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RESEARCH ARTICLE

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Influence of Citric Acid on Struvite Precipitation

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Struvite ($MgNH_4PO_4 \cdot 6H_2O$) is a mineral deposit which can be commonly crystallized on the surface of process pipes, pumps, and other industrial equipment and hence influence the performance and maintenance cost. However, struvite is also phosphate minerals that can be used as resources in an industrial fertilizer. This paper presents results of study on examining the controlled parameter (chemical additives) on struvite precipitation. $MgCl_2 \cdot 6H_2O$ and $NH_4H_2PO_4$ crystals were separately dissolved in doubly-distilled water to provide the struvite crystallizing solution of 0.03 M. The magnesium chloride and the ammonium dihydrogen phosphate salts would provide the struvite components i.e., Mg^{2+}, NH^{4+} and PO_4^{3-}, respectively. The experiments for struvite crystallization was conducted at ambient temperature of about 30 °C. It was done by mixing the two solutions in a glass beaker with stirring at 400 rpm. The acids were added in ppm amounts: 1.00; 10.00 and 20.00 ppm, respectively. The crystallization process was subsequently evaluated by the induction time through observing the pH reduction over time. It was shown that in all the experiments, the pH decreased over time depending on the parameters investigated. SEM analysis revealed that the struvite crystal has prismatic-shaped morphology. Struvite was the major crystalline phase found in the crystals as confirmed by XRPD Rietveld analysis. This study indicated that the citric acid can be beneficial for the mitigation of struvite scale.

Keywords: Citric Acid/Additives, SEM-EDX Analysis, Struvite, XRPD Rietveld Analysis.

1. INTRODUCTION

Struvite is a mineral deposit which is commonly found on the surface of process pipes, pumps and other industrial equipment.[1, 2] The deposition of struvite may lead to impairing the performance of equipment and increasing the maintenance cost. Such deposition, i.e., scale deposition on process equipment, has become important issues in wastewater treatment units.[1, 3] However, it has been long recognized that struvite can be utilized as fertilizer.[4]

On the other hand, struvite can be a result of biological mineralization in the incidence of urinary tract infection which is caused by urease-producing microorganisms.[5] Consequently, some research has also been directed to obtain a better understanding of struvite crystallization process in human and animal kidneys.[6, 7]

Struvite is a white orthorhombic crystal formed in a solution with a 1:1:1 molar ratio of its forming-components namely $[Mg^{2+}]$, $[NH_4^+]$ and $[PO_4^{3-}]$, according to the following equation:[1]

$$Mg^{2+} + NH_4^+ + HnPO_4^{-3+n} + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O + nH^+ \quad (1)$$

Further, spontaneous precipitation of struvite may be governed by the exceed solubility product of its components in solution, which can be written as follows:

$$[Mg^{2+}][NH_4^+][PO_4^{3-}] > K_{sp} \quad (2)$$

It has been reported that solution pH, supersaturation, temperature, and the presence of foreign ions play an important role in the extent of struvite precipitation and the characteristics of the crystalline solid.[1, 8, 9]

Furthermore, when the ion activities of Mg^{2+}, NH_4^+, and PO_4^{3-} in solution exceed the respective solubility product, spontaneous precipitation of struvite is possible. The extent of struvite precipitation and the characteristics of the precipitating solid depend on the solution pH, supersaturation, temperature, and the presence of foreign ions.

Consequently, extensive research has been carried out with the aim at inhibiting the struvite crystallization in pipelines and other equipment such as processing and/or storage tanks.[10–13] Here, the presence of citrate and phosphocitrate ions in synthetic wastewater has shown to provide a significant inhibitor of struvite formation, i.e., causing changes in size and morphology.[14] It was also found that citric acids were seen as a better inhibitor for struvite than other two carboxylic acids, namely tartaric and malic

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acids acid).[17] The purpose of the present research was to study the influence of citric acids on struvite precipitation. The crystalline product was then characterised using XRPD method for mineral composition and SEM/EDX for morphology and chemical elements.

2. METHODOLOGY

Three analytical grade chemicals (Merck™) were used for the experiments, without further purification, namely $MgCl_2 \cdot 6H_2O$ and $NH_4H_2PO_4$. These crystals were separately dissolved in double-distilled water to provide the struvite crystallizing solution of 0.03 M, which would subsequently provide the ions i.e., Mg^{2+}, NH^{4+} and PO_4^{3-}, respectively. The solutions obtained were filtered thoroughly 0.22 μm filter paper. Prior to every crystallization run, the pH of the solution was adjusted to 9 by drop-wise addition of 0.5 N KOH. The experiments for struvite crystallization was conducted at ambient temperature of about 30 °C. It was done by mixing the two solutions in a glass beaker with stirring at 400 rpm. To investigate the effect of citric acids ($C_6H_8O_7$) on struvite, this acid was added into one of the crystallizing solutions, i.e., the magnesium chloride solution. The acids were added in ppm amounts: 1.00, 10.00 and 20.00 ppm, respectively. The precipitation process was monitored by reducing the pH solution.[9] To assure repeatability, the experiments were performed in duplicate and the average values obtained were used.

2.1. Analytical Methods

The crystalline product was also characterised by X-ray powder diffraction (XRPD) (Philips 1830/40) for mineralogical phase composition. The scan parameters (5–85° 2θ, 0.020 steps, 15 s/step) were recorded. A PC-based search-match program (Philips X'Pert Plus) was employed for identifying possible crystalline phases of precipitates. The crystalline phase obtained by the extensive search match was subsequently validated by the Rietveld full profile fitting analysis available in the program. The parameters refinements of the XRPD data included:
(i) the 2θ° scale zero position,
(ii) the polynomial fitting for the background with six coefficients,
(iii) the phase scale factors,
(iv) the cell parameters,
(v) the peak asymmetry and the peak shape functions,
(vi) the atomic coordinate and anisotropic temperature factors.

The diffraction line widths (FWHM) as a function of tan θ using the known formula of Ref. [10] was adopted for Rietveld calculation while starting values of a, c and u was obtained from the values of measured quartz. The preferred orientation of the minerals present was also refined. The obtained values of the cell parameters and the calculated (wt %) levels of mineralogical phases were calculated by the program.

Elemental composition and morphology of the precipitates were examined by scanning electron microscopy (SEM, JEOL JSM 5200) equipped by EDX. For these examinations, dry-prepared loose particles of the precipitates with different particle sizes below 100 μm were embedded in epoxy on an Al-sample holder. Subsequently, the samples were sputtered with carbon for SEM analysis.

2.2. Thermodynamic Chemical Modeling

To approximate the solution equilibrium was performed by using the Visual MINTEQ software program version 3.0, which providing the predicted outcomes for the solid solubility and speciation of organic solutes produced in the solution. The model of mineral species was predicted by entering input parameters for fixed pH of 9 and a temperature of 30 °C. Consequently, the calculated ions and compound for Mg^{+2}, NH_3, NH_4^+, H_3PO_4, $H_2PO_4^-$, HPO_4^{-2}, PO_4^{-3}, and $MgNH_4PO_4$ was presented. The estimated mineral speciation was then validated by the XRPD Rietveld method.

3. RESULTS AND DISCUSSION

3.1. Kinetic and Growth Rate of Struvite

The decrease in the pH of the solution both in the absence and in the presence of citric acid is shown in Figure 1. As can be seen, in all cases the pH decrease sharply in the first ten minutes of the run. Subsequently, the decrease is gradual and levels off after 70 minutes. During the precipitation process, ions of Mg^{+2}, NH^{4+}, and PO_4^{-3} may form ion complexes, such as NH_3, NH_4^+, H_3PO_4, $H_2PO_4^-$, HPO_4^{-2}, $MgOH^+$, $MgNH_4PO_4$, $MgPO_4^-$, $MgH_2PO_4^+$ and $MgHPO_4$.

The majority of published works related on struvite nucleation were mostly conducted with reaction controlled in aqueous solution at constant temperature and various initial solution pH.[3–19] The supersaturated solution was made at constant temperature and pH.[15–20] Here, the precipitation of struvite occurred due to the liberation of H^+ at the expense of Mg^{2+}, and thus the pH solution reduced. Accordingly, the precipitation rate can be estimated by the increase in $[H^+]$ as demonstrated by the pH decrease.

The rate of the crystallization process was calculated using the pH data obtained, namely the decrease in Mg^{2+} concentrations as crystallization proceeded.[8] The linear form of the modified expression of first-order kinetic model (Fig. 2) as follows:[9]

$$\ln(C - C_{eq}) = -kt + \ln(C - C_0) \qquad (1)$$

where $C = [Mg^{2+}]$ at any time t (molar), C_{eq} $[Mg^{2+}]$ at equilibrium (molar), C_0 = initial $[Mg^{2+}]$ at time zero ($t = 0$) (molar), k = reaction rate constant (h^{-1}), t = crystallization time (min).

The lines of best fit for the experiments are shown in Table I. It can be seen that the lines fit with the first order rate equation, with rate values between 1.75 and 2.31 h^{-1}, which agree with the results of previous studies.[21, 22]

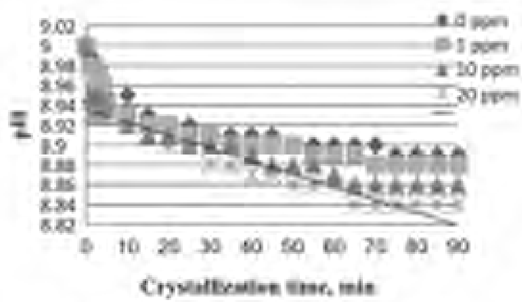

Fig. 1. The decrease in pH level during the crystallization time.

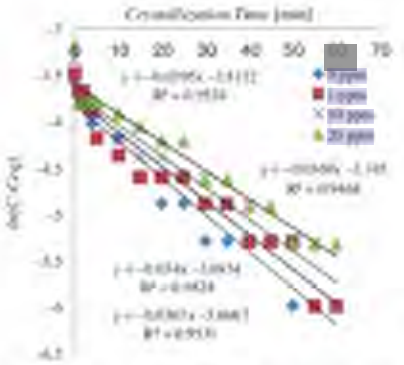

Fig. 2. Curve fitting of calculating (Mg^{2+}) to the first-order kinetic for the effect of citric acid concentrations (0, 1, 10 and 20 ppm) and the initial pH 9.

The increasing amount of additives reduce the rate constants. This effect corresponds to the previous findings on the scaling of gypsum in a piping system using similar organic acids.[24] They found that the growth of gypsum scale was apparently inhibited by the adsorption of the additives used onto the crystal surface. The reduction of reaction rates was manifested in the reduction of crystal growth.[24] Further, the mineral speciation of the precipitate can be predicted using Minteq, where the SI values for farringtonite, struvite, and struvite (K) were above zero in the pH 9. Here struvite and struvite (K) were minerals to be precipitated from the solutions.

3.2. Mineralogical Structure and Crystal Morphology of Precipitate

Initially, the XRPD search-match method identified that the precipitating solid with no additive matched with the PDF#71-2089 for struvite; the PDF#35-0812 for struvite-(K) [$KMgPO_4(6H_2O)$]; and PDF#76-1368 for sylvite (KCl). These identified minerals were subsequently verified by the full profile Rietveld refinement, as the overlapping peaks of phases in the search match or mistakenly assigned phases clearly can be observed in the difference plot of the calculated and the measured diffraction profile.[25,26] XRPD data of the crystalline solids obtained from the solutions with a variety of additive concentrations are shown in Figure 3(a). Each peak had been judged by the full profile Rietveld refinement and labeled with the mineralogical phase name. The XRPD signals provided direct the experimental evidence of the struvite and struvite-(K) minerals formed in the precipitating solid. In particular, the precipitates obtained with no additives showed peaks of sylvite. Sylvite grown in the precipitate could be ascribed to the precipitation of excessive potassium reacted with chloride ions and subsequently formed during the drying samples.

Table 1. First order rate constants for struvite crystallization.

400 rpm, T = 30 °C	Regression equation	Rate constant, (h^{-1})	R^2
0.00 ppm	$y = -0.0385x - 3.8582$	−2.31	0.9528
1.00 ppm	$y = -0.0365x - 3.8155$	−2.19	0.9451
10.00 ppm	$y = -0.0343x - 3.8187$	−2.06	0.9670
20.00 ppm	$y = -0.0291x - 3.8721$	−1.75	0.9762

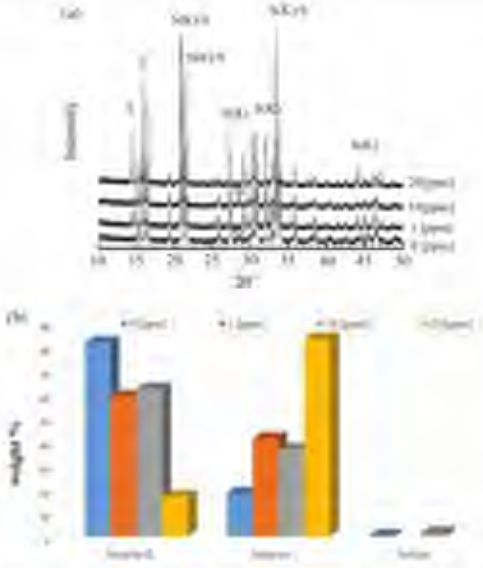

Fig. 3. (a) XRPD data of the crystalline solids obtained was from the solution with a variety of additive concentrations. (b) Quantity of crystals formed into the precipitating solids was evaluated by the XRPD Rietveld method.

The further addition of 1, 10 and 20 ppm citric acids in the solution at the 30 °C, struvite-(K) was found, as can be estimated from the peaks at 20.432 2θ° (PDF#35-0812), in addition to materials of struvite and sylvite. The XRPD pattern of struvite-(K)

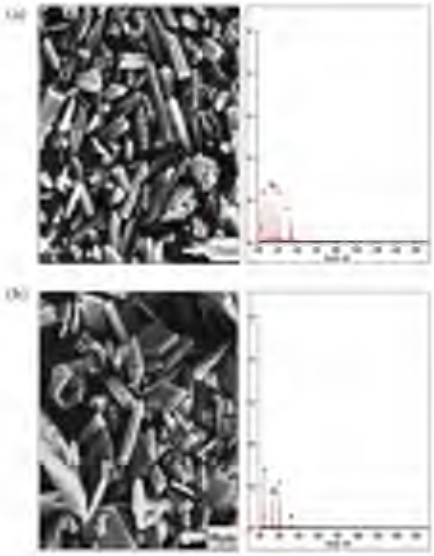

Fig. 4. (a) SEM-EDX image of a prismatic shaped crystal morphology obtained from the solution in the absence of additive; (b) SEM-EDX image of a prismatic shaped crystal morphology released from the solution in the presence of 1 ppm citric acid additive.

was identical and identified a close relationship to the mineral struvite. The patterns of struvite and struvite-(K) are quite similar and overlapped, but the complicated patterns could be practically identified during the XRPD Rietveld analysis.

The quantity of crystals formed into the precipitating solids was evaluated by the XRPD Rietveld method (Fig. 3(b)). In the absence of additive, there is an evidence for the major mineral of the struvite K (81.6 wt.%) and struvite (18.1 wt.%), but the minor minerals of sylvite (0.3 wt.%). A decreased amount of struvite K was observed as a result of the citric acid addition in 1, 10 and 20 ppm, as compared to those in the previous precipitating solids. Here struvite (83.5 wt.%) was the greatest amount of the mineral formed in 20 ppm additive.

Figure 4(a) shows the type of morphology for struvite family crystals precipitated out the solution in the absence of the citric acids at the temperature of 30 °C. The prismatic-shaped crystals about 20 μm in size was noticed, whereas the crystals precipitated in the presence of 1 ppm citric acid exhibited larger size (Fig. 4(b)). Because of the precipitation obstruction in the inhomogeneous crystallite size, some elongated crystals developed, compared with the crystals obtained by spontaneous precipitation in the absence of additives.[14]

4. CONCLUSIONS

It can be concluded that a mixture of struvite and struvite-(K) was the minerals controlling MAP and K ions recovery at 30 °C and initial pH 9. The impurity of sylvite can be formed into some precipitating solids. Struvite-family crystals can be grown from solution of artificial wastewater in the absence and presence of citric acid additives. The increasing amount of additives provided the difference in phase abundance, where struvite-K was the major minerals in the absence of additive, but struvite become major mineral in the presence of 20 ppm citric acid. From the comparison of this result, it can be observed that in the absence of citric acid, the crystals in most cases take the prism-shaped morphology. Moreover, the differences in results were noticed in their sizes due to the increasing amount of citric acid additives.

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