

A STUDY ON AMMONIUM NITROGEN REMOVAL IN UREA FERTILIZER PLANT SEWAGE

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Abstract

Struvite, magnesium ammonium phosphate hexahydrated (MAP) ($Mg NH_4 PO_4 \cdot 6H_2O$) is a white inorganic crystalline mineral that can be used as a slow releasing fertilizer. The present study evaluated the feasibility of using bittern as a by-product of salt manufacture, as a low-cost source of magnesium ions, to recover the ammonia from industrial wastewater. A lab-scale study was performed to investigate the efficiency of (MAP) precipitation using bittern at different pHs, from 7–11 at two different molar ratios of $Mg:NH_4:PO_4$ (1:1:1) and (1.6:0.6:1) on synthetic struvite in distilled water. The optimum pH, settling time and solid/liquid ratio have been studied. Application of liquid bittern to industrial wastewater treatment for ammonia removal was confirmed by XRD-spectra diffractograms of precipitate collected after bittern addition with final pH = 9.6 was compared to synthetic standard struvite.

Key Words: *ammonium, crystal, nitrogen, process, removal, struvite, tower, wastewater*

Ammonia stripping tower is commonly used in urea fertilizer plant to reduce levels of ammonium nitrogen concentration in its wastewater. Normally, the tower is equipped with a successive elevation of parallel splash-bars made of a timbered packing material to make wastewater stream into tiny liquid particles. The liquid particles are then allowed in contact with air resulting ammonia to release and reduce ammonium concentration in the liquid phase. However, this method is only efficient when a wastewater that has ammonia contents between 10 to 100 mg/L. For higher ammonia content (more than 100 mg/L), it may be more economical to use alternate techniques, such as steam stripping or biological method. Several methods have

been applied to remove ammonium nitrogen from industrial effluent including natural zeolite, membrane process, and electrodeionization process. Exploration of a cost-effective approach to recover a valuable material from a wastewater can deliver a breakthrough idea in wastewater treatment technology. One of the novel innovations is production of struvite crystal ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$) from waste. Struvite can improve soil fertilities by providing Mg, N, and P as micro and macronutrients. Struvite, as a slow-release fertilizer, has excellent qualities at certain conditions compare with standard fertilizers. Practically, struvite can be recovered from municipal landfill leachate, poultry manure wastewater, or urine. Struvite also can be produced using microbial fuel cells. Recently, struvite has been produce from fertilizer wastewater. This study was conducted by adding $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ molar ratio of 1:1:1, and solution pH of 9.5.

Elimination of ammonium concentration from urea fertilizer plant wastewater through struvite crystal ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$) formation by adding MgCl_2 , KH_2PO_4 , and KOH were studied. This method of elimination has two benefits, namely, reducing ammonium nitrogen content in the wastewater, as well as production of a valuable material (struvite crystal). Struvite is known as a slow-release fertilizer and less soluble. This report presents the ammonium removal efficiencies during struvite formation.

The growth of struvite production under different molar ratios of $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ and solution pH is also discussed. To find the efficiencies and measure the growth rates, lab-scale experiments were conducted in a batch crystallizer-reactor. SEM, XRD, and FTIR observation were also applied to investigate the characteristics of struvite. The reactant molar ratios of $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ of 1.2:1:1, 1:1:1.2, and 4-1:1:1 were evaluated. Each of the molar ratios was treated at the solution pH of 8, 9, and 10. It was found that, the highest ammonium removal efficiency was 94.7% at the molar ratio of 1.2:1:1 and pH of 9. Primarily, the growth rate of struvite formation complied with a first-order kinetic model. The rate constants (k_1) were calculated to be 2.6, 4.3, and 5.0 h^{-1} for solution pH of 8, 9, and 10, respectively. The findings of the study provide suggestion for an alternative sustainable recovery of ammonium nitrogen content in a urea fertilizer plant effluent.

The solution pH and molar ratio of $\text{Mg}^{2+}:\text{PO}_4^{3-}$ have significant factor on the solubility of struvite and ammonium nitrogen removal efficiency. Struvite can be precipitated at a wide range

of pH (from 7.0 to 11.5) and the effective of the ratio was 1:1 or 1.2:1. In the present study, the NH_4^+ -N removal from urea fertilizer plant wastewater to produce struvite crystal was investigated in presence of MgCl_2 , KH_2PO_4 , and KOH at pH (8-10) and $\text{Mg}^{2+}:\text{PO}_4^{3-}$ molar ratio of 1.2:1 and 1:1.2. Moreover, kinetic growth rates of struvite formation were calculated and characteristics of struvite crystal were performed by SEM, XRD, and FTIR.

1. Methodology

The experiment was conducted by using a raw urea fertilizer plant wastewater, MgCl_2 , and KH_2PO_4 . The raw wastewater was collected from a urea fertilizer plant located in Lhokseumawe City, Aceh Province, Indonesia. The wastewater as NH_4^+ contained ammonium nitrogen concentration of 824 ± 470 mg/L and pH was in range of 8.7 to 9.2. Stock solution of MgCl_2 as Mg^{2+} was prepared by dissolving crystals of MgCl_2 in distilled water. Stock solution of KH_2PO_4 as PO_4^{3-} was made in the similar procedure. The solutions were kept individually and mixed before conducting any experiment. KOH solution (1N) was used to adjust the pH of the reactant mixture to the preferred experimental conditions (pH 8, 9, and 10).

The experiment was performed in an erlenmeyer flask (as a batch crystallizer-reactor) of a capacity of 500 ml at room and at 120 rpm. The experiment was carried out for 60 min with 5 min interval sampling time. An amount of 3 ml aliquot of reactant solution was pipetted from the flask at respective sampling period and filtered. Subsequently, the filtered samples (supernatants) were analyzed for residual ammonium nitrogen. The concentration of NH_4^+ -N in the supernatant was analyzed by UV-vis spectrophotometer (Shimadzu UV-1700). The product struvite was filtered, oven dried overnight at 50°C , and weight analysis. The characteristics of struvite product were observed by SEM (JEOL JSM 6510), XRD (Shimadzu XRD 600), and FTIR (Shimadzu IR Prestige21). In order to study the mechanism of struvite formation, the first-order kinetic model was used to the experimental results as per method proposed by Rahman *et al.*, Nelson *et al.* and Quintana *et al.*

2. Results and discussions

2.1 Effect of molar ratio and solution pH

The effects of molar ratios of $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ and solution pH on the ammonium nitrogen

removal are presented in figure 1. The $Mg^{2+}:NH^+:PO^{3-}$ molar ratio of 1.2:1:1, 1:1:1.2, and 1:1:1 is given in figure 1a, figure 1b, and figure 1c, respectively. The ammonium nitrogen concentrations of 533 \pm 10 mg/L in average were applied in the experiments. The decrease of ammonium concentration in solution provides an indication of struvite formation. It was found that, the rate of ammonium reduction in bulk solution reached steady after 30 min in all experiments investigated.

The effect of the addition of excess magnesium concentration to the struvite crystallizer- reactor on the ammonium nitrogen removal is illustrated in figure 1a. During this experiment, the applied concentration of magnesium was 441 \pm 4 mg/L. The result shows that the ammonium removal efficiencies were 87.1%, 94.7%, and 90.6 % for pH of 8, 9, and 10, respectively. Similarly, the influence of the excess addition of phosphate concentration on ammonium removal is given in figure 1b. In this experiment, the added concentration of phosphate was 361 \pm 7 mg/L. It was found that the removal ammonium nitrogen efficiencies were 82.4%, 88.3%, and 86.7% at pH of 8, 9, and 10, respectively. These results demonstrated that the increase of the Mg^{2+} molar ratio from 1 to 1.2 improved the removal ammonium efficiency by 10%. Similar results have been obtained by Rahaman *et al.* The addition of chemical reactants to a waste water to produce struvite would be needed to provide an equimolecular condition of the reactants. Figure 1c provides ammonium removal for the molar ratio of $Mg^{2+}:NH^+:PO^{3-}$ of 1:1:1. The ammonium removal efficiencies were found of 84.6%, 93.8%, and 92.1% for pH of 8, 9, and 10, respectively. Yetilmezsoy and Zengin performed a series experiment and they concluded that the $Mg^{2+}:NH^+:PO^{3-}$ molar ratio of 1:1:1 would be sufficient for the nitrogen removal and struvite precipitation.

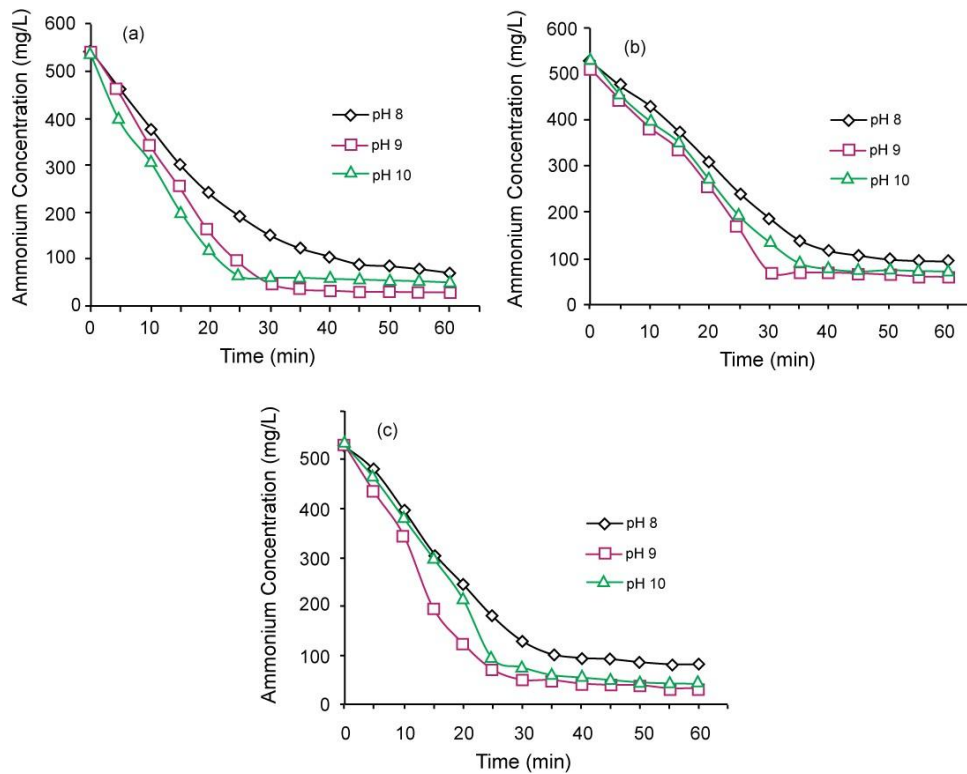


Figure 1. Effect of molar ratio and pH on the ammonium nitrogen removal. The molar ratios of $\text{Mg}:\text{NH}_4:\text{PO}_4$ in a) 1.2:1:1, b) 1:1:1.2, and c) 1:1:1.

Solution pH plays an important role for the removal of nutrient such as nitrogen and phosphorus from solution by struvite precipitation. The results in figure 1 show that solution pH affects the ammonium removal or struvite production. Increasing solution pH from 8 to 9 increased ammonium removal but insignificant upgrade at pH of 10 for all ratio reactants investigated. At the ratio $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ of 1:1:1, for solution pH of 8, ammonium removal efficiency was 84.6%. In addition, for solution pH of 9 and 10, ammonium removal efficiency were 93.8% and 92.1%, respectively. Similar result has been found by Hao *et al.* and Ariyanto *et al.* They mentioned that struvite can be precipitate at a broad range of pH, but the acceptable pH range between 7.5 to 9.0, and growth rate of struvite crystallization increased with an increase in solution pH about 8 to 9.

3.2 Kinetic model

Figure 2 presents the kinetic experimental data by plotting $\ln(C-C_s)$ versus time (t) which shows

a straight line with varied slopes. The correlation coefficients (R^2) between decreased concentration and reaction time were 0.997, 0.980, and 0.970 for solution pH of 8, 9, and 10, respectively. These results demonstrated that the application of first-order kinetic model is suitable for the experimental observation. From the results, it shows that the higher ammonium nitrogen removal efficiency was achieved at higher solution pH. The first-order removal rate constants (k_1) were calculated to be 2.6, 4.3, and 5.0 h^{-1} for solution pH of 8, 9, and 10, respectively. Ariyanto *et al.* investigated the influence of several of physico-chemical process parameters on kinetic of struvite crystallization using artificial wastewater. They obtained the rate constants were 3.7, 5.1, and 6.9 h^{-1} for solution pH of 8, 8.5, and 9, respectively. The presence of Ca^{2+} ion in solution inhibits struvite production by the formation of calcium phosphates.

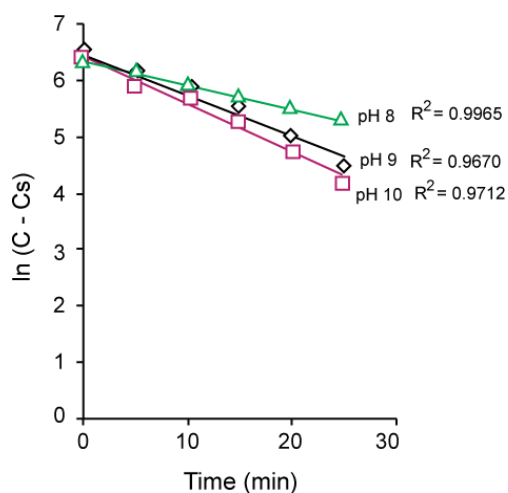


Figure 2. Plot of $\ln(C - C_s)$ versus time at

3.3 Characteristics of struvite crystal

The struvite product from this experiment as shown in figure 3 is white crystalline powder consisting equimolar concentration of magnesium, ammonium, and phosphate combined with six water molecules.



Figure 3. Struvite product from the experiment.

SEM analysis on struvite product (solution pH of 9 and $Mg^{2+}:NH_4^+:PO_4^{3-}$ molar ratio of 1:1:1) is presented in figure 4. The struvite product has a rod-like irregular structure. Similar struvite crystal formation has been reported by Le Corre *et al.* using synthetic liquor in a pilot scale crystallization reactor. XRD was used to analyze the crystal structure of struvite product as shown in figure 5 (left). It is notified that the XRD curve developed from this sample confirmed the database model for struvite particle. The FTIR was applied to examine potential charge and chemical bond of the struvite product. The FTIR spectrum of struvite product is presented in figure 5 (right). The absorption line spectrum appeared at 3589, 2949, and 2901 cm^{-1} are due to O-H, N-H, and NH^+ stretching vibrations.

The weak bands occurring at 2360 cm^{-1} in the spectrum can be confirmed as a result of H-O-H stretching vibrations of water molecules in the struvite crystal. The spectrum emerged around 1688, 1578, 1441 cm^{-1} have been indicated to N-H bending vibration. The stretching of P-OH (hydrophosphate) was confirmed at the spectrum of 1009 cm^{-1} . A medium absorption band at spectrum around 880 and 760 cm^{-1} reveals the oscillation patterns of vibration of the coordinated water and the metal-oxygen bond in the complex.

Similar descriptions of FTIR results of struvite crystal have been described by Chauhan *et al.*, Suguna *et al.* and Ariyanto *et al.* The FTIR spectrum also established that scissoring vibration of PO_4 at about 571 cm^{-1} , NH^+ at around 1441 cm^{-1} , and scissoring vibration of water at close to 1688 cm^{-1} . Therefore, it was confirmed that struvite crystal had been formed, and the result was comparable with the XRD examination.

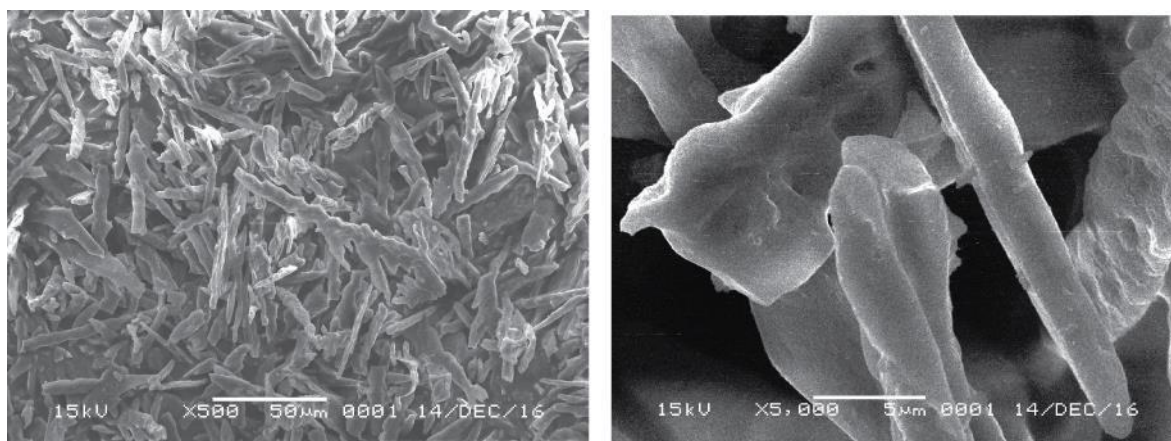


Figure 4. SEM of crystal struvite product.

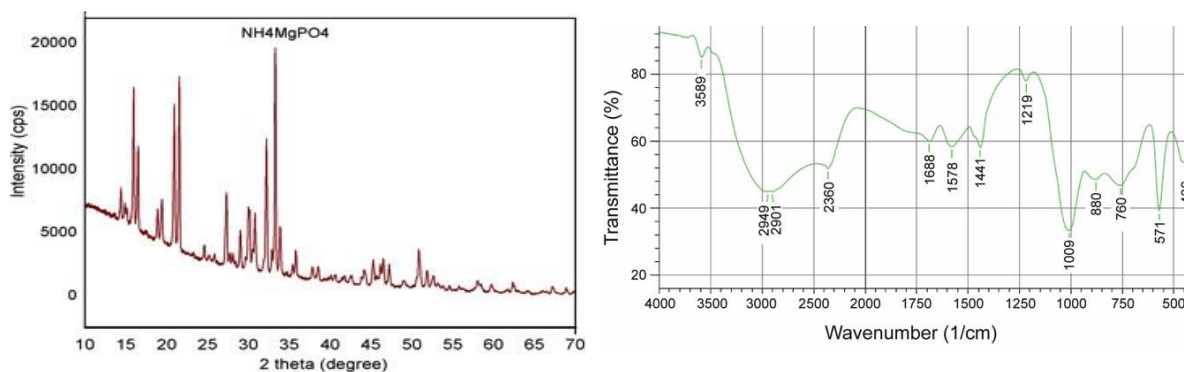


Figure 5. XRD pattern (left) and FTIR spectrum (right) of crystal struvite product.

Conclusion

The struvite crystal as fertilizer material was produced from a raw wastewater of urea fertilizer plant. The raw wastewater as ammonia source reacts with magnesium chloride (Mg^{2+} source) and potassium dihydrogen phosphate (PO^{3-} source) plus potassium hydroxide as pH adjustment to produce the crystal. Based on the result, ammonium nitrogen removal efficiency significantly depends on the molar ratio of $Mg:NH_4:PO_4$ and pH. The highest efficiency (94.7%) achieved at the molar ratio of 1.2:1:1 and pH of 9. The growth of struvite crystal fitted well with the first-order kinetic model. The lower rate constant found in this experiment is probably due to interference by other cations in the wastewater. Analysis of the powdered crystal by using XRD and FTIR confirmed the formation of struvite. This proposed method could be an alternative for the sustainability of urea fertilizer plant wastewater treatment technology through recovery of its ammonium nitrogen content.

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