SYNTHESIS OF STRUVITE USING A VERTICAL CANTED REACTOR WITH CONTINUOUS LAMINAR FLOW PROCESS

S Sutiyono¹, L Edahwati², S Muryanto³, J Jamari⁴, A.P. Bayuseno⁴
¹,²Universitas Pembangunan Nasional “Veteran” JawaTimur, Surabaya
³Department of Chemical Engineering, UNTAG University in Semarang.
³Department of Mechanical Engineering, Diponegoro University, Semarang
²edahwatiluluk@yahoo.co.id
⁴apbayuseno@gmail.com

Abstract. Struvite is a white crystalline that is chemically known as magnesium ammonium phosphorus hexahydrate (MgNH₄PO₄ꞏ6H₂O). It can easily dissolve in acidic conditions and slightly soluble in neutral and alkaline conditions. In industry, struvite forms as a scale deposit on a pipe with hot flow fluid. However, struvite can be used as fertilizer because of its phosphate content. A vertical canted reactor is a promising technology for recovering phosphate levels in wastewater through struvite crystallization. The study was carried out with the vertical canted reactor by mixing an equimolar stock solution of MgCl₂, NH₄OH, and H₃PO₄ in 1: 1: 1 ratio. The crystallization process worked with the flow rate of three stock solution entering the reactor in the range of 16-38 ml/min, the temperature in the reactor is worked on 20°, 30°, and 40 °C, while the incoming air rate is kept constant at 0.25 liters/min. Moreover, pH was maintained at a constant value of 9. The struvite crystallization process run until the steady state was reached. Then, the result of crystal precipitates was filtered and dried at standard temperature room for 48 hours. After that, struvite crystals were stored for the subsequent analysis by Scanning Electron Microscope (SEM) and XRD (X-Ray Diffraction) method. The use of canted reactor provided the high pure struvite with a prismatic crystal morphology.

1. Introduction
Struvite (or MAP) is a type of natural crystal containing magnesium, ammonium, and phosphate. (Elisabeth, 2000). The process of struvite formation is by reacting Mg²⁺, NH₄⁺, PO₄³⁻ corresponds to the general reaction. The reaction of crystalline struvite formation occurs when the concentration of magnesium, ammonium, and phosphorus in solution exceeds solubility product (Ksp) [1].

\[ \text{Mg}^{2+} + \text{NH}_4^+ + \text{PO}_4^{3-} + 6\text{H}_2\text{O} \rightarrow \text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O} \]

In the development of struvite precipitation is much applied to process the dominant waste containing ammonium or phosphate, such as on leachate, industrial flavor wastewater, industrial leather waste, and livestock feed waste, agricultural waste. Struvite precipitation may also be functioned to semiconductor wastewater [12].

The controlled struvite crystallization process is a technology that can be applied to remove phosphorus from sidestreams. The crystallization process is the process of forming solid crystals from a
homogeneous essence solution [12]. There are three components of magnesium, ammonium, and phosphate are the main ingredients in the struvite. Human and animal manure and manure are the two main sources of phosphorus that phosphorus can be recycled.

Struvite minerals can be used as a fertilizer because of its phosphate content contained therein. In addition, these struvite crystals have several benefits when compared with other minerals. One of the advantages is struvite fertilizer classified as slow-release fertilizer [5]. Struvite fertilizers can release the minerals needed by plants slowly, making this struvite fertilizer durable [2]. Struvite can be used as a slow release fertilizer with a high usage level, without the danger of damaging plant roots.

The previous researcher [10] created a continuous flow reactor with three layers of stainless steel mesh wire to provide aeration and settling zones. Struvite is obtained as much as 65 kg for 70 days of operation with an influent rate of 5.3 m³/day. Struvite obtained is ready to be used as a raw material of fertilizer. Moreover, struvite reveals different chemical stability behaviors at higher temperatures (>100°C) when it presents in an excessive water. When struvite is heated at more than 100°C for 24 hours, it will lose some ammonia ions and be partially transformed into bobierite (Mg₃(PO₄)₂.8H₂O) [3].

Further, struvite formation dominates at a pH value greater than 8. The excessive ammonium increases struvite precipitation and provides buffer pH of the solution. When diluted with pure water, the pure struvite is transformed into Mg₃(PO₄)₂, which has the lower solubility but it has a slower precipitation kinetics than struvite [9] [4]. Here, it is an important to improve the struvite production with the pH variation. In the study, the use of a vertical reactor using air as a stirrer was chosen based on the fact that the flow pattern in the reactor determines the reaction product of the solution. By performing a countercurrent process by inserting a synthetic struvite solution from the top of the reactor and the air is bubbled from under the reactor, the reaction becomes more homogenous thus the phosphorus removal outcome will be greater.

1.1 SEM Analysis
Scanning Electron Microscope (SEM) is an electron microscope that draws the surface of the specimen by scanning using high-energy electron rays in scans and raster patterns that attains the sizes detail less than 1 nm. The SEM process begins when the electrons interact with the atoms so that the specimen produces signals containing information about the topography of the specimen's surface, composition, and other characteristics such as electrical conductivity. Because the electron beam is very narrow, the SEM image has the depth that can produce a three-dimensional characteristic display that is useful for knowing the structure of the specimen's surface. SEM enables some magnification, from about 10 times to more than 500,000 magnification times, or about 250 times of the optical microscope's zoom capabilities [6].

1.2 XRD Analysis
XRD Test (X-Ray Diffractometry) is a characteristic tool for the identification of crystal structure, percentage and crystallinity rate of a yield [8]. The XRD measurement results in a graph of diffraction patterns. In addition, there are also diffraction angle values (2 theta), the distance between lattice values (d) and relative intensities of diffraction peaks in percent. [6].

2. Method
A synthetic solution of magnesium ammonium phosphate (MAP) was prepared by a ratio of 1:1:1 molar concentrations. The pH of the solution was varied into 8, 9, and 10 by using KOH solution. The entry of feed rates was set in the range of 16-38 ml/min, while the entry of air rate was kept constantly at 0.25 liters/min.
The crystallization process of struvite formation was carried out in a vertical reactor (as shown above), a bulkhead reactor with a continuous process. The reactor is planned with the volume 498.75 mL, height 50 cm with outer diameter 5 cm; 2.5 cm inner diameter. The inner reactor serves as a site for crystallization. A solution of eqimolar struvite was prepared (= solution A) as well as KOH as a controller of pH (Bsolution). Furthermore, solutions A and B were filled from the top of the reactor by adjusting the inlet of flow rate, after the two solutions reach three-quarters of the column height, the air is inserted from below the column at a certain speed. The process was run until the steady state was achieved. With this reactions that occur in the reactor is expected to form a struvite reaction to be more perfect. After the process was completed, the formed struvite precipitate was filtered and then dried at room temperature for 48 hours. The dried struvite was analysed using SEM equipped EDX for the morphology and chemical elements of the crystal, while the phase composition of the crystal was determined using the XRD Rietveld method.

3. Results and Discussion

The MgNH₄PO₄ solution was prepared by reacting MgCl₂, NH₄OH, and H₃PO₄ with Mg: NH₄: PO₄ ratio of 1: 1: 1 and having Mg 41.6%, NH₄ 7.8% and PO₄ 41.6%. After the struvite crystals were formed under pH 9, struvite crystals were dried at room temperature for XRF (X-Ray Fluorescent) analysis. Below is presented a graph of XRF analysis result at pH 9:

![Graph](image)

Figure 2. The relationship between temperature and phosphate levels produced at pH 9 with a ratio of concentrations of 1: 1: 1

The graph explains the relationship of the temperature effects on the phosphate levels. It is visible at temperatures between 25 and 30 that phosphate levels tend to increase and decrease at 40 OC. Struvite crystals have different behavior at high temperatures with excess water when struvite crystals are heated.
at high temperatures (<100 °C) with excess water for 24 hours, ammonia will disappear gradually, and will become bobierrite. Struvite crystals in excessive water cause in the loss of 5 water molecules and become monohydrate. (Bhuiyan et al., 2007). For feed rate 38 ml/min and temperature 20°C obtained the highest level of phosphate with 37.19%, while rate 16 ml/minute and a temperature of 40°C got PO4 level at least 28.15%.

Figure 3. SEM-EDX result at pH 9 and temperature (a) 20 ; (b) 30 ; and (c) 40 °C with molar ratio 1:1:1

Figure 4. XRD result at pH and temperature 20, 30, and 40 °C with molar ratio 1:1:1
From figure 3 and 4, the crystal struvite formed support by SEM result it proves that crystal struvite is the orthorhombic crystal.

4. Conclusion
The struvite crystallization process is one of the most desirable methods today to reduce waste in the industry. In this process, it is expected that the phosphate content obtained with XRF analysis can be used as a reference for further crystallization of struvite and can be used as raw material for struvite fertilizer. The result of the lowest phosphate content at feed rate was 16 ml/min and temperature 40°C with phosphate 28.15% and the best condition in this study was feed rate 38 ml/min and temperature 20°C with phosphate content of 37.19%. It can be concluded that the effect of incoming feed rate on the phosphate content produced is directly proportional. In this struvite crystallization process has the optimum temperature, those at 20°C has the highest phosphate concentration.

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