

Analysis of effect Magnesium Ammonium Phosphate (MAP) Concentration on Struvite Morphology in A Vertical Reactor

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Abstract. Struvite was a white crystal known as Magnesium Ammonium Phosphate Hexahydrate ($MgNH_4PO_4 \cdot 6H_2O$). In industry, struvite was found in the pipes crust which the hot fluid through passes. Struvite is often used as fertilizer because it contains phosphate content. The one of benefits of struvite crystals is slow release fertilizer, so it can be more durable, which is good for the growth of the plants. The Precipitation technology is currently one of the most widely applied technologies in struvite formation. The process of forming struvite is carried out by using a vertical reactor. The process started by mixing the equimolar solutions of $MgCl_2$, NH_4OH , and H_3PO_4 with a concentration ratio of 1: 1: 1 and 1: 1: 2. The process was carried out with the condition at the 30°C while the air inlet rate was 1.25 liters/min. The pH of the solution is pH 9 and controlled using NaOH solution. The process was carried out in the steady state condition. Then the solution was filtered and solid was dried at room temperature for 48 hours. From this study, the concentration ratio of 1:1:2 was obtained the best composition of struvite compared to the others ratio. The solid was analyzed by using the SEM-EDX instrument. The morphology of struvite was formed an irregular pyramid-like crystal or commonly referred to as an authorhombic shape.

Keyword: Struvite; Precipitation; SEM-EDX

1. INTRODUCTION

Struvite is an inorganic mineral crystal contain of Mg^{2+} ions, NH_4^+ ions, PO_4^{3-} ions (Iswahyudi, 2013). The Struvite or Magnesium Ammonium Phosphate (MAP) has the chemical formula $MgNH_4PO_4 \cdot 6H_2O$. (Hao et al, 2008). Struvite ($MgNH_4PO_4 \cdot 6H_2O$) also called a white crystal from the reaction between Mg^{2+} , NH_4^+ and PO_4^{3-} ions with a molar ratio of 1: 1: 1. Struvite has a solubility (K_{sp}) value of 7×10^{-14} - 3.89×10^{-10} (Ariyanto et al., 2015, Agrawal et al., 2018; J. R. Buchanan et al., 2013; and R Understanding et al., 2006). Struvite is widely used for plants such as grasses, tree seeds, ornamental plants, vegetables and garden grass as fertilizer and gets good results. Then, struvite also can be a very alternative fertilizer for some crops such as sugar which requires the magnesium content. Mostly, struvite will not damage the plant roots due to the characteristic of struvite which is a slow release fertilizer. Struvite has the following ionic reactions:



The process of forming struvite has been carried out by several researchers, including the formation of struvite used in phosphorus recovery in fluidized bed reactors and mixer reactors (Bhuiyan et al., 2008). In the fluidized bed reactor, there are seed crystals inside the reactor column to help the growth of struvite crystals (Durrant et al., 1999). However, the seed crystals that used in this process can reduce the purity of the product (Le Corre et al., 2009). In a mixer reactor, the struvite crystals formed can stick to the mixer. Increasing the speed of mixing process can be affect to an increase in energy consumption and can breakdown of struvite crystals that are formed due to the collision process between crystals and crystals with the surface of the reactor walls, baffles and impellers (Ariyanto et al., 2014; Frawley et al., 2012).

This study was conducted by using a vertical reactor with the conditions were a volume of 498.75 mL, the height of 50 cm with an outer diameter (OD) of 5 cm and inner diameter (ID) of 2.5 cm. The process of forming struvite was carried out by using the aeration as a mixer in the vertical reactor (Edahwati et al., 2018). Air flow effect the homogeneity in a solution. The more bigger the rate of air used, it can affect to reaches a homogeneous state condition and also affect the process of forming struvite crystals become more faster. Based on (Darmadi, 2014), purpose of the aeration to accelerate the a homogeneous condition and it can effect more faster the forming process struvite crystal. By giving the small air bubbles and letting it go up through the water (air into the water), it can affect the homogeneity condition in a solution.

2. RESEARCH METHODS

Prepare the solutions of $MgCl_2$, NH_4OH , and H_3PO_4 with a concentration ratio of 1: 1: 1 and 1: 1: 2, and the NaOH solution as a pH controller. The instrument of vertical reactors can be seen in **figure 1**. down below :

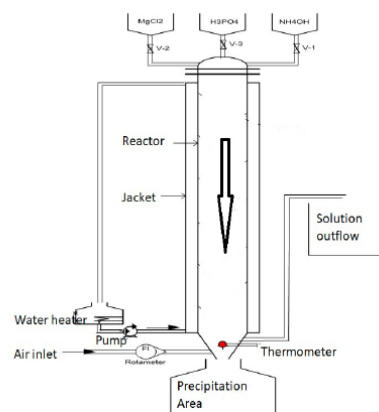


Figure 1. Schematic Diagram of Vertical Reactor

The solution of $MgCl_2$, NH_4OH , and H_3PO_4 was transferred to the reactor approximately $\frac{3}{4}$ of reactor's height. The air flow was fed into the reactor, as a countercurrent flow, with the rate of 1.25 ml/min. A NaOH solution, which used to control the pH around 9, was added. After the pH 9, the aeration process was continued until the condition become steady state. Then, the solution was filtered and the solids were dried at the room temperature for 48 hours. The morphology and composition of the dried struvite were analyzed by using scanning electron microscopy-electron diffraction X-Ray (SEM-EDX).

3. RESULT AND DISCUSSION

The effect of the MAP concentration ratio on the struvite morphology can be shown in **figure 2.** for the molar ratio of 1:1:1 and **figure 3.** for the molar ratio of 1:1:2

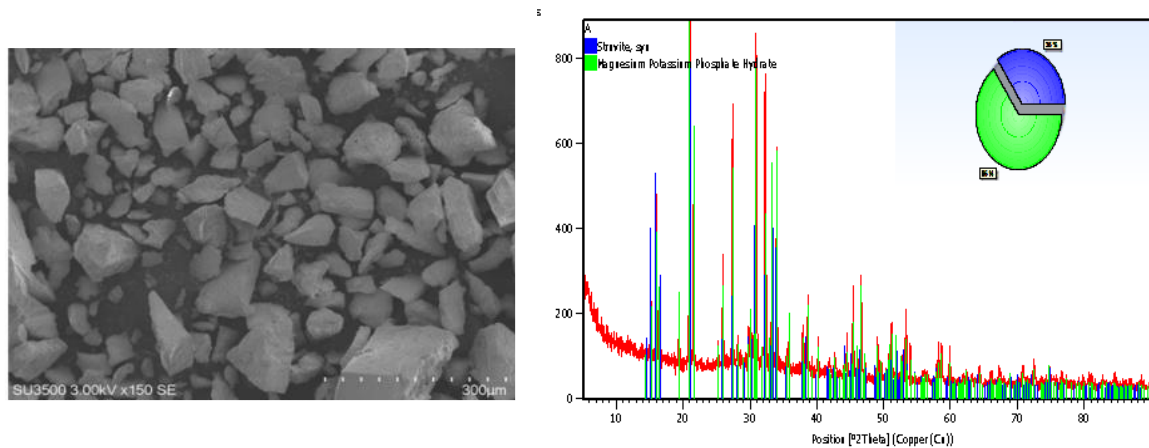


Figure 2. Result of SEM- EDX for molar ratio of 1:1:1

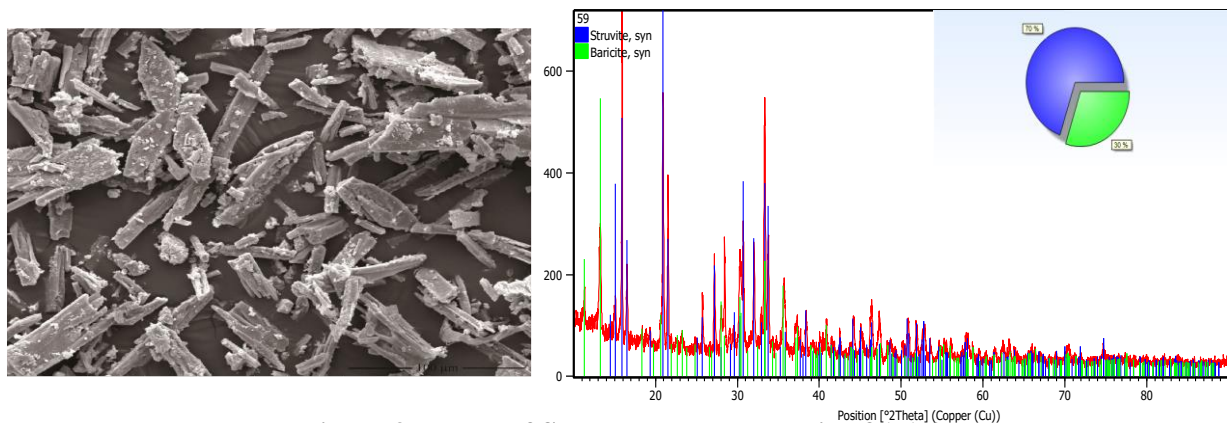


Figure 3. Result of SEM- EDX molar ratio of 1:1:2

Concentration indicates the effect of concentration or substances that play a role in the reaction process. The more bigger the concentration value, the more bigger the value of the reaction rate. This is because the amount of substance is getting bigger and the the opportunity to collision happens getting bigger. So, that effect the reaction rate more faster and the reaction will shift towards the reaction result and the amount of struvite crystals formed was increased.

The molar ratio of reactants, PO_4 and Mg ion is one of the parameters that can affect the process of crystal struvite formation, at the condition of spesific pH, the increasing of the molar ratio of Mg : NH_4 : PO_4 will also increase the degree of saturation to the formation of struvite and will effect the increasing the level of phosphate in the solution. Precipitation of struvite is mainly controlled by such factors as $Mg^{2+}/NH_4^+/PO_4^{3-}$ concentrations, pH and temperature. In the mixed solution, the optimal ratio of Mg: N: P was maintained at 1.2:3:1. Based on Haohhjh, the concentration ratio 1:1:1 can obtain > 90% of struvite content with the optimal pH range at 7.5-9.0.

Table 1. The Analysis Data using XRF Method for concentration ratio of 1: 1: 1

| Composition | Percentage (%) |
|-----------------|----------------|
| Mg | 23.86 |
| NH ₄ | 24.12 |
| PO ₄ | 25.17 |
| Ca | 20.09 |
| K | 6.76 |

Table 2. The Analysis Data using XRF Method for concentration ratio of 1: 1: 2

| Composition | Percentage (%) |
|-----------------|----------------|
| Mg | 26.53 |
| NH ₄ | 24.85 |
| PO ₄ | 36.74 |
| Ca | 9.87 |
| K | 2.01 |

Compare the **Table 1. and Table 2.**, it shows that the quantity of the MAP solution concentration ratio shows a significant effect on the percentage of removal PO₄³⁻. The percentage of PO₄³⁻ removal was obtained 36.74% at the MAP concentration ratio of 1:1:2, while a 25,17% was reached by using the concentration ratio of 1: 1: 1.

From the results of XRF analysis, approximately 70% of the struvite composition (Mg, NH₄ and PO₄) were obtained by using the concentration ratio of 1: 1: 2. The formation of struvite was shown by the formation of peaks on the graph. The peak can be seen a lot on the blue line go across the red line, it shows that the struvite formation occurs.

4. CONCLUSION

The struvite formation process using a vertical reactor and aeration was very important. The struvite, which is formed, has a type of irregular pyramid-like crystal. It is white color or commonly referred to as an orthorhombic shape. Using MAP solution with the concentration ratio of 1: 1: 2 was obtained the highly struvite composition, as well as the phosphate content formed.

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