CHEMICAL ENGINEERING TRANSACTIONS
VOL. 72, 2019

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Jeng Shiun Lim, Azizul Azri Mustaffa, Nur Nabila Abdul Hamid, Jiří Jaromír Klemeš

ISBN 978-88-95608-69-3; **ISSN** 2283-9216

DOI: 10.3303/CET1972038

Removal of Phosphorus in Rubber Wastewater – Design of Experiment for the Struvite Crystallization Reaction

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Recovering struvite crystal is one of the most interesting methods for removing phosphorus from wastewater to produce fertilizer. Phosphorus is removed from wastewater streams to prevent the ecologically harmful effects of eutrophication in receiving natural, so the recovery and reuse of phosphorus in rubber wastewater by struvite precipitation not only reduces the effects of phosphorus for the environment where the product MAP (Magnesium Ammonium Phosphate) is also a slow release fertilizer is very useful for agriculture. During the reaction process taking place, the parameters of pH, Mg^{2+}/PO_4^{3-} ratio and NH_4^+/PO_4^{3-} ratio gate the large influence on the formation of struvite. The design of experiment had been carried out using three factors based, multi-factorized experimental equation was. From the experimental equation, the experimental had been optimized for three factors. The optimization level of the parameters were determined as 9.0 for the pH, 1.25 for ratio of Mg^{2+}/PO_4^{3-} and 4.35 for ratio of NH_4^+/PO_4^{3-}. The obtained precipitation volume with optimum parameters was 0.3401 g/300 mL of rubber wastewater

1. Introduction

Phosphorus (P) is the basic element of life, including people dependent on phosphorus to stay healthy and productive, and as an essential nutrient for plants production. Moreover, there is no substitute for phosphorus in nature (United States Geological Survey, 2005).

Vietnam's rubber industry is growing in line with economic growth and contributed significantly to the GDP of the country. However, along with the rapid economic development, the environment problems caused by this industry are also worrying.

In Vietnam, it is estimated that rubber latex processing industry generates about 5.000.000 m^3 wastewater annually. This large amount of wastewater has high concentration of biodegradable organic substances such as: acetic acid, sugar, protein. The concentration of COD reached 2,500 – 35,000 mg/l, BOD: 1,500 – 12,000 mg/l, NH4-N: 200 – 400 mg/L, total phosphorus: 25- 40 mg/L (Mohammadi et al., 2010).

Wastewater from the rubber latex processing plants, if not thoroughly treated, will become as one of the reason that causes of the increasingly serious environment pollution such as: the exhaustion of oxygen leading to eradication of aquatic animals and plants, eutrophication deprives the aesthetics and water quality of source, the instruction into the groundwater adversely affects the quality of water, which use for domestic purposes and increases the cost of treatment (Doino et al., 2011).

Therefore, the recovery of phosphorus from wastewater streams is very necessary. Reducing the amount of phosphorus in wastewater is important for the environment. Various chemical and biological processes have been developed for P removal, such as metal precipitation, constructed wetland systems (Headley et al., 2000), biological nutrient removal processes (Stratful et al.,1999), enhanced biological phosphorus removal processes (Carlsson et al., 1997), and the struvite crystallization process (Munch and Barr, 2001). Among these processes, the struvite crystallization process is an ideal technique because it can simultaneously remove and recover P and N from wastewater (Ueno and Fujii, 2001). Moreover, when struvite is used as fertilizer, the extraction of rock phosphorus can be reduced (Zhu et al, 2014).

Struvite precipitation occurs under alkaline conditions according to the reaction have been shown in Eq(1) as follows:

Paper Received: 03 September 2018; Revised: 21 October 2018; Accepted: 09 December 2018

Please cite this article as: Huy N.V.T., Chi T.M., Phan T.L., Le A., 2019, Removal of phosphorus in rubber wastewater – design of experiment for the struvite crystallization reaction, Chemical Engineering Transactions, 72, 223-228 DOI:10.3303/CET1972038

$$Mg^{2+} + NH_4{}^{+} + PO_4{}^{3-} + 6H_2O \rightarrow MgNH_4PO_4.6H_2O \quad (1)$$

Eq(1) indicated that the struvite crystals to be created when the magnesium, ammonia and phosphate combined in water in a mole to mole to mole ratio of 1:1:1.
Struvite precipitation depends on two main factors: the molar ratio of $Mg:NH_4:P$ and the pH value of wastewater (Munch and Barr, 2001). The struvite crystallization process on influence of pH, temperature and supersaturation on struvite growth kinetics (Harrison et al., 2011).
The paper presents the results of the empirical study on influence of three factors: pH, molar ratios of $Mg^{2+}/PO_4{}^{3-}$ and $NH_4{}^{+}/PO_4{}^{3-}$ to the struvite precipitation reaction and struvite content obtained from the process the experiment was 3.401 g/300 mL wastewater.

2. Materials and methods

2.1 Experimental setup

In experiments, measured amounts of $MgCl_2{\cdot}6H_2O$ were added to 300 mL of wastewater, and stirred in a jar test apparatus. The reaction time was 30min at a mixing speed of 50 rpm. Sodium hydroxide (NaOH) of 3M were used for pH adjustment. To investigate the effect of NH_4-N concentration solution, ammonium chloride (NH_4Cl) was added to 300 ml of wastewater to get different molar ratios of NH_4-N:PO_4-P.

2.2 Wastewater

The experimental solutions were prepared by mixing accurately measured volumes of magnesium chloride, potassium dihydrogen phosphate and ammonium chloride dissolved in distilled water.
The parameters and conditions experiment are described in Table 1.

Table 1: The experimental parameters and conditions

No.	Parameters	Unit	Value
1	pH	-	8.5; 9.0; 9.5
2	$Mg^{2+}/PO_4{}^{3-}$	-	1; 1.25; 1.5
3	$NH_4{}^{+}/PO_4{}^{3-}$	-	1; 2.25; 3.5
4	Stirring speed	rpm/min	50
5	Temperature	˚C	30

2.3 Sampling and analysis

PO_4-P, NH_4-N were determined according to the Standard Methods. pH were measured by pH meter (Model: Sension 01 – Hach).
The MAP crystal solid sediment was collected from the bottom of reactor by centrifuging at 3000 rpm for 10 min. The obtained MAP solid mixture was dissolved into an acidic solution (pH 2.66 H_2SO_4) after which the supernatant was collected. The pH of the supernatant was then increased to 10.5 to derive pure MAP crystal formation. Subsequently, the white crystals were recovered from the solution.

2.4 Statistical modeling

The $PO_4{}^{3-}$-P in synthetically prepared wastewater was removed using struvite precipitation technology. A quadratic statistical modeling, response surface methodology (RSM), was applied to investigate the improvement availability for high-level removal of phosphorus by struvite precipitation. However, the general practice in determining the optimal conditions of struvite precipitation is by varying one parameter at one time while keeping the others constant. Such work is extremely laborious and time consuming. Therefore, the main purpose of this study was to develop, improve, and optimize struvite precipitation process using a response surface methodology optimization statistical model.

3. Results and discussion

3.1 Select the survey domain

When studying the conditions for the formation of struvite it is shown that this process is influenced by many factors such as temperature, rate of stirring, concentration of substance. pH, $Mg^{2+}/PO_4{}^{3-}$ and $NH_4{}^{+}/PO_4{}^{3-}$ strongly influence the formation of struvite. In this study, these three factors has been chosen to calculate in the domain. The correlation between the coding value and real value is shown in Table 2 and the Eq(2).

Table 2: The coding value and empirical elements

No	Variable	Symbol	Symbol encoding value		
			-1	0	+1
1	pH	X1	8.5	9	9.5
2	Mg^{2+}/PO_4^{3-}	X2	1	1.25	1.5
3	NH^{4+}/PO_4^{3-}	X3	1	2.25	3.5

3.2 Set up the model

The coding value, design results with the experimental planning matrix are shown in Table 3. Table 3 consists 20 experiments corresponding to 20 different values of three factors pH, Mg^{2+}/PO_4^{3-} and NH_4^+/PO_4^{3-} and resulting precipitation volume corresponds to the above values.
The effect to the three factors and the objective function (volume of precipitation obtained) were constructed by second order regression function for the objective function as Eq(2):

$$Y_i = \beta_0 + \sum_{i=0}^{k} \beta_i x_i + \sum_{i=0}^{k} \beta_{ii} x_i^2 + \sum_{i=0}^{k} \beta_{ij} x_i x_j \quad (2)$$

$Y_i$is the objective function and also is the precipitation volume;$\beta_0$is the coefficient of freedom;$\beta_{i,}\beta_{ii},\beta_{ij}$ are parameterized vector model that are defined empirically.
Statistics model is only meaningful and is use after satisfying statistical standards (Fisher).

Table 3: Experimental matrix with three factors, pH, Mg^{2+}/PO_4^{3-}, NH_4^+/PO_4^{3-}

No.	pH		Mg^{2+}/PO_4^{3-}		NH_4^+/PO_4^{3-}		Precipitation volume (g)
	Value	Symbol	Value	Symbol	Value	Symbol	
1	8.5	-1	1	-1	1	-1	0.1189
2	9.5	+1	1	-1	1	-1	0.1786
3	8.5	-1	1.5	+1	1	-1	0.1322
4	9.5	+1	1.5	+1	1	-1	0.1949
5	8.5	-1	1	-1	3.5	+1	0.1490
6	9.5	+1	1	-1	3.5	+1	0.1659
7	8.5	-1	1.5	+1	3.5	+1	0.1867
8	9.5	+1	1.5	+1	3.5	+1	0.2021
9	8.16	-1	1.25	0	2.25	0	0.0555
10	9.84	+1	1.25	0	2.25	0	0.1719
11	9	0	0.83	-1	2.25	0	0.2159
12	9	0	1.67	+1	2.25	0	0.1502
13	9	0	1.25	0	0.15	-1	0.1912
14	9	0	1.25	0	4.35	+1	0.3401
15	9	0	1.25	0	2.25	0	0.1392
16	9	0	1.25	0	2.25	0	0.1380
17	9	0	1.25	0	2.25	0	0.1569
18	9	0	1.25	0	2.25	0	0.1728
19	9	0	1.25	0	2.25	0	0.1623
20	9	0	1.25	0	2.25	0	0.1779

3.3 Analyze the meaning of the model with empirical

Analysis of model fit and significance of the model was assessed by ANOVA analysis in Table 4 and correlation indiced in Table 5.
The significance of the regression coefficients was determined by F standard, with value of $p< 0.05$ indicating significant regression coefficients.
The data in Table 4 showed that the value of “Model-F-value” was 4.18 and the model was statistically significant with a reliability of 98.21% ($p<0.0179$). In addition, the F standard was 7.14 ($p = 0.0251$) which indicated that the model was compatible with the experiment. The results in the study had shown that these factors influenced the formation of the struvite.
Table 5 showed the results of the analysis was fit and significance of the model with empirical data. The ANOVA results indicated that the R2 was of 78.99 %.

Table 4: Results of optimal ANOVA analysis

Source	Sum of Squares	df	Mean Square	F value	p value	
Model	0.042	9	$4.719x10^{-3}$	4.18	0.0179	significant
A – pH	$8.993x10^{-3}$	1	$8.993x10^{-3}$	7.96	0.0181	
B – Mg^{2+}/PO_4^{3-}	$3.582x10^{-6}$	1	$3.582x10^{-6}$	$3.171x10^{-3}$	0.9562	
C – NH_4^+/PO_4^{3-}	$7.951x10^{-3}$	1	$7.591x10^{-3}$	7.04	0.0242	
AB	$2.812x10^{-7}$	1	$2.812x10^{-7}$	$2.490x10^{-3}$	0.9877	
AC	$1.015x10^{-3}$	1	$1.015x10^{-3}$	0.90	0.3656	
BC	$2.453x10^{-4}$	1	$2.453x10^{-4}$	0.22	0.6512	
A2	$6.063x10^{-3}$	1	$6.063x10^{-3}$	5.37	0.0430	
B2	$2.315x10^{-4}$	1	$2.315x10^{-4}$	0.20	0.6604	
C2	0.016	1	0.016	14.07	0.0038	
Residual	0.011	10	$1.130x10^{-3}$			
Lack of fit	$9.908x10^{-3}$	5	$1.982x10^{-3}$	7.14	0.0251	significant
Pure error	$1.388x10^{-3}$	5	$2.776x10^{-4}$			
Total correlation	0.054	19				

Table 5: Results of the analysis of the fit of the model with experiment

Parameter	Value	Parameter	Value
Standard deviation	0.034	R – Squared	0.7899
Mean	0.017	Adj R – Squared	0.6008
C.V.%	19.77	Pred R – Squared	-0.4355
Press	0.077	Adeq Precision	9.917

Under the ratio condition of NH_4^+ /PO_4^{3-} was of 2.25, the optimum precipitation volume of struvite was depended on the pH of the reaction environment and the ratio of the concentration of Mg^{2+}/ PO_4^{3-} as showed in Figure 1. In Figure 2, the optimum point had been obtained during the survey of the pH and ratio of NH_4^+ /PO_4^{3-} under the condition of Mg^{2+}/PO_4^{3-} was set of 1.25 constant.

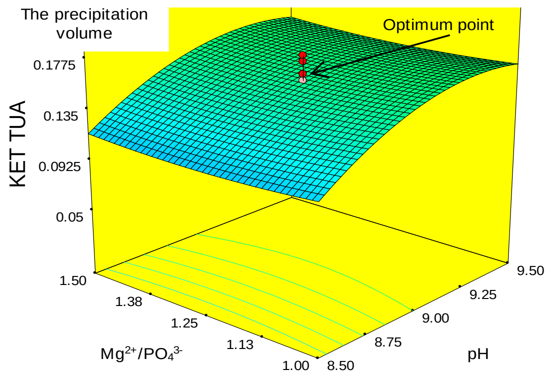

Figure 1: Surface response of pH & Mg2+/PO43- factors affected on the formation of struvite

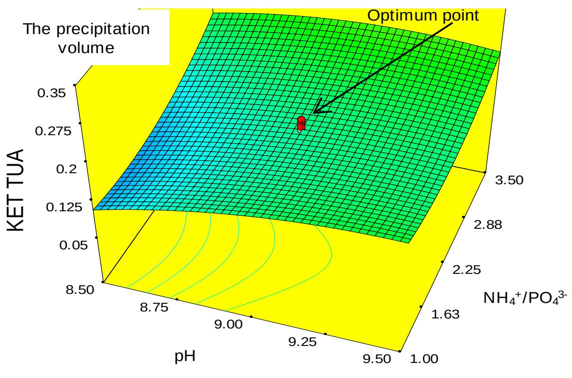

Figure 2: Surface response of pH& NH_4^+/PO_4^{3-}factors affected on the formation of struvite

Similarly, to survey the precipitation of struvite follows the ratio of Mg^{2+}/PO_4^{3-} and the ratio of NH_4^+/PO_4^{3-}, the experiment was carried out with the environment condition of pH was set of 9.00. The results of calculation response was showed in Figure 3 as follows:

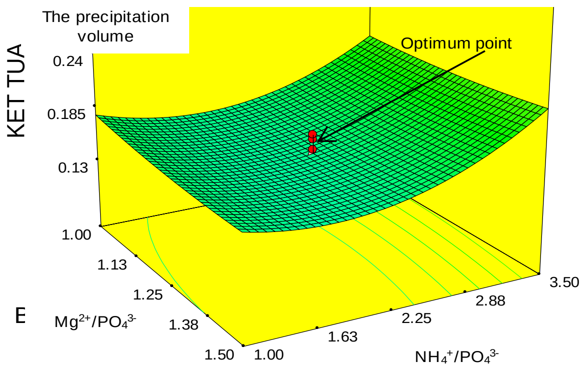

Figure 3: Surface response of the Mg^{2+}/PO_4^{3-}& NH_4^+/PO_4^{3-}factors affected on the formation of struvite

From the above analysis values, the expected function values given by the DX7 software are expressed in Eq(3).

$$Y = -7.0799 + 156675X_1 - 0.21575X_2 + 0.063683X_3 + 1.5 \times 10^{-3}X_1X_2 - 0.018020X_1X_3 + 0.01772X_3X_2 - 0.082042X_1^2 + 0.064134X_2^2 + 0.021256X_3^2 \quad (3)$$

Where Y is the expected precipitate; X_1 is value of pH; X_2 is value of Mg^{2+}/PO_4^{3-};$X_3$is value of NH_4^+/PO_4^{3-}.

3.4 MAP recovery from wastewater

For the solids tests, the sediments collected from the bottom of the process were purified using acid and alkali solutions. The properties of the recovered crystals were analyzed by the XRD analyses in Figure 4 and SEM showed in Figure 5.

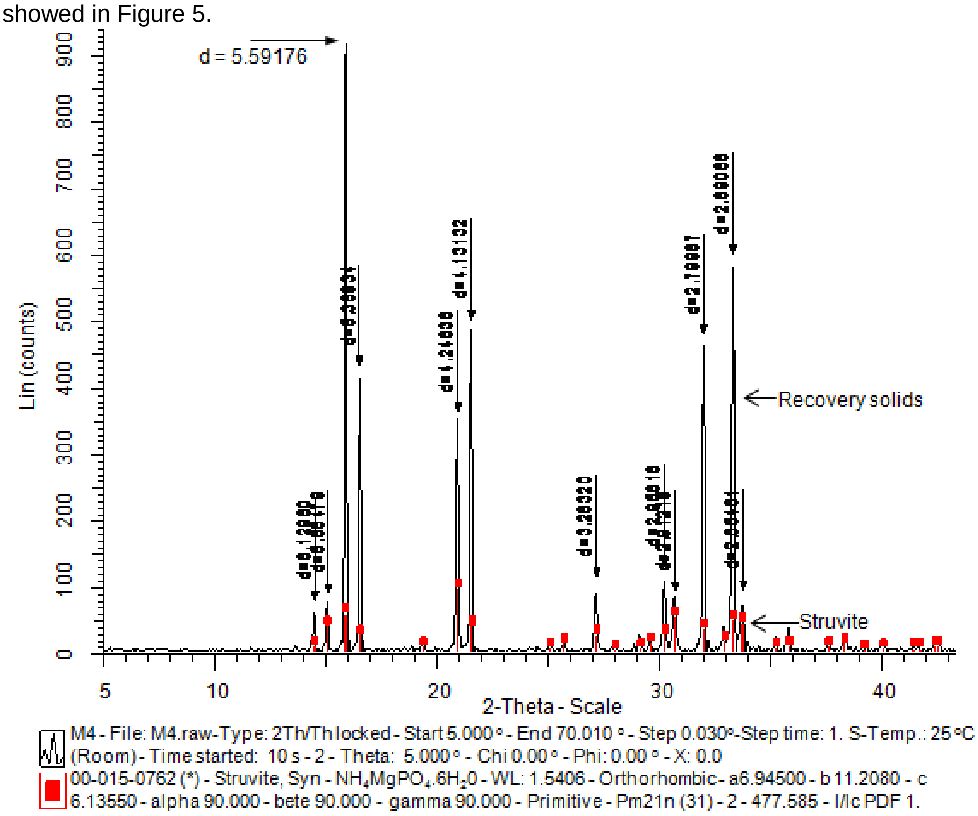

Figure 4: The X-ray diffraction analysis of the recovered crystals

The XRD pattern (position and intensity of the peaks) generated from the crystals matched the reference values, indicated that the precipitated crystals were MAP. The SEM analysis showed that the Struvite crystallized in the orthorhombic system and irregular-shaped. Crystals were in coarse shape and their size varied from couple of µm to several dozen of µm.

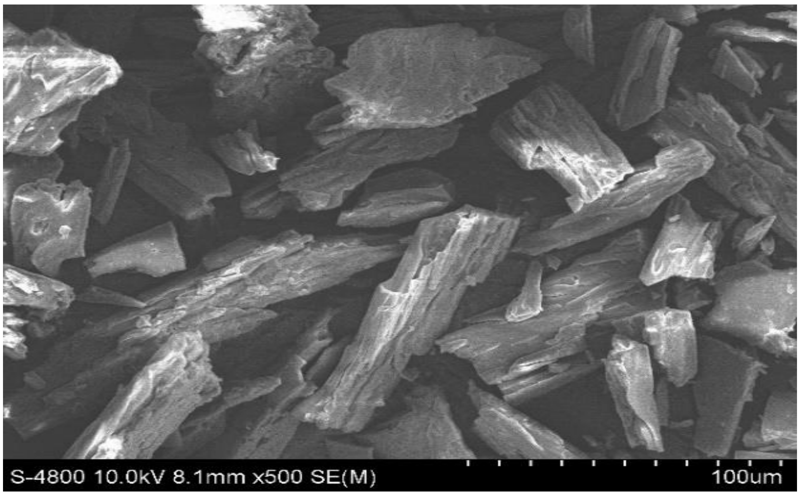

Figure 5: SEM picture of the recovered crystals

4. Conclusion

Using the mathematical model of experimental planning with surface response, the optimum concentration for the struvite precipitate medium was determined with three factors pH, Mg^{2+}/PO_4^{3-} and NH_4^+/PO_4^{3-}. The three factors as well as the interaction between these factors affected on the process of creating struvite. This method also determined the optimum level of the three factors: pH was 9.0; the ratio of $Mg^{2+}/PO_4^{3-}$was 1.25 and the ratio of NH_4^+/PO_4^{3-} was 4.35. The precipitation volume obtained with the optimum parameters was 0.3401g/300mLof the wastewater.

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