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Technical Note

Fate of phosphorus in diluted urine with tap water

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HIGHLIGHTS

- The urine dilution ratio with tap water should not exceed 50/50.
- The removed P accounted for 24% of total P under 50/50 urine solution.
- Struvite crystals with high purity were still obtained under 50/50 urine solution.
- Lowest P recovery efficiency was found at 25 °C with largest struvite crystal size.

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ABSTRACT

P loss during the fresh urine storage process is inevitable because of the presence of Ca and Mg. Dilution is one of the most important parameters influencing urine composition and subsequent P recovery. This study aimed to investigate the fate of P in urine with different dilution ratios (V_{water}/V_{urine}, i.e., 0/100, 25/75, 50/50 and 75/25). The results indicate that the percentage of P loss increased from 43% to 76% as the dilution ratio increased from 0/100 to 75/25 because of more Ca and Mg obtained from tap water. Meanwhile, P removal efficiency through struvite precipitation decreased from 51% to 8% because of lower supersaturation ratio as a result of dilution. Struvite crystals with high purity were still obtained even under a dilution ratio of 50/50 urine solution. Batch experiments were also performed to study the influence of temperature (15–35 °C) on P recovery and crystal size. For different dilution ratios of urine solutions, no significant discrepancy for the P removal efficiencies were observed at 15 and 35 °C, whereas the P removal efficiencies at 25 °C showed an increasing gap with those at 15 and 35 °C. The largest average crystal sizes were found at 25 °C, which was opposite to the trend of P removal efficiency.

1. Introduction

P recovery and reuse from urine have gained increasing attention because of the depletion of P reserves. The human body excretes 1.6–1.7 g of P per day, and most are found in urine (Schouw et al., 2002). Struvite precipitation is a reliable method for the recovery of 95% of P in urine (Wilsenach et al., 2007). White and odourless struvite crystals, which are compact and can be stored and transported easily, have been proposed as P fertiliser in agriculture (Johnston and Richards, 2003; Etter et al., 2011). Prior to P recovery from urine, urine hydrolysis occurs during the urine collection and storage process and triggers the precipitation of Ca and Mg in the form of carbonates and phosphates (Udert et al., 2003), thereby resulting in P loss. The hydrolysis of urea in fresh urine is catalysed by the enzyme urease, and the urine pH increases when ammonium and bicarbonate ions are produced during the urea hydrolysis process (1).

$$NH_2(CO)NH_2 + 2H_2O \rightarrow NH_3 + NH_4^+ + HCO_3^- \quad (1)$$

Some researchers have addressed the influence of storage conditions on the dynamics of urine and P recovery (Hellström et al., 1999; Tilley et al., 2008; Liu et al., 2014). Dilution, one of the most important parameters, induces urea hydrolysis (Tilley et al., 2008) but reduces P removal efficiency during the subsequent struvite precipitation process (Liu et al., 2014). Temperature also directly influences the solubility of struvite (Hanhoun et al., 2011) and thermodynamic properties (Ronteltap et al., 2007). However, Webb and Ho (1992) reported that temperature has less effect on struvite precipitation than other parameters, such as pH and nutrient concentrations. Thus, information on the influence of temperature on struvite formation remains unclear. In particular, the change in P recovery and crystal size from urine with temperature has not been well studied.

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Udert et al. (2003) studied the influence of dilution on the composition of precipitation during the urine storage process using a model, but did not involve subsequent P recovery. Previous urine dilution studies were carried out with distilled water (Tilley et al., 2008; Liu et al., 2014), not tap water. However, diluted urine with tap water in practice will increases the spontaneous precipitation in the collection system because of additional Ca and Mg, resulting in higher P loss, which might pose certain influence on P recovery by struvite formation. The quantification of P loss in the collecting and storage process and afterwards the P recovery through struvite will be essential to evaluate the feasibility of P recovery from diluted urine with the variation of dilution ratio.

Thus, this study aimed to investigate the fate of P in urine with different dilution ratios with tap water, and to evaluate the influence of dilution with tap water on the purity of struvite formed because the additional Ca provided from tap water may affect the struvite precipitation and decrease the purity of struvite crystals. Furthermore, the influence of temperature on P recovery and crystal size was investigated.

2. Materials and methods

2.1. Urine samples

Fresh urine collected from public urinals in the teaching building of the University of Chinese Academy of Sciences was stored for 3 wk to ensure that the urine was fully hydrolysed and the NH_4^+ concentration was maintained at a stable level, which ranged from 6400 to 6600 mg L^{-1}. Urine (15 L) was collected over a span of 24 h. The collected fresh urine was mixed into a composite sample in a 20 L jerry can and used for immediate ureolysis experiments. The basic characteristics of fresh urine are presented in Table 1. The tap water used in this study contained 142 mg L^{-1} Ca and 46 mg L^{-1} Mg, and had a pH of 7.5.

2.2. Experimental design

Storage experiments were presented in 2 L wide-mouth jars with screw-top lids. Four dilution ratios (V_{water}/V_{urine}, i.e., 0/100, 25/75, 50/50 and 75/25) with the addition of tap water were prepared with the jars closed during the storage experiments, and 1.6 L of samples of urine mixtures was used for each treatment. Each experiment was performed in triplicate, and the storage experiments were performed at 25 ± 1.0 °C in the laboratory.

The urine samples were withdrawn at the beginning and end of the storage process. Urine samples were filtered through 0.45 μm Millipore filters, acidified to pH 2 with 5% sulphuric acid solution and stored at 4 °C for analysis. The struvite precipitation experiments were carried out in 1 L beakers at three temperature conditions (15, 25 and 35 °C) using a thermostat container. According to previous studies on optimal conditions for struvite formation (Liu et al., 2013), magnesium chloride solution (1 M) as Mg resource was added into 500 mL of the filtered urine solutions to achieve a typical Mg/P molar ratio of 1.3 in stoichiometric conditions. Urine solutions were mixed with a submersible magnetic stirrer for 5 min and the precipitation time was 30 min. Urine samples were preserved as described above. The formed struvite crystals were filtered through a 5 μm sieve mesh, and dried in an oven at 40 °C for 48 h to avoid ammonia loss. The difference in the PO_4^{3-} concentrations of diluted fresh urine and hydrolysed urine was compared with that of diluted fresh urine to calculate the P loss percentage. The P removal efficiency was determined by comparing the difference in the initial and final PO_4^{3-} concentrations and the initial PO_4^{3-} concentration during the struvite precipitation experiments. The percentage of P removal was defined as the removed P through struvite formation, which accounted for the total P in fresh urine.

2.3. Analytical methods

The pH of all urine solutions was immediately measured using a HI98185A type pH meter (Hanna, Italy). Dried struvite crystals (0.1 g) were completely dissolved in 25 mL of 5% hydrochloric acid to analyse the elemental composition. PO_4^{3-} and NH_4^+ were analysed by colourimetric analysis according to the Standard Methods for the examination of water and wastewater (APHA, 1998). Elemental K, Na, Ca and Mg were analysed by inductively coupled plasma optical emission spectrometry (Leeman Prodigy, USA). The average crystal size was determined using laser diffraction (Mastersizer 2000, Malvern Instrument, UK). The average values and standard deviations of three replicate samples were calculated and shown in this study.

3. Results and discussion

3.1. Fate of P during the storage and struvite process

The pH of pure urine solutions increased from 6.7 to 9.3 after the storage process. The final pH values for the dilution ratios of 25/75, 50/50 and 75/25 urine solutions were approximately 9.2, 9.1 and 9.0, respectively. Table 2 shows that the P concentration in hydrolysed urine solutions sharply decreased and the P loss percentage increased from 43% to 76% with increasing dilution ratios from 0/100 to 75/25. This result indicated that a higher dilution ratio would consume more P in urine because of additional Ca and Mg provided by tap water, thereby resulting in a higher P loss percentage. However, our previous experiments showed that P loss percentages for the dilution ratios of 0/100, 50/50 and 25/75 urine solutions with the addition of distilled water are 49%, 50% and 53%, respectively (Liu et al., 2014). These results suggested that dilution with distilled water has little effect on P loss percentage, whereas dilution with tap water will further increase the P loss percentage of urine because of the presence of Ca and Mg from tap water. Thus, the amounts of P loss in diluted urine are mainly correlated with the amounts of Ca and Mg in fresh urine and tap water.

The remaining P concentration significantly decreased because of struvite formation under the Mg/P molar ratio of 1.3 (Table 3). The P removal efficiencies exhibited a decreasing trend as the dilution ratio increased from 0/100 to 75/25, and ranged from 88% to 32%. The P removal efficiencies were 88%, 85% and 67% for the dilution ratios of 0/100, 25/75 and 50/50 urine solutions, respectively, but reached an extremely low value (32%) for the dilution ratio of 75/25 urine solutions. The allocation of P in urine solutions with different dilution ratios is shown in Fig. 1a, which presents the percentage of P loss, P removal and remaining P concentration in solutions. The removed P by struvite formation accounted for 8–51% of the total P in the different dilution ratios of fresh urine.

Table 1
Characteristics of fresh urine (mg L^{-1}) (n = 3).

Parameters	pH	PO_4^{3-}	NH_4^+	Na	Ca	Mg	K
Mean ± Std	7	327 ± 2	259 ± 32	2570 ± 93	253 ± 31	145 ± 23	867 ± 43