research Abroad Fund in 2014 (C-D-2014-0724).

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