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Struvite Crystallization for Ammonium Removal from Cow Urine with Bulkhead Reactor

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ABSTRAK

Kandungan amonium dalam limbah urine sapi dapat merusak ekosistem perairan karena toksisitasnya. Kandungan amonium dapat dikurangi dengan menghilangkannya melalui kristalisasi struvite. Pada penelitian ini, struvite ($MgNH_4PO_4.6H_2O$) terbentuk dari reaksi senyawa magnesium, amonium, dan fosfat yang dijalankan menggunakan reaktor kolom bersekat. Laju udara menggerakkan larutan di dalam reaktor menyebabkan amonium bereaksi dengan reaktan membentuk struvite. Penelitian ini dilakukan untuk mendapatkan kondisi penurunan amonium terbaik pada limbah urine sapi. Penelitian berjalan dengan perbandingan molar larutan M: A: P (magnesium amonium fosfat) 3 : 1 : 1 dan laju aliran udara 0,4 L / menit dengan variasi laju aliran MAP 8,8; 11; 14,67; 22; 44 ml / menit dan variasi suhu 25, 35, 45, 55, 65˚C untuk menurunkan kandungan amonium. Semakin cepat laju aliran MAP, semakin rendah efisiensi penurunan amonium. Efisiensi penurunan amonium akan meningkat dengan meningkatnya suhu. Hasil terbaik yang diperoleh dalam penelitian ini adalah penurunan amonium pada limbah sebesar 77,97%. Hasil difraksi serbuk sinar-X (XRD) dan scanning electron microscope (SEM) adalah kristal yang diuji berupa struvite berbentuk batang atau memanjang. Analisis EDAX memberikan hasil persentase komponen pada struvite yaitu 14,28% Mg, 10,68% N, dan 18,19% P.

Kata kunci**:** urine sapi, struvite, penghilangan amonium

ABSTRACT

The presence of ammonium content in cow urine waste damages the aquatic ecosystem due to its toxicity. Ammonium content can be reduced by removing it through struvite crystallization. In this study, struvite ($MgNH_4PO_4.6H_2O$) was formed from the reaction of magnesium, ammonium, and phosphate compounds using a bulkhead reactor. The rate of air moving the solution in the reactor causes ammonium to react with reactants to form struvite. This research was conducted with M : A : P (magnesium ammonium phosphate) molar ratio solution is 3 : 1 : 1 and 0,4 L/min air flow rate with MAP flow rate variation of 8,8; 11; 14,67; 22; 44 ml/min and a temperature variation of 25, 35, 45, 55, 65˚C to decrease ammonium content. The faster the MAP flow rate, the lower the ammonium removal efficiency. The efficiency of ammonium removal will increase with increasing temperature. The best results obtained in this study were ammonium removal in the waste of 77.97%. The result of x-ray powder diffraction (XRD) and scanning electron microscope (SEM) is the crystals tested was a struvite with elongated or rod shape. EDAX analysis gave the percentage of components in struvite, namely 14.28% Mg, 10.68% N, and 18.19% P.

Keywords**:** cow urine, struvite, ammonium removal

1. INTRODUCTION

In Indonesia, cow are one of the most popular strategic livestock commodities in food security [1]. So it is not surprising that large amounts of waste are generated. In one day, each cow can produce 100-150 liters of liquid waste where this waste has not been managed properly, especially the urine. As a result of the waste from livestock activities to the environment will have a negative impact on public health, let alone the waste entering public waters where people use these waters for various needs of their daily life [2]. The content of cow urine is very complex, but the most disturbing and must be reduced levels is ammonium content. The presence of

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ammonium can cause damage to aquatic ecosystems because it is toxic so that it can cause the death of organisms [3].

The way to reduce the ammonium content in cow urine is to react it into struvite. Struvite ($MgNH_4PO_4.6H_2O$) is a crystalline mineral containing magnesium, ammonium, and phosphate compounds in an equimolar amount, struvite has potential to be used as fertilizer [4]. Struvite is generally a white crystal and the morphology is orthorombic with shapes such as rods, plates, and dendrites. The process of forming struvite crystals is carried out by crystallization, where in the formation of struvite crystals there will be a process of crystal nucleation and crystal growth. The crystallization process of struvite is influenced by several factors, such as temperature, pH, and solubility of the substance, stirring, also impurities in the solution [5]. This crystallization method can convert the struvite liquid into a solid that can be used for plant fertilizer. Struvite has the advantage of being a non-soluble fertilizer or commonly known as a slow release fertilizer. Struvite has three components in one crystal and these three components are needed by plants in general to meet their daily needs [6]. Struvite crystals are formed from the following reaction [7] :

$$Mg^{2+} + NH_4^{+} + PO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4.6H_2O$$

Struvite can be formed through a crystallization process. Crystallization is a process in which particles are formed from a homogeneous phase. Separation by crystallization technique is based on the release of the solvent from the solute in a homogeneous mixture or solution, so that crystals form the solute. Crystal formation is a complex process of solute purification (liquid or solid) which leads to a solid phase made of ordinary structures. Although the process is complex in which compounds are formed in crystals with thermodynamic equilibrium from solid-liquid and solid, the phenomenon of mass transfer between solid and liquid phases [8].

The formation of crystals is divided into two stages, namely nucleation and crystal growth. Nucleation occurs due to the joining of several molecules to form clusters. Nucleation occurs in systems where there is no crystal content [9]. Next is the crystal growth stage. The crystals will grow larger in size. If the crystal size is bigger, the solubility level will be smaller [10]. So that struvite crystals are formed when the concentration of magnesium, ammonium, and phosphate in the solution exceeds the solubility product [11].

The parameters of struvite formation include temperature, pH, molar ratio, and others. The effect of temperature is not too significant in the formation of struvite because temperature will affect the solubility of the struvite. The solubility product will increases with increasing the temperature. However temperature can have a clear effect on either ammonium or phosphate removal. Phosphate removal increased efficiently from 63% to 78% when the temperature increased from 15 to 35˚C [12]. The heating process causes the ammonium compound in the solution to change its phase to ammonia gas. pH is related to the level of solubility and saturation. The solubility of struvite can be reduced from 3000 mg/L to less than 100 mg/L for pH 5 to 7.5 [8]. The increase in pH causes the formation of more sediment layers due to the presence of strong and perfect ionic bonds because the activity of NH_3 and PO_4 ions is influenced by pH. By controlling the pH, it was found that the crystal solids weight increased [13]. The higher the pH value, the smaller the ammonium residual or the increase in ammonium removal efficiency. The addition of excess magnesium can increase the efficiency of removal in this process, but can also reduce the purity of the struvite formed. The greater the molar ratio, the higher the ammonium removal efficiency. The highest ammonium removal efficiency was in the ratio Mg: NH_4: PO_4 (MAP) which was 3: 1: 1 [14].

2. METHODS

2.1. Materials

The waste used is cow urine from farms in Balongpanggang, Gresik. The contents of the waste are shown in Tabel 1. In the formation of struvite, magnesium chloride ($MgCl_2$), phosphoric acid (H_3PO_4), and potassium hydroxide (KOH) are needed.

Table 1. The content of cow urine

Parameter	Unit	Test Result
Magnesium (Mg)	mg/L	107.71
Ammonium (NH4)	mg/L	4580.98
Phospate (PO_4)	mg/L	17

2.2. Methods

A bulkhead reactor as can be seen in Figure 1 is used for removing ammonium content of the waste by struvite crystallization . The reactor is designed with volume 498,75 mL. The reactor used air as agitator on the flow known as aeration process. The purpose of this process is to release ammonium from the waste [15]. The reactor operated with counter current flow, which the air will enter through the bottom of the reactor while the feed enters through the top of the reactor. Large air bubbles will be resize by the bulkhead in the reactor so that the size of the air bubbles is more uniform and made stirring process is more homogeneous. The heating process occurs in the reactor caused by heated water entering through the jacket of reactor.

MAP solution was prepared by mixing $MgCl_2$, cow urine, and H_3PO_4 with comparison of molar ratio (MAP) which was 3: 1: 1 and KOH 1N. MAP and KOH solution was entered into the reactor with various flowrates and temperatures. The airflow into the reactor is 0,4 L/min and 25˚C. The MAP solution was heated to 25˚C, 35˚C, 45˚C, 55˚C, and 65˚C. During the process, the temperature is controlled according to the variables using a thermocontrol that has a sensor. The sensor is installed in the hose where the solution comes out. Both of solution will react each other and struvite crystallization occurs until pH 9. The solution that came out was analyzed by spectrophotometric analysis to determine the ammonium content. The obtained struvite deposits were analyzed by XRD analysis for a qualitative of the sediment tested and SEM-EDX to determine the morphological form and contents in it.

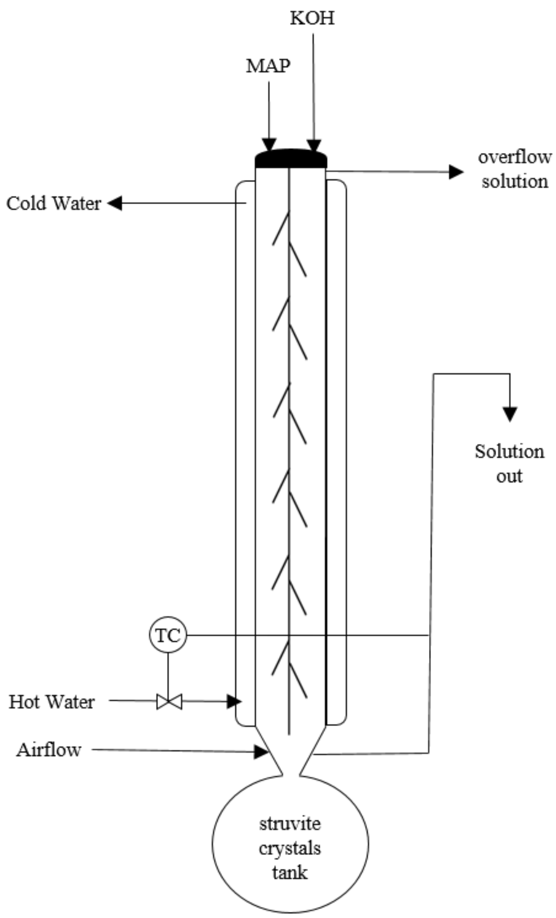

Figure 1. The design of bulkhead reactor

3. RESULTS AND DISCUSSION

3.1 Effect of MAP flow rate and temperature on ammonium removal (%)

Based on Figure 2, a graph of the relationship between MAP flow rate and ammonium removal at various temperatures is obtained. The results obtained were that the faster the

MAP flow rate resulted in the smaller ammonium removal.

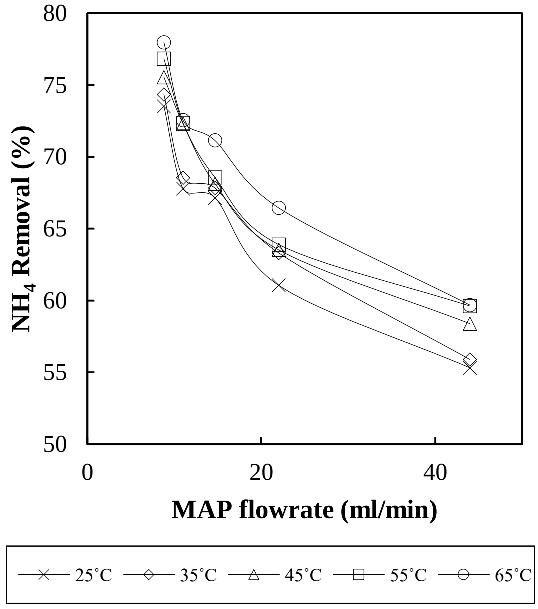

Figure 2. Effect of MAP flowrate on ammonium removal with various temperatures

This is because the MAP flow rate is inversely proportional to the residence time of the solution in the reactor. At a higher flow rate, the time for the solution in the reactor to stay faster to get out. The minimal contact time between the MAP solution and the KOH solution results in the ammonium compound in the MAP solution not converting completely to struvite [16]. The ammonium removal process cannot be maximized if the crystallization process of the formation of struvite does not occur in a longer time. The longer time gives the reactants the opportunity to react to one another.

The components of magnesium, ammonium, and phosphate will react with each other to form struvite. Excess magnesium is intended so that the phosphate and ammonium can react completely [17]. The unreacted compounds will exit the reactor. Some of the ammonium will be pushed by air and transformed into ammonia gas. However, this still does not remove ammonium completely because the large MAP flow rate causes the ammonium to be less converted. Based on Figure 2, the best ammonium removal was obtained at a flow rate of 8.8 ml/min and temperature of 65˚C.

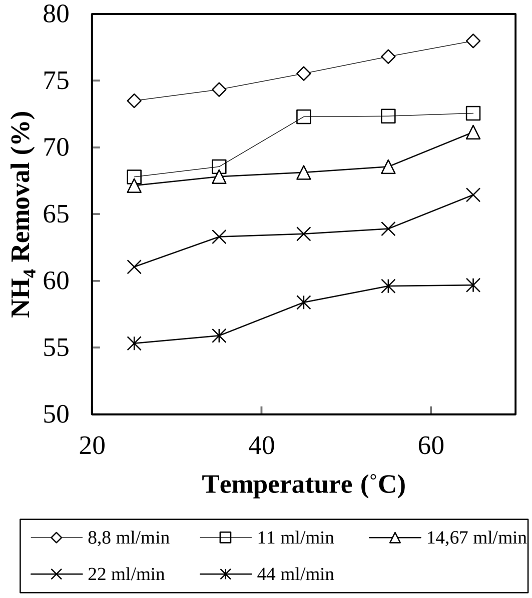

Figure 3. Effect of temperature on ammonium removal with various MAP flowrates

Based on Figure 3, a graph of the relationship between temperature and ammonium removal conversion is obtained in various MAP flow rates. The result is that the ammonium removal will increase with increasing temperature. As for each temperature, the smallest flow rate is able to remove the ammonium content in the waste better than the large flow rate, as previously explained. Temperature has an effect on ammonium removal, where the efficiency of ammonium removal can be greater if it is done at high temperatures [18]. The heating process in closed conditions causes ammonium to transform into ammonia gas (NH_3) [19]. Air will transport ammonia to be released to the top of the reactor column [20]. In this study, the best ammonium removal efficiency was obtained at a temperature of 65˚C to reach 77.97%. In another study, removal of ammonium by the struvite crystallization method resulted in a removal of almost 90% over the range of temperatures studied (25˚C-40˚C) in two step process [21]. Actually, this process in principle also incorporates the ammonia stripping process. With the combination of struvite crystallization and air as stirring, it is hoped that it can reduce the ammonium content in the waste so that the waste is safely disposed of in the environment. However, the waste disposal standard in Indonesia for quality standards for waste based on ammonium content (Permen LHK Nomor 68 Tahun 2016) is 10 mg/l. While the smallest ammonium content in this study was 1009 mg/l.

To reduce the ammonium content according to quality standards, it is necessary to recycle the solution feed so that ammonium that has not been converted to struvite can be drastically reduced in waste. In a five step process, NH_4 decreases initially at 92% and gradually decreased to 77% in the fifth step. The removal of NH_4 is decreased because a portion of the MAP solution has reacted previously at the initial step of the reaction. To get clean waste from ammonium, it is necessary to have a feed recycle stage and an appropriate MAP molar ratio at each step [22].

There are limitations when the recycle process is carried out on this reactor. In fact, this reactor works continuously. There is a need for further development of bulkhead reactors, for example the addition of a second reactor column after the solution has been discharged to the first column of the reactor or other relevant options can be applied to this reactor.

3.2 XRD and SEM-EDX analysis

The morphological characteristics of the struvite were observed using a scanning electron microscope (SEM). While the qualitative composition of the crystals can be identified by the XRD analysis method [23]. The results of the XRD analysis at a feed flow rate of 8.8 ml/min and a temperature of 65˚C are shown in Figure 4.

It can be explained that the struvite material has been formed. This is evidenced by the presence of a graphic peak (struvite diffraction pattern, Figure 4b) while the graphic peak is a diffraction pattern of the precipitate being tested (Figure 4a). The peaks in each struvite diffraction pattern have been filled by the peaks of the tested precipitate diffraction pattern. However, there were several peaks in the two diffraction patterns that did not match. The reason is that the tested sediment is not completely pure struvite, the tested sediment still contains other minerals that were formed during the crystallization process. The level of purity of the struvite is also determined from the condition of the materials used, the type of waste, and other parameters. The condition of the waste is initially brownish yellow and there are other complex contents in cow urine waste. This is what makes the resulting struvite impure.

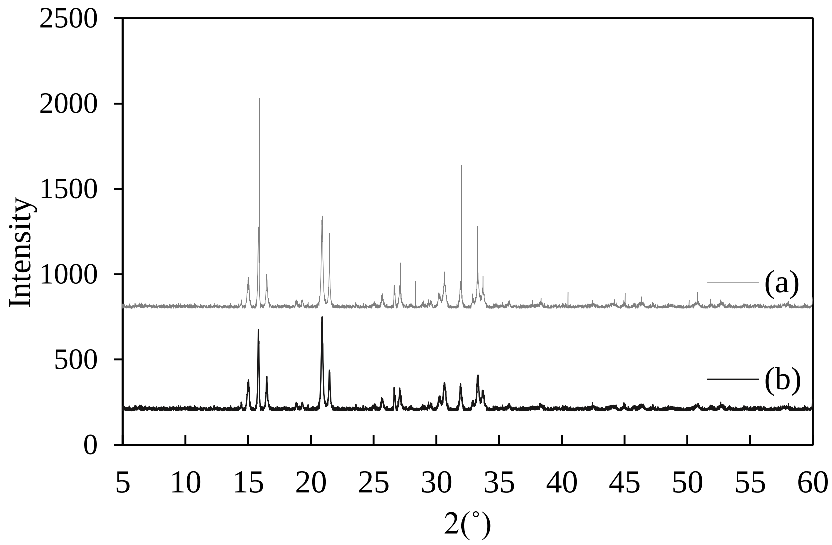

Figure 4. XRD (x-ray powder diffraction) analysis of (a) research result (b) struvite

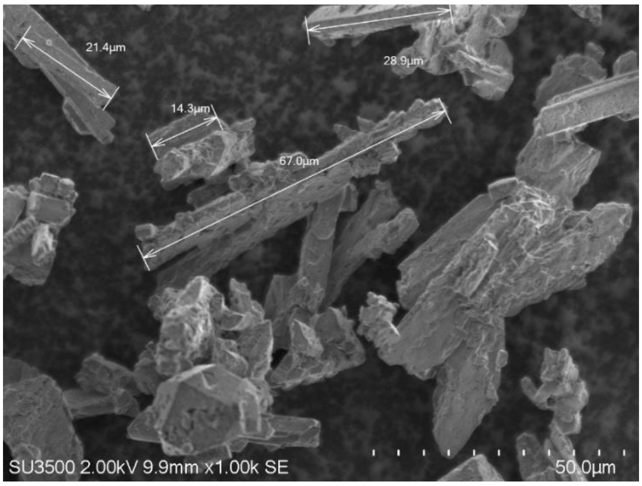

Figure 5. SEM analysis results

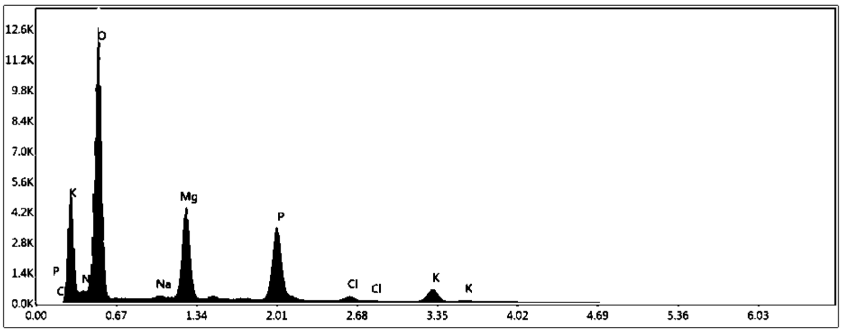

Figure 6. EDAX analysis of the powdered struvite crystallized

Figure 6 and Table 2 shows the existence of other components in the resulting struvite. The results of observations using SEM in Figure 5 were carried out with a magnification of 1000x. In theory, it is stated that struvite has a morphology such as orthorhombic crystals or a rod shape [24]. In this observation, struvite is rod-shaped with irregular ends, where the struvite still contains impurities or other minerals that were formed during the crystallization process [15].

Table 2. Analysis of struvite content under study

Component	% atom	% weight
Mg	11.35	14.28
N	14.74	10.68
P	11.35	18.19
O	157.74	47.79
Na	0.61	0.73
Cl	0.87	1.6
K	3.33	6.74

The elements sodium, chloride, and potassium have a small percentage, but these three elements are bound to the compounds that make up struvite. The resulting struvite has grade C according to SNI 02-3776-2005 with a minimum phosphate content of 14%. The struvite tested found P content of 18.19% by weight. With the presence of Mg and N content, plants can grow better.

4. CONCLUSIONS

The removal of ammonium by struvite crystallization with MAP ratio of 3: 1: 1 using bulkhead reactor obtained the best removal efficiency of 77.97% at the test point MAP flow rate 8.8 ml/min and temperature 65˚C, so that the process of reducing ammonium by forming struvite can reduce the ammonium levels in cow urine waste. But it has not met the quality standard of wastewater. The ammonium removal process can be carried out with high temperature variations and a smaller MAP flow rate to slow down the reaction time of the solution in the reactor. The resulting struvite has an elongated shape or rod shape with irregular ends.

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