Nutrient Recovery from Slaughterhouse Wastewater

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Abstract. Poultry slaughterhouse wastewater commonly contains high concentration of NH₄⁺ and PO₄³⁻. These nutrients can cause eutrophication and unpleasant odor problem if untreated properly. By adding some minerals, the nutrients can be recovered in the form of immiscible powder called struvite. Struvite precipitation process for nutrients recovery from waste sources is beneficial not only providing slow-releasing and high-quality fertilizer but also reducing soil and water pollution from rich-nutrients wastewater. Three parameters in struvite precipitation will be observed in this study which are pH, temperature, and PO₄³⁻/Mg²⁺ molar ratio. The optimum conditions obtained based on the highest removal efficiency of phosphate (99.3%) and ammonium (98.1%) are PO₄³⁻/Mg²⁺ ratio of 1:3; pH of 9.0; and temperature at 30℃. Meanwhile for kinetic study, the temperature increase will reduce the rate constant (k) value, while increasing pH tend to increase k values. The obtained powder of struvite has been confirmed by X-Ray diffraction (XRD) with expected impurity of MgCl₂ due to the excess usage during struvite precipitation process. This study is applicable for wastewater treatment plant which not only treating wastewater but also producing eco-friendly fertilizers.

1. Introduction

Nitrogen (N) and phosphorus (P) are important organic plant nutrients and also used for optimization of animal products. In agricultural sector, P and N play an important role in producing high quality fertilizers. These facts indicate a massive consumption of N and P worldwide and will lead to resource depletion in a short period of time.

Phosphate rock, the major source of P in fertilizer, is a nonrenewable resource, it is estimated that current global reserves will be exhausted in the next 50 to 100 years [1]. This alarming situation for agriculture industry and feeding a fast-growing world population. Thus, P and N recovery from waste sources is necessary.

One the other hand, the increasing demand of chicken meat for human consumption had increase dramatically. This demand requires a vast poultry production chain from chicken farm to slaughterhouses which lead to many sorts of waste including slaughterhouse wastewater. Hence, the treatment of this wastewater should be implemented in order to protect environment and prevent disease outbreak of pathogenic bacteria from animal wastes [2]. In a modern treatment principle, it is essential for not only reduce the pollutant but also recovery the valuable content in the waste stream.

Wastewater rich-in nutrients can be used as the major source for P and N recovery [3]. This nutrient recovery is considered as sustainable agriculture practices to close nutrient cycles [4]. One of common separation method for recovering valuable compound is chemical precipitation in which P and N can be recovered by struvite precipitation [1]. Struvite, a precipitate of phosphate and ammonia with magnesium, has a great potential as a fertilizer and might be a promising P and N source.

Struvite precipitation from wastewater is has multiple benefits by providing slow-releasing fertilizer and also reducing the risk of soil and water pollution [5]. This study is intended to determine the optimum conditions of struvite precipitation by some variables which are pH, temperature and Mg²⁺/PO₄³⁻ molar ratio to find the highest PO₄³⁻ and NH₄⁺ removal efficiency from synthetic poultry wastewater.
slaughterhouse wastewater. Then, kinetic modeling for struvite formation from synthetic wastewater using lab-scale batch experiment is also undertaken.

2. Materials and Methods

2.1. Materials

Poultry slaughterhouse wastewater (PSW) sampling from the wastewater treatment plant were used and analyzed the major content as the reference. The sampling site is located in Agro-Technology Innovation Center (PIAT) Gadjah Mada University. Sodium hydroxide (NaOH analytical grade) was used for pH adjustment. Magnesium chloride (MgCl₂, analytical grade, China), ammonium chloride, NH₄Cl (analytical grade) and potassium dihydrogen phosphate, KH₂PO₄ (analytical grade, Germany) were used as Mg²⁺, NH₄⁺ and PO₄³⁻ sources for preparing synthetic wastewater.

2.2. Methods

Batch precipitation experiment was conducted with the experiment variables including pH, temperature and Mg²⁺:PO₄³⁻ molar ratio with the variation of 7.5, 9 and 10.5 for pH, and 30, 40 and 50°C for temperature, and 1:1, 2:1 and 3:1 for the molar ratio. The batch experiments performed with three-necked round-bottom flask equipped with condenser tube, air pump for air introduction and mixing during struvite precipitation and water bath for heating equipment as shown in Figure 1. The analytical equipment are pH meter, thermometer, Ammonia High Range Portable Photometer (Hanna HI 96733), Phosphate High Range Portable Photometer (Hanna HI 96717), and Magnesium High Range Portable Photometer (Hanna HI 96752).

The slaughterhouse wastewater samples were collected and refrigerated at 4°C to preserve the waste condition. The wastewater samples were initially analysed for pH, temperature, PO₄³⁻, NH₄⁺ and Mg²⁺. The summary of experimental protocol for both synthetic and poultry slaughterhouse wastewater in all conditions was given in Figure 2.

Figure 1. Batch struvite precipitation setup
Figure 2. Flowchart of struvite precipitation experiment.

Efficiency of Phosphate removal is calculated by the following equation:

\[
\% P\ Removal = \frac{[C_{PO_4^{3-}}]_{t=0} - [C_{PO_4^{3-}}]_{t=t}}{[C_{PO_4^{3-}}]_{t=0}} \times 100\%
\]  

(1)

where,

\[
[C_{PO_4^{3-}}]_{t=0} = \text{concentration of PO}_4^{3-} \text{ at } t=0 \text{ (mg/L)}
\]

\[
[C_{PO_4^{3-}}]_{t=t} = \text{concentration of PO}_4^{3-} \text{ at } t=t \text{ (mg/L)}
\]

\[
\% P\ Removal = \text{efficiency of phosphate removal}
\]

Kinetics study was conducted intend to determine the rate constants of the struvite formation in the batch reactor. The following mass balance equations were generated for modelling PO$_4^{3-}$, NH$_4^+$, and Mg$^{2+}$ balance during struvite precipitation process toward the calculation of rate constant using the simulation of parameter fitting using Sums Square of Error (SSE) method of Matlab program.

The general mass balance of each reactants in the batch reactor is as follows,
−k \cdot C_a \cdot C_b \cdot C_c = \frac{dc_i}{dt}  \tag{2}

where,
\begin{align*}
i &= a (\text{PO}_4^{3-}), b (\text{NH}_4^+), c (\text{Mg}^{2+}) \\
C_a, C_b, C_c &= \text{concentration of } \text{PO}_4^{3-}, \text{NH}_4^+, \text{Mg}^{2+} \\
k &= \text{reaction rate constant.}
\end{align*}

In volume-constant batch reactor, the struvite formation can be assumed as second order reaction due to the high concentration of magnesium which leads to very low changes before and after reaction.

3. Results and Discussion

3.1. Effect of pH

In Figure 3, where (1a) represent phosphate (\text{PO}_4^{3-}) removal, and (1b) is for ammonium (\text{NH}_4^+) removal. As a result, the removal of phosphate and ammonium is dramatically increase in the first 20 minute and then remain steady at certain level. The overall removal efficiency of \text{PO}_4^{3-} and \text{NH}_4^+ in solution are significant approximately 80-90%. It is reported that, precipitation of phosphorus is highly dependent on the physical–chemical parameters of the solution, especially pH [8]. Various researchers have found that a higher phosphate and ammonium removal with the increasing of pH. This might emphasize the fact that the solubility of struvite decreases with increasing of pH, thus facilitating higher phosphate and ammonium removal and recovery for a given feed strength. However, the highest of phosphate removal is about 93% at pH of 10.5 and ammonium is around 87% at pH of 9. Further pH increases didn’t show an improvement of the removal efficiency [9] [10] [11]. The increase of pH may lead to the formation of other compounds than struvite [12].

![Figure 3](image)

**Figure 3.** The effect of pH on nutrients removal (1a) Phosphate (\text{PO}_4^{3-}) removal, and (1b) Ammonium (\text{NH}_4^+) removal.

3.2. Effect of temperature

From Figure 4, where (2a) illustrate phosphate (\text{PO}_4^{3-}) removal, and (2b) represent ammonium (\text{NH}_4^+) removal. According to the result, there was no enhancement of the nutrients removal efficiency proportional to the increasing of temperature. The removal efficiency of \text{PO}_4^{3-}, and \text{NH}_4^+ in solution are significantly obtained at the percent of approximately 90% and 80%, respectively. Significantly, the highest removal efficiency of phosphate is 91.9% and the one of ammonium is around 87.9% at the
temperature 30°C. It is indicated as the best condition for struvite precipitation. Thus, the increasing of temperature does not significantly affect to the removal of phosphate and ammonium.

\[ \text{(2a) Temperature, } ^\circ\text{C} \]

\[ \text{(2b) Temperature, } ^\circ\text{C} \]

Figure 4. The effect of temperature on nutrients removal (2a) Phosphate (PO}_{4}^{3-} removal, and (2b) Ammonium (NH}_{4}^{+} removal.

3.3. Effect of Mg^{2+}:PO_{4}^{3-} molar ratio

Nutrients removal with the different molar ratio of phosphate over magnesium ion is presented in Figure 5 where (3a) represent phosphate (PO}_{4}^{3-}) removal, and (3b) is Ammonium (NH}_{4}^{+} removal. It is illustrated the removal efficiency of the phosphate, and ammonium with different molar ratio of PO}_{4}^{3-}/Mg^{2+}.

\[ \text{(3a) Molar Ratio, } \]

\[ \text{(3b) Molar Ratio, } \]

Figure 5. The effect of PO}_{4}^{3-}/Mg^{2+} molar ratio on nutrients removal (3a) Phosphate (PO}_{4}^{3-}) removal, and (3b) Ammonium (NH}_{4}^{+} removal.
In the first 20 minutes, the effectiveness of phosphate and ammonium removal increases dramatically. The high efficiency could be due to the high concentration of all the reactants (phosphate, ammonium and magnesium ions) in the initial stage of the reactor. After that, the efficiency increases slowly and keep remaining stable at a particular efficiency level. Furthermore, the higher PO$_4^{3-}$/Mg$^{2+}$ concentration ratio, the more PO$_4^{3-}$, and NH$_4^+$ removal efficiency which are obtained for more than 90%, respectively. It could be due to the higher reactant concentration that will enhance the reaction rate of struvite precipitation. However, the highest removal of phosphate is 99% and 98% for ammonium removal at 1:3 of PO$_4^{3-}$/Mg$^{2+}$ ratio condition. Thus, it follows the previous findings that the increase of removal proportional to the increasing of molar ratio [$6,7$].

### 3.4. XRD analysis

![XRD analysis](image)

Figure 6. XRD of struvite sample; (4a) ratio 1:1; (4b) temperature 50°C; (4c) ratio 1:3; (4d) pH=10.5 and (4e) reference struvite (JCPDS Card No 1-077-2303).

Obtained powder was analyzed to confirm struvite crystal structure by using XRD. Figure 6 shows the diffraction pattern of the four struvite powder samples with different operating condition and reference struvite pattern. With this, the XRD pattern of (4a) represents the sample of controlled condition which
coded R1:1 and (4b) show the sample within condition of temperature 50°C, coded T50. These two patterns have major peaks at 2-theta (2θ) values of 15.8112°, 21.4497°, 31.9272°, and 32.0247°; 15.8161°, 21.4420°, 31.9197°, and 32.0178°, respectively. Similarly, in for (4c) which represent the sample of condition of ratio 1:3 where coded R1:3) and (4d) show the sample of condition of pH=10.5, coded pH10.5) have major peaks at 2-theta (2θ) values of 15.7933°, 16.4288°, 20.8238°, 21.4286°, 27.0670°, 31.9050°, 32.0033°, and 33.2308°; 15.8785°, 21.5037°, 32.0628°, and 33.2884°, respectively.

In line with the existing database that struvite crystals have major peaks of 2-theta at 16°, 21° and 32° (see Figure 6 (4e)). Thus, these four samples can be confirmed that struvite is obtained because the main diffraction peaks of the struvite standard-exist.

3.5. Kinetic study

Reaction rate constant is determined by simulation of data fitting by Sums Square of Error (SSE) method using equation 2. It is assumed that the reaction rate is first order with respect to each of the reactant except magnesium since its concentration is remain constant as observed by the experiment. Figure 7 (5a and 5b) shows the samples of curve fitting result obtained from the simulation. This curve fitting simulation result is conducted by using a data set of samples with 1:1 molar ratio of PO₄⁻³:Mg²⁺, pH=7.5 and temperature=30°C); where (5a) PO₄⁻³ concentration; and (5b) NH₄⁺ concentration. Since the reactions were done at different operating conditions, there are reaction rate constant variation. The obtained rate constants (k) are listed in Table 1.

![Figure 7](image)

**Figure 7.** Curve fitting simulation result using sample of condition (1:1 of PO₄⁻³:Mg²⁺ molar ratio, pH=7.5 and temperature=30°C); (5a) PO₄⁻³ concentration; (5b) NH₄⁺ concentration.

**Table 1.** The value of reaction rate constant (k) with different parameters.

| Parameters code | Rate constant (k), (L²/mol².s) | SSE          |
|-----------------|-------------------------------|--------------|
| R1:1            | 0.2506                        | 7.2810×10⁻⁵  |
| R1:2            | 0.2940                        | 1.3042×10⁻⁵  |
| R1:3            | 0.2961                        | 2.0538×10⁻⁶  |
| pH7.5           | 0.0408                        | 4.6412×10⁻¹  |
| pH9             | 0.2506                        | 7.2810×10⁻⁵  |
3.6. Nutrients removal from real PSW
Based on the study using synthetic wastewater, both phosphate and ammonium removal are obtained in similar level. Thus, the controlled condition (pH= 9, temperature= 30℃ and 1:1 of PO$_4^{3-}$/Mg$_2^+$ molar ratio) was applied for poultry slaughterhouse wastewater study.

According to Figure 8, the removal of phosphate reaches more than 80% while the removal of ammonium is obtained for about 50% within 30 min of reaction time. The low removal of ammonium is due to the limiting of the phosphate concentration in the wastewater. Thus, to increase the removal percentage of ammonium from wastewater, the addition phosphate is considered but should be in a certain dose to prevent the excess of its present in wastewater for further treatment or deposition in environment.

### Figure 8. Removal efficiency of nutrients (phosphate and ammonium) from poultry slaughterhouse wastewater.

Conclusions
According to the result in each parameter, the highest removal efficiency of phosphate and ammonium are obtained at 3:1 ratio of Mg$_2^+$/PO$_4^{3-}$; pH=9; and temperature 30℃. The result of kinetics parameter (k) is quite diverse due to the different condition. As obtained by the simulation, the reaction rates for pH 7.5 is 0.0408 L$^2$/mol$^2$.s, for 3:1 of Mg$_2^+$:PO$_4^{3-}$ molar ratio provided the reaction rate of 0.2961 L$^2$/mol$^2$.s and at 40℃ provided 0.0541 L$^2$/mol$^2$.s. The struvite formation has been successfully confirmed by X-Ray diffraction (XRD) with some impurity of MgCl$_2$ due to the excess usage during struvite precipitation process.

References
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