Potensiometric of Struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) Formation System from Biogas Waste in Electrolysis Cells

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Abstract. Struvite is a yellowish white or brownish yellow crystal. Struvite occurs in an alkaline environment. The reaction that occurs is the reduction of H^+ and at the anode is H_2O oxidation. The purpose of this study was to determine the maximum potential conditions of deposition of struvite which was contained in biogas waste by electrolysis process and to improve the quality of struvite fertilizer. The method was carried out with the electrolysis time condition of 30 minutes where the electrical voltages used were 1V, 3V, 5V, 7V, and 9V and the size of the electrodes used were 30 cm, 36 cm, 50 cm, 60 cm, 70 cm. From the research that has been done, it could be seen that the struvite formed was very small, the best conditions in this study at 5V voltage and 36 cm electrode area with a yield of 28.8%.

Keyword: Struvite, Biogas, Electrolysis Cells

1 Introduction

Struvite, a crystalline substance first identified in the 18th century, consists of magnesium ammonium phosphate ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) [1]. Struvite is a phosphate mineral that crystallizes in the orthorhombic system as a white to yellow or brownish white pyramid crystal or in the form of mica. Wastewater which contains a high amount of phosphorus and nitrogen would be a good source of struvite [2]. One of the ingredients that has the content is biogas waste. The advantages of struvite fertilizer besides being an environmentally friendly fertilizer the formation process is also made simple [3].

Pure struvite can be a fine white powder that is difficult to dissolve in water, while it is more soluble in acidic solutions [4]. Also, struvite can occur in various sizes of crystals in a yellowish or brownish white color. Struvite was first described in Hamburg, 1845, when it was discovered in a sewer system [5]. The molecular weight of struvite is 245.43 g/mol. According to its structure, struvite contains 12.6% phosphorus, 5.7% nitrogen, and 9.9% magnesium as an effective source of nutrition [6]. Struvite is known as a problematic compound in wastewater treatment plants and sludge treatment facilities which can cause weight gain from the system wall [7].

Biogas liquid waste (bio-slurry) is the final product of sewage treatment in the form of mud and is a high quality organic fertilizer that is rich in humus content [8,9]. Biogas liquid waste is an organic fertilizer which is very rich in elements needed by plants [9]. In addition to the elements N, P and K there are other elements in

biogas liquid waste including magnesium (Mg), calcium (Ca), copper (Cu), zinc (Zn), amino acids and others. Based on the analysis of the wet weight content in liquid fertilizer biogas waste namely C-organic 48%, N-total 2.9%, C/N 15.8%, P_2O_5 0.2%, K_2O 0.3% [9]

Electrolysis cells are cells that use electric current to produce desirable redox reactions and are widely used in our society. Rechargeable battery batteries are an example of electrolysis cell applications in everyday life. A battery that is being recharged converts the supplied electrical energy into the desired chemical product. Water, H_2O , can be decomposed by using electricity in the electrolysis cell. This process will break down water into its constituent elements [10].

At the anode an oxidation reaction occurs, that is, anions (negative ions) are drawn by the anode so that the number of electrons decreases, or the oxidation number increases. At the cathode a reduction reaction occurs, ie cations (positive ions) are drawn by the cathode and receive additional electrons, so the oxidation number decreases [11].

Factors Affecting Electrolysis

a. Use of catalysts

Catalysts such as H_2SO_4 and KOH simplify the process of decomposition of water into hydrogen and oxygen because the catalyst ions are able to affect the stability of water molecules into H and OH ions which are easier to electrolyze due to a decrease in the activation energy. These substances do not undergo lasting changes (not consumed in the electrolysis process). The use of sulfuric acid as a catalyst in the electrolysis process is the first choice compared to KOH . Because sulfuric acid

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releases H^+ which makes it easy to form hydrogen gas. Whereas KOH releases OH^- which inhibits the formation of hydrogen gas.

- b. Surface Area Dipped
 The more area that touches the electrolyte, the easier it is for an electrolyte to transfer electrons. So that a comparable relationship occurs if the area is immersed a little more difficult for the electrolyte to release electrons due to the lack of cross-sectional area that touches the electrolyte. So that the electron transfer works slowly in electrolyzing electrolytes.
- c. Metal Properties of Electrode
 The use of an electric field in a metal can cause all electrons to move freely in the metal, parallel to and in the opposite direction to the direction of the electric field. A measure of the ability of a material to conduct an electric current. If an electric potential difference is placed at the ends of a conductor, moving charges will move, producing an electric current.
- d. Concentration of reagents
 The greater the concentration of a reagent solution, the greater the reaction rate. This is because the higher percentage of catalyst can reduce the resistance to the electrolyte. So that electron transfer can more quickly electrolyze electrolytes and obtained a straight line drawn that there is a proportional relationship to the percentage of catalyst with electro transfer [10].

Over-potential is the difference in potential (voltage) between the half-reduction potential of a thermodynamically measured reduction reaction and the potential at which an oxidation-reduction reaction is observed [12].

Struvite general reaction:

Reaction at anode:

Cathode reaction:

Electric voltage or voltage is very influential in this electrolysis process. Voltage has a positive effect because the greater the voltage applied, the greater the metal that is drawn and attached to the cathode. The data shows that the increase in voltage between the two electrodes will increase the number of ionized atoms. In addition, the electric field between the two electrodes is getting bigger. In a large electric field, the ions or electrons will move faster. As a result, the formation of layers on the cathode will be faster [10].

Variations in pH and molar ratio were chosen with consideration of the smallest number of struvite precipitates formed and the smallest concentrations of phosphate and ammonium residuals [13]. Based on the predicted precipitate formed, the pH variation used in this study was 8 ; 8.2; and 8.5. This pH is the pH that will be maintained in a balanced state (equilibrium pH).

The choice of pH variations is due to pH 8 ; 8.2; and 8.5 formed the most struvite precipitate compared to other pH. Molar ratio factor is a factor that greatly influences the conditions of supersaturation in solution. The condition of supersaturation is strongly influenced by the concentration of each struvite-forming element. Adding excess magnesium can increase removal efficiency in this process.

2 Research Methods

The study was conducted at the Research Laboratory of the Chemical Engineering Department of the East Java "Veteran" Development University.

2.1 Material

The materials used were biogas waste from Pasuruan district, phosphoric acid (H_2PO_4), ammonium hydroxide (NH_4OH) and potassium hydroxide (KOH) purchased at chemical stores.

2.2 Equipment

The instrument used in this study was a series of electrolysis devices consisting of a power supply, a connecting cable between the electrodes and power supply, electrodes in the form of stainless steel and beakers.

2.3 Procedure

The first procedure was to prepare raw materials, namely biogas waste, because biogas waste was still in the form of slurry, so it needed to be filtered until there was no sludge and other impurities left in the waste. Then analyzed the levels of magnesium ammonium phosphate in the biogas waste filtrate before used.

Then towards the electrolysis process. The first stage was measuring 1000 ml of biogas waste to be placed in a beaker glass and then adding supporting materials namely phosphoric acid and ammonium hydroxide to balance the molar ratio between magnesium ammonium and phosphate. Next, adjust the pH of the biogas waste as specified, stir briefly. Then the steel electrode was connected to the power supply and then dipped in a glass beaker containing biogas waste, set the appropriate voltage so that the electrolysis process can take place and let stand for 30 minutes. After getting the filter sediment using filter paper and calculate the amount of struvite that settles. The last step was the analysis of struvite products that are formed.

The variables used in this study were free and permanent variables. The variable still used was biogas waste volume of 1000 ml, electrolysis time of 30 minutes, pH 10 and with a molar ratio of 1: 1: 1. The independent variable used was the voltage of 1V, 3V, 5V, 7V, 9V and the size of the electrodes were 10x5cm, 10x7 cm, 10x10 cm, 12x5 cm, 12x7 cm.

3 Results and Discussion

3.1 Electrode Area and Voltage on Deposition Weight

From the results of research conducted, struvite deposits formed and then filtered and dried at room temperature which was around 30-33°C for XRD analysis then performed. The struvite precipitate has a slightly blackish brown color powder, the amount produced was only around 3-4 grams and it smells unpleasant.

Table 1. The influence of Electrode Area and Voltage on the Weight of the Precipitate

Electrode Area (cm ²) Top	Sediment Weight (gr)				
	1 volt	3 volts	5 volts	7 volts	9 volts
30	4.522	2.221	3.259	3.024	4.096
36	5.306	3.331	2.406	3.23	3.182
50	2.682	3.272	3.552	4.949	2.803
60	2.952	3.998	2.89	2.674	3.385
70	2.158	4.064	3.621	2.075	3.878

Fig. 1. Electrode area and sediment weight in biogas waste

Based on Figure 1 there are fluctuating results. Sediment formed has increased and decreased which is not constant. Judging from the factors that influence the more surface is immersed, the more ion exchange occurs so that the resulting sediment will be even greater. The results of this study are not in accordance with the theory that the greater the area of the electrode does not always get the greater the precipitate results.

3.2 Electrode Area and Voltage on Struvite Levels

In Figure 2 it can be seen that the greater the applied voltage does not always have a higher struvite content. The best content in this study is at 5 volts with 12 x 3 cm electrode size which has a struvite content of 94.5%. This is certainly not in accordance with existing theories.

Table 2. Effect of Electrode Area and Voltage on Struvite Levels

Electrode Area (cm ²)	Struvite levels (%)				
	1 volt	3 volts	5 volts	7 volts	9 volts
30	78.33	40.86	88.53	58.17	80.48
36	74.4	61.28	94.5	56.52	62.53
50	87.57	60.2	86.48	42.7	55.08
60	86.21	73.56	91.12	60.98	66.52
70	90.2	74.77	86	65.8	76.2

Fig. 2. Electrode area and struvite levels in biogas waste

Figures 3 and 4 showed the results of struvite XRD analysis of biogas waste, synthesis struvite and hospital waste struvite. If struvite from biogas waste is compared with others, it will have similarities in the form of the graph. This shows the presence of struvite crystals contained in the results of this study. But in the picture there are still many impurities so that the resulting struvite was not pure. Generally struvite is white while in our observations our results was brown which indicates that impurities are still classified as many. This was also because biogas waste was characterized by having very complex compounds making it difficult to separate.

Fig. 3. XRD analysis results on the variable 36 cm 5 volts

Fig. 4. XRD Analysis of Hospital Struvite Synthesis and Struvite Waste

4 Conclusion

Based on the research data, it could be concluded that The results of struvite from biogas waste were not in accordance with the characteristics of struvite in general because biogas waste contains a lot of impurities and other substances that were difficult to separate; The best results of struvite formation in this study were at 5 volts and 36 cm electrode area with a yield of 28.8% and struvite content of 94.5%; The process of forming struvite by the electrolysis method is considered inappropriate and is not the right method.

This research was supported by Allah, the closest friend, family, and lecturers from National Development University "VETERAN" East Java.

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