CESARE'22

3rd Coordinating Engineering for Sustainability And Resilience
May 6th – May 9th, 2022, Irbid, Jordan
ISSN:2788-6204

PREDICTING INFLUENCE OF PROCESS PARAMETERS THROUGH MODELING STRUVITE PRECIPITATION USING VMINTEQ

Sarah S. Sinno[1], Kazi P. Fattah[2], and Hadeer S. Abdalla[3]

[1]Department of Civil Engineering, American University of Sharjah, Sharjah, United Arab Emirates
e-mail: g00088543@aus.edu;

[2]Department of Civil Engineering, American University of Sharjah, Sharjah, United Arab Emirates
e-mail: kfattah@aus.edu;

[3]Department of Civil Engineering, American University of Sharjah, Sharjah, United Arab Emirates
e-mail: hadeer.s.abdalla@gmail.com;

Keywords: Struvite, VMINTEQ, phosphorus, calcium, wastewater, nutrients recovery.

Abstract. *Phosphorus (P) and nitrogen (N) have a major role in the world food supply as essential nutrients for plants and crops growth. The rapid increase in population, and consequently, the increase in demand for fertilizers is putting a strain on the phosphorus production. On the other hand, population growth is increasing the production of nutrient rich wastewater, causing pollution in soil and waterbodies, and limiting the availability of clean water. Thus, the removal and recovery of nutrients from wastewater is now a necessity rather than just an option. A sustainable approach for nutrients recovery is the precipitation of struvite ($MgNH_4PO_4{\cdot}6H_2O$), which can function as a slow release fertilizer. The crystallization of struvite is affected by various factors from which this study is going to investigate: pH, Mg/P and Ca/Mg molar ratios using VMINTEQ modeling software. The struvite formation was predicted for a pH ranging between 7 and 11, Mg/P and Ca/Mg molar ratio between 0 and 2.5. Results showed that the optimum conditions for struvite crystallization is at pH 9 when Mg/P molar ratio is unity, and that the presence of Ca hinders the formation of struvite even with a Ca/Mg molar ratio as low as 0.2.*

1 INTRODUCTION

Phosphorus (P) and nitrogen (N) are essential nutrients for plants and crops growth, which gives them a major role in the world food supply. Phosphorus is a non-renewable and finite resource, where mineable P-rocks are the only available source for P, but researches expect that the phosphorus critical production point will occur in the 21st century [1]. Such phosphorus deficiency is expected to impact negatively on food production, leading to increased cost of food items. Nevertheless, phosphorus is abundant in domestic and livestock wastewaters which are known to be rich in nutrients. Such wastewater is recognized as major source for environmental pollution when not properly treated before being discharged. In recent years, large amounts of nutrients have been disposed in the environment causing over-enrichment of the soil, eutrophication of water bodies, and deterioration of water quality [2]. With the global population growing rapidly, the demand for food and consequently fertilizers is increasing drastically, and thus an increase in wastewater generation. As a result, the removal and recovery of nutrients from wastewater is a necessity rather than just an option. Among the sustainable approaches for nutrients recovery is the precipitation of struvite ($MgNH_4PO_4.6H_2O$). Struvite is being utilized as an alternative to chemical fertilizers, and its slow-release property allowed for reduced application and fertilization-associated costs. Crystallization of struvite depends on several factors, such as pH, molar ratios between nutrients, presence of competing ions, organic load, and solids content [3], [4]. The recovery of phosphorus from wastewater has multiple benefits – reduce the eutrophication potential, provide an alternative to mined phosphorus, and lower the operating costs of wastewater treatment plants as it contributed to the reduction of phosphates salts that block the pipes [5]. Thus, wastewater can now be regarded as a source for nutrients rather than just a waste and pollutant. While the influence of pH and magnesium to phosphorus molar ratio on struvite precipitation is well documented in the literature, there are few studies on the impact of competing ions on the chemical process [6]. The aim of this study is to use VMINTEQ software to model the crystallization of struvite and to determine the optimum conditions for recovery of the nutrients. The investigated factors include pH and change in molar ratios between magnesium and phosphate (Mg/P), as well as influence of calcium on struvite precipitation.

2 STRUVITE PRECIPITATION

Struvite is a white crystal that is also known as magnesium ammonium phosphate (MAP), which is formed as a precipitate according to Equation 1.The precipitate can be recovered through solid-liquid separation due to its low solubility in alkaline solutions [7].

$$Mg^{2+} + H_nPO_4^{3-n} + NH_4^+ + 6H_2O \rightarrow MgNH_4PO_4.6H_2O + H^{n+} \quad (1)$$

Several studies show the feasibility of recovering phosphorus from different wastewater and waste materials, such as urine, swine wastewater, dairy wastewater, municipal wastewater, poultry manure, digested dairy manure, sewage sludge, and landfill leachate [3], [5], [8]. High phosphorus removal rates were proven for different pH and magnesium to phosphorus molar ratios: 1.67 molar ratio at a pH of 8.8 resulted a 99% phosphorus removal rate from biological sludge [9], 1.2 molar ratio at a pH of 9 resulted in a 98.5% P removal rate from swine wastewaters [10], and a 1.5 molar ratio at a pH of 10 resulted in a 93% P removal from human urine [11]. Although studies have reported high phosphorus removal, the recovery may not be entirely as struvite, due to the precipitation of $Mg_3(PO_4)_2$ and $Mg(OH)_2$ at high pH which limits the presence of magnesium for struvite precipitation [12]. In addition to the magnesium limitation at high pH, wastewaters such as anaerobically digested dairy manure have high concentrations of calcium (up to 361 mg/l) whereas magnesium concentrations can go up to 1,800 mg/l having a Ca/Mg molar ratio of around 0.5 [13]. Although the added calcium does not reduce the phosphorus removal efficiency, it affects the purity of the struvite formed due to the precipitation of hydroxyapatite ($Ca_5(PO_4)_3OH$) according to Equation 2 [14].

$$5Ca^{2+} + 3PO_4^{3-} + H_2O \rightarrow Ca_5(PO_4)_3OH + H^+ \quad (2)$$

3 MODELING STRUVITE PRECIPITATION

Visual MINTEQ is a freeware chemical equilibrium model that can be used for the calculation of metal speciation, solubility equilibria, sorption, solids precipitation etc. for natural waters [5]. In this study, typical water constituents' concentrations of Mg^{2+}, NH_4^+, PO_4^{3-}, and Ca^{2+} were added in mmol/l. The only competitive ion added was calcium which was used to study the effect of calcium concentration on the struvite formation. Possible solid phases, presented in Table 1, were identified based on the components available in the solution defined. Based on the pH ranges and molar ratios investigated in the literature mentioned in section 2, it was decided to run the model for pH ranging between 7 and 11 with an increment of 0.5, Mg/P to ratio between 0 and 2.5 (increment of 0.2 between 0 and 1, and 0.5 increment between 1 and 2), and Ca/Mg ratio between 0 and 2.5 as well using the same increments listed before.

Table 1: Possible solid phases and their components

Possible precipitate	Components
Struvite ($NH_4MgPO_4 \cdot 6H_2O$)	Mg^{2+}, NH_4^+, PO_4^{3-}, H_2O
Brucite ($Mg(OH)_2$)	Mg^{2+}, H_2O, H^+
Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$)	Ca^{2+}, PO_4^{3-}, H_2O, H^+
Lime (CaH_2O_2)	Ca^{2+}, H_2O, H^+
Periclase (MgO)	Mg^{2+}, H_2O, H^+
Portlandite ($Ca(OH)_2$)	Ca^{2+}, H_2O, H^+
$Ca_3(PO_4)_2$	Ca^{2+}, PO_4^{3-}
$CaHPO_4$	Ca^{2+}, PO_4^{3-}, H^+
$Mg_3(PO_4)_2$	Mg^{2+}, PO_4^{3-}
$MgHPO_4.3H_2O$	Mg^{2+}, PO_4^{3-}, H_2O, H^+

ISSN:2788-6204

4 RESULTS AND DISCUSSION

After running the software using the variables defined earlier, the results were plotted in a 3D mesh using MATLAB for better visualization. The obtained plots are illustrated in Figure *1* and Figure *2*. Results show that the optimum conditions for struvite formation is the absence of Ca and Mg/P ratio of 1 and at a pH of 9. At pH higher than 10, struvite concentration decreases due to the formation of brucite ($Mg(OH)_2$), thereby limiting the Mg^{2+} available for the struvite crystallization. The range of pH between 8 and 9.5 had the highest struvite formation. With the addition of calcium, the struvite formation is completely hindered when Ca/Mg>2. In the optimum pH range (8 to 9.5) the addition of Ca, even with Ca/Mg molar ratios as low as 0.2 and 0.4, the reduction in struvite formation was on average 8% and 18%, respectively. A Ca/Mg molar ratio of 1 contributed to the reduction of struvite formed by almost 50%.

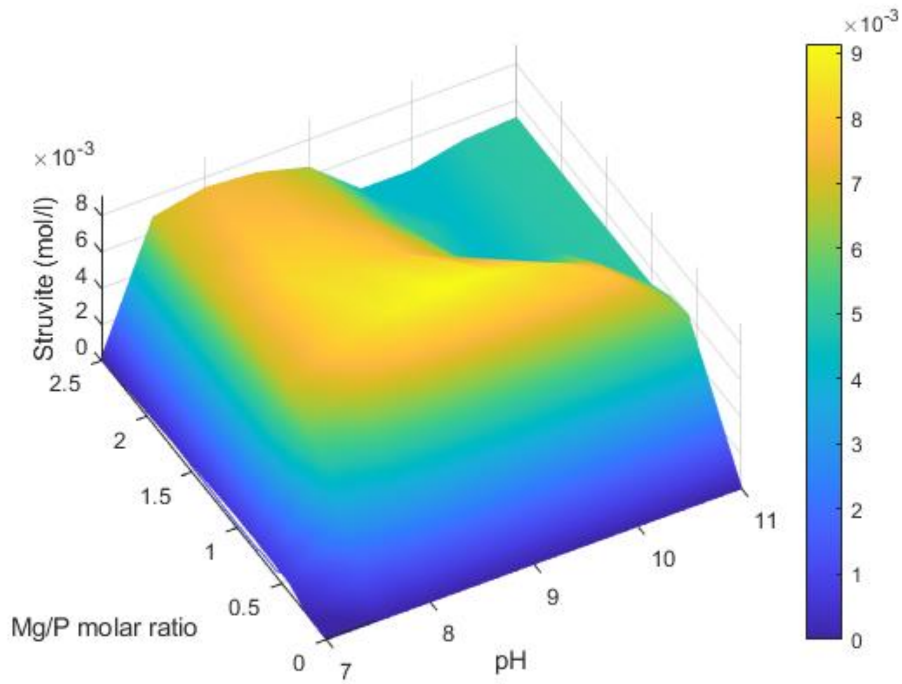

Figure 1: Influence of Mg/P molar ratio and pH on struvite formation.

ISSN:2788-6204

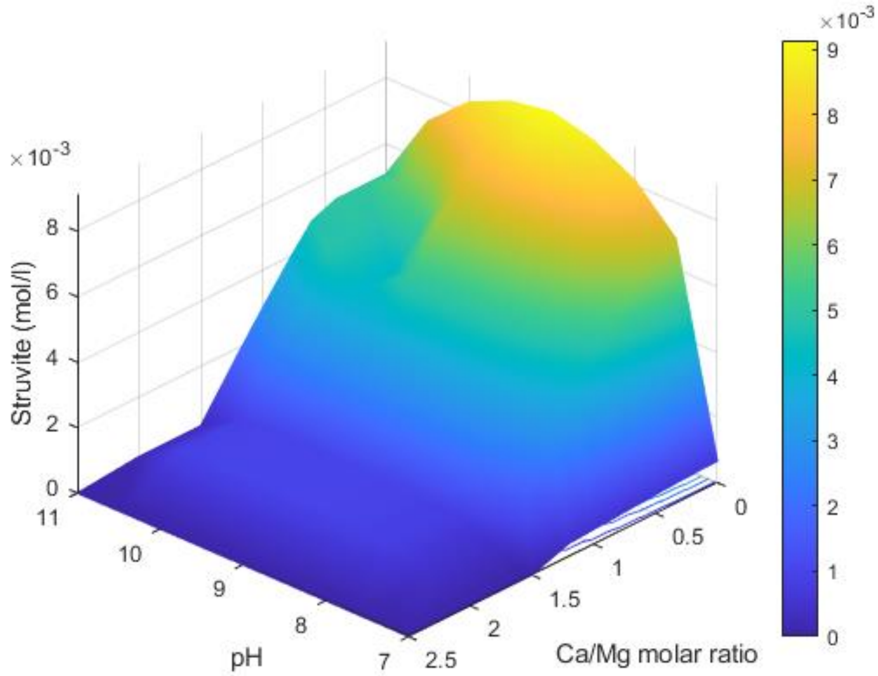

Figure 2: Influence of Ca/Mg molar ratio and pH on struvite formation.

5 CONCLUSION

With the depletion of natural nutrients resources, and the increase in wastewater production, it has become a necessity to start considering wastewater as a resource to recover and recycle nutrients through struvite crystallization. Struvite can be used as a slow releasing fertilizer and thus has an economic value. However, wastewaters do contain other ions that will hinder the precipitation of struvite. The model developed in this study has shown that the optimum conditions for struvite crystallization are pH between 8 and 9.5 and an Mg/P molar ratio of unity, the presence of Ca in small concentrations compared to Mg which hinders the struvite precipitation and reduces the purity of the struvite formed. Thus, pretreatment of wastewater is suggested to improve the conditions for struvite formation. The model's results are expected to be validated through a series of experiments using municipal wastewater and digested dairy manure as source of P and N in the future.

ACKNOWLEDGEMENT

The authors would like to thank the American University of Sharjah for the financial support through Grant# FRG20-M-E44.

REFERENCES

[1] D. Cordell, J.-O. Drangert, and S. White, "The story of phosphorus: Global food security and food for thought," *Glob. Environ. Change*, vol. 19, no. 2, pp. 292–305, May 2009, doi: 10.1016/j.gloenvcha.2008.10.009.

[2] R. J. Diaz and R. Rosenberg, "Spreading Dead Zones and Consequences for Marine Ecosystems," vol. 321, p. 5, 2008.

[3] R. Taddeo and R. Lepistö, "Struvite precipitation in raw and co-digested swine slurries for nutrients recovery in batch reactors," *Water Sci. Technol.*, vol. 71, no. 6, pp. 892–897, Mar. 2015, doi: 10.2166/wst.2015.045.

[4] K. P. Fattah and F. L. Chowdhury, "Early detection of struvite formation in wastewater treatment plants," *J. Environ. Eng. Sci.*, vol. 10, no. 1, pp. 19–25, Apr. 2015, doi: 10.1680/jees.14.00015.
[5] S. Kumari, S. Jose, and S. Jagadevan, "Optimization of phosphate recovery as struvite from synthetic distillery wastewater using a chemical equilibrium model," *Environ. Sci. Pollut. Res.*, vol. 26, no. 29, pp. 30452–30462, Oct. 2019, doi: 10.1007/s11356-019-06152-4.
[6] D. Kim, K. J. Min, K. Lee, M. S. Yu, and K. Y. Park, "Effects of pH, molar ratios and pre-treatment on phosphorus recovery through struvite crystallization from effluent of anaerobically digested swine wastewater," *Environ. Eng. Res.*, vol. 22, no. 1, pp. 12–18, Sep. 2016, doi: 10.4491/eer.2016.037.
[7] L. D. Xavier, M. C. Cammarota, L. Yokoyama, and I. Volschan, "Study of the recovery of phosphorus from struvite precipitation in supernatant line from anaerobic digesters of sludge," *Water Sci. Technol.*, vol. 69, no. 7, pp. 1546–1551, Apr. 2014, doi: 10.2166/wst.2014.033.
[8] O. Krüger, K. P. Fattah, and C. Adam, "Phosphorus recovery from the wastewater stream—necessity and possibilities," *Desalination Water Treat.*, vol. 57, no. 33, pp. 15619–15627, Jul. 2016, doi: 10.1080/19443994.2015.1103315.
[9] S. Shaddel, T. Grini, J.-P. Andreassen, S. W. Østerhus, and S. Ucar, "Crystallization kinetics and growth of struvite crystals by seawater versus magnesium chloride as magnesium source: towards enhancing sustainability and economics of struvite crystallization," *Chemosphere*, vol. 256, p. 126968, Oct. 2020, doi: 10.1016/j.chemosphere.2020.126968.
[10] H. Huang, G. Guo, P. Zhang, D. Zhang, J. Liu, and S. Tang, "Feasibility of physicochemical recovery of nutrients from swine wastewater: Evaluation of three kinds of magnesium sources," *J. Taiwan Inst. Chem. Eng.*, vol. 70, pp. 209–218, Jan. 2017, doi: 10.1016/j.jtice.2016.10.051.
[11] V.-G. Le, C.-T. Vu, Y.-J. Shih, X.-T. Bui, C.-H. Liao, and Y.-H. Huang, "Phosphorus and potassium recovery from human urine using a fluidized bed homogeneous crystallization (FBHC) process," *Chem. Eng. J.*, vol. 384, p. 123282, Mar. 2020, doi: 10.1016/j.cej.2019.123282.
[12] B. Li *et al.*, "Phosphorus recovery through struvite crystallisation: Recent developments in the understanding of operational factors," *J. Environ. Manage.*, vol. 248, p. 109254, Oct. 2019, doi: 10.1016/j.jenvman.2019.07.025.
[13] M. P. Huchzermeier and W. Tao, "Overcoming Challenges to Struvite Recovery from Anaerobically Digested Dairy Manure," *Water Environ. Res.*, vol. 84, no. 1, pp. 34–41, Jan. 2012, doi: 10.2175/106143011X13183708018887.
[14] A. Siciliano, C. Limonti, G. M. Curcio, and R. Molinari, "Advances in Struvite Precipitation Technologies for Nutrients Removal and Recovery from Aqueous Waste and Wastewater," *Sustainability*, vol. 12, no. 18, p. 7538, Sep. 2020, doi: 10.3390/su12187538.