Article

Recovery of Phosphate and Ammonium from Dairy Cow Urine by Struvite Crystallization with Vertical Reactor

Luluk Edahwati¹,a, Sutiyono¹, Rizqi Rendri Anggriawan¹b

¹Department of Chemical Engineering, Faculty of Engineering, UPN “Veteran” Jawa Timur
Jl. Rungkut Madya No.1, Gn. Anyar, Kec. Gn. Anyar, Surabaya, Indonesia
E-mail: a⁸lulukedahwati@gmail.com, b⁰rrendrianggriawan24@gmail.com

Received: 12th October 2020; Revised: 27th October 2020; Accepted: 30th November 2020;
Available online: 1th December 2020; Published regularly: October 2020.

Abstract

Excess phosphate (PO₄³⁻) and ammonium (NH₄⁺) in wastewater can cause environmental damages, such as pollutants and eutrophication in water. Dairy cow urine is a dangerous liquid waste that contains high amounts of phosphate and ammonium. The removal of PO₄ and NH₄ components can be done by crystallizing them into struvite fertilizers. Struvite (MgNH₄PO₄·6H₂O) is a mineral formed from magnesium, ammonium, and phosphate with the equimolar ratio. The crystallization process of struvite is carried out using a vertical reactor. MAP solution (magnesium ammonium phosphate) is prepared by reacting MgCl₂, H₃PO₄, and dairy cow urine with MAP molar ratio of 1 : 1 : 1 and KOH 1N. The study run in pH 8; 8.5; 9; 9.5; 10 and temperature variations of 25, 30, 35, 40, 45 °C in vertical reactor continuously. The struvite precipitate was filtered and dried, it is analyzed by XRF to determine the struvite composition and SEM to determine the morphology of the struvite. The results showed that the best percentage of phosphate and ammonium was at 45°C and pH 9.5, it was 33.2% and 27.9%.

Keywords: ammonium, phosphate, recovery, struvite, vertical reactors.

1. Introduction

The presence of high amounts of phosphate (PO₄³⁻) and ammonium (NH₄⁺) compounds in wastewater causes serious environmental problems. Ammonium excess is a very dangerous pollutant because it can cause the death of organisms [1]. While the excess of P (phosphorus) or phosphate components causes eutrophication where there is an uncontrolled increase in aquatic plants causing damage to the aquatic system [2]. One example of waste that contains high concentrations of phosphate and ammonium is dairy cow urine [3]. Dairy cow urine is the residual liquid from feed that has been digested and metabolized by the cow’s body. Cow urine contains nitrogen, sulphur, phosphate, ammonium, sodium, manganese, iron, silica, chlorine, magnesium, calcium, minerals, lactose, enzymes, hormones and acids. The composition of cow urine is almost same as human urine [4]. From its nutritional aspect, cow urine has a higher nutrient content compared to its solid feces [5]. Ammonium and phosphate content is large enough to make cow urine can be used as fertilizer struvite.

Struvite is a mineral formed from magnesium, ammonium, and phosphate with the equimolar ratio. The molecular formula of struvite is MgNH₄PO₄·6H₂O (magnesium ammonium phosphate hexahydrate). Struvite has morphology like orthorhombic crystal. Struvite is a white crystal, it can be shaped like a plate, but the shape can be either round or dendrite. Struvite dissolves slowly in neutral water. The ability of slow release struvite is used to substitute urea fertilizer which has side effects on deteriorating soil quality. Struvite crystals can
form if concentrations of magnesium, ammonium, and phosphate in solution exceed the solubility product (Ksp). Struvite formation reaction [6]:

\[
\text{Mg}^{2+} + \text{NH}_4^+ + \text{PO}_4^{3-} + 6\text{H}_2\text{O} \rightarrow \text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O} \quad (1)
\]

This crystallization can convert MAP solutions into struvite crystals and be used as fertilizer for plants. Struvite crystals formation through nucleation first. The crystal core will grow larger until it reaches a stable size. The process of making struvite by crystallization is a raw material in the form of waste containing one of the struvite-forming elements that is collected before being reacted. Then the waste is mixed with reactants containing other struvite-forming elements, flowed into the crystallization reactor. After mixing into a solution in the crystallization reactor in the flow of the aeration process, a struvite crystal will settle under the crystallization reactor section [7].

\[
\text{pH} \text{ is an important factor in the formation of struvite and the process of crystallization. An increase in pH causes more deposition to form due to strong and perfect ionic bonds because the activity of the NH}_3 \text{ and PO}_4^3- \text{ ions is influenced by pH. The increase of pH in solution is directly proportionally to the removal of ammonium and phosphate} \ [8]. \text{ The addition of excess magnesium can increase removal efficiency in this process, but also can reduce the purity of struvite formed} \ [9]. \text{ In addition, the aeration process is used to release or dissolved ammonium from solution. The air flow dilutes the NH}_4^+ \text{ gas phase concentration and increases the driving force to dissolve NH}_4^+ \text{ to separate the gas phase} \ [10]. \text{ The crystallization process using a stirred reactor is also not profitable because the struvite crystals formed will adhere to and stick to the stirrer so that the resulting product can be reduced. In addition, adhering to the product on the mixer can inhibit the movement of the mixer so that the mixer rotates more slowly. Research on the formation of struvite using an aeration process can remove a maximum of 83.7% of phosphate} \ [7].
\]

2. Material and Method

---

Dairy cow urine containing high amounts of ammonium so it can be used as ammonium source. Magnesium chloride (MgCl\(_2\)) as magnesium source, phosphoric acid (H\(_3\)PO\(_4\)) as phosphate source, and potassium hydroxide (KOH) solution is used as a pH controller.

A vertical reactor shown in Figure 1 is used for the crystallization process of struvite formation. The reactor is approved with volume 498.75 mL, height 50 cm with outer diameter 5 cm; inner diameter 2.5 cm. In this reactor, air is
used as a stirrer on the flow that is in the vertical reactor, so that MAP solution (Magnesium Ammonium Phosphate) that is in the reactor can be homogeneous.

MAP solution (Magnesium Ammonium Phosphate) is made by comparison of concentration ratios Mg: NH₄: PO₄ = 1: 1: 1 and KOH concentration of 1N. The reactor is filled with ¾ the reactor volume. Turn on the compressor to drain the air into the reactor. After the process was steady state, the struvite precipitate was filtered and dried. Record the weight and analysed using XRF and SEM.

3. Results and Discussion

Dairy cow urine is taken from a farm in Pasuruan, East Java. Cow urine has yellow to light brown color with a non-pungent odor. The results of the urine analysis are as follows:

| Parameter         | Unit | Test Result |
|-------------------|------|-------------|
| Magnesium (Mg)    | mg/kg| 170.57      |
| Ammonium (NH₄)    | mg/kg| 430         |
| Phosphate (PO₄)   | mg/kg| 100         |

Table 1. Dairy Cow Urine Analysis Results

It is known that the phosphate content in wastewater that exceeds quality standards can result in eutrophication. Eutrophication is an environmental problem caused by waste [11]. Besides that in the dairy cow urine, there is ammonium content if just dumped into the environment cause hazardous and damages.

3.1. The Effect of Temperature on Phosphate and Ammonium Content

Temperature can affect the solubility and morphology of struvite. High temperatures in crystallization usually cause controlled diffusion growth, while low temperatures cause integrated surface growth. In addition the growth rate of crystallization often increases at high temperatures and can affect the size and shape of the crystals [11].

In the graph shown by Figure 2, it can be explained that the percentage phosphate component for pH 8; 8.5; 9; 9.5; and 10 tends to increase at the temperature of 40°C and has decrease at the temperature of 45°C. It has been because the solubility product (Ksp) increases at high temperature. Most studies usually used a process temperatures from 25 to 35°C [12]. In addition, phosphorus removal efficiency increased from 63% to 78% when temperature increased from 5 to 50°C [13]. Its in line with this study, where at temperatures of 25 to 40°C resulting in an increase the efficiency of phosphate removal. Whereas at temperature of 45°C there is a decrease in phosphate removal.

![Fig. 2. Effect of temperature (°C) on phosphate content (%) in various pH](image-url)
Ammonium components are presented in Figure 3. With increasing temperature from 25 to 40°C, the percentage of ammonium increases to a peak at 40°C then decreases at 45°C. This is in line with the temperature recommendations in the formation of struvite and ammonium removal. The recommended temperature for removing ammonia from struvite is between 25 and 40°C. Because the heating of struvite was carried out in the sealed condition, most of the ammonia was possibly changed into NH₃ species [14].

3.2. The Effect of pH on Phosphate and Ammonium Content

pH is an important factor in the formation of struvite and the process of crystallization. Struvite precipitation potential significantly increases due to its solubility and decreases with the increasing of pH. Increase in pH produces higher nuclei population densities that might be the cause of producing smaller crystals. The struvite content decreased to around < 30-70% at over pH 9.5 [15]. Both of percentage ammonium and phosphate component in struvite, indicating that the higher of pH value occur an increase of the percentage component. Meanwhile, the peak of crystal growth in this study was at pH 9.5 and began to decline at pH 10 as presented in Figure 4 and Figure 5. At pH 10, the crystal nucleation may dominate the crystal growth of struvite, ultimately resulting in smaller crystals [16].

3.3. Morphologies of Struvite from Diary Cow Urine

Morphological characteristics of struvite were observed using by scanning electron microscopy (SEM). SEM draws the surface of struvite so that the morphological form of struvite can be enlarged resolution [15]. The results of observations using SEM at pH 9 are shown in Figure 6 at 700x magnification.
In theory, it is stated that struvite has a shape like an orthorhombic crystal or rod shape [10]. In this observation, the morphological shape of struvite is rod shape with a part of the rod line that is not sharp. But there is a few struvite in Figure 6 has irregular shape which mean the struvite obtained an impurities or other mineral formed during the crystallization [10].

4. Conclusions

The best percentage of phosphate and ammonium components in the struvite crystallization from dairy cow urine was obtained at temperature of 45°C and pH of 9.5, that was 33.2% phosphate and 27.9% ammonium.

Acknowledgement

The authors wish to express our gratitude to University of Pembangunan Nasional “Veteran” Jawa Timur for supporting this research programs.

References

[1] H. A. Aka, Suhendrayatna, and Syaubari, “Penurunan Kadar Amonia Dalam Limbah Cair Oleh Tanaman Air Typha Latifolia (Tanaman Obor),” J. Ilmu Kebencanaan, vol. 4, no. 3, pp. 72–75, 2017.
[2] B. Liu, A. Giannis, J. Zhang, V. W. Chang, and J. Wang, “Chemosphere Characterization of induced struvite formation from source-separated urine using seawater and brine as magnesium sources,” Chemosphere, vol. 93, no. 11, pp. 2738–2747, 2013.
[3] C. W. Purnomo, N. P. Kusumawardhani, and Y. N. Marpaung, “Phosphate recovery from dairy urine by struvite crystallization Phoshide Recovery From Dairy Urine By Struvite Crystallization,” in The 3rd International Seminar on Chemistry, 2018.
[4] H. Gulhan, A. Nakanekar, N. Mahakal, S. Bhople, and A. Salunke, “Gomutra (Cow Urine): a Multidimensional Drug Review Article,” Int. J. Res. Ayurveda Pharm., vol. 8, no. 5, pp. 1–6, 2017.
[5] V. N. Sari, M. Same, and Y. Parapasan, “Pengaruh Konsentrasi dan Lama Fermentasi Urin Sapi sebagai Pupuk Cair pada Pertumbuhan Bibit Karet (Hevea brasiensis Muell. Arg.),” J. Agro Ind. Perkeb., vol. 5, no. 1, p. 57, 2017.
[6] M. I. Ali and Rajshahi, Struvite crystallization from nutrient rich wastewater., no. July. 2005.
[7] E. Ariyanto, A. Melani, and T. Anggraini, “Penyisihan PO4 Dalam air Limbah Rumah Sakit Untuk Produksi Pupuk Struvite,” Jurnal.Ftumj, pp. 1–8, 2015.
[8] Iswahyudi, L. K. Muharrami, and Supriyanto, “Pengolahan Limbah Garam (Bittern) menjadi Struvite dengan Pengontrolan pH,” in Seminar Nasional: Menggagas Kebangkitan Komoditas Unggulan Lokal Pertanian dan Kelantan Fakultas Pertanian Universitas Trunojoyo Madura, 2013, pp. 708–715.
[9] W. P. dan I. W. Iswarani, “Recovery Fosfat dan Amonium Menggunakan Teknik Presipitasi Struvite,” J. Tok. ITS, vol. 7, no. 1, pp. 7–9, 2018.
[10] L. Edahwati, Sutiyono, N. Zahra, and H. Septiani, “Magnesium Recovery of Struvite Formation Based on Waste Salts (Bittern) with a Bulkhead Reactor,” Int. J. Eco-Innovation Sci. Eng., vol. 1, no. 01, pp. 1–5, 2020.
[11] Sutiyono, Lukul edahwati, K. Pratiwi, and A. Fanani, “Tofu Factory Liquid Waste for Making Struvite with Canted Vertical Reactors,” Int. J. Eco-Innovation Sci. Eng., vol. 1, no. 01, pp. 13–17, 2020.
[12] D. Crutchik and J. M. Garrido, “Kinetics of
the reversible reaction of struvite crystallisation,” *Chemosphere*, vol. 154, pp. 567–572, 2016.

[13] S. H. Lee, B. H. Yoo, S. J. Lim, T. H. Kim, S. K. Kim, and J. Y. Kim, “Development and validation of an equilibrium model for struvite formation with calcium co-precipitation,” *J. Cryst. Growth*, vol. 372, pp. 129–137, 2013.

[14] A. P. Bayuseno and W. W. Schmahl, “Thermal decomposition of struvite in water: qualitative and quantitative mineralogy analysis,” *Environ. Technol. (United Kingdom)*, vol. 0, no. 0, pp. 1–7, 2019.

[15] M. M. Rahman, M. A. M. Salleh, U. Rashid, A. Ahsan, M. M. Hossain, and C. S. Ra, “Production of slow release crystal fertilizer from wastewaters through struvite crystallization - A review,” *Arab. J. Chem.*, vol. 7, no. 1, pp. 139–155, 2014.

[16] K. Suzuki et al., “Removal and recovery of phosphorous from swine wastewater by demonstration crystallization reactor and struvite accumulation device,” *Bioresour. Technol.*, vol. 98, no. 8, pp. 1573–1578, 2007.