

Magnesium Recovery of Struvite Formation Based on Waste Salts (Bittern) with a Bulkhead Reactor

by Luluk Edahwati

Submission date: 26-Nov-2020 09:12AM (UTC+0700)

Submission ID: 1457306104

File name: 4.2.Magnesium_Recovery.pdf (297.32K)

Word count: 2479

Character count: 12041



Article

Magnesium Recovery of Struvite Formation Based on Waste Salts (Bittern) with a Bulkhead Reactor

Luluk Edahwati^{1,a}, Sutiyono¹, Nikmatuz Zahra^{1,b,*}, Herdiana Septiani¹

¹Chemical Engineering Department, Engineering Faculty, University of Pembangunan Nasional "Veteran" Jawa Timur

E-mail: ^alulukedahwati@gmail.com, ^{b,*}zahraniikmatuz11@gmail.com

Abstract. Waste salt or bittern is the residual liquid from the salt formation which cannot be precipitated again but can be obtained from the washing water remaining in the purification process. Bittern has high economic value of mineral salts such as $MgCl_2$, $MgSO_4$, KCl , and Br_2 . The element Mg in bittern can be used as a mineral forming struvite because magnesium is one of the components needed in the formation of struvite. Crystallization of the formation of struvite minerals occurs in equimolar concentrations of Mg^{2+} , NH_4^+ and PO_4^{3-} in an alkaline state. The column reactor is equipped with a bulkhead which functions as a stirrer inside the reactor and is assisted by incoming air. Struvite solution (MAP) reacted can be formed from phosphoric acid, ammonium hydroxide, and bittern or salt waste as a source of magnesium with a molar ratio of 2: 1: 1. The pH variations run in the range of 7 to 11 and the reactor inlet air velocity between 0.25-1.25 L/min in a closed column reactor that is operated continuously. The resulting dry sludge was analyzed by XRD method for mineral characterization, SEM to determine the morphology of the crystals and XRF to determine the composition of struvite mineral.

Keywords: recovery, bittern, struvite, magnesium, bulkhead reactor, air rate, pH.

International Journal of Eco-Innovation in Science and Engineering Volume 01 No. 01

Received Date 15th April 2020

Accepted Date 4th May 2020

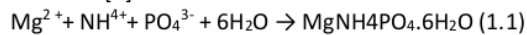
Published Date 15th May 2020

Online at <https://ijeise.upnjatim.ac.id/>

1. Introduction

Bittern is a concentrated liquid produced from salt pond waste or salt industry waste. Bittern are often directly thrown into the water by salt farmers while bittern is rich in magnesium and other components. According to (Sato et al, 2010) bittern contains various compounds such as magnesium sulfate ($MgSO_4$), sodium chloride (NaCl), magnesium chloride ($MgCl_2$), potassium chloride (KCl) and calcium chloride ($CaCl_2$). So far, bittern has been only used as a mixture to get old water instantaneously by back mixing, the term Madura salt farmer with a *cegean* method, but this technique has proven to worsen the quality of the salt product produced [8]. The magnesium contained in bittern is one of components to form struvite minerals which have many benefits, for example as fertilizer in agriculture.

Struvite is a crystal formed from reactions with the same molar concentration of magnesium, ammonium, and phosphate combined with six water molecules ($MgNH_4PO_4 \cdot 6H_2O$). The molecular weight of struvite is 245.43 gmol/ L, slightly soluble under neutral and basic conditions but easily soluble in acids. The solubility of struvite in the water is around 0.018 g/ 100 ml at 25°C. Struvite is considered a soft mineral with low specific gravity (1.7), not washed with rainwater so that it can be used as fertilizer material in flooded areas (Lee et al., 2009). Crystallization occurs in equimolar concentrations of Mg^{2+} , NH_4^+ and PO_4^{3-} in an alkaline state (base) based on the following reaction: [4]



1.1. Struvite Crystallization

In general, the aggregation process is divided into two phases, the transition phase when struvite crystals evolve from nucleation and the stages of crystal growth into aggregation. Then the second is the steady phase where the aggregate size does not increase significantly and fluctuate in a certain range [10]. The development of struvite crystals are influenced by some factors such as the initial crystal state of the compound, the thermodynamics of the liquid-solid equilibrium, the phenomenon of mass transfer between the solid and liquid phase and the reaction kinetic [7].

1.2. Factors that Influence Struvite Formation include:

1.2.1. Effect of pH

Struvite formation is strongly influenced by pH values. According to (Doyle, 2000) struvite formation occurs between a pH range of 7 to 11 [5]. pH values indicate two things in the formation of struvite,

namely the minimum solubility value and the value at which struvite initially begins to form. High pH values cause changes in ammonium to ammonia. The pH value of the solution is also the most important parameter in the struvite crystallization process. The formation of struvite occurs if the Ion Activity Product (IAP) of Mg^{2+} is greater than the Solubility Product (KSP). The IAP value is controlled by the pH of the solution, increasing the pH will increase the IAP value of the solution at the same concentration [3].

1.2.2. N: P: Mg Molar Ratio

Based on equation 1.1, the minimum molar ratio of precipitation occurrence of struvite [Mg^{2+}]: [NH_4^+]: [PO_4^{3-}] is 1: 1: 1. This means that the formation of struvite theoretically stoichiometry requires a minimum of [Mg^{2+}]: [NH_4^+]: [PO_4^{3-}] is 1: 1: 1 [9]. Magnesium (Mg) is an important constituent ion for the formation of crystalline struvites. Mg^{2+} ions can influence the saturation level of the solution and increase the reaction process of struvite crystal formation. At a certain pH, every increase in the molar ratio of Mg: PO_4 reactants will increase the degree of saturation to the formation of struvite and the percentage of removal of PO_4^{2-} in the solution increases [3].

1.2.3. Aeration Level

Aeration aims to release a number of ammonium dissolved or free from solution [2]. The air flow shakes the solution and creates a release path for dissolved ammonia to evaporate from the solution. In addition, the air flow dilutes the NH_4-N gas phase concentration and increases the driving force to dissolve NH_4-N to separate the gas phase. So, there is an increasing tendency for ammonia volatilization with increasing air flow rate.

1.3. Struvite crystallization reactor

In this study a bulkhead reactor was used with a continuous process. The principle of the bulkhead reactor uses counter-current flow, which the incoming feed from the top of the reactor and the air as a stirrer from under the reactor. The reactor is planned with the volume 498.75 mL, height 50 cm with outer diameter 5 cm; 2.5 cm inner diameter. This reactor has several parts. In the section above the reactor has 3 holes which for the entrance of MAP solution, NaOH solution and overflow solution. At the bottom of reactor there are also 3 holes for air inlet, to the struvite solution storage tank and to the sediment storage tank. This reactor is equipped with a bulkhead which functions as a stirrer inside the reactor and is assisted by entering air from the stabilizer tank which

is equipped with an air rate regulator which connected by a hose and there is a compressor to fill the air pressure in the stabilizer tank equipped with a barometer.

2. Material and Method

The materials used in this study are NH_4OH , H_3PO_4 , Bittern (obtained from PT. Garam (Persero) Segoromadu Gresik), which contain Magnesium (Mg): 23470 mg/L or 2,4%, Chloride (Cl): 18.2%, Phosphorus (P): 0.05%, Sulfur (S): 0.3%, Potassium (K): 0.59%, Sodium (Na): 4444961.68 mg/L or 44.449% and NaOH for the alkali source.

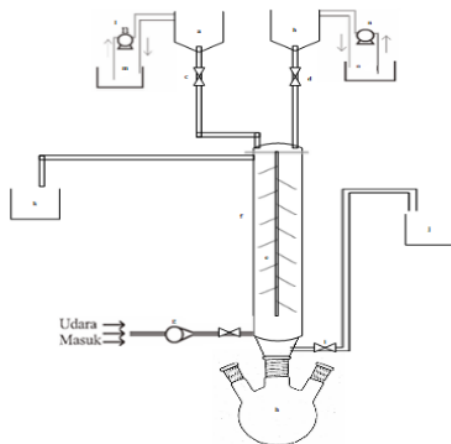


Fig. 1. Bulkhead Reactor

The crystallization process of struvite formation was carried out in a vertical reactor (as shown above), a bulkhead reactor with a continuous process. A solution of bittern, NH_4OH , and H_3PO_4 with 1:1:2 molar ratio was prepared (A solution) as well as NaOH as a controller of pH (B solution). Furthermore, solutions A and B were filled from the top of the reactor by adjusting the inlet of flow rate, after the two solutions reach three quarters of the column height, the air is inserted from below the column at a certain speed. The process was run until the steady state was achieved. With this reactions that occur in the reactor is expected to form a struvite reaction to be more perfect. After the process was completed, the formed struvite precipitate was filtered and then dried at room temperature for 48 hours. The dried struvite was analyzed using XRF for the chemical elements of the crystal, SEM for the morphology, while the phase composition of the crystal was determined using the XRD Rietveld method.

3. Results and Discussion

Table 1. XRF analysis results of the composition of struvite mineral

pH	Component %	Air Flow Rate (L/minutes)				
		0.25	0.5	0.75	1	1.25
7	Mg	7.6	8.1	9.8	9.2	8.9
8	Mg	7	8.4	10.1	9.5	9.3
9	Mg	8.2	9.9	13	10.7	11.6
10	Mg	10	10.5	11.9	11.5	11.3
11	Mg	11.5	11.9	12.7	12.6	12.2

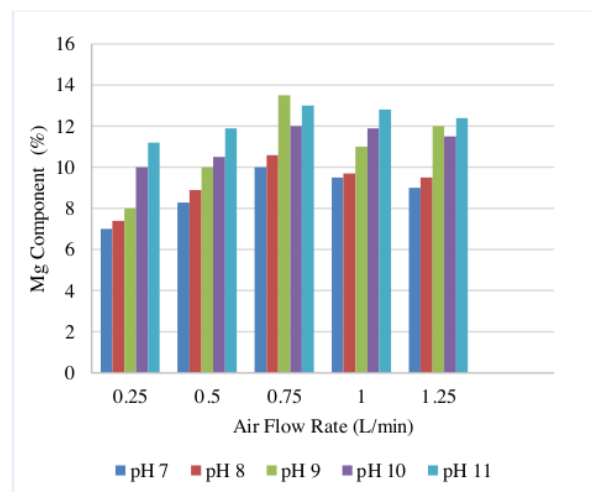


Fig. 2. Effect of air flow rate (L/min) on Mg content (%) in various pH variations

In the graph above it can be explained that the content of Mg for pH 7, 8, 9, 10, and 11 tends to increase at the air rate of 0.75 L/min and has a decrease to the air rate of 1.25 L/min. This is because the air supplied will act as a mixer which makes the solution in the reactor homogeneous. Where the greater the rate of air flow, the reaction formation of struvite crystals will be faster and the collisions between particles will be even greater. The best condition is the air rate of 0.75 L/min while the air rate of 1 and 1.25 L/min decreases but it is not significant because if the given air rate is too large then collisions between particles occur very quickly so that the mixing process becomes unfavorable and the reaction of struvite formation becomes unstable. According to the theory [1] it is said that the greater the stirring speed, the induction time will decrease and nucleation

will occur faster, whereas the too high stirring speed, magnesium removal can decrease due to the stability of struvite crystals which can decrease and cause crystals to break. According to (Rahman, 2013) the air rate is proportional to the formation of struvite crystals around 0.73 L/min [7].

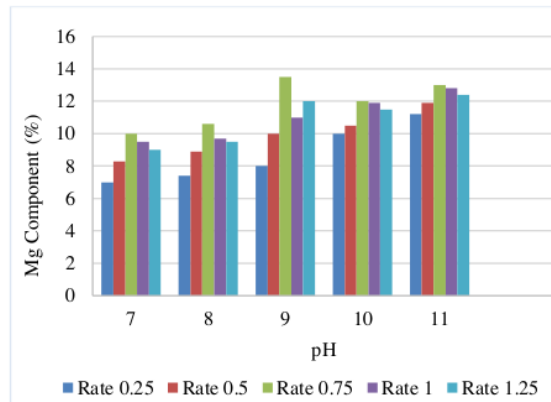
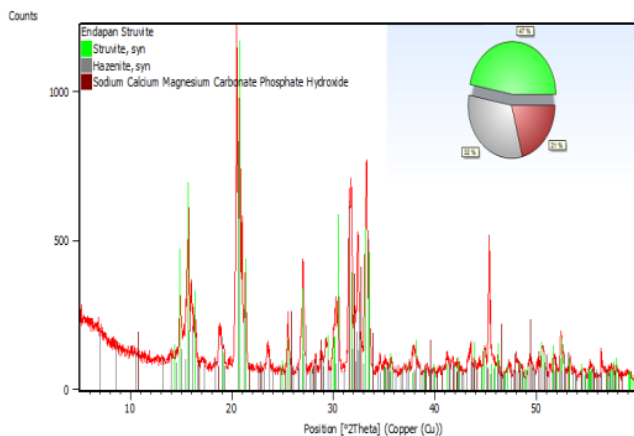


Fig. 3. Effect of pH on Mg content (%) in various variations in Air Rate (L/min)

The graphical form obtained at pH 7, 8, 10, and 11 is symmetrical in shape while at pH 9 with a rate of 0.75 L / min it experiences a high enough increase to exceed pH 11 this is because pH 9 is the optimum pH in the formation of struvite crystals . At pH 7 and 8 the



formation of struvite minerals can be said to be not optimal whereas at pH 10 and 11 the mineral content of struvite has decreased due to the increasing amount of impurities formed at high pH.

Fig. 4. Results of XRD analysis of struvite material at pH 9 with an air rate of 0.75 L/min

From the results of the analysis it can be explained that struvite material has been formed

which is evidenced by the existence of a graphic peak. From the results of XRD analysis, it is known that the content of struvite material produced from raw salt (bittern) waste is not pure because the waste raw material used has a fairly complex content that triggers the formation of other minerals during the process. The struvite content that is formed is 47%, while impurities that are formed impurities in 32% hazenite form and 21% sodium calcium magnesium carbonate phosphate hydroxide

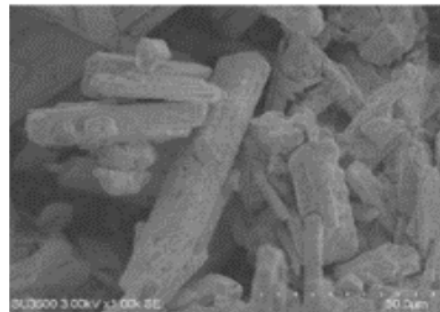


Fig.5. SEM analysis results of struvite material at pH 9 with an air rate of 0.75 L / min

Based on existing theories according to [1] it is said that pure struvite crystals have a rod shape with a pointed tip, the surface is clean and without defects. From this study, struvite crystals are found with rod and pointed ends, but the surface is not smooth and there are small lumps. The lump is an impurities mineral formed during the precipitation process. The impurity mineral from the XRD analysis results in the form of hazenite and sodium calcium magnesium carbonate phosphate hydroxide.

4. Conclusions

1. The optimal conditions of this study are at pH 9 and air rate 0.75 L/min where the magnesium content in the struvite minerals produced is 13 %.
2. The mineral content of struvite at pH above 9 has decreased due to the increasing amount of impurities formed at high pH.
3. The mineral content of struvite when air flow rate above 0.75 L/minis decreased because the high flow rate makes the reaction of struvite formation unstable.

Acknowledgement

The authors want to thank to Engineering Faculty, University of Pembangunan Nasional "Veteran" Jawa Timur for supporting this research programs.

References

- [1] A. R. Fitriana, I. Warmadewanthi, "Penurunan Kadar Amonium dan phospat pada Limbah Cair Industri Pupuk," *Jurnal Teknik ITS* Vol. 5, No. 2, 2016.
- [2] Darmadi, "Pengolahan Limbah Cair Pabrik Pupuk Urea Menggunakan Advanced Oxidation Processes," *Jurnal Rekayasa Kimia dan Lingkungan* vol. 10, no. 1, hal 1-6, 2014.
- [3] E. Ariyanto, A.Melani, T. Anggraini, "Penyisihan PO₄ Dalam Air Limbah Rumah Sakit untuk Produksi Pupuk *Struvite*," *Jurnal Teknik Kimia Universitas Muhammadiyah*. Vol 20, No 20: 1-4, 2015.
- [4] I. M. Jimenez, V. Celorrio, D. J. Fermin, J. Greenman, I. Ioannis, "Enhanced MFC power production and *struvite* recovery by the addition of sea salts to urine," *Water Researchers Journal*, 2016.
- [5] J. D. Doyle, R. Philp, S. A. Parsons, "Analysis of *Struvite* Precipitation in Real and Synthetic Liquors," *Institution of Chemical Engineers: Trans IChemE*, Vol 78, Part B, 2000.
- [6] M. Nadia, M. Zainuri, M. Effendy, "Prototype Pupuk Multinutrient Berbasis Phosphate Berbahan Dasar Limbah Garam (*Bittern*) sebagai Alternatif Solusi Penumbuh Pakan Alami," *Jurnal Kelautan* Vol 8, No. 2, 2015.
- [7] Md. M. Rahman, M. A. M. Salleh, U. Rashid, A. Ahsan, M. M. Hossain, C. S. Ra, "Production of Slow Release Crystal Fertilizer from Wastewaters Through *Struvite* Crystallization," *Arabian Journal of Chemistry*, pages 139-175, 2014.
- [8] Sidik, R. Fajar. "Variasi Produk Pupuk Majemuk dari Limbah Garam (*Bittern*) dengan Pengatur Basa Berbeda," *Jurnal Kelautan* Vol 6, p.2, 2013.
- [9] X. Zhang, J. Hu, H. Spanjers, B. Jules, V. Lier, "*Struvite* Crystallization Under a Marine / Brackish Aquaculture Condition," *Bioresource Technology* 218 pages 1151–1156, 2016.
- [10] Z. Ye, Y. Shen, S. Ye, Z. Zhang, Chen, C. Shaohua, J. Shi, "Phosphorus recovery from wastewater by *struvite* crystallization: Property of aggregate," *Journal of Environmental Science* 26, 999, 2014.

Magnesium Recovery of Struvite Formation Based on Waste Salts (Bittern) with a Bulkhead Reactor

ORIGINALITY REPORT

18%

SIMILARITY INDEX

5%

INTERNET SOURCES

15%

PUBLICATIONS

11%

STUDENT PAPERS

PRIMARY SOURCES

- 1** S Sutyono, L Edahwati, S Muryanto, J Jamari, A.P. Bayuseno. "Synthesis of Struvite using a Vertical Canted Reactor with Continuous Laminar Flow Process", Journal of Physics: Conference Series, 2018
Publication 9%
- 2** garuda.ristekbrin.go.id
Internet Source 5%
- 3** Md. Mukhlesur Rahman, Mohamad Amran Mohd. Salleh, Umer Rashid, Amimul Ahsan, Mohammad Mujaffar Hossain, Chang Six Ra. "Production of slow release crystal fertilizer from wastewaters through struvite crystallization – A review", Arabian Journal of Chemistry, 2014
Publication 4%

Exclude quotes On

Exclude bibliography On

Exclude matches < 2%

Magnesium Recovery of Struvite Formation Based on Waste Salts (Bittern) with a Bulkhead Reactor

GRADEMARK REPORT

FINAL GRADE

/0

GENERAL COMMENTS

Instructor

PAGE 1

PAGE 2

PAGE 3

PAGE 4

PAGE 5
