

# Phosphorus recovery from wastewater and sludge

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**Abstract.** Wastewater and sludge are potential resource of phosphorus (P) for fertilizer production. One method of recovering phosphorus is via chemical precipitation. In the study, phosphorus was recovered from wastewater and sludge. First, hydrolysis was carried out to release the phosphorus in the sludge by the addition of 1.0M acid (sulfuric acid) or base (sodium hydroxide) solution mixed for three hours at 200 rpm. The hydrolyzed sludge was filtered, and the pH of the solution was adjusted to 9.0. Precipitation for both wastewater and hydrolyzed sludge solution was carried out using magnesium chloride hexahydrate ( $MgCl_2 \cdot 6H_2O$ ) and ammonium chloride ( $NH_4Cl$ ). The mixture was stirred for an hour for crystallization. Precipitates were allowed to settle for 24 hours before it was filtered and dried in an oven at 55-58°C for 24 hours. The dried sample was grinded and characterized using Fourier transform infrared spectroscopy (FTIR), x-ray fluorescence (XRF), and scanning electron microscope with energy-dispersive x-ray spectroscopy (SEM-EDX).

## 1 Introduction

Many countries have implemented strict monitoring and removal of nutrients such as phosphorus and nitrogen from effluent wastewater. These nutrients pose serious environmental problems and could lead to eutrophication when left untreated [1].

Phosphorus (P) is an essential element for living organisms. But due to the depleting amount of phosphorus in phosphate rocks, there is a need to recover P from P-bearing wastes [2]. Wastewater and sludge are two possible sources for phosphorus recovery. Phosphorus removal from wastewater and/or sludge can be achieved through either biological or chemical means. The biological method utilizes the presence of polyphosphate-accumulating organisms (PAOs), while chemical method uses multivalent metal ions such as calcium ( $Ca^{2+}$ ), aluminum ( $Al^{3+}$ ), and iron ( $Fe^{3+}$ ) to form sparingly soluble precipitates [3]. Phosphorus recovered from both methods can be used for fertilizer. However, phosphorus recovered through biological means is preferable due to the absence of heavy metals that are harmful to humans at high concentrations.

Some literatures explored the recovery of phosphorus from waste in the form of struvite [4–6]. Wang et. al [4] stated that phosphorus could be recovered in the form of hydroxyapatite or struvite, but struvite is preferable since it requires less pretreatment before utilization. Struvite is a crystalline substance with a molecular formula  $MgNH_4PO_4 \cdot 6H_2O$ . It has the potential to be an alternative to commercial fertilizer due to its

advantageous properties. The substance contains elements such as magnesium, phosphorus, and nitrogen, which are essential to plant growth. Furthermore, it does not have any side effects compared to commercial fertilizers. Lastly, it has lower impurity than other phosphate fertilizers [2]. It has been proven that struvite can be precipitated from wastewater and sludge, and it is proven to be an effective fertilizer [4–6]. However, in general, struvite recovery or phosphorus recovery has not been explored in the Philippines.

The study will explore the recovery of phosphorus from wastewater and sludge in the form of struvite, and its potential application in the Philippine setting. This is achieved by investigating the effect of sludge type and effect of ammonium ( $NH_4^+$ ) source.

## 2 Materials and methods

### 2.1 Materials and reagents

98% Sulfuric acid ( $H_2SO_4$ ) was used for hydrolysis of sludge. On the other hand, magnesium chloride hexahydrate ( $MgCl_2 \cdot 6H_2O$ ) and ammonium chloride ( $NH_4Cl$ ) were utilized as magnesium and ammonia source for the precipitation of struvite. The phosphate as phosphorus content of the dewatered sludge sample was determined using HACH TNT vials.

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## 2.2 Collection of sludge samples

Dewatered sewage sludge, dewatered septage sludge, and influent wastewater were collected from a local treatment facility in Metro Manila. The sludge samples pass through primary treatment which utilizes fine screens to remove large and unwanted solid particles. Then it goes through the secondary treatment which involves the use of flocculating agent.

## 2.3 Release of phosphorus (P) from sludge

The study investigated the effect of acid and base in the release of phosphorus from sludge. 1 M of acid (sulfuric acid) or base (sodium hydroxide) was added to 50 mL of sludge, and the solution was mixed for 1 hour at 200 rpm. After mixing, undissolved particles were allowed to settle before the solution was filtered.

## 2.4 Struvite precipitation

Initial pH of the hydrolyzed solution was recorded. If necessary, sodium hydroxide was added to adjust the pH to 9.00. Magnesium chloride hexahydrate ( $MgCl_2 \cdot 6H_2O$ ) and ammonium chloride ( $NH_4Cl$ ) were added to the solution as magnesium and ammonium source, respectively. The solution was mixed for 1 hour at 200 rpm and the precipitates were allowed to settle overnight. Filtered precipitates were dried in an oven at 55 – 58°C for 24 hours and grinded.

## 2.5 Material characterization

The precipitates were analyzed using Fourier transform infrared spectroscopy (FTIR), scanning electron microscope with energy-dispersive x-ray spectroscopy (SEM-EDX) and x-ray fluorescence (XRF).

## 3 Results and discussion

### 3.1 Effect of sludge type

Initially, the plan was to investigate the phosphorus recovery of dewatered sewage sludge samples only. However, it was estimated using the HACH TNT Vials that the phosphate as phosphorus ( $PO_4\text{-P}$ ) concentration is around 13 ppm. The diluted  $PO_4\text{-P}$  concentration may be the reason why no visible precipitates are formed after the addition of  $MgCl_2 \cdot 6H_2O$  since there might be other ions that could have combined with the phosphate ions. Dewatered sewage sludge was then used for the exploratory study since it is believed that it contains more phosphate content.

### 3.2 Effect of reagent used for hydrolysis

The effect of reagents such as sodium hydroxide (NaOH) and sulfuric acid ( $H_2SO_4$ ) was investigated. Sulfuric acid has been used in previous studies to release phosphorus from sludge [4,5]. The problem with using sulfuric acid

is the release of interfering ions such as  $Fe^{3+}$  and  $Ca^{2+}$  are also released and could bind and form unwanted precipitates [3]. This further reduces the formation of struvite. The effect of sodium hydroxide for phosphorus release is also investigated.

From the experiments, it was observed that white, flaky precipitates are only formed from sludge hydrolysed with sodium hydroxide only when bicarbonates are added as a treatment process to remove calcium ions from the solution. However, it is unlikely that struvite is formed. Sludge hydrolysed with sulfuric acid formed light brown precipitates even with or without the addition of  $NH_4Cl$ . Material characterization was conducted on the samples and it was determined that unwanted products were formed. The results will be discussed in the following section.

### 3.2 Effect of addition of ammonia source

#### 3.2.1 Fourier transform infrared spectroscopy (FTIR)

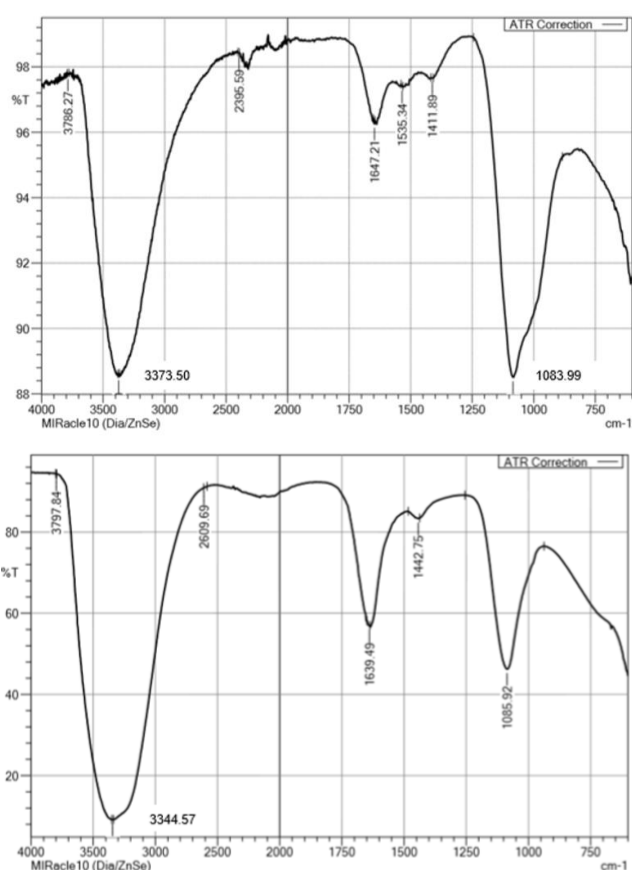
Table 1 below is the list of reported IR frequencies in determining the presence of struvite in the precipitates based from previous literatures.

**Table 1.** Literature source for struvite determination using FTIR analysis.

Source	Assignments	Reported IR Frequencies ( $cm^{-1}$ )
[7]	H-O-H stretching vibration of water crystallization	3280 - 3550
	H-O-H stretching vibration of cluster of water molecules of crystallization	2060 - 2460
	H-O-H bending modes of vibration	1590 - 1650
	Wagging modes of vibration of coordinated water	808
	$\nu_1$ symmetric stretching vibration of $PO_4^{3-}$ units	930 - 995
	$\nu_2$ symmetric bending vibration of $PO_4^{3-}$ units	404 - 470
	$\nu_3$ asymmetric stretching vibration of $PO_4^{3-}$ units	1017 - 1163
	$\nu_4$ asymmetric bending modes	509 - 554
	Metal-oxygen bonds	400 - 650
	Deformation of OH linked to $Mg^{2+}$	847
[8]	Broad asymmetric band attributed to O-H and N-H stretching vibrations	2200 - 2800
	N-H bending vibrations	1440, 1570, and 1650
	$\nu_2$ modes of $PO_4^{3-}$ ions	569, 1003, and 1050
	$\nu_3$ and $\nu_4$ modes of $PO_4^{3-}$ ions	471

Results from the FTIR analysis for samples without and with ammonia source are shown in **Fig. 1** below. Both graphs show the presence of  $\text{PO}_4^{3-}$  units at  $1083.99\text{ cm}^{-1}$  and  $1085.92\text{ cm}^{-1}$ , respectively. Peaks observed between  $3433.15$  and  $3373.50\text{ cm}^{-1}$  in **Fig. 1a** and between  $2609.69$  and  $3797.84\text{ cm}^{-1}$  in **Fig. 1b** indicate stretching vibrations of water vibration. Peaks at  $1416.05$  and  $1595.07\text{ cm}^{-1}$  in **Fig. 1a** could indicate N-H bonds. This could mean that the ammonia content in the sludge combined with Mg and  $\text{PO}_4^{3-}$  units during the precipitation experiment. Meanwhile, peak  $1442.75\text{ cm}^{-1}$  in **Fig. 1b** indicate N-H bonds.

However, further verification is needed to prove that struvite is present in the samples. The wavenumbers indicated in **Table 1** might correspond to other functional groups. Other methods are important for material characterization.

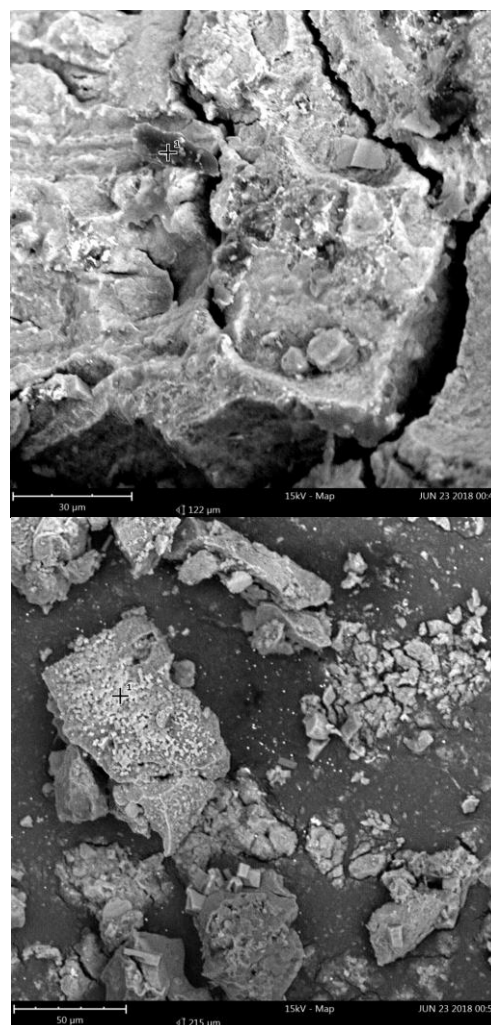


**Figure 1.** FTIR results for samples without (top) and with (bottom) addition of ammonia source.

### 3.2.2. Scanning electron microscope with energy dispersive x-ray (SEM-EDX) analysis

SEM-EDX analysis was used to determine the structure and elemental content of the precipitates. Pure struvite has an orthorhombic structure, and the structure changes at decreasing purity [8,9]. **Fig. 2** shows the image of the precipitates from the experiment. The structure of struvite crystal changes depending on the purity. Suguna et. al [8] presented rectangular bar-shaped pure struvite crystals. Rahman et. al [10] showed struvite crystals can be cube-like, rod-like, and irregular. Based from the

sources [8,10], it can be concluded that the precipitates are unlikely struvite.



**Figure 2.** FTIR results for samples without (top) and with (bottom) addition of ammonia source.

EDX was utilized to determine atomic concentration in the samples. **Tables 2** and **3** show the results for the samples without and with ammonia source. From the results, it could be concluded that a different product was formed. Interferences such as sodium (Na), sulfur (S), chlorine (Cl), calcium (Ca), iron (Fe), and aluminum (Al) are present in both samples. In addition, it could be due to inadequate amount of magnesium, phosphorus, and nitrogen in the sample. The ideal stoichiometric Mg:N:P ratio is 1:1:1. However, Shiba and Ntuli [5] stated that a ratio of 1:3:4 would be ideal for struvite precipitation from sludge.

### 3.2.3. X-ray fluorescence analysis

**Table 3** shows the elemental analysis of samples using x-ray fluorescence analysis. Negative results were found similar to SEM-EDX. Interferences such as calcium (Ca), iron (Fe), sulfur (S), chlorine (Cl), and others are present in both samples.

**Table 2.** Elemental analysis for samples with and without ammonia source using SEM-EDX.

Without Ammonia Source		With Ammonia Source	
Element	Atomic Conc. (%)	Element	Atomic Conc. (%)
O	62.276	O	33.501
Na	17.034	Na	23.461
S	9.433	Cl	12.858
Fe	2.338	C	12.371
Ca	2.241	Mg	5.217
Al	1.874	S	3.219
P	1.784	Mo	2.486
Mn	1.174	Fe	1.957
Si	0.738	Al	1.855
Br	0.587	Nb	0.963
Nb	0.521	Na	0.924
		Zr	0.612
		P	0.577

**Table 3.** Elemental analysis for sample with and without ammonia source using XRF.

Without Ammonia Source		With Ammonia Source	
Analyte	Result (%)	Analyte	Result (%)
Ca	21.477	Cl	68.522
Fe	18.425	S	9.924
S	17.082	Fe	9.871
Al	14.958	Ca	3.262
P	11.775	Mn	2.769
Mn	5.192	Zn	2.696
Zn	4.511	P	1.868
Si	4.316	Si	0.842
Mg	1.305	Cu	0.128
Cu	0.394	Others	0.118
Others	0.564		

### 3.3 Phosphorus recovery from wastewater

The possibility of precipitating struvite from wastewater was investigated. pH of the sample was adjusted to 9.0.  $MgCl_2 \cdot 6H_2O$  and  $NH_4Cl$  solutions were added and the solution was mixed for 1 hour. No precipitates were formed in the experiment and this may be due to low  $PO_4-P$  concentration of the sample.

## 4 Conclusion

The study explores the possibility of precipitating struvite from the current condition of wastewater and sludge in the Philippines. Several parameters such as reagent and ammonia concentration were varied and evaluated. The results from the FTIR are promising since there is a possibility that struvite was formed from the experiments. However, negative results were observed based from SEM-EDX and XRF. Reasons for not being able to precipitate struvite could lie from the amount of phosphorus in the wastewater and/or sludge, the presence of contaminants such as iron, calcium, and aluminum which easily bind with phosphate, and the molar ratio of Mg:N:P. For future work, it is recommended to use cation exchange resins

[4,5] to eliminate interferences such as iron and aluminum and increase the magnesium and ammonia concentration. In addition, the use of biological nutrient removal technologies (BNRT) could help in increasing phosphorus concentration in sludge.

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