

**Recovery of Nutrients from Anaerobic Digester
Supernatant using Magnesium-Rich Waste
Material**

**A thesis submitted in fulfilment of the requirements for the
degree of Master of Engineering**

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DECLARATION

I certify that except where due acknowledgement has been made, the work is that of the author alone; the work has not be submitted previously, in whole or in part, to qualify for any academic award; the content of the thesis is the result of work which has been carried out since the official commencement date of the approved research program.

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ABBREVIATIONS AND NOTATIONS

Abbreviations

- BNR – Biological Nutrient Removal
- EBPR – Enhanced Biological Phosphorus Removal
- ESEM – Environmental Scanning Electron Microscope
- MAP – Magnesium Ammonium Phosphate
- rpm – Revolutions per minute
- XRD – X-ray Diffraction
- USEPA – United States Environmental Protection Agency

Notations

- α_i – Ionization fraction
- [C] – Concentration of reactant
- [C]₀ – Initial concentration of the reactant
- C_i – Free ion concentration
- dHr – The change of enthalpy
- k – Kinetic rate constant
- K_{SO} – Activity solubility product
- K_{SP} – Thermodynamic solubility product
- LogKs – Logarithmic value of the equilibrium constant
- LogK_{sp} – Negative logarithmic value of the solubility product
- n – Order of reaction
- P_S – Conditional solubility product
- γ_i – Activity coefficient
- t – Time

ABSTRACT

Formation of magnesium ammonium phosphate (struvite, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$), which has commercial value as fertiliser, is a sustainable technology for ammonia and phosphate removal and recovery from anaerobic digester supernatant. Considering that magnesium concentration relative to ammonia and phosphate concentrations in the supernatant is low, magnesium dosage is usually required to force struvite formation. This research was conducted to investigate the optimum reaction conditions and the feasibility of Mg-rich waste material as a magnesium source for ammonia and phosphate removal and recovery as struvite from anaerobic digester supernatant.

Struvite formation was carried out by adding Na_2HPO_4 and MgCl_2 or magnesium-rich waste material at different conditions: (i) pH; (ii) reaction time; (iii) molar ratios ($\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$). Confirmation of struvite formation and measurement of struvite precipitation's particles size were analysed by XRD and ESEM, respectively. Economic analysis was conducted to estimate the cost of using Mg-rich waste material in the process. A chemical equilibrium software Visual MINTEQ was used for predicting struvite formation using high range of the pH and molar ratio.

Increasing the mixing rate and the reaction time had little effect on ammonia and phosphate removal. Crystal growth had only a minor relationship to the reaction time. pH change with time indicated that induction time was extremely short. The optimum pH was between 9 and 9.5. The reaction time of 10

minutes was adequate for struvite formation due to a high reaction rate. The $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ ratio of 1.2:1.0:1.0 was found to be the optimum molar ratio in order to use Mg^{2+} and PO_4^{3-} dosage efficiently. The chemical equilibrium software Visual MINTEQ successfully predicted struvite formation. The prediction indicated that struvite formation was at a wide pH range from 6.5 to 11.5. $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$, $\text{Mg}_3(\text{PO}_4)_2$ and Brucite ($\text{Mg}(\text{OH})_2$) formed with struvite, but struvite was still the main product. The removal of ammonia and phosphate was achieved over 98.00% using Mg-rich waste material as a magnesium source at pH 9.5 and the $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ ratio of 1.2:1.0:1.0. Precipitates analysis using XRD showed that nearly pure struvite formed. Economic evaluation indicated that Mg-rich waste material as the magnesium source can reduce the total cost compared with MgCl_2 .

Chapter 1 Introduction

1.1 Background

The limitation of phosphorus use and the reduction of environmental impacts have become central concerns for sustainable wastewater treatment. Anaerobic digester is the most common method to stabilize wastewater. High concentrations of ammonia and phosphate ions in the supernatant of anaerobic digester cause environmental pollution (Demirer and Chen, 2005). In order to develop a sustainable methodology, researchers have studied the potential reuse of ammonia and phosphate. The common techniques for ammonia and phosphate removal and recycling of wastewater are general chemical precipitation and biological removal, but they do not produce valuable by-products. The use of magnesium ammonium phosphate (struvite, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) has been shown to be more effective for the removal and recovery of ammonia and phosphate from wastewater because of its high reaction rate and reaction efficiency (Celen and Tuerker, 2001). In addition, struvite precipitation has economic value as a low release fertilizer (Booker *et al.*, 1999, Nelson *et al.*, 2003, Shu *et al.*, 2006). This technology has been applied for ammonia and phosphate recovery from supernatants of anaerobic digesters (Celen and Tuerker, 2001, Marti *et al.*, 2008, Pastor *et al.*, 2008, Uludag-Demirer and Othman, 2009). Struvite precipitation has also been studied in relation to treatment of landfill leachate (Gunay *et al.*, 2008, Li and Zhao, 2003), swine wastewater (Burns and Moody, 2002, Çelen *et al.*, 2007, Nelson *et al.*, 2003, Wang *et al.*, 2005), anaerobic digester side-streams (Battistoni *et al.*, 1997, Kumashiro *et al.*, 2001, Münch and Barr, 2001) and dairy

manure (Uludag-Demirer *et al.*, 2005). The magnesium ammonium phosphate recycling system has been developed at laboratory scale and applied to full-scale plants. In Europe and Japan, this nutrient recovery technology has been accepted by large municipal sewage-handling facilities (Battistoni *et al.*, 2001, Battistoni *et al.*, 2006, Kumashiro *et al.*, 2001, Türker and Çelen, 2007, Ueno and Fujii, 2001, Uludag-Demirer and Othman, 2009, Yoshino *et al.*, 2003).

Recently, researchers have sought to find a suitable and economic magnesium source for this nutrient recovery system because of the high operating cost of the addition of magnesium (Celen and Tuerker, 2001, Gunay *et al.*, 2008, Türker and Çelen, 2007). Magnesium sources such as $MgCl_2$, $Mg(OH)_2$ and $MgSO_4$ have been tested and employed for struvite precipitation (Altinbas *et al.*, 2002a, Li and Zhao, 2003, Münch and Barr, 2001). Some low-cost materials have been used as an alternative source of magnesium ions, such as low grade MgO , bittern, seawater, and $MgCO_3$ (Chimenos *et al.*, 2003, Gunay *et al.*, 2008, Kumashiro *et al.*, 2001, Lee *et al.*, 2003, Li and Zhao, 2003).

1.2 Objectives

The main goal of this study was to investigate the feasibility of the use of Mg-rich waste material as a magnesium source for ammonia and phosphate recovery, in the form of struvite, from anaerobic digesters supernatant.

The objectives of this study are:

- To determine struvite crystal growth and induction time.

- To assess how would the parameters pH, molar ratios of $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ and the reaction time affect ammonia and phosphate removal and recovery.
- To evaluate the potential of using the chemical equilibrium software Visual MINTEQ to predict struvite formation.
- To determine ammonia and phosphate removal and recovery using Mg-rich waste material, and compare with that using analytical grade MgCl_2 .
- To determine the potential economic value of Mg-rich waste material compared with that obtained using a high purity grade MgCl_2 as a source of magnesium.

1.3 Thesis outline

This thesis consists of eight chapters, and additional material is included as appendices and references.

Chapter 1 describes the background relating to ammonia and phosphate removal and recovery, sets the objectives of the research and provides the outline of the thesis.

Chapter 2 provides a basic understanding of struvite precipitation. It includes the kinetics of struvite formation, parameters affecting struvite formation, the development of the technology and the economic value of struvite

Chapter 3 presents the detailed methods and materials which are used in the experiments, while Chapter 4 reports struvite formation at different operating

conditions (the reaction time and the mixing rate) and determination of induction time using pH change with time.

Chapter 5 describes the effects of pH, the reaction time and molar ratios on ammonia and phosphate removal and recovery from anaerobic digester supernatant and the optimum conditions for struvite precipitation are discussed.

Chapter 6 presents chemical equilibrium software Visual MINTEQ used for the prediction of struvite formation at different pH and molar ratios. The residual concentrations of ammonium, magnesium and phosphate are considered, and ammonia and phosphate removal are analysed. The amount and type of solids formed after reaction are also considered to determine the pH and molar ratio effects.

Chapter 7 presents the efficiency of struvite formation from anaerobic digester supernatant using Mg-rich waste material. The effects of the pH and molar ratio are studied. An economic analysis is also presented to evaluate the feasibility of using Mg-rich waste material.

Chapter 8 presents the conclusions and recommendations for future work based on the present study results.

Chapter 2 Literature Review

2.1 Introduction

This chapter presents the background of the research. It includes the techniques of ammonia and phosphate removal and recovery and the basic theory, development and application of struvite precipitation techniques. The main parameters of struvite precipitation and the kinetics of struvite relating to nucleation and growth are presented. The technological application of struvite and its economic analysis are also included in this chapter. Problems arising from this technique and current trends in its development are discussed at the end of this chapter.

2.2 Ammonia and phosphate removal and recovery technologies

The development of ammonia and phosphate removal technology was a response to the issue of eutrophication dating from the 1950s. The recovery of phosphate from wastewater has been attracting attention because the reserves of phosphorus rock are limited (Steen, 1998). A number of phosphate recycling techniques have been employed and are practised widely. The most common techniques used for ammonia and phosphate removal and recovery from wastewater are chemical precipitation, biological phosphorus removal, and crystallization (Morse *et al.*, 1998). Removal was initially achieved by chemical precipitation, which remains the leading technology today. However, biological phosphorus removal has become firmly established, and crystallisation technology has also progressed towards commercialisation and technologies

extending chemical precipitation to assist nutrient removal are beyond the pilot stage.

Chemical precipitation is a simple physical and chemical process, which has been established widely in the world recently. Aluminium or iron salt is suitable for adding to wastewater, and an insoluble metal phosphate is settled out by sedimentation (Morse *et al.*, 1998). For example, metal salts such as aluminium sulphate ($\text{Al}_2(\text{SO}_4)_3$), ferric chloride (FeCl_3), ferrous (bivalent), and ferric sulphates ($\text{Fe}_2(\text{SO}_4)_3$) are commonly used to precipitate phosphate (Stumm *et al.*, 1996). However, it is technically and economically unfeasible for recycling phosphate (Battistoni *et al.*, 2002). The technology has the disadvantages of the use of chemicals and excess sludge production.

Biological phosphate removal technique (i.e. BNR, EBPR) use micro-organisms to accumulate phosphates as polyphosphates for their own metabolism (Driver *et al.*, 1999, Mulkerrins *et al.*, 2004). This technique can reduce phosphate concentration in wastewater efficiently, the phosphate precipitates is not efficient for wastewaters with high phosphate concentrations (de-Bashan and Bashan, 2004, Battistoni *et al.*, 2002).

The main crystallisation technologies are selective ion exchange (i.e. the RIM-NUT process) (Liberti *et al.*, 1986), precipitation in a stirred reactor (Laridi *et al.*, 2005, Stratful *et al.*, 2004) and precipitation in fluidised bed reactors or air-agitated reactors (Battistoni *et al.*, 2005, Münch and Barr, 2001). Phosphate is available in crystals of some compounds such as calcium phosphate or struvite

($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) from wastewater effluent. Struvite and calcium phosphate are phosphate fertilizers (Gaterell *et al.*, 2000). Several laboratory and pilot-scale studies have been carried out to assess the potential of such methods in removing and recovering phosphate as a reusable product, and some have been tested at full scale in The Netherlands (Giesen, 1999) and Italy (Battistoni *et al.*, 2005). Japan has produced struvite from anaerobically-digested sludge liquors and it has been sold to fertiliser companies (Gaterell *et al.*, 2000).

2.3 The development and applicability of struvite precipitation

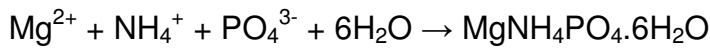
Struvite was originally considered a problem in wastewater treatment plants. Rawn (1939) found that struvite accumulated in the digested sludge supernatant lines, causing trouble and expense for the wastewater treatment plant. Borgerding (1972) reported that certain locations in digested sludge piping systems tended to form struvite. These locations included those with the greatest surface-to-volume ratio, energy input, rough surfaces and local low pressure (pump suction, venturiers and pipe bends). Since struvite accumulation limits the capacity and efficiency of pipes and other related equipment, different strategies have been investigated to control struvite accumulation. For example, struvite deposition has been controlled by dilution with water effluent, thermal treatment, jet washing (Borgerding, 1972), chemical dosing of iron salts (Mamais *et al.*, 1994) or the addition of chemical inhibitors (Buchanan *et al.*, 1994). However, the operational costs of these strategies are considerable.

On the other hand, struvite precipitate has been found to have potential as a marketable product for the fertilizer industries (Booker *et al.*, 1999). It also reduces both ammonia and phosphate concentrations in wastewater. Researchers began to investigate struvite precipitation in controlled conditions and locations. They focused on the prevention of scaling, alternative ammonia and phosphate removal and recovery techniques from wastewater effluent and its economic value as a fertilizer (Booker *et al.*, 1999, Doyle and Parsons, 2002, Gaterell *et al.*, 2000). Investigators have determined struvite precipitation at batch and pilot scale, and some field-scale applications in treatment plants (Nelson *et al.*, 2003). In Europe and Japan, this nutrient recovery technology is already accepted by large municipal sewage-handling facilities (Battistoni *et al.*, 2001, Battistoni *et al.*, 2006, Kumashiro *et al.*, 2001, Türker and Çelen, 2007, Ueno and Fujii, 2001, Uludag-Demirer and Othman, 2009, Yoshino *et al.*, 2003). Farm-scale struvite precipitation has not been developed, so struvite precipitation technique has yet to benefit from current practices.

The technology of ammonia and phosphate removal and recovery as struvite has been applied widely and effectively. It has been reported in relation to landfill leachate (Gunay *et al.*, 2008, Li and Zhao, 2003), swine wastewater (Burns and Moody, 2002, Çelen *et al.*, 2007, Nelson *et al.*, 2003, Wang *et al.*, 2005), anaerobic digester side-streams (Battistoni *et al.*, 1997, Kumashiro *et al.*, 2001, Münch and Barr, 2001) and dairy manure (Uludag-Demirer *et al.*, 2005). Struvite precipitation has also been applied to ammonium and phosphate recovery from supernatant of anaerobic digester sludge (Çelen and Türker, 2001, Marti *et al.*, 2008, Pastor *et al.*, 2008, Uludag-Demirer and Othman, 2009).

2.4 Background of struvite formation

Magnesium ammonium phosphate hexahydrate ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) (MAP) is commonly known as struvite. The struvite crystal has a unique orthogonal structure (Doyle *et al.*, 2000), and its solubility product constant range from 5.50×10^{-14} to 3.98×10^{-10} (Doyle and Parsons, 2002). A scanning electron micrograph of struvite crystals is shown in Figure 2.1 (Bouropoulos and Koutsoukos, 2000). Struvite forms according to the general reaction shown in Equation 2.1. The formation constant of struvite is 1.41×10^{13} (Buchanan *et al.*, 1994).



(2.1)

$$K_{\text{SP}} = [\text{Mg}^{2+}] [\text{NH}_4^+] [\text{PO}_4^{3-}]$$

(2.2)

$$K_{\text{SO}} = (\alpha_{\text{Mg}^{2+}} \gamma_{\text{Mg}^{2+}} C_{\text{T}, \text{Mg}^{2+}}) (\alpha_{\text{NH}_4^+} \gamma_{\text{NH}_4^+} C_{\text{T}, \text{NH}_4^+}) (\alpha_{\text{PO}_4^{3-}} \gamma_{\text{PO}_4^{3-}} C_{\text{T}, \text{PO}_4^{3-}})$$

(2.3)

$$P_{\text{S}} = C_{\text{T}, \text{Mg}} C_{\text{T}, \text{NH}_4} C_{\text{T}, \text{PO}_4} = \frac{K_{\text{SO}}}{\alpha_{\text{Mg}^{2+}} \alpha_{\text{NH}_4^+} \alpha_{\text{PO}_4^{3-}} \gamma_{\text{Mg}^{2+}} \gamma_{\text{NH}_4^+} \gamma_{\text{PO}_4^{3-}}}$$

(2.4)

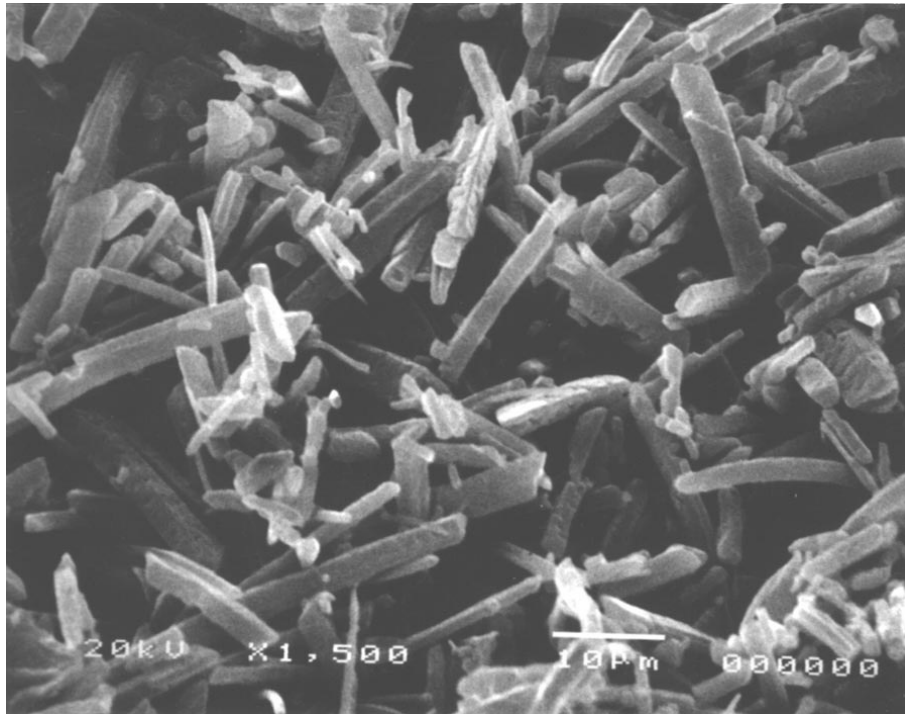


Figure 2.1: Scanning electron micrograph of struvite crystals precipitated spontaneously in aqueous supersaturated solutions, pH 8.5

Stumm and Morgan (1996) and Snoeyink and Jenkins (1980) formulated the thermodynamic solubility product (K_{SP}) (Equation 2.1) and the conditional solubility product (P_S) (Equation 2.4). When $P_S > K_{SP}$, struvite precipitation will form from the supersaturated solution, otherwise the solution is under-saturated. However, K_{SP} takes no account of pH, ion activity and ionic strength. Therefore, the K_{SP} value can be expressed as an activity solubility product K_{SO} (Mullin, 1997), which takes into account the free ion concentration (C_i), ionization fraction (α_i) and the activity coefficient (γ_i) of the struvite constituents (Mg^{2+} , NH_4^+ and PO_4^{3-}). The conditional solubility product (P_S) and the thermodynamic solubility product (K_{SO}) are illustrated in the solubility status of field effluent (Equations 2.3).

2.5 Kinetics of struvite formation

Struvite precipitation can be separated into two major steps: nucleation and crystal growth. Nucleation occurs when ions combine to form crystal embryos that can act as the foundation for growth into detectable crystals. Growth results from the assimilation of ions into the lattice structure established by the crystal embryo foundation (Ohlinger *et al.*, 1999).

The precipitation potential of struvite is highly dependent on K_{SP} and the pH of the solution. When pH increases, the dissolution equilibrium curve for struvite decreases, allowing a greater degree of struvite precipitation to occur (Ohlinger *et al.*, 2000). The rate of struvite formation depends upon the conditional solubility product (K_{SP}) of struvite which is directly proportional to the product of Mg^{2+} , NH_4^+ , and PO_4^{3-} ions in solution.

The kinetics of homogenous chemical reactions can be described as Equation 2.5 (Smith, 1970).

$$-\frac{d[C]}{dt} = k[C]^n$$

(2.5)

Where $[C]$ is the concentration of reactant, k is the rate constant and n is the order of reaction. If the equation is integrated for the first, second and third order, it yields the following integrated equations respectively:

$$\ln[C] = \ln[C]_0 - kt \quad \text{For the first order}$$

(2.6)

$$\frac{1}{[C]} = \frac{1}{[C]_0} + kt \quad \text{For the second order}$$

(2.7)

$$\frac{1}{2[C]^2} = \frac{1}{2[C]_0^2} + kt \quad \text{For the third order}$$

(2.8)

When the left-hand sides of Equations 2.6-2.8 are plotted against time t , a straight line for correct reaction order is obtained. $[C]_0$ is the initial concentration of the reactant.

Studies by Ohlinger *et al.* (2000) and Nelson *et al.* (2003) identified that struvite kinetics of crystal growth followed first order kinetics with rate constants ranging from 4.2 to 12.3 h^{-1} , depending on the solution pH. In contrast, Turker and Celen (2007) reported that struvite nucleation followed second order kinetics.

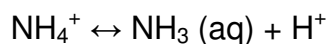
2.6 Parameters effect on struvite formation

The main components of the reaction solution are Mg^{2+} , NH_4^+ and PO_4^{3-} , but there are still a variety of complex ions patterns in wastewater, including MgOH^+ , $\text{MgH}_2\text{PO}_4^+$, MgHPO_4 , H_3PO_4 , H_2PO_4^- , HPO_4^{2-} , MgPO_4^- , NH_3 (Bouropoulos and Koutsoukos, 2000). Parameters influencing struvite precipitation from wastewater include the pH, molar ratio, ions in the wastewater, reaction time,

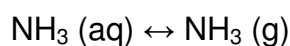
the mixing rate and temperature. The key process parameters of reactions are the pH and concentration of reactants.

2.6.1 Effect of pH

The pH of the solution is the most significant factor for struvite precipitation, and not only affects the amount of struvite precipitation, but also its purity. Increasing pH and the reactant concentration can reach solution saturation. However, increasing the pH of the solution is more appropriate for feasible and desirable applications. Snoeyink and Jenkins (1980) stated that the concentrations of Mg^{2+} , NH_4^+ and PO_4^{3-} ions can be affected by the pH of the solution. Mg^{2+} hydroxide complexes ($MgOH^+$, $Mg(OH)_3^-$, etc) can be formed when the pH of solution is increased, and NH_4^+ ion can form $NH_3(g)$ (Equations 2.19 and 2.10). $NH_3(g)$ can be volatile to air. On the other hand, the concentration of PO_4^{3-} ion is expected to increase as the solution becomes more basic. In addition, the pH of the solution controls struvite solubility. Snoeyink and Jenkins (1980) reported that struvite solubility decreases with increasing the pH, but it begins to increase when the pH rises above pH 9, since the ammonium ion concentration will decrease and the phosphate ion concentration will increase. Booker *et al.* (1999) reported a similar result.



(2.9)



(2.10)

A chemistry equilibrium model MINTEQA2 was used to model struvite formation (Buchanan *et al.*, 1994). These researchers found that struvite precipitation occurred within a pH range of 7.0 to 11.0, with minimum struvite solubility at pH 9. Ali *et al.* (2003) also predicted struvite precipitation by Visual MINTEQ, and found that struvite formed at the pH range from 7 to 10.5. They reported that struvite was the only solid formed in the pH range of 7.75 to 9.27. Newberyite ($\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$), Brucite ($\text{Mg}(\text{OH})_2$) and Farringtonite ($\text{Mg}_3(\text{PO}_4)_2$) formed at below or above pH, which affected the amount of struvite precipitation.

As Table 2.1 shows, the optimum pH for struvite precipitation ranges from 8.5 to 9.5. It differs somewhat because of the different types of wastewater and treatment processes. Miles and Ellis (2001) investigated struvite precipitation for anaerobically-digested swine wastewater at pH from 9.0 to 9.5, with 88% NH_4^+ -N recovery. Nelson *et al.*, (2003) reported that maximum phosphate recovery occurred at a pH range from 8.9 and 9.25 using anaerobic swine lagoon liquid. They found that phosphate recovery achieved 85% at pH 9 and the $\text{Mg}^{2+}:\text{PO}_4^{3-}$ molar ratio of 1.2:1 and phosphate concentration in the effluent can be reduced to 2 mg/L.

The two most common methods of pH adjustment are chemical amendment and aeration stripping of carbon dioxide. NaOH, $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ are the common reagents used to adjust the pH of the solution pH, although NaOH has been suggested as the more effective chemical (Fujimoto *et al.*, 1991).

The above studies have shown that the pH of the solution is the most important parameter for struvite precipitation from wastewater. Because of the different experimental systems used to date, the optimum pH for struvite formation is from 8.5 to 9.5.

2.6.2 Effect of molar ratio

Struvite can form and precipitate in solution when $Mg^{2+}: NH_4^+: PO_4^{3-}$ molar ratio is adjusted to 1.0:1.0:1.0 according to Equation 2.1. However, other magnesium, phosphate compounds may be formed because of the complex compounds in wastewater, such as $MgHPO_4 \cdot 3H_2O$ (Newberyite), and $Mg_3(PO_4)_2 \cdot 8H_2O$ (Bobierrite). The addition of magnesium and phosphate is required to maximize ammonia recovery from wastewater. In addition, increasing magnesium addition can enhance struvite precipitation at the same time reducing phosphate dosage. It can also decrease residual phosphorous concentration in the solution. However, if the concentration of magnesium is increased up to a certain value, phosphorus removal will not change (Jaffer *et al.*, 2002). Katsuura (1998) believes that phosphate removal does not change when the $Mg^{2+}: NH_4^+: PO_4^{3-}$ molar ratio is more than 1.3:1.0:1.0 at pH 9.0. Nelson *et al.* (2003) reported that the Mg^{2+} concentration addition did not have a significant impact on phosphorus removal. Therefore, magnesium addition and phosphate addition should be controlled to ensure the feasibility of struvite precipitation from wastewater. The optimum molar ratio for struvite precipitation is summarized in Table 2.1. Most research to date has indicated that the optimum $Mg^{2+}: NH_4^+: PO_4^{3-}$ molar ratio is between 1.0:1.0:1.0 and 1.6:1.0:1.0 (Nelson *et al.*, 2005, Altinbas *et al.*, 2002b,

Celen and Turker,2001, Mile and Ellis,2001,Ryu *et al.*, 2008, Burns *et al.*, 2003, Battistoni *et al.*, 2001, Yoshino *et al.*, 2003).

2.6.3 Effect of reaction time

As the formation of struvite is a chemical reaction, it is completed quickly. Stratful *et al.* (2001) reported that only 4% more PO_4^{3-} ions were removed between 1minute and 180 minutes, and the reaction time did not have a significant effect on struvite production. Booker *et al.* (1999) found that the reaction was completed within a few minutes. The reaction time of 10 minutes for struvite precipitation is consistent with that of Burns *et al.* (2003) and Celen (2006), who tested the reaction time for struvite precipitation from swine manure slurries. Lee *et al.* (2003) also reported that struvite precipitation occurred rapidly and was completed within 10 minutes.

Table 2.1: A summary of the optimum pH and $Mg^{2+}:NH_4^+:PO_4^{3-}$ for struvite formation

Type of wastewater	Molar ratio $Mg^{2+}:NH_4^+:PO_4^{3-}$	Initial concentrations(mg/L)		Removal (%)		Optimum pH	References
		NH_4^+ -N	PO_4^{3-} -P	NH_4^+ -N	PO_4^{3-} -P		
Anaerobic swine lagoon	1.6:1.0:1.0	533	55.4		96	8.9	Nelson <i>et al.</i> (2003)
		272	63.8	—	91	9.25	
Anaerobically-treated municipal and landfill wastewater	1.0:1.0:1.0	735	5.8	84	—	9.2	Altinbas <i>et al.</i> (2002b)
Effluent from anaerobic digester treating molasses-based industrial wastewater	1.2:1.0:1.2	1088.9	7.8	97	—	8.5	Celen &Turker (2001)
Supernatant from an anaerobic digestion of sludge from a sewage treatment plant	1.1: 1.0:1.0	441-602	198-242	—	92	8.4-8.5	Yoshino et tal. (2003)
Anaerobically-digested swine wastewater	1.25: 1.0:1.0	2882	—	88	—	9.0-9.5	Miles & Ellis (2001)
Semiconductor wastewater	1.2:1.0:1.0	143.5	142.5	78	—	9.2	Ryu <i>et al.</i> (2008)
Supernatant from swine slurries	1.6:1.0:1.0	—	~1000(high)		98	8.6	Burns <i>et al.</i> (2003)
		—	~230(low)	—	96		
Anaerobic sludge supernatant	—	1090	58.2	—	80	8.78	Battistoni <i>et al.</i> (2001)

Table 2.2: Summary of sources of magnesium sources used for struvite precipitation as published in the literature

Type of wastewater	Mg sources added	Molar ratio Mg ²⁺ :NH ₄ ⁺ :PO ₄ ³⁻	Initial concentrations(mg/L)		Removal (%)		pH	References
			NH ₄ ⁺ -N	PO ₄ ³⁻ -P	NH ₄ ⁺ -N	PO ₄ ³⁻ -P		
Anaerobic digestion sludge supernatant from a sewage treatment plant	MgSO ₄ ·7H ₂ O	1.1:1.0:1.0	441-602	198-242	—	92	8.4-8.5	Yoshino <i>et al.</i> (2003)
Synthetic wastewater	seawater	1.3:1.1: 1.0	—	—	54	—	10.0	Lee <i>et al.</i> (2003)
Synthetic wastewater	bittern	1.3:1.1: 1.0	—	—	39	—	9.6	Lee <i>et al.</i> (2003)
Side-streams from AD treating sludge	Mg(OH) ₂	1:1:1.3:1.0	790	61	6	94	8.5	Munch & Barr (2001)
Wastewater from cochineal insect processing	Low grade MgO	1.0:1.0:1.0	2320	3490	89	100	8.5-9.0	Chimenos <i>et al.</i> (2003)
Anaerobic treatment effluent from baker's yeast industry	MgCl ₂ ·6H ₂ O	1.0:1.0:1.0	735	5.8	84	—	9.2	Altinbas <i>et al.</i> (2002a)
Landfill leachate	MgCO ₃	1.0:1.0:1.0	2100	—	91	—	8.6	Gunay <i>et al.</i> (2008)
Landfill leachate	MgSO ₄ ·7H ₂ O	1.0:1.0:1.0	2750	—	70	—	9.0	Li & Zhao (2003)
Landfill leachate	MgCl ₂ ·6H ₂ O	1.0:1.0:1.0	2750	—	92	—	9.0	Li & Zhao (2003)
Landfill leachate	Bittern	1.0:1.0:1.0	2900	—	80	—	8.38	Li & Zhao (2003)
Side-streams from digested sludge	Seawater	1.6:1.0:1.0	517	26.4	17	76	7.76	Kumashiro <i>et al.</i> (2001)

2.7 Magnesium sources and economic analysis

Struvite has been suggested as a valuable fertiliser because it has been found to display excellent qualities under specific conditions when compared with standard fertilizers (Ghosh *et al.*, 1996). These qualities are related to the slow release of nutrients due to struvite's solubility characteristics. According to Münch and Barr (2001) and Gaterell *et al.* (2000), the qualities of struvite include its low solubility and nitrogen and phosphorus components, although extensive field trials are yet to be undertaken using struvite as a fertiliser or as a fertiliser additive. In addition, struvite contains low heavy metal content when compared to phosphate-bearing rocks that are mined and supplied to the fertiliser industry (Driver *et al.*, 1999).

Costs of production of struvite vary, for example it is around \$140 per tonne in Australia and to \$460 per tonne in Japan. The market value of struvite ranges from \$9 to \$1885 per tonne (Doyle and Parsons, 2002) as shown in Table 2.3. Jaffer *et al.* (2002) showed that for full-scale recovery of struvite to be economic in United Kingdom (UK), struvite would have to be marketable at \$283 to outweigh the costs of chemicals for magnesium dosage and pH adjustment.

The concentration of magnesium in wastewater effluents, with potential for struvite formation, is limiting, i.e. lower than the concentrations of ammonium and phosphate (Giesen, 1999, Lee *et al.*, 2003, Nelson *et al.*, 2003). Therefore Mg must be added to the solution for the precipitation to occur. It has been found that the cost of magnesium salts required to achieve the designated molar ratios is a major economic constraint to the application of struvite

precipitation for nutrients recovery. Researchers have attempted to find suitable and economic magnesium sources for this application, recovery of nutrients in the form of struvite. For this purpose, various magnesium sources (i.e. MgCl_2 , $\text{Mg}(\text{OH})_2$ and MgSO_4) have been tested and employed for struvite precipitation at different scales (Liu *et al.*, 2008, Wilsenach *et al.*, 2007). Most studies have used analytical grade MgCl_2 as the magnesium source for struvite precipitation. Low-cost materials have been tested as the magnesium sources, including low grade MgO , bittern and seawater, as shown in Table 2.2. Chimenos *et al.* (2003) used low-purity MgO as a magnesium source to recover the high concentrations of nitrogen and phosphorus in wastewater because of its low price and efficiency. Kumashiro *et al.* (2001) used seawater as a magnesium source for struvite precipitation at a pilot scale. Bittern is another natural source of magnesium which is produced by the evaporation of seawater. Lee *et al.* (2003) applied bittern for struvite formation to achieve a high removal rate of phosphorus, but the removal of ammonia was limited by the imbalance in the ratio of nitrogen and phosphorus.

Table 2.3: Cost of producing and selling struvite (Doyle and Parsons, 2002)

Country	Description	Cost (converted to US dollar/tonne)	References
Australia	Cost of production of 1 tonne of struvite	140	Booker <i>et al.</i> (1999)
Australia	Suggested market value for struvite	877	Booker <i>et al.</i> (1999)
Australia	Conservative estimate of struvite as 'boutique' fertilizer	261	Munch <i>et al.</i> (2001)
Australia	Suggested market value for struvite	198-330	Munch and Barr (2001)
Japan	Operational costs for producing 1 tonne	460	Kumashiro <i>et al.</i> (2001)
Japan	Cost of purchasing 1 tonne of struvite	276	Munch and Barr (2001)
Japan	Suggested value of struvite	1885	Taruya <i>et al.</i> (2000)
Japan	Cost of purchasing 1 tonne of struvite	250	Gaterell <i>et al.</i> (2000)
Japan	Final product produced from struvite	500	Gaterell <i>et al.</i> , 2000
UK	Cost of struvite as an ingredient	9	Gaterell <i>et al.</i> (2000)
UK	Cost of phosphate rock	40-50	Driver <i>et al.</i> (1999)
UK	Suggested market value for struvite	283	Jaffer <i>et al.</i> (2002)

2.8 Chapter summary

This chapter reviewed the techniques used by researchers at laboratory, pilot and full scale to remove and recover ammonia and phosphate as struvite precipitation. Struvite precipitation is still not widely applied in practice and most of studies were conducted at laboratory scale and in a few field trials. The main problem is the high cost of chemicals, the low purity of struvite precipitation, and the relative lack of practical research in the agricultural field. In addition, magnesium dosage is the major cost of the process.

This chapter identifies that the use of a low priced magnesium source in struvite precipitation would reduce operating costs. Further research should focus on reducing production operating costs, improving yield and purity of struvite, sampling recovery procedures and the application of struvite as a fertilizer in agricultural practically.

Chapter 3 Materials and Methods

3.1 Introduction

The literature review in Chapter 2 indicated that maximizing ammonia and phosphate removal and recovery as struvite precipitation and finding a low cost magnesium source are the main issues of the application of struvite precipitation technology. This chapter describes the experimental methods and materials used for laboratory tests. A chemical equilibrium software Visual MINTEQ was used for testing ammonia and phosphate recovery as struvite precipitation from the supernatant of anaerobic digesters.

3.2 Materials

3.2.1 Characteristics of supernatants

Anaerobic digester supernatant samples were collected from Melton and Eastern wastewater treatment plants in Melbourne, Australia. They were centrifuged at 4000 rpm for 15 minutes and filtered through a glass fibre filter paper (quality advance 0.6 μ m). The solid-free solution was acidified using H₂SO₄ and stored at 4°C in a refrigerator for later use in the experiments, which were carried out during a period of a month. The constituents of anaerobic digester supernatant were measured according to Standard Methods (Clesceri *et al.*, 1998), and the results are shown in the Tables 3.1 and 3.2. Supernatants from both wastewater plants were dark brown in colour.

Table 3.1: The composition of anaerobic digester supernatant from Melton Wastewater Treatment Plant in Melbourne, Australia

Parameter	Concentration(mg/L)
Ammonia	731.85
PO ₄ ³⁻	319.00
Soluble COD	120.33
Mg ²⁺	35.67
Na ⁺	107.40
Fe ²⁺	109.11
K ⁺	2.64
Ca ²⁺	97.72
pH	7.32

Table 3.2: The composition of anaerobic digester supernatant from Eastern Wastewater Treatment Plant in Melbourne, Australia

Parameter	Concentration(mg/L)
Ammonia	1349.92
PO ₄ ³⁻	352.60
Soluble COD	250.50
Mg ²⁺	16.45
Na ⁺	160.00
K ⁺	81.00
Ca ²⁺	105.23
pH	8.13

3.2.2 Characteristics of Mg-rich waste material

Table 3.3 shows the compositions of Mg-rich waste material which was purchased from one waste material recycling company (Rain Storm). This magnesium source contains high concentration magnesium, followed by potassium and sodium. It also contains a small amount of iron and calcium. The concentrations of ammonia and phosphate relative to the amount of magnesium are very small.

Table 3.3: The composition of Mg-rich waste material

Parameters	Concentration(mg/L)
Mg ²⁺	112.44×10 ³
Na ⁺	4.38×10 ³
K ⁺	147.34×10 ³
Fe ²⁺	4.87
Ca ²⁺	272.44
Ammonia	1.57
PO ₄ ³⁻	130.00

3.3 Experimental methods

3.3.1 Ammonia and phosphate removal from synthetic solutions using analytical grade MgCl₂

This part of the experimental program was to determine ammonia and phosphorous removal and induction time, reaction time and struvite formation from a synthetic solution (i.e. Mg²⁺, NH₄⁺ and PO₄³⁻ constituents dissolved in deionised water). The mixing rate and the reaction time experiments were conducted to determine the experimental conditions at which struvite formation can be evaluated. The mixing rate effect on struvite formation was carried

investigated at rates between 80 to 250 rpm. Struvite formation was investigated for reaction times from 3 to 25 minutes. Determination of induction time used the pH change over time.

All reactions were carried out using batch reactors at room temperature (21 °C-24 °C). Magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) and ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) were used as a source of Mg^{2+} , and PO_4^{3-} to form struvite, and all of them were of analytical grade. The pH was controlled by the addition of sodium hydroxide (NaOH) and hydrogen chloride (HCl), and measured using a pH meter (Thermo Orion, Model 550A). After the reaction time, precipitates were filtered through 0.2 μm pore size Whatman membrane (for synthetic solution) and dried at room temperature. When anaerobic digester supernatant was used for induction time determination, the precipitates were filtered through a glass fibre filter paper (quality advance 0.6 μm) Whatman membrane (for anaerobic digester supernatant). Residual concentrations of Mg^{2+} , NH_4^+ and PO_4^{3-} in solution after filtration stage were analysed by the following methods. The concentrations of ammonia and phosphate were analysed using a HACH DR/4000 spectrophotometer. The concentration of Mg^{2+} was analysed using atomic absorption spectrophotometer (Varian SpectrAA-600). The collected precipitates were analysed by environmental scanning electron micrograph (ESEM). All experiments were carried out in duplicate.

3.3.2 Ammonia and phosphate removal from anaerobic digester supernatant using analytical $MgCl_2$

Based on the initial composition of the supernatant solution (Table 3.1), Magnesium was the limiting reactant. Mg^{2+} and PO_4^{3-} dosages of 35.67mg/L and 319.00mg/L respectively, were required to be increased to desired molar ratio of $Mg^{2+}:NH_4^+:PO_4^{3-}$. The concentrations of ammonia and phosphate in the supernatant were checked before each experiment was carried out. Ammonia concentration ranged from 716.00 mg/L to 740.00 mg/L, and phosphate concentration was in the range from 34.00 to 37.00 mg/L. The concentration of NH_4^+ was kept constant at its original level in all experimental runs. The experimental design consisted of three stages was to identify the conditions for maximizing ammonia and phosphate removal and the associated quality of struvite precipitation. These stages comprised determination of the effect of the reaction time, pH and molar ratios. To investigate the effect of pH on ammonia and phosphate removal and recovery from anaerobic digester supernatant, experiments were carried out at pH range of 8.0 to 10.5 at the $Mg^{2+}: NH_4^+:PO_4^{3-}$ ratio of 1.0:1.0:1.0. To determine the reaction time required to assess ammonia and phosphate removal throughout the course of this study, experiments were carried out using different reaction times of 5.0 to 60.0 minutes. To determine molar ratio at which ammonia and phosphate removal is maximum and the associated precipitate quantity and quality, experiments using different magnesium and phosphate dosages were carried out at the reaction time identified in the second stage of the experimental program described in this section.

All of the experiments were carried out at batch conditions in 250 mL beakers using supernatant volumes of 100 mL. Beaker contents were mixed using a magnetic stirrer. All reactions took place at room temperature (21 °C-24 °C). The concentrations of Mg^{2+} and PO_4^{3-} were adjusted to the required molar concentration using $MgCl_2 \cdot 6H_2O$ and NaH_2PO_4 solution, respectively. All reagents were of analytical grade. For all tests where pH was adjusted, NaOH was used to raise the pH, and measured using a pH meter. After reaction time, the precipitates were filtered through glass fibre filter (quality advance 0.6 μ m) Whatman membrane and dried at room temperature. Residual concentrations of Mg^{2+} , ammonia and phosphate in solution after filtration stage were analysed by the following methods. Phosphate and ammonia were analysed by a HACH DR/4000 spectrophotometer. Magnesium was analysed using atomic absorption spectrophotometer (Varian SpectrAA-600). The dry precipitates were characterized by X-ray diffraction (XRD) analysis. All experiments were carried out in duplicate.

3.3.3 Ammonia and phosphate removal and recovery from anaerobic digester supernatant using Mg-rich waste material

Based on the initial composition of the supernatant solution (Table 3.2), Mg^{2+} and phosphate concentration 16.45 mg/L and 352.60 mg/L respectively, were required to be increased to desired levels. Both of them were lower than the ammonia concentration (1349.92 mg/L). The concentrations of ammonia and phosphate were checked again before each experiment on different days. Ammonia concentration was in the range from 1347.00 mg/L to 1350.00 mg/L, and phosphate concentration was at the range from 348.00 mg/L to 362.00

mg/L. The concentration of ammonia was kept constant at its original level in all experimental runs. Three different tests were designed to determine the feasibility of using Mg-rich waste material for ammonia and phosphate removal and recovery as struvite: the pH, the reaction time and molar ratios. To establish required equilibrium time, the experiments were carried out at pH 9.0 and the equal molar ratio using 5-60 minutes. Magnesium and phosphate concentrations were increased by Mg-rich waste material and Na_2HPO_4 . To test the pH effect, an investigation evaluated the feasibility of ammonia and phosphate removal and recovery at the range from 7.0 to 11.0 and the equal ratio. To determine ammonia and phosphate removal and recovery with increasing magnesium dosage, the different molar ratios of $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ from 1.0:1.0:1.0 to 2.0:1.0:1.0 were used for struvite formation at pH 9.5.

All of the experiments were carried out as batch reactions in 250 mL beaker with supernatant of 100 mL. Beaker contents were mixed using a magnetic stirrer. All reactions took place at room temperature (21°C-24°C). The concentrations of Mg^{2+} and phosphate were increased with Mg-rich waste material and NaH_2PO_4 . For all tests where pH was adjusted, NaOH and HCl were used to raise the pH. After reaction, precipitates were filtered through a glass fibre filter (quality advance 0.6 μm) Whatman membrane and dried at room temperature. Residual concentrations of Mg^{2+} , ammonia and phosphate in solution after filtration stage were analysed by the following methods. Phosphate and ammonia were analysed by a HACH DR/4000 spectrophotometer. Magnesium was analysed with atomic absorption spectrophotometer (Varian SpectrAA-600). The collected precipitates were

characterized by X-ray diffraction analysis and ESEM. All batch experiments were carried out in duplicate.

3.3.4 Prediction of struvite formation using chemical equilibrium Visual MINTEQ model

Visual MINTEQ is a chemical equilibrium computer program that has an extensive thermodynamic database that allows for the calculation of speciation, solubility, and equilibrium of solid and dissolved phases of minerals in an aqueous solution (Gustafsson, 2008). Visual MINTEQ is a Windows version of MINTEQA2 ver 4.0, which was released by the USEPA in 1999. MINTEQA2 is a chemical equilibrium model for the calculation of metal speciation, solubility equilibrium etc. for natural waters. The original version of MINTEQ was developed at Battelle Pacific North Western Laboratory (PNL) by combining the fundamental mathematical configuration of MINTEQ with WATEQ3 (Allison *et al.*, 1991).

The chemical equilibrium software Visual MINTEQ was used to predict the potential for struvite formation as a function of pH and magnesium dosage. Using the composition of anaerobic digester supernatant as input, the model's output was used to estimate what minerals could be formed. Each model prediction was run at a temperature of 25 °C and a negligible ionic strength. The Visual MINTEQ database does not include struvite. Struvite was added to the database through a database management tool. The possible solids formation can be chosen using the "specify possible solid phase" tool. These steps were done before running Visual MINTEQ to predict struvite formation. Otherwise the model will predict that no solids formation will occur.

3.3.4.1 Database management in Visual MINTEQ

The requirements for adding struvite to database are species name, species ID number, logKs, dH_r, charge of species, and number of components in this species. LogKs is the logarithmic value of the equilibrium constant of reaction, it is the negative logarithmic value of the solubility product constant (-LogK_{sp}) (Allison *et al.*, 1991). Ohlinger (1999) from his research found -LogK_{sp} was 13.27. Nelson (2003) reported the value of -LogK_{sp} equal to 13.15. Soneyink and Jenkins (1980) suggested -LogK_{sp} was 12.60. A value of 13.27 for -LogK_{sp} was used in Visual MINTEQ input file in this study. This study was carried at room temperature, and the change in enthalpy (dH_r) used was zero. Species ID number (1960009) was suggested by the database management tool. The database for struvite in Visual MINTEQ input file is shown in Table 3.4.

Table 3.4: Database of struvite

Species	Struvite
Species ID number	1960009
logKs	-13.27
dH _r	0
Charge	0
NO. of components in this species	4
Molar weight(g/mol)	245.414

3.3.4.2 Specifying possible precipitates for MINTEQ Model

The possible solids that may be formed were specified using the “specify possible solid phase” tool before running the software. Ali *et al.* (2003) used Visual MINTEQ to predict solids in supersaturated solutions at different pH values. The results showed that struvite was the dominant solid in the pH range of 7.0 to 10.5. Celen *et al.* (2007) discussed the possible precipitates which included magnesium phosphate species, calcium phosphate species, calcium carbonate species and other salts. The possible precipitates were chosen from Visual MINTEQ database. The results are shown in Table 3.5.

Table 3.5: Possible precipitates in the system

Species	Possible precipitates
Magnesium phosphate species	MgNH ₄ PO ₄ ·6H ₂ O, MgHPO ₄ ·3H ₂ O
Calcium phosphate species	CaHPO ₄ ·2H ₂ O(DCPD)
Calcium carbonate species	—
Other salts	MgCO ₃ , MgCO ₃ ·3H ₂ O, Mg(OH) ₂

3.3.4.3 Prediction of struvite formation at different reaction conditions

Using MINTEQ Equilibrium Model

The samples were collected from Eastern Wastewater Treatment Plant in Melbourne. The characteristics of anaerobic digester supernatant were shown in Table 3.2. The concentration of Mg²⁺ was predicted to increase by Mg-rich waste material. The characteristics of this magnesium source were shown in Table 3.3. Typically, the concentration of ammonia in the supernatant is higher

than Mg^{2+} and PO_4^{3-} concentrations. In order to force struvite formation, the molar ratio of NH_4^+ , Mg^{2+} and PO_4^{3-} should be at 1.0:1.0:1.0. Mg-rich waste material was used to increase Mg^{2+} concentration. A very small amount of this magnesium source addition can reach the equal molar ratio, since magnesium concentration in this material was extremely high. Na^+ and K^+ concentrations were also high compared to Fe^{2+} and Ca^{2+} shown in Table 3.3. However, Fe^{2+} was only 4.87mg/L. Therefore, Na^+ , K^+ and Ca^{2+} were calculated to input along with Mg^{2+} addition.

The concentrations of Mg^{2+} , NH_4^+ and PO_4^{3-} were introduced to a Visual MINTEQ input file. Visual MINTEQ was operated at two different settings:

- Visual MINTEQ was run at the pH range from 6.0 to 14.0 at 25 °C to investigate the pH effect on ammonium and phosphate removal and the amount and purity of struvite formation.
- Visual MINTEQ was run at molar ratio from 1.0:1.0:1.0 to 2.0:1.0:1.0 at pH 9.5 and 25°C to investigate the optimum magnesium dosage for struvite formation and ammonium and phosphate removal.

The Visual MINTEQ model provides the concentrations of Mg^{2+} , NH_4^+ and PO_4^{3-} remaining in solution and the percentages of ammonium and phosphate removal for each specified conditions.. Also, the model output included the amount and types of solids formed. The results and discussion are presented in Chapter 6.

3.4 Chapter summary

This chapter presents the details of experiments including materials and experimental methods. The section of materials presents the components in the supernatants and Mg-rich waste material. The section of experimental methods has four parts which were designed to assess ammonia and phosphate removal and recovery as struvite formation. Ammonia and phosphate removal from synthetic solution using analytical MgCl_2 will be presented in Chapter 4. Struvite formation using the supernatant to maximize ammonia and phosphate removal and evaluate Mg-rich waste material feasibility will be presented in Chapter 5 and Chapter 7, respectively. The chemical equilibrium software Visual MINTEQ was used for modelling struvite formation using the components of supernatant and Mg-rich waste material, and the results obtained from running Visual MINTEQ will be presented in Chapter 6.

Chapter 4 Ammonia and Phosphate removal from synthetic solutions using analytical chemicals

4.1 Introduction

Chapter 3 identified the methodologies that were selected to study operating conditions and their influence on removal of ammonia and phosphorous and the associated struvite formation. This chapter reports on the experimental results. The images of crystals size were taken using ESEM. The ESEM data collected are analysed with aim of achieving the research objective posed in this thesis: assess struvite crystal growth and induction time. The research component has two parts that were detailed in the preceding methodology in Chapter 3. To access the main operating conditions influence on struvite formation, the mixing rate and the reaction time tests were carried out using a synthetic solution laboratory scale batch reactors.

4.2 Effect of operating conditions

4.2.1 Mixing rate

An optimal mixing rate is required to initiate and form a precipitant. To assess the effect of the mixing rate on struvite formation, 5 stirring speeds of 80, 100, 150, 200 and 250 rpm were investigated in this case of the experimental program. After each experiment, the residual concentrations of Mg^{2+} , ammonia and phosphate were determined.

Table 4.1: The residual concentrations of ammonia, phosphate and magnesium using different stirring speeds at pH 9.0 and the $Mg^{2+}:NH_4^+:PO_4^{3-}$ ratio of 1.0:1.0:1.0

Stirring speeds (rpm)	Ammonia (mg/L)	Phosphate (mg/L)	Magnesium (mg/L)
80	32.54	168.50	49.34
100	31.33	178.75	48.96
150	30.96	151.75	47.80
200	30.84	151.00	47.51
250	29.99	146.00	47.20

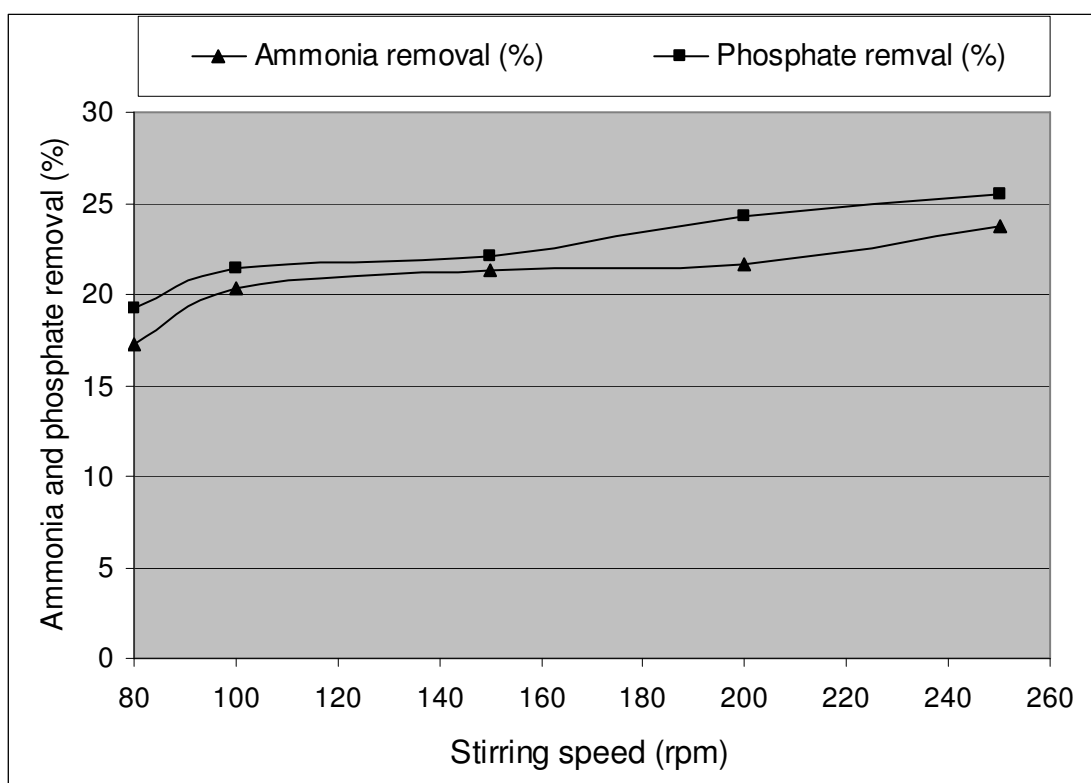


Figure 4.1: Ammonia and phosphate removal (%) using different stirring speeds at pH 9.0 and the $Mg^{2+}:NH_4^+:PO_4^{3-}$ ratio of 1.0:1.0:1.0

Table 4.1 shows the residual concentrations of ammonia-N, phosphate and magnesium using 5 different stirring speeds - 80 rpm, 100 rpm, 150 rpm, 200

rpm and 250 rpm, respectively. Figure 4.1 shows that the percentages of ammonia and phosphate removal using different stirring speed at same pH 9.0 and $Mg^{2+}:NH_4^+:PO_4^{3-}$ ratio of 1.0:1.0:1.0. From Figure 4.1, even the stirring speed increased more than double from 100 rpm to 250 rpm, only 3.40% ammonia and 4.47% phosphate increase in removal was observed. This means that the mixing rate may slightly improves the ammonia and phosphate removal. Increasing in the stirring speed is not necessary when it reaches a certain speed to consider economic benefit. Therefore, the stirring speed would be controlled at between 100 rpm and 150rpm. Low concentrations of the synthetic solution were employed in this part of the experimental program. The stirring speed of 100 rpm will be used for the experiments involving high concentrations of ammonia and phosphate (i.e. anaerobic digester supernatant).

4.2.2 Reaction time

Determination of the reaction time involved carrying out experiments at $Mg^{2+}:NH_4^+:PO_4^{3-}$ of 1.0:1.0:1.0, pH 9.0 and measuring the residual concentrations of magnesium, ammonia, phosphate after different time intervals. Residual concentrations after reaction times of 3- 25 minutes were investigated. A different reactor was used for each reaction time. The results obtained are shown in Figures 4.2 and 4.3. The images from ESEM for crystal size of precipitants are shown in Figure 4.4 (a)-(f).

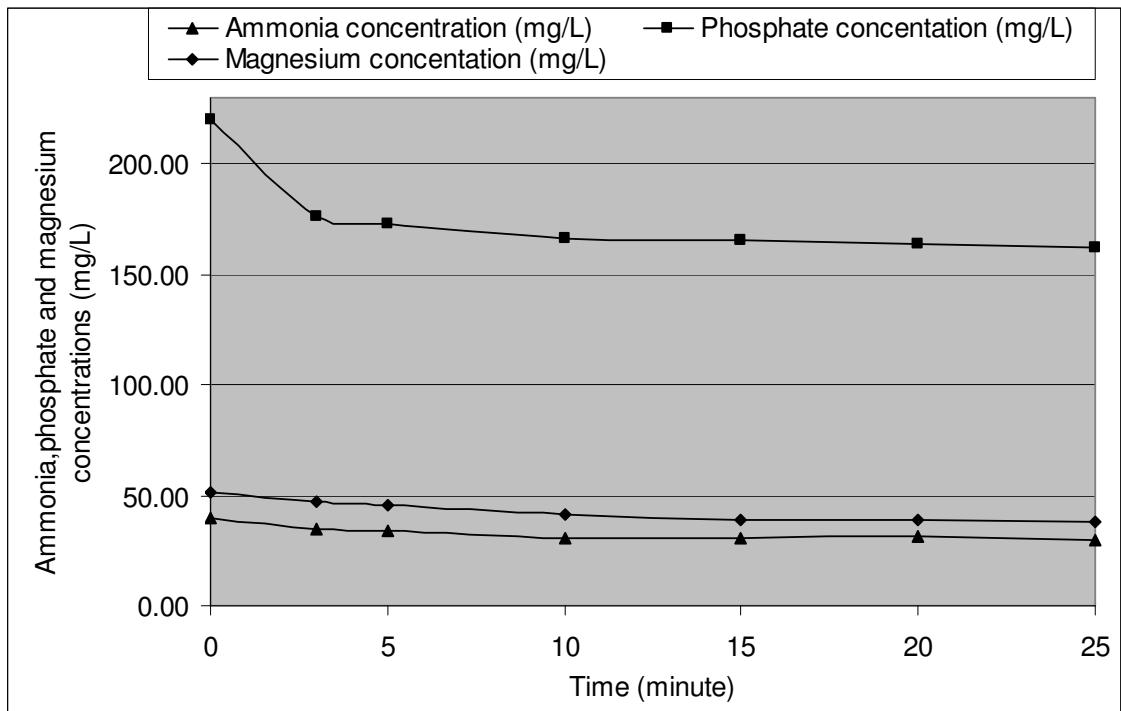


Figure 4.2: The residual concentrations of ammonia, phosphate and magnesium after different reaction times (0-25 minutes) at pH 9.0 and the $Mg^{2+}:NH_4^+:PO_4^{3-}$ ratio of 1.0:1.0:1.0

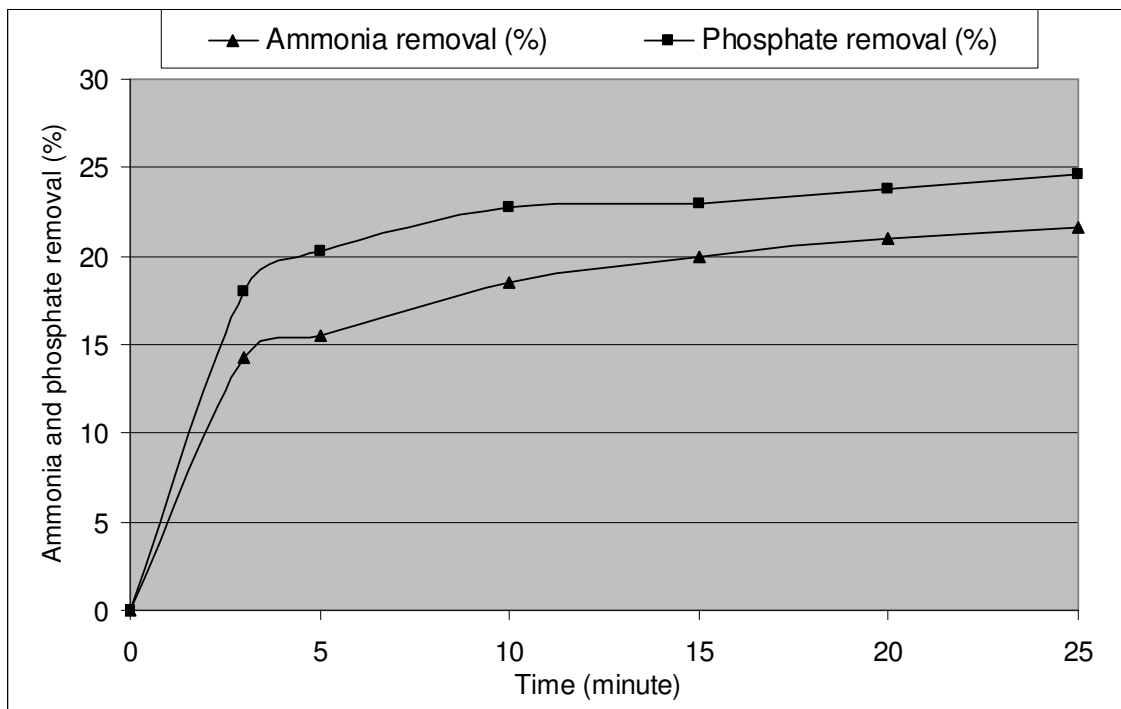
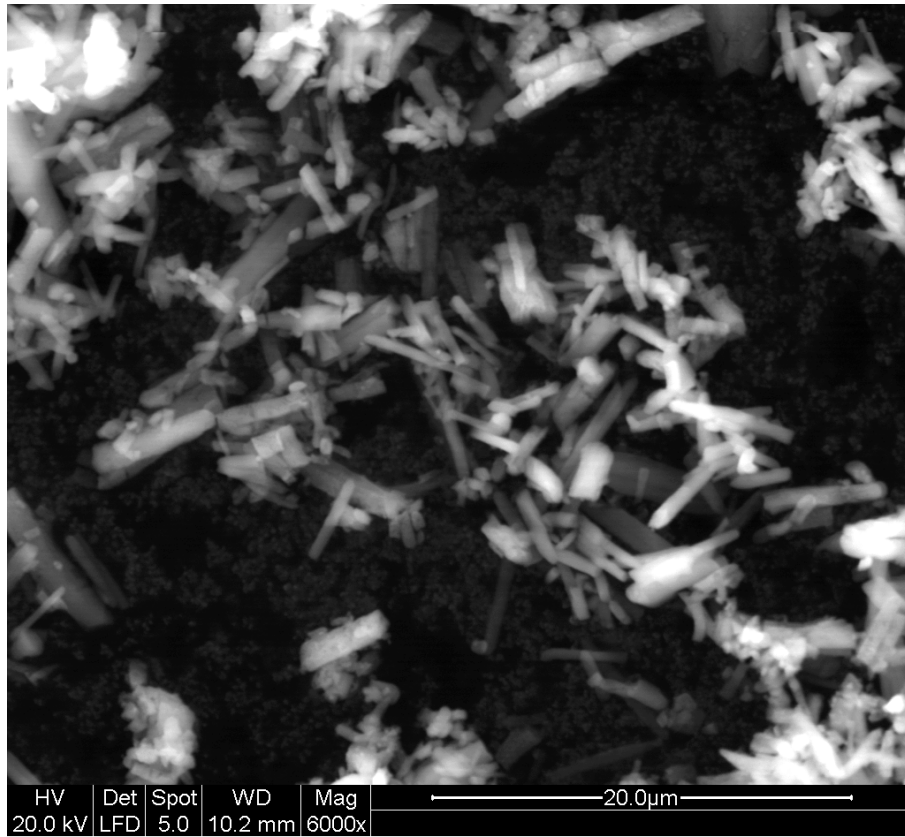


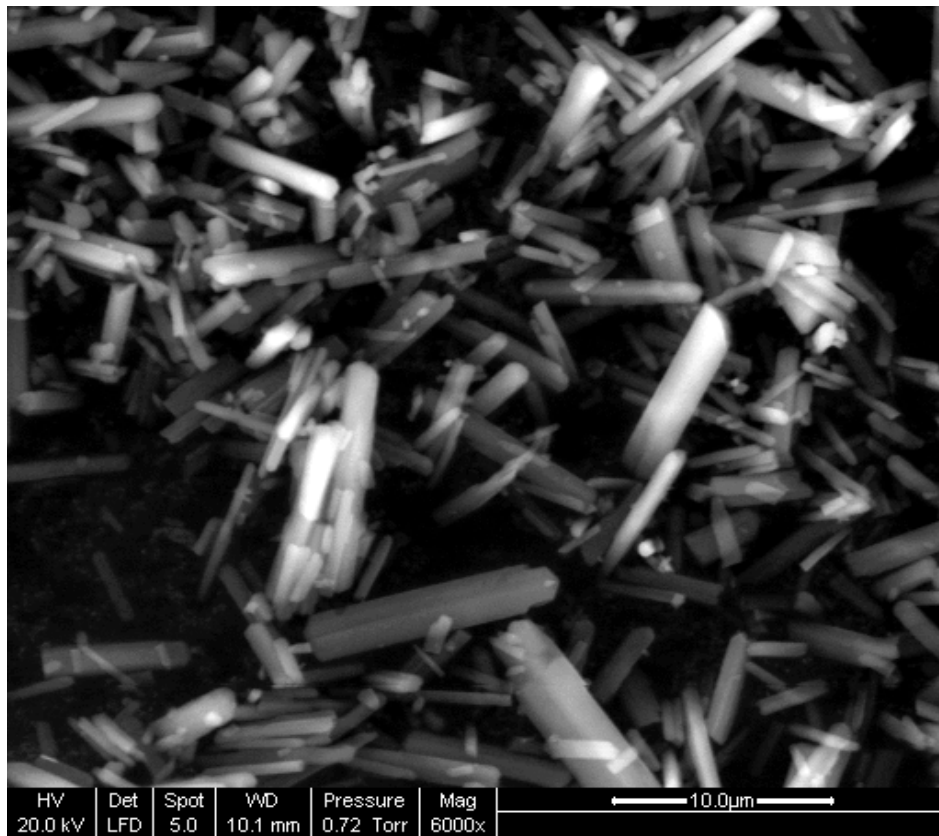
Figure 4.3: Ammonia and phosphate removal (%) after different reaction times (0-25 minutes) at pH 9.0 and the $Mg^{2+}:NH_4^+:PO_4^{3-}$ ratio of 1.0:1.0:1.0

Figure 4.2 shows the residual concentrations of ammonia, phosphate and magnesium after different reaction times between 0 and 25 minutes, and Figures 4.3 presents the percentages of ammonia and phosphate removal based on the residual ion concentrations after reaction. The percentages of ammonia and phosphate removal were significant between 0 and 3 minutes. This indicates that nucleation occur at a relatively short time. It is observed that 14.24% of ammonia and 18.01% of phosphate removal in 3 minutes. When the reaction time was more than 5 minutes, the percentages of ammonia and phosphate removal increased slightly, especially for reactions times longer than 10 minutes. Only 3.12% and 1.80% increase in ammonia and phosphate removal were observed with the increase in reaction time from 10 to 25 minutes (Figure 4.3). It can be seen that only a very small amount of ammonia and phosphate removal increased using longer reaction time, 10 minutes to 25 minutes.

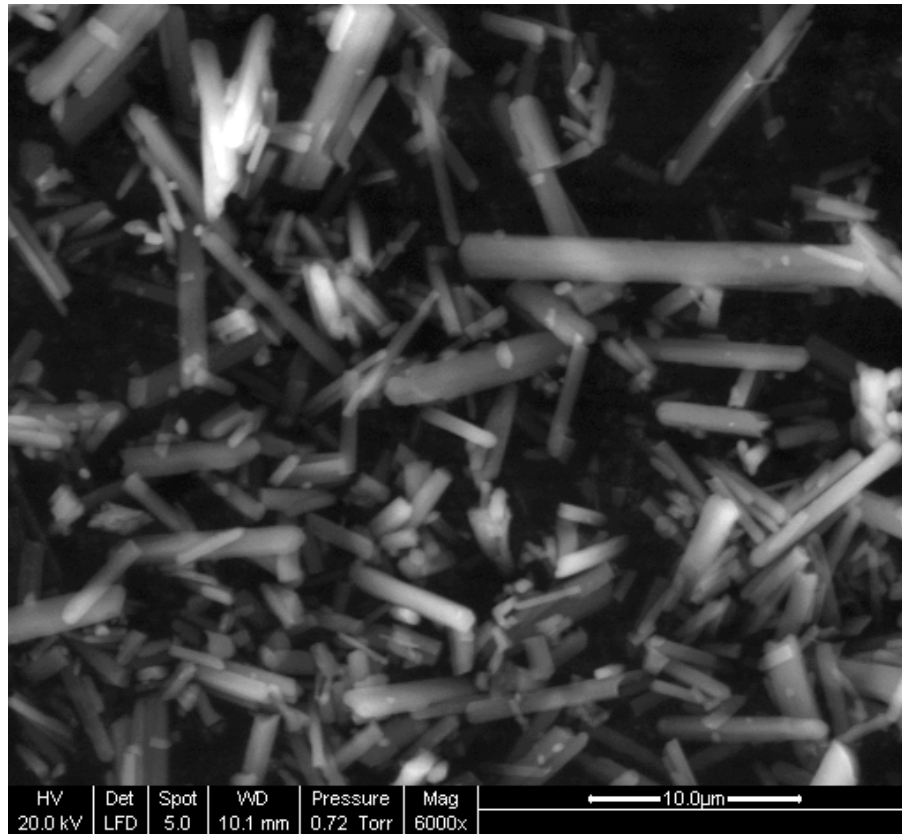
Huang *et al.* (2006) studied reaction time and reported that it depends on the struvite crystal nucleation rate and growth rate, which are affected by the surface diffusion, the saturation level of the solution and the mass transfer efficiency. The crystal needs sufficient time in the reactor to grow and aggregate to the desired size, provided that other operational conditions are maintained. Therefore, a finite reaction time is required for struvite crystal formation. However, it is not necessary to use longer times to form struvite crystal. The longer reaction time did not achieve a better removal effect.



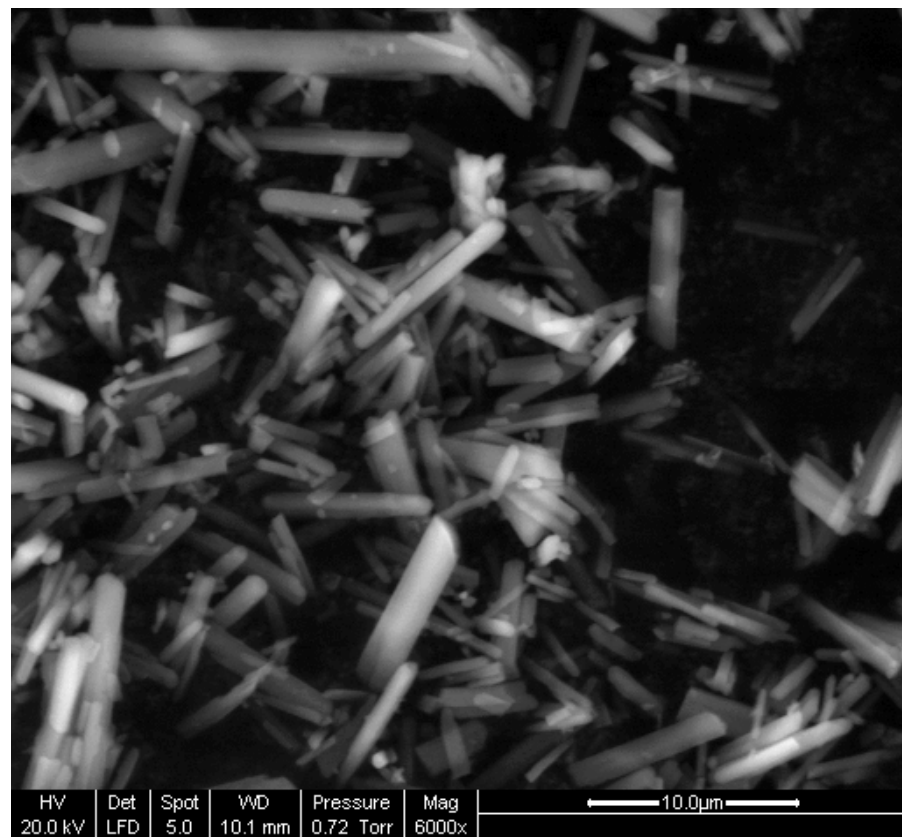
(a)



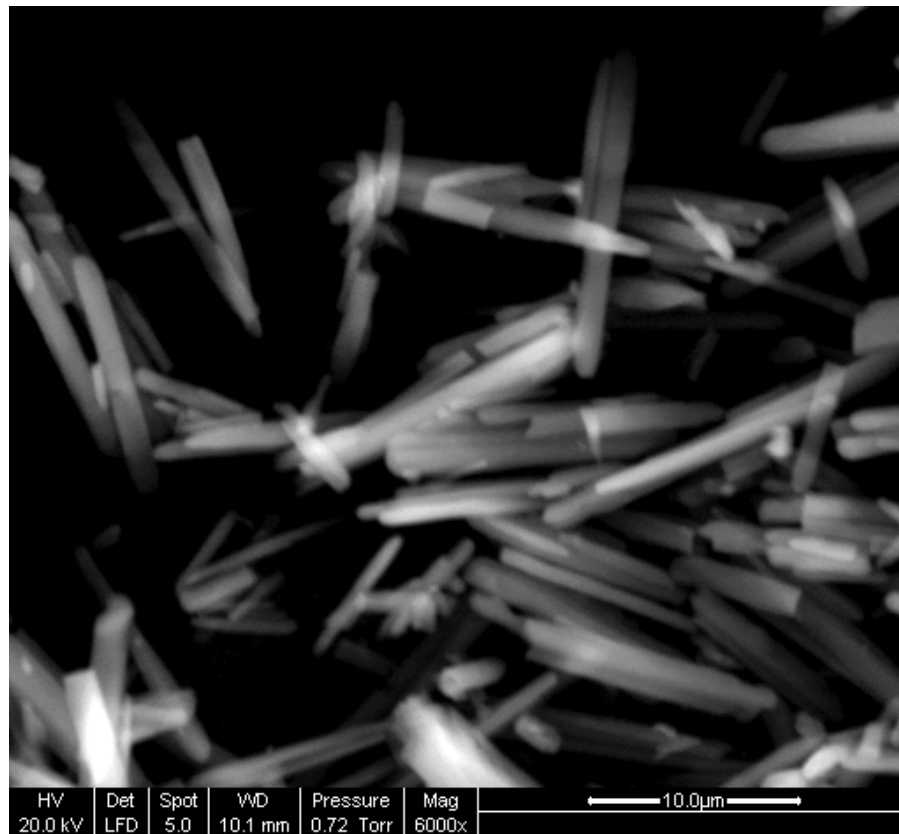
(b)



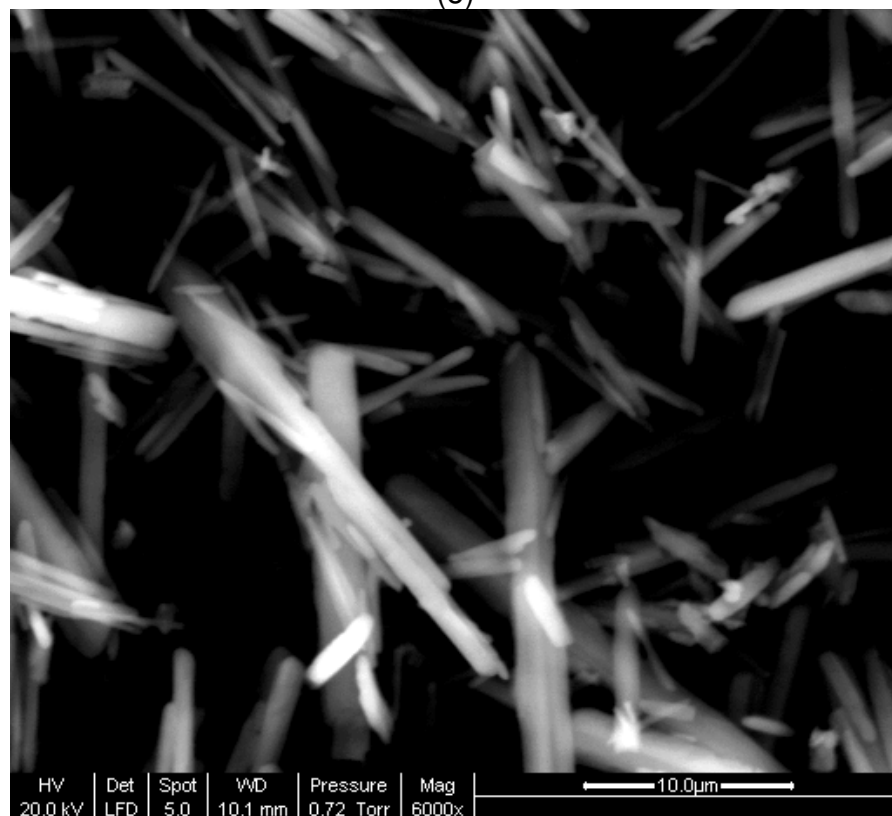
(c)



(d)



(e)



(f)

Figure 4.4(a)-(f): Environmental Scanning electron microscope (ESEM) images of crystals size using (a) 3 minutes, (b) 5 minutes, (c) 10 minutes, (d) 15 minutes, (e) 20 minutes and (f) 25 minutes of the reaction time

Figure 4.4 (a)-(e) shows the images of crystals size after 5, 10, 15, 20 and 25 minutes. The crystal size of particles after 5 minutes (Figure 4.3-(b)) was uniform. Most crystals size after 5 minutes were smaller compared to the crystals after 25 minutes (Figure 4.3-(e)). When the reaction time increased from 5 to 15 minutes, more large particles were formed, but there are still small ones crystals present. The crystal size was uniform (Figure 4.4-(d) and (e)) for the reaction times of 20 and 25 minutes, and there were small particles present. The crystal size was about 10 μm . Stratful *et al.* (2001) studied the reaction time effect on struvite formation in a waste water rich in nutrients. They showed the crystal size at 1 minute, 60 minutes and 180 minutes. They reported that the crystal size grew from 0.1mm to 3mm within 180 minutes. However, reaction time increase had a negligible effect on phosphate removal. In the present study, it was observed that reaction time has little effect on ammonia and phosphate removal, after the initial 10 minutes. Also it was observed that the crystal size changed slightly after 15 minutes, using synthetic solution.

Reaction time was controlled at a designated time to ensure ammonia and phosphate removal and crystal growth, as the longer reaction time was not effective. It is better to use shorter times for further experiments as this has a positive economic outcome.

4.3 Determination of induction time

This part of the study was to determine pH changes with time between 0 to 30 minutes for ammonia and phosphate removal both from the synthetic solution and anaerobic digester supernatant, respectively. Initial experiments at pH 9.0

used changes in solution pH to indicate the start and rate of struvite precipitation. The pH variations during the experiments are shown in Figures 4.5 and 4.6.

The interval between pH adjustment and the first pH change is defined as the induction time. From Figure 4.5, the pH remained unchanged until the induction period. Induction times estimated from pH graphs for an initial pH 9.0 were less than 1.5 minutes. Determination of induction time using the supernatant with Mg-rich waste material showed that the pH began to change at less than 0.5 minutes (Figure 4.6). After several minutes, there was no significant pH change for both of experiments.

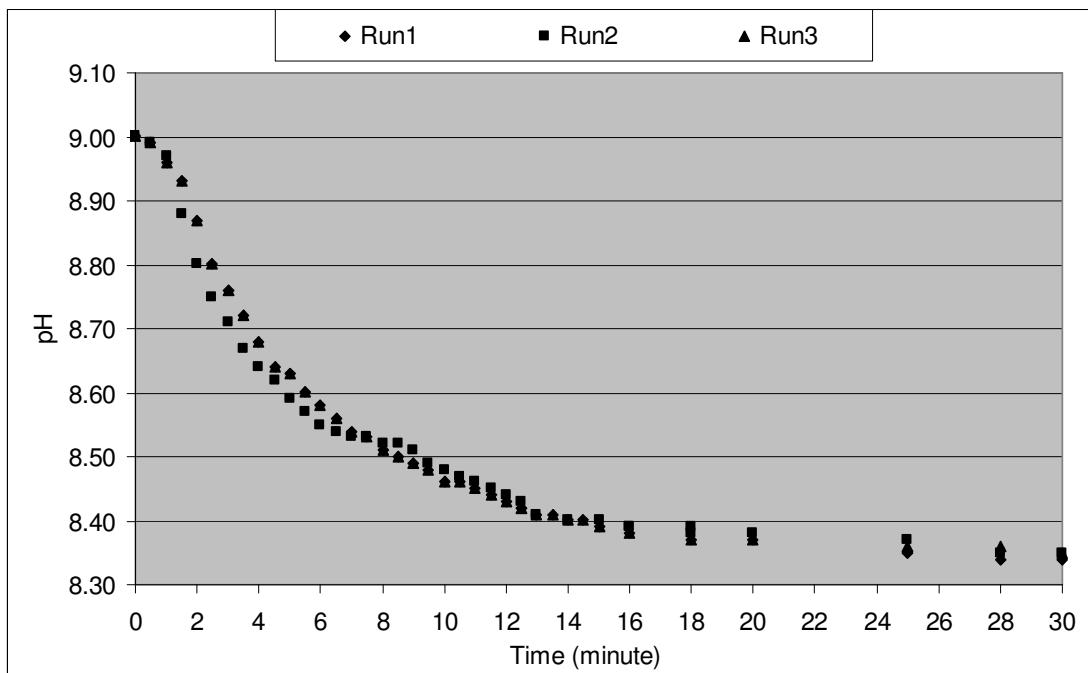


Figure 4.5: Change in pH over 30 minutes reaction time for the synthetic solution

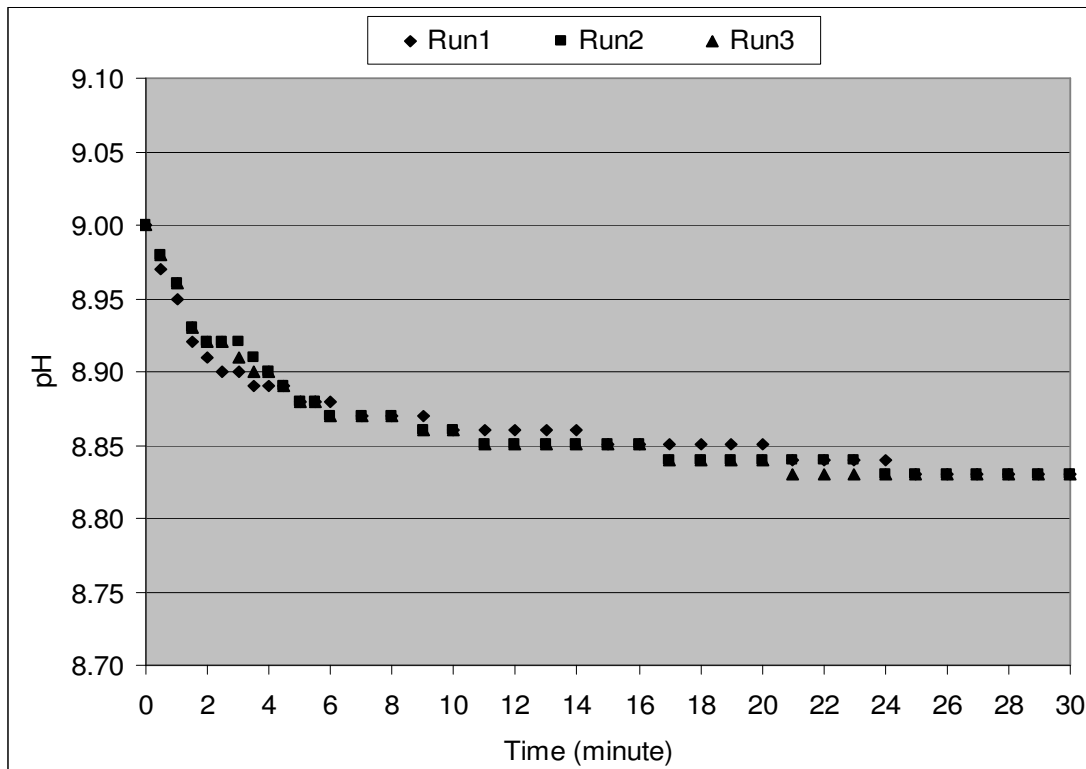


Figure 4.6: Change in pH level over 30 minutes for anaerobic digester supernatant

Comparing induction time determination from previous studies showed that induction time varies with reaction conditions such as, temperature and initial concentrations. Le Corre *et al.* (2007) studied the kinetics of struvite formation at laboratory scale in synthetic solutions. They reported that pH measurement can be used for the prediction of kinetics of struvite formation, and the higher concentrations leading to shorter induction time. They showed a similar trend using magnesium concentrations from 1.20×10^{-3} mol/L to 2.30×10^{-3} mol/L, and the induction time decreased from 5 minutes to less than 0.5 minute. Bouropoulos and Koutsoukos (2000) also studied induction time and reported that induction time decreased from 125 minutes to 6 minutes using magnesium concentrations from 2.75×10^{-3} mol/L to 4.00×10^{-3} mol/L. These two research work used synthetic solutions for induction time determination. In the present study, the concentration of magnesium in the synthetic solution was 4.50×10^{-3}

mol/L. Magnesium concentration was adjusted to 55.40×10^{-3} mol/L to reach the equal $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ molar of 1.0:1.0:1.0 ratio. Induction time is different because of the variation in solution and reaction conditions. It is noted that final pH values after reaction for the synthetic solution and the anaerobic digester supernatant are different. The pH dropped from 9 to 8.33 for the synthetic solution and from 9 to 8.83 for the anaerobic digester supernatant. This is most likely due to the characteristics of the supernatant including alkalinity and other buffering compounds (Tables 3.1 and 3.2).

4.4 Chapter summary

This chapter reports the reaction time and the mixing rate effect on struvite formation using a synthetic solution. Ammonia and phosphate removal were tested at different conditions. Crystal size growth also was analysed for different reaction times. The induction time was determined using a synthetic solution and anaerobic digester supernatant, respectively. The main results obtained were as follows.

- The experimental observations for the mixing rate test and reaction time test showed that increasing mixing rate and reaction time had a negligible effect on ammonia and phosphate removal. Based on crystal size comparison, the longer reaction time was not effective in improving crystal growth.
- The experimental determination of induction time showed that induction time is extremely short. It was 1.5 minutes for the synthetic solution and 0.5 minutes for anaerobic digester supernatant.

Chapter 5 Ammonia and Phosphate Removal from Anaerobic Digester Supernatant using analytical MgCl_2

5.1 Introduction

Chapter 4 determined the mixing rate and the reaction time effect on ammonia and phosphate removal from the synthetic solution. This chapter was to determine ammonia and phosphate removal from anaerobic digester supernatant. The aim of this chapter is to investigate the effect of the presence of various constituents, typically present in anaerobic digester supernatant, on the removal of ammonia and phosphate and the formation of struvite. As mentioned in Chapter 2, the pH and $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ molar ratios are the main factors for struvite precipitation. In order to achieve the above aims, the effect of pH and $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ ratio on the removal of ammonia and phosphate from the supernatant using analytical chemicals ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and NaH_2PO_4) were tested. Reaction time was also evaluated.

5.2 Effect of pH

To investigate the effect of pH on ammonia and phosphate removal and recovery from the supernatant, the residual concentrations of ammonia and phosphate were determined after each experiment. Removal of ammonia and phosphate was calculated based on the change between the initial concentration and the residual concentration. Experiments were carried out with a reaction time of 25 minutes at the pH range of 8.0 to 10.5 and an equal ratio ($\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}=1.0:1.0:1.0$). Based on the experimental results, the optimum

pH for struvite formation was identified. Figures 5.1 and 5.2 present the residual concentration and removal of ammonia and phosphate, respectively, at a pH range from 8.0 to 10.5. Table 5.1 shows the percentages of ammonia and phosphate removal and the amount of precipitates at this range of pH.

Table 5.1: Ammonia and phosphate removal and the amount of precipitates

pH	Ammonia removal (%)	Phosphate removal (%)	Precipitates (g)
8.0	76.70	79.15	1.5801
8.5	78.14	79.25	1.7155
9.0	87.79	88.95	2.2725
9.5	88.56	84.10	2.5132
10.0	87.29	69.66	3.1260
10.5	86.20	65.78	3.3040

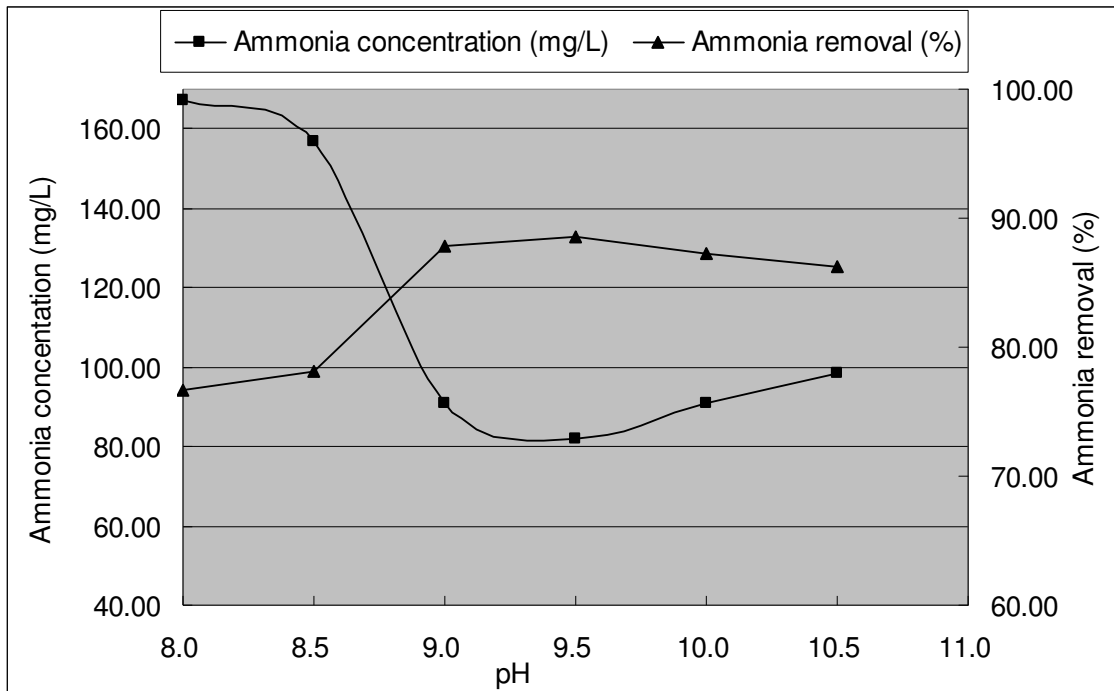


Figure 5.1: Ammonia residual concentration and removal at a pH range of 8.0 to 10.5 and the $Mg^{2+}:NH_4^+:PO_4^{3-}$ ratio of 1.0:1.0:1.0.

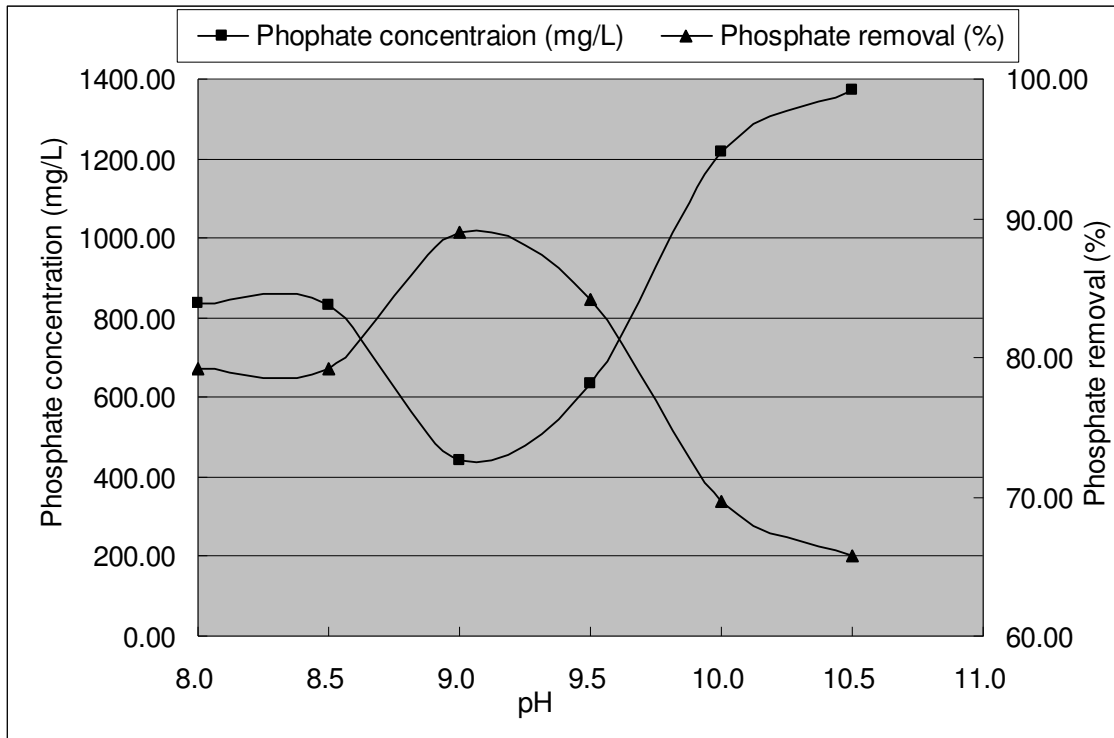


Figure 5.2: Phosphate residual concentration and removal at a pH range of 8.0 to 10.5 and the $Mg^{2+}:NH_4^+:PO_4^{3-}$ ratio of 1.0:1.0:1.0

As discussed in Chapter 2, the pH of solution affects the solubility of struvite (Snoeyink and Jenkins, 1980). For example, experiments in this part were carried out at the same temperature, stirring speed and molar ratio of $Mg^{2+}:NH_4^+:PO_4^{3-}$. Ammonia and phosphate removal were only affected by the pH of the solution. As shown in Figures 5.2 and 5.1, both ammonia and phosphate concentrations varied with the increasing pH. The maximum ammonia and phosphate removal occurred at a pH of 9.5 and 9.0, respectively. The removal of ammonia and phosphate achieved were 87.79% and 88.95%, respectively at pH 9.0, and 88.56% of ammonia and 84.10% of phosphate was removed at pH 9.5. The pH of 9.0 - 9.5 can be considered as the optimum pH range for ammonia and phosphate removal from the anaerobic digestion supernatant. It is also observed that increasing the pH from 8 to 10.5 resulted in 10% increase in ammonia removal and 14% drop in phosphate removal

decreased by 14%, yet the amount of precipitate doubled from 1.508g to 3.304g. This could be explained in terms of formation of more ammonia-based compared to phosphate-based precipitates at these conditions..

The optimum pH observed in present study is in agreement with optimum pH ranges in the published literature. The researchers suggested that the optimum pH for struvite formation range from 8.5 to 9.5 as shown in Table 2.1 (page 18). Booker *et al.* (1999) reported that concentrations of nitrogen and phosphorus changed with increasing pH, and that optimum pH for struvite precipitation is from 9.0 to 9.4. Nelson *et al.* (2003) found that the pH for maximum phosphate recovery was from 8.90 to 9.25 for two effluents from an anaerobic swine lagoon.

5.3 Effect of reaction time

This section assesses ammonia and phosphate removal for different reaction times (5, 10, 15, 25, 40, and 60 minutes) at pH 9.0 and equal molar ratio ($\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ 1.0:1.0:1.0). Based on the experimental results, the optimum reaction time for struvite formation was identified. This was followed by measuring the residual concentrations of ammonia and phosphate, and removal of ammonia and phosphate removal. Figures 5.3 and 5.4 show the experimental results.

Table 5.2: Ammonia and phosphate removal and the amount of precipitates using different reaction time

Time (minutes)	Ammonia removal (%)	Phosphate removal (%)	Precipitates (g)
0	0.00	0.00	0.0000
5	72.88	82.50	1.7519
10	81.78	82.97	1.8042
15	84.66	84.58	1.9607
25	87.29	88.08	2.1810
40	87.72	89.19	2.2766
60	87.97	89.97	2.3022

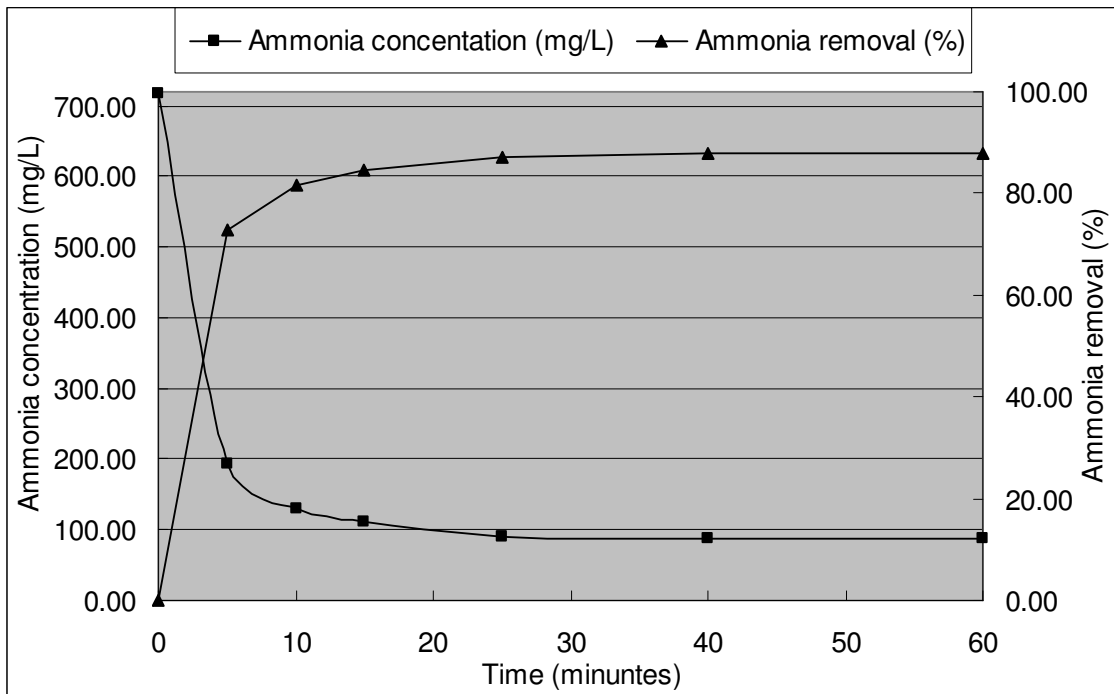


Figure 5.3: Ammonia residual concentration and removal using different reaction times at pH 9.0 and the $Mg^{2+}: NH_4^+: PO_4^{3-}$ ratio of 1.0:1.0:1.0

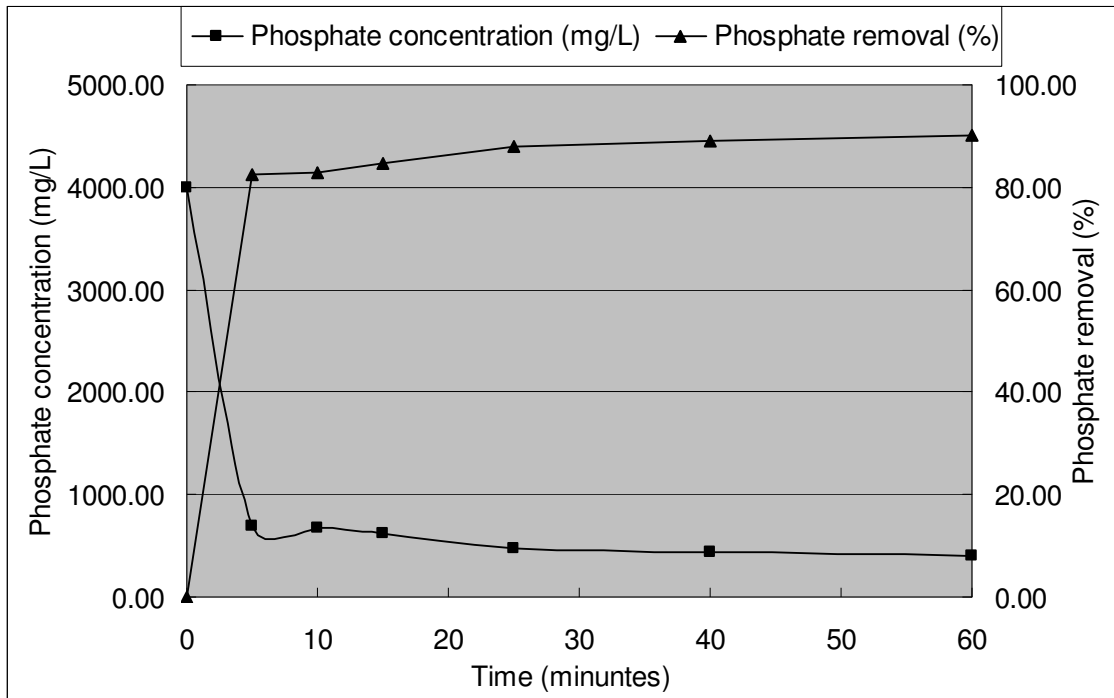


Figure 5.4: Phosphate residual concentration and removal using different reaction times at pH9.0 and the $Mg^{2+}:NH_4^+:PO_4^{3-}$ ratio of 1.0:1.0:1.0

As seen in Figures 5.3 and 5.4, both ammonia and phosphate concentrations dropped significantly within 5 minutes, whereas changed slightly for reaction times longer than 10 minutes. The residual ammonia concentrations were 130.54 mg/L after 10 minutes and 86.21 mg/L after 60 minutes, respectively (Figure 5.3). The residual phosphate concentrations were 681.75 mg/L after 10 minutes and 401.50 mg/L after 60 minutes (Figure 5.4). The removal of ammonia and phosphate were 81.78% and 82.97% during the first 10 minutes. There was little difference in ammonia and phosphate removal between 10 minutes and 60 minutes. Ammonia removal was only 6.45% higher, and phosphate removal was only 7.07% higher.

To conserve the mixing rate and processing time, 10 minutes reaction time was applied for struvite precipitation from the supernatant. This was in agreement

with the result reported by Lee *et al.* (2003). They reported that struvite formation reacted rapidly and was complete within 10 minutes. A reaction time of 10 minutes for struvite formation was also applied by Burns *et al.* (2003) and Celen (2006), who tested the reaction time for struvite formation from swine manure slurries. Other researchers also studied ammonia and phosphate removal and recovery using different reaction times. Stratful *et al.* (2001) reported that there was only 4% more PO_4^{3-} ions being removed between 1 minute and 180 minutes, and the reaction time did not have a significant effect on the struvite product. Booker *et al.* (1999) found that the reaction was completed within a few of minutes.

5.4 Effect of molar ratios

Initial Mg^{2+} , ammonia and phosphate concentrations in the supernatant from anaerobic digester were 35.67 mg/L, 319.00 mg/L and 731.85 mg/L, respectively. The ammonia concentration was much higher than Mg^{2+} and PO_4^{3-} concentrations. Therefore, magnesium and phosphate sources had to be added in all experimental runs to force struvite formation, and the concentration of ammonia was not adjusted. The experimental design allowed observation of the effects of magnesium and phosphate sources dosage on ammonia and phosphate removal as struvite. Experiments were carried out at the same reaction time of 10 minutes and a pH of 9.5 according to previous results.

5.4.1 Effect of magnesium dosage

The concentration of Mg^{2+} was the lowest when compared to initial ammonia and PO_4^{3-} concentrations in the supernatant. The addition of Mg^{2+} is necessary to force struvite formation in all experimental runs. The concentration of Mg^{2+} was increased to increase the molar ratio of from 1.0:1.0:1.0 to 1.6:1.0:1.0. $NH_4^+ : PO_4^{3-}$ was kept at 1.0:1.0 for all experiments. Figures 5.5 and 5.6 present ammonia and phosphate residual concentrations and removal for molar ratios of $Mg^{2+}:NH_4^+:PO_4^{3-}$ at 1.0:1.0:1.0 to 1.6:1.0:1.0. Table 5.3 shows the percentages of ammonia and phosphate removal and the amount of precipitates for this molar ratio range.

Table 5.3: Ammonia and phosphate removal and the amount of precipitates for $Mg^{2+}:NH_4^+:PO_4^{3-}$ from 1.0:1.0:1.0 to 1.6:1.0:1.0

$Mg^{2+}:NH_4^+:PO_4^{3-}$	Ammonia removal (%)	Phosphate removal (%)	Precipitates (g)
1.0	85.23	96.73	1.7524
1.2	86.39	97.54	1.7781
1.3	88.20	97.54	1.7856
1.4	89.43	98.67	1.7960
1.6	90.71	98.53	1.8102

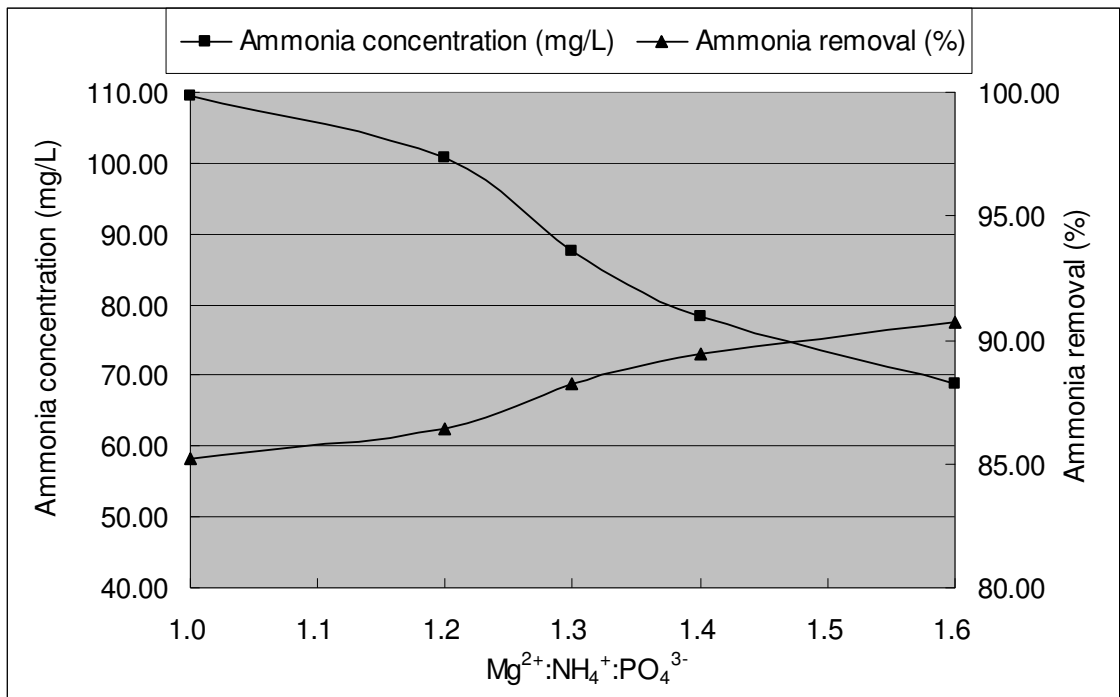


Figure 5.5: Ammonia residual concentration and removal for $Mg^{2+}:NH_4^+:PO_4^{3-}$ from 1.0:1.0:1.0 to 1.6:1.0:1.0 at pH 9.5

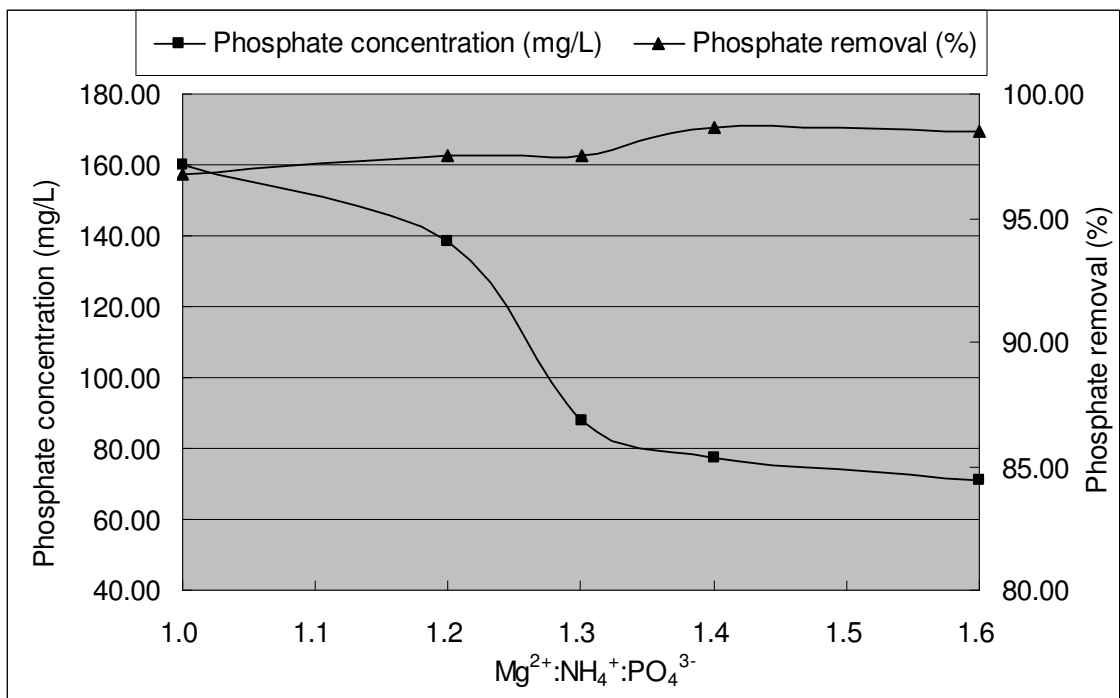


Figure 5.6: Phosphate residual concentration and removal for $Mg^{2+}:NH_4^+:PO_4^{3-}$ from 1.0:1.0:1.0 to 1.6:1.0:1.0 at pH 9.5

As seen in Figures 5.5 and 5.6, 85.23% of ammonia removal and 96.73% of phosphate removal were achieved at the $Mg^{2+}:NH_4^+:PO_4^{3-}$ ratio of 1.0:1.0:1.0, while 90.71% ammonia and 98.53% phosphate were removed at the $Mg^{2+}:NH_4^+:PO_4^{3-}$ ratio of 1.6:1.0:1.0. Only 5.48% and 1.80% increase in ammonia and phosphate removal for an increase in the $Mg^{2+}:NH_4^+:PO_4^{3-}$ molar ratio from 1.0:1.0:1.0 to 1.6:1.0:1.0. Therefore, Magnesium addition is required to force struvite precipitation, but it improved ammonia and phosphate removal slightly. Katsuura (1998) stated that the phosphate removal did not change when $Mg^{2+}:PO_4^{3-}$ molar ratio was more than 1.3:1.0 at pH 9.0. Nelson *et al.* (2003) also reported that the Mg^{2+} concentration addition in excess did not have a significant impact on the phosphorus removal. It also can be seen that phosphate removal was higher than ammonia removal at all ranges of molar ratios used. When magnesium dosage increased, the phosphate may combine with magnesium to form other magnesium phosphate species such as $Mg_3(PO_4)_2$, more other solids formation in precipitate can affect the amount and purity of struvite production.

Most researchers reported that the optimum $Mg^{2+}:PO_4^{3-}$ molar ratio for struvite formation was between 1.1:1.0 and 1.6:1.0 (Burns *et al.*, 2003, Lee *et al.*, 2003, Yoshino *et al.*, 2003). Magnesium dosage is added to reach the $Mg^{2+}:NH_4^+:PO_4^{3-}$ ratio of 1.0:1.0:1.0 and struvite is formed. However, this is the theoretical molar ratio. The presence of other ions in wastewater would impact struvite formation in practice. To consider the efficient and economic treatment for wastewater, the $Mg^{2+}:NH_4^+:PO_4^{3-}$ ratio of 1.2:1.0:1.0 is sufficient to remove and recover ammonia and phosphate from anaerobic digester supernatant.

Ammonia and phosphate removal as struvite formation from anaerobic digester supernatant can reach 86.39% and 97.54% respectively at an $Mg^{2+}:NH_4^+:PO_4^{3-}$ ratio of 1.2:1.0:1.0.

5.4.2 Effect of phosphate dosage

Struvite formed at the molar ratios of $PO_4^{3-}:NH_4^+:Mg^{2+}$ (1.25:1.0:1.0, 1.11:1.0:1.0, 1.0:1.0:1.0, 0.91:1.0:1.0, 0.83:1.0:1.0, and 0.77:1.0:1.0) was measured to investigate ammonia and phosphate removal for increased dosages of PO_4^{3-} . Figure 5.7 presents the residual concentrations of ammonia and ammonia removal at this range of $PO_4^{3-}:NH_4^+:Mg^{2+}$. The residual concentrations of phosphate and phosphate removal are shown in Figure 5.8. Table 5.4 shows the percentages of ammonia and phosphate removal and the amount of precipitates.

Table 5.4: Ammonia and phosphate removal and the amount of precipitates for $PO_4^{3-}:NH_4^+:Mg^{2+}$ from 0.77:1:1 to 1.25:1:1

$PO_4^{3-}:NH_4^+:Mg^{2+}$	Ammonia removal (%)	Phosphate removal (%)	Precipitates (g)
1.25	97.64	96.71	1.4129
1.11	92.65	97.01	1.2999
1.00	87.67	96.21	1.1697
0.91	82.31	98.03	1.1133
0.83	78.41	97.67	1.0248
0.77	73.26	97.60	0.9438

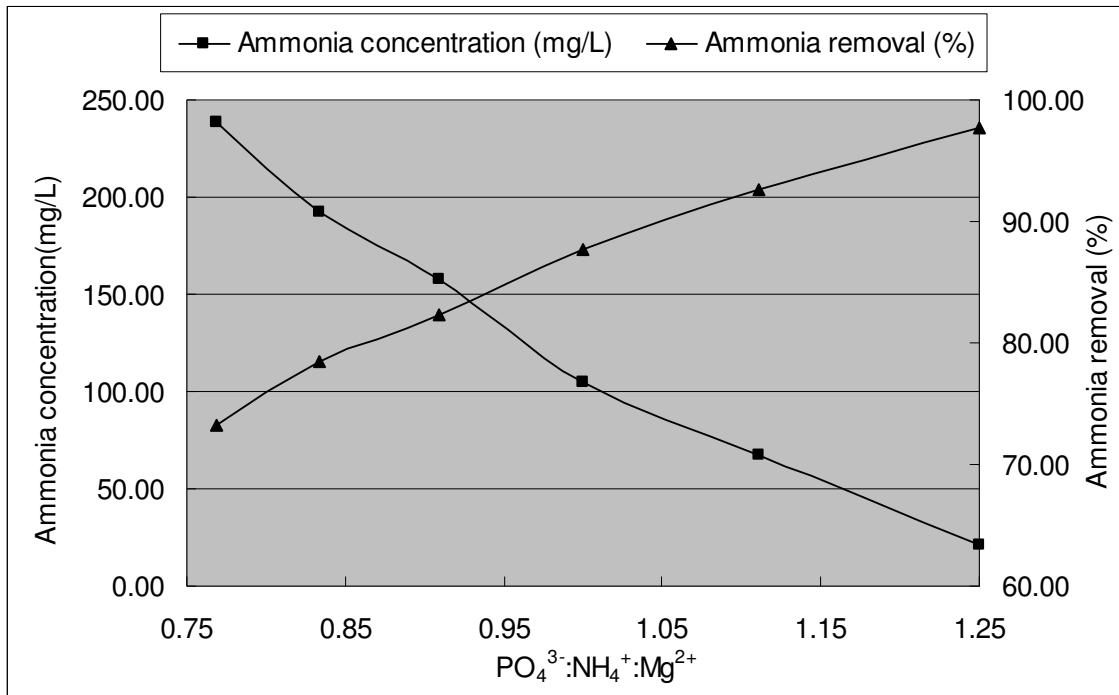


Figure 5.7: Ammonia residual concentration and removal for PO₄³⁻:NH₄⁺: Mg²⁺ from 0.77:1.0:1.0 to 1.25:1.0:1.0 at pH 9.5

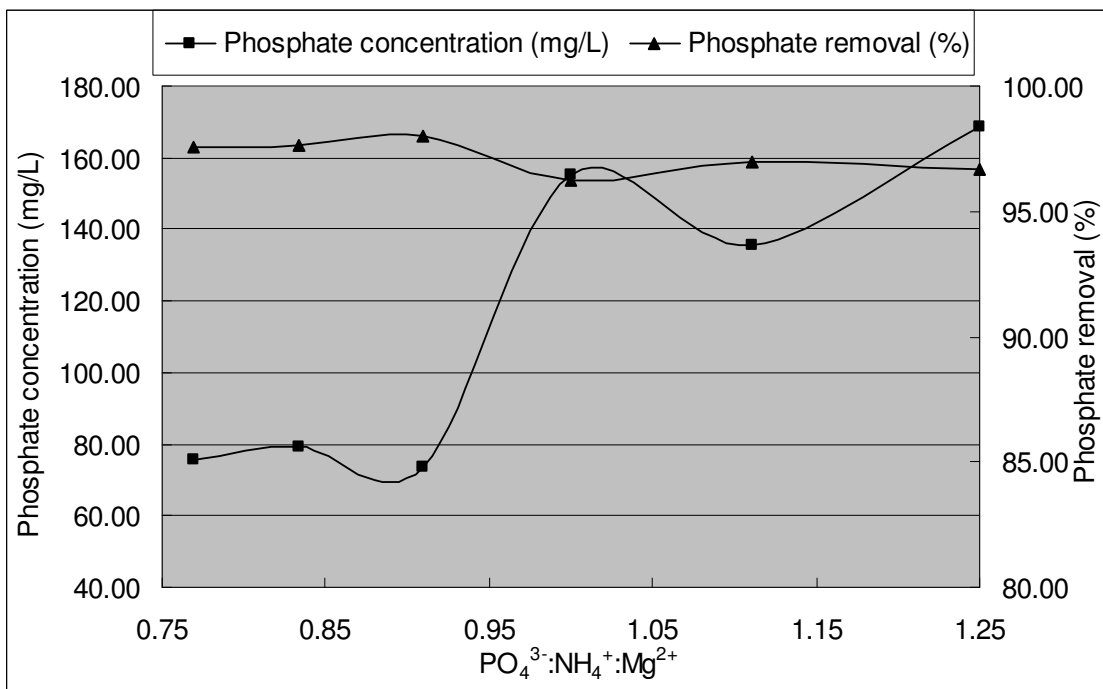


Figure 5.8: Phosphate residual concentration and removal for PO₄³⁻:NH₄⁺: Mg²⁺ from 0.77: 1.0:1.0 to 1.25:1.0:1.0 at pH 9.5

Ammonia removal increased gradually with the increase of $\text{PO}_4^{3-}:\text{NH}_4^+:\text{Mg}^{2+}$ (Figure 5.7). Using a 1.25:1.0:1.0 molar ratio of $\text{PO}_4^{3-}:\text{NH}_4^+:\text{Mg}^{2+}$, only 20.95 mg/L ammonia was left in the supernatant after reaction. The removal of ammonia reached 97.64%. This means that more ammonia removal was reached with the addition of phosphate. Phosphate removal remained at around 97.00% during this molar ratio range (Figure 5.8).

High ammonia removal was reached when more phosphate source was added to the solution. However, the residual concentration of phosphate increased with the increasing phosphate addition. The aim in present study is to remove ammonia as well as phosphate. Increasing phosphate dosage over the equal molar ratio is not efficient and effective for ammonia and phosphate removal from the supernatant.

5.5 Precipitates analysis

Precipitates collected from experiments were analysed with XRD to confirm as struvite under different reaction conditions. Figures 5.9 and 5.10 show the results of XRD analysis for precipitates using pH 9.0 and 9.5 at the $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ ratio of 1.0:1.0:1.0 compared with standard struvite. Both of them almost matched struvite standard. It indicates that almost all ammonia and phosphate was recovered as struvite precipitation from the supernatant at pH 9.0 and pH 9.5, and nearly pure struvite formed at these reaction conditions.

Figures 5.11, 5.12 and 5.13 present the results of XRD analysis compared with standard struvite for $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ ratio of 1.2:1.0:1.0, 1.3:1.0:1.0 and

1.6:1.0:1.0, respectively, at pH 9.5. The results of XRD analysis for precipitates collected at these reaction conditions almost matched standard struvite. Only trace amounts of other solids present in the precipitate. It was not possible to have an exact match with the patterns for possible solids in XRD database. The impurities that may be present in struvite precipitation were not identified in present study.

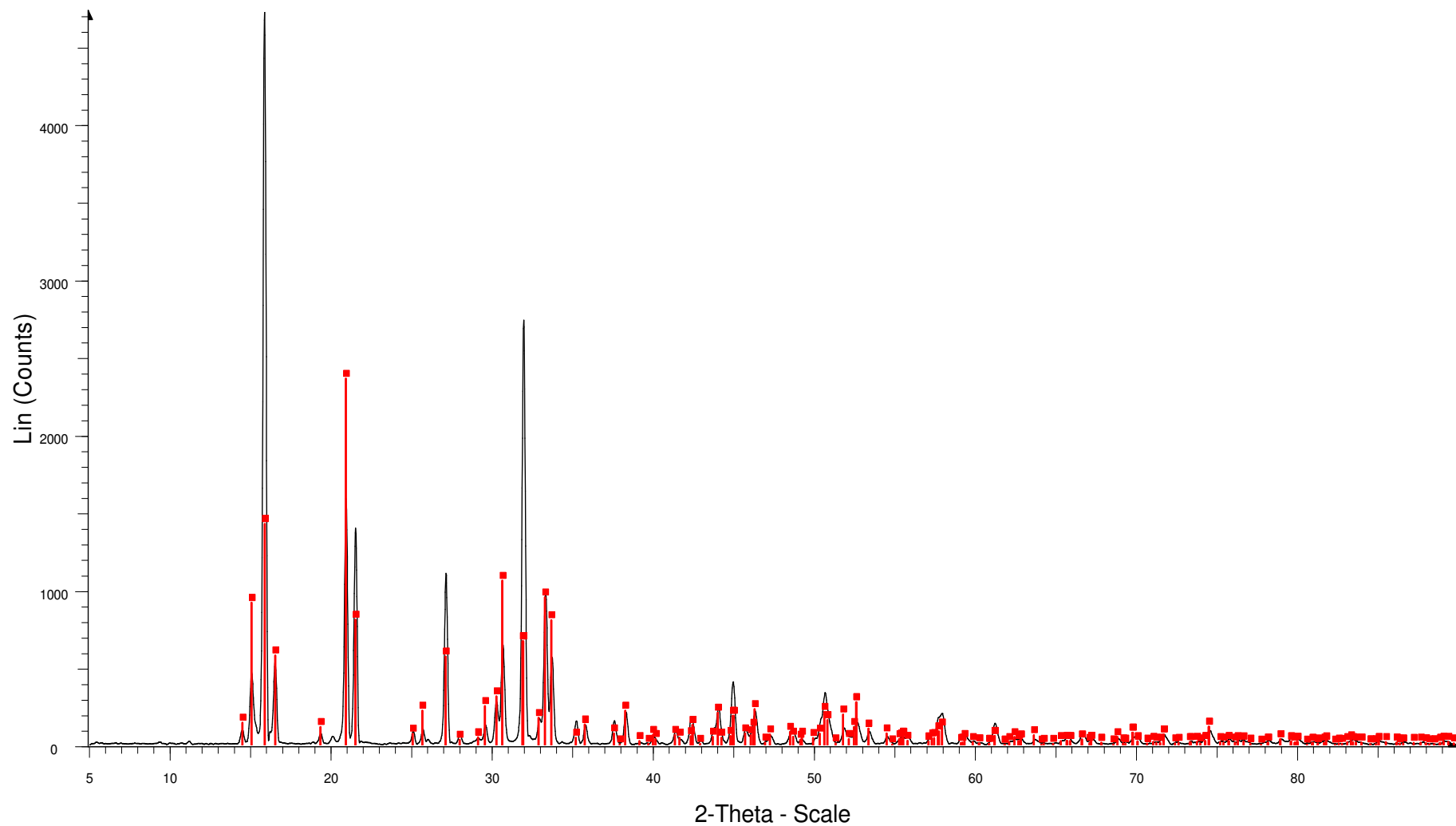


Figure 5.9: X-ray Diffraction Pattern for precipitate formed at pH 9.0, the $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ ratio of 1.0:1.0:1.0 compared with standard struvite pattern

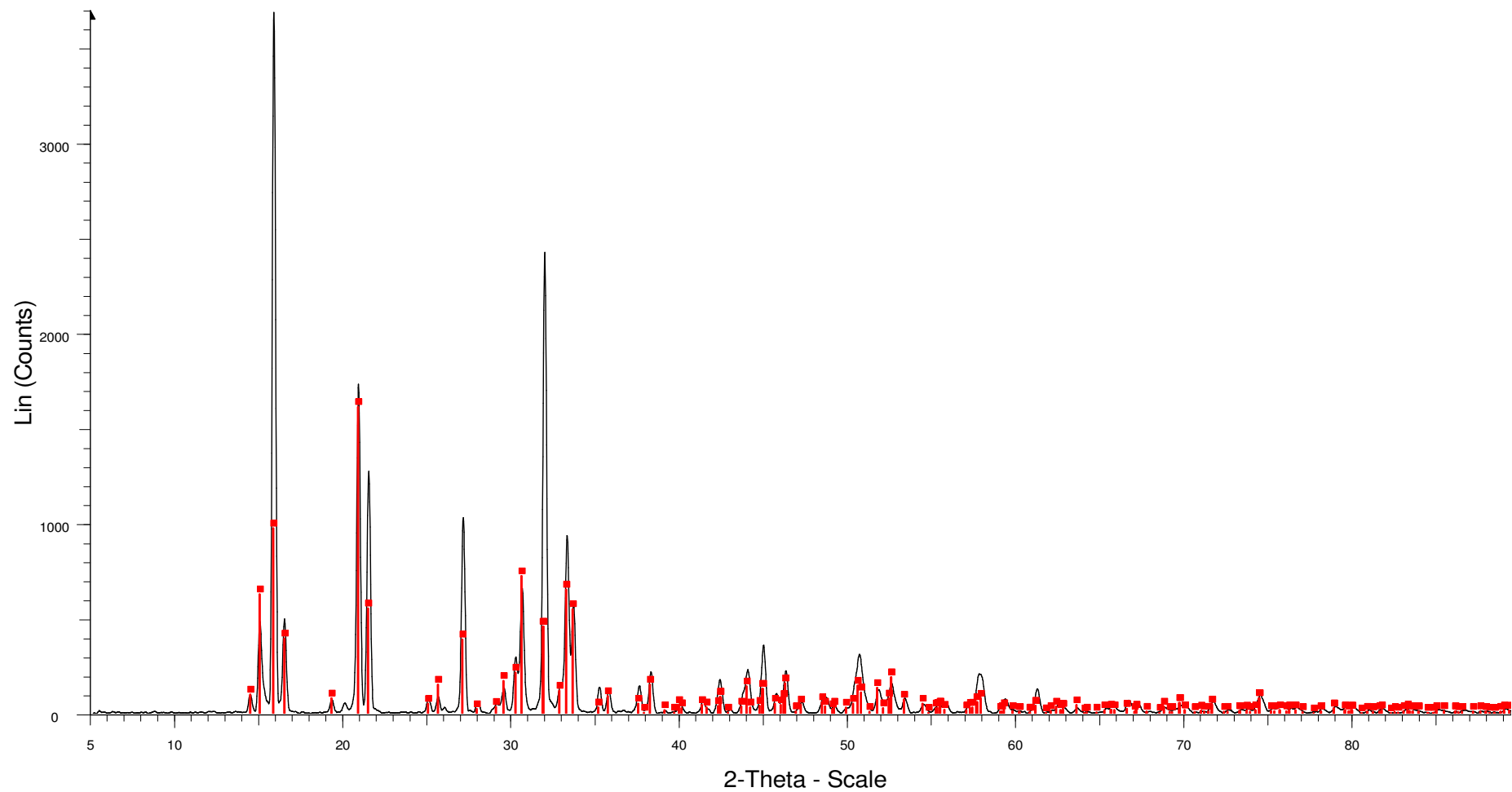


Figure 5.10: X-ray Diffraction Pattern for precipitate formed at pH 9.5, the $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ ratio of 1.0:1.0:1.0 compared with standard struvite pattern

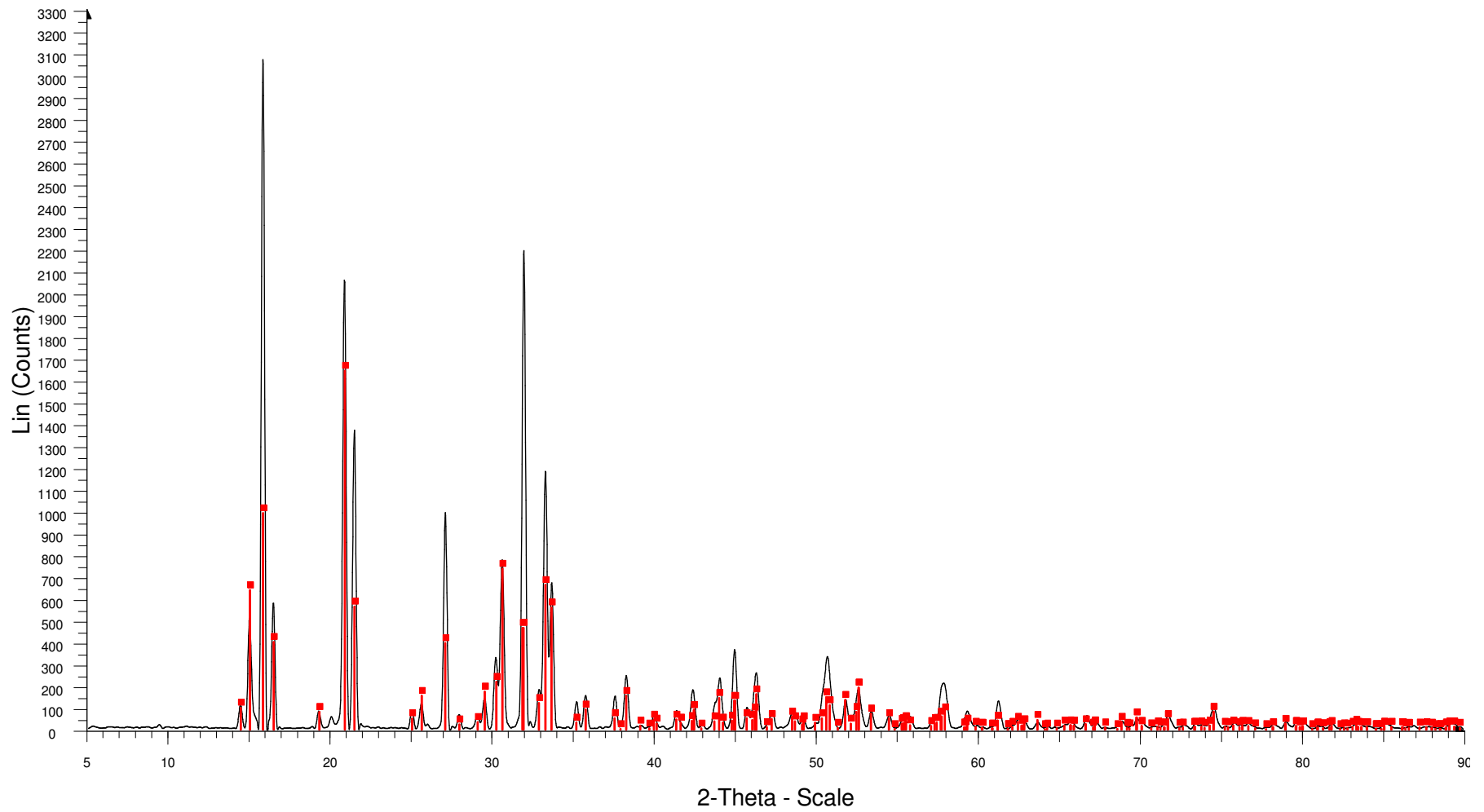


Figure 5.11: X-ray Diffraction Pattern for precipitate formed at pH 9.5, the $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ ratio of 1.2:1.0:1.0 compared with standard struvite pattern

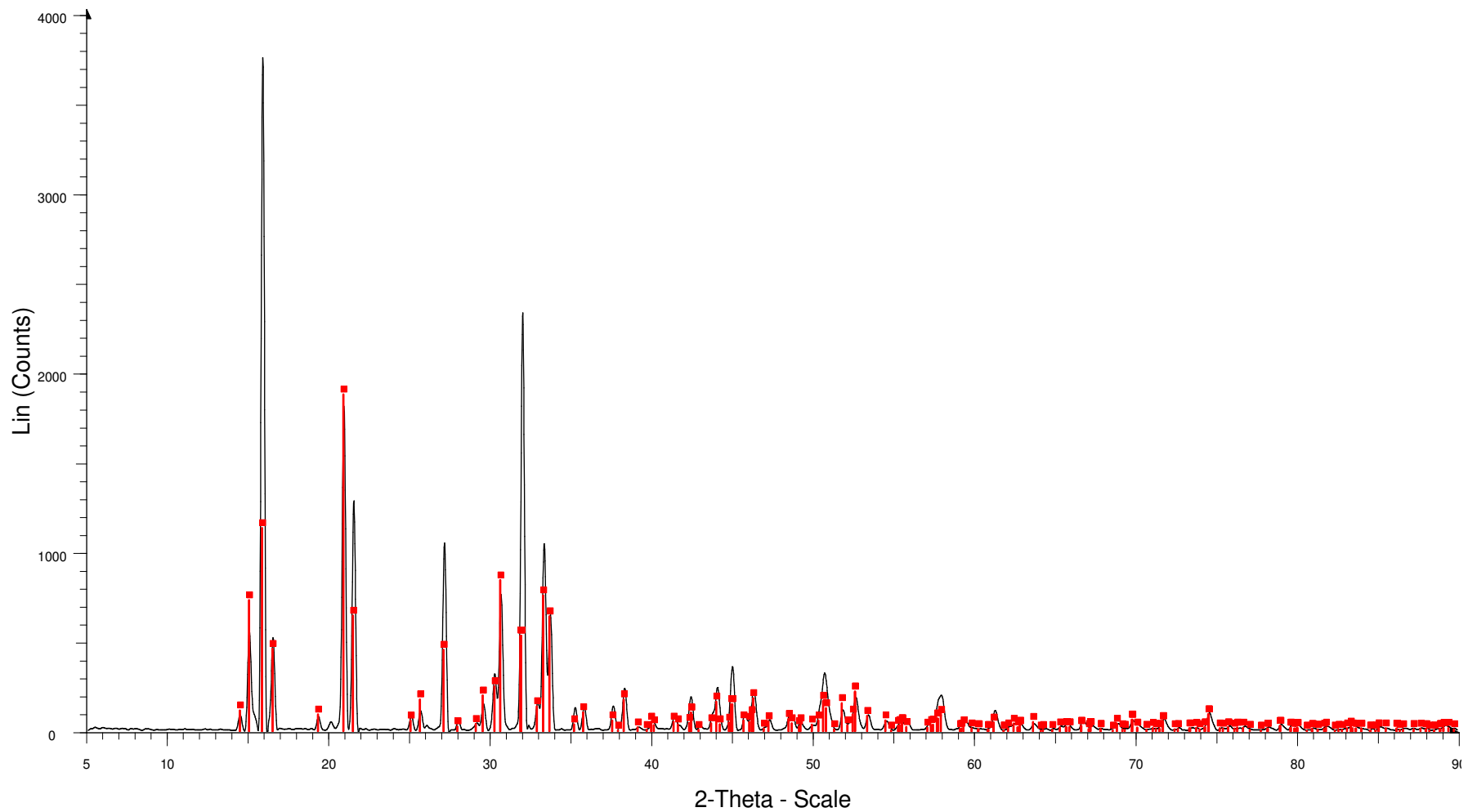


Figure 5.12: X-ray Diffraction Pattern for precipitate formed at pH 9.5, the $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ ratio of 1.3:1.0:1.0 compared with standard struvite pattern

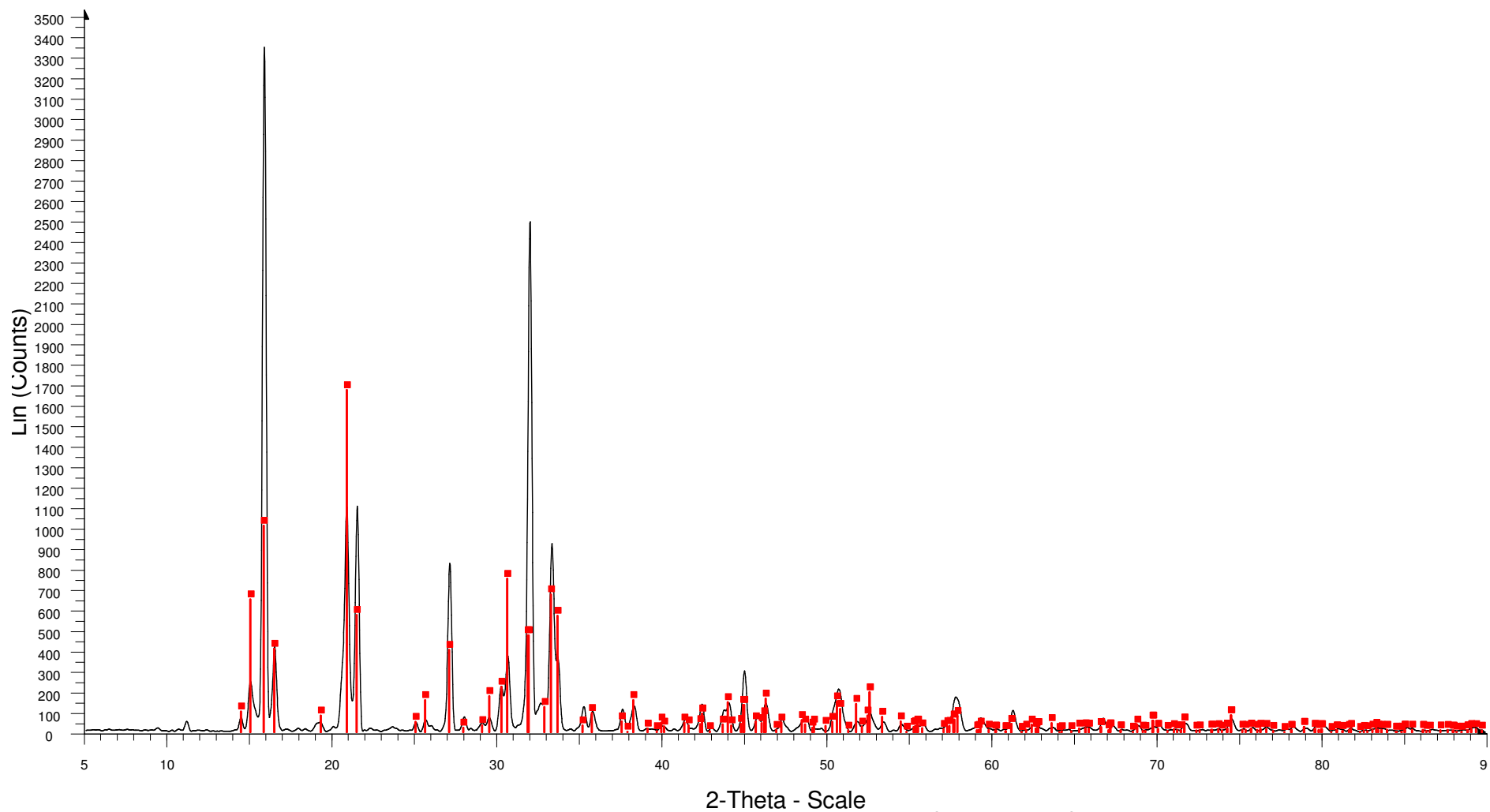


Figure 5.13: X-ray Diffraction Pattern for precipitate formed at pH 9.5, the $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ ratio of 1.6:1.0:1.0 compared with standard struvite pattern

5.6 Chapter summary

Chapter 5 showed the experimental results of struvite formation at different reaction conditions. The optimum reaction conditions (pH, the reaction time and molar ratio) for ammonia and phosphate removal and recovery as struvite from anaerobic digester supernatant were discussed. Analytical grade chemicals $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and NaH_2PO_4 were used as magnesium and phosphate sources, respectively. The following can be concluded:

- The increasing pH improved ammonia and phosphate removal. The optimum pH observed at pH between 9.0 and 9.5.
- Struvite formation occurred rapidly within 5 minutes. The removal of ammonia and phosphate increased slightly during the period 10-60 minutes. Therefore, the reaction time of 10 minutes was considered adequate for ammonia and phosphate removal as struvite from supernatant to save energy.
- The higher dosages of Mg^{2+} and PO_4^{3-} sources did not show additional ammonia and phosphate removal improvement. To save capital investment and maximise the removal of ammonia and phosphate, the $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ ratio of 1.2:1.0:1.0 was considered as the optimum molar ratio for ammonia and phosphate removal and recovery. Ammonia and phosphate removal can reach 86.39% and 97.54% respectively at the $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ ratio of 1.2:1.0:1.0 and pH 9.5.
- Precipitates analysis has shown that high pure struvite precipitations were achieved at pH 9.0 and 9.5 whilst the ratio of $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ would be at 1.0:1.0:1.0 and 1.2:1.0:1.0, respectively.

Chapter 6 Struvite Formation Prediction Using Chemical Equilibrium Visual MINTEQ Model

6.1 Introduction

Chapter 5 determined the ammonia and phosphate removal and recovery from anaerobic digester supernatant at different conditions. This Chapter utilises the Chemical Equilibrium model Visual MINTEQ to predict struvite formation. Several software products can be used for predicting struvite formation such as MINEQL+ and MINTEQA2 which has been used to model struvite precipitation in wastewater and to measure the pH effect on minimum struvite solubility (Buchanan *et al.*, 1994, Ohlinger *et al.*, 1998). MINTEQA2 was used by Miles and Ellis (2001) to model NH_4^+ removal from wastewater. Visual MINTEQ was used to design nutrients recovery for piggery effluent streams (Ali *et al.*, 2003). Celen *et al.* (2007) also employed Visual MINTEQ to maximize struvite formation from liquid swine.

The aim of this chapter was to predict conditions for optimum struvite precipitation potential using the chemical equilibrium model of Visual MINTEQ. Solids formation and ammonium and phosphate removal at different pH and different molar ratios were also discussed in this Chapter.

6.2 Modelling at different pH

The effect of pH on struvite formation investigated with Visual MINTEQ was discussed in this section. Details of this process were presented in Chapter 3. The initial concentrations of ammonium, phosphate and magnesium were

predicted as ions concentrations from Eastern Wastewater Plant (Table 3.2). Phosphate and magnesium concentrations were predicted to increase to reach the $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ ratio of 1.0:1.0:1.0 by adding Na_2HPO_4 and Mg-rich waste material. Visual MINTEQ was run at the pH range from 6.0 to 14.0 at 25 °C to investigate the residual ammonium, phosphate and magnesium concentrations in the output and their removal. The results are shown in Figures 6.1 and 6.2 and Table 6.1. The amount and type of solids formed are presented in Figure 6.3 and Table 6.2.

Table 6.1: Removal of ammonium, phosphate and magnesium at a pH range 6.0 to 14.0 predicted by Visual MINTEQ

pH	Ammonium (%)	Phosphate (%)	Magnesium (%)
6.0	0.00	82.58	83.68
6.5	57.23	88.08	89.25
7.0	86.53	90.53	91.73
8.0	95.57	95.33	96.59
8.5	96.80	96.55	97.83
9.0	97.42	97.17	98.47
9.5	97.62	97.37	98.67
10.0	97.40	97.28	98.64
10.5	94.91	96.79	99.15
11.0	91.39	91.16	99.80
11.5	72.09	71.90	99.95
12.5	0.00	0.00	100.00
13.0	0.00	0.00	100.00
14.0	0.00	0.00	100.00

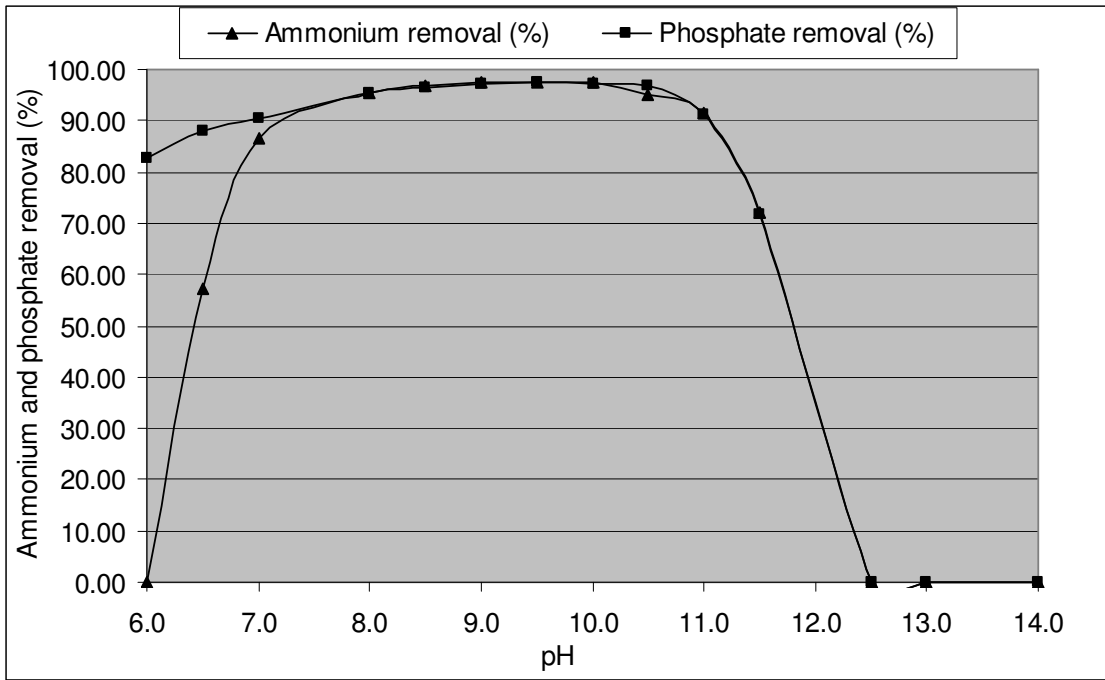


Figure 6.1: Ammonium and phosphate removal (%) predicted by Visual MINTEQ at the pH range from 6.0 to 14.0

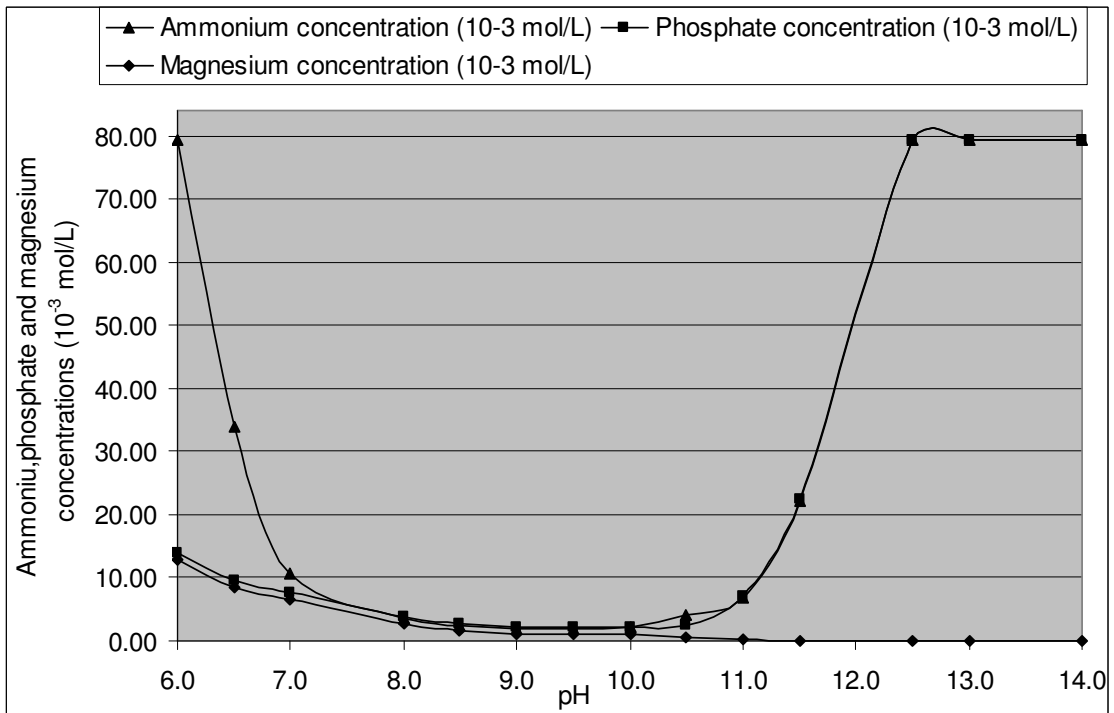


Figure 6.2: The ammonium, phosphate and magnesium concentrations (10^{-3} mol/L) dissolved in the solution after reaction predicted by Visual MINTEQ at the pH range from 6.0 to 14.0

Table 6.2: Solids formation at the pH range from 6.0 to 14.0

pH	MgHPO ₄ ·3H ₂ O (10 ⁻³ mol/L)	Struvite (10 ⁻³ mol/L)	Mg ₃ (PO ₄) ₂ (10 ⁻³ mol/L)	Brucite (Mg(OH) ₂) (10 ⁻³ mol/L)
6.0	65.60	0.00	0.00	0.00
6.5	24.62	45.35	0.00	0.00
7.0	3.35	68.56	0.00	0.00
8.0	0.00	75.72	0.00	0.00
8.5	0.00	76.69	0.00	0.00
9.0	0.00	77.19	0.00	0.00
9.5	0.00	77.35	0.00	0.00
10.0	0.00	77.17	0.05	0.00
10.5	0.00	75.20	0.84	0.00
11.0	0.00	72.41	0.00	5.82
11.5	0.00	57.11	0.00	21.23
12.5	0.00	0.00	0.00	78.39
13.0	0.00	0.00	0.00	78.39
14.0	0.00	0.00	0.00	78.39

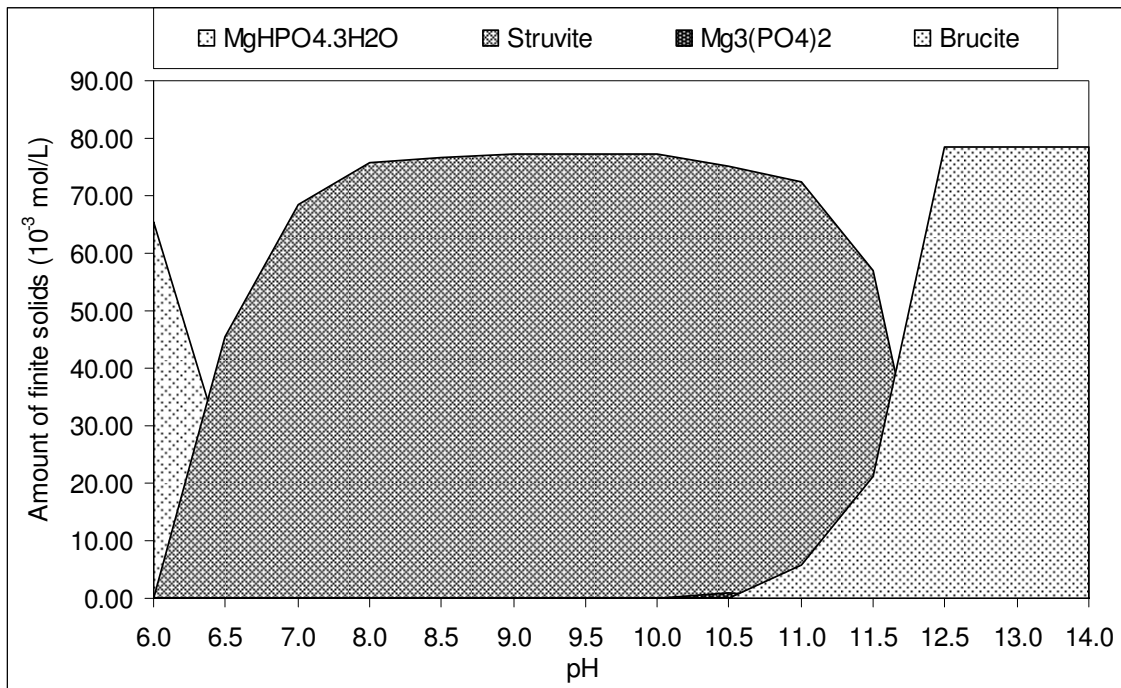


Figure 6.3: Solids formation predicted by Visual MINTEQ at the pH range from 6.0 to 14.0

From Figure 6.1 and Table 6.1, ammonium and phosphate removal changed with the pH increase. Removal was significant with over 90.00% of ammonium and phosphate at the pH range from 7.0 to 11.0. Maximum ammonium and phosphate removal achieved more than 97.00% ammonium and phosphate removal occurred at pH 9.5, and the amount of struvite precipitation was $77.35 \times 10^{-3} \text{ mol/L}$. Only $1.89 \times 10^{-3} \text{ mol/L}$ ammonium and $2.09 \times 10^{-3} \text{ mol/L}$ phosphate dissolved in the solution at pH 9.5 (Figure 6.2). This agreed well with Buchanan *et al.* (1994) who confirmed the findings that struvite formation at the pH range of 7.0 to 11.0 using MINTEQA2, with the minimum solubility at pH 9.0.

Table 6.2 and Figure 6.3 show the amount and types of solids formation modelling with Visual MINTEQ. Struvite was precipitated in the pH range from 6.5 to 11.5, and it was the only solid formed at pH between 7.0 and 9.5 (Table 6.2). This indicated that ammonium and phosphate only form as struvite in this pH range. In addition, the amount of struvite production increased after raising pH from 7.0 to 10.0. As much as $70 \times 10^{-3} \text{ mol/L}$ of struvite was formed in this pH range (Table 6.2). $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ precipitated at $\text{pH} < 8.0$, and $\text{Mg}_3(\text{PO}_4)_2$ and Brucite ($\text{Mg}(\text{OH})_2$) appeared at $\text{pH} > 10$. The pH influence on these possible species formation was also studied by Ali *et al.* (2003). They reported that struvite is the only crystal formation at the pH range of 7.75 to 9.27, and Newberyite ($\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$), Brucite ($\text{Mg}(\text{OH})_2$) and Farringtonite ($\text{Mg}_3(\text{PO}_4)_2$) formed at below pH 6.75 or above 9.27.

The pH value can affect ammonium and phosphate removal and the amount and purity of struvite formation from the solution. Other possible solids

precipitate from solution formed when pH is at low range or very high range. In addition, their formation can consume the magnesium source and affect the purity of struvite precipitation.

6.3 Modelling at different molar ratios

This section was to investigate the optimum amount of magnesium for struvite precipitation. The optimum pH 9.5 was discussed in the last section. The molar ratio of $Mg^{2+}:NH_4^+:PO_4^{3-}$ increased from 1.0:1.0:1.0 to 2.0:1.0:1.0. Table 6.3 and Figures 6.4 and 6.5 show ammonium, phosphate and magnesium removal and their residual concentrations at this ratio range. Table 6.4 and Figure 6.6 show the different types of solids and amounts of solids at this ratio range.

Table 6.3: The removal of ammonium (%) and phosphate (%) predicted by Visual MINTEQ at the $Mg^{2+}:NH_4^+:PO_4^{3-}$ ratio from 1.0:1.0:1.0 to 2.0:1.0:1.0

$Mg^{2+}:NH_4^+:PO_4^{3-}$	Ammonium (%)	Phosphate (%)
1.0:1.0:1.0	97.62	97.37
1.1:1.0:1.0	96.76	99.61
1.2:1.0:1.0	95.17	99.86
1.3:1.0:1.0	93.90	99.92
1.4:1.0:1.0	92.82	99.94
1.6:1.0:1.0	91.01	99.96
1.8:1.0:1.0	89.49	99.97
2.0:1.0:1.0	89.10	99.97

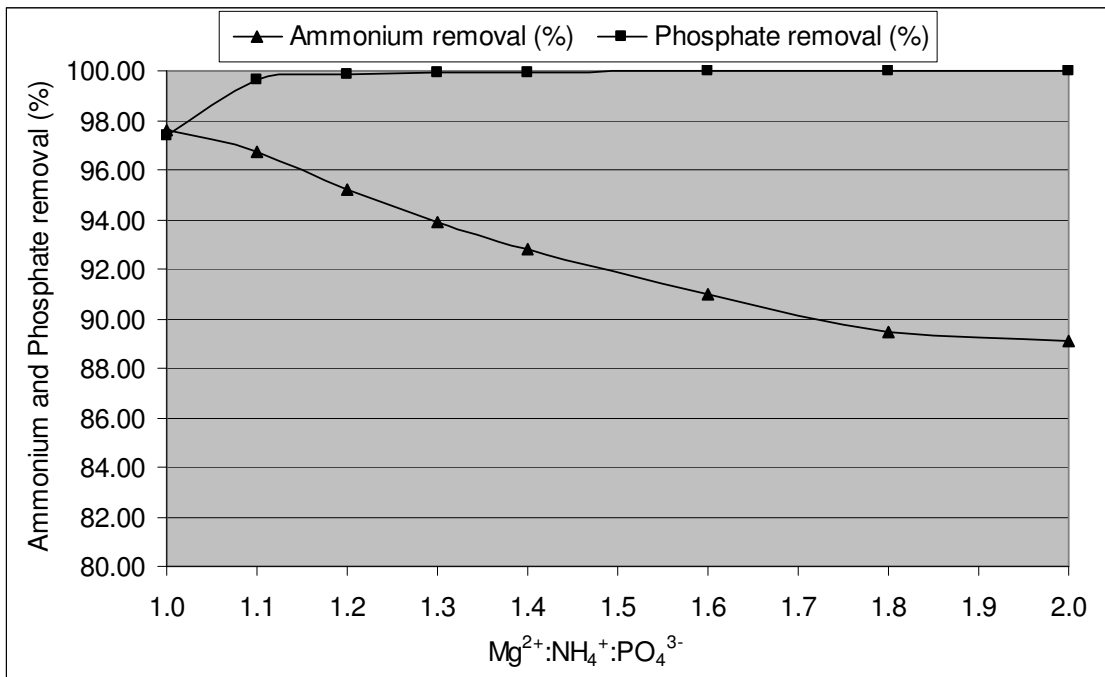


Figure 6.4: Ammonium removal (%) and phosphate removal (%) predicted by Visual MINTEQ at the Mg²⁺:NH₄⁺:PO₄³⁻ ratio from 1.0:1.0:1.0 to 2.0:1.0:1.0

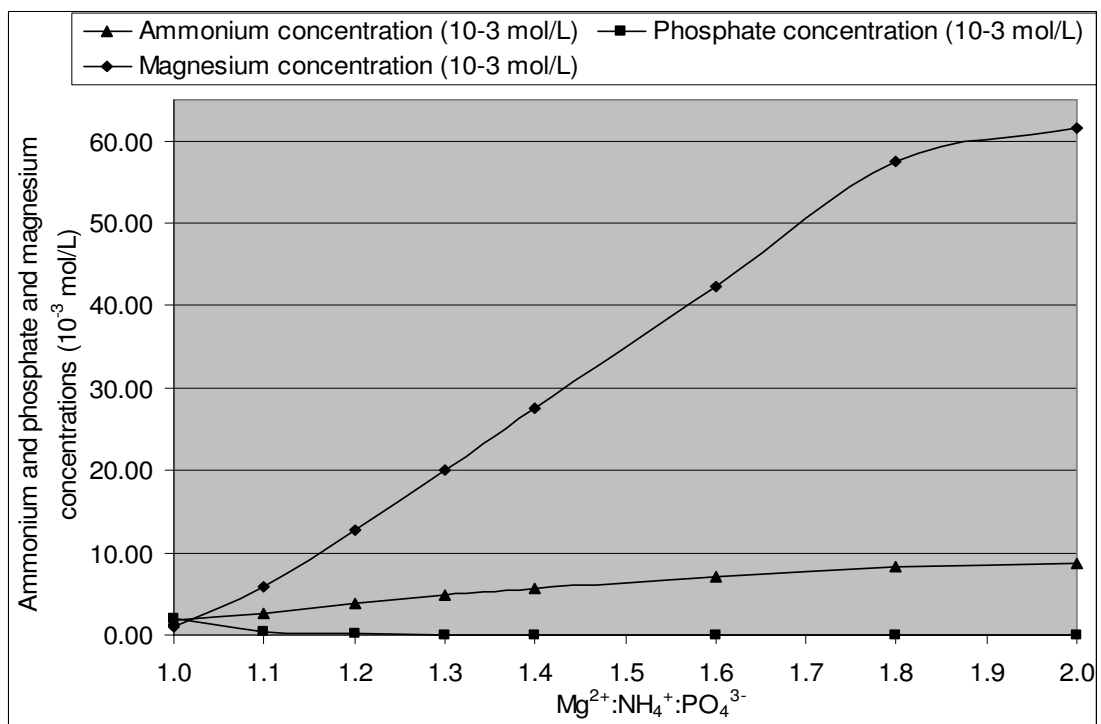


Figure 6.5: Ammonium, phosphate and magnesium concentrations (mol/L) dissolved in the solution predicted by Visual MINTEQ at the Mg²⁺:NH₄⁺:PO₄³⁻ ratio from 1.0:1.0:1.0 to 2.0:1.0:1.0

Table 6.4: The type and amount of solids formed at the $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ ratio from 1.0:1.0:1.0 to 2.0:1.0:1.0

$\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$	Struvite (10^{-3} mol/L)	$\text{Mg}_3(\text{PO}_4)_2$ (10^{-3} mol/L)	Brucite ($\text{Mg}(\text{OH})_2$) (10^{-3} mol/L)
1.0:1.0:1.0	77.35	0.00	0.00
1.1:1.0:1.0	76.67	1.22	0.00
1.2:1.0:1.0	75.41	1.96	0.00
1.3:1.0:1.0	74.41	2.48	0.00
1.4:1.0:1.0	73.55	2.92	0.00
1.6:1.0:1.0	72.12	3.64	0.00
1.8:1.0:1.0	70.91	4.25	0.00
2.0:1.0:1.0	70.60	4.41	11.36

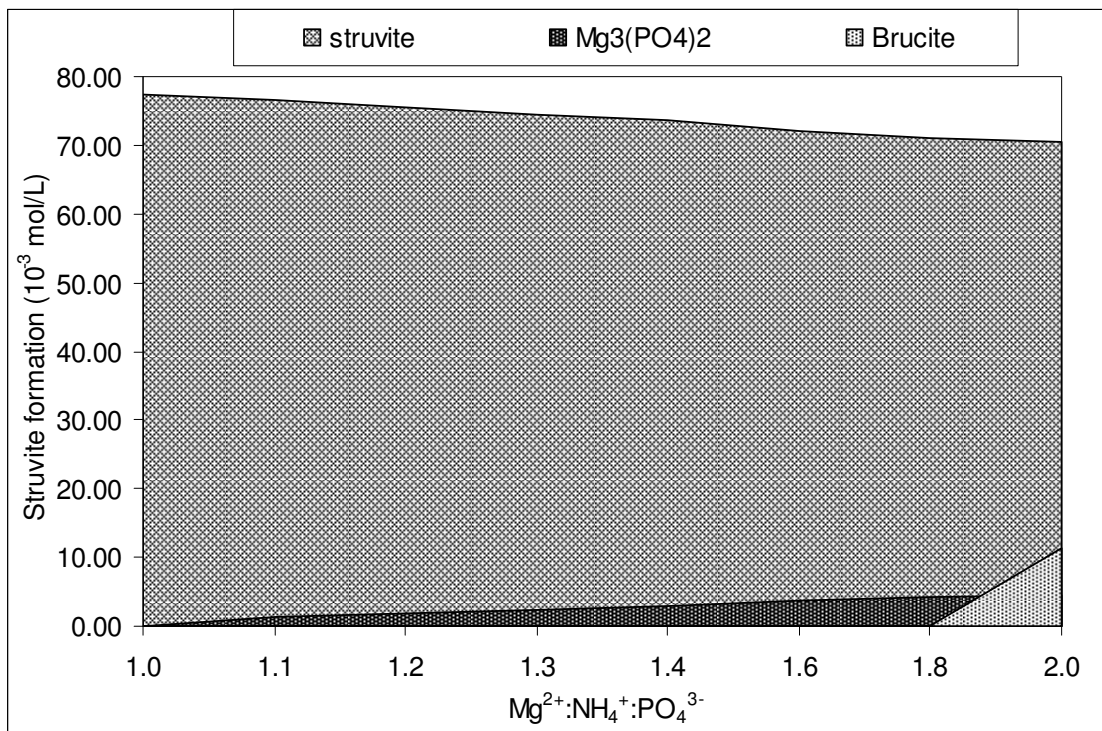


Figure 6.6: Solids formed predicted by Visual MINTEQ at the $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ ratio from 1.0:1.0:1.0 to 2.0:1.0:1.0

Phosphate removal reached extremely high levels at the $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ ratio of 1.0:1.0:1.0 and almost all phosphate was removed the $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ ratio from 1.1:1.0:1 to 2.0:1.0:1.0 (Figure 6.4). On the other hand, the removal of ammonium decreased steadily with magnesium addition (Figure 6.4). Over 97.00% ammonium and phosphate removal were achieved at the $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ ratio of 1.0:1.0:1.0. At the ratio of 1.2:1.0:1.0, 95.17% ammonium and 99.86% phosphate were removed (Table 6.3). It can be seen that the increase of the $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ ratio from 1.0:1.0:1.0 to 2.0:1.0:1.0 improved phosphate removal slightly, and was not helpful for ammonium removal from the supernatant.

From Table 6.4, the amount of struvite precipitation decreased with increasing molar ratios. The other solids could form with magnesium addition. $\text{Mg}_3(\text{PO}_4)_2$ precipitated with struvite when $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ was over 1.1:1.0:1.0. Brucite ($\text{Mg}(\text{OH})_2$) also formed with struvite and $\text{Mg}_3(\text{PO}_4)_2$ when $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ reached 2.0:1.0:1.0. But struvite still was the main solid in precipitate at the whole range (Figure 6.6). There are 76.67×10^{-3} mol/L struvite and 1.22×10^{-3} mol/L $\text{Mg}_3(\text{PO}_4)_2$ at molar ratio 1.1:1.0:1.0, and 70.60×10^{-3} mol/L struvite, 4.41×10^{-3} mol/L $\text{Mg}_3(\text{PO}_4)_2$ and 11.36×10^{-3} mol/L Brucite ($\text{Mg}(\text{OH})_2$) precipitated from wastewater when the molar ratio was at 2.0:1.0:1.0 (Table 6.4). Therefore, increasing magnesium dosage does not enhance the amount of struvite precipitation from the supernatant.

6.4 Chapter summary

This chapter has predicted struvite formation using the chemical equilibrium software Visual MINTEQ. A wide range of the pH and molar ratios were run through Visual MINTEQ. Ammonium and phosphate removal and solids formation has been discussed. Based on the results from this part of the study, the following can be concluded:

- The pH can affect ammonium and phosphate removal and the amount and purity of struvite formation from the solution. The other possible solids precipitate from solution formed when pH is at low range or very high range. In addition, their formation can consume the Mg source and affect the purity of struvite precipitation. To optimise struvite production and enhance its purity, the reaction pH would be controlled at the optimum pH range. The pH range for ammonium and phosphate removal and recovery as struvite formation was from 7.0 to 11.5, and no other solids were formed at the range from 7.0 to 9.5. The maximum production was 77.35×10^{-3} mol/L of struvite precipitation at 9.5, and over 97.00% of ammonium and phosphate were removed. $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$, $\text{Mg}_3(\text{PO}_4)_2$ and Brucite ($\text{Mg}(\text{OH})_2$) were found in the solid phase in addition to struvite.
- Magnesium addition improves phosphate removal slightly, and it is not helpful for ammonium removal and struvite precipitation production. Over 97.00% ammonium and phosphate were removed at the equal molar ratio, and 95.17% ammonium and 99.86% phosphate were removed at the $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ ratio of 1.2:1.0:1.0. Additional, $\text{Mg}_3(\text{PO}_4)_2$ and

Brucite ($\text{Mg}(\text{OH})_2$) can be formed with struvite precipitation increasing magnesium addition, but struvite was the main product in the precipitate. Overall, the chemical equilibrium software Visual MINTEQ can be employed successfully to assist ammonium and phosphate removal and recovery as struvite. Visual MINTEQ can model the large range of the pH and molar ratios. Its output shows the residual concentrations of ions and the percentage of ions precipitated from the solution. The amount and types of solids formation are also shown in the output. The results of this Chapter will be compared with the experimental results in Chapter 7.

Chapter 7 Ammonia and Phosphate Removal and Recovery from Anaerobic Digester Supernatant using Mg-rich waste material

7.1 Introduction

Chapter 5 have determined the optimum conditions for ammonia and phosphate as struvite from anaerobic digester supernatant. Magnesium chloride was used as the magnesium source. Chapter 6 described the chemical equilibrium software Visual MINTEQ to predict struvite formation using the supernatant with Mg-rich waste material. The aim of this Chapter is to evaluate the feasibility of struvite formation using Mg-rich waste material as the magnesium source from anaerobic digester supernatant. The reaction time, pH and magnesium dosage for struvite formation using Mg-rich waste material were determined in the laboratory. The samples were collected from Eastern Wastewater Treatment Plant in Melbourne which contained 1349.92 mg/L ammonia, 352.60 mg/L phosphate and 16.45 mg/L magnesium. Since the concentration of ammonia was higher than Mg^{2+} and phosphate concentrations, magnesium and phosphate concentrations were increased by Mg-rich waste material and Na_2HPO_4 to force struvite formation. Precipitates were analysed using XRD and ESEM. Economic analysis was used to evaluate the feasibility of using Mg-rich waste material for struvite formation from anaerobic digester supernatant.

7.2 Reaction time test

This part work was to test ammonia and phosphate removal as struvite using different reaction times at the same other reaction conditions (pH=9.0, $Mg^{2+}:NH_4^+:PO_4^{3-}=1.0:1.0:1.0$). The residual concentrations of ammonia and ammonia removal and the residual concentrations of phosphate and phosphate removal are shown in Figures 7.1 and 7.2, respectively.

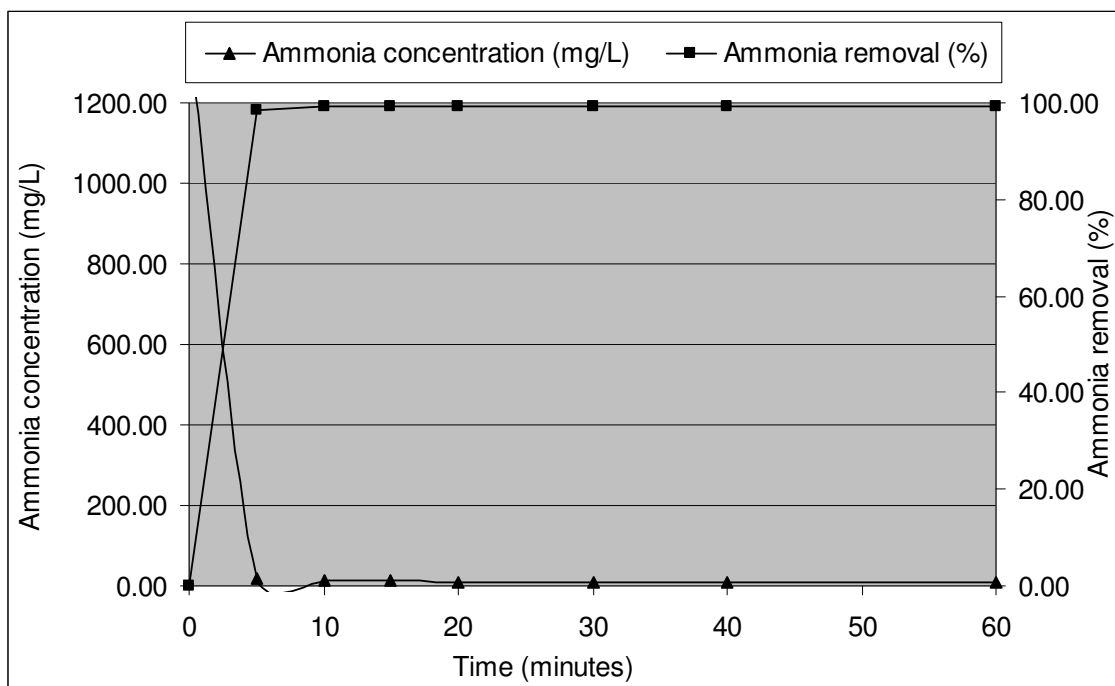


Figure 7.1: Reaction time effect on the residual ammonia concentration and ammonia removal using Mg-rich waste material (pH=9.0, $Mg^{2+}:NH_4^+:PO_4^{3-}=1.0:1.0:1.0$)

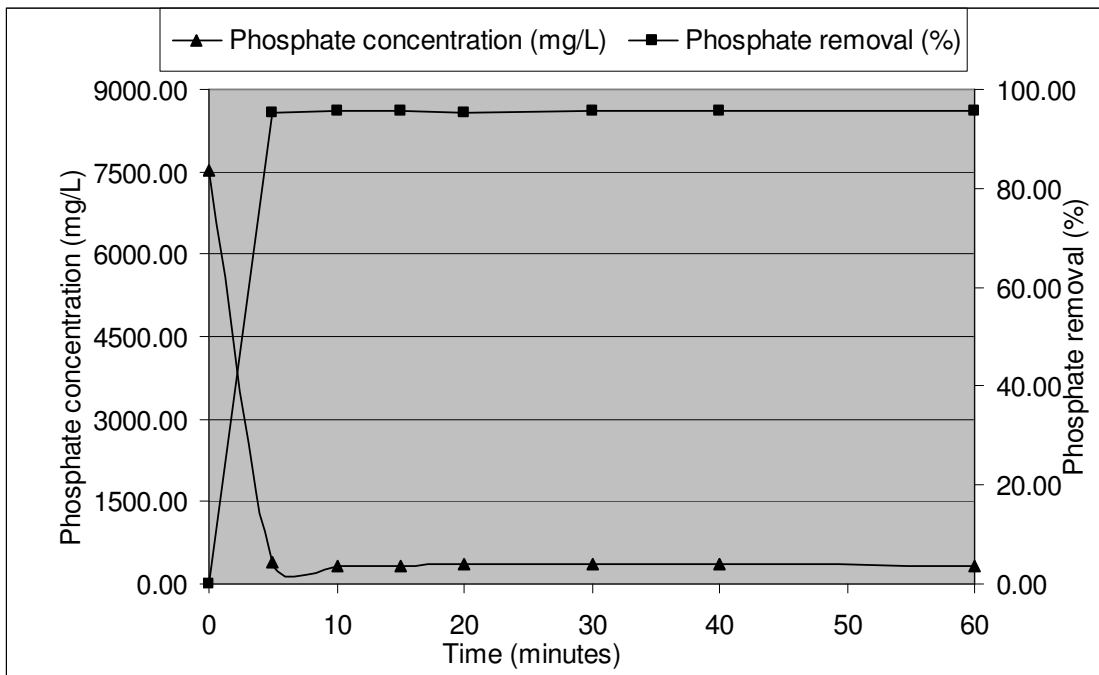


Figure 7.2: Reaction time effect on the residual phosphate concentrations and phosphate removal using Mg-rich waste material (pH=9.0, $Mg^{2+}:NH_4^+:PO_4^{3-} = 1.0:1.0:1.0$)

Both the residual ammonia concentration and the residual phosphate concentration decreased immediately between 0 and 5 minutes when pH was adjusted to 9.0 after magnesium and phosphate source addition (Figures 7.1 and 7.2). The removal of ammonia and phosphate reached 95.16% and 98.63% respectively within 5 minutes. After 60 minutes, the removal of ammonia and phosphate was 95.60% and 99.15%. There was only slightly improvement to ammonia and phosphate removal from 5 minutes to 60 minutes. Comparing of the results indicated that struvite was formed rapidly and extremely high ammonia and phosphate removal was achieved by 5 minutes. There was only slight ammonia and phosphate removal improvement from 5 minutes to 60 minutes. It was also faster than the reaction using the supernatant from Melton Wastewater treatment plant which was discussed in the Chapter 5. The fast reaction could be because of the ammonia concentration of the samples from

Eastern Wastewater Treatment Plant, which was about twice of that available in the supernatant from Melton Wastewater Treatment Plant used in Chapter 5. To consider the rapid reaction rates, a reaction time of 10 minutes was enough for all experiments. There were over 95.00% ammonia and almost phosphate removal using 10 minutes at this part of the study.

7.3 The pH test

The high pH range from 7.0 to 11.0 was tested to analyse pH effect on struvite formation using Mg-rich waste material at the equal molar ratio. Figures 7.3 and 7.4 show the results from experiments.

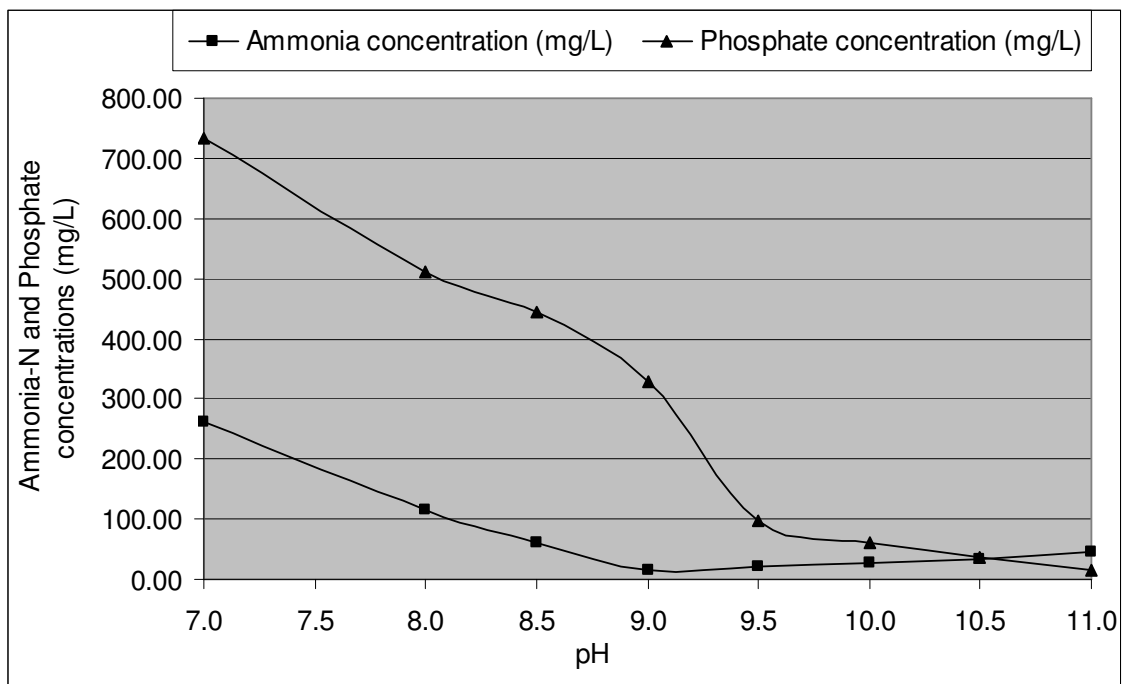


Figure 7.3: The residual ammonia and phosphate concentrations at pH from 7.0 to 11.0 ($Mg^{2+}:NH_4^+:PO_4^{3-} = 1.0:1.0:1.0$)

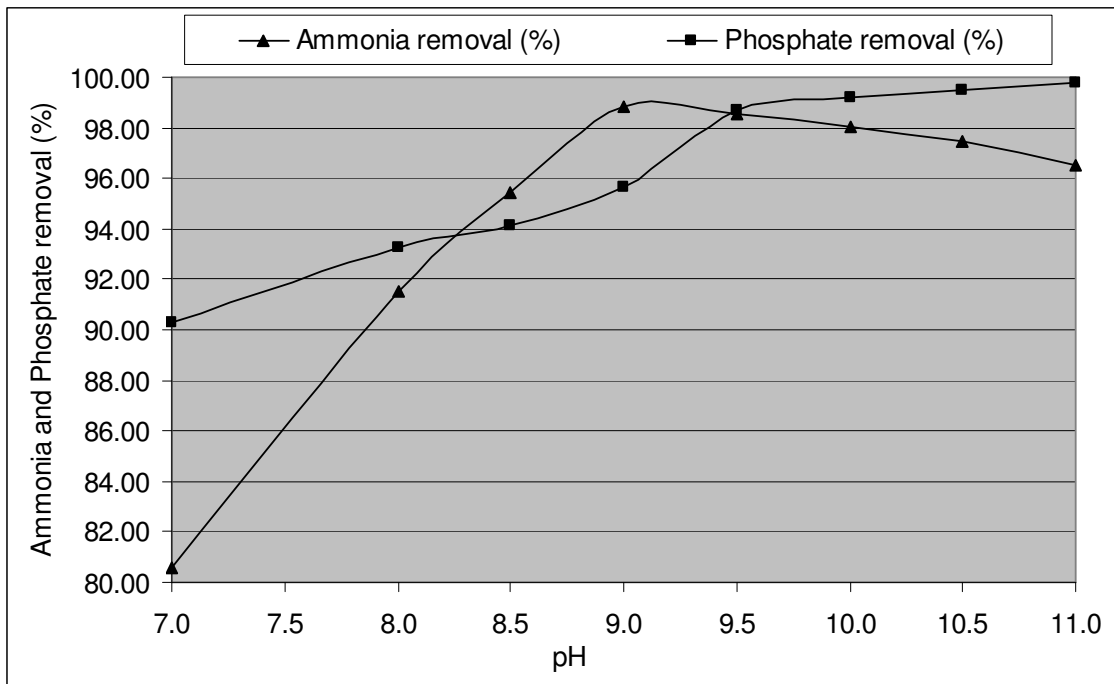


Figure 7.4: Ammonia and phosphate removal (%) using Mg-rich waste material at pH from 7.0 to 11.0 ($Mg^{2+}:NH_4^+:PO_4^{3-} = 1.0:1.0:1.0$)

Figure 7.3 presents the residual concentrations of ammonia and phosphate after the reaction using the pH range from 7.0 to 11.0. Figure 7.4 shows ammonia and phosphate removal calculated from the residual concentration. From Figure 7.3, the low ammonia residue concentration was achieved in the solution when the pH was over 8.5. The residual concentration of phosphate was also low when the pH was over 9.5. There were 19.85 mg/L ammonia and 98.63 mg/L phosphate remained in the solution using pH 9.5. As shown in Figure 7.4, both of ammonia and phosphate removal were improved at pH between 7.0 and 9.0. The removal of ammonia was 98.87% at pH 9.0 and 98.53% at pH 9.5, compared with 80.60% at pH 7.0. However, ammonia removal began to decrease with $pH > 9.0$ (Figure 7.4). Phosphate removal increased from 90.30% at pH 7.0 to 99.80% at pH 11.0, and it achieved 98.53% at pH 9.0 and 98.69% at pH 9.5 (Figure 7.4). Over 98.00% ammonia and

phosphate were removed at the pH between 9.0 and 9.5. This indicated that almost all the ammonia and phosphate was removed when the pH was adjusted to pH 9.0 or pH 9.5.

The chemical equilibrium software Visual MINTEQ has been used to predict the possible solids formed from the supernatant at the large range of the pH in Chapter 6. From the results, $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$, $\text{Mg}_3(\text{PO}_4)_2$ and Brucite ($\text{Mg}(\text{OH})_2$) formed at $\text{pH} < 7$ or $\text{pH} > 9.5$. The possible solids formations were chosen from database before running Visual MINTEQ in the Chapter 6, so they were limited to several types. More species may form due to the complex components of the supernatant and Mg-rich waste material. Musvoto *et al.*, 2000 found that $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ precipitated at lower pH (< 6), and Brucite ($\text{Mg}(\text{OH})_2$) formed at the high pH. In addition, the presence of Ca^{2+} in the supernatant may lead to calcium species formation such as $\text{Ca}_3(\text{PO}_4)_2$, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ and CaHPO_4 (Uludag-Demirer and Othman, 2009). Therefore, to guarantee both ammonia and phosphate removal and recovery as struvite from the supernatant, the pH of 9.5 was used for magnesium dosage test.

7.4 Magnesium dosage test

This was an investigation to determine the dosage of Mg-rich waste material for ammonia and phosphate removal as struvite at $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ from 1.0:1.0:1.0 to 2.0:1.0:1.0 and at pH 9.5. The results are shown in Figures 7.5 and 7.6. The amounts of precipitates using different magnesium dosage are shown in Table 7.1.

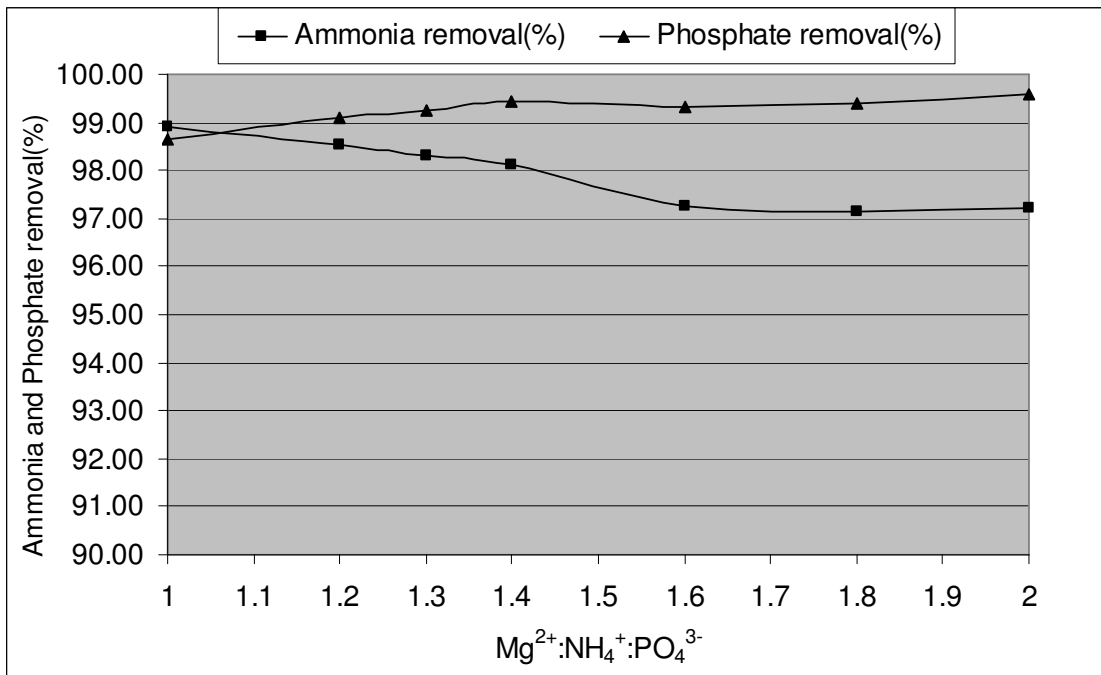


Figure 7.5: Ammonia and phosphate removal using Mg-rich waste material at the Mg²⁺:NH₄⁺:PO₄³⁻ ratio from 1.0:1.0:1.0 to 2.0:1.0:1.0 (pH=9.5)

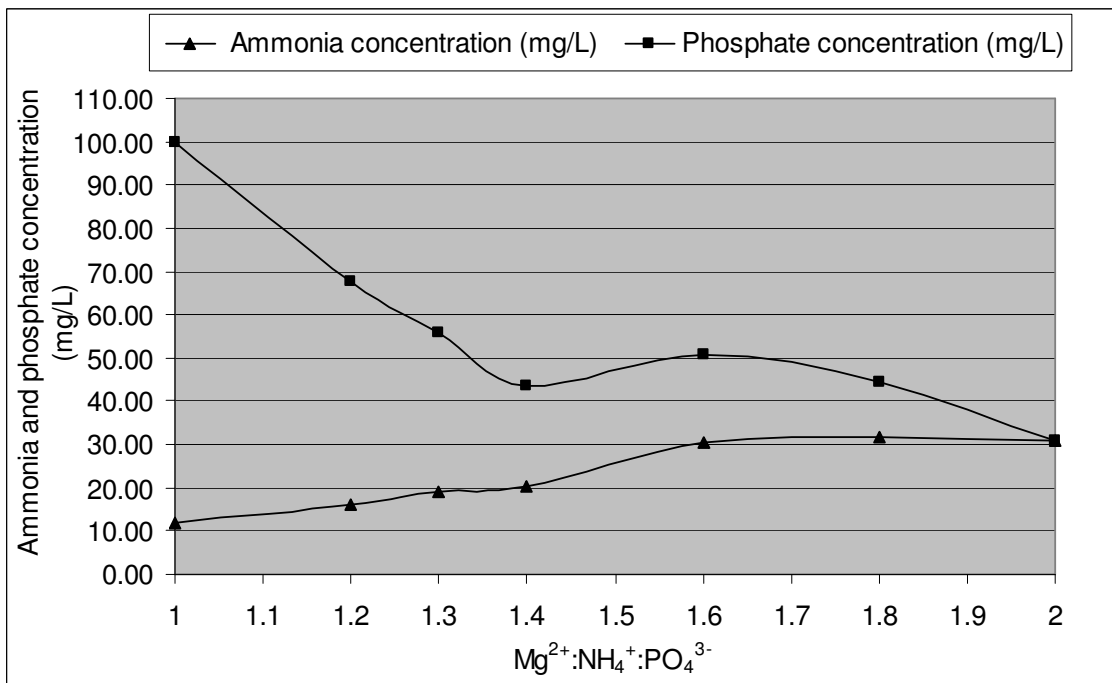


Figure 7.6: The residual ammonia and phosphate concentrations using Mg-rich waste material at the Mg²⁺:NH₄⁺:PO₄³⁻ ratio from 1.0:1.0:1.0 to 2.0:1.0:1.0 (pH=9.5)

Table 7.1: Precipitates formed from 100 ml supernatant using Mg-rich waste material at pH 9.5

$Mg^{2+}:PO_4^{3-}:NH_4^+$	precipitates(g)
1.0:1.0:1.0	1.2132
1.2: 1.0:1.0	1.2629
1.3: 1.0:1.0	1.2467
1.4: 1.0:1.0	1.1210
1.6: 1.0:1.0	1.2538
1.8: 1.0:1.0	1.2987
2.0: 1.0:1.0	1.3045

From Figures 7.5 and 7.6, both ammonia and phosphate removal was over 97.00% at $Mg^{2+}:NH_4^+:PO_4^{3-}$ from 1.0:1.0:1.0 to 2.0:1.0:1.0. Ammonia and phosphate removal achieved 98.92% and 98.63% at the $Mg^{2+}:NH_4^+:PO_4^{3-}$ ratio of 1.0:1.0:1.0, and 98.54% and 99.10% at the $Mg^{2+}:NH_4^+:PO_4^{3-}$ ratio of 1.2:1.0:1.0. The removal of phosphate increased slightly with magnesium addition, but the removal of ammonia decreased slightly with addition of Mg-rich waste material. As shown in Table 7.1, masses precipitated from 100 ml supernatant at molar ratios from 1.0:1.0:1.0 to 2.0:1.0:1.0 were between 1.200 g and 1.3000 g. Precipitates collected from experiments were less than the typical amount. Small amount of precipitates were lost during filtration. The amounts of precipitates formed at from 1.0:1.0:1.0 to 2.0:1.0:1.0 were 1.2132 g and 1.3045 g, respectively.

Increased magnesium dosage can increase slightly phosphate removal, but ammonia removal and the amount of struvite precipitation are not improved. Magnesium dosage was double, precipitate masses were improved slightly.

Additionally, with magnesium addition increase, $Mg_3(PO_4)_2$ and Brucite ($Mg(OH)_2$) may be formed as predicted using chemical equilibrium software Visual MINTEQ (Chapter 6). Other solids formations affect the purity of struvite formation. Therefore, excess magnesium dosage is not necessary as discussed in Chapter 5 and Chapter 6. It is better to introduce a certain amount of the magnesium source to force struvite formation and maximize ammonia and phosphate removal. Ammonia and phosphate removal can reach over 98.00% at the equal molar ratio, but the complex common in wastewater still needs to be considered. To guarantee ammonia and phosphate removal effectively and magnesium addition efficiently, the $Mg^{2+}:NH_4^+:PO_4^{3-}$ ratio of 1.2:1.0:1.0 could be chosen as the optimum molar ratio. Characterization of precipitates was presented in the next section, and the impurity of struvite precipitation also was analysed.

7.5 Characterization of precipitates

Precipitates collected from each experiment were air dried at room temperature for 48 hours, and were identified using XRD diffraction analysis. The results were compared with a standard struvite which is in XRD database. To find out the impurity of struvite precipitation, the results of XRD were also compared with the possible solids formation in the precipitates. Figure 7.7 shows the XRD pattern of precipitate using the $Mg^{2+}:NH_4^+:PO_4^{3-}$ ratio of 1.0:1.0:1.0 at pH 9.5 was compared with standard struvite. Figures 7.8 and 7.9 show the XRD patterns of precipitates using the $Mg^{2+}:NH_4^+:PO_4^{3-}$ ratio of 1.0:1.0:1.0 and 1.2:1.0:1.0 at pH 9.5 was compared with standard struvite. Figure 7.10 shows

the images of precipitates using the $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ ratio of 1.0:1.0:1.0 at pH 9.5.

As shown in Figures 7.7, trace amounts of other solids were in the precipitate at the $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ ratio of 1.0:1.0:1.0. When the molar ratio of $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ increased to 1.2:1.0:1.0, the pattern of the precipitate approximately matched standard struvite pattern (Figure 7.9). Newberyite could be one possible solid formed with struvite precipitation at the $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ of 1.0:1.0:1.0 and 1.2:1.0:1.0 (Figures 7.8 and 7.9). It indicated that nearly pure of struvite were formed using Mg-rich waste material at pH 9.5 and the $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ ratio of 1.0:1.0:1.0 and 1.2:1.0:1.0.

From Figure 7.10, struvite precipitation is present as a cubic shape. As discussed in Chapter 2, Doyle *et al.* (2000) produced struvite in aqueous supersaturated solutions, and reported that struvite has a unique orthogonal structure. Dunn *et al.* (2004) also confirmed this shape for the struvite structure. In this study, anaerobic digester supernatant was used for struvite formation at a short time of 10 minutes. Struvite may also be present as spherical or dendrite or cubic shapes (Ali, 2005).

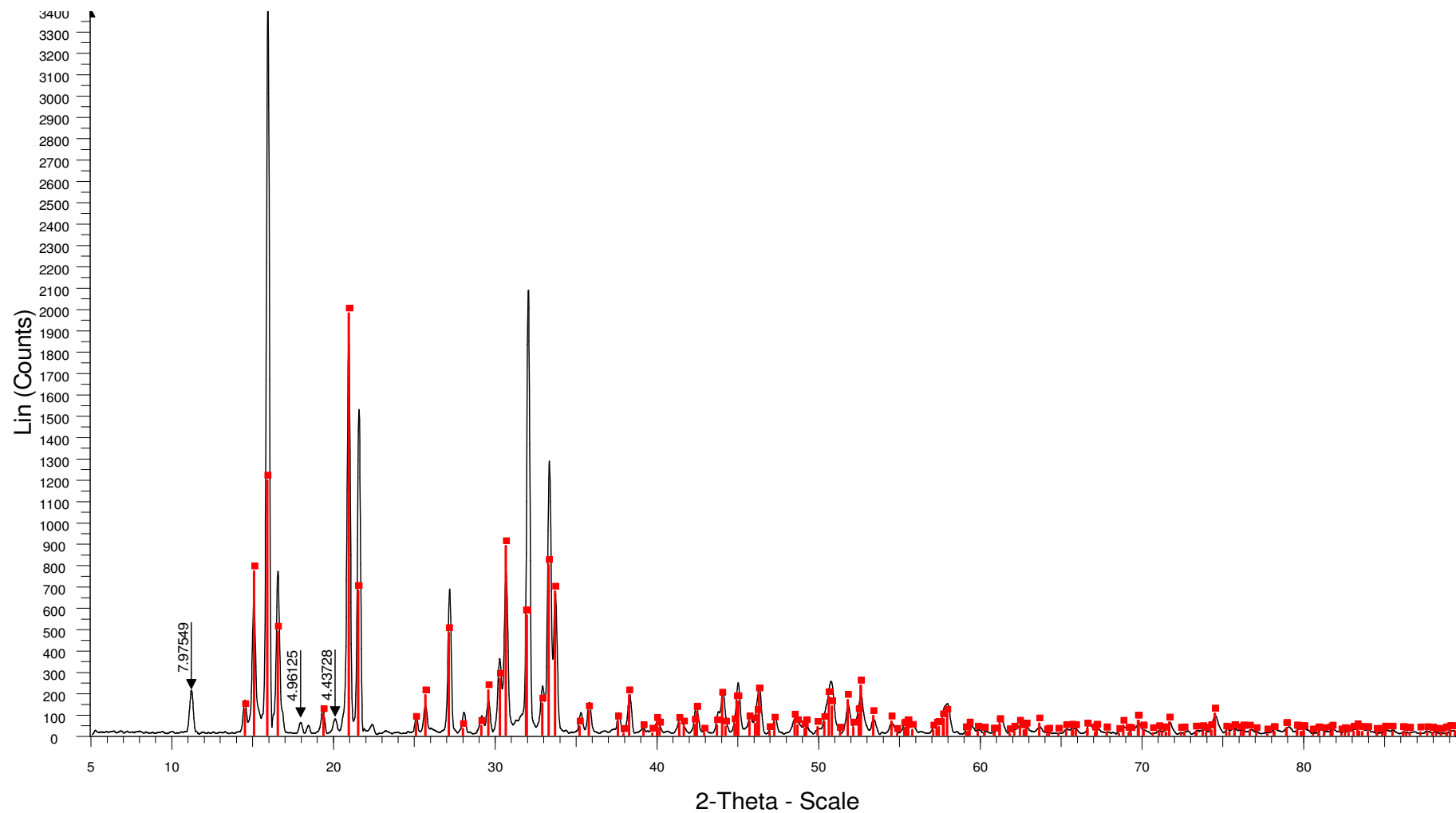


Figure 7.7: X-ray Diffraction Pattern for precipitate formed at pH 9.5, the $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ ratio of 1.0:1.0:1.0 compared with standard struvite pattern

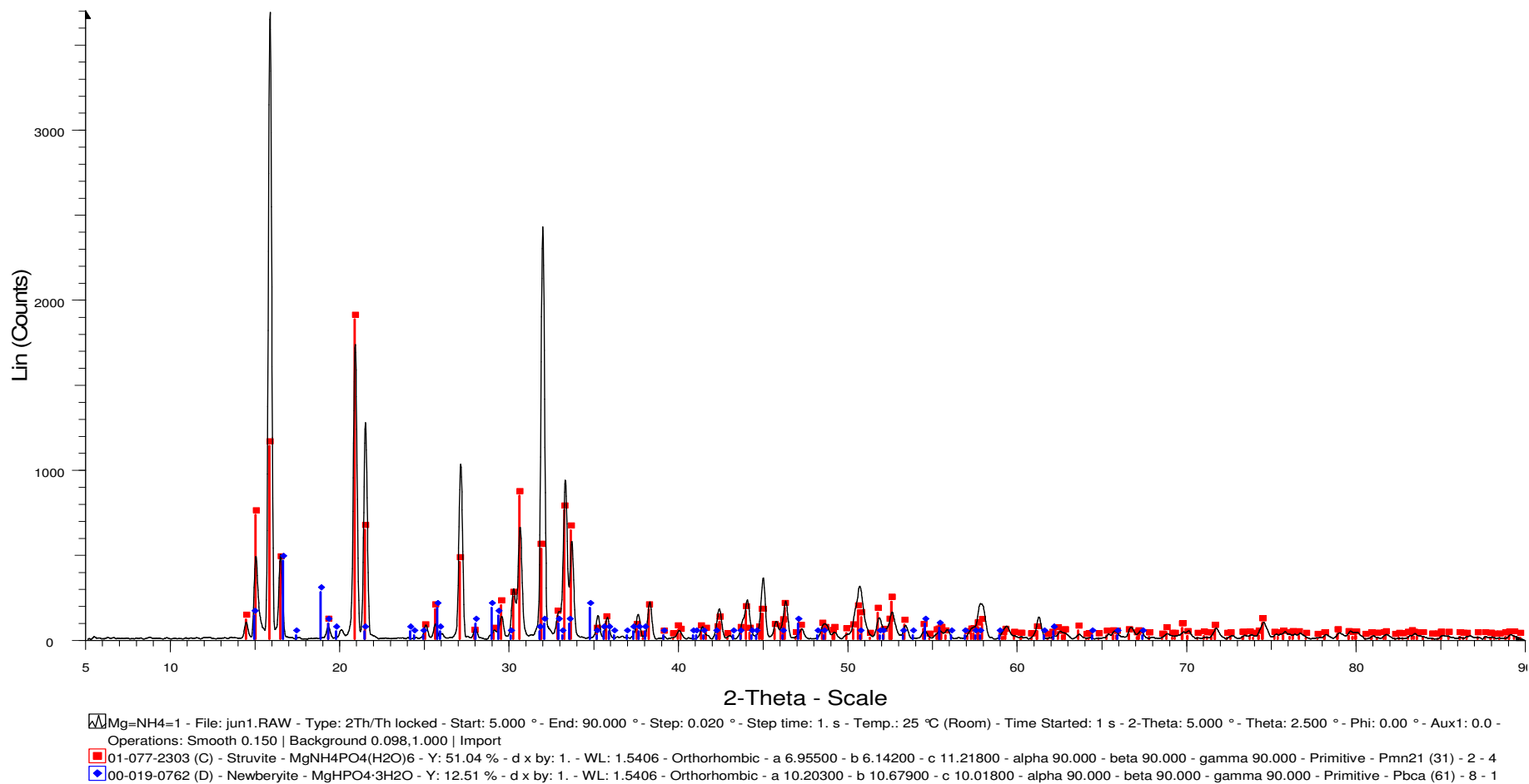


Figure 7.8: X-ray Diffraction Pattern for precipitate formed at pH 9.5, the $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ ratio of 1.0:1.0:1.0 compared with standard struvite pattern and Newberyite ($\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$) pattern

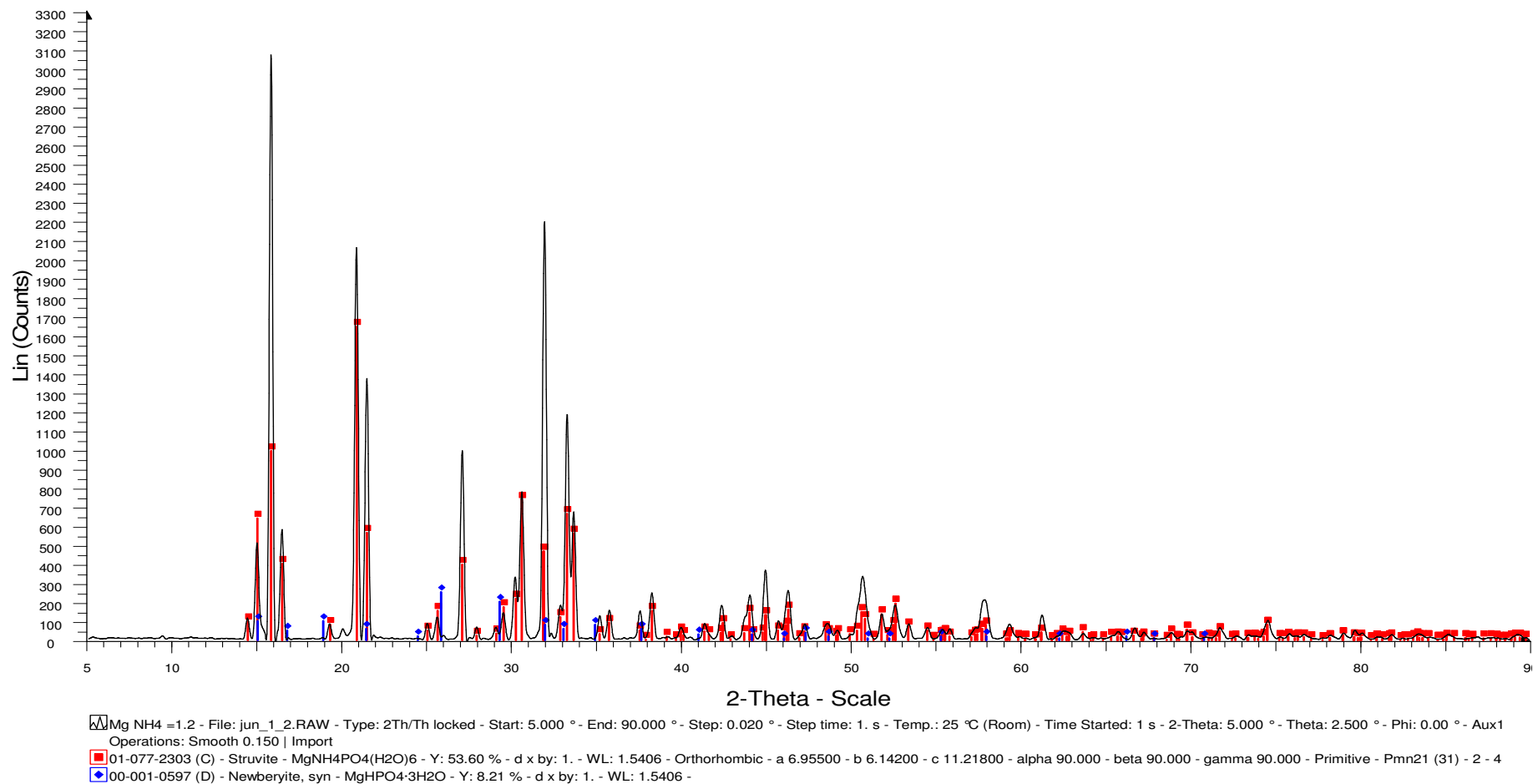


Figure 7.9: X-ray Diffraction Pattern for precipitate formed at pH 9.5, the $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ ratio of 1.2:1.0:1.0 compared with standard struvite pattern and Newberyite ($\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$) pattern

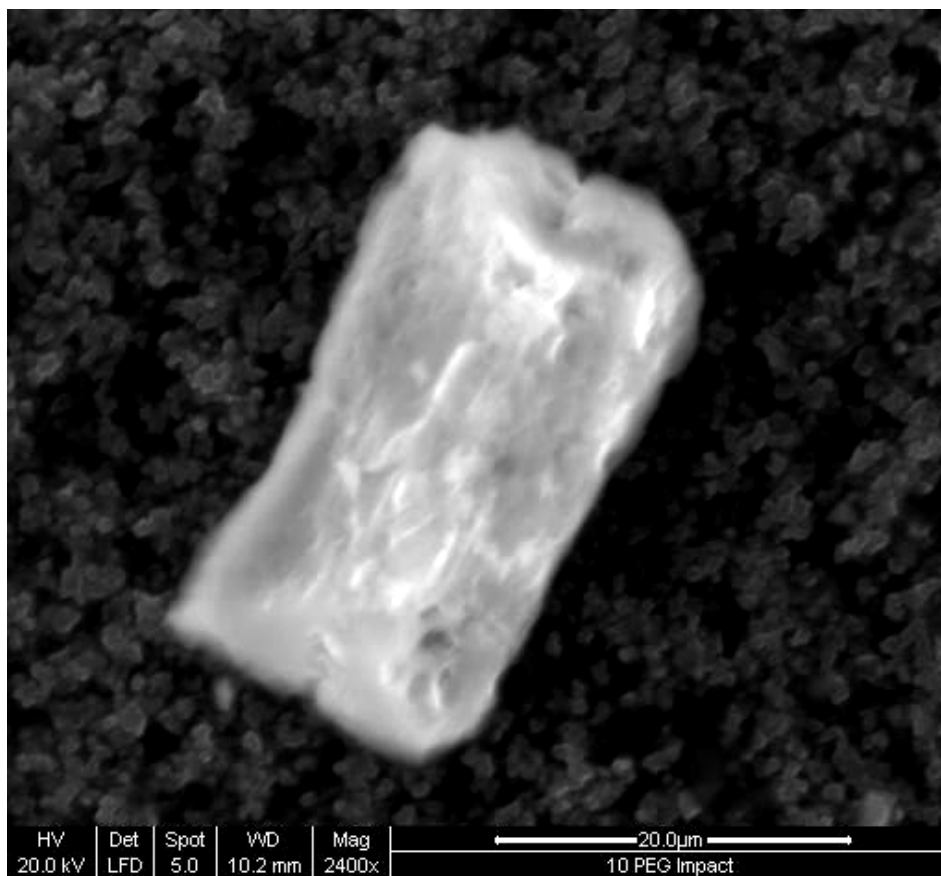
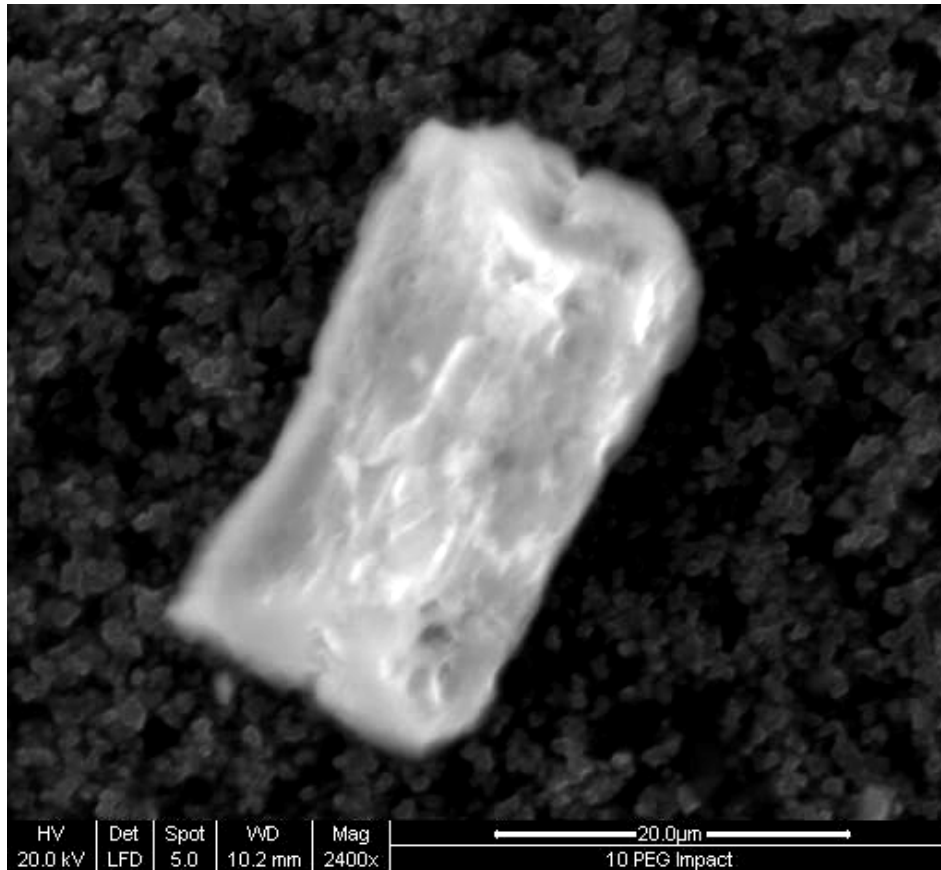


Figure 7.10: Images of struvite precipitation using the $Mg^{2+}:NH_4^+:PO_4^{3-}$ ratio of 1.2:1.0:1.0 at pH 9.5

7.6 Economic analysis

In this study, economical analysis was undertaken conducted to evaluate the cost of Mg-rich waste material compared with MgCl_2 . The economic feasibility using Mg-rich waste material was also discussed. Based on the results in Chapter 5 and Chapter 7, the optimum reaction conditions for ammonia and phosphate removal and recovery as struvite were pH 9.5, the reaction time of 10 minutes and the $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ ratio of 1.2:1.0:1.0. Anaerobic digester supernatant from Melton Wastewater Treatment Plant contains 731.85 mg/L ammonia, 319.00 mg/L PO_4^{3-} and 35.67 mg/L Mg^{2+} . The pH of the supernatant was 7.32. The pH adjustment using NaOH was necessary for the production of struvite. Based on these concentrations, the molar ratio of $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ is 1:32.6:2.5, so magnesium and phosphate addition were required to reach the molar ratio of 1.2:1.0:1.0 to form struvite precipitation. Therefore, ammonia and phosphate removal and recovery from the supernatant requires one of the following chemicals: Na_2HPO_4 , $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ or Mg-rich waste material and NaOH. In this assessment, investment costs such as the mixing rate and equipment were not taken into account and only the cost of chemicals was analysed.

The economic analysis was based on the experimental results using 100 mL supernatant. If 1 m³ supernatant is used for recovering nutrient as struvite using $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 10.23 kg $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 5.63 kg Na_2HPO_4 and 2.0 kg NaOH would be added to the solution to reach a molar ratio $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ of 1.2:1.0:1.0 and pH 9.5 (Table 7.2). On the other hand, if 1m³ supernatant is used for recovering nutrient as struvite using Mg-rich waste material, 10.74 L

MgCl₂.6H₂O, 5.63 kg Na₂HPO₄ and 2.0 kg NaOH would be added to solution to reach the optimum reaction conditions (Table 7.3). The costs are shown in Table 7.2 and 7.3. The economic comparison of magnesium source using MgCl₂ and Mg-rich waste material is shown in Figure 7.11.

Table 7.2: Economic analysis of struvite precipitations using MgCl₂ from 1m³ supernatant

Chemicals	Price (\$/kg or \$/L)	Amount (kg/m ³ or L/m ³)	Cost (\$/m ³)	Percent of total cost %
MgCl ₂ .6H ₂ O	1.21	10.23	12.38	83.25
NaH ₂ PO ₄	0.40	5.63	2.25	15.13
NaOH	0.12	2.00	0.24	1.61
total(\$/m ³)			14.87	

Table 7.3: Economic analysis of struvite precipitates using Mg-rich waste material from 1 m³ supernatant

Chemicals	Price (\$/kg or \$/L)	Amount (kg/m ³ or L/m ³)	Cost (\$/m ³)	Percent of total cost %
Mg-rich waste material	0.30	10.74	3.22	56.39
NaH ₂ PO ₄	0.40	5.63	2.25	39.40
NaOH	0.12	2.00	0.24	4.20
total(\$/m ³)			5.71	

From Tables 7.2 and 7.3, when MgCl₂.6H₂O was used as the magnesium source, the cost of this process was 14.78 \$/m³. The cost of MgCl₂ was 83.25% of the overall cost. Mg-rich waste material was relatively cheap compared to MgCl₂. Its price is only 0.30 \$/L. When it was used as the magnesium source for

struvite formation, the overall cost was 5.71\$/m³ (Table 7.3). The cost of Mg-rich waste material was 56.39% of the overall cost. From Figure 7.11, the additional magnesium source was the main cost element for struvite formation compared to those of Na₂HPO₄ and NaOH. The cost of the process per 1m³ supernatant using Mg-rich waste materials was low in comparison to the use of MgCl₂. Economic analysis showed that cost of struvite precipitation with Mg-rich waste material was 61.60% cheaper than with MgCl₂. The cheaper magnesium source, Mg-rich waste material, can be used for decreasing the overall cost of struvite precipitation process.

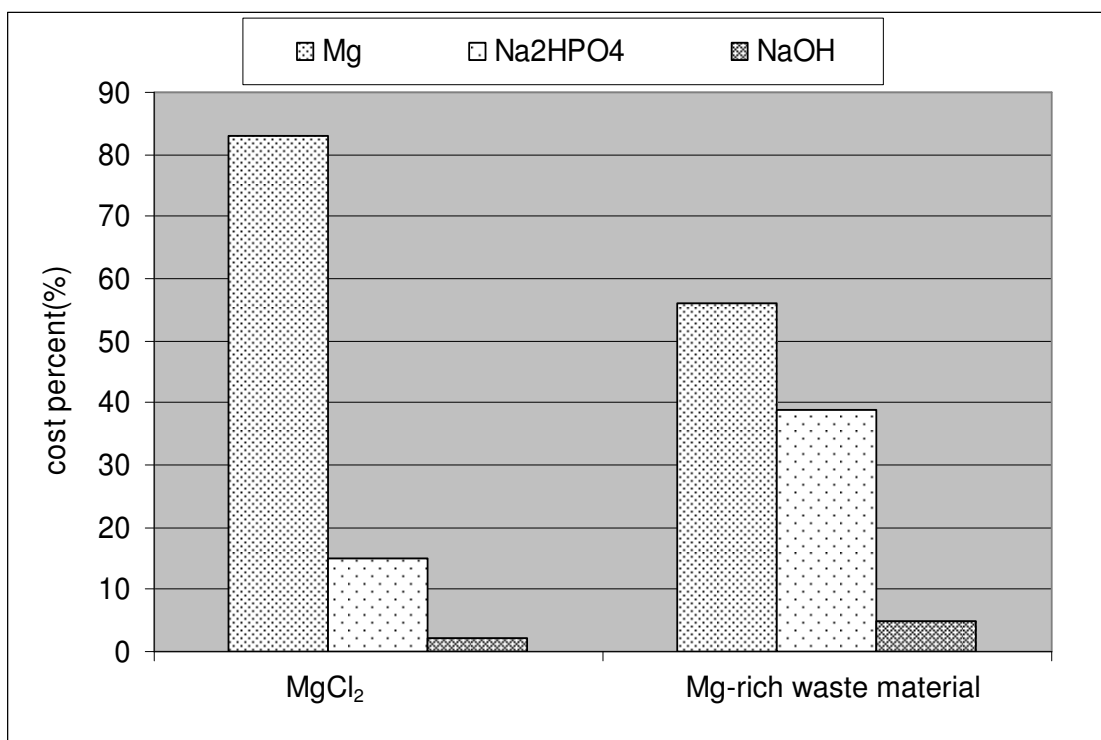


Figure 7.11: Economic comparison of Mg source using MgCl₂ and Mg-rich waste material

7.7 Chapter summary

This Chapter shows the results of Mg-rich waste material used as the magnesium source for ammonia and phosphate removal and recovery as struvite from anaerobic digester supernatant using different reaction conditions.

Based on the results, the following can be concluded:

- The reaction time test shows that precipitates formed immediately and reached equilibrium about 5 minutes using the high ammonia concentration supernatant. Over 95.00% ammonia and phosphate were removed from anaerobic digester supernatant using 10 minutes.
- Determination of the pH revealed that the pH was significant for ammonia and phosphate removal and recovery. Ammonia and phosphate removal can be achieved over 98.00% at the pH between 9.0 and 9.5. The pH of 9.5 was considered as the optimum pH.
- The magnesium dosage test found that excess magnesium dosage was not necessary for struvite formation. Increasing magnesium dosage improved phosphate removal slightly, but it is not helpful for ammonia removal.
- XRD diffraction was used for struvite confirmation and precipitate purity determination. From the results, precipitates almost match standard struvite. Ammonia and phosphate removal and recovery as struvite precipitation is a major mechanism when Mg-rich waste material was added to anaerobic digester supernatant.
- The results from economic analysis showed that the magnesium source was the main cost for ammonia and phosphate removal and recovery as struvite from anaerobic digester supernatant. The low cost Mg-rich waste

material as a magnesium source for 1 m³ supernatant can reduce the total cost to 5.71\$/L, which was cheaper 61.60% compared to MgCl₂.

Mg-rich waste material was effective for ammonia and phosphate removal and recovery as struvite precipitation. Almost all ammonia and phosphate removal was achieved when the pH and molar ratio was adjusted to the optimum conditions. It also reduced the total cost due to its cheap price.

Chapter 8 Conclusions and Recommendations for Future Work

8.1 Conclusions

8.1.1 Ammonia and phosphate removal from synthetic solutions using analytical $MgCl_2$

The results from testing mixing rates found that the mixing rate higher than 100 rpm had little effect on ammonia and phosphate removal. The reaction time test found that only 3.12% and 1.80% increase in ammonia and phosphate removal from 10 to 25 minutes. ESEM images of precipitates also indicated that increasing reaction time for more than 10 minutes has no effect on struvite crystals growth. Struvite induction time (also referred to as nucleation), defined as the time at which the initial change to pH, was found to be 1.5 minutes in synthetic solution and 0.5 minutes in anaerobic digester supernatant. The extremely short induction time in the supernatant can be due to the presence of background material in the supernatant. .

8.1.2 Ammonia and phosphate removal from anaerobic digester supernatant using analytical $MgCl_2$

The removal and recovery of ammonia and phosphate in the form of struvite from anaerobic digester supernatant using analytical grade $MgCl_2$ were investigated for different pH, reaction times and molar ratios. Assessing ammonia and phosphate removal at different reaction times, the results found that over 80.00% of ammonia and phosphate removal occur during the first 10 minutes. The removal of ammonia and phosphate increased only 6.45% and 7.07% with reaction time from 10 to 60 minutes. The results obtained showed

that the optimum pH was between 9.0 and 9.5. There were 87.79% of ammonia removal and 88.95% of phosphate removal at pH 9.0, and 88.56% of ammonia and 84.10% of phosphate was removed at pH 9.5. The removal of ammonia and phosphate with different magnesium and phosphate dosages were to determine the effect of molar ratios. It was found that an excess magnesium and phosphate dosage were not efficient or economic for ammonia and phosphate removal from the supernatant. The molar ratio of $Mg^{2+}:NH_4^+:PO_4^{3-}$ was optimized at 1.2:1.0:1.0. XRD analysis compared precipitates with standard struvite found that high pure struvite precipitation achieved at the optimum reaction conditions.

8.1.3 Struvite formation prediction using chemical equilibrium visual MINTEQ model

The third part of this project predicted struvite formation using Visual MINTEQ. Struvite formation from anaerobic digester supernatant using Mg-rich waste material was predicted at different pH and molar ratios. The concentrations of ammonium and phosphate remaining in solution after struvite formation were collected. The percentage of ammonium and phosphate removal collected and calculated. The amounts and types of solids formation after each run were collected to observe how the reaction conditions affect the purity of struvite precipitation. The pH range for struvite formation was from 6.5 to 11.5. The maximum struvite formation occurred at pH 9.5, and over 97.00% of ammonium and phosphate were removed. Other solids such as $MgHPO_4 \cdot 3H_2O$, $Mg_3(PO_4)_2$ and Brucite ($Mg(OH)_2$) could be formed struvite. Excess magnesium addition was not significant for improving the removal and recovery of ammonium and

phosphate. Almost all ammonium and phosphate can be removed at the $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ ratios of 1.0:1.0:1.0 and 1.2:1.0:1.0.

8.1.4 Ammonia and phosphate removal and recovery from anaerobic digester supernatant using Mg-rich waste material

Finally, Mg-rich waste material was used as a magnesium source to remove and recover ammonia and phosphate as struvite from anaerobic digester supernatant. Based on the results from this study, Mg-rich waste material was found to be effective in removing and recovering ammonia and phosphate in the form of nearly pure struvite product. Ammonia and phosphate removal at pH 9.5 and the $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ ratio of 1.2:1.0:1.0 reached 98.00% after 10 minutes.

Economic analysis was used for evaluating the feasibility of Mg-rich waste material as a magnesium source. It was found that magnesium source was the main cost for ammonia and phosphate removal and recovery as struvite precipitation from anaerobic digester supernatant. The total cost for the production of struvite using Mg-rich waste material can be reduced by 61.6% compared with that using analytical MgCl_2 as a magnesium source.

8.2 Recommendations for future work

This research has studied the optimum reaction conditions for ammonia and phosphate removal and recovery as struvite, and to evaluate the feasibility of Mg-rich waste material used as the magnesium source. Some research questions could not be addressed because of the limitation of time or they were

beyond the scope of this research work. Recommendation for future work including:

- Fertilizing potential of struvite. The results found in this study focus on the optimization of ammonia and phosphate removal and recovery and the feasibility of Mg-rich waste material used as the magnesium source. The laboratory study of struvite formation from anaerobic digester supernatant resulted in high purity of struvite. However, the application of struvite for vegetable growth is very important to investigate the feasibility of struvite as fertilizer. A set of pot trial tests comparing struvite precipitation with N & P model fertilizer is highly recommended in future work.
- The continuous flow reactor. Chemicals addition and the pH adjustment were designed using the batch reactor at laboratory scale in the present study. Parameter effects on ammonia and phosphate removal and recovery as struvite at continuous flow environment is significant for the application of this technique. Struvite formation in the continuous flow reactor is strongly recommended.
- Effect of magnesium dosage on induction time. The present research only studied determination of induction time using the pH change over time. The effect of magnesium dosage on induction time is recommended. In addition, further research on the rate constant of struvite formation kinetics is highly recommended.

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