

## RESOURCE RECOVERY FROM ANAEROBICALLY DIGESTED LIQUOR OF WASTEWATER SCREENINGS

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**ABSTRACT.** *Phosphorus is a limited resource which is predicted to be exhausted at some point during the 21<sup>st</sup> century. However, it is present in wastewaters at concentrations that come close to supplying the nation's annual requirements for fertiliser. Therefore, this study was conducted to study the potential of wastewater screenings which has received little attention that produced during wastewater treatment, for phosphorus recovery. Many papers have addressed the recovery of phosphate or ammonia as struvite from different type of waste. The most prominent usage of struvite (magnesium ammonium phosphate hexahydrate) is as a slow-release fertiliser, suitable as replacement for chemical fertiliser, for agricultural application. In this study, digested liquor was obtained from anaerobically digested of wastewater screening. The experiments were carried out with and without chemical amendment to study the feasibility of phosphorus recovery, at different Mg:P molar ratio, i.e. 1.56:1 (without chemical amendment), 2:1 and 3:1 (with chemical amendments). Precipitation at 1.56:1 showed that phosphorus removal efficiency was 68% and recovered 0.52g amorphous calcium carbonate. Precipitation at 2:1 reduced phosphorus removal efficiency to 53% and the recovered solid was found to be calcium phosphate, with 0.33g precipitate. Precipitation at 3:1 was not economically interesting for P recovery as shown by its lowest removal efficiency and highest chemical usage. The results demonstrated that the presence of calcium and carbonate ion in the digested liquor highly interfere with phosphorus recovery in the form of struvite.*

**KEYWORDS.** Phosphorus recovery; wastewater screenings; anaerobically digested liquor; precipitation technique.

### INTRODUCTION

Phosphorus (P) is a limited resource which is anticipated will be exhausted in the 21st century (Cordell *et al.*, 2009; Smil, 2000; Herring & Fantel, 1993). While natural sources like oil can be substituted with other sources when its reserves peak (such as wind, solar, or thermal energy), P has no substitute and cannot be manufactured or synthesized. The main source of phosphorus is extracted from the phosphate rock in the earth's crust, which is concentrated in a few countries namely, China, Morocco, the United States and Russia which together hold more than 70% of the global phosphate deposits (USGS, 2009). Due to the depleting P resource and higher extraction cost, there are increasingly studies have been undertaken to recover P from waste streams, including swine wastewater (Song *et al.*, 2014; Huang *et al.*, 2011; Jordaan *et al.*, 2010), industrial wastewater (Yan *et al.*, 2013; Jaffer *et al.*, 2002; Tünay *et al.*, 1997), and urine (Zhang *et al.*, 2014; Zang *et al.*, 2012; Wilsenach *et al.*, 2007). The best way to recover P from solid waste is to solubilise it in the form of liquid. The

use of anaerobic digestion (AD) technique to extract and solubilise P from solid waste has been extensively reported for the past 20 years. There are a number of studies have been reported in using anaerobic digested liquor from various type of solid wastes to recover P, but as yet non from wastewater screenings has been reported. As this material has received little attention, research on treatment of wastewater screenings by anaerobic digestion is rare.

Digestion of screenings can produce a liquid or biosolids mixture which is high in nitrogen and phosphorus that are valuable fertiliser components. AD will solubilise the nutrient and make them easy to recover. Currently, the removal and recovery of phosphate from anaerobically digested liquor (ADL) has been widely studied by using crystallisation or precipitation technique (Gaudie *et al.*, 2014; Song *et al.*, 2011; Pastor *et al.*, 2010; Le Corre *et al.*, 2007; Yoshino *et al.*, 2003; Battistoni *et al.*, 2002; Münch & Barr, 2001; 2000; Booker *et al.*, 1999). This technique has also been gaining attention as it can reduce nutrient load by preventing spontaneous solid deposits which can cause operational failure in the wastewater treatment plants (Doyle *et al.*, 2000; Ohlinger *et al.*, 1999; Mohajit *et al.*, 1989). Most of the phosphate salts produced from the precipitation technique is in the form of struvite, a white substance that shows potential as a slow-release fertiliser. The current study aims to examine the potential of anaerobically digested liquor of wastewater screenings, for phosphorus recovery in order to turn this waste into useful resources.

## MATERIALS AND METHODS

### *Anaerobically digested liquor (ADL)*

The ADL in this study was obtained from a mesophilic reactor digesting wastewater screenings. Prior to precipitation process, the ADL was centrifuged at 4000 rpm for 30 minutes. Following centrifugation, the effluents were filtered through a 0.45  $\mu\text{m}$  membrane filter and transferred into glass bottles. The filtered ADL then divided into two portions to be used in precipitation with and without chemical amendment. The addition of chemicals was according to the molar ratio of  $\text{PO}_4^{3-}$ ,  $\text{NH}_4^+$  and  $\text{Mg}^{2+}$  ions at 1:1:1 in solution. Initial concentrations of soluble phosphate ions ( $\text{PO}_4^{3-}$ ), ammonium ions ( $\text{NH}_4^+$ ), magnesium ions ( $\text{Mg}^{2+}$ ) and calcium ions ( $\text{Ca}^{2+}$ ) were determined, respectively. The initial characteristics of the ADL used for precipitation with and without chemical amendment are summarised in Table 1. The molar ratio for precipitation process with chemical amendment was set at 2:1 and 3:1 and the chemical used was magnesium chloride ( $\text{MgCl}_2$ ).

### *Precipitation process*

A precipitation reactor (PR) of 2.5 L volume with a conical bottom, made of transparent acrylic with a liquid circulation tube, a drain valve at the bottom and a peristaltic pump was used in this study. Initially 2.0 L of measured ADL was poured into a 2.0 L beaker and the pH was adjusted to 9.0 using 5.0 M NaOH and 2.0 M HCl and then transferred into the PR. The precipitation process was performed according to the method described by Le Corre *et al.*, (2007) and Song *et al.*, (2011). The precipitation process was performed with and without chemical amendment, depends on the molar ratio of  $\text{PO}_4^{3-}$ ,  $\text{NH}_4^+$  and  $\text{Mg}^{2+}$ . Two types of magnesium,  $\text{Mg}(\text{OH})_2$  and  $\text{MgCl}_2$ , are generally used in the chemical amendment process. In this study  $\text{MgCl}_2$  was chosen because it dissociates faster than  $\text{Mg}(\text{OH})_2$  and results in shorter precipitation times. After the precipitation process, the precipitate was allowed to settle for 30 min before drained through the valve situated on the bottom of the reactor and separated from the liquid phase by centrifugation at 4000 rpm for 20 minutes. The supernatants were then decanted and the precipitate that formed was collected by filtration through a 0.45  $\mu\text{m}$  membrane filter. Residual concentrations of  $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{PO}_4^{3-}$  and  $\text{Ca}^{2+}$  in the supernatant

were analysed. The precipitates separated from both centrifugation and filtration methods were dried in an incubator at 37°C for 24h and weighed. The collected dried precipitates were analysed for content and sent for XRD analysis.

**Table 1. Characteristics of ADL for the precipitation process.**

ADL character	Precipitation without chemical amendment	Precipitation with chemical amendment	
	Initial concentrations mg/L (mMol/L)	Initial concentrations mg/L (mMol/L)	
Molar ratio Mg:P	1.56:1	2:1	3:1
Mg <sup>2+</sup>	346.0 (14.4)	326.4 (13.6)*	489.6 (20.4)*
NH <sub>4</sub> <sup>+</sup>	126.0 (7.0)	126.0 (7.0)	126.0 (7.0)
PO <sub>4</sub> <sup>3-</sup>	879.4 (9.3)	644.1 (6.8)	644.1 (6.8)
Ca <sup>2+</sup>	231.5 (5.8)	147.3 (3.7)	147.3 (3.7)
Alkalinity (as CaCO <sub>3</sub> )	2000	1500	1500

### **Analytical methods and instrumentation**

All the analytical parameters were carried out following the procedures outlined in APHA (2005). The composition of the precipitates was characterised using X-ray diffraction (XRD) and the phosphorus removal and recovery assessment was done according the modified formula of Song *et al.*, (2011) as shown in Equation 1.

$$\text{PO}_4\text{-P removal efficiency} = \frac{\text{PO}_4 \text{ influent} - \text{PO}_4 \text{ effluent}}{\text{PO}_4 \text{ influent}} \quad \text{Eq. 1}$$

## **RESULTS AND DISCUSSION**

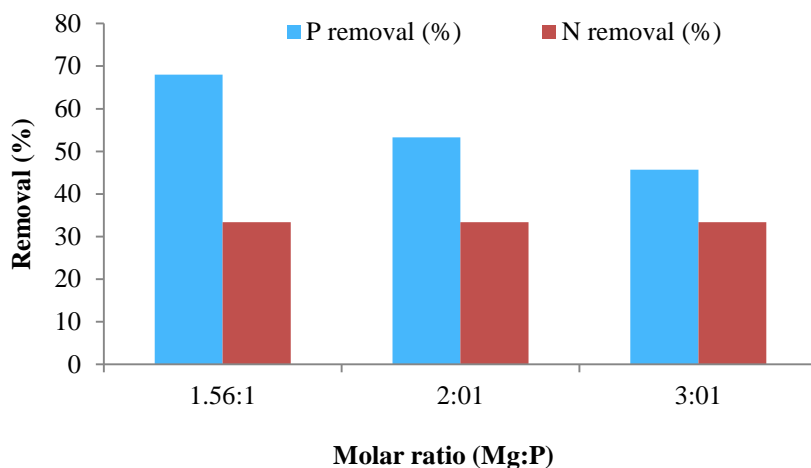
### **Phosphorus recovery from ADL of wastewater screenings**

The potential for P recovery was performed by precipitation process using ADL of wastewater screenings, with and without chemical addition. Compared to the supernatants used in previous studies, the concentration of PO<sub>4</sub><sup>3-</sup> ions in this present study was very high, thus a high phosphate precipitation was expected. Previous studies mentioned that wastewater tends to be high in NH<sub>4</sub><sup>+</sup> but deficient in Mg<sup>2+</sup>. However in the present study, the concentration of Mg<sup>2+</sup> was almost 3 fold higher than NH<sub>4</sub><sup>+</sup> (Table 1). The high concentration of Mg<sup>2+</sup> may due to the fact that the screenings used in this study was collected from an inlet work in Knostrop WWTP that processes waste collected from the south of Leeds, which is predominantly an industrial area. This might also reflect the higher P concentration compared to previous works.

### **Precipitation without chemical amendment**

The first set of the experiments was carried out without chemical amendment, because soluble concentrations of PO<sub>4</sub><sup>3-</sup>, NH<sub>4</sub><sup>+</sup> and Mg<sup>2+</sup> ions were sufficient for the precipitation. After almost 1h of reaction, the precipitate became heavier and settled to the bottom of the reactor. Theoretically, struvite will precipitate when the molar ratio of PO<sub>4</sub><sup>3-</sup>, NH<sub>4</sub><sup>+</sup> and Mg<sup>2+</sup> ions are present at least 1:1:1 in solution. However, previous studies have showed that Mg<sup>2+</sup> concentration must be in excess relative to PO<sub>4</sub><sup>3-</sup> in order to induce high P removal and struvite precipitation (Chimenos *et al.*, 2003; Wang *et al.*, 2005; Jaffer *et al.*, 2002; Maekawa

*et al.*, 1995; Stratful *et al.*, 2001; Burns *et al.*, 2003; Jordaan *et al.*, 2010; Song *et al.*, 2011). In the present study, the initial molar ratio of the ADL was 1.56:1, so  $Mg^{2+}$  was sufficient to ensure high P removal and recovery. Therefore, no chemical amendment was performed. It was found 68% and 33% of P and N, respectively were removed by the precipitation (Figure 1), and 0.52 g solids were recovered.



**Figure 1. Removal efficiency of P and N at molar ratios studied.**

#### ***Precipitation with chemical amendment***

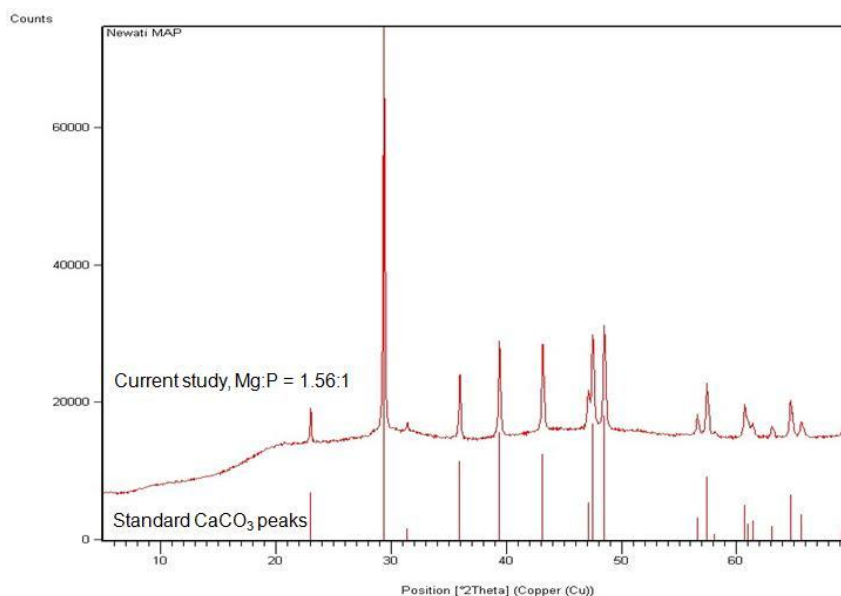
A similar physical observation was found from precipitation with chemical amendment as described before. At an increased Mg:P ratio of to 2:1 achieved by chemical amendment, P removal efficiency decreased from 68% to 53% (Figure 3), with 0.33 g solids were recovered. Previous observations have revealed high N:P will increase P removal. But in this current study, this does not affect P removal when the molar ratio of N:P increased from 0.76 to 1.03. A decrease in P removal efficiency at a higher Mg:P molar ratio suggests the presence of various ions in the ADL. If the solution contains negative ions, insoluble magnesium ammonium phosphate (struvite) will be more adhesive (Maekawa *et al.*, 1995) because struvite is reported has possessing a high negative charge at alkaline pH (Le Corre *et al.*, 2007; Bouropoulosa & Koutsoukos, 2000), consequently increasing P removal. However, a decrease in P removal efficiency in current study suggests that positive ions were also present which inhibited the precipitation process and decreased P removal efficiencies. For N removal, the results showed that molar ratios did not affect removal efficiency, i.e. 33% for all ratios studied. Table 2 reveals that there were significant losses of ions involved when the molar removed were compared with the recovered precipitate. It also found that the precipitation process shows no improvement at increased Mg:P to 3:1.

**Table 2. Concentrations of mole removed and recovered solids at different molar ratios.**

Mg:P	$Mg^{2+}$			$PO_4^{3-}$			$NH_4^+$		
	Rem.	Rec.	Lost %	Rem.	Rec.	Lost %	Rem.	Rec.	Lost %
<b>1.56:1</b>	3.93	0.39	90	6.30	0.76	88	2.33	0.54	76
<b>2:1</b>	8.36	5.90	29	3.60	0.43	88	2.33	0.97	58
<b>3:1</b>	13.85	4.59	67	3.10	0.37	88	2.33	1.17	50

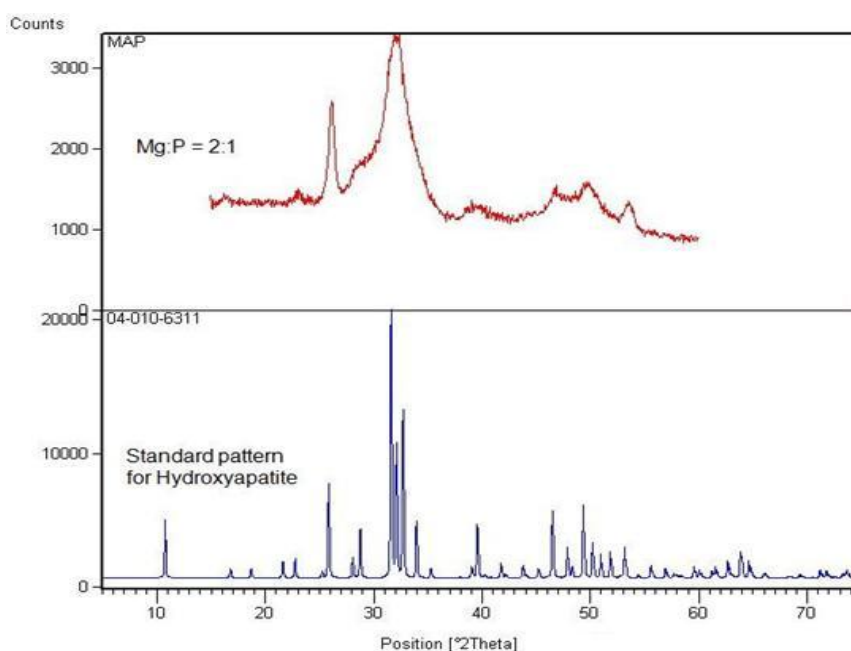
### ***Determination of the recovered product***

In order to find the type of the precipitate that produced by the precipitation process, XRD analysis was performed on the recovered precipitate. Figure 2 shows a large non-flat background indicates high levels of amorphous material. It confirms that the only crystalline material present is calcium carbonate,  $\text{CaCO}_3$  (also known as calcite) which is a very strong match with all peaks where the collected data can be attributed to this phase.



**Figure 2. XRD patterns of the recovered solid (1.56:1).**

The precipitate produced from the controlled precipitation (2:1 of Mg:P ratio) was also identified. The experimental results found that the recovered solid was not struvite even though  $\text{Mg}^{2+}$  concentration was higher than  $\text{Ca}^{2+}$  with 0.27:1 of Ca:Mg molar ratio. The XRD analysis identified it was calcium phosphate, in the form of hydroxylapatite (Figure 3). The XRD pattern matched the standard pattern for hydroxylapatite. The broad peaks suggest other type of calcium phosphate minerals may incorporate and overlap hydroxylapatite.



**Figure 3. XRD results at 2:1.**

The formation of calcium carbonate and calcium phosphate occurred instead of phosphate salts may be due to the higher concentration of  $\text{CaCO}_3$  rather than phosphate in the ADL as shown in Table 1. Nevertheless, formation of calcium carbonate and calcium phosphate was not unusual in wastewater treatment process. The precipitated calcium phosphate can be used in manufacturing slow-release phosphate fertiliser and as a soil conditioner. Substantial removal of phosphorus but low removal of nitrogen from the digested liquor increased the N:P ratio in the final effluent and could be applied directly on land without accumulating P in the soil.

## CONCLUSIONS

Precipitation experiments were carried out using ADL of wastewater screenings in a precipitation reactor. High concentrations of soluble  $\text{PO}_4^{3-}$  and  $\text{NH}_4^+$  with adequate  $\text{Mg}^{2+}$  in the ADL provide an excellent opportunity to achieve P recovery as struvite. The concentrations were found even higher than the concentration in wastewater that have been reported in literature. The ADL precipitation found 0.52 g solids was recovered when a chemical source was not added, where the Mg:P was 1.56:1. At this molar ratio, 68% P and 33% N were removed from the ADL. However, the brown-white precipitate was found to be amorphous calcium carbonate after confirmation by XRD analysis. This indicates that  $\text{PO}_4^{3-}$  and  $\text{Mg}^{2+}$  were not completely involved in the precipitation. Given the information from previous studies mentioning that  $\text{Mg}^{2+}$  must be higher than  $\text{PO}_4^{3-}$  in order to induce high P recovery in the form of struvite, the Mg:P ratio was increased to 2:1 and 3:1 by adding  $\text{MgCl}_2$ .

It would be expected that when Mg is added, P will be removed with a high efficiency, in the form of struvite. However, when the Mg:P increased to 2:1 and then to 3:1, the P removal efficiency was found to decrease to 53% and 46%, respectively. There was no effect on N removal efficiency with 33% for all ratios studied. The precipitate from 2:1 was then analysed but not for 3:1 given that the removal efficiency was the lowest and not economically viable due to its higher chemical usage. The identification analysis proved that the 0.33 g of recovered solids at 2:1 Mg:P molar ratio, was calcium phosphate (hydroxylapatite) with no indication of struvite formation.

Formation of calcium carbonate and calcium phosphate in an attempt to precipitate struvite from the ADL shows that the presence of carbonate and calcium ions had a large impact on struvite formation. However, the recovered calcium phosphate still can be used in manufacturing slow-release phosphate fertiliser, a soil conditioner and even can be applied directly on land for agricultural purposes. Overall, from this study, recovery of phosphorus from waste streams will not only alleviate environmental problems, but also ease the stress on depleted resources, i.e. phosphorus.

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