Effect of magnesium dose on amount of pharmaceuticals in struvite recovered from urine

Patiya Kemacheevakul, Surawut Chuangchote, Sosuke Otani, Tomonari Matsuda and Yoshihisa Shimizu

ABSTRACT

Phosphorus (P) recovery was carried out through struvite precipitation from urines. Human urine, however, contains not only high nutrients for plants, such as P and nitrogen, but also pharmaceuticals and hormones. In this work, effects of magnesium (Mg) dose (in terms of Mg:P ratio) on P recovery efficiency and pharmaceutical amounts contained in struvite were investigated. Batch-scale experiments of synthetic and human urines revealed that struvite precipitation formed more *X*-shaped crystals with an increased molar ratio of Mg:P, while the amount of pharmaceuticals (tetracycline, demeclocycline, and oxytetracycline) in struvite decreased with an increased molar ratio of Mg:P. The lowest pharmaceutical amounts in struvite were found at the Mg:P ratio of 2:1 from both samples. Moreover, the maximum P recovery efficiency, quantity and purity of struvite were found in the range of 1.21 to 2:1. It indicated that the molar ratio of Mg:P has a significant impact on struvite precipitation in terms of pharmaceutical amounts in struvite; morphology, quantity and purity of struvite; and P recovery.

Key words | magnesium molar ratio, pharmaceutical, phosphorus recovery, struvite, urine

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INTRODUCTION

Phosphate rock is an important source of phosphorus (P), one of the main nutrients for agriculture. Phosphate rock, however, is a non-renewable resource, just as oil is (Cordell *et al.* 2009). The nature of a non-renewable resource means that, eventually, it will reach a peak and then decrease annually, resulting in a wide gap between supply and demand (Hubbert 1949). Fortunately, P has the ability to be recycled by recovery from municipal and other waste sources, and can still be applied to agriculture or soil applications (Münch & Barr 2001). Human urine is a good waste source for the recovery of agricultural nutrients, especially P and nitrogen (N). The main proportion of the major agricultural nutrients in municipal wastewater originates from urine, approximately 50–90% (Maurer *et al.* 2003). Some researchers reported on the recovery of nutrients from human urine (Gethke *et al.* 2006; Wilsenach *et al.* 2007; Etter *et al.* 2011). However, not many actual implementations have been reported in the literature.

Struvite precipitation is one of the sustainable methods for P recovery from human urine. Struvite consists of magnesium–ammonium–phosphate hexahydrate ($MgNH_4PO_4{\cdot}6H_2O$), which is a white crystalline powder. Consequently, it has a potential use as a slow-release fertilizer in agriculture (Parsons *et al.* 2001). The precipitation of struvite can occur when the concentrations of phosphate (PO_4^{3-}), magnesium (Mg^{2+}), and ammonium (NH_4^+) ions are more than the soluble product (expressed as solubility product constant, Doyle & Parsons 2002). However, struvite precipitation is limited by pH, temperature, concentrations of Mg^{2+}, NH_4^+, PO_4^{3-}, and other ions such as calcium (Ca), and mixing energy (Bouropoulos & Koutsoukos 2000; Le Corre *et al.* 2005). Moreover, in a previous work (Kemacheevakul *et al.* 2012, 2014), we found that struvite which was recovered from human urine contained some pharmaceuticals, especially, tetracycline (TC) (note that TC is used to represent the tetracycline pharmaceutical, while 'TCs' refers to a group of pharmaceutical antibiotics). TC antibiotics, such as TC, demeclocycline (DMC), and oxytetracycline (OTC), are medicines broadly used against microbial infections (Novák-Pékli *et al.* 1996). TCs have a

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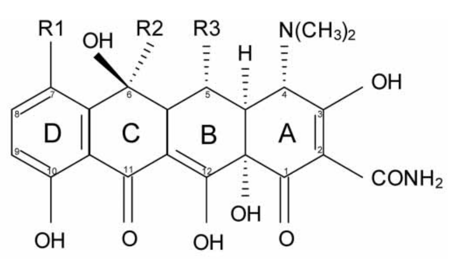
unique structure as illustrated in Figure 1, and can undergo chelation with metallic cations (Jezowska-Bojczuk *et al.* 1993). Mg is one of the three important ingredients for struvite precipitation. A number of researchers have investigated the optimum Mg dose for struvite precipitation in human urine. Recently, Ronteltap *et al.* (2010) reported that struvite precipitation from human urine in a continuously stirred tank reactor made it possible to remove dissolved phosphate by more than 98% with Mg:P around 1.33:1. Etter *et al.* (2011) also claimed that a molar ratio of Mg:P around 1.1:1 could recover P by over 90%. However, no research has been conducted on the effect of Mg dose on the amount of pharmaceuticals contained in struvite. Therefore, the purpose of this work is to gain a better understanding of the effect of Mg on P recovery efficiency and the amount of pharmaceuticals (i.e. TC, DMC, and OTC; see structures in Figure 1) in struvite together with the morphology and purity of struvite. Furthermore, the maximization of amounts of P recovered and the minimization of pharmaceuticals in struvite are the aims of this work.

MATERIALS AND METHODS

Sample preparation

The batch experiments consisted of two types of urine (i.e. synthetic and human) to determine the effect of Mg dose on P recovery efficiency and the amounts of TCs that remain in precipitates obtained from the urines. The synthetic urines were used to control the composition of urine for comparable parameters in the samples, while human urines were used for confirmation of the results. The precipitates are normally struvite crystals and other compounds



Tetracycline (TC): R1=R3=H, R2=CH_3
Demeclocycline (DMC): R1=Cl, R2=R3=H
Oxytetracycline (OTC): R1=H, R2=CH_3, R3=OH

Figure 1 | Chemical structures of selected TC antibiotics.

(i.e. calcium phosphate), which are nutrients and metals in the form of insoluble minerals (Tilley *et al.* 2008). Struvite constitutes more than 90% of the formed precipitates. Therefore, in the rest of this report, the precipitates are referred to as struvite. Synthetic urines were prepared according to the composition reported by Harada *et al.* (2006). Human urines were collected using cleaned stainless steel barrels from 10 to 13 healthy males aged between 22 and 32 years in a 24-hour period. Pharmaceutical standards, TC (Wako Pure Chemical Industries, Osaka, Japan), OTC (Wako Pure Chemical Industries, Osaka, Japan) and DMC (LKT Laboratories, Inc., Minnesota, USA), were analytical and high purity grade (>95%). Each TC, OTC, or DMC standard was dissolved in methanol and stored in the dark at $-20\,^{\circ}C$. Synthetic and human urines were spiked with 7 μg/L TC, OTC, or DMC solution and mixed well (Kemacheevakul *et al.* 2012).

Mg dose experiments

Five different molar ratios of Mg:P, including 0.X:1 (initial Mg:P ratio in each urine, where $X = 5$ and 6 in the case of synthetic and human urines, respectively, without addition of extra Mg), 1:1, 1.2:1, 1.5:1, and 2:1, were investigated. It should be noted that the composition of synthetic human urine was the composition from Harada *et al.* (2006) (Mg:P = 0.5:1), while the Mg:P ratio of actual human urine could not be controlled. Therefore, the initial Mg:P ratios were relatively different. Synthetic and human urines (500 mL) were decanted into 1 L glass beakers for each Mg molar ratio experiment at room temperature ($20 \pm 1\,^{\circ}C$). The Mg source, magnesium chloride powder ($MgCl_2.6H_2O$), was added into each beaker following the five different Mg:P ratios. The amounts of Mg added to synthetic urines for each Mg:P ratio were directly calculated by using the chemical composition of synthetic urine, while the added amounts of Mg in human urines were calculated by using the results for the analysis of common parameters which is explained in the 'Analytical methods' section. It was reported that a suitable pH of urine for struvite precipitation was between 9.4 and 9.7 (Harada *et al.* 2006). Therefore, the pH of all samples in this work was adjusted to 9.6 ± 0.3 by using sodium hydroxide. The synthetic and human urines were mixed at a rapid speed of 300 rpm for 10 minutes, followed by a slow mixing at 50 rpm for 12 hours. After the mixing process, the supernatant and precipitates were separated by using glass fiber filters (GF/B, Whatman, UK) with 1 μm pore size. The supernatant and precipitates were analyzed for pharmaceutical contents and common parameters as explained later.

Crystal morphology

After struvite precipitation at different Mg:P ratios, the samples were filtered by GF/B (1 μm pore size) and dried in an oven at 105 °C for 1 hour. The morphology and structure of struvite from synthetic and human urines were characterized by using a scanning electron microscope (SEM, JEOL JSM-6500FE) operating at an acceleration voltage of 10 kV. Prior to SEM characterization, the prepared samples were mounted directly onto sample stubs and positioned in the electron beam.

Analytical methods

To analyze the pharmaceutical amounts, the supernatant and struvite samples were spiked with isotopically labeled compounds, which were TC-d_6 (Toronto Research Chemicals, Ontario, Canada) and carbamazepine-d_{10} (Cambridge Isotope Laboratories, Massachusetts, USA) for 7 μg/L and 50 μg/L, respectively. The struvite was dissolved by phosphoric acid whereas the supernatant's pH was adjusted in acid condition. Ethylenediaminetetraacetic acid (EDTA, 1 g/L) disodium salt was then added to all samples. Afterwards, the samples were filtered by using Phenex-NY 25 mm syringe filters with 0.2 μm pore size and were concentrated by using Strata-X cartridge (30 mg, 1 mL) solid phased extraction from Phenomenex (California, USA). It should be noted that prior to the use of the cartridge, the cartridge was pre-conditioned; that is, the cartridge was rinsed by 1 mL methanol, 1 mL 0.5 N HCl, followed by 1 mL MilliQ water. The samples (1 mL) were loaded through cartridges by gravity. The cartridges were then dried under vacuum and finally eluted with 1 mL methanol. The extracts obtained were evaporated under a gentle N stream at 37 °C and reconstituted to 150 μL in 30% acetonitrile in MilliQ water (Kemacheevakul *et al.* 2012). The final samples were analyzed by liquid chromatography–tandem mass spectrometry. Separation of the analytes was performed by a high-performance liquid chromatograph (HPLC, Waters Alliance 2695) interfaced with a Micromass Quattro Ultima Pt mass spectrometer (Waters Corp., Massachusetts, USA).

In the case of the common parameters, which include N (in the form of ammonia nitrogen, NH_4–N), P (in the form of orthophosphate, PO_4–P), Mg, calcium (Ca), K, and sodium (Na), struvite was dissolved by sulfuric acid before the analysis of common parameters while the separated supernatant samples were analyzed without any treatment. NH_4–N and PO_4–P concentrations were measured by using an auto-analyzer from Seal Analytical Ltd (Wisconsin, USA) whereas Mg, Ca, K, and Na concentrations were measured by a personal ion analyzer-1000 from Shimadzu (Kyoto, Japan). All concentrations were calculated in the unit of mg/L. All chemicals and reagents used were of analytical grade and obtained from Wako Pure Chemical Industries (Osaka, Japan).

RESULTS AND DISCUSSION

Effect of Mg dose on the morphology of struvite

Figure 2 reveals the SEM images of the dried samples from synthetic urine at different Mg:P ratios. The precipitates at the ratio of 0.5:1 (Figure 2(a)) were the agglomeration of needle-like crystals with small spherical forms which aggregated into irregularly shaped clusters similar to amorphous calcium phosphate (Lee & Kumta 2010; Dorozhkin 2010). Figure 2(b) (Mg:P = 1.0:1) shows that the morphology changed to a more X-like shape. The needle-like crystals could still be observed in the precipitates. At a higher molar ratio of Mg:P (1.2:1), Figure 2(c) demonstrates that the precipitates were mainly X-like crystals. Similarly, Figures 2(d) and 2(e) (Mg:P = 1.5:1 and 2.0:1, respectively) also reveal the same results, showing no significant difference in morphology from Figure 2(c) (X-like shape). The needle-like and X-like crystals are described as a typical form of struvite crystal (Wilsenach *et al.* 2007; Ronteltap *et al.* 2010). It was preliminarily concluded that the higher dose of Mg altered the formation of struvite crystals from needle-like to X-like shapes.

In the case of human urine, the precipitates at Mg:P ratio of 0.5:1 (Figure 3(a)) were tubular and trapezoidal crystals together with small clumps of organic matter and bacterial flocs, similar to a work reported by Clapham *et al.* (1990). The trapezoidal shape is also typical of another struvite crystal (Münch & Barr 2001). In the same tendency as synthetic urine at ratio 1:1, the precipitates changed the morphology to a more X-like shape as shown in Figure 3(b). The precipitates at ratio 1.2:1 were mainly X-like crystals; nevertheless, the size of these crystals (Figure 3(c)) was slightly smaller than the crystals in Figure 3(b). The X-like shaped crystals were also found in the precipitates at ratios 1.5:1 and 2.0:1 as shown in Figures 3(d) and 3(e), respectively. However, the comparison of size of crystals

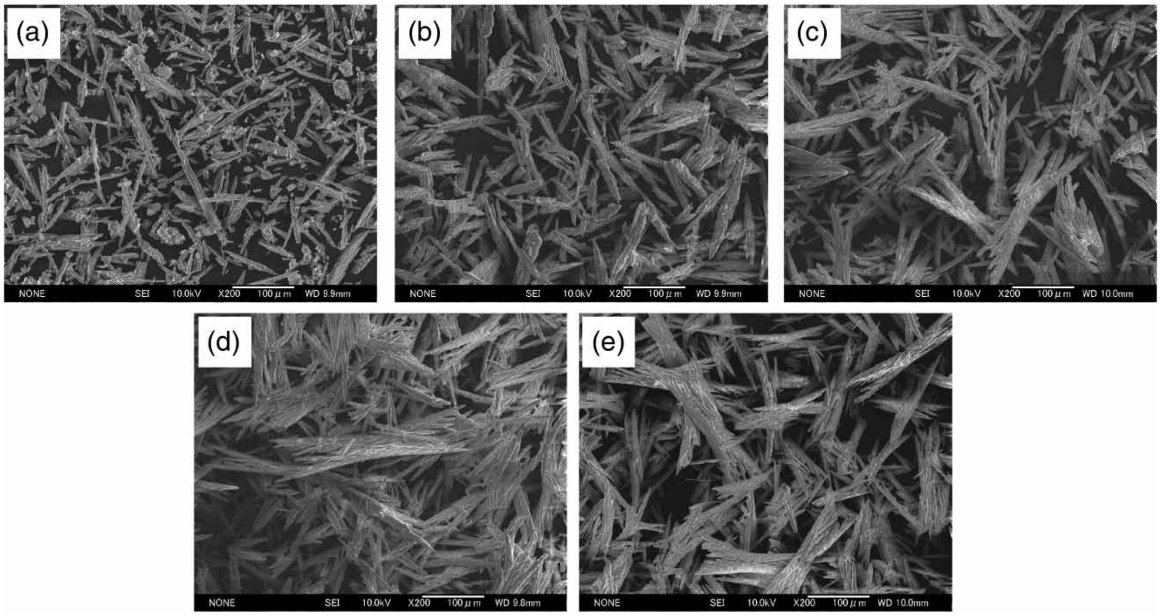


Figure 2 | SEM images (200×) of precipitates from struvite precipitation in synthetic urine at different Mg:P molar ratios: (a) 0.5:1; (b) 1.0:1; (c) 1.2:1; (d) 1.5:1; and (e) 2.0:1.

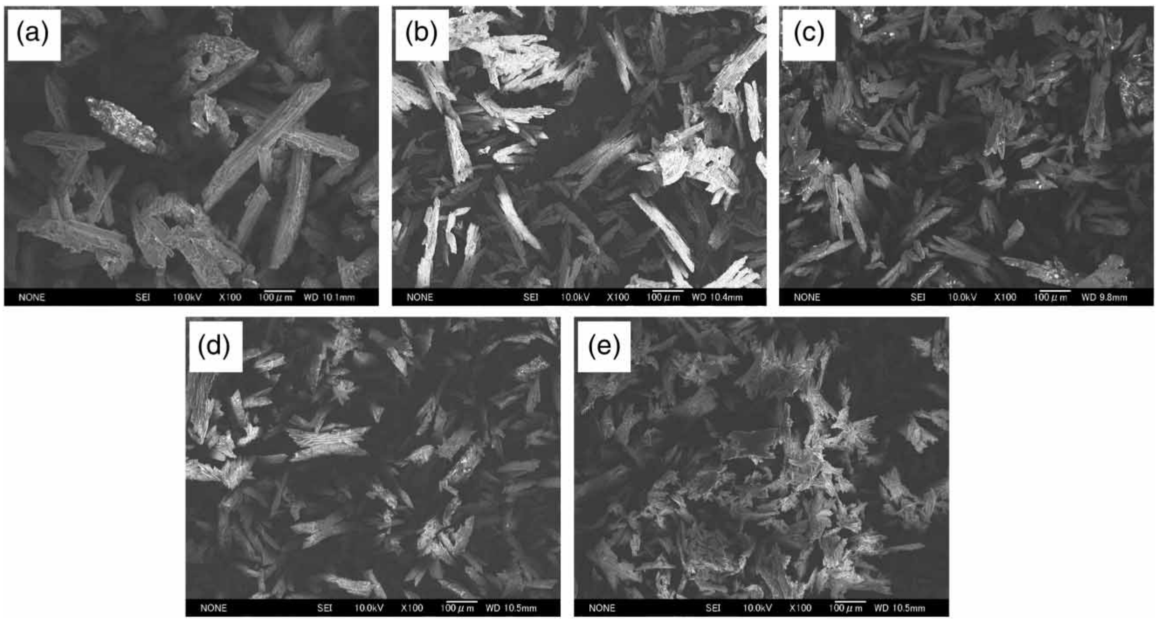


Figure 3 | SEM images (×100) of precipitates from struvite precipitation in human urine at different Mg:P molar ratios: (a) 0.6:1; (b) 1.0:1; (c) 1.2:1; (d) 1.5:1; and (e) 2.0:1.

in Figures 3(c)–3(e) shows that the length tends to decrease with an increase in Mg:P ratio whereas the width increases. Ronteltap *et al.* (2010) explained that higher supersaturation (e.g. weak mixing, high Mg:P ratios, and low temperature) leads to smaller particle sizes. This indicated that the Mg:P ratio had an effect on the morphology and size of struvite crystals recovered from urine.

Effect of Mg molar ratio on the amount of pharmaceuticals in struvite

The experiments of different Mg:P molar ratios in synthetic and human urines were carried out at a constant pH of 9.6 and at the same temperature. The results from this study are shown in Table 1. It should be noted that percent masses in

Table 1 | The percent masses of pharmaceuticals in the supernatant (filtrate) and the re-dissolved struvite crystals based on the initial spiked amounts at different Mg molar ratios

		TC (%)		DMC (%)		OTC (%)	
Mg:P		Synthetic urine	Human urine	Synthetic urine	Human urine	Synthetic urine	Human urine
0.X:1[a]	Supernatant	2.7	5.4	6.3	3.9	27.1	22.1
	Struvite	81.8	94.3	77.7	88.7	56.8	67.6
	Recovery	84.5	99.7	84.0	92.6	83.9	89.7
1.0:1	Supernatant	N.D.[b]	3.0	5.5	0.3	18.1	9.8
	Struvite	99.6	99.6	75.3	90.0	64.8	68.5
	Recovery	99.6	102.6	80.8	90.3	83.0	78.3
1.2:1	Supernatant	76.1	3.5	76.3	3.2	92.4	10.4
	Struvite	14.4	96.6	13.7	82.4	N.D.[b]	68.7
	Recovery	90.5	100.1	90.0	85.6	92.4	79.0
1.5:1	Supernatant	79.7	13.9	81.5	17.4	95.9	38.9
	Struvite	1.9	90.2	7.1	73.5	N.D.[b]	49.3
	Recovery	81.6	104.1	88.6	90.9	95.9	88.2
2.0:1	Supernatant	82.7	64.3	90.3	63.4	98.7	94.4
	Struvite	0.2	33.8	2.9	20.4	N.D.[b]	5.4
	Recovery	82.9	89.1	93.2	83.8	98.7	99.8

[a]$X = 5$ and 6 for synthetic and human urines, respectively.
[b]N.D.: non-detectable value.

Table 1 were calculated by comparing to the initial amount of pharmaceuticals that were spiked into the urines. For an example, in synthetic urine, from 100% TC spiked into urine, TC allocated in the struvite and supernatant was 81.8% and 2.7%, respectively, after precipitation. For synthetic urine, we found that TC and DMC at Mg:P of 0.5:1 were contained in the struvite in significant amounts, which were 81.8% and 77.7%, respectively, while OTC amounts contained in struvite were relatively lower than the other two compounds (56.8%). TCs have a high affinity for metallic multivalent cations, such as Mg^{2+} or Ca^{2+}, to form chelate complexes (Tongaree *et al.* 2000; Kishida 2011). Mg is one of the most important component for struvite precipitation; therefore, it is possible that TCs can form chelate complexes with Mg in struvite. The chelation can occur at the A ring (tricarbonyl) or the B–C–D ring (phenolic β-diketone) of TCs (Anderson *et al.* 2005) as shown in Figure 1. Tongaree *et al.* (1999) explained further that chelation interactions increased with increasing pH, which can explain the higher chance of chelation in our experiments, which were carried out at quite high pH (9.6). Moreover, the increasing of Mg:P ratio to 1:1 resulted in the highest pharmaceutical amounts in struvite except that the DMC was a bit lower than that of the Mg:P of 0.5:1, around 2.4%. This result is in accordance with the amount of precipitates increasing with an increasing Mg:P ratio (Table 2); hence, the pharmaceuticals had more opportunity to form or adsorb in struvite.

Table 2 | Amount of struvite recovered, P recovery efficiency, and percentage of P in struvite from synthetic and human urines at various Mg:P molar ratios

	Struvite (g)[a]		P recovery efficiency[b] (%)		P in struvite (% by mass)	
Mg:P molar ratio	Synthetic urine	Human urine	Synthetic urine	Human urine	Synthetic urine	Human urine
0.X:1[c]	0.99	0.56	51.4	27.5	22.7	22.8
1.0:1	1.66	1.72	89.8	69.9	25.3	18.8
1.2:1	1.79	2.05	95.5	86.2	23.2	19.4
1.5:1	1.84	2.19	94.3	87.7	22.7	18.5
2.0:1	1.80	2.19	94.8	88.5	23.1	18.7

[a]Weighted amounts of precipitate normalized by 1 L of urine sample.
[b]P recovery efficiency was calculated from P in struvite and compared with total PO_4–P, where total PO_4–P concentration was 440 mg/L and 462 mg/L in synthetic and human urine, respectively.
[c]$X = 5$ and 6 in for synthetic and human urines, respectively.

The amount of pharmaceuticals in struvite at Mg:P of 1.2:1 dropped to 14.4%, 13.7%, and a non-detectable value for TC, DMC, and OTC, respectively. The reason for this observation is that the remaining amount of Mg in the supernatant after struvite precipitation was a relatively high amount at a higher molar ratio of Mg:P, which led pharmaceuticals to remain in the supernatant instead of struvite. As described above, TCs can form chelate complexes with Mg^{2+} in urines. When the amount of Mg^{2+} increases while the amount of PO_4^{3-} and NH_4^+ are constant, the probability that the TCs–Mg chelates will incorporate in the precipitates will decrease. Therefore, the pharmaceutical amounts in struvite gradually decreased with an increasing Mg:P ratio to 1.5:1 and 2:1. The lowest amounts of TC, DMC, and OTC in struvite were 0.2%, 2.9%, and a non-detectable value, respectively. A similar trend with synthetic urine was observed in the case of human urine. The results of human urine in Table 1 show that TC and DMC were the highest amounts at Mg:P of 1:1, whereas OTC was the highest amount at Mg:P of 1.2:1, which was higher than that of 1:1, but only by 0.2 percentage point. The pharmaceutical amounts in struvite slowly decreased when the ratio of Mg:P was increased to 1.5:1. At the molar ratio of Mg:P of 2:1, TC, DMC, and OTC amounts dropped to 33.8%, 20.4%, and 5.4%, respectively. This revealed that the molar ratio of Mg:P has a direct influence on the amount of pharmaceuticals in struvite.

Figure 4 shows the percentage of pharmaceutical amounts in precipitates (struvite), at different Mg:P molar ratios, from synthetic and human urines. Although, the amount of pharmaceuticals in struvite from both urines seemed to be the highest at Mg:P of around 1:1, the percentages of pharmaceutical amounts in struvite (w/w) tended to decrease with an increasing Mg:P ratio as shown in Figure 4. The percentages of pharmaceutical amounts in struvite decreased because the amounts of struvite increased at a higher molar ratio. Among the three selected pharmaceuticals, OTC contained in struvite was lower in quantity than the other two compounds because OTC may have less-suitable sites for chelation with metallic cations than have TC and DMC. All results in Table 1 and Figure 4 indicate that the molar ratio of Mg:P 2:1 is the optimum for struvite precipitation because of the low pharmaceutical amounts contained in struvite from both synthetic and human urines. The use of a higher ratio of Mg:P is not recommended because the amount of pharmaceuticals in struvite recovered will be not much different, but material cost for Mg will be higher.

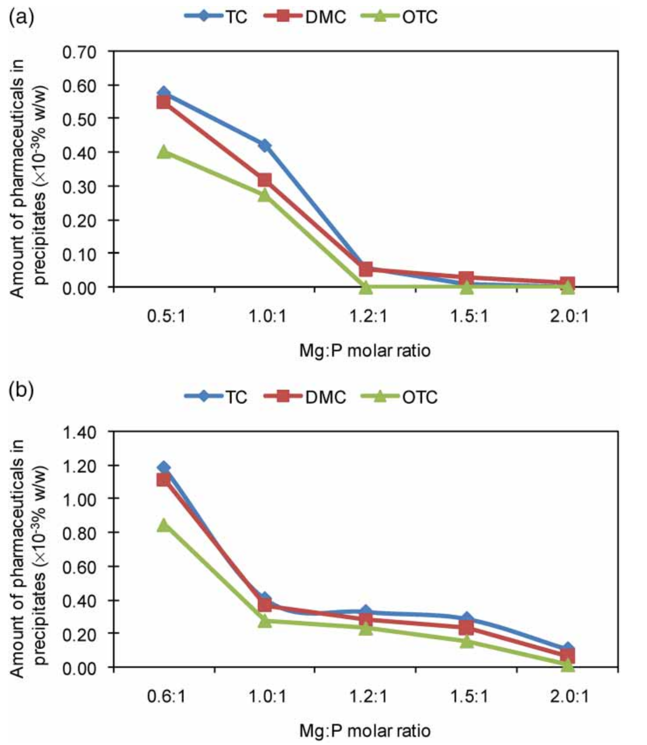


Figure 4 | The percentage of pharmaceutical amounts (TC, DMC, and OTC) in precipitates (struvite) at different Mg:P molar ratios from (a) synthetic and (b) human urines.

Presence of impurities in precipitated struvite

Other ions in urine which are not the ions for the formation of struvite (NH_4^+, Mg^{2+}, and PO_4^{3-}) are called 'impurity ions', and they also have a significant impact on struvite precipitation (Le Corre *et al.* 2005). In this research, we focus on Ca, potassium (K), and sodium (Na) as the selected impurity ions. To study the effect of Mg dose on the amount of impurity ions in struvite, the experiments were carried out at different molar ratios of Mg:P. The results in Table 3 demonstrate that the highest amount of Ca was contained in struvite at the initial Mg:P ratios (0.5:1 or 0.6:1), which were 2.55% and 14.65% (of the weight of the precipitated struvite) from synthetic and human urines, respectively. The difference of Ca in struvite from synthetic and human urines at the initial Mg:P ratios is because the initial concentrations of synthetic and actual urine were different. Ca in the synthetic urines is, again, from the reference (Harada *et al.* 2006), whereas Ca in the actual urines depends on many factors, especially the food that the human consumed. This high amount of Ca in struvite at the initial Mg:P ratio resulted in the different morphology of precipitates (Figures 2(a) and 3(a)) compared with those from other conditions as discussed in the section 'Effect

Table 3 | Percentage of calcium, sodium, and potassium in precipitates from synthetic urine and human urine

	Ca (% by mass)		Na (% by mass)		K (% by mass)	
Mg:P molar ratio	Synthetic urine	Human urine	Synthetic urine	Human urine	Synthetic urine	Human urine
0.X:1[a]	2.55	14.65	N.D.[b]	0.92	2.13	1.85
1.0:1	N.D.[b]	4.26	N.D.[b]	0.34	2.33	2.68
1.2:1	N.D.[b]	2.42	0.13	0.33	2.71	2.61
1.5:1	N.D.[b]	0.46	0.12	0.23	2.64	2.64
2.0:1	N.D.[b]	N.D.[b]	0.12	0.33	2.83	2.94

[a]$X = 5$ and 6 for synthetic and human urines, respectively.
[b]N.D.: non-detected value.

of Mg dose on the morphology of struvite'. At higher molar ratios' of Mg:P from 1.0:1 to 2.0:1, the results show that Ca amounts in struvite from synthetic urine could not be detected, while those from human urine gradually decreased with an increasing Mg:P ratio and could not be detected at the ratio of 2.0:1. According to the initial Mg:P ratio, which was the ratio without addition of extra Mg, the molar ratio of Ca: Mg in urine was the highest when compared with the other higher Mg:P ratios. Therefore, the higher Ca:Mg ratio leads to the formation of the Ca precipitates rather than struvite. Le Corre *et al.* (2005) explained that increasing the Ca concentration can reduce the size of struvite crystals. Moreover, some impurities can be easily adsorbed on the surface of the crystals, and then retard the rate of struvite precipitation (Kabdaşli *et al.* 2006; Kim *et al.* 2009). In the case of Na, only small amounts were contained in struvite from synthetic and human urines (<1%). Similar to Na, less than 3% K was found in struvite from both samples. It indicated that Na and K have no significant impact on struvite crystallization as long as their concentrations are not significantly higher than those typically observed in urine.

From the results in Table 3, we could roughly calculate the purity of struvite by subtracting the amounts of selected impurities from the total mass. The purity of struvite increased with increasing Mg:P ratio, from 95% to around 97% and from 83% to 97% in the case of synthetic and human urines, respectively. The increasing of the Mg:P ratio also increased the Mg:Ca ratio. Battistoni *et al.* (2000) and Wang *et al.* (2005) suggested that efficiency of struvite precipitation can be achieved with increasing Mg: Ca ratios, which confirmed our experiments. We can conclude that the higher the Mg:P ratio, the better the quality of struvite. The highest purity of struvite recovered from urine was around 97%, where the ratios of Mg:P are in the range of 1:1–2:1 and 1.5:1–2:1 for synthetic and human urines, respectively.

Amount of struvite recovered and P recovery efficiency

Table 2 shows amount of struvite recovered, P recovery efficiency, and percentage of P in struvite from synthetic and human urines at various Mg:P molar ratios. At the initial molar ratio of Mg:P (0.5:1 and 0.6:1 for synthetic and human urines, respectively), it appears that small amounts of struvite can precipitate, which were 0.996 g and 0.56 g from synthetic and human urines, respectively. This is because of the low Mg: P ratio, which is not enough Mg for struvite precipitation. Lee *et al.* (2003) mentioned that the ideal molar ratio of Mg:P:N for struvite precipitation is 1:1:1. With the increase of Mg:P ratio to 1.0:1, we found that more struvite could precipitate (1.66 g and 1.72 g from synthetic and human urines, respectively). At molar ratios of Mg:P of 1.2:1 and above, the results reveal that the amounts of struvite are almost the same. The maximum weight from synthetic urine was 1.84 g at the ratio of Mg:P of 1.5:1, whereas the maximum weight from human urine was 2.19 g at the ratios of Mg:P of 1.5:1 and 2:1.

Struvite precipitation is a very efficient method of P recovery from urine (Wilsenach *et al.* 2007). In our experiments, the amount of P recovered from urines was determined by PO_4–P concentrations. It was found that PO_4–P concentrations in re-dissolved struvite from synthetic and human urines rapidly increased with the increase of the Mg:P ratio from the initial ratio to 1:1 as shown in Figure 5. At the higher Mg:P ratios (1:1–2:1), it was found that the concentration of PO_4–P in re-dissolved struvite from synthetic urine was quite constant; conversely, the concentration of PO_4–P in re-dissolved struvite from human urine gradually increased and was then constant at Mg:P ratios of 1.5:1–2:1. At molar ratios of Mg:P of 1.2:1–2:1, the maximum P recovery efficiency was observed, which was in the ranges of 94.3%–95.5% and 86.2%–88.5% from synthetic and human urines, respectively (Table 2). The P recovery efficiency from synthetic urine was slightly higher than that from human urine.

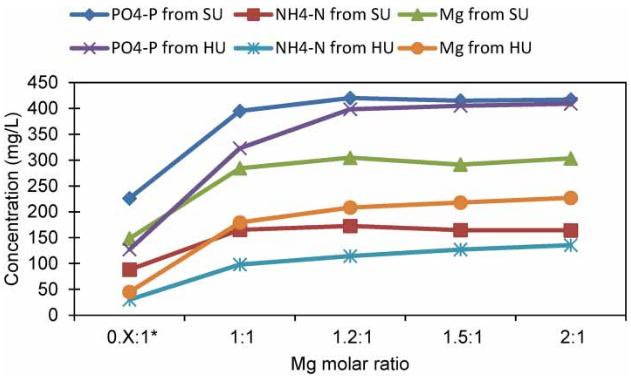


Figure 5 | The concentration of PO_4–P, NH_4–N, and Mg in struvite from synthetic and human urines (SU and HU, respectively) at different Mg:P molar ratios (*$X = 5$ and 6 for synthetic and human urines, respectively).

This is because human urine contains organic matter and other impurities, which retard the growth rate of struvite precipitation (Le Corre *et al.* 2005; Kabdaşli *et al.* 2006).

Table 2 also shows the amounts of P in struvite at various Mg:P ratios in term of percentage by mass, which indicates that the highest percentage of P was at the molar ratios of Mg:P of 1.0:1 and 0.6:1 for synthetic and human urines, respectively. However, struvite contained high pharmaceutical amounts at these molar ratios and could precipitate with only small amounts as discussed previously (Table 2). Moreover, struvite was obtained with low purity at the molar ratio of Mg:P of 0.6:1. Therefore, the molar ratios of Mg:P of 1.0:1 and 0.6:1 for synthetic and human urines, respectively, were not suitable ratios for struvite precipitation. In contrast, the Mg:P molar ratios from 1.2:1 to 2:1 were the optimum conditions for struvite precipitation in terms of P recovery efficiency, purity, and amount of struvite. However, if the amount of pharmaceuticals in struvite is also considered, the molar ratio of Mg:P of 2:1 is a suitable ratio for all factors.

Struvite precipitation recovers not only P, but also Mg and N. The concentrations of Mg and NH_4-N in re-dissolved struvite exhibit similar trends to PO_4–P concentrations as shown in Figure 5. It was found that the molar ratios of N:P were 1.6:1 and 1.5:1 in synthetic and human urines, respectively, which were higher than the ideal molar ratio for struvite precipitation, 1:1 (Lee *et al.* 2003). Therefore, the concentration of NH_4–N in synthetic and human urine was enough for struvite precipitation.

CONCLUSIONS

In the present work, the effect of Mg dose on the amount of pharmaceuticals and P recovery efficiency in struvite recovered from urine has been investigated. Various molar ratios of Mg:P were applied in the precipitation of struvite from synthetic and human urines. It has been shown that the molar ratio of Mg:P has a significant impact on struvite precipitation in term of pharmaceutical amounts in struvite, morphology, P recovery efficiency, quantity and purity of struvite. The pharmaceutical amounts in struvite decreased with the increase of the Mg:P ratio because, when the amount of Mg^{2+} increases while the amount of PO_4^{3-} and NH_4^+ are constant, the probability that the TCs–Mg chelates will incorporate in the precipitates will decrease. The lowest amount of pharmaceuticals (TC, DMC, and OTC) in struvite was found at the Mg:P ratio of 2:1 from both samples. The maximum P recovery efficiency, quantity and purity of struvite were found at the Mg:P ratios in the range of 1.2:1–2:1. The results indicated that the optimum Mg:P ratio for struvite precipitation was 2:1, where low pharmaceuticals contained in struvite, high P recovery efficiency (>94% and 88% in case of synthetic and human urines, respectively), and high struvite purity of around 97% for both synthetic and human urines were obtained. The results from both synthetic and human urines showed strongly similar trends. It can be concluded that other compounds in actual human urine did not have significant effects on the struvite precipitation and TCs removal.

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