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The role of reagent adding sequence in the NH$_4^+$-N recovery by MAP method

Caiqing He, Yunnen Chen✉, Chen Liu, Yang Jiang, Ruoyu Yin & Tingsheng Qiu

Ammonium-nitrogen (NH$_4^+$-N) recovery from high concentration of NH$_4^+$-N-containing wastewater by struvite (MgNH$_4$PO$_4$·6H$_2$O, MAP) precipitation method has been realized, but whether NH$_4^+$-N recovery under different reagent adding sequence of NaOH, solid Mg salt and P salt can generate different effects, remains ambiguous. In view of the problem, four modes to add reagents were investigated in detail on the formation of struvite. The results show that the Mode IV (M-IV, i.e. using 50% NH$_4^+$-N wastewater to dissolve completely the Mg salt and the P salt, respectively and then simultaneously poured into a beaker to mix the solution evenly and adjust the pH to 9.5.) has the highest NH$_4^+$-N recovery efficiency (90.80%) and the maximum mass of precipitates (896 mg) because of the more amount of alkali and initial seed formation. From the morphology of the obtained precipitates, it can be seen that sample M-IV is more loose and porous than the others. XRD patterns show that the four products under the different modes basically agree with the standard MAP.

Water environment deterioration and eutrophication of natural water bodies such as rivers, lakes and wetlands in China have been caused wide public concern in the last few decades[1]. High concentration NH$_4^+$-N is commonly present in textile, fertilizer, petrochemical, pharmaceutical industrial wastewater[2–5]. Meanwhile, nitrogen (N) is one of the indispensable nutrients for crops[6,7]. Therefore, it is necessary to recover NH$_4^+$-N from wastewater containing NH$_4^+$-N. Several methods have been applied to pretreat wastewater containing high concentration NH$_4^+$-N, such as steam-stripping / air-stripping means[8], biological denitrification technology[9,10] and MAP method. Struvite precipitation method[11–14] is considered to be an attractive treatment option due to its simple operating, high efficiency, low cost, and can recover NH$_4^+$-N as slow-release fertilizer[15–17], but different reaction conditions directly affect the recovery efficiency of struvite.

Many researchers have been working to improve the reaction conditions of struvite precipitation, include the solution of pH[18], the molar ratio of Mg, P, N[3] and combined struvite precipitation and microwave irradiation[19]. To the best of my knowledge, the sequence of adding reagents is an important aspect of the mineral flotation influencing factors studied by Zhang Qidong[20] and Wang Jizhen[21]. But there have been few reports on the effect of the order of reagent addition on NH$_4^+$-N recovery and removal. In addition, in practical applications, the reagent addition sequence introduced in this article is mainly applicable to actual wastewater with little or no Mg salt and P salt, such as coking wastewater[19] and hydrometallurgy wastewater[22].

Based on the aforementioned information, the effect of the reagent addition sequence of solution on the formation of struvite was investigated. The corresponding precipitation products were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD).

Results and discussion

The effect of reagent addition sequence on NH4$^+$-N recovery efficiency.   The NH$_4^+$-N concentration of solution, pH, and the molar ratio of Mg, P, and N were 500 mg L^{-1}, 9.5, and 1.3:1:1, respectively. The reaction mechanism of struvite formation can be expressed as the following formula:

$$NH_4^+ + Mg^{2+} + HPO_4^{2-} + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O \downarrow + H^+ \tag{1}$$

It can be seen from Fig. 1 that the sequence of reagent addition has a great influence on the NH$_4^+$-N recovery efficiency. Among the four modes, the M-IV has the highest NH$_4^+$-N recovery efficiency, up to 90.80%. The NH$_4^+$-N recovery efficiency in the other three modes is 66.17%, 60.70%, and 84.08%, respectively.

Jiangxi Key Laboratory of Mining & Metallurgy Environmental Pollution Control, Jiangxi University of Science and Technology, Ganzhou, 341000, PR China. ✉e-mail: cyn70yellow@gmail.com
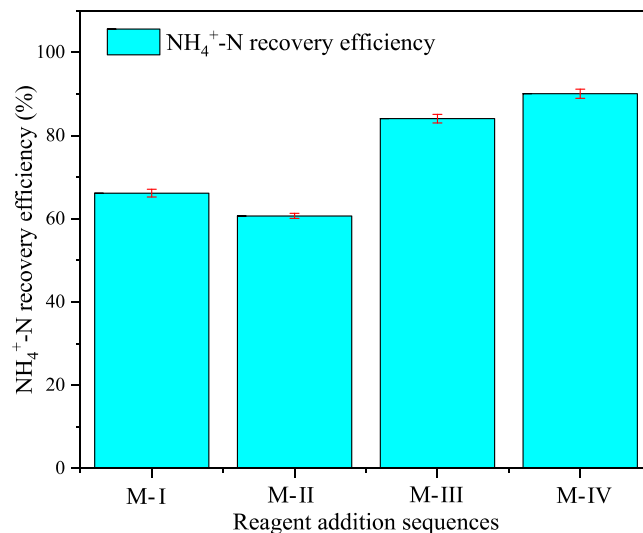
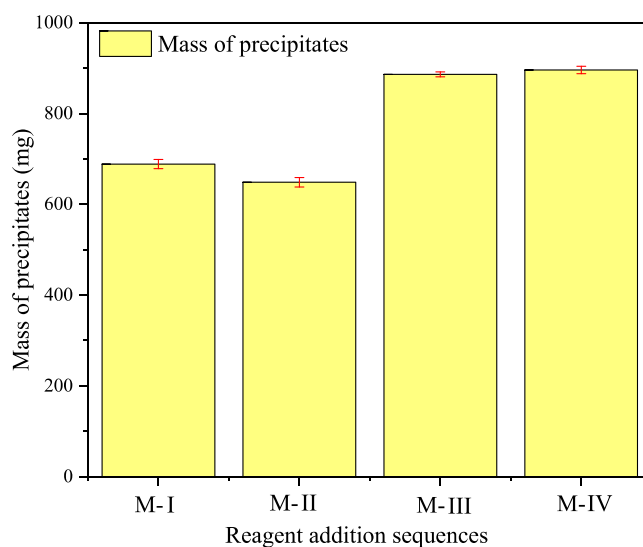**Figure 1.** NH_4^+-N recovery efficiency (%) under four modes.

Figure 2. Mass of precipitates (mg) under four modes.

The significant difference in the recovery efficiency of NH_4^+-N may be related to the sequence of pH adjustment of the solution. As elucidated by Eq. (1), when the Mg salt and the P salt reacted with the NH_4^+-N wastewater to form struvite crystallization, the pH of solution will decrease. It is reflected in the Fig. 1 that when the pH was adjusted after reagent reaction (M-III and M-IV), the NH_4^+-N recovery rate were larger than that of pH value adjusted before the reaction (M-I and M-II). When the NaOH solution was used to adjust the pH to 9.5, it was confirmed that the latter two (M-III, 2.4 ml and M-IV, 2.4 ml) used more alkaline solution than the first two (M-I, 1.3 ml and M-II, 1.2 ml). This is a powerful explanation of why the latter two (M-III and M-IV) are significantly better than the former two (M-I and M-II) for NH_4^+-N recovery rate. Consequently, one of the mechanisms by which different reagent addition sequences lead to different ammonia nitrogen recovery rates can be attributed to the discrepancy in the final NaOH addition amount. Additionally, other possible causes will be explained in the next section on the effect of reagent addition sequence on precipitates mass recovery.

The effect of reagent addition sequence on mass of precipitates. From Fig. 2 can be seen that the sequence of reagent addition has also great influence on the yield of precipitates. Among the four modes, the M-IV has the highest mass of sediment, up to 896 mg. The amount of sediment in the other three modes is 689 mg (M-I), 649 mg (M-II), and 886 mg (M-III), respectively. Compared with Fig. 1, it can also be observed that the higher NH_4^+-N recovery efficiency, the more precipitates are produced.

Meanwhile, the reason why the M-IV is better than the M-III is probably that the difference in seed amount of crystals formation, which is conducive to the increase of precipitation[23]. For M-IV, it was ensured that Mg salt and P salt solids were dissolved in NH_4^+-N wastewater, respectively, before adjusting the pH to 9.5, then
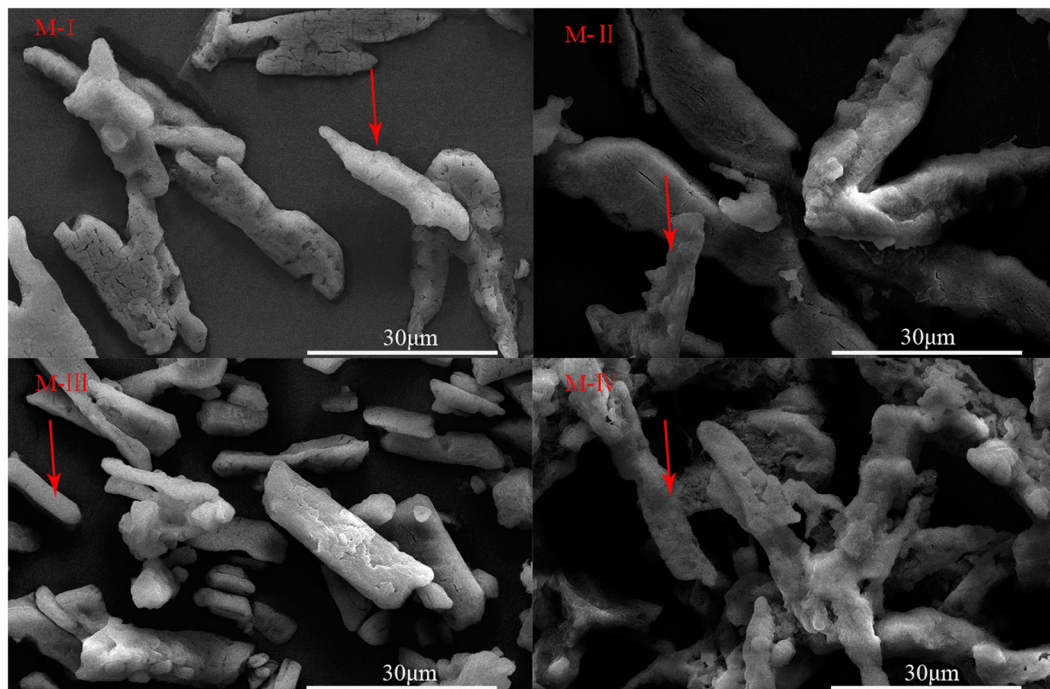
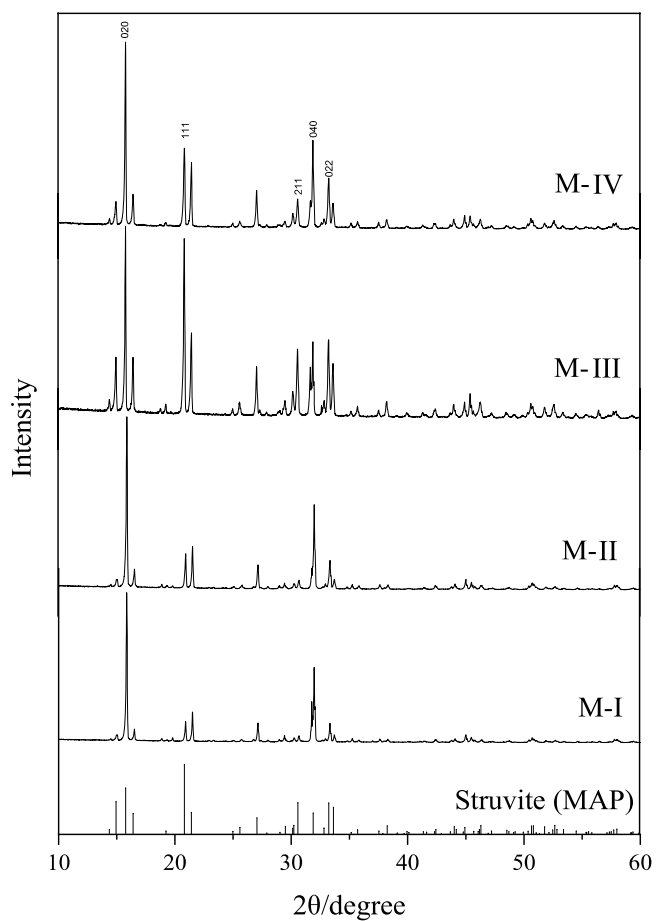**Figure 3.** SEM images of products under different reagent addition sequences.

Figure 4. The XRD spectra of products under different reagent addition sequences.
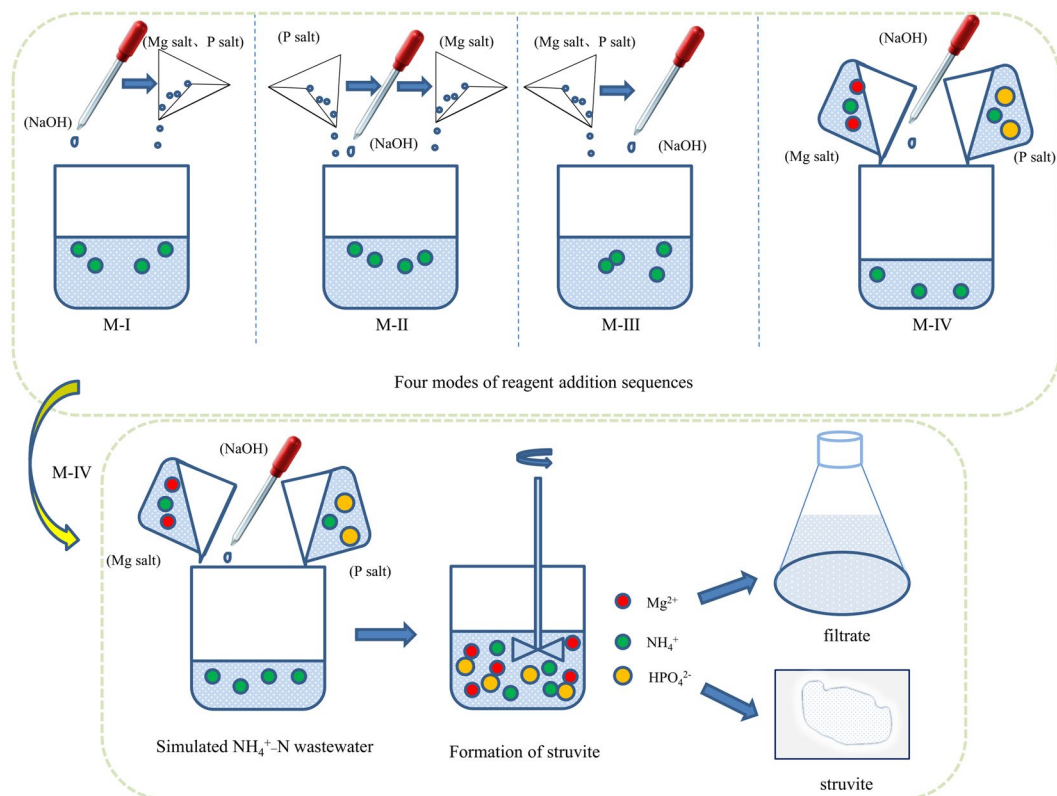
Figure 5. Four modes of reagent addition sequences schematic diagram of struvite formation.

the three reagents reacted with each other and formed the initial crystal seed[24]. By contrast, P salts took longer (30 seconds–1 minute) to dissolve completely than Mg salts when Mg salt and P salt reagents added into NH_4^+-N wastewater, which affected the formation of crystal seed, leading to a bit lower mass of precipitates in M-III than that of M-IV[25].

SEM analyses. Figure 3 shows the SEM images of products obtained under different reagent addition sequences. According to the results shown in Fig. 3, the morphology of products formed in four modes was quite different. In particular, the orthorhombic crystal phases of M-II and M-IV differ greatly, in which M-II is broad and dense and M-IV thin and loose. This is because in order to promote the formation of precipitation, the compaction degree of solids is affected, thus becoming loose and difficult to further precipitate. This result is similar to Song *et al.*[26]. This also in accord with the results analyzed in Fig. 1. The amount of sodium hydroxide has an effect on the morphology.

X-ray diffraction. Figure 4 shows the XRD spectra of products obtained under different reagent addition sequences. As can be seen from the XRD diffractogram (Fig. 4), the (020), (111) and (040) reflections of the four spectra are almost identical with the standard struvite spectrum, which can be confirmed that struvite crystal is the mainly component in the obtained precipitates according to JCPDS files (15–0762). For the peak's intensity of (022) and (211) reflection, M-III and M-IV were stronger than that of M-I and M-II. This is due to the more sodium hydroxide retained by M-III and M-IV, which is consistent with the results obtained in Fig. 1.

Conclusions

The experimental results showed that the sequence of reagent addition has a great influence on NH_4^+-N recovery and mass of precipitates. The optimal NH_4^+-N recovery efficiency (90.80%) appeared in M-IV, that is, using 50% NH_4^+-N wastewater to dissolve completely the Mg salt and the P salt, respectively and then simultaneously poured into a beaker to mix the solution evenly and adjust the pH to 9.5. The mechanism for M-IV mainly resulted from the more alkali than M-I and M-II, and the more amount of initially crystal seed formation than M-III.

Materials and Methods

Materials. All reagents were of analytical grade and purchased in Shantou Xiqiao Science Co., Ltd., Guangdong, China. P salt and Mg salt used in the experiment were disodium hydrogen phosphate dodecahydrate ($Na_2HPO_4 \cdot 12H_2O$) and magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$), respectively. Ammonium chloride (NH_4Cl) was used to prepare simulated NH_4^+-N wastewater. The initial pH of solution was adjusted with $1\,mol\,L^{-1}$ NaOH and HCl. All solvents were deionized water.

Procedures of experiments. Under room temperature (25 ± 2°C), four modes of reagent addition sequences are as follows: Three 200 ml beakers were filled with 100 ml 500 mg L^{-1} synthetic NH$_4^+$-N wastewater. In the beaker I (M-I), the initial pH of solution was adjusted to 9.5 firstly, then added solid Mg salt and P salt at the same time and stirred to dissolve completely. In the beaker II (M-II), solid P salt was added and stirred to dissolve completely, then adjusted the pH of the mixture to 9.5, following Mg salt was added and stirred to dissolve completely. For the beaker III (M-III), Mg salt and P salt were added at the same time and then stirred to dissolve completely, following adjusted the pH of the solution to 9.5. As for the beaker IV (M-IV), Mg salt and P salt were first added into a 100 ml beaker containing 50 mL of NH$_4^+$-N wastewater and then stirred to dissolve completely, respectively. Next simultaneously poured into a 200 ml beaker to mix the solution evenly and adjust the pH to 9.5. Four modes of reagent addition sequences and schematic diagram of struvite formation have shown as Fig. 5.

The mixed solution of the four beakers was stirred by a magnetic stirrer to promote the formation of precipitates and then standing for 30 min to make the precipitation complete. After that, precipitation yield was obtained after filtrating through a 0.45-μm filter membrane, washing by deionized water three times and drying in an oven at 50°C. The content of NH$_4^+$-N in the filtrate was determined. All batch experiments were performed in triplicate and the average was taken as the experimental results.

Analytical methods. The morphology of the precipitates was characterized using a scanning electron microscope (SEM, MLA650F, FEI, Hillsboro, USA). The crystal patterns of the synthesized struvite was obtained by X-ray diffractometer with Cu-Kα radiation (40KV, 40 mA), from radiation angle 10–60°(XRD, DX-2700, Shjingmi, Shanghai, China). The content of NH$_4^+$-N in solution was measured by visible spectrophotometer (722 N, INESA, Shanghai, China) with a wavelength of 420 nm according to Nessler's reagent spectrophotometry method.

The calculation Eq. (2) for the recovery of NH$_4^+$-N is:

$$Y = \frac{C_O - C_t}{C_O} \times 100 \tag{2}$$

where Y (%) is the recovery efficiency of NH$_4^+$-N, C_0 refers to the initial NH$_4^+$-N concentration (mg L^{-1}) and C_t refers to the equilibrium NH$_4^+$-N concentration (mg L^{-1}) of the solution.

References

1. Liu, W. & Qiu, R. Water eutrophication in China and the combating strategies. *J. Chem. Technol. Biotechnol.* **82**, 781–786 (2007).
2. Abu Hasan, H. *et al*. Removal of ibuprofen, ketoprofen, COD and nitrogen compounds from pharmaceutical wastewater using aerobic suspension-sequencing batch reactor (ASSBR). *Sep. Pur. Technol.* **157**, 215–221 (2016).
3. Chen, Y., Liu, C., Guo, L., Nie, J. & Li, C. Removal and recovery of phosphate anion as struvite from wastewater. *Clean Techn Environ Policy* **20**, 2375–2380 (2018).
4. Fu, L. Y., Wu, C. Y., Zhou, Y. X., Zuo, J. E. & Ding, Y. Treatment of petrochemical secondary effluent by an up-flow biological aerated filter (BAF). *Water Sci. Technol.* **73**, 2031–2038 (2016).
5. Zhang, S., Peng, Y., Wang, S., Zheng, S. & Guo, J. Organic matter and concentrated nitrogen removal by shortcut nitrification and denitrification from mature municipal landfill leachate. *J. Environ. Sci.* **19**, 647–651 (2007).
6. Liu, T., Hu, S., Yuan, Z. & Guo, J. High-level nitrogen removal by simultaneous partial nitritation, anammox and nitrite/nitrate-dependent anaerobic methane oxidation. *Water Res.* **166**, 115057 (2019).
7. Huang, H., Liu, J. & Jiang, Y. Crystallization and precipitation of phosphate from swine wastewater by magnesium metal corrosion. *Sci Rep* **5**, 16601 (2015).
8. Xiong, J. *et al*. Recovery of NH3-N from mature leachate via negative pressure steam-stripping pretreatment and its benefits on MBR systems: A pilot scale study. *J. Cle. Pro.* **203**, 918–925 (2018).
9. Asadi, A., Zinatizadeh, A. A., Van Loosdrecht, M. & Younesi, H. Nitrogen removal by ANAMMOX and simultaneous nitrification–denitrification (SND) processes in a novel single airlift bioreactor. *RSC Adv.* **6**, 74367–74371 (2016).
10. Sri Shalini, S. & Joseph, K. Combined SHARON and ANAMMOX processes for ammoniacal nitrogen stabilisation in landfill bioreactors. *Bioresour. Technol.* **250**, 723–732 (2018).
11. Doyle, J. D. & Parsons, S. A. Struvite formation, control and recovery. *Water Res.* **36**, 3925–3940 (2002).
12. Yetilmezsoy, K. & Sapci-Zengin, Z. Recovery of ammonium nitrogen from the effluent of UASB treating poultry manure wastewater by MAP precipitation as a slow release fertilizer. *J. Hazard. Mater.* **166**, 260–269 (2009).
13. Simoes, F., Vale, P., Stephenson, T. & Soares, A. The role of pH on the biological struvite production in digested sludge dewatering liquors. *Sci Rep* **8**, 7225 (2018).
14. Wang, F. *et al*. Phosphate Recovery from Swine Wastewater by a Struvite Precipitation Electrolyzer. *Sci Rep* **9**, 8893 (2019).
15. Lee, S.-H. *et al*. Enhancement of struvite purity by re-dissolution of calcium ions in synthetic wastewaters. *J. Hazard. Mater.* **261**, 29–37 (2013).
16. Siciliano, A. Assessment of fertilizer potential of the struvite produced from the treatment of methanogenic landfill leachate using low-cost reagents. *Environ Sci Pollut Res.* **23**, 5949–5959 (2016).
17. Min, K. J., Kim, D., Lee, J., Lee, K. & Park, K. Y. Characteristics of vegetable crop cultivation and nutrient releasing with struvite as a slow-release fertilizer. *Environ Sci Pollut Res.* **26**, 34332–34344 (2019).
18. Stratful, I., Scrimshaw, M. D. & Lester, J. N. Conditions influencing the precipitation of magnesium ammonium phosphate. *Water Res.* **35**, 4191–4199 (2001).
19. Huang, H., Liu, J., Xiao, J., Zhang, P. & Gao, F. Highly Efficient Recovery of Ammonium Nitrogen from Coking Wastewater by Coupling Struvite Precipitation and Microwave Radiation Technology. *ACS Sustainable Chem. Eng.* **4**, 3688–3696 (2016).
20. Zhang, Q. Fundamental study on regulation and control floatability difference of molybdenite and talc. (Northeastern University, 2016).
21. Wang, J. Study on flotation and separation intensification of complex refractory scheelite and its reaction mechanism. (Northeastern University, 2015).
22. Peng, C. *et al*. Study on the mechanism of copper–ammonia complex decomposition in struvite formation process and enhanced ammonia and copper removal. *J. Environ. Sci.* **51**, 222–233 (2017).

23. Muhmood, A. *et al.* Biochar seeding promotes struvite formation, but accelerates heavy metal accumulation. *Sci. Tot. Environ.* **652**, 623–632 (2019).
24. Kataki, S., West, H., Clarke, M. & Baruah, D. C. Phosphorus recovery as struvite: Recent concerns for use of seed, alternative Mg source, nitrogen conservation and fertilizer potential. *Resources, Con. Recycl.* **107**, 142–156 (2016).
25. Zhang, T., Ding, L., Ren, H. & Xiong, X. Ammonium nitrogen removal from coking wastewater by chemical precipitation recycle technology. *Water Res.* **43**, 5209–5215 (2009).
26. Song, Y. *et al.* Nutrients removal and recovery by crystallization of magnesium ammonium phosphate from synthetic swine wastewater. *Chemosphere* **69**, 319–324 (2007).

Acknowledgements

Author contributions

H.C.Q. and C.Y.N. wrote the main manuscript text. L.C. and J.Y. prepared all figures. All authors discussed the data, interpreted the results and reviewed the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

Correspondence and requests for materials should be addressed to Y.C.

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