

Ammonium removal from wastewater via struvite pyrolysate recycling with Mg(OH)₂ addition

Rongtai Yu, Subin Cheng, Hongqiang Ren, Yanru Wang, Lili Ding, Jinju Geng, Ke Xu and Yan Zhang

ABSTRACT

Magnesium ammonium phosphate (MAP) pyrolysate recycling technology was investigated with Mg(OH)₂-mediated pyrolysis. The results revealed that the removal ratio of ammonium was stable at about 75%, and could be increased to 79% after additional acidolysis. The phosphate concentration in the supernate was low at 2 mg/L. The optimum conditions for ammonia release were a 1:1 molar ratio of Mg(OH)₂:NH₄⁺, a heating temperature of 110 °C and a heating time of 3 h. With continual additions of Mg(OH)₂ to release ammonia, magnesium phosphate (Mg₃(PO₄)₂) was suggested as a possible derivative. However, with Mg(OH)₂-mediated pyrolysis, the growth and nucleation of MAP was inhibited during MAP pyrolysate recycling.

Key words | ammonium, Mg(OH)₂, residual phosphate, struvite pyrolysate recycling, wastewater

Rongtai Yu
Hongqiang Ren (corresponding author)
Yanru Wang
Lili Ding
Jinju Geng
Ke Xu
Yan Zhang

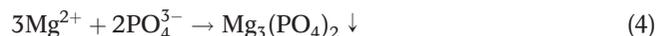
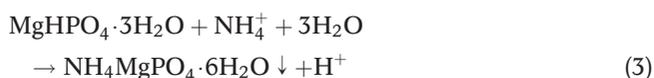
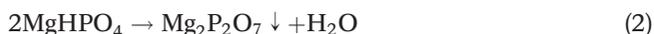
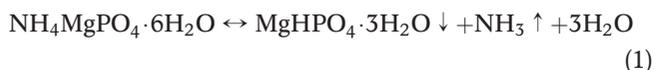
State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing 210023, Jiangsu, China
E-mail: hqren@nju.edu.cn

Subin Cheng
College of Civil Engineering, Tongji University 200092, Shanghai, China

Rongtai Yu
Jingdezhen Ceramic Institute, Jingdezhen 333001, Jiangxi, China

INTRODUCTION

Ammonium ion is a commonly found nitrogen species, and removing it from wastewater, especially industrial sewage, has become increasingly important (Yang *et al.* 2004). For the recycle of nitrogen and phosphate, struvite chemical precipitation has been widely investigated (Sugiyama & Yokoyama 2005; Zhang *et al.* 2009). The high costs of magnesium and phosphate reagents are the principal reasons for the lack of practical application of magnesium ammonium phosphate (MAP) chemical precipitation, and residual phosphate is a real problem. The recycle of MAP pyrolysate as magnesium and phosphate salts was studied to reduce the reagent consumption (He *et al.* 2007; Türker & Çelen 2007). The reaction equation of MAP pyrolysis and MAP pyrolysate recycling can be written as follows.



Recently, in order to increase the ammonia release rate, a NaOH solution was added during MAP pyrolysis. Zhang *et al.* (2009) found that the ammonia release ratio was more than 90%, whereas He *et al.* (2007) reported that the ammonia release ratio reached more than 97% with NaOH-mediated pyrolysis. However, the concentration of phosphate in the supernate was very high (above 100 mg/L), and it is not offered as an effective solution in the literature. Another economic obstacle to removal of ammonium out of wastewater by MAP precipitation is the decrease in the ammonium removal ratio with the increase of the number of recycles. The ammonium removal ratio was reported to be 84% in the first recycle versus 62% in the sixth recycle by He *et al.* (2007), while Türker & Çelen (2007) reported a similar decline, from an initial 92% with progressive decrease to 77% in the fifth stage.

Presently, the components of the amorphous MAP pyrolysate have only been theoretically predicted, rather than verified by experiment, especially the presence of magnesium

hydrogen phosphate (MgHPO_4) and pyrophosphate ($\text{Mg}_2\text{P}_2\text{O}_7$). Sugiyama & Yokoyama (2005) reported that MgHPO_4 could not have generated magnesium phosphate ($\text{Mg}_3(\text{PO}_4)_2$) during MAP pyrolysis; $\text{Mg}_3(\text{PO}_4)_2$ is thought to be one of the products resulting from continual addition of magnesium hydroxide ($\text{Mg}(\text{OH})_2$) for the removal/recovery recycling system for ammonium.

Addition of seed crystals can increase the rate of MAP crystallization and significantly shorten the reaction crystallization time. In other studies, suitable methods to measure the crystallization rate were not used, and only the ammonium removal rate was used as a measure of the crystallization rate of MAP (Kim et al. 2006, 2007; Zhang et al. 2009; Liu et al. 2011); so the MAP crystallization rate as a result of seeding cannot be quantified.

In this investigation, the effects of a new mediated $\text{Mg}(\text{OH})_2$ reagent were studied, and MAP pyrolysate and its derivatives were experimentally characterized. MAP grain sizes from seed-crystal-inoculated reactions were calculated using the Scherrer equation, and particle sizes were assessed using a nano-particle analyzer. The inclusion of an acidolysis step to release magnesium and phosphate ions from $\text{Mg}_3(\text{PO}_4)_2$ and/or $\text{Mg}_2\text{P}_2\text{O}_7$ was studied also during MAP pyrolysate recycling.

MATERIALS AND METHODS

Composition of raw wastewater

Raw wastewater was collected from a fertilizer plant located near Nanjing, and stored in a 25 L container at 4 °C until required. The ammonium concentration in the raw wastewater was $1,197 \pm 20$ (mg/L), chemical oxygen demand was 560 ± 10 (mg/L) and pH was 7.86 ± 0.1 ; no phosphate was detected.

Formation of MAP

MAP crystalloid was formed as follows. Ammonium chloride (NH_4Cl) and disodium hydrogen phosphate ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$) of analytical purity were dissolved in deionized water (1,000 mL), and magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) was added to the solution to obtain a 1:1:1 $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ molar ratio. The reaction solution was magnetically stirred for 30 min at pH 9.5, and then allowed to settle for 30 min. The reaction mixture was then filtered through a 0.45 μm membrane filter and washed three times with deionized water to remove sodium chloride.

The precipitate was collected and dried in an oven at 40 °C for 48 h.

MAP pyrolysis experiments with $\text{Mg}(\text{OH})_2$ addition

MAP pyrolysis experiments were performed with $\text{Mg}(\text{OH})_2$ addition as follows. The MAP precipitate was mixed with $\text{Mg}(\text{OH})_2$ powder, ground for 10 min, and heated in an oven at temperatures from 70 to 190 °C for 1 to 5 h, using $\text{Mg}(\text{OH})_2:\text{NH}_4^+$ molar ratios of 0.5:1–3:1. In this manner, the effects of temperature, time, and $\text{Mg}(\text{OH})_2:\text{NH}_4^+$ molar ratio on ammonia release were studied.

The MAP pyrolysate was dissolved in sulfuric acid solution, and pH was adjusted to 6.5–7.5 with 2.5 N NaOH to determine the residual ammonium concentration according to standard methods. The formula for the ammonia release ratio (X), as a percentage, was as follows.

$$X\% = \frac{(\text{NH}_{4\text{tot}} - \text{NH}_{4\text{residual}})}{\text{NH}_{4\text{tot}}} \times 100 \quad (5)$$

MAP pyrolysate loading and stirring time experiments

(1) MAP was pyrolysed by heating in an oven at 110 °C for 3 h. (2) Loading experiments. MAP pyrolysate was added to simulated wastewater (NH_4^+ , 500 mg/L) at $\text{Mg}^{2+}:\text{NH}_4^+$ molar ratios of 0.8:1–1.3:1, where Mg^{2+} concentrations were calculated on the basis of MgHPO_4 as the major constituent. The reaction solution was mechanically stirred for 60 min at pH 9.5, then allowed to settle for 60 min. (3) Stirring time experiments. MAP pyrolysate was added to simulated wastewater (NH_4^+ , 500 mg/L) at a 1:1 $\text{Mg}^{2+}:\text{NH}_4^+$ molar ratio at pH 9.5. The reaction solution was magnetically stirred from 30 to 90 min, and then allowed to settle for 60 min. (4) Sulfuric acid (H_2SO_4) was added to adjust pH to 6.5–7.5 to determine the concentrations of ammonium and phosphate ions in the supernate.

MAP pyrolysate recycling experiments

(1) Formation of MAP. $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ were added to the fertilizer wastewater (500 mL) with magnetic stirring for 30 min at pH 9.5; the mixture was allowed to settle for 30 min. The precipitate was filtered through a 0.45 μm membrane filter and washed three times with deionized water to remove organic compounds co-precipitated from the wastewater, and then dried in an oven at 40 °C for 48 h. (2) MAP pyrolysis.

Mg(OH)₂ powder was added to MAP, with a 1:1 Mg(OH)₂:NH₄⁺ molar ratio, ground for 10 min, and heated in an oven at 110 °C for 3 h. (3) Recycling the pyrolysate as magnesium and phosphate salts. The MAP pyrolysate was added to the fertilizer wastewater (500 mL), the mixed solution was agitated by a six-in-one electromotive stirrer for 90 min at pH 9.5, and allowed to settle for 60 min. The collected MAP precipitate was recycled, and step (2) and (3) were repeated. (4) Acidolysis. The MAP pyrolysate from steps (2) was added to the H₂SO₄ solution to acidolysis by heating at 120 °C for 2 h at an optimum pH of 1 (Zhang *et al.* 2004). The hydrolysate was dumped back into the fertilizer wastewater (500 mL), and step (2) and (3) were repeated. The process – pyrolysis, precipitation, and acidolysis – was repeated twice.

After the recycling experiments, H₂SO₄ was added to adjust the pH to 6.5–7.5 to determine the concentrations of ammonium, magnesium and phosphate ions in the supernate.

Seed crystal experiments

Seeding crystal experiments were performed concomitantly with MAP pyrolysate recycling experiments. Pre-formed MAP, as a seeding material, was added to wastewater in advance. The reaction conditions for the seed crystal experiments were the same as those of the MAP pyrolysate recycling experiments.

Analytical methods

The concentrations of ammonium, magnesium and phosphate ions were measured according to the standard methods (APHA 1998). The characterizations of MAP precipitate and pyrolysate were performed by X-ray diffraction (XRD, D8 Advance Bruker), Fourier transform infrared spectroscopy (FTIR, Nicolet 5700 Thermo Electron Corp) and nano-particle size analysis (Mastersizer 2000, Malvern).

RESULTS

MAP pyrolysis in the presence of Mg(OH)₂

Figure 1 (A) and (B) describes the effects of Mg(OH)₂:NH₄⁺ molar ratio, heating temperature and reaction time on ammonia release. Dry pyrolysis was used in this study. MAP precipitate was mixed with Mg(OH)₂ powder under specified experimental conditions (Mg(OH)₂:NH₄⁺ molar

ratios 0.5:1–3:1; heating temperatures from 70 to 190 °C; and reaction time of 1–5 h). The results showed that, at 100 °C, the ammonia release ratio exceeded 91% at a 1:1 Mg(OH)₂:NH₄⁺ molar ratio, which increased slowly with temperature increase, the same as the Mg(OH)₂:NH₄⁺ molar ratio and reaction time. When the Mg(OH)₂:NH₄⁺ molar ratio was from 1:1 to 2:1, the ammonia release ratio was from 91 to 93% at 100 °C, and from 89 to 92% at heating time from 2 to 5 h at a 1:1 Mg(OH)₂:NH₄⁺ molar ratio. From an economic perspective, the optimum molar ratio of Mg(OH)₂ to NH₄⁺ was 1:1, temperature was 110 °C and reaction time was 3 h.

MAP can be decomposed by acid dipping or direct heating at 300 °C (Yang *et al.* 2004; Zhang *et al.* 2004), as well as by addition of alkali to release ammonia. Related literature described the addition of NaOH during MAP pyrolysis (Türker & Çelen 2007; Zhang *et al.* 2009). At 110 °C for 3 h, the ammonia release ratio was more than 90% at a 2:1 NaOH:NH₄⁺ molar ratio (Zhang *et al.* 2009); at 100 °C for 4 h, the ammonia release efficiency reached a level of >97% at a 1:1 NaOH:NH₄⁺ ratio (He *et al.* 2007). It was reported that dittmarite (NH₄MgPO₄·H₂O) was formed with excess water during MAP pyrolysis (Lonsdale & Sutor 1966; Sutor 1968; Boistelle *et al.* 1983). At the same time, during MAP pyrolysate recycling, the phosphate concentration in the supernate is very high under NaOH-mediated pyrolysis conditions. These problems can be solved by adding Mg(OH)₂ powder in the pyrolysis step to form Mg₃(PO₄)₂ during recycling runs.

MAP pyrolysate loading and stirring time experiments

These experiments probed the effects of MAP pyrolysate loading and stirring time on ammonium removal; the results are shown in Figure 2. When the molar ratio of Mg²⁺:NH₄⁺ (Figure 2(A)) was changed from 0.8:1 to 1.3:1, the ammonium removal rate was increased, from 76.96 to 87.78%. The phosphate concentration in the supernate was also increased. The ammonium removal rate was 82.56% at a 1:1 Mg²⁺:NH₄⁺ molar ratio. From the perspectives of the phosphate concentration in the supernate and cost-effectiveness, the optimal MAP pyrolysate dosage used in this study was Mg²⁺:NH₄⁺ molar ratio of 1:1.

The parameter of Mg²⁺:NH₄⁺:PO₄³⁻ molar ratio was very important for MAP precipitation. However, the concentration of Mg²⁺ and PO₄³⁻ in the MAP pyrolysate was difficult to determine because not only MgHPO₄ was found but also Mg₂P₂O₇ and even Mg₃(PO₄)₂ were formed. Huang *et al.* (2011) reported that the MAP pyrolysate

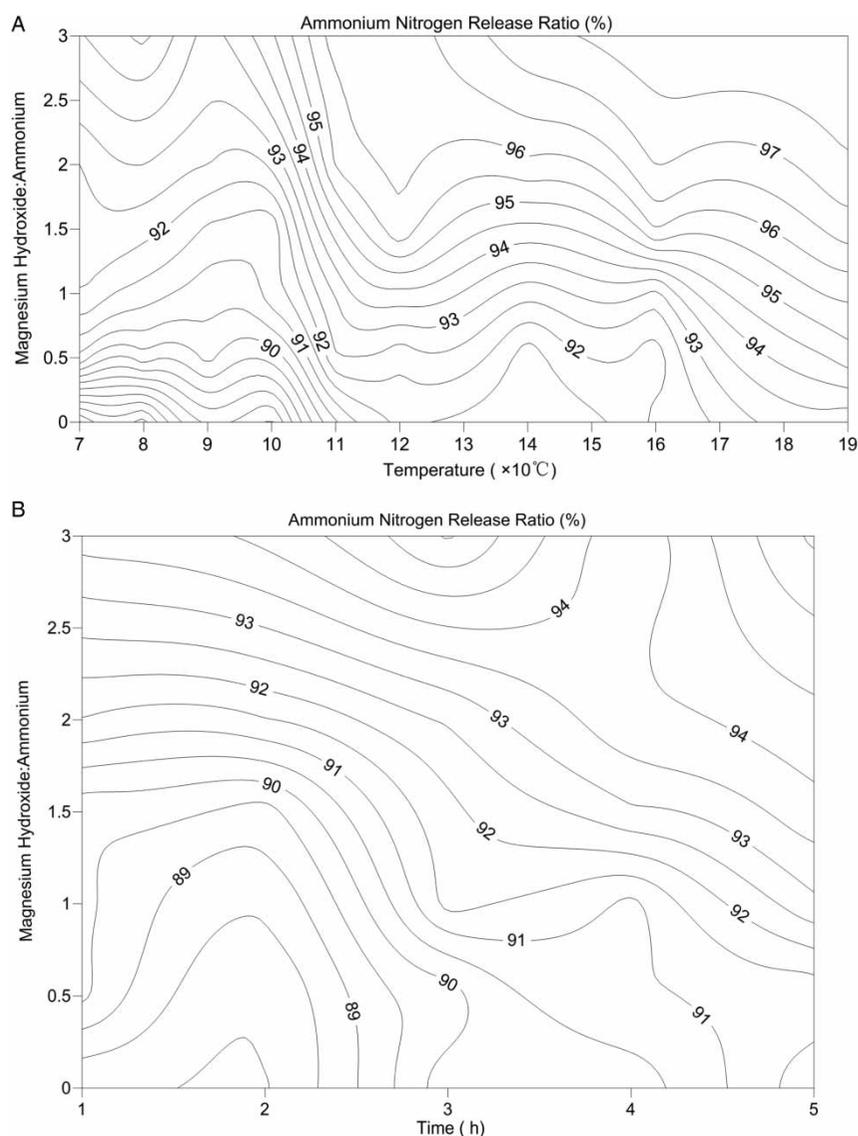


Figure 1 | Ammonia release ratio with $\text{Mg}(\text{OH})_2$ -mediated pyrolysis at different $\text{Mg}(\text{OH})_2:\text{NH}_4^+$ molar ratio, temperatures and times. (A) Effect of different $\text{Mg}(\text{OH})_2:\text{NH}_4^+$ molar ratio and temperature on $\text{NH}_4\text{-N}$ removal (time = 2 h). (B) Effect of different $\text{Mg}(\text{OH})_2:\text{NH}_4^+$ molar ratio and time on $\text{NH}_4\text{-N}$ removal (temperature = 100 °C).

dosage was varied in experiments with different wastewaters but parameters affecting the MAP pyrolysate dosage were not established. In this study, MAP pyrolysate dosage was added at 1:1 $\text{Mg}^{2+}:\text{NH}_4^+$ molar ratio, where the Mg^{2+} concentrations were calculated based on MgHPO_4 .

Stirring time was an important factor for MAP precipitation. MAP precipitation would be incomplete without sufficient stirring time, whereas the phosphate concentration in the supernate would be increased with prolonged stirring, which is not economical also. As shown in Figure 2(B), the ammonium removal rate and the supernate phosphate concentration showed little change with stirring time prolongation, but struvite

precipitation was an incompleted reaction for 30 min and the grain size was very small at our pre-experiment (data not shown). The energy consumption would be increased with too long a stirring time. In this study, the best stirring time was 60 min.

MAP pyrolysate recycling experiments

The results of MAP pyrolysate recycling with $\text{Mg}(\text{OH})_2$ -mediated pyrolysis are shown in Figure 3. The ammonium removal ratio could be maintained at about 75%, and the effect of MAP pyrolysate recycling was not very significant. The ammonium removal ratio was not distinctly different

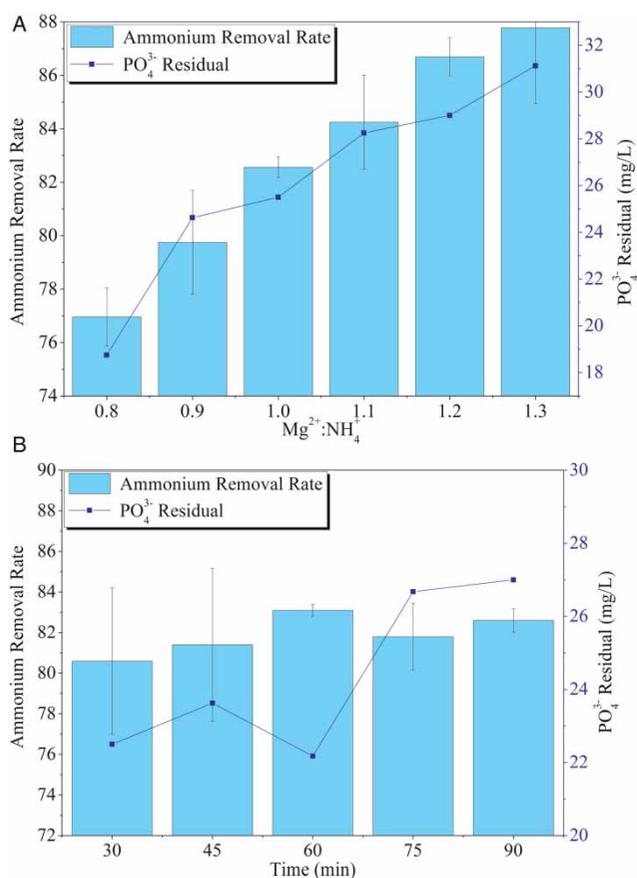


Figure 2 | The effect of MAP pyrolysate loading (A) and stirring time (B) on ammonium removal ratio.

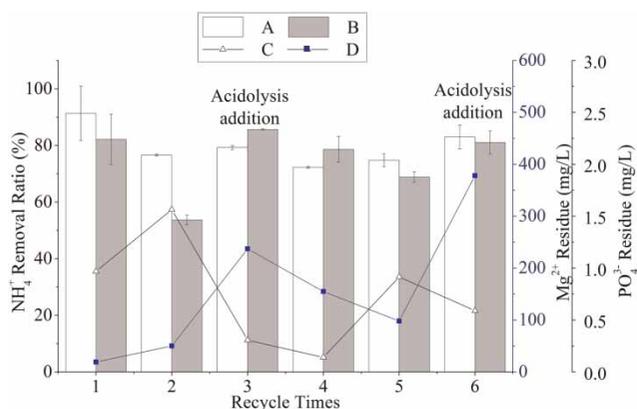


Figure 3 | $\text{NH}_4\text{-N}$ removal ratio and residues of PO_4^{3-} and Mg^{2+} in the supernate under different conditions. (A) $\text{NH}_4\text{-N}$ removal ratio with $\text{Mg}(\text{OH})_2$ addition. (B) $\text{NH}_4\text{-N}$ removal ratio without $\text{Mg}(\text{OH})_2$ -mediated pyrolysis. (C) PO_4^{3-} residue in the supernate, with $\text{Mg}(\text{OH})_2$ -mediated pyrolysis. (D) Mg^{2+} residue in the supernate, with $\text{Mg}(\text{OH})_2$ -mediated pyrolysis.

from that of MAP direct pyrolysis, but was more stable than the latter. The ammonium removal ratio was slower to decline with the increase in the number of recycles, from 91.3 to 76.6%, versus 82.1 to 53.7% for direct pyrolysis,

over the second recycling run. The ammonium removal ratio increased after additional acidolysis, from 74.8 to 83.0% with $\text{Mg}(\text{OH})_2$ -mediated pyrolysis, versus 68.8 to 81.0% with direct pyrolysis. The biggest advantage with $\text{Mg}(\text{OH})_2$ -mediated pyrolysis lies in the phosphate concentration in the supernate, which was less than 2 mg/L, as residual phosphate is one of the key control factors in MAP practical application. However, the magnesium ion concentration in the supernate was very high, reaching 100 mg/L (Figures 3(C) and (D)); the reason was that $\text{Mg}(\text{OH})_2$ was continuously added as a medium. The magnesium ion concentration became higher as the number of recycling repetitions increased, especially after additional acidolysis, reaching 235.2 mg/L in the third recycle and 378.0 mg/L in the sixth recycle. $\text{Mg}_3(\text{PO}_4)_2$ was readily formed with such high magnesium ion concentration.

Sugiyama & Yokoyama (2005) reported that $\text{Mg}_2\text{P}_2\text{O}_7$ was a possible product of MAP pyrolysis. $\text{Mg}_3(\text{PO}_4)_2$ was readily formed upon stoichiometric addition of $\text{Mg}(\text{OH})_2$ during MAP pyrolysate recycling. As $\text{Mg}_2\text{P}_2\text{O}_7$ and $\text{Mg}_3(\text{PO}_4)_2$ accumulated, the ammonium removal rate during MAP pyrolysate recycling was decreased gradually as the number of recycles increased. As reported, the ammonium recovery ratio was initially 92% and progressively decreased to 77% in the fifth stage (Türker & Çelen 2007). Ammonium removal rates of 84 and 62% in the sixth cycle were achieved for synthetic wastewater and landfill leachate, respectively (He et al. 2007). In this study, by addition of an acidolysis step to release Mg^{2+} and PO_4^{3-} from $\text{Mg}_2\text{P}_2\text{O}_7$ or $\text{Mg}_3(\text{PO}_4)_2$, the ammonium removal ratio was investigated during MAP pyrolysate recycling. In this manner, the ammonium removal ratio was 91.3% with $\text{Mg}(\text{OH})_2$ -mediated pyrolysis, versus 83.0% with direct pyrolysis in the sixth cycle.

Seed crystal experiments

In the literature, there are plenty of seed materials for struvite crystallization, such as pre-formed MAP crystals (Wu & Bishop 2004; Kim et al. 2007), sand and silica or quartz sand (Kim et al. 2006) and stainless steel (Le et al. 2007). Pre-formed MAP was added to our solution at the beginning of the experiment as a seeding inoculant in this study. The results are shown in the Supporting Information Figure S2 (available online at <http://www.iwaponline.com/wst/068/540.pdf>).

The size of single-crystal nanoparticles or crystallites in nanocrystalline bulk materials can be calculated using the Scherrer equation (Scherrer 1918) with XRD refinement;

the Scherrer equation is $D_{hkl} = K\lambda / (B_{hkl} \cos\theta)$, where D_{hkl} is the crystallite size in the direction perpendicular to the lattice planes, hkl are the miller indices of the planes being analyzed, K is a numerical factor frequently referred to as the crystallite-shape factor, λ is the X-ray wavelength, B_{hkl} is the width (full-width at half-maximum) of the X-ray diffraction peak in radians, and θ is the bragg angle. In our study, the values $K = 0.89$ and $\lambda_{Cu} = 0.15406$ were used in the fitting of the XRD data, and the B_{hkl} and θ values were obtained.

The grain sizes (derived using the Scherrer equation) of MAP without seeding were 1.9 nm with $Mg(OH)_2$ -mediated pyrolysis, versus 2.0 nm with seeding. The rate of crystallization was increased by 8.0%. The grain sizes of MAP with $Mg(OH)_2$ -mediated pyrolysis were smaller than those obtained through direct pyrolysis: 1.9 nm versus 2.1 nm respectively. The results showed that the rate of MAP crystallization was promoted with seeding, but was inhibited during MAP precipitation with $Mg(OH)_2$ -mediated pyrolysis. The same conclusion emerged from the particle size test (Figure S3, available online at <http://www.iwaponline.com/wst/068/540.pdf>): the particle size of MAP from $Mg(OH)_2$ -mediated pyrolysis was smaller than that of direct pyrolysis, $d(0.5) = 22.8 \mu m$ versus $d(0.5) = 31.5 \mu m$, respectively.

DISCUSSION

The high costs of magnesium and phosphate reagents and residual phosphate are the principal reasons for the obstruction of practical application of MAP chemical precipitation. The recycling of MAP pyrolysate as magnesium and phosphate salts was a possible solution for the first problem. MAP could be decomposed at above $70^\circ C$ to release ammonia, and MAP pyrolysate has good removal efficiency for ammonium. As the release rate of ammonia is very poor by direct pyrolysis, a NaOH solution was added to stimulate to release ammonia (He *et al.* 2007; Türker & Çelen 2007; Zhang *et al.* 2009). However, with heating in excess water, struvite would be transformed into dittmarite, $MgNH_4PO_4 \cdot H_2O$. Dittmarite is thermally more stable than struvite (Sarkar 1991; Bhuiyan *et al.* 2008). In order to release ammonia under a relatively low temperature, an anhydrous powder ($Mg(OH)_2$) was investigated in our study. The other reason to use $Mg(OH)_2$ instead of NaOH was that residual phosphate in the supernate was very high during MAP pyrolysate recycling. Although there is no effect on the removal of residual phosphate with NaOH-mediated pyrolysis, it was different

with $Mg(OH)_2$ -mediated pyrolysis. The superfluous Mg^{2+} would be supplied by residual $Mg(OH)_2$ in the MAP pyrolysate, $Mg_3(PO_4)_2$ would be formed and the phosphate concentration in the supernate was decreased, as shown in this study; the phosphate concentration was less than 2 mg/L.

The problem emerged that ammonium removal ratio gradually declined with the increase in the number of recycles and a feasible solution was not put forward to solve the problem in the literature. With the rise of temperature, struvite would be decomposed and transformed into magnesium hydrogen phosphate (Bhuiyan *et al.* 2008), which was shown to form magnesium pyrophosphate also (Sugiyama & Yokoyama 2005). The formation of magnesium pyrophosphate is associated with temperature and increasing number of MAP pyrolysate reuse cycles. As we know, the ammonium removal efficiency of magnesium pyrophosphate is very poor, and this fact can explain the decrease in the ammonium removal ratio with the increase in the number of recycles. In order to solve the problem, acidolysis was put forward to release magnesium ion and phosphate from magnesium pyrophosphate in this study, which would form struvite with ammonium in wastewater. The effect of additional acidolysis during MAP pyrolysate recycling was good in our investigation (Figure 3).

Sedimentation property is a key factor in the application of MAP precipitation. Newberyite (Lonsdale & Sutor 1966; Boistelle *et al.* 1983; Wierzbicki *et al.* 1997), $MgHPO_4 \cdot 3H_2O$, would nucleate and form during the first phase of the reaction, whereas MAP would dissolve as a result of the sharp decrease in pH. With residual $Mg(OH)_2$, the solution pH during the first phase does not drop sharply, and the effects of newberyite crystals on the nucleation and growth of MAP crystal are not clear. This is a flaw in MAP pyrolysate recycling combined with $Mg(OH)_2$ -mediated pyrolysis. However, the crystallite size could be increased by seeding, which was investigated in our research. As the solubility of $Mg(OH)_2$ is low in water, residual $Mg(OH)_2$ would play a role in simultaneous seeding.

CONCLUSIONS

The addition of an acidolysis step and a new alkali reagent, $Mg(OH)_2$, were investigated to improve the removal of ammonium from fertilizer wastewater. The ammonia release rate with $Mg(OH)_2$ -mediated pyrolysis was not distinctly different from that of direct pyrolysis. However, the ammonium removal rate from wastewater was more stable with $Mg(OH)_2$ -mediated pyrolysis than that of direct

pyrolysis, and the phosphate concentration in the supernate was very low, less than 2 mg/L. The rates of MAP crystallization and nucleation were increased by seed crystals. But the changes were subtle, because residual $\text{Mg}(\text{OH})_2$ powder in MAP pyrolysate can also act as inoculating seed during MAP pyrolysate recycling.

ACKNOWLEDGEMENTS

This study was supported by the Natural Science Foundation of China (No. 51178216) and the Science and Technology Support Program of the Social Development Projects of Jiangsu Province (BE2011774).

REFERENCES

- APHA 1998 *Standard Methods for the Examination of Water and Wastewater*, 19th edn. American Public Health Association/American Water Works Association/Water Environment Federation, Washington, DC, USA.
- Bhuiyan, M. I., Mavinic, D. S. & Koch, F. A. 2008 Thermal decomposition of struvite and its phase transition. *Chemosphere* **70**, 1347–1356.
- Boistelle, R., Abbona, F. & Lundager Madsen, H. E. 1983 On the transformation of struvite into newberyite in aqueous systems. *Phy. Chem. Minerals* **9**, 216–222.
- He, S., Zhang, Y., Yang, M., Du, W. L. & Harada, H. 2007 Repeated use of MAP decomposition residues for the removal of high ammonium concentration from landfill leachate. *Chemosphere* **66**, 2233–2238.
- Huang, H. M., Song, Q. & Xu, C. 2011 Removal of ammonium from aqueous solutions using the residue obtained from struvite pyrogenation. *Water Sci. Technol.* **64**, 2508–2514.
- Kim, E. H., Yim, S. B. & Jung, H. C. 2006 Hydroxyapatite crystallization from a highly concentrated phosphate solution using powdered converter slag as a seed material. *J. Hazard. Mater.* **136**, 690–697.
- Kim, D., Ryu, H. D., Kim, M. S., Kim, J. & Lee, S. I. 2007 Enhancing struvite precipitation potential for ammonia nitrogen removal in municipal landfill leachate. *J. Hazard. Mater.* **146**, 81–85.
- Le, C. K. S., Valsami-Jones, E., Hobbs, P., Jefferson, B. & Parsons, S. A. 2007 Struvite crystallisation and recovery using a stainless steel structure as a seed material. *Water Res.* **41**, 2449–2456.
- Liu, Z. G., Zhao, Q. L., Wei, L. L., Wu, D. L. & Ma, L. M. 2011 Effect of struvite seed crystal on MAP crystallization. *J. Chem. Technol. Biotechnol.* **86**, 1394–1398.
- Lonsdale, K. & Sutor, D. J. 1966 Newberyite in ancient and modern urinary calculi: identification and space group. *Science* **154**, 1353–1354.
- Sarkar, A. K. 1991 Hydration/dehydration characteristics of struvite and dittmarite pertaining to magnesium ammonium phosphate cement systems. *J. Mater. Sci.* **26**, 2514–2518.
- Scherrer, P. 1918 Bestimmung der Größe und der inneren struktur von kolloidteilchen mittels röntgenstrahlen.– göttinger nachrichten (Determination the size and the internal structure of colloid particles by X-ray). *Math.-Phys.* **2**, 98–100.
- Sugiyama, S. & Yokoyama, M. 2005 Removal of aqueous ammonium with magnesium phosphates obtained from the ammonium-elimination of magnesium ammonium phosphate. *J. Colloid. Interf. Sci.* **292**, 133–138.
- Sutor, J. 1968 Newberyite – its formation in human urinary calculi. *Nature* **218**, 295.
- Türker, M. & Çelen, I. 2007 Removal of ammonia as struvite from anaerobic digester effluents and recycling of magnesium and phosphate. *Bioresour. Technol.* **98**, 1529–1534.
- Wierzbicki, A., Sallis, J. D., Stevens, E. D., Smith, M. & Sikes, C. S. 1997 Crystal growth and molecular modeling studies of inhibition of struvite by phosphocitrate. *Calcif. Tissue Int.* **61**, 216–222.
- Wu, Q. Z. & Bishop, P. L. 2004 Enhancing struvite crystallization from anaerobic supernatant. *J. Environ. Eng. Sci.* **3**, 21–29.
- Yang, M., Wu, C. Q., Zhang, C. B. & He, H. 2004 Selective oxidation of ammonium over copper-silver-base catalysts. *Catal. Today* **90**, 263–267.
- Zhang, T., Ding, L. L., Ren, H. Q. & Xiang, X. 2009 Ammonium nitrogen removal from coking wastewater by chemical precipitation recycle technology. *Water Res.* **43**, 5209–5215.
- Zhang, S. J., Yao, H. H., Feng, X. X. & Yang, M. 2004 Repeated use of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ residues for ammonium removal by acid dipping. *Desalination* **170**, 27–32.

First received 22 May 2013; accepted in revised form 28 August 2013. Available online 24 October 2013