



Effects of pH, molar ratios and pre-treatment on phosphorus recovery through struvite crystallization from effluent of anaerobically digested swine wastewater

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ABSTRACT

Struvite precipitation has been proven to be an effective method in removing and recovering ammonia nitrogen (N) and phosphate phosphorus (P) from wastewater. In this study, effects of pH, molar ratios and pre-treatment of effluent of anaerobically digested swine wastewater were investigated to improve struvite crystallization. The magnesium : ammonium : phosphate ratio of 1.2 : 1.0 : 1.0 was found to be optimal, yet the molar ratio in the wastewater was 1 : 74.9 : 1.8. From the analysis, the optimum pH was between 8.0 and 9.0 for maximal phosphate P release and from 8.0 to 10.0 for maximal ammonia N and phosphate P removal from real wastewater. Analysis from Visual MINTEQ predicted the pH range of 7-11 for ammonia N and phosphate P removal and recovery as struvite. For pre-treatment, microwave pre-treatment was ineffective for phosphate P release but ultrasound pre-treatment showed up to 77.4% phosphate P release at 1,000 kJ/L of energy dose. Precipitates analysis showed that phosphorus and magnesium in the collected precipitate had almost same values as theoretical values, but the ammonia content was less than the theoretical value.

Keywords: Ammonia and phosphate recovery, Magnesium ammonium phosphate, Pre-treatment, Struvite, Ultrasonic treatment

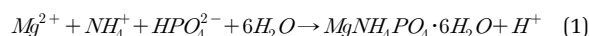
1. Introduction

Recently livestock wastewater treatment and recycling in South Korea have become a big issue as animal wastewater generation has reached to about 46,000 Mm³/y. Also, the wastewater from the pig farming industry poses serious social and economic problems due to the negative effect on the environment with respect to treatment and recycling of swine wastewater [1-2]. The treatment and recovery of nutrient from the waste stream is important, since swine wastewater contains high concentrations of nitrogen and phosphorus that cause eutrophication in water bodies. Recently, the depletion of phosphorus resources has been a big issue, which has been discussed on a global basis [3], although it is estimated that 7,000 billion kg of phosphate rock still exists [2].

Phosphorus as well as nitrogen in swine wastewater after anaerobic digestion has been widely used as a liquid fertilizer in Korea.

However, the quick-release fertilizer application is a principal source of nitrogen and phosphorus pollution in the farming field, causing water pollution. Alternative methods, however, such as crystallization and adsorption processes have been developed to recover nutrients to high quality [4-6]. Among these techniques, the crystallization process of the magnesium ammonium phosphate (MAP, also known as struvite) is considered to be one of the better techniques, as struvite crystallization is cost-effective and yields high-quality nutrients, used as valuable slow-release fertilizers [7-9].

Struvite (MgNH₄PO₄·6H₂O) is a crystalline substance consisting of magnesium, ammonium, and phosphate ions in equal molar concentrations. Struvite crystal is commonly formed as scale after anaerobic digestion on pipe walls and reactor vessels. The chemical equation for struvite crystal formation is as follows [10]:



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Struvite precipitation from wastewater is influenced by a large number of parameters such as pH of the reaction, molar ratio, interfering ions in the feed, reaction time, types of chemicals added, types of the reactor used and temperature. From these, the reaction pH and molar ratios of reactants, namely magnesium : ammonium : phosphate molar ratios, are the main factors for struvite precipitation.

The pH of the reaction plays a significant role during struvite precipitation process, and not only affects the amount of struvite precipitation, but also its purity. Increasing the pH and the reactant concentration can reach solution saturation but increasing the pH of the solution is more feasible and allows for more varied applications [11]. Struvite can be precipitated at a wide pH range (from 7.0 to 11.5), but the suitable pH range is from 8.0 to 9.5. Struvite precipitation is a physico-chemical process that can occur over a range of pH values bounded by the speciation of struvite components so that the concentrations of magnesium, ammonium and phosphate ions can be affected by the pH of the solution [12]. A variety of magnesium and phosphate complex ions patterns in the reactor solution, including MgOH^+ , $\text{Mg}(\text{OH})_3^-$, $\text{MgH}_2\text{PO}_4^+$, MgHPO_4 , H_3PO_4 , H_2PO_4^- , HPO_4^{2-} , MgPO_4^- can be formed when the pH of solution is varied [13].

The pH of the solution in the struvite precipitation reactor influences struvite solubility. With increasing the pH, the struvite solubility decreases, but the solubility begins to increase when the pH rises above pH 9; this is because the ammonium ion concentration decreases and the phosphate ion concentration increases [12, 14]. As various factors such as reaction pH, ionic strength and temperature affect struvite solubility, which in turn determines the supersaturation ratio [15]. It is the excess supersaturation in the liquid that is the major parameter in predicting struvite precipitation potential [16]; therefore, it is important to use chemical equilibrium-based models to calculate and predict the practical conditions for struvite formation. There is a geochemical equilibrium speciation model MINTEQA2 that could be used to model struvite formation [17]. For calculating metal speciation, solubility equilibria, sorption, etc., for natural waters, visual MINTEQA2 is available as a freeware chemical equilibrium model.

For the anaerobically digested effluent of swine wastewater from livestock, there is generally less magnesium and phosphate ions compared with ammonium ion. It is then necessary to add a source of magnesium and phosphate ions to enhance the struvite crystallization process. The concentration of phosphate ion is expected to increase through solubilization of total phosphorus. The first step, thus, is to enable phosphate P release from solid phases to increase the recovery of phosphorus by the struvite crystallization process. The general methods to facilitate phosphate P release are physical and chemical techniques [18-20]. Among these techniques, alkaline-ultrasonic pre-treatment is preferred as it also disintegrates the solid from swine wastewater and enhances the anaerobic digestion process [21-22].

The objectives of this study were to investigate the effect of pH and molar ratios for magnesium, ammonium, and phosphate ions on ammonia N and phosphate P removal and recovery. Also alkaline-ultrasonic pre-treatment was applied to the struvite crystallization process to enhance nutrient recovery.

2. Materials and Methods

2.1. Materials

The anaerobically digested effluent of swine wastewater used in the study was from the P-city swine wastewater treatment plant in Korea. The effluent of swine wastewater was concentrated at 4°C for 24 h and its main characteristics are shown in Table 1. Based on the initial composition of the effluent solution, magnesium and phosphate ions concentrations were very low, and they needed to be increased to reach the desired molar ratios for magnesium, ammonium, and phosphate ions. For both synthetic and real wastewater, the concentrations of magnesium, ammonium and phosphate ions were adjusted to the required molar concentration using $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, NH_4Cl and KH_2PO_4 solutions, respectively. All reagents were of analytical grade. To investigate the effect of reaction pH, 2 N HCl and 2 N NaOH were used to adjust the pH, and the pH was monitored with a pH meter. In addition, the pH influenced the phosphorus fractions [22-23].

Table 1. Characteristics of the Effluent from the Anaerobically Digested Swine Wastewater

	Concentration
pH	8.17
T-N (mg/L)	2,350
$\text{NH}_3\text{-N}$ (mg/L)	1,775
T-P (mg/L)	612
$\text{PO}_4\text{-P}$ (mg/L)	221

2.2. Crystallizations Experiments

A lab-scale airlift reactor with a working volume of 5 L was used for struvite crystallization. The schematic diagram of the experimental apparatus for struvite crystallization is shown in Fig. 1. The reactor operated with a 10 min hydraulic retention time for the mixing zone and 3 h for the whole reactor. The obtained struvite cake from the process was dried at room temperature to form a powder.

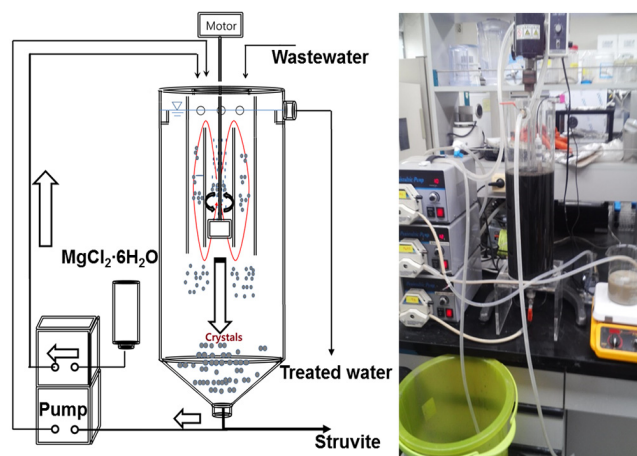


Fig. 1. Experimental equipment for struvite crystallization.

2.3. Pre-treatment for Phosphate P Release

Ultrasonic pre-treatment was performed for phosphate P release with STH-750S ultrasound (Sonitopia, Korea) with operating frequency of 20 kHz and maximal power of 750 watt. Microwave pre-treatment device had a microwave frequency of 2,450 MHz with maximal power of 600 watt. During pre-treatment, the supplied energy density ranged from 100 to 20,000 kJ/L. The energy density of pre-treatment device can be defined with following Eq. (2) (the energy density conditions of pre-treatment are shown in Table 2):

$$\text{Energy density (kJ/L)} = \frac{\text{Power} \times t}{1000 \cdot V} \quad (2)$$

where *Power* is in watt, *t* (time) in s, and *V* (sample volume) in L.

Table 2. Energy Density Used in Pre-treatment

Energy density (kJ/L)	Electricity (watt)	Contact time (s)
100	33	300
200	67	300
500	167	300
1,000	333	300
2,000	667	300
5,000	750	667
10,000	750	1,334
20,000	750	2,667

2.4. Analysis and MINTEQ Model

The concentrations for total nitrogen (T-N), ammonia N, pre-treatment for organic phosphate measurement were determined by the following standard methods [24]. To study the release of phosphate ions concentration at different ultrasonic doses with ultrasonic disintegration, total phosphorus (T-P) and ortho-phosphate P (PO₄³⁻-P) levels in the effluent of the swine wastewater were established by the Persulfate Digestion Method in HACH methods 10072. The phosphorous concentrations were determined by the ascorbic acid method, using a UV-V is spectrophotometer at 800 nm (Smart Plus SP-1900PC, Woongki Science, Seoul, Korea). The pH meter (Orionstar, Thermo Scientific, Waltham, MA, USA) was calibrated after each experiment. The potential for struvite formation as a function of pH was predicted by using chemical equilibrium freeware Visual MINTEQ 3.0 developed by the U.S. Environmental Protection Agency. Using the composition of the anaerobically digested effluent of swine wastewater from P-city as input, the model's.

3. Results and Discussion

3.1. Effect of MAP Molar Ratios on Struvite Formation

In this research, the effects of Mg²⁺ : NH₄⁺ : PO₄³⁻ molar ratios on struvite crystallization using synthetic swine anaerobic digester wastewater were analyzed based on indications from previous work [25-27]. At the start of the experiment, using a 0.1 NaOH

solution, the initial pH of the digester effluent sample was adjusted to 9.0. Table 2 shows the effect of molar ratios on ammonia and phosphate ions removal. Molar ratio of Mg²⁺ : NH₄⁺ : PO₄³⁻ for the effective removal seemed to be 1.2 : 1.0 : 1.1.

Nelson et al. reported that adding magnesium ions did not play an important role in phosphorus removal [11]. Therefore, external addition of magnesium and phosphate should be controlled to ensure the feasibility of struvite precipitation from wastewater. Rahman et al. had a wide range of PO₄³⁻ and Mg²⁺ ratios tested for struvite precipitation, but in most cases, the effective ratio was 1 : 1 or 1 : 1.2 [28]. Most research to date has reported that the optimum molar ratio of Mg²⁺ : NH₄⁺ : PO₄³⁻ for struvite precipitation is between 1.0 : 1.0 : 1.0 and 1.6 : 1.0 : 1.0 [28], although phosphate removal is not affected when Mg²⁺ : NH₄⁺ : PO₄³⁻ molar ratio is more than 1.3 : 1.0 : 1.0 at pH 9.0 in a full-scale plant [26].

There was a significant difference between ion removals in real and synthetic effluents of swine wastewater anaerobic digester. Ammonia N removal efficiency from synthetic wastewater was over 90%, while real wastewater had lower than 50% ammonia N removal. Addition of magnesium ion facilitated ammonia N removal up to ratio of 1.2 and then it negatively influenced it. However, more ammonia N was removed than would be predicted based on the magnesium removal and the chemical formula for struvite as shown in Fig. 2.

Table 3. Molar Ratios of Mg²⁺ : NH₄⁺ : PO₄³⁻ for Ammonia and Phosphate Removal

NH ₄ ⁺	Mg ²⁺	PO ₄ ³⁻	NH ₄ ⁺ removal (%)	PO ₄ ³⁻ Removal (%)
1.0	1	1	86.9	97.1
		1.1	88.7	88.2
		1.2	88.4	83.4
		1.3	90.4	76.4
		1.5	91.2	70.3
		2	83.8	61.1
	1.1	1	88.8	99.2
		1.1	92.7	96.9
		1.2	93.6	89.4
		1	87.5	99.8
		1.2	94.5	98.9
		1.2	95.8	95.9
1.3	1	87.4	99.4	
	1.3	98.6	98.2	
	1.5	97.6	41.8	
	2	95.4	78.3	
	1	92.3	99.9	
	1.5	98.4	99.3	
1.5	1.5	98.3	95.3	
	2	97.7	93.9	
	1	89.9	99.5	
	2	98.1	99.4	
2	1.5	98.7	99.4	
	2	99.0	95.0	

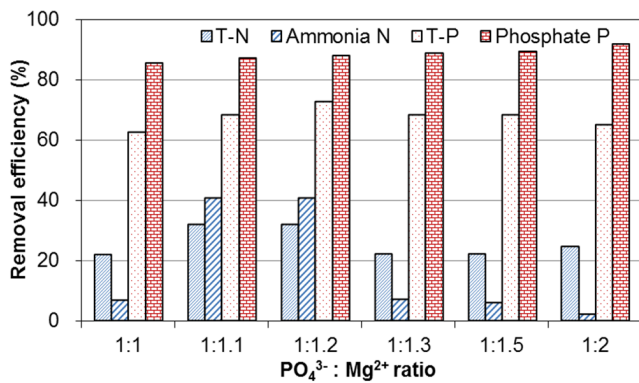


Fig. 2. Nitrogen and phosphorus removal according to $\text{PO}_4^{3-} : \text{Mg}^{2+}$ ratio for the effluent of swine wastewater anaerobic digester at pH 9.

Initial levels of magnesium, ammonium and phosphate ions in the effluent of swine wastewater anaerobic digester were 32, 1,775, and 221 mg/L (molar ratio 1 : 74.9 : 1.8), respectively. The ammonium ion concentration was much higher than magnesium and phosphate ions concentrations. Therefore, magnesium and phosphate ions sources had to be adjusted to completely remove the ammonium ion. The experimental design allowed observing the effects of magnesium and phosphate ions source dosage on ammonia N and phosphate P removal as struvite. Experiments were carried out with 10 min in the mixing zone and 3 h for the whole reactor retention time and a pH of 9.0 according to previous results.

The addition of magnesium and phosphate ions was required to maximize ammonia recovery from the effluent of swine wastewater anaerobic digester. The removal efficiency reached over 95%, and it was almost the same for the synthetic effluent. Moreover, increasing added magnesium likely attributed to both improvement of struvite precipitation and reduction of phosphate P dose. Over dosing of magnesium could also contribute to decreased residual phosphorous concentration in the effluent and phosphate recovery. However, if the concentration of magnesium was increased up to a certain value, phosphorus removal would not change [29].

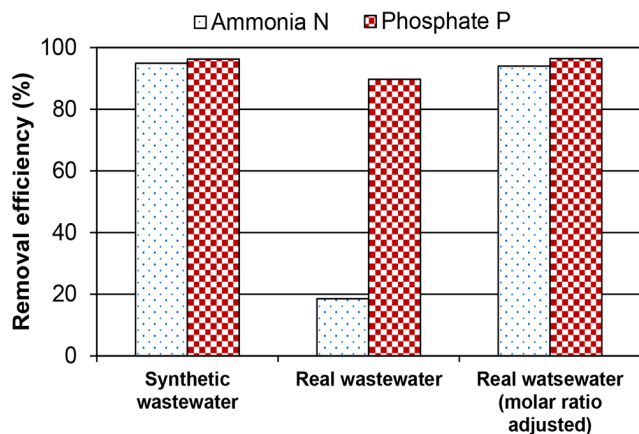


Fig. 3. Addition of PO_4^{3-} and Mg^{2+} to real wastewater for enhanced recovery.

3.2. Effect of pH on Ammonia N and Phosphate P Removal

The ideal pH range for struvite precipitation could occur at a wide pH range of 7.0 to 11.5. However, the suitable pH range for struvite formation is 8 to 9.5 [30]; this is consistent with many other reports [17, 29]. Interfering ions in solution also affect the pH range for struvite precipitation and nutrient removal. To investigate the effect of pH on ammonia N and phosphate P removal and recovery from the effluent of swine wastewater anaerobic digester, the residual concentrations of ammonia N and phosphate P were examined after each experiment. Removal of ammonia N and phosphate P was calculated based on the change between the initial concentration and the residual concentration. Experiments were carried out under the same reactor conditions at the pH range of 6.0 to 12.0 and an equal ratio ($\text{Mg}^{2+} : \text{NH}_4^+ : \text{PO}_4^{3-} = 1.0 : 1.0 : 1.0$).

Based on the batch experiment, the optimum pH for struvite precipitation was investigated. Fig. 4 and Fig. 5 display the removal efficiencies, depending on the pH, for ammonia N and phosphate P in synthetic and real wastewaters, respectively. For synthetic wastewater, as shown in Fig. 4, both ammonia N and phosphate P removal efficiencies depended on the reaction pH, and the maximum ammonia N and phosphate P removal occurred at pH 9.0 and 11.0, respectively. For real wastewater, from Fig. 5, the optimal

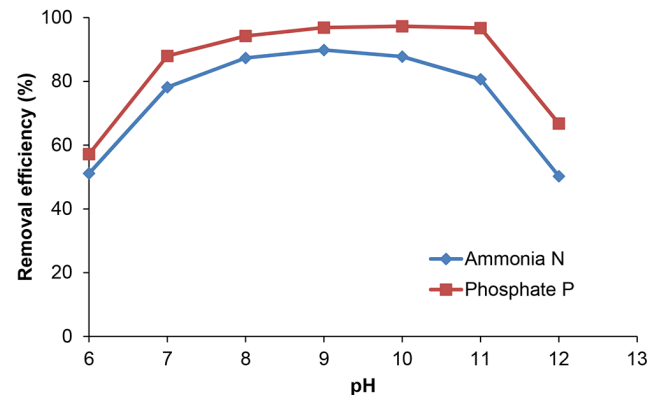


Fig. 4. Ammonia N and P phosphate removal according to pH for synthetic wastewater.

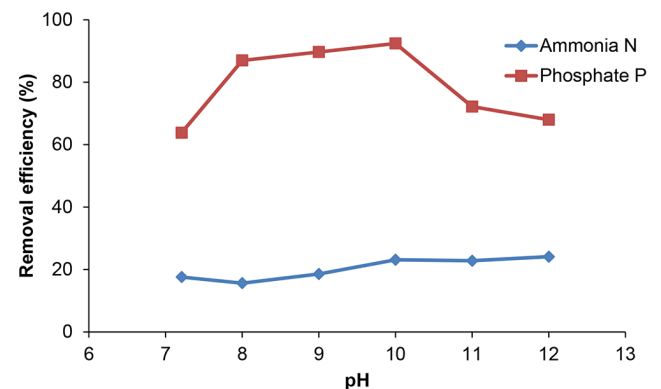


Fig. 5. Ammonia N and phosphate P removal according to pH for real wastewater.

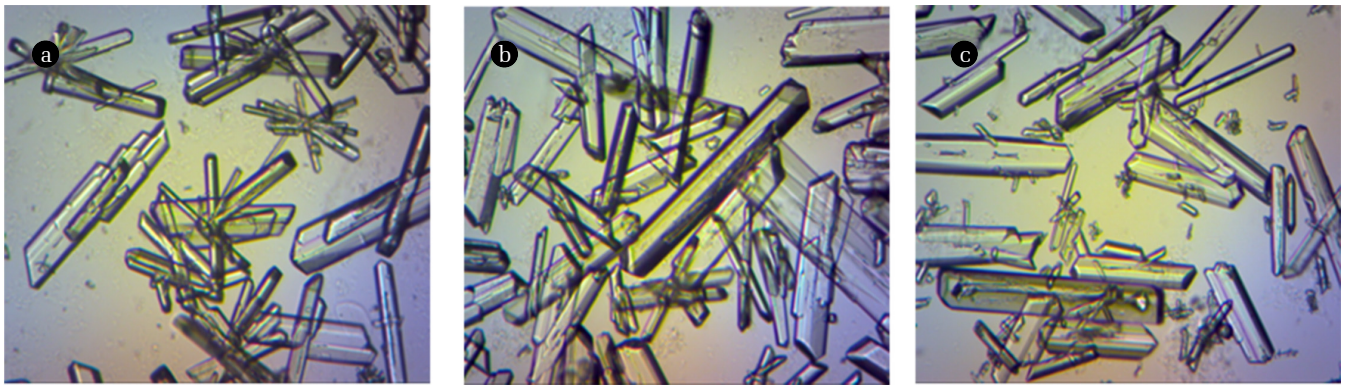


Fig. 6. Struvite crystals (1000X); a) pH 8, b) pH 8.5, c) pH 9.

range of phosphate P was reduced to between pH 8 and pH 10. The maximum removal efficiency of phosphate P achieved were over 95% in both wastewater types, while the maximum ammonia N removal efficiency was very low in real wastewater due to the high initial concentration of ammonia N. Thus, the pH of 8.0-10.0 can be considered as the optimum pH range for both ammonia N and phosphate P removal from the effluent of swine wastewater anaerobic digester.

Fig. 6 shows the optical microscope images of the struvite crystals at various reaction pH values. This indicates larger struvite crystals seen in higher pH values. Moreover, the increased size affected struvite formation, and led to more precipitates forming at high pH values. This could be explained in terms of more ammonia-based precipitates forming compared to phosphate-based precipitates at these conditions.

3.3. Pre-treatments Affecting Phosphate P Release

Acid-alkaline pre-treatments were applied for phosphate P release from the effluent of swine wastewater anaerobic digester of P-city. In this experiment, the initial pH was 7.2 and the pH was changed with HCl and NaOH for the test pH range of 2.0-12.0. Acid-alkaline pre-treatments were carried out under the same conditions so that the ammonia N and phosphate P removals could be tested in terms of the pH conditions of the wastewater. As shown in Fig. 7, both T-P and phosphate P concentrations increased with

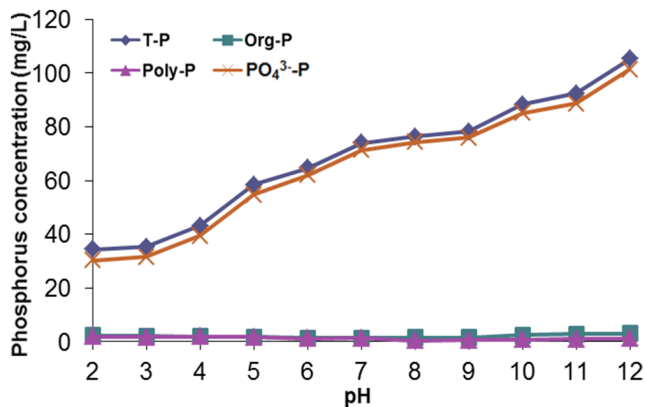


Fig. 7. Change of phosphorus concentration according to pH.

the increasing reaction pH, while poly-P concentration was slightly decreased with the increasing pH. Fig. 8 shows the change of phosphorus fraction according to pH. Maximum phosphate P release was observed at pH between 8.0-9.0.

In this work, the effect of ultrasonic and microwave pre-treatment was also studied for changes in phosphate P release from the effluent of swine wastewater anaerobic digester. The range of the supplied energy density was from 100 kW/L to 20,000 kW/L. From this analysis, phosphate P levels increased by increasing ultrasonic energy density (up until 1,000 kJ/L); however, microwave

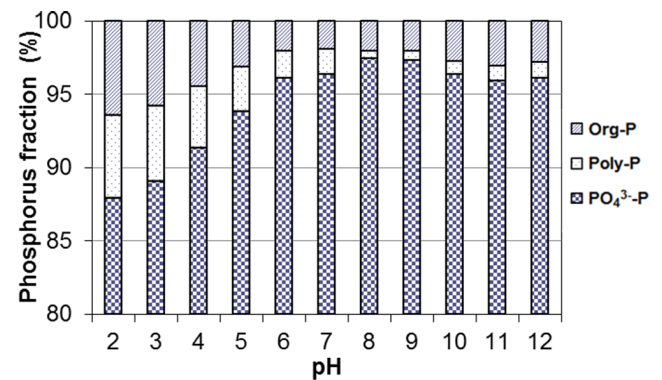


Fig. 8. Change of phosphorus fraction according to pH.

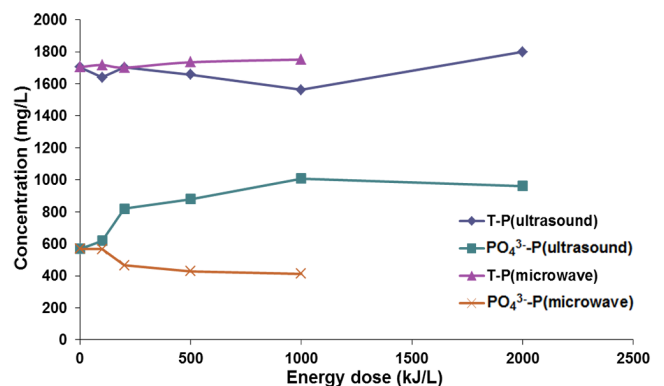


Fig. 9. Phosphate P release from swine wastewater according to energy density.

pre-treatment did not lead to any increases. At 1,000 kJ/L of energy dose by using ultrasound, the highest phosphate P release (at 77.4%) was observed (Fig. 9).

3.4. Composition of Recovered Struvite

Precipitates from the anaerobically digested effluent of swine wastewater collected from the experimental reactor were analyzed for the composition of struvite. The contents of phosphorus and magnesium were similar to theoretical values but the ammonia content was less than the theoretical value. This observed low ammonia content could likely be attributed to precipitation of other minerals, such as potassium struvite ($\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$) instead of magnesium ammonium phosphate due to introduction of potassium (KH_2PO_4) for phosphate P supply.

For samples from the effluent of swine wastewater anaerobic digester of P-city, Visual MINTEQ 3.0 was applied to concentrations of Mg^{2+} , NH_4^+ and PO_4^{3-} at the pH range of 6.0 to 13.0 at 25°C to investigate the effect of pH on the amount and purity of struvite formation from ammonia N and phosphate P removal in the wastewater. Fig. 10 shows the levels and types of supersaturated solids modeled by Visual MINTEQ. From the analysis, struvite would be precipitated in the pH range 6.5 to 12.5, and as the ion activity product (IAP) exceeded the minimum equilibrium constant of solubility [31], struvite crystals would be formed in the pH 7.5 to 10.5.

Table 4. Composition of Recovered Struvite

	Theoretical	Sewage (Ueno and Fujii, 2001)	This study
Mg^{2+}	9.9	9.7	9.9
NH_4^+	7.3	7.3	4.1
PO_4^{3-}	38.7	39.5	39.6

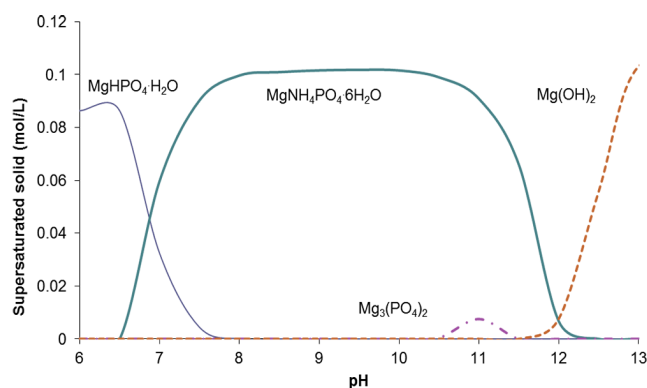


Fig. 10. Solids formation predicted at the pH range 6.0 to 13.0.

4. Conclusions

In this study, a wide range of molar ratios and pH values were tested to determine optimum struvite recovery in terms of efficiency. Microwave and ultrasonic pre-treatments were also investigated for phosphate P release from solid phases for increased recovery of phosphorus from wastewater. From this analysis, the optimum molar ratio of $\text{Mg}^{2+} : \text{NH}_4^+ : \text{PO}_4^{3-}$ for the effective removal

was 1.2 : 1.0 : 1.1. For real wastewater, the optimal pH range of phosphate P was found to be between 8 and 10. The pH range of 8 to 9 was found to lead to maximum phosphate P release and could be the optimum condition for phosphorus recovery. Ultrasound pre-treatment had the highest phosphate P release of 77.4% at 1,000 kJ/L of energy dose but the microwave pre-treatment had no effect under the tested conditions. Contents of phosphorus and magnesium in the collected precipitate were similar to theoretical values but the ammonia content was less than the predicted value. The modeling by Visual MINTEQ pointed to struvite as the dominant solid phase in the pH range 7 to 11.

Acknowledgements

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