Kinetics Analysis of Synthesis Reaction of Struvite With Air-Flow Continuous Vertical Reactors

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Abstract. Kinetics reaction is a knowledge about a rate of chemical reaction. The differential of the reaction rate can be determined from the reactant material or the formed material. The reaction mechanism of a reactor may include a stage of reaction occurring sequentially during the process of converting the reactants into products. In the determination of reaction kinetics, the order of reaction and the rate constant reaction must be recognized. This study was carried out using air as a stirrer as a medium in the vertical reactor for crystallization of struvite. Stirring is one of the important aspects in struvite crystallization process. Struvite crystals or magnesium ammonium phosphate hexahydrates (MgNH₄PO₄•6H₂O) is commonly formed in reversible reactions and can be generated as an orthorhombic crystal. Air is selected as a stirrer on the existing flow pattern in the reactor determining the reaction kinetics of the crystal from the solution. The experimental study was conducted by mixing an equimolar solution of 0.03 M NH₄OH, MgCl₂ and H₃PO₄ with a ratio of 1: 1: 1. The crystallization process of the mixed solution was observed in an inside reactor at the flow rate ranges of 16-38 ml/min and the temperature of 30°C was selected in the study. The air inlet rate was kept constant at 0.25 liters/min. The pH solution was adjusted to be 8, 9 and 10 by dropping wisely of 1 N KOH solution. The crystallization kinetics was examined until the steady state of the reaction was reached. The precipitates were filtered and dried at a temperature for subsequent material characterization, including Scanning Electron Microscope (SEM) and XRD (X-Ray diffraction) method. The results show that higher flow rate leads to less mass of struvite.

1. Introduction
Kinetics reaction is the branch of chemistry that studies about chemical reaction. The differential of the reaction rate can be determined from the reactant material or the formed material. The reaction mechanism of a reactor may include a stage of reaction occurring sequentially during the process of converting the reactants into products. Meanwhile, the rate of chemical reaction is the number of moles of reactants per unit volume in units of time [15]. The kinetic equation of the reaction is divided into two equations i.e the kinetic velocity of the homogeneous reaction and the heterogeneous. In this study, the researchers determined the kinetic’s data using struvite solution. In our body can also form struvite that can harm us. In the body, struvite can be formed naturally in the process of formation of urine. Even struvite that settles in our bodies can lead to a disease that kidney stone disease [5].
According to [11], the experimental observations for struvite precipitation kinetics with different stirrer speeds clearly indicate that the mixing intensity used in this study has an influence on the reaction kinetics constants. This study using the vertical reactor as a crystalline struvite crystal formation’s medium. The crystalline struvite in the present study was formed from synthetic waste comprising MgCl₂, NH₄OH, H₃PO₄ and using KOH as a pH. Researchers tried to find the kinetic of reaction struvite crystals and calculate the reaction constant in the continuous process of crystallization struvite by using the vertical reactor. The precipitates were filtered and dried at a temperature for subsequent material characterization, including Scanning Electron Microscope (SEM) and XRD (X-Ray diffraction) method. The results show that higher flow rate leads to less mass of struvite.

The process of struvite crystals formation by using the crystallization process. Crystallization is the process by which solid particles are formed from the homogeneous phase [4]. The formation of these struvite crystals uses a continuous process. In the previous research [14], struvite forming process has been carried out using continuous flow stirred tank reactor and after Batch Process is done, the result is better than batch process. Then According to previous researchers [7], Mg₂⁺ : NH₄⁺ : PO₄³⁻ influenced in the experiment and speed gradient. According to [12] with different Mg: P ratios indicating that the higher the ratio (in the range 1.0-1.6), the better the struvite formation efficiency. So the kinetics precipitation also influential. Then according to [13], the reaction rate decreases with increasing precipitation time with minimum phosphorus and magnesium concentrations. Kinetics of the struvite crystallization process are influenced by temperature. The struvite solubility product increases as the temperature increases. Moreover, an increase in the reaction temperature causes an increase in the reaction rate parameter. Besides, the kinetics of the struvite reaction are influenced by the pH of the aqueous solution because the availability of struvite ions is affected by pH. [2].

1.1 Type Of Kinetics Reaction
1. Homogeneous Reaction
A homogeneous reaction is a reaction involving a phase reaction mixture. The reaction velocity can be expressed as the volume of the reaction mixture, so mathematically the reaction rate can be written as follows:

\[-r_A = 1/V = dN_A/dt\]

In addition to the speed of the reaction the whole material becomes:

\[-\frac{-r_A}{a} = \frac{-r_B}{b} = \frac{-r_R}{r} = \frac{-r_S}{s}\]

2. Heterogeneous Reactions
Heterogeneous reactions are reactions that involve multiple phases in the reaction. [18].

1.2 Residence Time Of Reactor With Continuous Process
In a continuous process, known as residence time. According to [1]. The theory of residence time relates to how the incoming particle flows through it and leaves a system. It intuitively looks reasonable to expect that not all particles have the same residence time. For constant density, levenspiel shows that:

\[\tau = \frac{Vol}{Q}\]

where:
\[\tau = \text{Residence Time (minute)}\]
\[V = \text{Volume (cc)}\]
\[Q = \text{Debit (cc/minute)}\]

1.3 Crystallisation of Struvite
Struvite is magnesium Ammonium phosphate (MgNH₄PO₄·6H₂O) which usually crystallizes in reversible reactions and produces orthorhombic crystals with Mg²⁺ : NH₄⁺ : PO₄³⁻. [2]. The reaction of struvite formation may be expressed as follows:

\[Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4\cdot6H_2O\]

Struvite occurs spontaneously in solution when the content in Mg²⁺, NH₄⁺ and PO₄⁻ reaches a 1:1:1 molar ratio under specific conditions of pH, temperature, mixing energy and presence of foreign
ions [3]. Although conditions affecting success of P removal and recovery as struvite and their consequences on thermodynamics of precipitation have been widely investigated [11][9], knowledge on kinetics of struvite precipitation, that is to say on rates at which struvite forms, is still limited [10]. Struvite crystallisation can be divided in two major steps: nucleation and crystal growth [6].

2. Method

In this study, researchers use a vertical reactor as a medium for the formation of struvite crystals. Struvite crystals or magnesium ammonium phosphate hexahydrates (MgNH4PO4•6H2O) is commonly formed in reversible reactions and can be generated as an orthorhombic crystal.

Air is selected as a stirrer on the existing flow pattern in the reactor determining the reaction kinetics of the crystal from the solution. The first thing to do is make the Magnesium Ammonium Phosphat (MAP) with the concentration ratio Mg: NH4: PO4 = 1: 1: 1 and KOH 1N solution. Then compile set of tools as attached in Fig. 1. Then fill the reactor vertical with MAP reached the ¾ height of the reactor and KOH to control the pH of the solution. Turn on the stovem with temperature setting 30°C. Set the incoming MAP rate of 15, 20, 25, 30, 40 ml / min and KOH rate. Set the MAP and KOH rates in 1: 2 ratio. Turn on the compressor to drain the air into the reactor, set the air rate to 0.25 ml / min. Collect the mixture of MAP and KOH and measure the pH of mixed MAP and KOH solution to reach pH 8, 9, 10 and wait until 5 minutes. Then collect the result and filter using filter paper. Dry the struvite’s crystal and record the weight of the precipitate. Analyze the sediment.

3. Result and Discussion

3.1 Determine the Order Reaction

The observed variation pH for crystallization struvite during the study was given for pH 8, 9, and 10. The study was carried out at a temperature of 30 °C. After analyzing the struvite crystals, the final concentration of struvite (Ca) is obtained as shown in Table 1. With the variation of pH, the conversion price (Xa) increases with the increase of pH. Then, with the data so that it can be determined the determination of the reactions. it can be seen that the determination of reaction kinetics in this struvite crystal leads to first order.
Table 1. Calculation Order Reaction

| pH | Residence Time (minute) | Temperature (T) 30°C | CA0 (%) | C_A (%) | Xa   | -ln (1-Xa) |
|----|-------------------------|----------------------|---------|---------|------|-----------|
|    | 33.25                   | 0.43609              | 0.41928 | 0.007667 | 0.00769615 |
| 8  | 24.3975                 | 0.43609              | 0.42271 | 0.01591 | 0.01603794 |
| 9  | 19.95                   | 0.43609              | 0.42291 | 0.016391 | 0.0165265  |
|    | 16.625                  | 0.43609              | 0.423   | 0.016607 | 0.01674643 |
|    | 12.46875                | 0.43609              | 0.42395 | 0.01889 | 0.01907084 |
|    | 33.25                   | 0.43609              | 0.4029  | 0.0317  | 0.03221319 |
| 9  | 24.3975                 | 0.43609              | 0.403   | 0.03146 | 0.03196502 |
|    | 19.95                   | 0.43609              | 0.4031  | 0.031219 | 0.03171691 |
|    | 16.625                  | 0.43609              | 0.4032  | 0.030979 | 0.03146887 |
|    | 12.46875                | 0.43609              | 0.40325 | 0.030859 | 0.03134487 |
|    | 33.25                   | 0.43609              | 0.37912 | 0.088851 | 0.09304881 |
| 10 | 24.3975                 | 0.43609              | 0.381   | 0.084333 | 0.08810221 |
|    | 19.95                   | 0.43609              | 0.38275 | 0.080127 | 0.08351955 |
|    | 16.625                  | 0.43609              | 0.385   | 0.074719 | 0.07765825 |
|    | 12.46875                | 0.43609              | 0.38711 | 0.069648 | 0.07219269 |

3.2 Calculated of Order Reaction and Result Scanning electron micrographs (SEM) of struvite

Figure 2. Graphic τ (Residence Time) vs –ln(1-Xa) and Result Scanning electron micrographs (SEM) of struvite at the pH of 8

Figure 3. Graphic τ (Residence Time) vs –ln(1-Xa) and Result Scanning electron micrographs (SEM) of struvite at the pH of 9

Figure 4. Graphic τ (Residence Time) vs –ln(1-Xa) and Result Scanning electron micrographs (SEM) of struvite at the pH of 10

The graphic between τ (residence time) and -ln (1-Xa) shows a straight graph containing R² which the value close to 1 as shown in fig.2, fig.3, and fig.4. This proves that the kinetics of the struvite synthesis reaction follow the order first and with the variation of pH (8,9,10).
Table 2. Calculation % Error

| pH | $R^2$ | R  | Y = k  | t  + | 1/Ca0 | % Kesalahan R |
|----|-------|----|--------|-----|--------|---------------|
| 8  | 0.87625 | 0.93608 | $y = 0.0005$ | x  + | 0.02131 | 6.39%         |
| 9  | 0.96775 | 0.98374 | $y = 0.00004$ | x  + | 0.07775 | 1.62%         |
| 10 | 0.94358 | 0.97138 | $y = 0.00101$ | x  + | 0.10838 | 2.86%         |

While in table 2 we can be obtained data rate reaction constant at each pH is for pH 8 = 0.0005; pH 9 = 0.00004; and pH 10 = 0.00101 and for pH 8, pH 9, pH 10 got percentage of error respectively that is 6.39%; 1.62%; 2.86%. So that has the smallest percent error is at pH 9, where pH 9 is the best conditions for struvite formation.

4. Conclusion
After plotting between $\tau$ (residence time) and -$\ln (1-Xa)$ at the 1st reaction order, a straight graph containing $R^2$ values approaches 1, this proves that the kinetics of the struvite synthesis reaction follow the first order and with the pH variation (8,9,10) obtained the price of% mistake consecutively is 6.39%; 1.62%; 2.86%. It can be concluded that at pH 9 % obtained the smallest error that is equal to 1.62%, so this condition is the best condition in the process of crystalline struvite formation. While the reaction rate constant obtained at the first order of reaction at pH variation (8,9,10) was 0.5.10⁻³, respectively; 0.04.10⁻³; 1.01.10⁻³ min⁻¹. The best results of struvite crystals formed at pH 9. Based on the results of scanning electron micrographs (SEM) analysis at pH 9 obtained a struvite content of 27.85%.

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