Simultaneous recovery of phosphorus and nitrogen from inorganic fertilizer wastewater

Dinh Huu Phu[1], Le Tuyet Ngoc[1], Le Nguyen Quang Tu[1], Do Thi Minh Hieu[1,2], Nguyen Quang Long[1,2*], and Minh-Vien Le[1,2**]

[1] *Faculty of Chemical Engineering, Ho Chi Minh City University of Technology (HCMUT), 268 Ly Thuong Kiet – Dist.10 - Ho Chi Minh City, Vietnam*
[2] *Vietnam National University, Linh Trung – Thu Duc – Ho Chi Minh City, Vietnam*
[*] *Corresponding author. E-mail: nqlong@hcmut.edu.vn*
[**] *Corresponding author. E-mail:lmvien@hcmut.edu.vn*

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Conventional method for removal of N and P from industrial wastewater by biological treatment requires a long hydraulic- retention- time (HRT) and strict conditions for protecting the microorganisms. This study focuses on N and P recovery by struvite ($MgNH_4PO_4.6H_2O$) precipitation method which is a fast chemical process. In order to control the specs of the sample, a simulated wastewater solution was prepared according to the parameters of inorganic fertilizer wastewater. The influence of pH (7-9), Mg/P molar ratio (1-1.6) and N/P molar ratio (1.2-2) in struvite recovery efficiency was evaluated and the obtained struvite samples were characterized using X-ray diffraction (XRD), scanning electron micrograph (SEM). Response surface methodology (RSM) was utilized in Box-Behnken experimental design and data analysis to obtain a mathematic for P and N recovery. The XRD and SEM results confirmed the formation of struvite structure with the particle size about 7-50 micrometers. The obtained struvite contained nutrients N, P2O5 and MgO which can be used directly in fertilizer formulation. The mathematic models for P recovery and N recovery were obtained from analyzing experimental data with p-value <0.05. Basing on the proposed parameters (pH=9, Mg/P=1.4 and N/P=1.2) obtained from the mathematic model, 98% of phosphorous from an actual fertilizer wastewater sample (pH=8.3, N/P=1.2, P=2.98 g L^{-1}) can be recovered. The obtained mathematic model and the suggested technical conditions can be applied for simultaneous recovery ammonium and phosphate from practical wastewater with high concentrations such as in fertilizer industry.

Keywords: fertilizer industry, nitrogen recovery, phosphorous recovery, process optimization, struvite

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1. Introduction

Because of the rapid population growth and high demand for food, the fertilizer industry must increase production to meet the need which causes the depletion of non-renewable resources and discharges a large amount of fertilizer wastewater into the environment. Wastewater from fertilizer industry often contains large amounts of NH_4^+ and PO_4^{3-} which cause oxygen reduction in the water due to the decomposition of microorganisms resulting in unpleasant odors and environmental pollution [1]. The high pollution of wastewater combined with stringent environmental regulations has created an increasing interest in the development of alternative treatment methods.

Currently, there are numerous nitrogen and phosphorus treatment technologies in use, each with its own advantages and limitations. Sequence Batch Reactor is a system used to treat nitrogen and organic-rich biological wastewater with high ability to remove nitrogen and phosphorus but it has complicated manual operation and automatic control system programming, air blower system easily clogged due to mud [2]. Although this technology is highly efficient, membrane bioreactor technology has a high investment cost to purchase membranes and is not applicable to wastewater with color or many chemicals [3]. Furthermore, the membrane is easy to get clogged which is time-consuming and requires manual maintenance. The Up-flow Anaerobic Sludge Blanket tank is designed for the treatment of wastewater with a high concentration of organic pollution and low solids content [4]. However, its performance depends on factors such as temperature, pH, and toxins in wastewater [5]. Although being more energy efficient than other aerobic technology in treating wastewater with high organic matter content, the output water quality of Anaerobic – Anoxic – Oxic wastewater treatment technology depends on many factors such as microbiological treatment efficiency, activated sludge settling capacity, temperature, pH, mixed liquor suspended solids sludge concentration [6]. Ammonia stripping technology is a physicochemical method to remove the gaseous phase from the liquid phase that is simple yet efficient to handle ammonia with high concentration [7]. However, the pH level in wastewater may cause NH4+ to convert into NH3 which causes secondary air pollution [8].

The recovery of phosphorus and nitrogen through struvite precipitation is one of the highly feasible and effective methods in recent years [9, 10]. This struvite is encouraging to be used in bioponics for growing vegetables in a hydroponic type system [11]. Struvite or magnesium ammonium phosphate (MAP) is a white crystalline compound with orthorhombic pattern. Its composition of magnesium, ammonium and phosphate makes it a potentially product for the fertilizer industry [12, 13]. The production of struvite utilized the following reaction (1) with a 1:1:1 molar ratio [14, 15].

$$Mg^{2+} + NH_4^+ + H_nPO_4^{3-n} + 6H_2O \longrightarrow MgNH_4PO_4.6H_2O + nH^+ \tag{1}$$

where, n = 0,1 or 2 depends on the pH of the solution.

With the solubility product constant in water of 7.8×10^{-15}, struvite has the potential of a slow release fertilizer which reduces the application dose from 20 to 30% but still has the same nutrient efficiency with conventional fertilizer [16, 17]. Struvite exhibits less nutrient loss due to soil erosion, evaporation, or adherence to soil and improves fertilizer use efficiency [18]. Nutrients (Mg, N and P) are provided throughout the plant's development cycle, helping plant roots grow well and stick deeply, contributing to increased plant resistance. As nutrients are slowly released overtime, nutrients loss are significantly reduced, especially nitrogen and nitrate loss through NO_3^- leaching and NH_3 volatilization [16]. Thus, it contributes to the reduction of greenhouse gases such as N2O and the risk of groundwater and air pollution. Struvite as a slow release fertilizer reduces toxicity, does not cause plant death due to nutritional shock when newly applied, does not degrade and kills soil microorganisms. In addition, slow release fertilizer also improves soil quality, increases the germination rate of plants [19].

Practically, it is required to optimal the process of struvite precipitation to achieve the highest production yield from wastewater. However, the general practice in determining the optimal conditions of struvite precipitation is extremely laborious and time-consuming as one parameter is varied at one time while keeping the others constant. One of the most well-known methods is the response surface methodology (RSM) [20, 21]. In previous studies, RSM combined with central composite design (CCD) was applied to study the effect of factors pH, concentration of ammonium, phosphate, magnesium and calcium on phosphorus recovery from real swine wastewater [22–24]. The RSM in conjunction with the Box-Behnken design was also used as a statistical tool to determine the effect of temperature, pH and concentration of added citric acid on the process of struvite precipitation [25].

This paper arms to provide a mathematic model from experimental data for prediction of N and P recovery by struvite precipitation method. This paper focuses on the recovery of N and P from simulated solution containing high concentration of N and P, which can be found in inorganic fertilizer wastewater. The influencing factors such as pH, Mg/P molar ratio and N/P molar ratio were investigated through the use of RSM combined with the Box-Behnken to optimize various reaction parameters for phosphorus and nitrogen removal during struvite precipitation. The practical parameters for application of struvite precipitation process will be proposed and discussed in this paper.

2. Materials and methods

2.1. Experimental set-up and struvite process

Experiments for simultaneous N, P recovery process using struvite precipitation technology were based on simulated wastewater prepared in the laboratory using the set-up as shown in Fig. 1. Experiments were duplicated for each run and the reported data were the average values obtained from the duplicated experiments. By keeping phosphorus content at 3000 ppm (about 9100 ppm phosphate),

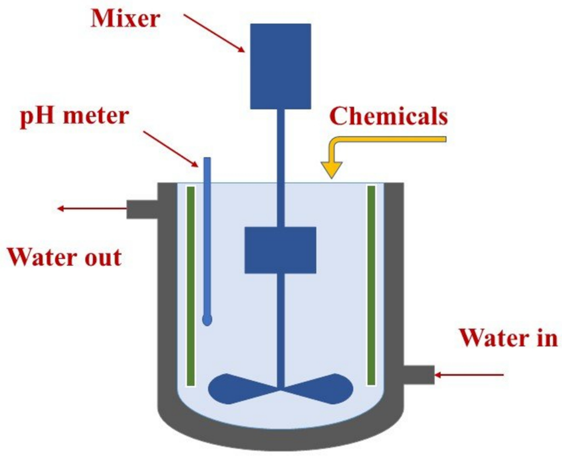

Fig. 1. Experimental set-up for struvite precipitation process

the simulated wastewater solutions were prepared by adding $MgCl_2.6H_2O$, $(NH_4)_2HPO_4$ and $Na_2HPO_4.12H_2O$ to 250 ml of deionized water according to the designed values described in section 2.2. The chemical $(NH_4)_2HPO_4$, $MgCl_2.6H_2O$, $Na_2HPO_4.12H_2O$, NaOH at the purity more than 99% purchased from Xilong Chemical Co. The chemical was used for experiments without further purification. After stirring the solution for 15 minutes, pH of the sample was adjusted using NaOH solution (40 wt.%) in drop-wise mode till to stably achieve the value which described in section 2.2. Then, the sample was stirred for 1 hour at 450 rpm. At the end of the reaction, the sample was aged for 1 hour at room temperature and then filtered to separate the precipitate from the liquid. The precipitation was dried at 40°C for 48 hours.

Nitrogen and phosphorus recovery were calculated by the following formula (2):

$$\begin{aligned} H(P) &= \frac{\left(\left[PO_4^{3-}\right]_0 - \left[PO_4^{3-}\right]_e\right)}{\left[PO_4^{3-}\right]_0} \times 100 \\ H(N) &= \frac{\left([NH_4^+]_0 - [NH_4^+]_e\right)}{[NH_4^+]_0} \times 100 \end{aligned} \tag{2}$$

where $[PO_4^{3-}]_0$, $[NH_4^+]_0$, and $[PO_4^{3-}]_e$, $[NH_4^+]_e$ were the ion concentrations of the solutions before and after the struvite precipitation.

2.2. Experiment design

Firstly, the Box-Benken design was applied to facilitate the optimization of the parameters efficiently with the minimum number of experiments, as well as allows the analysis of the interaction between the parameters. It was found that struvite can be precipitated at a wide range of pH (7.0-11.5) [26] Many studies have shown that there is an increase in P-removal ratio with an increase in pH, from pH7-pH9, get the highest yield of removals between pH 9 to 10 and decreased at pH >10 [27]. Hao et al. [28] stated that a highly purified (99.7%) struvite was formed at pH 7.0-7.5, decreased to around 3070% at pH 8.09.0 and decreased to <30% at over pH 9.5. Adnan et al. [29] also stated that the NH4 and PO4 removal was proportional up to pH 9.0, but the suitable pH range was 7.5-9.0 [30]. For Mg: P ratio, Tang et al. [31] reported that Mg:P ratio between 1 and 2 increases the degree of supersaturation. A further increase of Mg: P ratio did not significantly increase the phosphorus removal efficiency but increased the chemical dosage cost. In addition, N:P ratio in the real wastewater was predetermined as highest as 2:1. In this study, pH (A), Mg/P molar ratio (B), N/P molar ratio (C) were selected as independent variables. These parameters were studied at three levels: -1 (low level), +1 (high level) and 0 (used for center point). The target function is nitrogen and phosphorus recovery efficiency. Basing on the literature and preliminary experiments, the levels and ranges of the factors used in this study are presented in Table 1.

The number of experiments calculated by Design Expert 11.0 software is 15 experiments as shown in Table 2. Investigating and selecting three experiments at the center with three independent variables and two responding surfaces which are the recovery efficiency of nitrogen and phosphorus.

2.3. Physical and chemical analysis

The morphology, size and shape of samples obtained after precipitation were determined by scanning electron microscopy (SEM) performed on Hitachi Fe-SEM S4800. To identify the phase composition of the sample obtained after precipitation we use the X-ray powder diffraction (XRD) method with an X-ray diffraction meter (D8 Advance, Brucker, Germany), with CuKα radiation (λ = 1.5418 Å) generated at 40 kV and 40 mA. The elemental composition (total N, total P and Mg) of final precipitates struvite was measured by complete dissolution of product in 0.1M HCl solution with assistance of ultra-sonicated vibration for 15 min and the ion concentrations were measured as described above. Mg content was measured by titration method using EDTA. The total N content in the wastewater and in struvite was measured by Kjeldahl Apparatus (Behr, S2-Germany) according to Standard Methods [32]. The total P was determined according to the Ammonium Molybdate Spectrophotometric Method on the Hitachi spectropho-

Table 1. Scope and variation of factors

Real variables	Code	Level		
		-1	0	+1
pH	A	7	8	9
Mg/P molar ratio	B	1	1.3	1.6
N/P molar ratio	C	1.2	1.6	2

Table 2. Box-Behnken matrix and analyzed experimental data

Std	Run	Factor 1 A: pH	Factor 2 B: Mg/P molar ratio	Factor 3 C: N/P molar ratio
13	1	8	1.3	1.6
10	2	8	1.6	1.2
12	3	8	1.6	2
6	4	9	1.3	1.2
9	5	8	1	1.2
14	6	8	1.3	1.6
2	7	9	1	1.6
3	8	7	1.6	1.6
15	9	8	1.3	1.6
5	10	7	1.3	1.2
4	11	9	1.6	1.6
8	12	9	1.3	2
11	13	8	1	2
1	14	7	1	1.6
7	15	7	1.3	2

tometer U-2910, similar to Weijia Gong et al. (2018) [33] pH of solutions was measured with portable pH meter (HI 83141, Hanna, Italy).

2.4. Statistical and data analysis

Analysis of variance (ANOVA), which provides such as the lack of fit of the model (Lack of fit), the correlation coefficient R^2, the F coefficient (Fisher), is used to determine the suitability of the model. With a large F value and a small p-value, the analytical results will be considered reliable. For example, if the p-value is 0.01, the probability of a correct conclusion is 99%. In the analysis of Design-Expert 11.0, if the p-value is less than 0.05 then the model is considered to be effective. After the experiments were completed, a quadratic polynomial regression equation was used to illustrate the relationship between the predicted response and the process parameters (Eq. (3)):

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i_{i=1}}^{k} \sum_{j>1}^{k} \beta_{ij} X_i X_j \qquad (3)$$

where: Y represents the predicted response, β_0 is the constant term, β_i is the linear coefficient, β_{ii} is the quadratic coefficient and β_{ij} is the interaction coefficient, X_i is the i-th independent factor affecting the target function Y. After examining the technological factors affecting nitrogen and phosphorus recovery efficiency by Design Expert software, it is necessary to standardize these parameters to obtain high nitrogen and phosphorus recovery efficiency with economic benefit and feasible operation procedure. This regression equation can be used in optimization calculations.

3. Results and discussion

3.1. Experimental data and mathematical analysis

The experimental data are shown in Table 3 where the recovery efficiency of phosphorus (Response 1 P(R)%) and nitrogen (Response 1 N(R)%) was calculated by determining the concentration in the solutions after and before treatment.

The results of ANOVA variance analysis are shown in Tables 4 and 5. The F value of phosphorus and nitrogen recovery efficiency were 112.21 and 70.75, respectively, with a low probability value ($p < 0.05$) also indicates a high significance of the model for both responses. In ANOVA, the cor-total sum-of-square is the sum of model sum-of-square and residual sum-of-square. The residual sum-of-square or the sum-of-square due to error is the total of lack-of-fit sum-of-square and pure-error sum-of-square. The second row of Table 4 and Table 5 the model was statistically significant due to the small p-value. Moreover, it is indicated that the pure-error, which is the amount of difference between replicate runs at center point, was low and the model's error is mainly due to the lack-of-fit. Since the lack-of-fit was

Table 3. Box-Behnken matrix and analyzed experimental data

Std	Run	Factor 1 A: pH	Factor 2 B: Mg/P	Factor 3 C: N/P	Response 1 P(R)%	Response 2 N(R)%
13	1	8	1.3	1.6	92.1	53.2
10	2	8	1.6	1.2	95.17	84.16
12	3	8	1.6	2	96.23	49.22
6	4	9	1.3	1.2	97.75	87.74
9	5	8	1	1.2	81.16	74.76
14	6	8	1.3	1.6	90.5	55.14
2	7	9	1	1.6	85.1	72.7
3	8	7	1.6	1.6	87.33	56.38
15	9	8	1.3	1.6	91.23	53.27
5	10	7	1.3	1.2	81.2	62.88
4	11	9	1.6	1.6	99.94	82.33
8	12	9	1.3	2	99.81	64.37
11	13	8	1	2	81.9	45.86
1	14	7	1	1.6	73.21	43.76
7	15	7	1.3	2	82	39.01

not significant, the model's error can be acceptable. Furthermore, the independent parameters of pH, Mg/P and the quadratic effect of Mg/P for phosphorus and nitrogen recovery were significant with p value <0.05, as shown in Table 4 and Table 5. In addition, the high correlation coefficient R2 of 0.9684 and 0.9815 for phosphorus and nitrogen recovery performance (in Fig. 2) continue to show a good correlation between experimental and predictive models.

In Design-Expert 11.0, the significant factors (where $p < 0.05$) were chosen to establish the relationship model are shown in Equations (4) and (5). The calibration plots of the quadratic regression model of the experiment compared with the theory of each recovery efficiency are shown in Fig. 2. It can be seen that the results obtained from the Equations (4) and (5) were in agreement with the experimental data. The R-squared was 0.9815 and 0.9684 for the case of phosphorous recovery and nitrogen recovery, respectively.

$$\mathrm{Y(P)} = -35.00794(\mathrm{Mg/P})^2 + 114.89563(\mathrm{Mg/P}) + 7.35750\mathrm{pH} - 58.40520 \tag{4}$$

$$\mathrm{Y(N)} = 29.17969(\mathrm{N/P})^2 + 55.12500(\mathrm{Mg/P})^2 + 4.96125\mathrm{pH}^2 - 128.08750(\mathrm{N/P}) - 128.73750(\mathrm{Mg/P}) - 66.24125\mathrm{pH} + 470.71750 \tag{5}$$

For illustration, the correlations of nitrogen and phosphorous recovery with the two main technical parameters are also represented by response surface plots and contour plots in Figs. 3 and 4. The effect of individual parameter is shown in Figs. 5 to 7. It can be seen from Figs. 3 and 4 that optimal points are not observed in the response surface plots for both N and P recovery in the interested range. However, the limitation, the trend and approximated values of N and P recovery can be easily and visually obtained from the plots. Additionally, as reflected from the contour plots, one can have ideas for controlling the two parameters to obtain certain recovery efficiencies. For example, it can be seen from the Fig. 3b that, to recover 90% of phosphorus there are many conditions which are points on the contour 90%.

3.2. Effect of factors on nitrogen and phosphorus recovery

Figs. 5 to 7 show the effect of pH, Mg/P molar ratio, and N/P molar ratio on the nitrogen and phosphorus recovery. The pH of solution is an important factor for the crystallization of MAP. As shown in Fig. 5, when pH increased from 7 to 9, the phosphorus and nitrogen recovery rate increased from 83.21% to 97.97% and from 45.63% to 71.88%, respectively. It can be seen that pH affects the balance of ions involved in the crystallization process. The increase in pH can change the balance of the struvite components, leading to changes in the inter-saturated state. In terms of the dynamics of the nucleation, crystal growth and ultimate the size distribution of struvite. Moreover, with an increase in pH, the solubility of struvite decreased which is favorable for the formation of a struvite precipitate [34–36]. Therefore, the recovery efficiencies of both phosphorous and nitrogen were increased at high pH.

The Mg/P ratio had shown a strong effect on the phosphorus recovery efficiency and a weak impact on the nitrogen recovery efficiency. In Fig. 6b, the phosphorus recovery efficiency increased by 14.26% when the ratio of Mg/P increased from 1 to 1.6. However, under the same change, the recovery efficiency of nitrogen only increased slightly

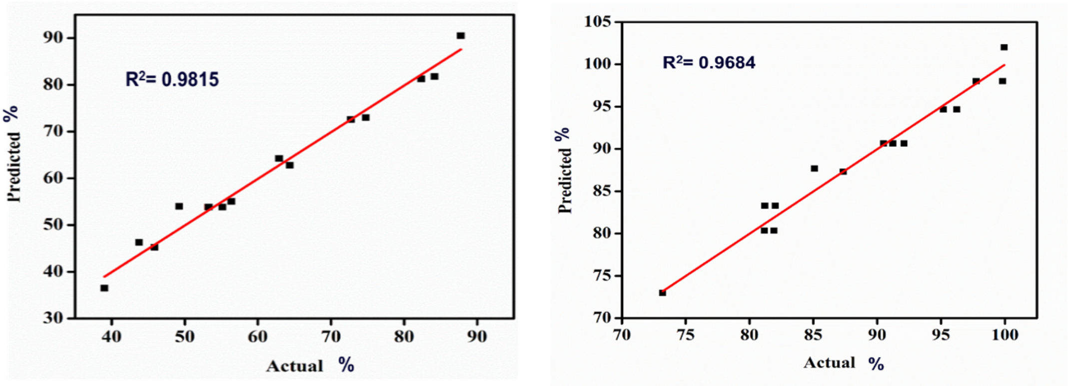

Fig. 2. Comparison plot of quadratic regression model of experimental compared with theory for nitrogen recovery efficiency (left) and phosphorus recovery efficiency (right)

Table 4. ANOVA results for phosphorus recovery efficiency response

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	880.53	3	293.51	112.21	< 0.0001	significant
A-pH	433.06	1	433.06	165.57	< 0.0001	
B-Mg/P	410.41	1	410.41	156.91	< 0.0001	
B^2	37.06	1	37.06	14.17	0.0031	
Residual	28.77	11	2.62			
Lack of Fit	27.49	9	3.05	4.76	0.1856	not significant
Pure Error	1.28	2	0.6416			
Cor Total	909.31	14				

Table 5. ANOVA results for nitrogen recovery efficiency response

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	3303.90 6	550.65	70.75	< 0.0001	significant	
A-pH	1381.01	1	1381.01	177.43	< 0.0001	
B-Mg/P	153.21	1	153.21	19.68	0.0022	
C-N/P	1542.35	1	1542.35	198.15	< 0.0001	
A^2	90.88	1	90.88	11.68	0.0091	
B^2	90.88	1	90.88	11.68	0.0091	
C^2	80.48	1	80.48	10.34	0.0123	
Residual	62.27	8	7.78			
Lack of Fit	59.85	6	9.97	8.24	0.1122	not significant
Pure Error	2.42	2	1.21			
Cor Total	3366.17	14				

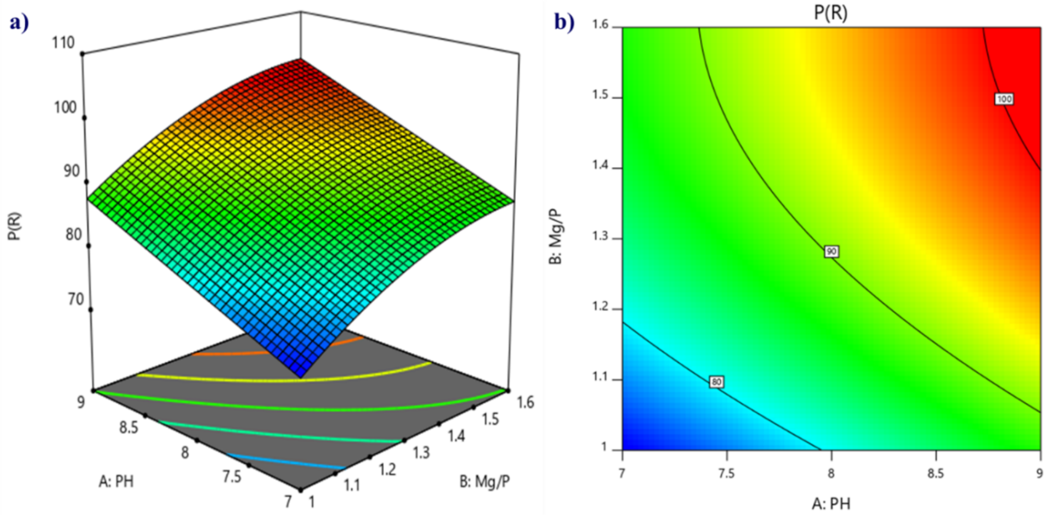

Fig. 3. (a) A typical surface response plot and (b) contour plot for the phosphorus recovery

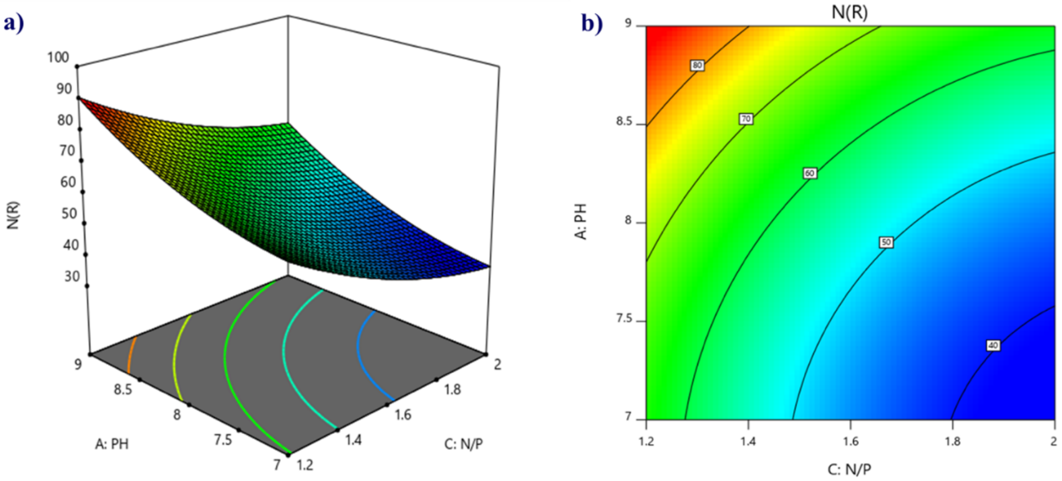

Fig. 4. (a) A typical surface response plot and (b) contour plot for the nitrogen recovery

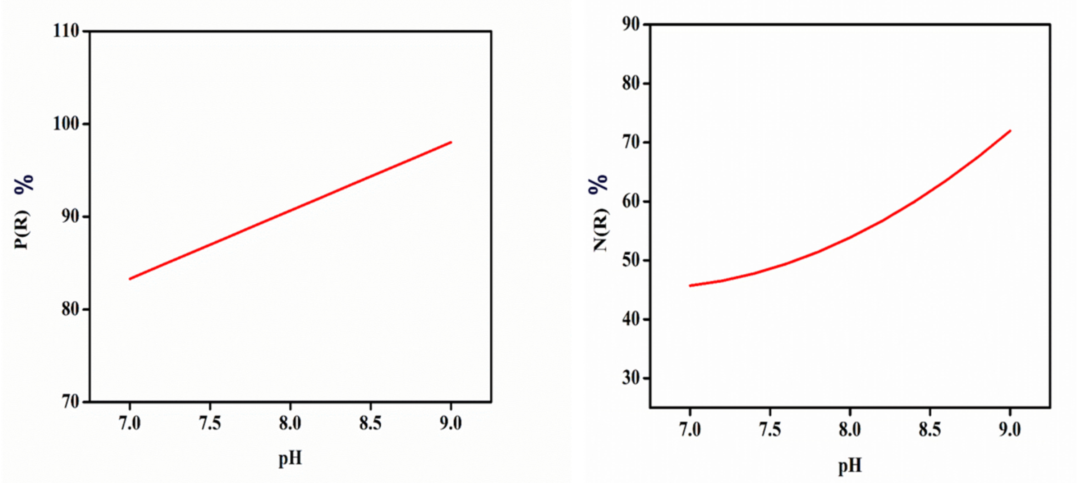

Fig. 5. The effect of pH on the phosphorus (left) and nitrogen (right) recovery efficiency

by 8.8%, as shown in Figure 6a. The above analysis shows that the recovery of nitrogen and phosphorus from simulated fertilizer wastewater can be promoted by increasing the molar ratio of Mg^{2+} and PO_4^{3-} in solution. Nevertheless, increasing a large amount of magnesium ion is not economical.

Mathematic regression Eqs. (4) and (5) showed the effect of the N/P molar ratio on N, P recovery. The N/P molar ratio influenced N recovery significantly, while it was not an effective parameter in P recovery. As seen in Figure 7 when the N/P ratio changed from 1.2 to 2.0 the nitrogen recovery reduced rapidly from 72.45% to 44.64%. In fact, in chemical composition of struvite ($MgNH_4PO_4.6H_2O$) the N/P molar ratio is 1. The high N/P molar ratio in the solution can lead to high recovery of phosphorous. However, the remaining nitrogen in the solution was also high. As a result, the nitrogen recovery of the process decreased.

3.3. Characterization of struvite

In this study, four samples, whose molar ratios of Mg/P molar ratio, N/P molar ratio, and pH are [1-2-8]; [1.6-2-8]; [1-1.6-9]; [1.3-1.6-8] respectively, were selected for comparative analysis of their purity and morphological structure. X-ray diffraction spectra generated from the samples are relatively consistent with the database model of struvite as shown in Figure 8. The XRD pattern of four samples exhibited characterization peaks at [15.80°, 20.87°, 31.91°]; [15.80°, 20.86°, 31.92°]; [15.82°, 20.87°, 31.95°] and [15.80°, 20.86°, 31.92°] which are corresponding to the characterization peaks of struvite at 2-theta value of [16°, 21°, 32°]. Therefore, it can be confirmed that the samples are mainly struvite.

The morphology and surface structure of the four struvite samples are shown in Fig. 9 The crystals stacked, had signs of fracture and had an irregular shape with length between 7.58 and 49.28 μm. Due to the pressure in the crystalline structure causing by the impurities covering the struvite crystal surface, many crystals cracked and created uneven surface morphology, deformed edges. In addition, the preparation procedure also affected the struvite structure and morphology. It also important note that the wide particle size distribution of obtained struvite in micrometer range is not affected to prepare NPK fertilizer granulation by rotating drum or compaction or making NPK fertilizer in powder [37]. Therefore the obtained struvite can be fine for using as a raw material for making fertilizer.

3.4. Discussion on parameters for N and P recovery from fertilizer wastewater

In actual fertilizer wastewater, pH, concentration of N and P vary depending on factory and also the period of production of a typical fertilizer. In the fertilizer industry phosphorous recovery is significantly more important than the nitrogen recovery because the phosphorus is a non-renewable resource and is being exploited at an increasing rate to meet fertilizer demand for agricultural production. Among phosphorous-containing inorganic fertilizer, struvite or MAP ($MgNH_4PO_4.6H_2O$) is an important raw material for producing slow-release fertilized since the solubility product constant of this compound is 7.8×10^{-15} [38]. Therefore, simultaneous recovery of N and P in the form of struvite is a value-added environmental treatment method.

For P recovery, according to the mathematic regression model as shown in Eq. (5), the efficiency of P recovery depends on pH and Mg/P molar ratio. The effect of N/P

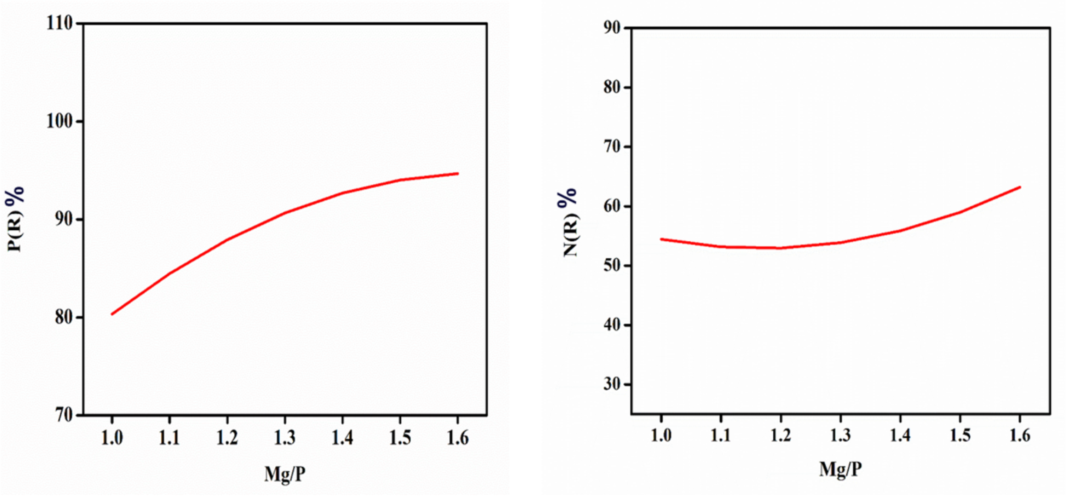

Fig. 6. The effect of Mg/P ratio on the phosphorus (a) and nitrogen (b) recovery efficiency

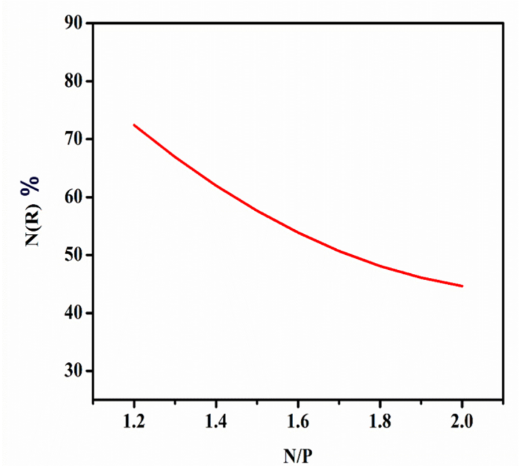

Fig. 7. The effect of N/P molar ratio on the nitrogen recovery efficiency

molar ratio was not significant in the range of investigation (N/P molar ratio: 1.2 – 2.0). It was reflected from Fig. 7 that the P recovery (and also N recovery) was increased at high pH. Increasing pH of the fertilizer wastewater requires certain amount of chemicals which is alkaline, usually NaOH, for raising pH and acid, usually HCl or H_2SO_4, for neutralizing the effluent before flowing to the water reservoir. In order to avoid using acid for neutralization, chosen pH for the struvite process should be the maximum allowable pH according to the country environmental regulation. In Vietnam, the pH limitation of the industrial effluent in is from 6-9 (QCVN 40:2011/BTNMT). Additionally, the P recovery can also be improved by increasing Mg/P molar ratio. It means that adding more Mg-containing salt such as cheap and available $MgCl_2$ can facilitate the precipitation

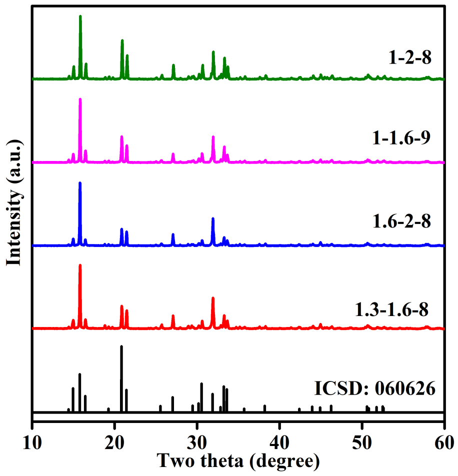

Fig. 8. XRD pattern of struvite samples

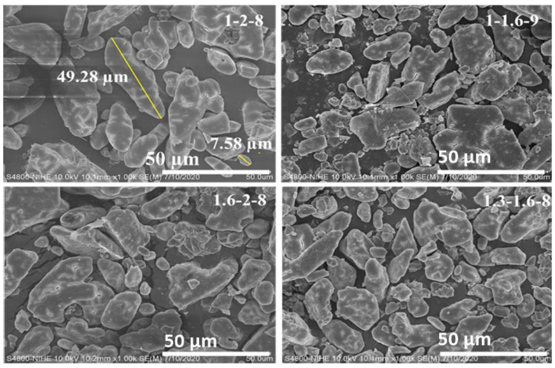

Fig. 9. SEM images of struvite samples with [Mg/P - N/P - pH] are [1-2-8], [1-1.6-9], [1.6-2-8] and [1.3-1.6-8]

of struvite. Fig. 10 shows proposed parameters for struvite process to simultaneous recovery of N and P from an example of fertilizer wastewater which was collected from an NPK fertilizer factory in the South of Vietnam. There are two proposed parameter sets for the struvite process. The first set of pH and Mg/P molar ratio is for the purpose of completely recovering the phosphorous from the wastewater. The second set of pH and Mg/P molar ratio is for the purpose of minimizing added chemicals which optimizes the cost for the treatment process. It can be seen that the calculated phosphorous recoveries obtained from the mathematic regression model were in agreement to the experimental data as shown in Fig. 10. Theoretically at N/P > 1.0 and Mg/P > 1.0 the recovery of P should be 100% because the chemical formula of the struvite is $MgNH_4PO_4.6H_2O$. However, since pH of the solution was maintained at basic condition and the solution was stirred for quite long time (1 hour) then aged for another 1 hour, it is possible that a part of NH^{4+} has been converted to gaseous NH_3 and a part of Mg^{2+} has been converted to precipitated $Mg(OH)_2$. Therefore the P recovery in experimental data and from the model were not 100%. It means that these values were lower than theoretical values. Moreover, since the differences between phosphorus recovery in real case and prediction were not significant, it can be concluded that the interferences of other ions in the actual fertilizer wastewater can be neglected during the struvite process.

In fact, the actual wastewater from the fertilizer company contained other ions such as K^+, Cl^-, and SO_4^{2-}. However, while most of the salts, which can be generated from those ions, are soluble in water, struvite is the only compound almost insoluble in water due to the significantly low solubility product constant (7.8×10^{-15}). Additionally, as observed from experiments the struvite precipitation process was immediately happen when pH was adjusted. As reviewed by Li et al. [39] these ions affected only the induction time of the struvite precipitation process. Therefore, the interference of the other ions can be neglected during the struvite precipitation. As a result, in the case of using actual wastewater, the obtained phosphorus recovery from experiment was in agreement with the calculated one (Fig. 10). It is also worth noting that more analysis may be required if the actual wastewater is not come from NPK fertilizer companies.

4. Conclusions

The struvite formation during simultaneous recovery of nitrogen and phosphorous has been study experimentally. The XRD and SEM results confirm the formation of struvite structure with the particle size about 7-50 micrometers. By experimental design and data analysis, mathematic regression models for P recovery efficiency and N recovery efficiency from simulated wastewater containing high concentration of N and P were obtained. The effects of pH, Mg/P molar ratio and N/P molar ratio on the P, N recovery were discussed. The pH and Mg/P molar ratio are the significant factors influencing P recovery efficiency, while all three factors are controlled factors for N recovery efficiency. Basing on the mathematic model, two parameter sets were proposed for an example of actual fertilizer wastewater to completely recover phosphorous or minimize added chemicals.

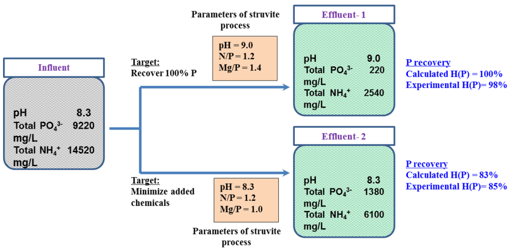

Fig. 10. The proposal for struvite process for an example fertilizer wastewater

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