Effect of the Optimized Temperature and pH Solution on the Crystallization of Struvite

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Abstract. A computational model was developed and applied to investigate struvite crystallization with design parameters of temperature 30, 35 and 40°C and pH solution. This study used visual MINTEQ to optimize the operating parameters for controlling crystallization of struvite by the addition of maleic acid in liquid waste. The results showed both struvite and struvite-K minerals were the main minerals that control recovery of Mg²⁺, NH₄⁺, and PO₄³⁻ ions. Ammonium (NH₄⁺) removal was obtained of 55.938% at a temperature of 30°C and pH 9 so that it could be used as fertilizer and reduce the environmental impact. The identification of struvite crystals by the Rietveld XRPD method and irregular prismatic crystal morphology were shown in crystal struvite using SEM-EDX analysis.

Keywords: Maleic acid, Struvite, SEM-EDX, Temperature

1. Introduction
Temperature is one of the factors that can influence struvite crystallization and affect the solubility of struvite and crystal morphology. Struvite solubility products were determined by the radioisotope method, at temperatures between 10-50°C increased from 0.542.10⁻¹⁴ to 3.73.10⁻¹⁴ [1]. Burns and Finlayson obtained the same tendency for measurement of pH and concentration, with increasing solubility is from 0.7.10⁻¹⁴ to 1.45.10⁻¹⁴ at 25°C and 45°C [2]. Because its solubility is associated with crystals can occur in supersaturated solutions, at high temperature the crystals are more difficult to settle. Struvite solubility increases in the temperature range 25-35°C and then decreases at 40°C [3]. Phosphate conversion rates and struvite solubility product values can be proposed using a thermodynamic model based on numerical equilibrium predictions from the study system MgNH₄PO₄·6H₂O in the temperature range of 15-35 °C [4]. Guangan J et al have applied struvite precipitation from anaerobic digester waste in the wastewater treatment plant, its systematic operation parameters can be optimized using Visual MINTEQ chemical-balance model [5]. Temperature can affect struvite crystallization, depending on the parameters chosen. Struvite crystallization can recover large amounts of ammonium from wastewater treatment [6],[3]. Struvite formation process is carried out by reacting Mg²⁺, NH₄⁺, and PO₄³⁻. Struvite is generally a white crystal and struvite crystallization has long been recognized as a fertilizer [6]. Carboxylic acids are weak organic acids and widely used as additives in the crystallization process. In previous studies three types of carboxylic acids (citric
acid, maleic acid and tartaric acid) were used as additives in the process of crystallization of calcium sulfate at concentrations of 0 - 20 ppm. The experimental results show that at the same concentration (20 ppm) citric acid is better than the two other carboxylic acids (maleic acid and tartaric acid) as effective inhibitors of struvite crystal growth even with low molar concentrations [7]. As done by Prisciandaro and colleagues that with low concentrations, citric acid can slow the nucleation of calcium sulfate and its effect is very strong [8]. Previous studies have also shown that citric acid can significantly inhibit the growth of struvite crystals despite the low additive concentration namely at 200 rpm stirrer rotation round with a temperature of 30° C with a maximum growth rate inhibition of 77% [9]. Here, the growth rate of struvite crystals is affected by various parameters as temperature, pH, stirring speed, and additives [10], [11], [9]. Therefore in this research, parameter optimization is used that affects the crystallization process for chemical equilibrium reactions. The purpose of this study is to find an effective crystallization process by influencing temperature, pH of the solution, stirring speed, and additives to struvite crystals.

2. Research methods

2.1 Materials

Struvite crystallization was developed from mixed solutions of magnesium chloride hexahydrate and ammonium phosphate, which were supplied with analytical grade of chemicals (MerckTM). The solution water was prepared in a 500 ml for the mixing MgCl₂.6H₂O and NH₄H₂PO₄. The maleic acid was also used as additives. Then each was pH adjusted to 9 by addition KOH. In this work, the effect of temperature 30, 35, and 40° C, maleic acid concentration 20 ppm, and stirring speed 300 rpm was evaluated. Each stock solution was then separated through a paper filter, and dried in a desiccator at room temperature.

2.2 Analytical methods

Struvite crystal characterization was performed by analyzing the crystal results obtained using the X-ray powder diffraction (XRPD) method to view the mineral phase and using a scanning electron microscope (SEM) equipped with EDX to view morphology and composition.

2.3 Thermodynamic model of chemical equilibrium

MINTEQ version 3.0 visual program is run to prediction of species for chemical composition of the solution [12]. The estimated composition in solution shown as this program (Table 1). Model prediction of species calculated using a pH value of 9 and a temperature of 30, 35, 40° C as input parameters and then confirmed use the Rietveld X-ray powder diffraction (XRPD) method.

| Table 1. Estimated composition in solution |
| No | Ions     | molal  |
|----|----------|--------|
| 1. | Mg⁴⁺     | 0.2040 |
| 2. | NH₄⁺     | 0.3418 |
| 3. | PO₄³⁻    | 0.1829 |
| 4. | K⁺       | 0.2116 |
| 5. | Cl⁻      | 0.0964 |

3. Results and Discussion

3.1 Modeling result

Mineral crystallization was calculated using the MINTEQ program with the values in Table 1. The chemical composition model was calculated in the program with the mineral speciation results listed in Table 2. During the crystallization process, Mg²⁺, NH₄⁺, and PO₄³⁻ can form complex ions MgOH⁺, MgCl⁺, Mg(NH₄)₂²⁺, MgPO₄⁺, MgHPO₄⁺, KH₂PO₄⁺, KPO₄⁻², HPO₄⁻², H₂PO₄⁻, MgPO₄⁻, MgHPO₄⁻, KHPO₄⁻, K₂HPO₄⁻, K₂PO₄⁻, Mg(NH₃)₂²⁺, NH₃ in the system. This complex ion is in accordance with the
findings of previous studies [13]. Figure 1 shows mineral speciation results predicted by Visual MINTEQ calculation. The saturation index (SI) value is presented in this study to estimate the possibility of mineral speciation formation. Therefore for mineral growth and accumulation, positive SI values are needed. As can be seen, the optimized temperature at a specified temperature of 30°C has a positive SI value to obtain struvite crystals. At pH 9, some crystals can form struvite-(K), struvite, MgH\(\text{PO}_4\)\(_2\)H\(_2\)O and Mg\(_3\)\(\text{PO}_4\)\(_2\). The influence of temperature on formation of struvite minerals and others is not very visible. The crystals that are formed are affected by the pH of the solution, the concentration of magnesium and phosphate.

### Table 2. Model prediction of species for chemical composition of the solution

| Component | Species name | % of total concentration (30°C) | % of total concentration (35°C) | % of total concentration (40°C) |
|-----------|--------------|---------------------------------|---------------------------------|---------------------------------|
| Mg\(^{2+}\) | Mg\(^{2+}\) | 16.778                          | 16.488                          | 16.021                          |
| MgOH\(^+\) | MgOH\(^+\)  | 0.089                           | 0.133                           | 0.196                           |
| MgCl\(^-\) | MgCl\(^-\)   | 4.764                           | 4.804                           | 4.840                           |
| Mg(NH\(_3\))\(^+\) | Mg(NH\(_3\))\(^+\) | 0.566                           | 0.759                           | 0.596                           |
| MgPO\(_4\) | MgPO\(_4\)  | 2.611                           | 2.885                           | 3.175                           |
| MgHPO\(_4\) (aq) | MgHPO\(_4\) (aq) | 75.192                         | 74.932                          | 74.632                          |
| KH\(_2\)\(\text{PO}_4\) (aq) | KH\(_2\)\(\text{PO}_4\) (aq) | 0.026                           | 0.027                           | 0.027                           |
| KPO\(_4\) | KPO\(_4\)  | 0.012                           | 0.013                           | 0.015                           |
| HPO\(_4\) | HPO\(_4\)  | 4.756                           | 4.475                           | 4.220                           |
| H\(_2\)PO\(_4\) | H\(_2\)PO\(_4\) | 0.066                           | 0.061                           | 0.056                           |
| MgPO\(_4\) | MgPO\(_4\)  | 2.912                           | 3.217                           | 3.540                           |
| MgHPO\(_4\) (aq) | MgHPO\(_4\) (aq) | 83.845                         | 83.555                          | 83.221                          |
| KHPO\(_4\) | KHPO\(_4\)  | 6.418                           | 6.628                           | 6.838                           |
| K\(_2\)HPO\(_4\) (aq) | K\(_2\)HPO\(_4\) (aq) | 1.951                           | 2.009                           | 2.066                           |
| K\(_2\)PO\(_4\) | K\(_2\)PO\(_4\) | 0.012                           | 0.012                           | 0.012                           |
| NH\(_4\)\(^+\) | NH\(_4\)\(^+\) | 55.875                          | 47.479                          | 39.498                          |
| Mg(NH\(_3\))\(^+\) | Mg(NH\(_3\))\(^+\) | 0.676                           | 0.906                           | 1.141                           |
| NH\(_3\) | NH\(_3\)  | 43.449                          | 51.614                          | 59.360                          |

Figure-1. Mineral speciation results predicted by Visual MINTEQ calculation
3.2 Mineralogical characterization
The results of the analysis of x-ray powder diffraction (XRPD) formed at temperature of 30 and 40°C. These results indicate that peaks of struvite and Struvite-(K) at low intensities were obtained at temperature 30 and 40°C and the mineral can be formed at low concentrations. Furthermore, the comparison of the results of the analysis of phosphate/magnesium concentrations was confirmed using the visual MINTEQ program (Table 2).

![Figure-2. SEM and EDX spectrum at temperature 30°C](image)

Struvite crystal formation at temperature 30°C was obtained using SEM-EDX analysis. Crystal morphology is irregular prismatic, shown as crystals with the addition of additives. The typical form of struvite crystals (Figure 2) [14]. The resulting both struvite and struvite (K) structures can be seen from the presence of K, Mg, N, O, P ions, which are shown by the EDX spectrum in figure 2.

4. Conclusions
Visual MINTEQ was chosen to mineral speciation predicted in solution. Results showed both struvite and struvite-K minerals were the main minerals that control recovery of Mg$^{2+}$, NH$_4^+$, and PO$_4^{3-}$ ions. Ammonium (NH$_4^+$) removal was obtained of 55.938% at a temperature of 30°C and pH 9 so that it could be used as fertilizer and reduce the environmental impact. The identification of struvite crystals by the Rietveld XRPD method and irregular prismatic crystal morphology were shown in crystal struvite using SEM-EDX analysis.

5. References
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