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# Comparison of different K-struvite crystallization processes for simultaneous potassium and phosphate recovery from source-separated urine

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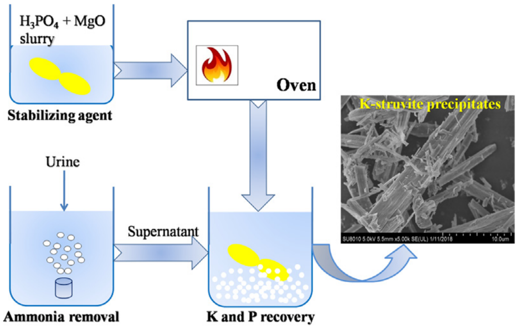
## HIGHLIGHTS

- K and P were recovered from urine by K-struvite precipitation.
- High nutrients recovery efficiencies were achieved by using low-grade MgO (LG-MgO).
- Na:K molar ratio has a marked effect on the competitive precipitation of Na and K.
- Using the stabilizing agent formed by LG-MgO and $H_3PO_4$ was optimal for K recovery.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Controlled K-struvite crystallization is an attractive technology to simultaneously recover phosphate and potassium from urine. This study investigated the recovery of phosphate and potassium from source-separated urine by K-struvite crystallization using different use models of low-grade MgO (LG-MgO): LG-MgO alone (model 1, M1), LG-MgO plus phosphorus acid (model 2, M2), and a pre-formed stabilizing agent by adding LG-MgO plus phosphorus acid (model 3, M3). Results showed that 100% phosphate and 25% K could be recovered from urine by M1. M2 at an MgO:K:P molar ratio of 4:1:1.6 provided a maximum P and K recovery efficiency at 100% and 70%. M3 achieved a same K-removal efficiency as M2, but the phosphate recovery efficiency was lower than that of M2 due to the dissolution of phosphate in the stabilizing agent. K-struvite crystallization was closely accompanied by severe co-precipitation of Na-struvite. Increasing the Na concentration markedly improved the ability of Na co-precipitation, but the variation of pH did not affect the competition precipitation of K and Na. When the Na:K molar ratio was >10, the precipitation of Na was more than that of K. A process performance evaluation indicated that M3 is more suitable for simultaneous K and P recovery from source-separated urine.

## 1. Introduction

Phosphorus (P) and potassium (K) are essential macro-nutrient for cells, crops, living animals and human beings. Most phosphorus and

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potassium current being used are sourced from mineral rock, which are nonrenewable resources being predicted to run out shortly (Gilbert, 2009; Li et al., 2018). What is more, the world population will increase to 9–10 billion by 2050 (Wang and Zhao, 2010), indicating that more food are required. Therefore, additional P and K sources must be developed to ensure the stable and sustainable development of agriculture.

Urine is in rich of P and K, and thus an important agricultural nutrient source in developing countries (Decrey et al., 2011; Udert and Wächter, 2012). However, direct urine application in large scale is unsuitable because of its inconvenient transportation and storage. As reported, source-separated urine can be quickly degraded to ammonia and bicarbonate, during which large amounts of ammonia volatilizes and the solution pH increases, producing unpleasant gases (Udert et al., 2003). In addition, source-separated urine may be cross-contaminated by the faecal material containing large amounts of pathogens such as bacteria, protozoa, viruses and parasitic worms (WHO, 2006). Therefore, it is essential to concentrate and stabilize nutrients in urine for convenient and safe use (Udert et al., 2006; Lienert et al., 2007).

Struvite ($MgNH_4PO_4 \cdot 6H_2O$) crystallization is an attractive technology for the enrichment of P and nitrogen (N). Through the addition of external magnesium source, most of the phosphate and a part of ammonia in urine can be recovered (Li et al., 2016). Nevertheless, because of the recyclability of N, the recovery of N does not have the same resource urgency as P recovery. It is more meaningful to recover K and P simultaneously by the formation of K-struvite ($MgKPO_4 \cdot 6H_2O$). K-struvite is an isomorphous analogue of struvite that also serves as slow-release fertilizer (Larsen et al., 2013). However, the presence of ammonia in urine can greatly inhibit the formation of struvite (Gao et al., 2018). Therefore, prior to K-struvite precipitation, ammonia needs to be removed. In previous literature, Xu et al. (2015) and Gao et al. (2018) investigated the recovery of phosphate and potassium from synthetic urine after deamination by K-struvite precipitation and reported high recovery efficiencies. Zhang et al. (2017) used a pilot-scale K-struvite fluidized bed reactor to simultaneously recover P and K from urine and achieved 20–35% of K removal and 80–90% of P removal. Unfortunately, since the K molar concentration in urine is much greater than that of P (Griffith et al., 1976), the equimolar composition of struvite (Mg, K, and P) requires both magnesium and phosphate addition for efficient K recovery.

Nowadays, pure magnesium salts or both magnesium and phosphate salts are often added for K recovery, which can heavily influence the economic feasibility of K-struvite crystallization in urine (Yao et al., 2017). Although some researchers have used lower-cost magnesium sources such as bittern (Huang et al., 2014), sea water (Li et al., 2019), calcined magnesite (Krähenbühl et al., 2016), seawater nanofiltration concentrate (Lahav et al., 2013) and sea salts (Merino-Jimenez et al., 2017) in struvite precipitation for ammonia removal, no investigation has yet focused on the recovery of K using a low-grade magnesium source. Low-grade MgO (LG-MgO) is often used as the magnesium source in struvite crystallization due to its wide range of sources and cost-effectiveness (Romero-Güiza et al., 2015). To determine the feasibility of using LG-MgO as the magnesium source in K-struvite crystallization, the present study conducted experiments to evaluate and better understand K recovery from source-separated urine with ammonia pretreatment using LG-MgO obtained from natural magnesite calcination. Experiments were performed by three use models of LG-MgO: the use of LG-MgO alone (model 1, M1), LG-MgO plus concentrated phosphoric acid (model 2, M2), and a stabilizing agent pre-formed by LG-MgO and concentrated phosphoric acid (model 3, M3). This study focused on nutrients recovery efficiency and the reaction mechanism of K-struvite crystallization in urine by the three models. Since Na-struvite (magnesium sodium phosphate heptahydrate, $MgNaPO_4 \cdot 7H_2O$) may co-precipitate with K-struvite, thereby reducing the K-recovery efficiency from urine (Xu et al., 2015), the competitiveness of K and Na precipitation was investigated. In addition, based on the above investigations, the comprehensive performance of the three models on the nutrients recovery from urine was evaluated and compared.

## 2. Materials and methods

### 2.1. Urine and reagents

Source-separated urine was collected from the public toilets in the teaching building of Yanshan University, P.R. China. To avoid the inhibition of ammonia nitrogen on K-struvite crystallization, the collected urine was pretreated by adjusting pH to 11.5 with NaOH and by air-stripping at 45 °C. The characteristics of treated urine are as follows: pH 10.3 ± 0.1, $K^+$ 49.8 ± 2.8 mM, $PO_4$-P 23.4 ± 1.1 mM, $Na^+$ 298 ± 10.3 mM, $NH_4^+$ 1.1 ± 0.03 mM, $Mg^{2+}$ 0.06 ± 0.03 mM, $Ca^{2+}$ 0.08 ± 0.01 mM. LG-MgO was derived from the calcination of magnesite mineral, with specific preparation process and corresponding composition given elsewhere (Huang et al., 2017a). All other reagents including $H_3PO_4$ (85%), NaCl, KCl, $Na_2HPO_4 \cdot 12H_2O$, and $MgCl_2 \cdot 6H_2O$ were of analytical grade and purchased from Tianjin Chemical Reagent Company, China.

### 2.2. Experimental procedures

Three different LG-MgO use modes are investigated: the use of LG-MgO alone (model 1, M1), LG-MgO plus concentrated phosphoric acid (model 2, M2), and a stabilizing agent that pre-produced by LG-MgO and concentrated phosphoric acid (model 3, M3). All experiments were conducted at 25 °C in duplicate.

#### 2.2.1. Model 1

500 mL treated urine was first fed into a 1000-mL beaker with a magnetic stirrer, LG-MgO was added at an Mg:K molar ratio of 2:1. The mixture was stirred at 200 rpm for 240 min. At every 20 min, the solution pH was measured and a 5 mL sample was collected and filtrated through a 0.45-μm membrane filter for composition analysis.

#### 2.2.2. Model 2

500 mL treated urine was fed into a 1000-mL beaker with a magnetic stirrer, LG-MgO and H3PO4 were added at different Mg:K:P molar ratios (3:1:1–5:1:2). The mixture was then treated following the same procedure as described in Section 2.2.1.

#### 2.2.3. Competitive precipitation of $Na^+$ and $K^+$

To determine the effect of $Na^+$ on K-struvite crystallization, a synthetic solution with a $K^+$ concentration of 49.8 mM was used, and the experiments were performed by adding $Na_2HPO_4 \cdot 12H_2O$ and $MgCl_2 \cdot 6H_2O$ to the synthetic solution at an Mg:K:P molar ratio of 1.6:1:1.6. While keeping the K concentration constant, the Na:K molar ratio was adjusted to a range of 5–30 by NaCl addition. The effect of pH on the competition precipitation was investigated in 250 mL stirred beakers at a pH of 10–12. The following experimental procedures were similar to those detailed in Section 2.2.1.

#### 2.2.4. Model 3

To produce the stabilizing agent (SA), 20 g LG-MgO was added to a 200-mL beaker with 40-mL pure water. At a stirring rate of 100 rpm, concentrated $H_3PO_4$ was fed slowly to the LG-MgO slurry with an Mg:P molar ratio of 1:1. The mixed slurry was then agitated for 1 h and dried at 80 °C for 48 h. Finally, the dried compounds were crushed to a particle size of about 100 μm and used as the precipitator for P and K recovery. 100 mL urine was then added to a 200-mL beaker with a magnetic stirrer. To make full use of phosphorus in urine, $MgCl_2 \cdot 6H_2O$ was added at an Mg:P molar ratio of 1:1 prior to SA addition. Then, SA was dosed with a range of 3.2–11.2 g/L. The solution was stirred for a desired time (30–120 min) with a pH ranging between 8.5 and 12. Finally, the