Effect of hydraulic retention time and seed material on phosphorus recovery and crystal size from urine in an air-agitated reactor

Xiaoning Liu, Zhengyi Hu, Jinzhi Wang and Guoqi Wen

ABSTRACT

Phosphorus (P) recovery from urine is affected by various parameters. This study evaluates the effects of hydraulic retention time (HRT) and seed material on P recovery and crystal size in an air-agitated reactor. Results show that ortho-phosphate removal and struvite recovery efficiencies were 96.3% and 89.5%, and 97.1% and 93.0%, after five runs of HRTs of 1 and 2 h, respectively. Low loss of crystals from effluent urine solutions indicates high struvite recovery efficiency and is correlated with the structure and design of the reactor. The average particle size decreased from 40.0 to 31.7 μm as the HRT increased from 1 to 2 h. The two types of seed materials (zeolite and molecular sieve) did not affect the ortho-phosphate removal efficiency but affected the struvite crystal size. In particular, multi-stage addition of zeolites increased the average crystal size from 33.7 to 57.0 μm.

INTRODUCTION

Nutrient discharges into water bodies by human activities have increased eutrophication problems. The concern for diminishing phosphorus (P) rock reserves has increased because P is an indispensable resource for a secure crop production to feed an increasing global population. These two facts justify the development of struvite crystallisation, which is a new alternative technology for sustainable and economical P recovery from wastewater. Studies on struvite formation from urine have been performed on a laboratory scale (Lind et al. 2000; Ban & Dave 2004) and small pilot scale (Ronteltap et al. 2010; Etter et al. 2011). Urine accounts for approximately 50% of the total P load in municipal wastewater but contributes less than 1% to the total wastewater volume (Larsen & Gujer 1996). Struvite formation from urine, which is regarded as a special P-rich stream, does not require pH adjustments (Ronteltap et al. 2010). Thus, P recovery from urine in the form of struvite is feasible and economical.

P recovery and crystal growth from wastewater and urine are usually affected by various parameters, such as mixing strength, retention time, seed materials and Mg/P molar ratio. Wilsenach et al. (2007) found that mixing speed had no effect on struvite formation in synthetic urine. Liu et al. (2015) indicated that P removal efficiency increased as mixing speed increased from 80 to 160 r/min in urine, whereas no change was observed when mixing speed increased from 160 to 240 r/min. Seed materials are used to optimise the size of struvite crystals obtained from wastewater (Battistoni et al. 2002; Ali & Schneider 2006) and to contribute to the final particle size distribution (Shimamura et al. 2005). In Europe and Japan, municipal facilities use seeding with sand to increase particle size and enhance P recovery (Ueno & Fujii 2004; Battistoni et al. 2002). Liu et al. (2015) found a lack of significant change when seed materials were added to urine in a laboratory test. From an economic point of view, large crystals should be obtained to facilitate the recovery, transport and commercial operation of the final product (Pastor et al. 2008). Therefore, the necessary conditions must be established to optimise struvite formation to minimise the running process and make it cost-effective.

However, the effect of seed material on P recovery and crystal size from urine has not been studied. The batch pilot experiments described in this paper aim to evaluate the effects of hydraulic retention time (HRT) and seed material used in P recovery and average crystal size produced in an air-agitated reactor.
MATERIALS AND METHODS

Human urine, magnesium resource and seed materials

The pure urine used in this study was obtained from the public toilet urinal near Baoding City Railway Station, Hebei Province, China. The collected urine was then stored in 25 L jerry cans with lids for one month. The pH of the hydrolyzed urine ranged from 9.2 to 9.4, the orthophosphate (PO$_4^{3-}$/C$_{0}$-P) concentration ranged from 184 to 232 mg/L and the ammonium nitrogen (NH$_4^+$-N) concentration ranged from 6,250 to 6,810 mg/L. Calcium (Ca) and magnesium (Mg) concentration decreased sharply to 12.6 and 5.2 mg/L, respectively, during the storage process because of the precipitation reaction with P in the urine. Magnesium chloride (MgCl$_2$·6H$_2$O, analytical grade) used as a Mg resource was added for struvite precipitation. Two types of seed materials, zeolite (A, 0.5 to 1 mm) and molecular sieve (B, 1 to 2 mm), were purchased from Luanping Zeolite Company in Hebei province and Shanghai Yuqing Trade Limited Company, respectively.

Design and performance of the air-agitated reactor

All experiments were conducted in an air-agitated reactor made of polymethyl methacrylate with a total volume of 2.6 L (Figure 1). The reactor had a diameter of 80 mm and a height of 500 mm. The top part was composed of two concentric columns and the diameters of the inner and the external columns were 80 and 120 mm, respectively. Effluent was discharged in the upper part of the external column and allowed to flow to the internal column through four holes of 8 mm diameter. This column prevented fine particles from washing out. A valve was used to close off the bottom of the reactor containing the precipitated product.

The hydrolyzed pure urine and MgCl$_2$·6H$_2$O solution (0.5 mol/L) were continuously pumped to the reactor using a peristaltic pump, leading to an average Mg/P molar ratio of 1.3 achieved during all experiments. The Mg/P molar ratio of 1.3 was obtained on the basis of previous studies of optimal conditions for struvite formation in urine (Liu et al. 2013). The urine and magnesium solutions were mixed in the reactor by injection of air at a flow of 1 L/min using an aeration pump through a gas sparger. Struvite crystals formed at the bottom of the reactor were filtered using a nylon filter bag (5 μm) and harvested at the end of each experiment. The collected crystals were dried at 40 °C (to prevent the N loss which occurs in the form of ammonia during the drying of struvite crystals) for 48 h, resulting in the final dried product. Effluent samples obtained at an interval of 1 h in triplicate were filtered through 0.45 μm membrane filters, acidified with 5% sulphuric acid solution and then stored at 4 °C for analysis.

The performance of the reactor was evaluated by analysing the PO$_4^{3-}$/P removal efficiency, struvite recovery efficiency and average crystal size. On the basis of thermodynamic equilibrium, the PO$_4^{3-}$/P removal efficiency was calculated from the difference in PO$_4^{3-}$/P concentrations of the influent and effluent of the reactor. The final dry weight of the struvite formed in the reactor was recorded. To calculate the struvite recovery efficiency, the obtained
masses were compared with the theoretical mass of struvite based on the equilibrium consideration.

**Experimental design**

The experimental conditions for seven experiments are shown in Table 1. The first pair of experiments was conducted to evaluate the effect of two different HRTs (1 and 2 h) on P recovery and struvite crystal size (Experiments 1 and 2). The desired HRT was controlled by varying the feed flow rate. Experiment 3 was used as a control without adding seed materials. The two seed materials (A: zeolite; B: molecular sieve) over four separate experiments (Experiments 4 to 7) were then compared. Seed materials were added to the reactor once (5 g, one-stage addition) and periodically added at an interval of 1 h (0.5 g each time, multi-stage addition) prior to the chemical reaction. At the beginning of each experiment, the feed flow, Mg flow and air flow rates were set to fixed values and the experiment lasted for five runs of HRTs of 1 and 2 h. All of the experiments were performed at 22 ± 1.0°C in the laboratory.

**Sample analysis**

The pH values of the urine solutions were measured immediately using a HI98185A-type pH meter (Hanna, Italy), and 0.10 g dried struvite was dissolved completely in 50 mL 5% hydrochloric acid solution to analyse the elemental composition. The PO$_4^{3-}$-P and NH$_4^+$-N were analysed using colorimetric analysis according to the Standard Methods of the American Public Health Association (1998). Elemental potassium (K), sodium (Na), Ca and Mg were analysed using inductively coupled plasma optical emission spectrometry (ICP-OES, Leeman Prodigy, USA). For the struvite crystals formed in the all experiments, the average crystal size and crystal size distribution (normal distribution) were determined using laser diffraction (Mastersizer 2000, Malvern Instruments, UK).

The average and standard deviation values of the data were obtained. The effect of HRT and seed material on the crystal size was analysed by one-way analysis of variance. All statistical tests were considered significant at $P < 0.05$. When the treatments were significant, Least Significant Difference (LSD) tests were used to check for the differences among individual treatments. Statistical analyses were performed using Origin Pro 8.6.

**RESULTS AND DISCUSSION**

**Effect of HRT on P recovery and crystal size**

The results represent changes in the PO$_4^{3-}$-P removal efficiency under HRTs of 1 and 2 h in an air-agitated reactor (Experiments 1 and 2, Figure 2(a)). The residual PO$_4^{3-}$-P concentration decreased sharply during crystal formation and the PO$_4^{3-}$-P removal efficiency exceeded 84.0% within 1 h. PO$_4^{3-}$-P removal efficiency also showed an increasing trend with time under both the HRTs of 1 and 2 h; however, these changes were not significant. After five runs of HRTs of 1 and 2 h, the effluent PO$_4^{3-}$-P concentrations were 7.9 and 6.1 mg/L, respectively, and the PO$_4^{3-}$-P removal efficiencies were 96.3 and 97.1%, respectively. Münch & Barr (2001) found that HRT has no effect on struvite formation during P removal from anaerobic digester side streams. It is the release rate of PO$_4^{3-}$-P into the solution, and not simply the feed rate of total P in urine, that determines the saturation index (SI) (Schneider et al. 2003) and P removal efficiency. This result may also be attributed to the fact that the reaction of struvite in urine occurs quickly. The formation of struvite from urine

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**Table 1** Operational condition for various experiments

<table>
<thead>
<tr>
<th>Experiments</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial PO$_4$-P Conc. (mg/L)</td>
<td>196.2</td>
<td>184.0</td>
<td>217.4</td>
<td>190.4</td>
<td>190.7</td>
<td>227.4</td>
<td>232.0</td>
</tr>
<tr>
<td>HRT (h)</td>
<td>1.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Mg/P molar ratio</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td>Run time (HRT)</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Seed material</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>A1</td>
<td>A2</td>
<td>B1</td>
<td>B2</td>
</tr>
<tr>
<td>Air flow (L/min)</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

A1: One-stage addition zeolite; A2: Multi-stage addition of zeolite; B1: One-stage addition molecular sieve; B2: Multi-stage addition of molecular sieve; ‘-’ means without adding seed materials.
The struvite recovery efficiency in the air-agitated reactor was 89.5 and 93.0% under HRTs of 1 and 2 h, respectively (Table 2). Longer HRT can yield higher struvite recovery efficiencies in this reactor. Losses were inevitable but were expected to represent a smaller mass fraction of the produced struvite given that these losses mainly resulted from the small crystals that were washed out and had adhered to the reactor wall (see below). Britton et al. (2008) studied P recovery from anaerobic digester supernatants in a wastewater treatment plant and obtained struvite recovery efficiencies of 86 and 87% from two reactors. Bhuiyan et al. (2008) found that 83 ± 2.0% of the theoretical mass of total struvite harvested may be recovered during operation and this difference may have occurred because of the loss of a number of fine crystals with the effluent. The air-agitated reactor in this study showed high results in terms of PO$_4^{3-}$-P removal and struvite recovery efficiencies because of its structure and design. The small hole connecting the inner and external columns might reduce the discharge of large amounts of fine crystals with the effluent. White crystal precipitation was also observed on the wall and at the bottom of the external column, which was eventually deposited at the bottom of the external column. These two factors prevented a large loss of fine crystals with the effluent and improved the struvite recovery efficiency.

The results show that changes in HRT have a direct effect on the average particle size and particle size distribution (Figures 2(b) and 2(c)). Longer HRT because of lower influent flow rate led to smaller mean particle sizes. The average particle size significantly decreased from 40.0 to 31.7 μm as the HRT increased from 1 to 2 h. Doino et al. (2011) found that increasing the flow rate resulted in increased particle size in a mechanically stirred fluidised bed reactor. The growth rate of crystals is essentially controlled by mass transfer and surface integration mechanisms (Mersmann 2001). Mass transfer refers to the transport of solutes from the solution to the crystal surface by diffusion, convection or both, and surface reaction refers to the incorporation of materials into the crystal lattice through surface integration (Le Corre et al. 2009).

![Figure 2](image-url)  
**Figure 2** | Effect of HRT on (a) PO$_4^{3-}$-P removal efficiency, (b) average crystal size and (c) crystal size distribution in the reactor (n = 3).

<table>
<thead>
<tr>
<th>HRT</th>
<th>Struvite recovered (g)</th>
<th>Theoretical struvite produced (g)</th>
<th>Struvite recovery efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 h</td>
<td>19.03</td>
<td>21.26</td>
<td>89.5</td>
</tr>
<tr>
<td>2 h</td>
<td>20.73</td>
<td>22.30</td>
<td>93.0</td>
</tr>
</tbody>
</table>
High influent rates improve the turbulence and contribute to the processes of mass transfer and surface integration, resulting in increased crystal size, and thus provide high separation performance and efficiency, which might be more economical and efficient for struvite crystallisation in a given reactor. However, high influent rate may also reduce the struvite recovery efficiency given the higher likelihood of particle loss in the effluent. Based on obtaining more crystal production, an HRT of 2 h was thus regarded as the basis for the subsequent experiments.

**Effect of seed materials on P recovery and crystal size**

Figure 3(a) presents the effect of seed materials on P removal efficiency in the air-agitated reactor. PO$_4^{3-}$-P removal efficiency ranged from 94.7 to 97.2% after 10 h under an HRT of 2 h, and the residual PO$_4^{3-}$-P concentration ranged from 6.1 to 11.3 mg/L. Although PO$_4^{3-}$-P removal efficiency generally showed an increasing trend with time, there was a lack of significant change observed in it after adding the seed materials. This result is in accordance with the studies conducted by Burns *et al.* (2003) and Rahaman *et al.* (2008), who pointed out that seed materials did not significantly enhance the P recovery process from wastewater. The reason might be that crystals form quickly, and rapidly attained equilibrium and nuclei formation before growth could occur on the surface of the seed materials (Rahaman *et al.* 2008).

However, in this study, we found that adding the seed materials affected the average crystal size and crystal size distribution (Figures 3(b) and 3(c)). The average crystal size significantly increased from 33.7 to 57.0 μm with multi-stage addition of zeolite, whereas it was 44.7 μm with one-stage addition of zeolite. However, adding molecular sieves did not significantly affect the average crystal size. Multi-stage addition of zeolite showed the largest effect on crystal growth and size. Seeds in the solution act as a diffusive medium that enhances crystal growth by allowing layering of newly formed crystallites onto the surface of the seeds (Ali & Schneider 2006). Le Corre *et al.* (2007) stated that utilisation of seed materials could effectively improve growth by enabling the agglomeration of fine struvite particles on the seed materials. Therefore, the seed material is a reliable tool to obtain larger crystals for P recovery. In our previous batch experiments, we found similar results showing that adding seed material in urine had no obvious effect on the P removal efficiency, but contributed to the formation of struvite clusters (Liu *et al.* 2013).

Multi-stage addition of zeolite and molecular sieve achieved larger average crystal sizes than one-stage addition because the seed material might disappear and be buried by subsequent layering of newly formed crystals during the
growth of crystals in a continuous process. This result implies that seed materials should be added periodically during a continuously running process, resulting in a larger diffusive media area and thus larger struvite crystals. The improved effect of zeolite on crystal growth may be correlated with the size of the seeds. The specific surface area of seeding materials has been speculated to be one of the factors that affect P removal (Ohlinger et al. 1999). Therefore, zeolites featuring smaller sizes, which implies larger specific areas, can provide an adequate number of reaction surfaces to accelerate crystal growth. Formed struvite particles, because of their larger specific area and similar structure, were used as alternative seed materials. Shimamura et al. (2003) observed the growth of struvite crystals from 0.79 to 1.18 mm within 12 d with the addition of fine struvite crystals as seed materials to a reactor.

Larger particle sizes are easier to separate and less prone to washing out than smaller particles (Ronteltap et al. 2010). Ronteltap et al. (2010) also reported that the average crystal size obtained from urine ranges from 36 to 136 μm and that maximum supersaturation is achieved between a pH of 9 and 10, which corresponds well with the minimum particle size. Thus, the average crystal size obtained from urine was smaller compared with those obtained from wastewater in prior research (Stratful et al. 2001, 2004). Mixing conditions can create segregation and attrition which affect the nucleation rate and result in a change in crystal number, size and distribution (Triger et al. 2012). Compared with the propeller stirrer reactor we used in another experiment (Liu et al. 2014), air flow is more energy-efficient, which causes lower turbulence and slower dissipation, resulting in higher supersaturation that favours nucleation over crystal growth (Mersmann 2001), and in turn, resulting in smaller crystal sizes. However, low turbulence with air injection prevents the outflow of fine crystals produced in the reaction zone of the reactor. Furthermore, crystals cannot easily agglomerate because of negative zeta potentials in hydrolyzed urine with high pH; thus, larger crystals are not easily formed during struvite crystallisation in urine (Bourououlos & Koutsoukos 2000; Ronteltap et al. 2010).

High purity struvite could be obtained in this study given that the main impurity found in the formed struvite were Ca, Na and K, which were present only with average weights of 0.71, 0.31 and 0.13%, respectively. Larger crystal sizes have been found in continuous reactors running for longer periods of time, e.g., several days (Ueno & Fujii 2001; Adnan et al. 2003). The experiments described in this study were not intended for long-term reactor operation. Thus, our study lacked several features that may be required in a system meant for long-term practical operation. Operation of the reactor for longer periods of time is further required to assess the feasibility of struvite crystallisation (e.g., crystal size, hardness and morphology) in urine.

**CONCLUSIONS**

The air-agitated reactor used in this study effectively recovered P from urine. After five runs of HRTs of 1 and 2 h, PO₄³⁻-P removal and struvite recovery efficiencies exceeded 91.2 and 89.5%, respectively, with pure struvite crystals. HRT did not clearly affect P removal efficiency because of the rapid crystal formation in the urine solution. The average particle size significantly decreased from 40.0 to 31.7 μm as the HRT increased from 1 to 2 h. Adding seed materials did not affect P removal efficiency but had a positive effect on the agglomeration of fine struvite particles. Multi-stage addition of zeolite facilitated an efficient diffusion integration, leading to a significant growth of larger struvite crystals (from 33.7 to 57.0 μm).

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