

Looking Beyond Struvite for P-Recovery

Xiaodi Hao,^{†,*} Chongchen Wang,[†] Mark C. M. van Loosdrecht,[‡] and Yuansheng Hu[†]

[†]Key Laboratory of Urban Stormwater System and Water Environment/R & D Centre for Sustainable Wastewater Treatment (Beijing University of Civil Engineering and Architecture), Ministry of Education, Beijing 100044, P. R. China

[‡]Department of Biochemical Engineering, Delft University of Technology, Julianalaan 67, 2628 BC Delft, The Netherlands



Phosphorus, a nutritional element for all life forms for which no substitute exists, is a natural resource in short supply. It is estimated that the remaining accessible reserves of phosphate rock will run out in 50 years, if the growth of demand for fertilizers remains at 3% per year.^{1,2} Reducing usage will help the reserves last longer, but the biggest gains will probably be made from the recovery of phosphates, both from wastewaters and livestock waste.¹ With regards to wastewater, such recovery would have the additional benefits of minimizing eutrophication and alleviating the scaling of process equipment at wastewater treatment plants. For these reasons, nutrient removal from wastewater has recently become integrated with phosphate recovery.^{2,3}

Struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) is generally considered as the optimal phosphate mineral for recovery as it contains 51.8% of P_2O_5 (based on MgNH_4PO_4) and could potentially be used as a slow-release fertilizer. If the economic and life cycle costs are taken into account, however, it becomes clear that phosphate recovery as struvite is likely not the best approach, for the following reasons: (1) production of P-mineral with a high content of struvite from real wastewater is a difficult and costly process; and (2) struvite is not superior to other phosphate-based compounds in fertilization efficiency, nor is it an exclusive form of raw materials favored by the fertilizer industry.

In literature and practice, struvite precipitation is usually performed under alkaline conditions, which are created by dosing alkalinity or CO_2 stripping.³ It is often taken for granted that precipitates harvested at a pH range between 9.0 and 10.7 are struvite-like compounds when there are appropriate molar

ratios among magnesium, ammonium and phosphate. In particular, X-ray diffraction (XRD) is often used to characterize the harvested crystalline precipitates, mainly by comparing the position and intensity of peaks with the struvite reference.⁴ If the diffraction patterns match the struvite reference to a certain extent, precipitates are then “confirmed” as being struvite. However, because XRD is not a quantitative method and amorphous precipitates are easily overlooked, many may be misled into believing that the harvested precipitate is struvite when, in fact, it is not.⁴

Indeed, the extensively reported struvite produced at high pHs (>9.0) could actually be phosphate-based compounds containing a lower content of struvite or no struvite at all, which can clearly be revealed by element analyses of the precipitates, as illustrated in Figure 1. It shows that the optimal

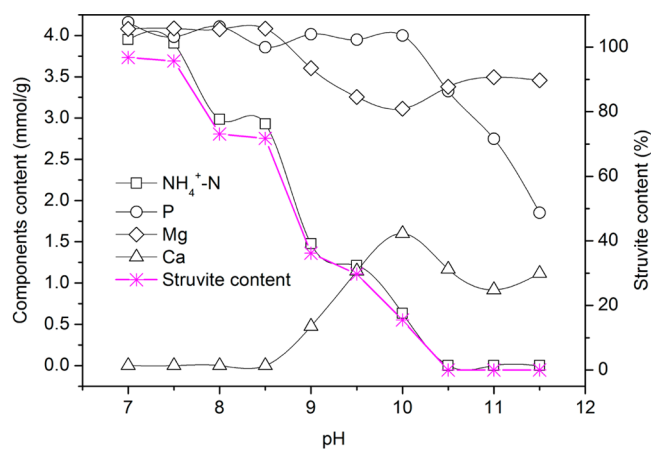


Figure 1. Elemental analyses of the precipitates from synthesized wastewater at different pHs⁴ (Components content: element molar (mmol)/weight of the precipitates (g)).

pH range for forming struvite crystal (struvite content >90%) is actually close to a neutral pH,⁴ rather than the alkaline pH usually cited in literature reports. Precipitates with a high struvite content (>95%) were only obtained at pH 7.0–7.5. At pH 8.0–9.0, the struvite content decreased to around 30–70%, and over pH 9.5, the content decreased sharply to <30%. An even higher pH (>10.5) resulted in the complete disappearance of struvite in the precipitates (Figure 1). The decline of NH_4^+

Received: March 15, 2013

Revised: March 25, 2013

Accepted: March 25, 2013

Published: April 10, 2013

content in the precipitates along with the increase of pH probably results from the conversion of NH_4^+ ions to NH_3 . Moreover, a small amount of K-struvite (MgKPO_4) could be formed as well; the occurrence of Ca^{2+} strongly indicates that applying high pHs in real wastewater would introduce impurities into the precipitates due to coprecipitation of the foreign ions (Figure 1).

A neutral pH level favors the formation of pure struvite, but the precipitation rate is significantly reduced, leading to longer reaction times. We acquired a single crystal of struvite (99.7% in purity) in a process taking approximately three months under ambient temperatures (25–30 °C) and controlled conditions.⁴ Obviously, such a long reaction time will hamper the application of struvite production in practice. Thus, some methods are suggested for the acceleration of the reaction rate in order to produce struvite swiftly. Among these, electrochemical deposition, use of crystal seeds and increasing thermodynamic driving force are proposed as having the potential to accelerate formation of pure struvite at neutral pH levels. Electrochemical deposition could effectively accelerate formation of struvite, but the process is expensive and energy-intensive. Introducing crystal seeds could reduce the induction time of struvite crystallization, but it leads to more complicated processes, due to the selection and control of seed material, seed size, dose, etc. A suitable amount of K^+ could enhance the thermodynamic driving force on struvite formation, but overdosing would have an adverse effect on struvite crystallization and even promote the formation of a mixture of MgKPO_4 and $\text{Ca}_3(\text{PO}_4)_2$. Furthermore, no matter what methods are applied to accelerate the formation of struvite, rapid precipitation could cause precipitated particles to become smaller, and thus reduce the potential of crystal growth and collection.

In general, phosphorus recovery is unnecessarily oriented to struvite from the practical application viewpoint. As a slow-release fertilizer, struvite is in fact rarely used directly in agriculture. In addition, previous studies have indicated that struvite is approximately equal to monocalcium phosphate ($\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$) and dicalcium phosphate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) in fertilization efficiency;⁵ however, the cost of producing struvite is much higher than that of producing these two compounds. In industrial fertilizer production, phosphate rock is usually processed using two methods: the wet (chemical) process and/or the electric furnace (thermal) process, in which there is no strict selectivity for the raw materials. Thus, the fertilizer industry finds no favor with struvite as long as the feedstock contains an appropriate content of P_2O_5 (30–40% favored).

Hence, phosphate recovery should not be too strongly focused on struvite, and could be aimed at any acceptable forms of phosphate-based compounds by the fertilizer industry, depending on onsite circumstances. Accordingly, efforts should also go to develop technologies based on other phosphate-based compounds in future research, and perhaps the use of (composted) sludge should also be considered for fertilization.

AUTHOR INFORMATION

Corresponding Author

*Phone: +86-131 61347675; fax: +86-10-68322128; e-mail, xdhao@hotmail.com.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This study was financially supported by the National Natural Science Foundation of China (50978013) and by the Funding

Project for Academic Human Resources Development in Institutions of Higher Learning under the Jurisdiction of Beijing Municipality (PHR20100508).

REFERENCES

- (1) Gilbert, N. The disappearing nutrient. *Nature* **2009**, *461* (8), 716–718.
- (2) Elser, J.; Bennett, E. Phosphorus cycle: A broken biogeochemical cycle. *Nature* **2011**, *478*, 29–31.
- (3) Le Corre, K. S.; Valsami-Jones, E.; Hobbs, P.; Parsons, S. A. Phosphorus recovery from wastewater by struvite crystallization: A review. *Crit. Rev. Environ. Sci. Technol.* **2009**, *39* (6), 433–477.
- (4) Hao, X. D.; Wang, C. C.; Lan, L.; van Loosdrecht, M. C. M. Struvite formation, analytical methods and effects of pH and Ca^{2+} . *Water Sci. Technol.* **2008**, *58* (8), 1687–1692.
- (5) Johnston, A. E.; Richards, I. R. Effectiveness of different precipitated phosphates as phosphorus sources for plants. *Soil Use Mgmt* **2003**, *19* (1), 45–49.