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Effects of calcium and ferric ions on struvite precipitation: A new assessment based on quantitative X-ray diffraction analysis

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ABSTRACT

The precipitation of struvite ($MgNH_4PO_4 \cdot 6H_2O$) from waste streams has attracted considerable attention due to its potential for recovering phosphorus for fertilization. As struvite is primarily acquired by means of precipitation and crystallization from aqueous solutions, it is important to evaluate the roles of common metal ions, particularly those that are commonly found in wastewater, in the struvite crystallization process. This study was performed to quantitatively evaluate the effects of calcium and ferric ions on struvite crystallization using the Rietveld refinement method, which is based on the analysis of X-ray diffraction data. The results indicate that both calcium and ferric ions significantly inhibit the formation of struvite crystals, and the effects vary under different pH conditions. There was a negative linear correlation between the struvite weight content in the precipitates and the Ca/Mg molar ratio in the initial solution. However, ferric ions were confirmed to be a more efficient inhibitor of struvite crystallization. Ca^{2+} and Fe^{3+} further modified the needle-like struvite into irregular shapes. An unambiguous and quantitative understanding of the effects of foreign ions on struvite crystallization will help to reliably improve the quality of struvite products recovered from wastewater and the control of struvite deposits in water and sludge piping systems.

1. Introduction

Struvite (MAP, $MgNH_4PO_4 \cdot 6H_2O$) crystallization is one of the main mechanisms that can lead to severe clogging problems in the sludge piping systems of many wastewater treatment plants (WWTPs). Struvite was first identified as a crystalline material by Rawn in a study of municipal wastewater digestion problems (Rawn et al., 1939). Since then, pipe blockages due to struvite deposition in wastewater treatment plants have been commonly reported (Pitman et al., 1991; Williams, 1999; Borgerding, 1972), resulting in the need to replace pipework (Ohlinger et al., 1998). However, the formation of struvite is also considered to be a highly promising strategy for recovering phosphorus (P) as a potential slow-release fertilizer. These high-quality struvite materials have been widely tested for their nutrient leaching properties and are considered to be suitable for fertilizer application, particularly in moderately alkaline and acidic soils (Massey et al., 2007). Struvite is a convenient source of nitrogen (N) and P from wastewater, and with the rapid depletion of phosphate rock resources, it could be applied as an ecofertilizer to compete against traditional fertilizers if its crystallization process could be well controlled (Rahman et al., 2014).

The struvite crystallization process includes nucleation and crystal growth processes that are affected by physicochemical factors such as the pH, supersaturation ratio, temperature, and mixing, and by the existence of foreign ions. Among these factors, few studies have focused on the influences of foreign ions on struvite crystallization (Le Corre et al., 2009). Kabdaszli et al. (2006) evaluated the effects of Na^+, SO_4^{2-}, CO_3^{2-}, and Ca^{2+} on the induction time of struvite precipitation. All of the tested ions clearly retarded the struvite crystallization, except for a very minor effect observed for the carbonate ions. Le Corre et al. (2005) undertook a series of struvite precipitation experiments to assess the effect of calcium ions on the struvite shape, crystal size, and purity. The pH was measured during the entire process and was used as an indicator of the struvite formation rate. The purity of struvite was analyzed by energy dispersive X-ray spectroscopy (EDS) to provide a comparison of the elemental distribution. Muryanto and Bayuseno (2014) investigated the struvite crystallization kinetics with interference from Zn^{2+} and Cu^{2+} and found that both ions at ppm levels can

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inhibit the struvite crystallization rate and that Zn^{2+} was a more effective antiscalant for struvite control. In our study, calcium ion was selected to observe its influence on struvite crystallization because calcium is often observed in the wastewater treatment process, particularly in settled sludge liquors (Ca/Mg molar ratio ranging from 1.4 to 3.7) (Parsons et al., 2001). Moerman et al. (2009) reported intensive interference from calcium in the formation of struvite and the phosphorus removal efficiency from pilot- and full-scale agro-industry wastewater. Calcium phosphate precipitation is regarded as another essential route of phosphorus removal and recovery. It is thus crucial to accurately report the composition of products achieved from solutions that contain Ca^{2+} and Mg^{2+}. Iron (Fe) chemicals are commonly used in wastewater treatment for coagulation, flocculation, and removal of phosphorus. In particular, ferric salts have been dosed into sludge anaerobic digestion systems to control the emission of hydrogen sulfide (H_2S) into biogas (Charles et al., 2006; Ge et al., 2012; Gutierrez et al., 2010). Ferric ions are widely known for their effects on crystal growth, such as the alteration of needle-shaped $NH_4H_2PO_4$ crystals into tapered prisms (Mullin, 1972). This method has been used to control struvite scale formation in anaerobic sludge digesters (Mamais et al., 1994). Therefore, this work focuses on calcium and ferric ions as they have a high potential to co-exist in struvite precipitation, which normally involves a combination of enhanced biological phosphorus removal (EBPR) and sludge digestion techniques (Battistoni et al., 2002; Cusick et al., 2014; Musvoto et al., 2000).

Although previous studies have identified various characteristics of struvite products derived from a wide variety of solution compositions, much less work has been done to provide information on the phase composition of struvite-containing precipitates. In this study, the phase compositions of products obtained from P-enriched solutions were directly analyzed by quantitative X-ray diffraction (QXRD) to quantify the effects of calcium and ferric ions on struvite crystallization. Together with scanning electron microscope (SEM) and Raman testing, a scientific understanding of the struvite crystallization mechanism and crystal growth behavior will provide a promising avenue for the effective recovery of quality struvite products from waste streams as a renewable nutrient resource.

2. Materials and methods

2.1. Batch experiments

Analytical grade magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$), ammonium chloride (NH_4Cl), and potassium dihydrogen phosphate (KH_2PO_4) were selected to produce struvite precipitation. The chemicals were dissolved in distilled water to prepare stock solutions at a concentration of 0.1 M. $CaCl_2$ and $FeCl_3$ were used to investigate the influences of calcium and ferric ions on struvite crystallization. In each experiment, 100 mL stock solutions of $MgCl_2$, NH_4Cl, and KH_2PO_4 were agitated in a 600 mL beaker at a fixed rotation speed, with the molar ratio of Mg, N, and P fixed at 1:1:1. For the calcium ion influence experiments, the molar ratios of Ca to Mg were designated as 1:5, 1:3, 1:2, 1:1, 1.25:1, and 2:1, and the experiments were performed under a wide pH range (7.5, 8.0, 9.0, 10.0, and 11.0), which has been suggested as the possible condition for struvite precipitation based on a variety of wastewater-derived sources (Wang et al., 2005). For the ferric ion influence experiments, the Fe^{3+} dosages were designated as 1 ppm, 5 ppm, 100 ppm, 200 ppm, and 372 ppm, with an Fe/Mg molar ratio of 1:5, at two pH values (7.5 and 9.0) due to the limited solubility of ferric compounds in alkaline conditions and strong flocculation properties. The initial pH of the mixture solution was acidic (pH 4.2 ± 0.1), so 1 M NaOH solution was added to adjust the system pH to the designated values. The solutions were agitated for 30 min and allowed to settle for 12 h, followed by filtration of the precipitates through 0.45 μm filters. The precipitates were dried at room temperature for 2 days before the subsequent characterizations. The liquor samples were also collected for the elemental analysis.

2.2. Analytical methods

The precipitates derived from the processes mentioned above were ground into powder and examined by XRD to determine their phase compositions. A Bruker D8 diffractometer (Bruker Co. Ltd.) equipped with a Cu X-ray tube was used to collect the diffraction patterns in step sizes of 0.02°, ranging from 10° to 110° at a 2θ angle. XRD analysis was also used to quantify the phase compositions of the samples using the Rietveld refinement method by fitting the full-profile experimental XRD data with a calculated diffraction pattern (Wiles and Young, 1981; Young, 1993). More specifically, by adding internal standards in known proportions, the absolute abundance of crystalline phases and amorphous phase(s) in a mixed sample can be calculated through intensity fitting of the respective peaks (Guirado et al., 2000). Calcium fluoride (CaF_2) has no overlapping peaks with the studied phases and was chosen as the internal standard due to its high crystallinity. Topas 4-2 software (Bruker, Mannheim, Germany), which is based on the Rietveld refinement method, was used in this work to conduct the phase quantification task. Four reliability index parameters, i.e., the pattern factor (Rp), the weighted pattern factor (Rwp), the expected error (Rexp), and the goodness of fit (GOF), are commonly utilized to evaluate the quality of refinement work. They are defined by the following equations:

$$R_p = \frac{\sum |Y_i(obs) - Y_i(calc)|}{\sum Y_i(obs)} \tag{1}$$

$$R_{wp} = \left\{ \frac{\sum \omega_i [Y_i(obs) - Y_i(calc)]^2}{\sum \omega_i [Y_i(obs)]^2} \right\}^{\frac{1}{2}} \tag{2}$$

$$R_{exp} = \left\{ \frac{\sum N_d - N_p}{\sum \omega_i [Y_i(obs)]^2} \right\}^{\frac{1}{2}} \tag{3}$$

$$GOF = \frac{R_{wp}}{R_{exp}} \tag{4}$$

where $Y_i(obs)$ and $Y_i(calc)$ are the observed and calculated data at data point i, respectively; ω_i is the weighting given to data point i; N_d is the number of data points, and N_p is the number of parameters.

The linear regression analysis of the quantitative data was conducted using ORIGIN software (version 9.0). The morphology of the samples was observed with an SEM (Hitachi S-4800 FEG and LEO 1530 FEG SEM) combined with elemental mapping with an EDS system. The highly amorphous precipitates were also examined by Raman spectroscopy. The Raman spectra were measured on a Renishaw inVia Raman microscope (Renishaw, UK) using a He–Ne laser (633 nm, 17 mW). Phosphorus concentrations in the liquid samples were measured by UV spectrophotometry at 700 nm based on the molybdenum-blue ascorbic acid method. The concentrations of magnesium and calcium ions were determined by inductively coupled plasma–optical emission spectrometry (ICP-OES, Perkin Elmer Optima 8000).