

Struvite formation, analytical methods and effects of pH and Ca²⁺

X.-D. Hao, C.-C. Wang, L. Lan and M. C. M. van Loosdrecht

ABSTRACT

Struvite formation is mainly controlled by concentrations of Mg²⁺, NH₄⁺ and PO₄³⁻, pH, temperature, and other ions like Ca²⁺. Experiments evaluating the effects of pH and Ca²⁺ on struvite formation indicated that XRD is only a qualitative method to analyze the struvite content in precipitating compounds, which was also reflected in microscopic images. The element analyses preceded by a dissolution method were introduced to quantitatively determine the struvite content and were shown to be an efficient enough method. Based on element analyses, the struvite content could be calculated according to the N content in the precipitations, based on the molar ratios (1:1:1) of Mg, N and P in pure struvite (MgNH₄PO₄·6H₂O). It was found that the optimal pH ranges for the struvite content >90% were respectively at 7.5 ~ 9.0 with ultra pure water as solute and at 7.0 ~ 7.5 with tap water (mainly consisting of ground water) as solute. Applying a pH > 8.0 in real wastewater containing Ca²⁺ might result in impure struvite contents in the precipitate due to the effect of Ca²⁺.

Key words | Ca²⁺, dissolution method, element analyses, pH, Struvite, XRD

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INTRODUCTION

Chemical precipitation of struvite (MgNH₄PO₄·6H₂O) from phosphate-rich wastewater (anaerobic supernatant, urine and/or animal wastes) is increasingly getting global attention for resource recovery and closing nutrient cycles. Recovered struvite is considered and practiced as a direct or an indirect valuable fertilizer. Some processes recovering struvite have been theoretically and experimentally investigated by chemists, biochemists and civil engineers (Taylor *et al.* 1963; Abbona *et al.* 1982; Ohlinger *et al.* 1998; Hao & van Loosdrecht 2006; Ronteltap *et al.* 2007; Wilsenach *et al.* 2007; Pastor *et al.* 2008). Precipitation of struvite is mainly controlled by such factors as Mg²⁺/NH₄⁺/PO₄³⁻ concentrations, pH and temperature. The influences of Ca²⁺ and other factors on precipitation of struvite have been also investigated (Stratful *et al.* 2001; Le Corre *et al.* 2005).

The mineral composition of struvite precipitation are traditionally characterized by X-ray diffraction (XRD) (Stratful *et al.* 2001; Doyle *et al.* 2003; Le Corre *et al.* 2005;

Kim *et al.* 2007; Sundaramoorthi & Kalaninathan 2007; Pastor *et al.* 2008) and by scanning electron microscopy coupled with energy dispersive X-ray analysis (SEM-EDS) (Le Corre *et al.* 2005). However, XRD might be only a qualitative method to judge if struvite is present in precipitates, simply by comparing the positions and intensities of XRD peaks, as described in limited literature (Doyle *et al.* 2003; Le Corre *et al.* 2005; Kim *et al.* 2007; Sundaramoorthi & Kalaninathan 2007; Pastor *et al.* 2008). No one has yet stated that the exact content of struvite in precipitates was determined by XRD. In principle, detailed calculations based on the results of XRD could determine the content of struvite. In practice, however, the calculating work is not so easy due to complicated and uncertain compositions in precipitates. For the reason, a potential method determining the content of struvite needs to be developed along with its formation and effects of pH and Ca²⁺.

MATERIALS AND METHODS

Materials

Analytical grade chemicals such as NaH₂PO₄·2H₂O, MgSO₄·7H₂O, NH₄Cl and NaOH were used as the reagents forming struvite. A relatively pure struvite crystal (99.0% in the content) was used as a reference compound, which was commercially purchased from Alfa-Aesar (US).

Struvite formation

Reactant solution I: 5 mmol NaH₂PO₄·2H₂O was dissolved in 0.5-L ultra pure water; Reactant solution II: 6 mmol MgSO₄·7H₂O and 15 mmol NH₄Cl were dissolved in 0.5-L ultra pure water. Reactant II was moved into a 1.5-L plastic beaker, and then Reactant solution I was gradually poured in the beaker. A magnetic stirrer at the bottom of the beaker was used for stirring. In the mixed solution, the optimal ratio of Mg: N: P was maintained at 1.2:3:1 (Wang *et al.* 2007). After reaction for 30 min at the ambient temperature of about 25°C, precipitating compounds were formed by adjusting pH with two NaOH solutions (a supersaturated NaOH solution followed by 1 M NaOH solution) from 6.5 to 11.5 respectively. After each pH adjustment, the solutions were continuously mixed for another 30 min with a lower speed (to prevent formed crystals from crushing), and then aged for an hour to obtain bigger crystals. Finally, the precipitations were filtered with a filter paper and washed with ultra pure water for 2 times to remove potential soluble impurities like ammonium compounds. The filtrated precipitations were naturally dried and stored in desiccators at the ambient temperature (25°C).

Under completely the same conditions described above, another series of experiments were performed with tap water as solute instead of ultra pure water. The tap water in Beijing mainly consists of ground water, with a high mineral content: $c(\text{Ca}^{2+}) = 2.17 \text{ mM}$ and $c(\text{Mg}^{2+}) = 1.34 \text{ mM}$.

Crystal characterization and image analyses of the precipitations

Crystal characterization of the dried precipitations was performed by X-ray diffractometer (Rigaku D/max IIIA),

and microscope image analyses were taken under a high-resolution color digital camera (Zeiss: AxioCam MRc5).

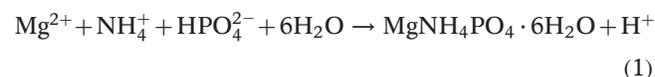
Element analyses of the struvite content in the precipitations

A dissolution method was testified to implement the element analyses of the precipitations. Clear solutions were prepared by dissolving 40 mg of the precipitations with a little amount of HCl (pH < 1), and then diluted to 250 ml with ultra pure water. The clear solutions should be adjusted to a suitable pH before conducting element analyses. Phosphate was analyzed using Inductively Coupled Plasma Atomic Emission Spectrometer (He & Zhang 2002), and Mg²⁺, Ca²⁺ and NH₄⁺-N were determined using Ion Chromatograph (Thomas *et al.* 2002).

RESULTS AND DISCUSSION

XRD and image analyses of potential struvite

In principle, struvite formation should be accompanied with the presence of Mg²⁺, NH₄⁺ and PO₄³⁻. However, our experiments indicated that the precipitations of struvite resulted in a rapid pH decrease, as also observed in other literatures (Boistelle *et al.* 1983; Schuiling & Andrade 1999), which reveals that HPO₄²⁻ rather than PO₄³⁻ would participate in the reaction of struvite formation, as expressed as follows:



In fact, struvite formation is mainly controlled by pH, initial relative ionic (Mg, N and P) concentrations and other ions like Ca. Among them, pH might be a key factor to control struvite formation (shape, morphology and purity). For this reason, the experiments were carried out to evaluate the effect of pH on struvite formation at the ambient temperature (25°C) and at a constant stirred speed, with Mg:N:P = 1.2:3:1.

The experiments were firstly carried out with ultra pure water being a solute, and pH was adjusted from 6.5 to 11.5 respectively. At pH < 7.5, no visible precipitations were observed due to the low concentrations of Mg, N and P

compounds. At pH > 7.5, white precipitations emerged in the solution. In order to test the impact of such ions as Ca²⁺ on struvite formation, the experiments were repeated using tap water as solute with the same concentrations of Mg, N and P compounds. XRD and microscopic images were applied to characterize the morphology of the formed crystals, as shown in Figure 1.

No apparent differences (*i.e.* position and intensity) can be observed by comparing the XRD patterns of the precipitations from the ultra pure water solutions with the pH range of 7.5–9.0, with those from the tap water solutions with the pH range from 7.0–8.5. The XRD patterns identify that these precipitations should be struvite. Figure 1 also illustrates that the images of the precipitating crystals were clear and bigger at lower pH values. When pH was higher than 9.0 with the ultra pure water solutions, some impurities such as Mg(OH)₂ ($K_{sp} = 5.1 \times 10^{-12}$) and Mg₃PO₄ ($K_{sp} = 1.0 \times 10^{-24}$) probably emerged in the precipitations, which indicates more noisy XRD patterns with reduction in peak intensities and with change in peak positions, and which also shows more irregular patterns in the microscopic images. In other words, the existence of Ca²⁺ in the tap water solutions at higher pH values would contribute to more impurities like Ca₃PO₄ ($K_{sp} = 2.1 \times 10^{-33}$) and even CaHPO₄ ($K_{sp} = 1.8 \times 10^{-7}$) (Yigit & Mazlum 2007), besides Mg(OH)₂ and Mg₃PO₄ found in the ultra pure water solutions.

The microscope images also show that the transparent rod-like crystals were only observed in the ultra pure water solutions with the pH range of 7.5–9.0 and in the tap water solutions with the pH range of 7.0–8.5. In both solutions with higher pH, the precipitations became white and even colorful powders (no crystals at all). Therefore, the precipitations at higher pH values are not pure struvite.

Element analyses determining the struvite content

In order to determine the struvite content in the precipitations, a dissolution method was tested to conduct the element analyses of the precipitations. The results of the element analyses of the precipitations from the ultra pure water solutions are shown in Figure 2. The element analyses of the purchased struvite sample indicate that the measured molar concentrations of N (0.6456 mM), P (0.6464 mM) and Mg (0.6532 mM) were very close to the calculated

molar concentrations (0.6520 mM) of each element (N/P/Mg). This means that the method of the element analyses could be reliably used to indirectly determine the struvite contents for other dissolved samples.

Figure 2 indicates that along with increasing pH in the original solutions the NH₄⁺-N content in the precipitations decreased gradually at pH ≤ 10.5 and decreased sharply at pH > 10.5. The NH₄⁺ ratio in solutions depends on its equilibrium with NH₃, as shown in Equation 2. At higher pHs, the NH₄⁺ ratio tends to decrease and nitrogen tends to volatilize from solutions in the gaseous form of NH₃ (Andrade & Schuiling 2001). Therefore, struvite is hardly formed at higher pHs.



As shown in Figure 2, the P content did not change until pH = 11.0. The content of Mg did not change at all over the pH range in the experiments. However, precipitation of impurities such as Mg₃PO₄ and Mg(OH)₂ occurred at higher pHs. Both the element analyses (Figure 2) and XRD analyses (Figure 1) could reveal the presence of such impurities as Mg₃PO₄ and Mg(OH)₂.

Figure 3 shows the results of the element analyses of the precipitations from the tap water solutions. Along with increasing pH, the NH₄⁺-N content in the precipitations decreased rapidly. At pH ≥ 10.5, there was no NH₄⁺-N in the precipitations at all, which implies that no struvite was present in the precipitations any more. At pH ≤ 8.5, the Ca content could not be detected in the precipitations. At pH > 8.5, however, the Ca content emerged suddenly, as described in a literature (Le Corre *et al.* 2005), which reveals that struvite formation was seriously limited by Ca compounds (Ca₃PO₄, CaHPO₄, etc.) at pH > 8.5. Moreover, other impurities like Mg₃PO₄ and Mg(OH)₂ might coexist under the conditions of pH > 8.5. The Ca content present in the precipitations even affected the P content at pH ≥ 10.0, which also reflects the effect on struvite formation.

Calculations for the struvite content in the precipitations

As shown in Equation 1, the molar ratio of N, P and Mg in struvite is 1:1:1. As mentioned above, however, P and Mg tend

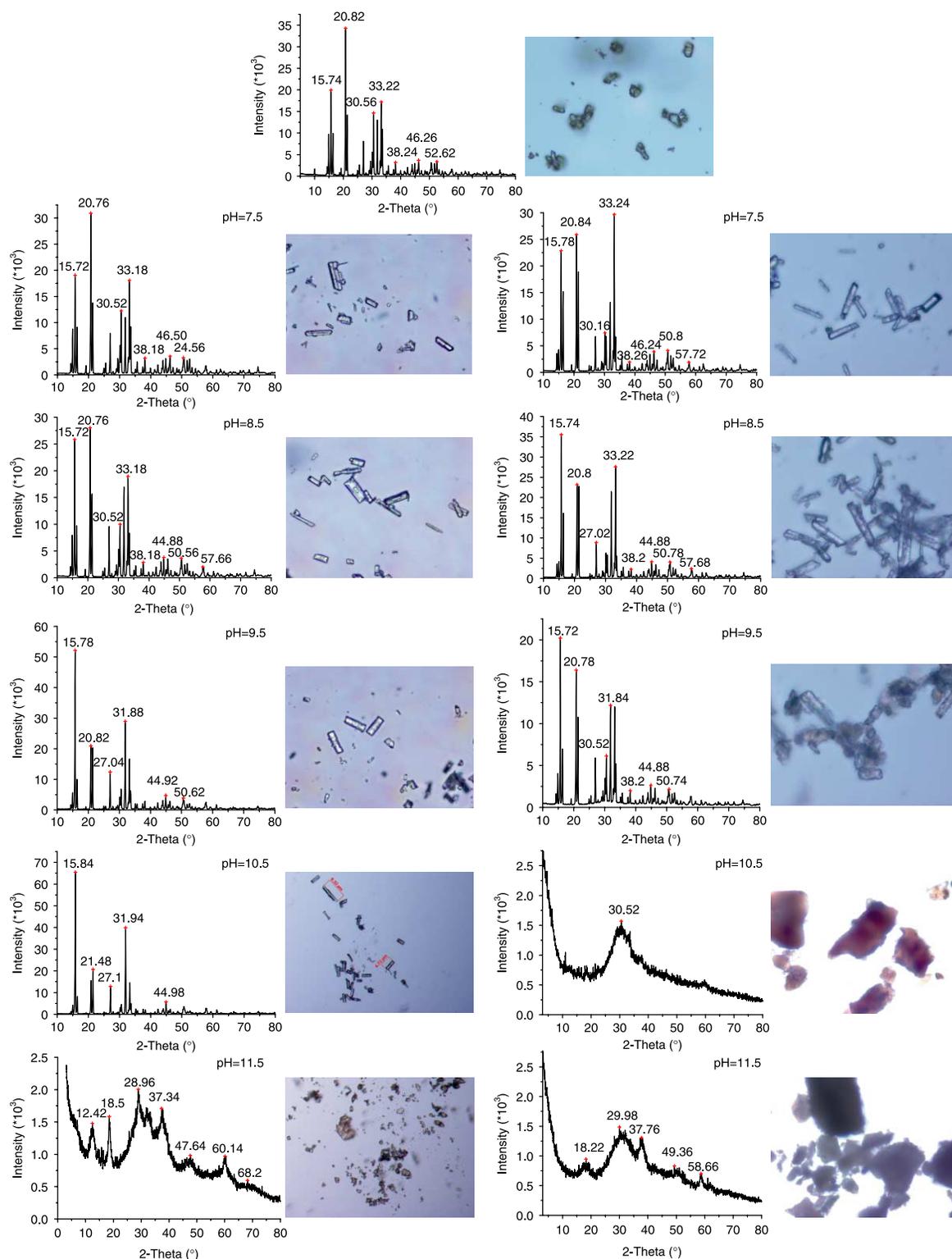


Figure 1 | Impacts of pH on the morphology of struvite crystals formed in the ultra pure water and tap water: XRD and microscopic images.

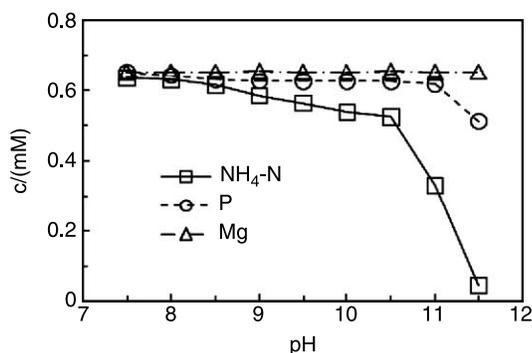


Figure 2 | Element analyses of the dissolved precipitations from the ultra pure water solutions.

to be bound into some impure compounds rather than struvite at the existence of Ca and at higher pHs. For the reason, the N content could become the only reference element to calculate the struvite content in the precipitations. In other words, a mole of N could be equivalent to a mole of struvite due to its molecular formula ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$). Therefore, the struvite content can be calculated as below:

$$\text{Struvite content (\%)} = \frac{n_{\text{nitrogen}} \times M_{\text{struvite}}}{m_{\text{precipitations}}} \times 100\% \quad (3)$$

where, $m_{\text{precipitations}}$ = mass of the precipitations; n_{nitrogen} = molar amounts of nitrogen; M_{struvite} = molar mass of struvite.

The content of the pure struvite purchased from Alfa-Aesar (US) was calculated with Equation 3 at the level of 98.9%, which matches well with the labeled content (99.0%) of the pure struvite. Thus, Equation 3 can be reliably used to determine other struvite contents of the precipitations, and the calculated results are shown in Figure 4.

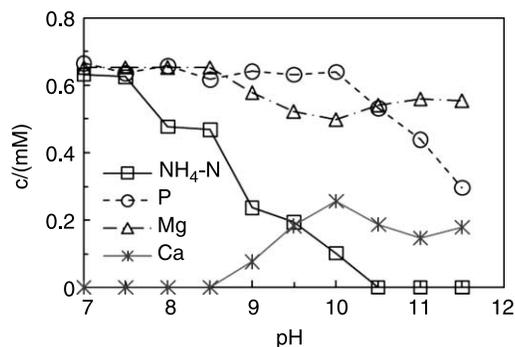


Figure 3 | Element analyses of the dissolved precipitations from the tap water solutions.

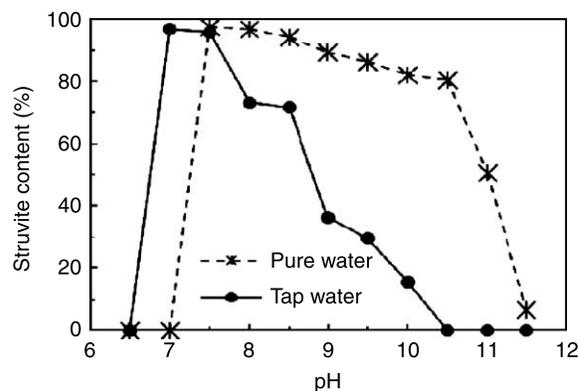


Figure 4 | Impact of pH on the struvite contents in the precipitations.

As shown in Figure 4, the struvite contents in the precipitations from the ultra pure water solutions decreased gradually in the pH range from 7.5 to 10.5, and then decreased sharply at $\text{pH} > 10.5$.

Figure 4 also indicates that the struvite contents in the precipitations from the tap water solutions were controlled not only by pH but also by the Ca content in the original solutions. The struvite contents in the precipitations were 96.8% and 95.7% at $\text{pH} = 7.0$ and 7.5 respectively. At $\text{pH} > 7.5$, the struvite content decreased sharply, up to 15.5% at $\text{pH} = 10.5$. An even higher pH (> 10.5) resulted in the complete disappearance of struvite in the precipitations.

In principle, $\text{CaNH}_4\text{PO}_4 \cdot 7\text{H}_2\text{O}$ is probably formed in precipitations when Ca ion exists in reaction solutions (Takagi *et al.* 1984). If this situation happens, calculating the struvite content based on NH_4^+ -N could result in an error. However, the element analyses in our experiments reveal that no calcium compounds produced at $\text{pH} \leq 8.5$ (Figure 3), which means that the above calculations of the struvite content at ≤ 8.5 are accurate enough. The errors might emerge at $\text{pH} > 8.5$ due to a small amount of $\text{CaNH}_4\text{PO}_4 \cdot 7\text{H}_2\text{O}$.

CONCLUSIONS

Based on the experiments forming struvite and XRD/microscopic images/element analyses, some main points can be concluded as follows.

1. XRD is only a qualitative method to analyze the presence of struvite in the precipitations.
2. The element analyses preceded by a dissolution method could be a quantitatively efficient method to determine the struvite content in the precipitations.
3. The struvite content in the precipitations was controlled by both pH and Ca²⁺ in the original solutions. The optimal pH ranges for the struvite content >90% were found respectively at 7.5 ~ 9.0 for the ultra pure water solutions and at 7.0 ~ 7.5 for the tap water (mainly consisting of ground water) solutions. A high Ca²⁺ content in tap water resulted in more calcium compounds rather than struvite in the precipitations.
4. With real wastewater containing Ca²⁺, it seems difficult to form a relatively pure struvite precipitation at pH 8.0.

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