Article

Tofu Factory Liquid Waste for Making Struvite with Canted Vertical Reactors

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Abstract. Struvite is a white crystal, chemically known as magnesium ammonium phosphate hexahydrate (MgNH₄PO₄·6H₂O). Tofu factory liquid waste is waste that can be reused because of its content. Tofu factory liquid waste can potentially pollute the environment. This research aims to analyze the manufacture of struvite by utilizing the phosphate content contained in the liquid waste of tofu factories using vertical canted column reactors which can reduce environmental pollution due to liquid waste of tofu factories. This study uses a vertical canted column reactors by mixing an equimolar 1: 1: 1 MgCl₂: NH₄OH: H₃PO₄ solution. Struvite crystallization process operates at a temperature variation of 30°C,35°C,40°C,45.50°C and a pH of 8, 9,10,11,12 by maintaining the air rate of 0.5 liters minute⁻¹ and a MAP (Magnesium Ammonium Phosphate)flow of 56 ml minutes⁻¹ as a whole. The crystallization process runs until a steady state condition is reached. Then, the struvite crystals obtained were filtered and dried at room temperature for 24 hours. After that struvite crystals were analyzed using XRF, XRD, and SEM. The results of the study obtained the best phosphate conversion of 24.935% at 30°C and pH 8.

Keywords: Struvite, vertical canted reactor , Tofu Factory Liquid Waste.
1. Introduction
Tofu factory waste must be recycled. Tofu factory waste consists of two types, namely solid waste and liquid waste. Tofu factory solid waste is obtained from the washing process and by-products in the process of making tofu that is solid and obtained from squeezed soybean pulp. While the liquid waste of the tofu factory is obtained from the process of soaking, washing soybeans, washing the process of tofu production equipment, filtering and pressing or making tofu. Produce, not so much solid waste that occurs (0.3% of soybean raw materials). Tofu waste consists of 25-35% of tofu produced. Tofu factory liquid waste has a variety of organic materials and also found gases such as (O₂), hydrogen sulfide (H₂S), ammonia (NH₃), carbon dioxide (CO₂), and methane (CH₄) [1]. In addition, tofu factory liquid waste also contains nutrients, namely N 1.24%; P₂O₅ 5.54%; K₂O 1.34% and C-organic 5.803% which are essential elements needed by plants [2].

Struvite is a crystal containing magnesium, ammonium, and phosphate. Struvite formation process is carried out by reacting Mg⁡⁺⁺, NH₄⁺, and PO₄³⁻. Struvite has chemical formula that is magnesium ammonium phosphate hexahydrate (MgNH₄PO₄.6H₂O). Struvite formation reaction:

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

Struvite is generally a white crystal. White struvite crystals can’t be found as sludge rather than solids. Struvite can be used as fertilizer. One advantage if struvite is used for fertilizer is struvite fertilizer as a slow-release fertilizer. Struvite fertilizer can release minerals needed by plants, so struvite fertilizer becomes more durable. Struvite can be used as a slow release fertilizer with a high level of use, without the danger of damaging plant roots [4]. The process of forming struvite can be divided into two stages, namely nucleation and growth. Nucleation in struvite occurs when constituent ions combine to form a crystal nucleus. The formation of the crystal core can be formed when the concentrations of magnesium, ammonium, and phosphate exceed the solubility of the resulting product which is expressed by the Ksp value (the solubility product constant). Ksp for struvite ranged from 5.5x10⁻¹⁴ to 2.51x10⁻¹³ [5]. The crystallization process commonly used to recover phosphorus is a fluidized bed reactor [6]. The canted vertical reactor is used instead of the stirred reactor. In this tool there are barriers made of used plastic which are sliced curved and equipped with small teeth along the arch. The teeth are intended as a breaker of large gas bubbles into small pieces. So that, the position of the barriers in the column does not falter and is not easily pushed upward by gusts of gas, then in the middle of the jagged arch a plastic support is mounted and then hot-chained. The second reinforcing rod is patented at the end of the ellipse at an angle of 30° and the third at the junction of the serrations with the first support, with an angle of approximately 70° [7].

2. Material and Method

Fig. 1. Series of vertical canted reactor devices

Information:
A. MA Storage Tank (MgCl₂ + NH₄OH)
B. The MA storage tank overflows
C. Tofu Mill Liquid Waste Storage Tanks
D. Overflow of Tofu Mill Liquid Waste Storage Tank
E. KOH Storage Tank
F. Struvite Overflow Solution Storage Tank
G. Water Storage Tank
H. Electric Cooker
I. Insulated Reactor
J. Pumpkin Neck Three
K. Reactor Jacket
L. Rotarometer
M. Thermo Control
N. Air

The material used is tofu factory liquid waste that has just been taken and not through the
treatment process first. 1N KOH solution is used as a pH adjustment. MgCl₂ and NH₄OH reacted with phosphate-containing waste.

Magnesium ammonium phosphate solution with a ratio of 1: 1 molar is prepared first. KOH solution is used to adjust the pH to fit the desired variable, which is 8, 9, 10, 11, and 12 using 1N KOH solution. Then the MAP flow (MAP solution) will be fed to the reactor with a bevelled column by adjusting the flow rate of 56 ml / min and the air flow of 0.5 L / min.

MAP solution and KOH solution will be fed through the top and then into the reactor inlet. The reactor is planned with the volume 498.75 ml, height 50 cm with outer diameter 5 cm; 2.5 cm inner diameter(figure 1). After that, the two materials are mixed and homogenized with the help of air and a bulkhead inside the reactor. After a steady state has been reached, wait for 5 minutes. The results are in a three neck flask and a struvite overflow storage tank. Then it filtered using filter paper to obtain crystals. Dry and note the crystal weight.

### 3. Results and Discussion

#### 3.1 Tofu’s Factory Liquid Waste

Liquid waste used is the final process of making tofu liquid waste, without any dilution or mixing. Waste used is also not specifically treated first. Tofu mill liquid waste is obtained from tofu-making centers in the area of East Java. In this study used fresh waste. This was chosen so that the characteristics of the waste did not change. Waste used in this study has a yellow color with a sour and sweet odor. In this research, tofu factory liquid waste will replace phosphate in the manufacture of magnesium ammonium phosphate (MAP) solution. The results of the tofu mill liquid waste analysis used are as follows:

| Parameter       | Unit | Test Result |
|-----------------|------|-------------|
| Magnesium (Mg)  | mg/L | 69.98       |
| Phosphate (PO₄³⁻)| mg/L | 190.62      |
| Ammonia free (NH₃-N)| mg/L | 24.65       |

Phosphate content (PO₄³⁻) in wastewater raises problems with the quality of waste such as eutrophication [8]. Eutrophication is an environmental problem caused by waste, besides that in the liquid waste of tofu factory there is also a dangerous NH₄ content if it is just thrown away into the environment.

#### 3.2 The Effect of Temperature on Percent Phosphate Conversion

Temperature can affect the solubility and morphology of struvite. Crystal growth can be influenced by temperature because can affect the relative diffusion rate of crystals and surface integrate. High temperatures in crystallization usually lead to controlled diffusion growth, whereas low temperatures cause controlled surface integrate growth. In addition, the growth rate of crystallization often increases at high temperatures and can affect the size and shape of crystals [9].

The observations in Figure 2 show that after 35°C, percent phosphate conversion has decreased significantly. At a temperature of 30°C and pH 8 struvite has a good percent phosphate conversion that is equal to 24.93%. The increase in temperature will affect the solubility of struvite, if the temperature increases, the solubility also increases. Struvite crystals have different characteristics. It is shown that the higher the temperature, the phosphate conversion also decreases. Struvite crystal have different behaviour 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 bobierite [4].

#### 3.3 The Effect of pH on Percentage Phosphate Conversion

The degree of acidity or pH is an important factor in the formation of struvite. The pH value will affect the solubility of struvite and its thermodynamic properties. An increase in pH can increase the nucelation rate of struvite crystals [10]. Removal of PO₄ in wastewater is influenced by the pH of the solution and further influences the formation of struvite. The increasing solution pH, the more crystalline deposits are formed [8].

To see more clearly the effect of percent phosphate conversion to temperature is illustrated though figure 3.

Observation Results Based on Figure 3, the best phosphate conversion was obtained at a temperature of 30 °C and pH 8 of 24.93%. Shown by graph 4, there was a decrease in phosphate conversion after pH 10, starting from 19.50%; 15.33%; 14.03%. An increase in the pH of the solution from 8-9 results in 80% phosphate recovery efficiency and a decrease occurs when the pH is above 10 [11]. That is because at pH above 10 will tend to form Mg (OH)₂, thereby reducing the availability of Mg ions which can reduce the productivity of struvite crystal formation [3].
3.4. Characteristics of Struvite Crystal Products

Scanning Electron Microscope (SEM) in 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 [4]. The characteristics of struvite crystals were observed using SEM with optimum conditions selected at pH 8 and a temperature of 30°C.

![Graph](image)

**Fig. 2.** Effect of temperature (°C) on percent phosphate conversion with various pH

![Graph](image)

**Fig. 3.** Effect of pH on percent phosphate conversion with various temperatures (°C)

![Images](image)

**Fig. 4.** Struvite form at magnification (a) 150x (b) 500x (c) 1000x (d) 1500x
shown in the figure 4. Pure struvite crystals will have a rod shape with a pointed tip and a clean surface without defects [12]. The results of observation in Figure 4 irregular struvite crystals which mean the struvite crystals obtained are not pure.

XRD Test (X-Ray Diffractometry) is a characteristic tool for the identification of crystal structure, percentage and crystallinity rate of a yield. The XRD measurements result in a graph of diffraction pattern. In addition, there are also diffraction angle values (2 theta), the distance between lattice values and relative intensities of diffraction peaks in percent [4]. XRD analysis was used to determine that the struvite obtained was crystal by showing the peak pattern in the XRD result.

4. Conclusions
The best phosphate conversion in the manufacture of struvite from tofu factory wastewater was obtained at a temperature of 30°C and a pH of 8 that was 24.935% of phosphate. The higher the pH, the percent weight of the phosphate obtained is lower. The higher the temperature, the lower percent of phosphate obtained.

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