Nutrient Removal and Recovery by the Precipitation of Magnesium Ammonium Phosphate

By

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A Thesis Submitted for the Degree of

Master of Philosophy

DECLARATION

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ABSTRACT

Phosphate and ammonium are the main nutrient sources in wastewater, contributing to eutrophication of water bodies. Removal of these nutrients from wastewater using conventional technologies is a challenge in water industry. Many processes have been developed to remove these two nutrients. On the other hand, phosphorus from nature is not infinite, which will be running out in about 50 – 100 years. Therefore recycling phosphorus is becoming an issue, as well as a challenge, for researchers all over the world.

This research is to investigate a chemical process technology to recover the nutrients by the precipitation of magnesium ammonium phosphate (MAP), which is valuable product and nutrient fertiliser. This is a new process based on the chemical equilibrium, which is greatly affected by pH of the solution, concentrations of Mg^{2+}, NH_4^+, PO_4^{3-}, and other ions and organic matters included in the wastewater. In order to implement this process, the optimal pH, and the best molar ratio of Mg^{2+}, NH_4^+ and PO_4^{3-} must be adequately studied.

In this thesis, the optimal pH and optimization of the molar ratio of $Mg^{2+}:NH_4^+:PO_4^{3-}$, were studied based on synthetic wastewater. It was found that the best pH range was 9-9.5, and the best molar ratio was $Mg^{2+}:NH_4^+:PO_4^{3-}=1.3:1:1.1$ Visual MINTEQ 3.0 software was then introduced to predict the possible solids precipitated and additional alkaline required in order to maintain the optimal pH value during experiments. Laboratory scale experiments were carried out under the same conditions of model input. Struvite yielded from laboratory experiments was tested and confirmed by SEM and X-ray diffraction. The results indicated that the experimental results agreed well with that of model prediction within the error deviation. Reagent addition rate and temperature were also tested in terms of removal efficiency and morphology of the precipitates. These two factors can affect size and morphology of crystals, but have limited impact on the removing efficiency compared to pH and concentration.

The main advantages of this technology are to recover nutrients and to prevent eutrophication. Preliminary results of operational factors of laboratory scale MAP system have been discussed and presented. Conclusions and recommendations were also made in this work.

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List of Abbreviations

STPs: Sewage treatment plants

SDE: Sludge dewatered effluent

WWTP: wastewater treatment plant

MAP: Magnesium ammonium phosphate

SEM: Scanning electron microscopy

XRD: X-ray diffraction

AD: Anaerobic digestion

LCFAs: Long chain fatty acids

EPA: Environmental protection agency

BNR: Biological nutrient removal

PAOs: Polyphosphate accumulating organisms

A^2/O: Anaerobic-aerobic-oxic

ICW: Integrated constructed wetland

SBRs: Sequencing bench reactors

UASB: Upflow anaerobic sludge blanket

RSM: Response surface technology

CCD: Central composite design

TS: Total solids

PS: Solubility product

HAP: Hydroxyapatite

OCP: Octacalcium phosphate

TCP: Tricalcium phosphate

DCP: Monetite

DCPD: Brushite

CBA: Cost-benefit analysis

List of Equations

Chapter 1

Introduction

1.1 Background

As a result of constantly tightening wastewater discharge limits, existing sewage treatment plants (STPs) in Australia have found themselves facing the ever increasing challenge of meeting these strict new limits using conventional technologies. Eutrophication of waters caused by nitrogen and phosphorus has become a focus of concern as they present a serious environmental issue, harming marine ecosystems and contributing to global warming (Figures 1 and 2). On the other hand, nitrogen and phosphorus are the most important and essential nutrients for plants. Hence, ability to recover and remove these highly valuable components from wastewater would contribute towards sustainable development. Apart from process efficiency, energy demand and potential greenhouse gases emissions are the critical criteria for selection of appropriate means to achieve this goal.

Sludge dewatering effluent (SDE) is a small stream from the sludge dewatering and digester processing in STPs. The SDE contains high loadings of ammonia (750-1500 mg $N–NH_4$ /L) and phosphorus (100-400 mg $P–P_3O_4$ /L). Although the SDE is only around 2% of the total flow of raw sewage, it contributes 10 - 30% of the nitrogen load and 10 - 80% of the phosphorus load, and significant operation costs to WWTPs (Jardin *et al.,* 2006). Current processes can mainly result in returning nutrients to the environment, allowing no or little recovery. For instance, SDE Bolivar STP in SA Water currently returns 600 kg ammonium /day to main stream, resulting in AUD$2940/day or AUD$1,058,400 annually if this nutrient-rich stream is treated by a conventional biological nutrient removal (BNR) process. Like many water industries in Australia, SA Water is urgently seeking a sustainable approach to not only remove, but importantly to recover the nutrients from the SDE.

Sustainability and gradual depletion of natural resources are the main reasons why nutrient recovery from wastewater has been receiving an increasing attention of researchers over the last few decades as a viable source of industrial raw material for manufacture of phosphate fertilizers or other materials (Adnan *et al.,*2003). Among others, ammonium and phosphorus can be recovered from the waste in form of magnesium ammonium phosphate (MAP, struvite). It has many uses, ranging from slow-release fertilizer, fire-resistant material or in cement. Latest studies have indicated struvite's potential application in detergent, cosmetics and animal feed. Struvite precipitates spontaneously in water environments where high concentrations of soluble magnesium, phosphorus and ammonium are present in the molecular ratio of $1(Mg^{2+}):1(NH_4^+):1(PO_4^{3-})$. Additional essential conditions are low concentrations of suspended solids and pH above 7.5 (de-Bashan and Bashan *et al.* 2004; Antakyali *et al.* 2005). As a matter of fact, uncontrolled formation of struvite fouls pipes and other inner surfaces in the treatment process, which makes the operation of plant inefficient and costly, because the struvite must be dissolved chemically or broken down manually. On the other hand, the SDE with high ammonia and phosphate contents presents a suitable source and environment for successful controlled formation of struvite. The deficient magnesium in SDE can be supplemented by addition of cheap magnesium chloride or bittern, which helps increase solution pH (Lee *et al.,* 2003). To date, struvite has been successfully harvested from wastewater at industrial scale in Japan (Ueno and Fujii *et al.,* 2001), Holland (Paques B.V. *et al.,* 2009) and USA (William *et al.,* 1999). Various design difficulties, such as precipitation and pH control, the formation of fine crystals and somewhat unfavourable economics of the process are the main issues that are yet to be resolved (Othman *et al.,* 2009). However, MAP process presents already the most potential way to recover a major part of phosphorus and to a less extent nitrogen from the SDE giving rise to a valuable product.

Figure1.1 Eutrophication problems (Algae)

Figure 1.2 Consequence of eutrophication

This thesis project investigated the main factors that could affect the precipitation of magnesium ammonium phosphate (MAP, struvite), such as the concentration of NH_4^+, PO_4^{3-}, Mg^{2+}, pH, temperature, and feeding rate. Artificial wastewater and dewatering effluent from Bolivar wastewater treatment plant (WWTP), Adelaide will be employed. Chemical equilibrium model Visual MINTEQ 3.0 was applied in this project to predict the formation of struvite and dosage of NaOH needed to maintain pH value. The results obtained in this study provide information in regards to the influences of these factors and can be used for the production trial in order to recover NH_4^+ and PO_4^{3-}. This process can mitigate the eutrophication problem, and balance nitrogen and phosphorous cycle. This technology is appraised in terms of removal and recovery of NH_4^+ and PO_4^{3-}.

1.2 Aim and objectives

This project aims to embrace the issues associated with nutrients removal within Australian sewage treatment plants and to develop a low-cost MAP process for the recovery of nitrogen and phosphorus from high-strength sludge dewatering effluent. The considered MAP process meets critical criteria, being not only highly efficient, but also environmentally sound and energetically efficient. The suggested highly efficient yet financially beneficial nutrient management scheme will be based on a combination of the most promising technology into a compact and easy to operate system. Process development will deliver process operation modelling for a pilot-scale investigation.

Objectives:

1. Survey the removal and/or recovery technologies of NH_4^+-N and PO_4^{3-}-P from wastewater.
2. Identification and optimization of operating parameters of MAP process for N and P recovery in a laboratory scale system.
3. Application of thermodynamic chemical equilibrium models to optimise the formation and crystallization of MAP.

1.3 Thesis outline

This thesis has been completed by 6 Chapters. Chapter 4 and 5, as main sections of this thesis, are prepared and presented as separated journal paper version.

Chapter 1 presents the background, project aim and objectives.

Chapter 2 focuses on the literature reviews devoted to describing wastewater treatment processes and research work that has been done by previous researchers. The effects of different factors on the process have been discussed in conjunction with materials and methods which were employed. Computer models designed and developed by other researchers to predict MAP crystallization were also discussed in this chapter. Overall, this chapter is dedicated to appraising and highlighting previous research and providing theoretical framework for this project.

Chapter 3 presents the materials and methodologies used in this project compared to the previous researches. All experiments in this work were designed specifically. Details of each experiment, including sample preparation, qualitative analysis, scanning electron microscopy (SEM) observation, and ingredients analysis were also introduced.

Chapter 4 focuses on the experimental results and discussion. This chapter details the laboratory investigations for the optimization of pH and the performance of different Mg^{2+} :NH_4^+ :PO_4^{3-} molar ratio for production of MAP and removal of NH_4^+ and PO_4^{3-}. Characteristics of struvite precipitated from synthetic wastewater were described and detected by X-ray diffraction. The size and morphology of struvite were characterised by SEM. The composition and purity of the crystallization were discussed in association with optimization studies.

Chapter 5 concentrates on the modelling of struvite precipitation process. The modelling result and experimental data were compared and discussed.

Chapter 6 draws conclusions and provides recommendations for future research in this field. Moreover, the outcomes from this research are summarized.

Chapter 2

Literature Review

2.1 Introduction

The wastewater treatment technologies have been developed and applied for more than 100 years (Speece *et al.*, 2008) since the first digester was reported in India in 1859. Other processes, such as, anaerobic digestion, aerobic digestion, composting, and incineration, have also been developed and designed for treating wastes. In addition, tertiary treatment was applied in order to recycle water, and to remove/recover nutrients from wastewater.

This chapter presents wastewater treatment technologies that have been applied to remove ammonium and phosphate. Current state of these removal and recovery processes is reviewed and summarised. The following sections will explain them in detail.

2.2 Wastewater treatment processes

Most wastewater treatment plants worldwide could be operated as a three-step process in order to make the effluent suitable for discharge or reuse. The three-step process includes physical treatment, biological treatment and tertiary treatment. A typical treatment process is sketched as shown in Figure 2.1.

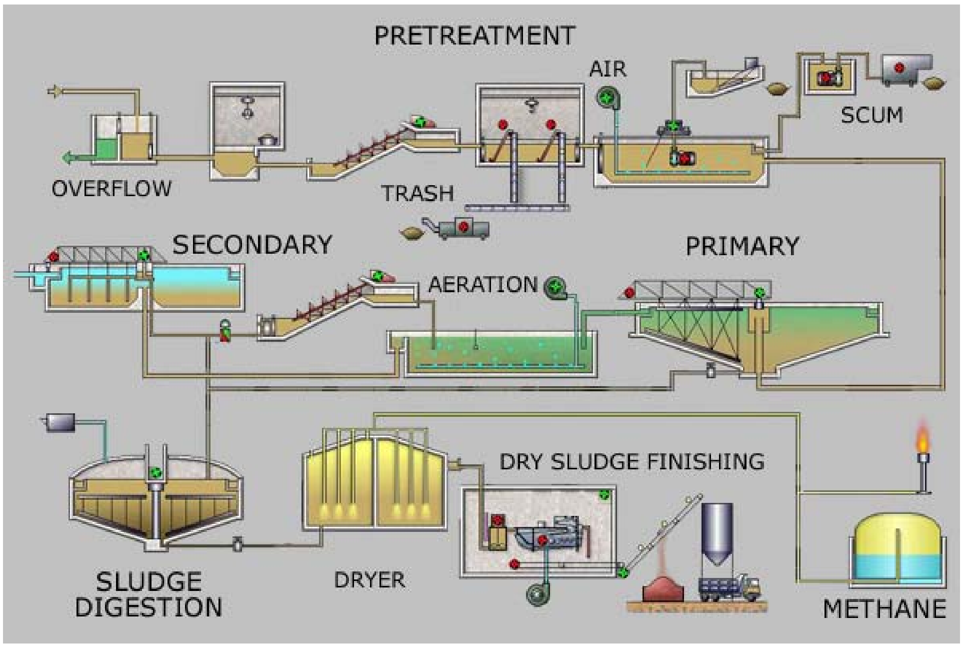

Figure 2.1 A typical large scale sewage treatment plant.

2.2.1. Physical treatment

Physical treatment is conducted by a settling or floating process which is applied to settle down suspended matters, grit, oil, and grease. Other lighter pollutants will be floating on the surface, and then membrane technologies are utilized to filtrate phosphorous particulates. In this step, part of dissolved phosphorous components as well as total suspended solids could be removed.

2.2.2 Biological treatment

A biological process can be carried out by a single and or combined system of anaerobic digestion, aerobic digestion, composting and incineration. Among them, anaerobic digestion and activated sludge are the most widely used processes/technologies when treating municipal wastewater.

Aerobic digestion

Aerobic process is a process in which bacteria consume organic matters and transform them into CO_2 and bacterial biomass. The cost of this process is normally very high because of the energy used for running blowers, pumps and motors. However, this disadvantage has been lessened by modern technology to some extent, such as aeration filter system using air. In activated sludge tanks or flocculation phases, coarse bubble diffusers are the most widely used. Diffusion systems or jet aerators could also be applied to oxidize sludge, which are cost effective, but there is plugging problem during the process.

Composting

Composting is a process that can also be considered as aerobic process. Carbonhydrates, such as sawdust, straw or wood chips, will be mixed with activated sludge with the presence of oxygen, when bacteria consume solids and carbonhydrtae sources in the wastewater, a large quantity of energy would be generated.

Incineration

Incineration is not a very commonly used process because it could generate odour, and consume additional resources to burn sludge. There are two most common systems which are stepped multiple hearth incinerators and fluidized bed incinerators. The composting process and incineration process will not be discussed in details in this thesis.

Anaerobic digestion

Anaerobic digestion (AD) process has been applied for sewage treatment for more than 100 years. The first digester was built in India in 1859 reported by Speece *et al.,* (2008). It is a well developed and the most widely used biological process applied in treatment of municipal, industrial and agricultural wastewater. The application of this technology will not be affected by the physical form and composition of the wastes. This process has been applied in many areas, such as municipal wastewater (Doĝan *et al.,* 2008), domestic wastewater (Ergüder and Demirer *et al.,* 2008), waste activated sludge (Romano and Zhang *et al.,* 2008; Demirer and Othman *et al.,* 2008), animal wastewater (Demirer and Chen *et al,* 2004; Karim *et al.,* 2005), and food waste (Kim *et al.,* 2006).

There are four phases in AD as shown in Figure 2.2, including hydrolysis/liquefaction, acidogenesis, acetogenesis and methanogenesis. A typical process was shown in Figure 2.2. In this process, the organic matters in wastewater were converted into inorganic chemicals and gas by the function of different bacteria working together. Well developed and maintained groups of bacteria will enhance the performance of converting wastewater into beneficial products, as reported by Dennis and Burke *et al.*, (2001).

In the first stage of anaerobic digestion, complex and/or insoluble organics, such as carbohydrate, proteins, fats, etc. will be transformed into sugars, amino acids and long chain fatty acids (LCFAs). Basically, the organic waste is broken into a soluble chemical form that can be used by bacteria at this stage. The bacteria which consist of obligate and facultative anaerobes are responsible for hydrolysis and removing a small quantity of oxygen applied into the digester (Parawira *et al.*, 2004). The second phase is the acidogenesis process. In this process, simpler forms of organic matters are converted into short chain fatty acids by microorganisms, such as propionic acid, Butyric acid, etc., By consuming decomposed organic matters by anaerobic digester, H_2 and CO_2 will be produced in this process (Gerardi *et al.,*2003; Parawira *et al.,*2004). Acetogenesis is the third phase, which changes higher organic acids into acetate, H_2 and CO_2. Whether the biogas is produced successfully or not is greatly impacted by this intermediate conversion because acids generated here can’t be consumed straight away by methanogens. The acetogens bacteria are the driver of biochemical reactions associated with this phase. However, they are sensitive to concentrations of organic and other operating parameters (Parawira *et al.,* 2004). The last step in this process is methanogenesis, H_2 and CO_2 and acetate produced in the acetogenesis process are utilised by methanogens to generate methane and CO_2 (Parawira *et al.*, 2004). Methanogens are also very sensitive to reaction situations and operational parameters (Parkin and Owen *et al.*, 1986).

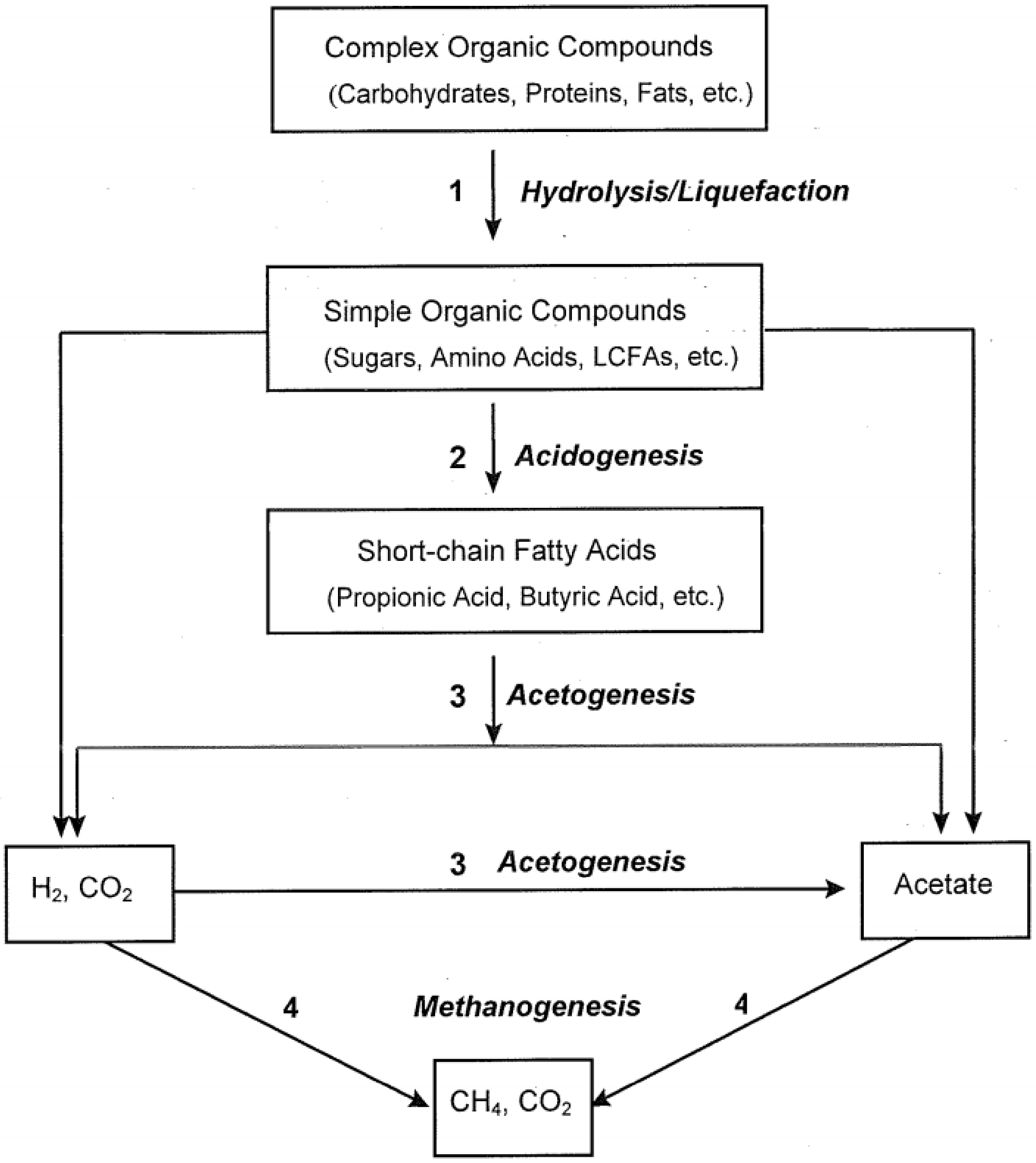

Figure 2.2 Process diagram of anaerobic digestion (Gerardi *et al.*, 2003)

The main outcome of AD and aerobic digestion is to degrade organic matters and remove carbon hydrate-based components, while nitrogen and phosphorus still remain in the sludge. According to EPA legislation, nitrogen and phosphorus must be removed in order to meet the discharge regulations.

2.2.3 Tertiary treatment

Tertiary treatment includes odour management, disinfection, filtration, lagooning, nitrogen and phosphorus removal and/or recovery. The removal and recovery of nitrogen and phosphorous has been a critical issue. It is well known that excessive amount of nutrients like NH_4^+ and PO_4^{3-} will result in severe environmental problems, such as, eutrophication, contamination of land and underground water (Battistoni *et al.*,2005; Liikanen and Martikainen, 2003; Han *et al.*,2011). Many studies have focused on the removal of NH_4^+-N and PO_4^{3-}-P from wastewater to meet EPA legislation.

Nitrogen removal

Biological and physical/chemical processes have been applied to remove nitrogen from wastewater. The main reactions in a biological process are nitrification and denitrification. Ammonification (organic nitrogen converted into ammonium nitrogen) and nitrogen uptake for cell growth (Jeyanayagam *et al.*, 2005) are recently developed biological technology for nitrogen removal. Nitrification, a two-step aerobic process, is the process for converting ammonium to nitrite, and finally to nitrate (WEF 1998). The nitrification can transform one nitrogen form to another successfully; however, nitrogen is not significantly removed in this process. In order to remove nitrogen, denitrification is introduced following the nitrification step (Tchobanoglous *et al.*, 2003). In a denitrification process, nitrate is converted to nitrogen gas by bacteria under anoxic conditions. After the denitrification process, the concentration of nitrogen is dramatically reduced as shown in Figure 2.3.

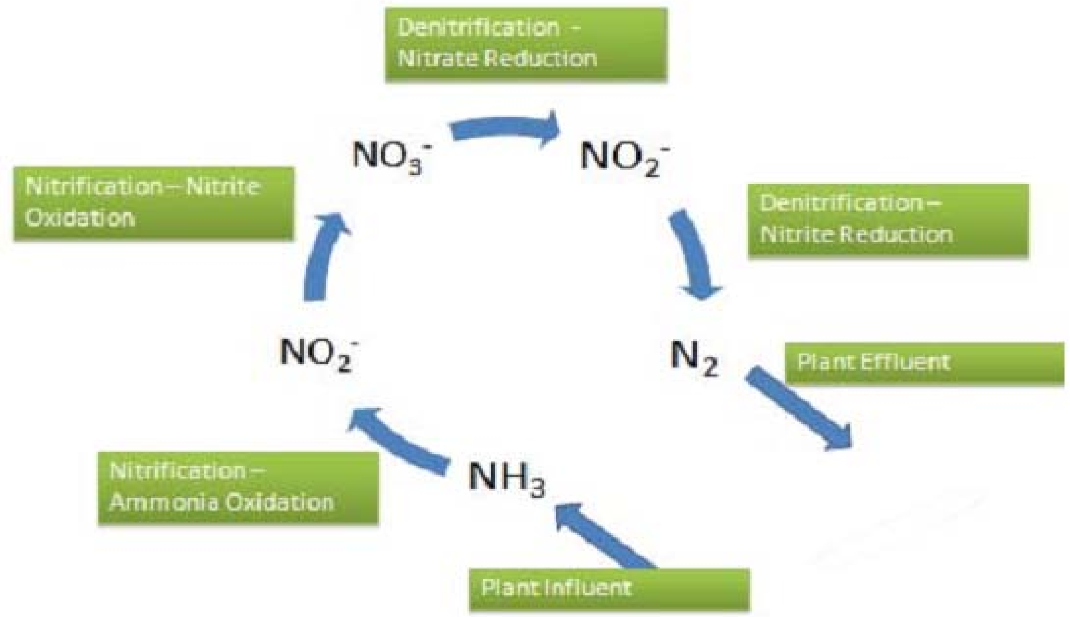

Figure 2.3 Nitrogen cycle in wastewater treatment plants (Starman *et al.*, 2009)

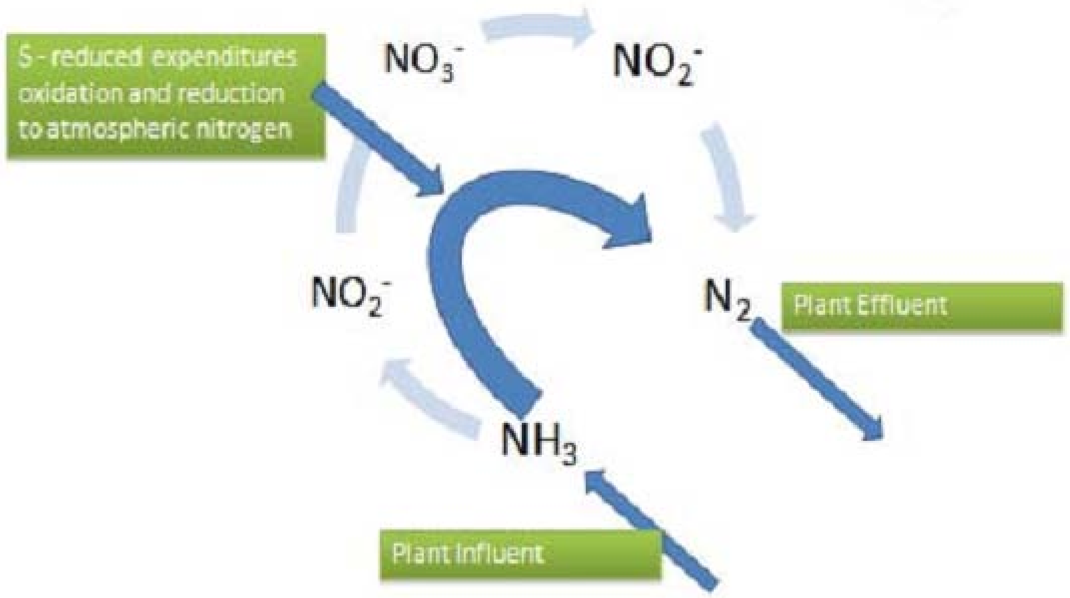

Figure 2.4 Nitrogen shortcut in enhanced biological nutrient removal (Starman *et al.*, 2009)

Anammox is a relatively new technology; the process flow diagram is shown in Figure 2.4. Anammox (anaerobic ammonium oxidation) process presents a recent innovation in the field of nitrogen removal from wastewater (Jetten *et al.,* 1999). The anammox process is the first wastewater treatment process based on notoriously slow-growing microorganisms that has reached the commercial and full-scale level (Van der Star *et al.,* 2007b). However, there are a few primary scientific challenges and technique bottleneck preventing successful mass application and widespread implementation of anammox, including low stability and long start up period of the process due to the slow growth, and inhibition sensitivity of the anammox bacteria. First, anammox bacteria are highly sensitive to nitrite and oxygen and there is a general lack of well-established guidelines for process monitoring and control (Van der Star *et al.,* 2007a). Second, the predominant practice of starting up anammox reactors is by inoculation with active biomass from already operational anammox reactors. Indeed, most operational full-scale anammox systems are centred in Europe (Van der Star *et al.,* 2008), which might not be readily amenable for repeated seeding for full-scale anammox systems elsewhere in the world, for instance, in Australia. Additionally, as the anammox bacteria are strictly anaerobes and autotrophs, they are very difficult to be cultured. To promptly establish anammox reactor systems, appropriate seeding sludge or starter cultures must be selected and used, and sufficient amount of anammox bacteria must be efficiently retained in the reactor. However, rational procedures for start-up and optimization of anammox reactors have not been developed yet (Tsushima *et al.,* 2007).

While the newly discovered anammox process opens up new possibilities for nitrogen removal from wastewater, the major obstacle for its implementation is the slow growth rate of the anammox bacteria, which makes the anammox process difficult to apply for practical wastewater treatments (Abma *et al.*, 2005). Therefore, it is essential to retain sufficient amounts of anammox bacteria in reactors. Many studies were carried out to enrich the anammox organisms, either by different methods such as biofilm or granulation (Ni *et al.*,2010), or by different types of anammox reactors, such as, sequencing batch reactors (Strous *et al.*,1998; Dapena-Mora *et al.*,2004), fluidized bed reactors (Strous *et al.*,1997), fixed bed biofilm reactors (Fux *et al.*,2004; Kindaichi *et al.*,2007; Tsushima *et al.*,2007b), up-flow anaerobic sludge blanket reactors (Ahn *et al.*,2004), membrane sequencing batch reactors (Trigo *et al.*,2006), and anammox non-woven membrane reactor (Ni *et al.*,2010). Most studies in the literature focused on the realization of anammox process in laboratory-scale reactors, while scarce research has been done on the pilot-scale to start up the process as soon as possible.

The physical/chemical nitrogen removal process consists of aeration stripping, ion exchange process and membrane separation process (WEF, 1998). Due to high cost of raw materials and maintenance, these physical/chemical processes have been not used widely and are being replaced by biological process (WEF, 1998).

In the aeration and air stripping process, the waste is first treated by air stripping; this process is shown in Figure 2.5.

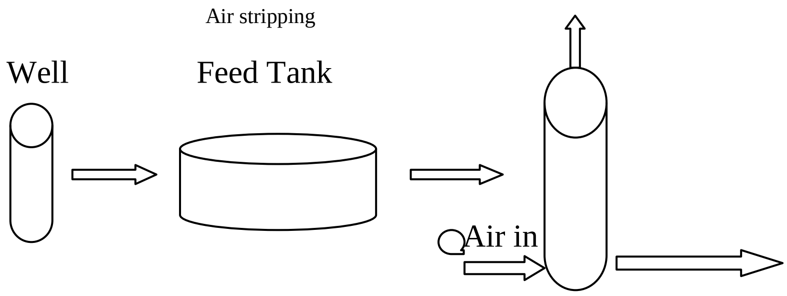

Figure 2.5 Air stripping treatment process

The air stripping process is used to eliminate high concentrations of ammonium from wastewater. If it is operated effectively, the volatile organic matter in wastewater can be removed up to 90 percent (Wikipedia, Google). However this process has some shortcomings. For example, when dissolved oxygen in water is raised to the saturation condition, it will cause the corrosion or air binding in filters. Another common problem is slow removal hydrogen sulphide and overuse of energy. Lastly is that nitrogen can't be recycled. If NH_3 is not absorbed by hydrogen sulphide or hydrogen chloride, it will be released to air which is a greenhouse gas, contributing climate change and global warming. Four main types of aerators are shown in the following Figures (Figure 2.6, 2.7, 2.8, 2.9):

Figure 2.6 Cone aerators

Figure 2.7 Draft aerator

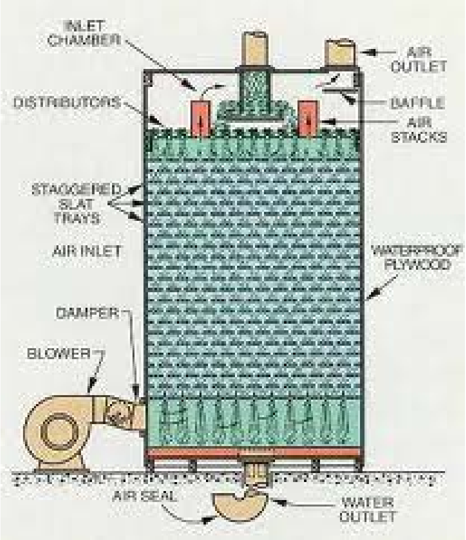

Figure 2.8 Cascade aerator

Figure 2.9 Spray aerator

In the ion exchange process, the typical ion-exchange reactions for natural and synthetic ion-exchange materials are given below (Wastewater treatment textbook):

$$Z\,Na_2 + \begin{matrix}Ca^{2+}\\ Mg^{2+}\\ Fe^{2+}\end{matrix} \Longrightarrow Z\ \begin{matrix}Ca^{2+}\\ Mg^{2+}\\ Fe^{2+}\end{matrix} + 2Na^{+} \tag{2.1}$$

Equation 2.1 Typical ion-exchange reactions (Wastewater engineering treatment and reuse forth edition).

Phosphorus removal

There are two processes applied to remove phosphorus, namely chemical process and biological process. Phosphorus can be removed by an enhanced biological phosphorus removal process. This process depends on phosphorus uptake by aerobic heterotrophs which can absorb orthophosphate much more than its growth requirements (Jeyanayagam *et al.,* 2005). The functional bacteria, named as polyphosphate accumulating organisms (PAOs), are enriched and will store large amount of phosphorus within their cells. The percentage of PAOs in the solution has great impact on the efficiency of this system.

The chemical process is based on the precipitation of phosphorus using salts. The most widely used salts are ferric and aluminium (Tchobanoglous *et al.*, 2003). Lime as an additional resource has also been applied by many investigators. Foreign reagents are added to the wastewater in this step. These ions react with PO_4^{3}-P and the reacted products settle out of wastewater. Then P is removed and stored in sludge. In addition, other methods have been developed, such as iron reactive filtration system (Möller *et al.*, 2006) and enhanced coagulation process (Woodard *et al.,* 2006). These processes can achieve as low as 0.03mg/L of phosphate in effluent (Woodard *et al.,* 2006). The chemical process can be operated in a small and compact reactor and can be operated much easily and stably compared to the biological process.

Anaerobic-aerobic-oxic (A^2/O) process and integrated constructed wetlands are very common processes to remove NH_4^+ and PO_4^{3-} (Javier *et al.,* 2010). In A^2/O process, phosphorus can be uptaken by microbial activities in an anaerobic reaction step. A large amount of phosphorus is released in the process. Polyphosphate is synthesized in the bacterial cells in vivo and stored there, finally in the sedimentation tank. The removal of phosphorus and nitrogen is achieved through sludge discharge, A^2/O system is viewed with less surplus sludge and stable operation, but with a long sludge aging time. The A^2/O system flow chart is shown in Figure 2.6.

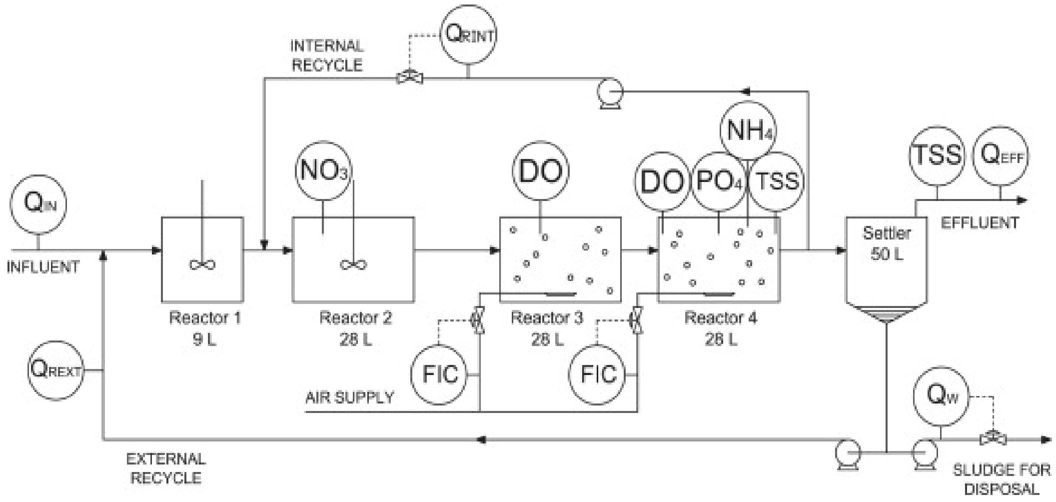

Figure 2.10 Scheme of the A^2/O simulated plant for simultaneous C/N/P removal. (Javier *et al.*, 2010)

While integrated constructed wetlands are built to remove NH_4^+-N and PO_4^{3-}-P from wastewater, this process occupies large amount of land area. However, the removal efficiency of NH_4^+-N and PO_4^{3}-P is normally low, and ammonium nitrification in saturated filtration beds is limited (Vymazal *et al.,* 2007). In addition to that, the main concern of this process is its long-term performance (Brix *et al.,* 2007). Pictures of integrated constructed wetlands are shown in Figure 2.11.

Other processes designed to remove NH_4^+-N and PO_4^{3}-P from wastewater are sequencing batch reactors (SBRs), the PhoStrip process, response surface study and electrodialysis process, etc. In this thesis, these processes won’t be mentioned in detail.

Figure 2.11 Representative integrated constructed wetland (ICW) system 11 in winter 2006: (a) sedimentation tank; (b) site overview; and (c) inlet arrangement to the first ICW cell. (Zhang *et al.*, 2008)

2.3 NH_4^+-N and PO_4^{3-}-P recovery by the precipitation of magnesium ammonium phosphate

Recently, the most intensively studied technology for recovery of ammonium and phosphate is a crystallization process through chemical precipitate reaction among ammonium, phosphate, and magnesium in wastewater. Due to this crystallization reaction, the precipitates addicted to the inner surface of pipes and resulted in blockage. Some wastewater treatment plants have experienced this blockage problem (Borgerding *et al.,* 1972; Mohajit *et al.,* 1989; Horenstein *et al.,* 1990; Mamais *et al.,* 1994, Ohlinger *et al.*, 1998). Jaffer *et al.*, (2001) performed experiments based on sewage from Slough STW, UK. They designed and operated a precipitation reactor as shown in Figure 2.12. They found that this process was very efficient to remove PO_4^{3-} from the centrifuge liquors.

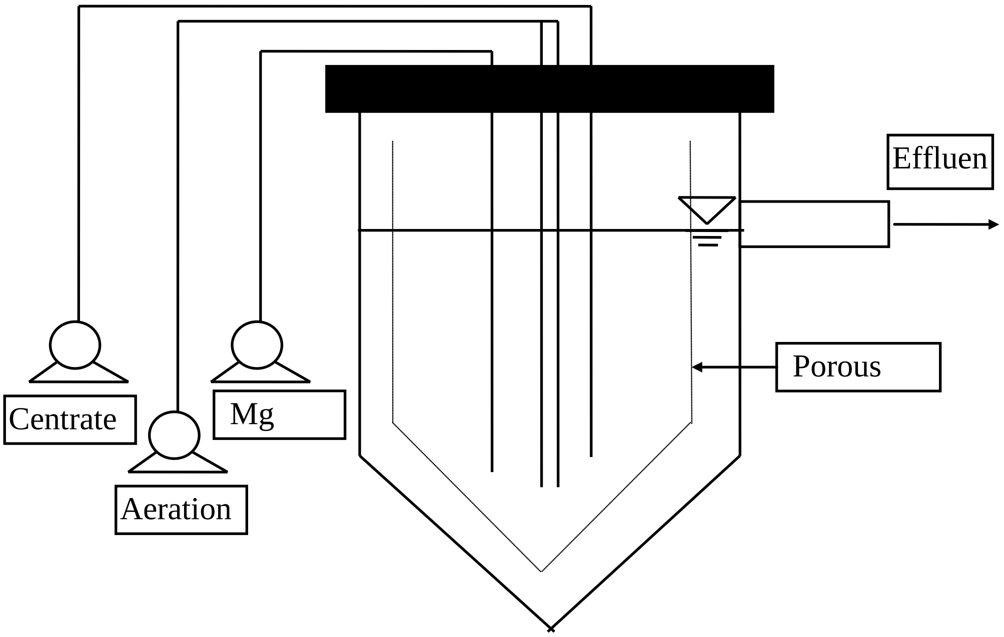

Figure 2.12 Reactor designed by Jaffer *et al.*,(2001)

The chemical species that may be formed in solution are probably $MgHPO_4 \bullet 3H_2O$ (newberyite), $MgNH_4PO_3 \bullet 6H_2O$ (MAP, struvite), $Mg_3(PO_4)_2 \bullet 8H_2O$ (bobierrite) and $Mg_3(PO_4)_2 \bullet 22H_2O$. Ca^{2+} is another most common cation, reacting with PO_4^{3-} to form following compounds: $Ca_5(PO_4)_3OH$ (hydroxyapatite), $Ca_3(PO_4)_2$ (whitelockite), $CaHPO_4 \bullet 2H_2O$ (Brushite), $CaHPO_4$ (monenite), $Ca(OH)_2$, $Ca_8(HPO_4)_2(PO_4)_4 \bullet 5H_2O$ (octacalcium phosphate). Furthermore, $MgCO_3$ (Magnesite), $MgCO_3 \bullet 3H_2O$ (nesquehonite), $CaMg(CO_3)_2$ (dolomite), $CaMg_3(CO_3)_4$ (huntite), and $Mg(OH)_2$ (brucite) may also be precipitated in the solution under certain conditions (Uludag-demirer *et al.,* 2009). Some of the chemicals, which contains NH_4^+ and PO_4^{3-} sources, can be used as fertiliser, such as $MgNH_4PO_3{\bullet}6H_2O$, $Ca_3(PO_4)_2$, especially $MgNH_4PO_3{\bullet}6H_2O$,. Not only can this method remove NH_4^+-N and PO_4^{3}-P at the same time, but also recover these two nutrients in a sustainable manner. The study of this process is becoming more and more attractive.

Previous researchers have indicated that MAP precipitation reaction could occur in different types of wastewaters as long as the concentrations of magnesium, ammonium, and phosphate reach saturation. Most importantly, this process can be applied in industrial wastewater (Diwani *et al.*, 2007), swine manure (Yetilmezsoy *et al.*, 2008), landfill leachates (Kim *et al.,* 2007), sewage (Jaffer *et al.,* 2001), and semi-conductor wastewater (Warmadewanthi and Liu *et al.,* 2009). Diwani *et al.,* (2007) tested and applied MAP cakes obtained from synthetic wastewater and industrial wastewater to fertilise grass in the field. Their results appraised the application of MAP as a fertilizer. Yetilmezsoy *et al.,* (2008) applied struvite precipitated from effluent of UASB treating poultry manure wastewater to three testing plants. Their results indicated that the struvite recovered from the sludge could be used as a valuable fertilizer for agriculture. Landfill leachates have been applied by Li *et al.,* (1999) and Kim *et al.,* (2007) to precipitate struvite in Hongkong. They found that large amount of ammonium could be crystallized by adding foreign Mg source with the pH controlled at 8.5 and 9. Another study performed with anaerobic swine lagoon effluent to precipitate struvite has proven that struvite solubility can be minimised by increasing the Mg^{2+}/PO_4^{3-} ratio with the pH value at 9 (Nelson *et al.,* 2000). By conducting laboratory and field experiments with swine waste, Burns *et al.,* (2001) found that when $MgCl_2$ (64%) was added to the waste pond, the soluble phosphorous was reduced 76% and 90% in laboratory and field experiments respectively.

Human urine has been studied by applying freezing-thawing method and MAP precipitation method (Ganrot *et al.*, 2007). The experiment results revealed that freezing-thawing could affect the removal of ammonium, and the removal of NH_4^+ and PO_4^{3-} was affected by the addition of MgO. Etter *et al.*, (2011) also worked on human urine in Nepal by fabricating his own reactor (Figure 2.13) to remove NH_4^+ and PO_4^{3-}. They concluded that a low cost and high efficient reactor could be applied and fabricated in Nepal to remove NH_4^+ and PO_4^{3-} from human urine based on tests on the granulation of struvite at laboratory scale and flocculation based on five different flocculants. It can be drawn that this technology is applicable to remove NH_4^+-N and PO_4^{3-}-P from urine, leather tanning wastewater (Tunay *et al.*, 1997) and agro-industry wastes (Moerman *et al.*, 2009).

Other reaction process or reactors have also been developed and used in order to remove NH_4^+-N and PO_4^{3-}-P effectively and efficiently. The following reactors are applied by researchers (Shown in Figure 2.14, 2.15, and 2.16).

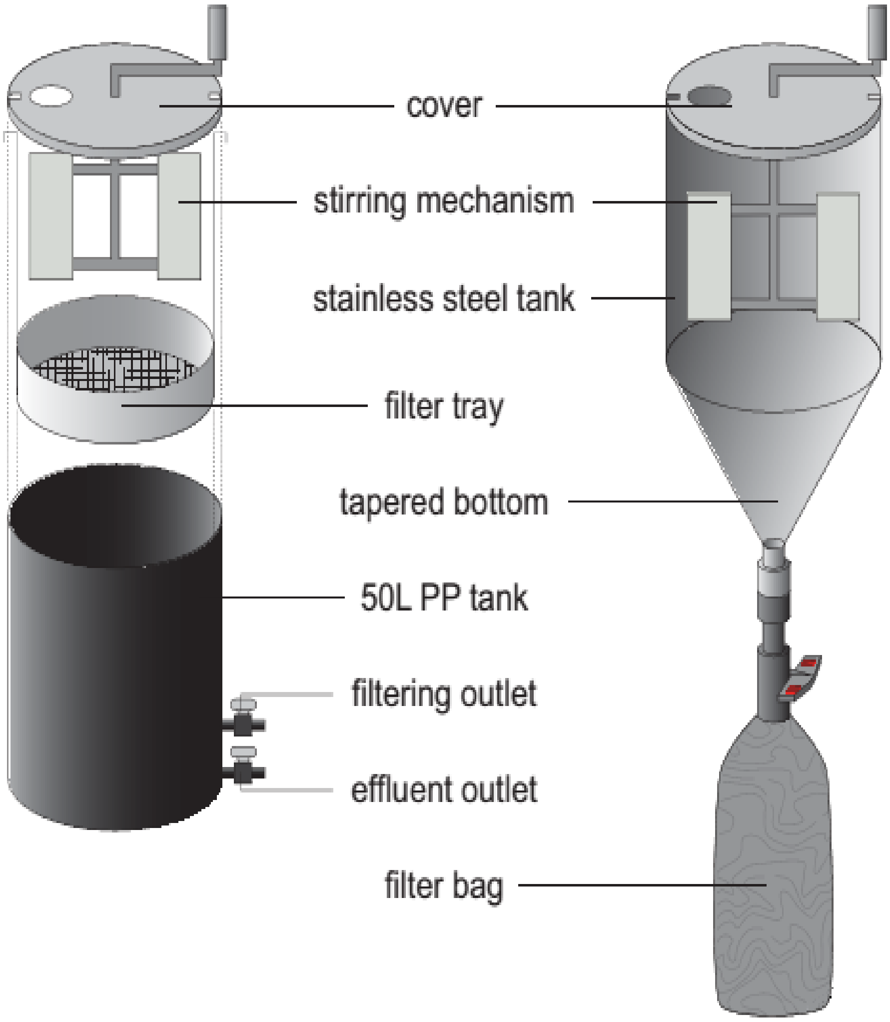

Figure 2.13 Reactor fabricated by Etter *et al.,* (2011)

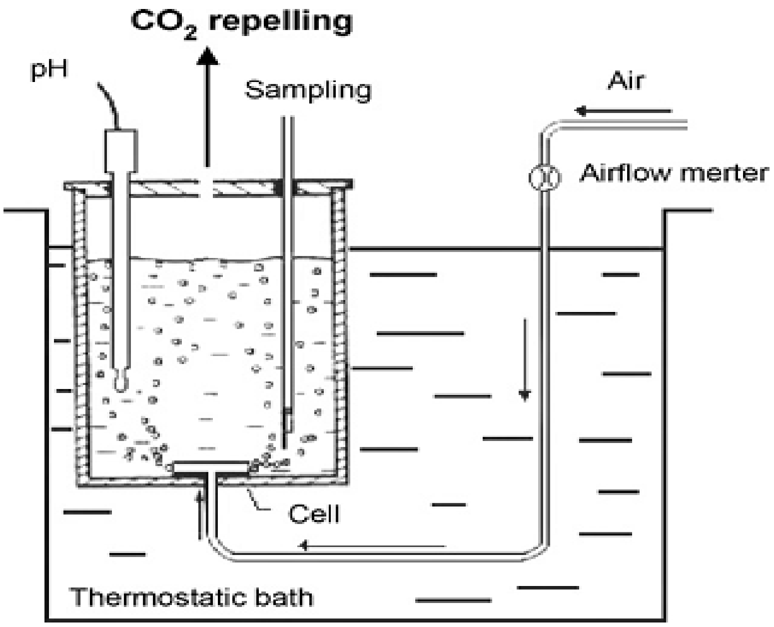

Figure 2.14 Reactor applied by Korchef *et al.*, (2011)--dissolved carbonate removal technique.

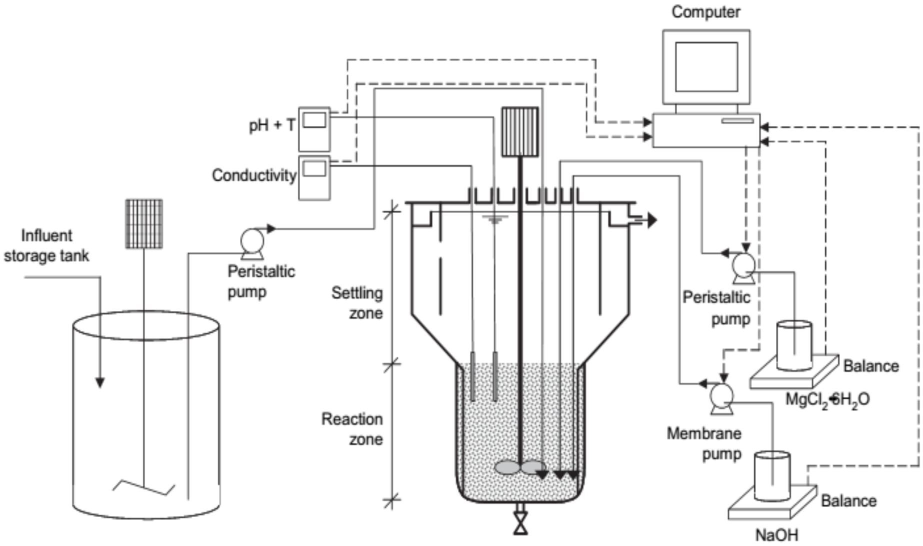

Figure 2.15 Crystallization pilot plant developed by Martí *et al.*, (2010)

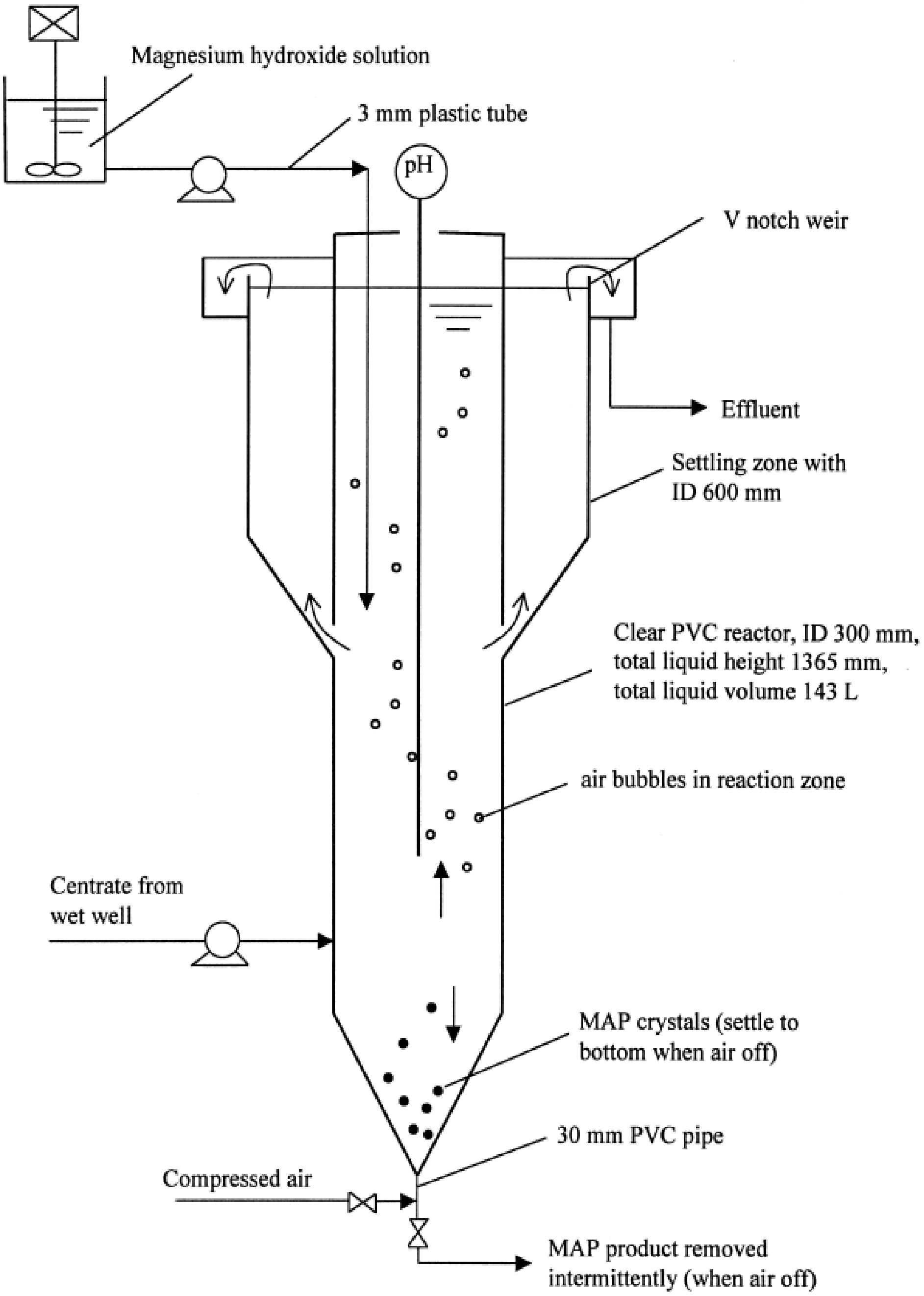

Figure 2.16 Reactor designed by Münch *et al.*, (2001)

2.4 Factors influencing MAP precipitation process

The principle of recovering magnesium ammonium phosphate in precipitation process can be stoichiometrically described as the following reaction equation (Michalowski *et al.,* 2006):

$$Mg^{2+} + NH_4^{+} + H_nPO_4^{n-3} + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O \downarrow + n\,H^{+} \qquad (2.2)$$

($n=0, 1, 2$. n depends on the pH of the solution.)

Many studies have been done to develop and operate a precipitation process by adding additional reagents at equilibrium conditions (Burns *et al.,* 2001; Jaffer *et al.,* 2001; Celen *et al.,* 2007; Altinbas *et al.,* 2002; Uludag-Demirer *et al.,* 2005). Equation 2.2 shows that the stoichiometric molar ratio of Mg^{2+} :NH_4^{+} :PO_4^{3-} is 1:1:1, and this reaction is highly pH dependent. Factors affecting this formation process are pH of the solution, the concentrations of Mg^{2+}, NH_4^{+}-N and $H_nPO_4^{n-3}$ ($n=0, 1, 2$), temperature, reagent addition rate of foreign reagents, and stirring rate.

pH

pH is a predominant operating factor which has significant impact on driving the precipitation reaction, and importantly precipitate formation and crystallization. In order to maximize the struvite formation efficiency and purity, pH must be maintained at certain range. The effect of pH on the crystallization process has been studied by Zhang *et al.,* (2009), Abbona *et al.,* (1982) and Nelson *et al.,* (2003). Based on laboratory experiments, a critical pH value 5.85 was reported by Abbona *et al.,*(1982). At pH lower than 5.85, newberyite was precipitated first, while struvite was formed first when pH was higher than 5.85. Zhang *et al.,* (2009) conducted experiments with landfill leachates with the molar ratio of Mg^{2+}: NH_4^{+}: PO_4^{3-} = 1:1:1.

They found that the optimal pH was 9.5. NH_4^+ removal efficiency was lower at pH < 9.5. However, $Mg_3(PO_4)_2{\bullet}22H_2O$ and $Mg(OH)_2$ rather than struvite were crystallized when pH was higher than 9.5. Nelson *et al.,* (2003) compared results of experiments from two treatment plants and found that the best pH value for struvite precipitation was 8.9 and 9.25 respectively, he also reported that the best pH was not affected by the molar ratio of Mg^{2+} : PO_4^{3-} removal was significantly affected by pH.

The optimal pH has been investigated by previous researchers for the precipitates process, Diwani *et al.,* (2007) observed the best pH was 9.6 with a range of 9-10 in their experiments. Zhang *et al.,* (2009), Nelson *et al.,* (2003), and Abbona *et al.,* (1982) recognized the pH of the solution dropped immediately once the reaction happened. In order to maintain the precipitation reaction in a continuous process with a stable high yield of struvite, additional alkaline needs to be added to adjust the pH. They also reported other crystals would be precipitated if the pH was too high. This result agreed well with that reported by Buchanan *et al.,* (1994) who found that the minimum struvite solubility was at pH 9. However, in consideration of ionic strength, reaction constant (k_{sp}) and magnesium complexes, the minimum solubility for struvite was 10.3 as reported by Ohlinger *et al.,* (1998). The best pH 10.7 was also obtained by Stumm and Morgan *et al.,* (1970). Tunay *et al.,* (1995) has found that a suitable pH range was 8-10. However, based on laboratory-scale experiments, pH between 9.94 and 13.26 has been confirmed by Shin and Lee *et al.,* (1997). In general, high removal efficiency can be achieved in the range of pH between 8 and 13. This is also the benchmark for pH consideration when experiments were performed in this project.

Magnesium source and concentration

The effect of Mg^{2+} concentration in solution has been widely investigated (Nelson *et al.,* 2003, Quintana *et al.,* 2005). Zhang *et al.,* (2009) did experiment with the fixed molar ratio of NH_4^+ and PO_4^{3-} as 1:1. When the molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-} was increased from 1:1:1 to 1.25:1:1, the removal efficiency of ammonium increased and then dropped, which meant the concentration of Mg^{2+} could affect precipitation reaction, therefore the removal efficiency. Zhang *et al.,* (2009) compared different chemical combinations of Mg^{2+} and PO_4^{3-}, and concluded that the combination of $MgCl_2{\cdot}6H_2O$ + $Na_2HPO_4{\cdot}12H_2O$ could lead to the highest ammonium removal. Pastor *et al.,* (2008) reported that the removal efficiency can be higher than 80% and would be increased further by increasing the $Mg/H_nPO_4^{n-3}$ ($n=0, 1, 2$) molar ratio. Lee *et al.,* (2009) also found that continuous formation of struvite can be obtained when the molar ratio of magnesium and phosphate salts is either more than 0.07m (Mg^{2+}/ PO_4^{3-}) or less than 0.05 M (Mg^{2+}/ PO_4^{3-}). Quintana *et al.,* (2005) pointed out that the amount of struvite increased with an increase in magnesium concentration under magnetic stirring and aeration. In light of cost, normally a slight extra Mg^{2+} source can be added to ensure a high removal efficiency of NH_4^+ and PO_4^{3-}.

Ammonium concentration

There might be sufficient NH_4^+ available in the waste effluent if it is used for MAP formation. Thus, addition of ammonium sources may be unnecessary. However, the concentration of NH_4^+ could be important in terms of struvite formation and crystallization. Zhang *et al.,* (2011) investigated the effect of NH_4^+ concentration on the crystallization process for NH_4^+ recovery by applying the thermodynamic modelling of PHREEQC programme. He found that the saturation index of MAP is affected by Mg^{2+}/ NH_4^+ molar ratio and the initial NH_4^+ concentration. Generally, NH_4^+ removal is slightly complicated under neutral and/or alkaline conditions, if Mg^{2+} concentration is supersaturated. NH_4^+ would be removed in two ways, as shown in Equation 2.3 (Korchef *et al.,* 2010).

$$(NH_4^+)_{\text{total removal}} = (NH_4^+)_{\text{removal by MAP}} + (NH_4^+)_{\text{removal by volatilization}} \tag{2.3}$$

Phosphate concentration

The concentration of phosphate is also a critical parameter which affects the MAP formation process. A high concentration of phosphate would result in increasing removal efficiency of Mg^{2+} and NH_4^+ while keeping the concentration of Mg and ammonium constant. The phosphate concentration decreases with the increase in pH and molar ratio of Mg^{2+} :PO_4^{3-} (Nelson *et al.,* 2003). Zhang *et al.,* (2009) found that the increase in the concentration of phosphate could result in reducing the concentration of NH_4^+ in the residual. However, phosphate could react with other metals, which will cause the impurity of MAP. Korchef *et al.,* (2010) suggested that the effect of phosphate concentration on the formation process still needs further study especially when magnesium concentration is kept constant.

Feeding sequence

When the constituent ions reach their saturation, the crystallization takes place in this MAP precipitation process. However, the feeding sequence of foreign reagents could have a significant impact on the purity of crystals (Michalowski *et al.*, 2006). Kim *et al.*, (2006) proposed that the feeding sequence would affect the performance of precipitation process. They designed eight experiments with different feeding sequences as shown in Table 2.3. Their results showed that high pure struvite could be obtained by adding Mg^{2+} and PO_4^{3-} before pH control. Kim *et al.*, (2006) also discovered that seed addition enhanced struvite precipitation in his experiment.

Table 2.1 Experiments designed by Kim *et al.*, (2006) to determine the effect of feeding sequence.

Experiment	Addition sequence
A1	pH$\rightarrow Mg^{2+} \rightarrow PO_4^{3-}$
A2	pH$\rightarrow PO_4^{3-} \rightarrow Mg^{2+}$
A3	pH$\rightarrow Mg^{2+}$ and PO_4^{3-}
A4	$Mg^{2+} \rightarrow$pH$\rightarrow PO_4^{3-}$
A5	$PO_4^{3-} \rightarrow$pH$\rightarrow Mg^{2+}$
A6	$Mg^{2+} \rightarrow PO_4^{3-} \rightarrow$pH
A7	$PO_4^{3-} \rightarrow Mg^{2+} \rightarrow$pH
A8	$Mg^{2+}$and $PO_4^{3-} \rightarrow$pH

Stirring rate

The effect of stirring rate on the MAP precipitation has been investigated by some researchers (Wilsenach *et al.,* 2007, Kim *et al.,* 2009, Fattah *et al.,* 2008). In general, the stirring rate can shorten the reaction time. However, the crystal solids in the precipitating solution needs a longer time to settle down. Benisch *et al.,* (2002) announced that the precipitation process started from the nucleation of crystal embryos, followed by crystal growth. Pastor *et al.,* (2010) stated that the AMP formation could be completed by two steps: nucleation process and crystallization process, leading to a very complex mechanism controlled by physical--chemical factors. These parameters are pH, concentration of Mg^{2+}: NH_4^+: PO_4^{3-} , temperature, the presence of other ions, and stirring speed. Ohlinger *et al.,* (1999) also studied the formation kinetics using artificial solutions and wastewater. They found out that the nucleation process was a reaction-controlled process, which was basically affected by the saturation of the solution, while crystal growth rate was transport-controlled. Nelson *et al.,* (2003) studied the formation kinetics of struvite using anaerobic swine lagoon liquid by using a continuously stirred batch reactor. Laboratory experiment results showed that the first order reaction expression is the following Equation 2.4, and then the linear first order equation (Equation 2.5) was obtained by integrating Equation 2.4:

$$-\mathrm{d}C/\mathrm{d}t = k\,(C - C_{\mathrm{eq}}) \tag{2.4}$$

$$\mathrm{Ln}(C - C_{\mathrm{eq}}) = -kt + \ln\,(C_0 - C_{\mathrm{eq}}) \tag{2.5}$$

Uludag-Demirer *et al.,* (2009) also investigated the kinetics of the AMP formation. There are two reaction orders recognized. Order 1 was based on phosphate (Ohlinger et al, 2000 and Nelson *et al.,* 2003) and Order 2 was based on the concentration of magnesium (Rahaman et *al.,* 2008) at the pH of 8.3, 8.5 and 8.7, respectively. Ohlinger *et al.,* (1999) discovered that the accumulation of the struvite didn't follow the nucleation kinetics but growth kinetics, which imply that the super saturation degree can accelerate the nucleation speed and well stirring could expedite the crystal growth.

Zhang *et al.,* (2009) proposed the kinetics of chemical process as Equation 2.6.

$$-\frac{\mathrm{d[C]}}{\mathrm{dt}} = \mathrm{k[C]^n} \qquad (2.6)$$

Based on Equation 2.6, rate law for the first order, the second order and the third order reactions can be expressed in the following equations:

First order: $\ln\,[C] = \ln\,[C]_0 - kt,$ (2.7)

Second order: $\frac{1}{[C]} = \frac{1}{[C]o} + kt.$ (2.8)

Third order: $\frac{1}{2[C]2} = \frac{1}{2[C]o2} + kt.$ (2.9)

The kinetics for MAP formation was studied based on the above equations by applying landfill leachates in Zhang's study (2009), who found that the kinetic of this process was a first order kinetic model. Other kinetic models studied by researchers are summarised in the following Table 2.2.

Table 2.2-The kinetic parameters calculated for MAP formation in different studies.

Type of wastewater	Mg:N:P	pH	Ion measured in the study	Order of the reaction	Rate constant of the reaction	References
Synthetically prepared wastewater	1.3:42.9:1	8.5	PO_4^{3-}e	1	213 /h	Rahaman et al., (2008)
Effluent of anaerobic digester treating Molasses	1:1:1	8.5	Mg^{2+} e	2	17.76*103L/mol h	Turker and Celen(2007)
Anaerobic swine	1.9:15.3:1	8.4	PO_4^{3-}e	1	3.7/h	Nelson et al., (2003)
Lagoon liquid	2.8:28.3:1	8.7			7.9/h	
	3.2:36.2:1	9			12.3/h	
Municipal wastewater	1:1:1	8.3	PO_4^{3-}	1	4.2/h	Ohlinger et al.(2000)

Temperature and other parameters

In addition to pH and concentrations of Mg^{2+}, NH_4^+ and $H_nPO_4^{n-3}$, some other operating parameters such as temperature were also studied by previous researchers. Abbona *et al.,* (1982) found that the majority of crystallization was newberyite rather than struvite when the temperature was risen from 25 ºC to 37 ºC. Temperature affects the solubility of chemicals and reaction activities in the solution. Supersaturation (Ren *et al.*,2010, Ali *et al.*,2008), nature of materials (Somathilake *et al.*,2009, Parsons *et al.,*2008), heavy metals, and other ions including Ca^{2+} and sulphate (Kim *et al.*,2009, Hao *et al.*,2008) will also have impact on the precipitation process. All these parameters need to be considered carefully when the precipitation process is conducted using wastewater.

2.5 Characteristics of struvite

Struvite is a type of white or light yellow crystal that is sparingly soluble under neutral and/or alkaline conditions. It is a valuable product with slow-releasing activities. An image of struvite crystal is shown in Figure 2.17:

Figure 2.17 Picture of pure struvite crystals

However, further study of MAP particles shows that the morphologies of struvite are quite different under different situations, especially when other ions co-exist. The sizes are different based on different wastewaters and different precipitation conditions. Figures 2.18, 2.19, 2.20, 2.21 are a few of examples of struvite images presented from different researchers.

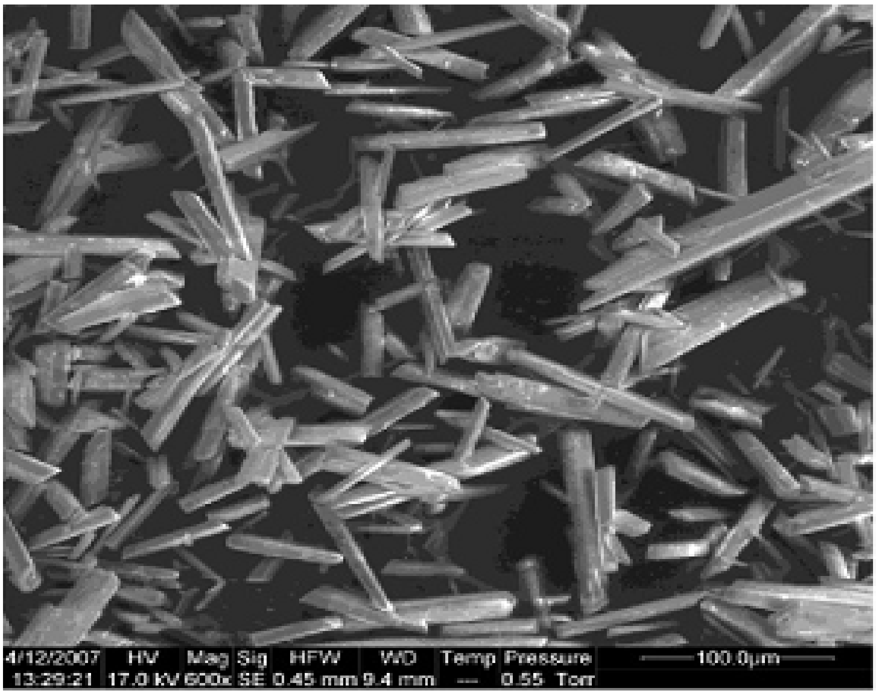

Figure 2.18 SEM Images of struvite obtained by Korchef *et al.*,(2011) in his experiments

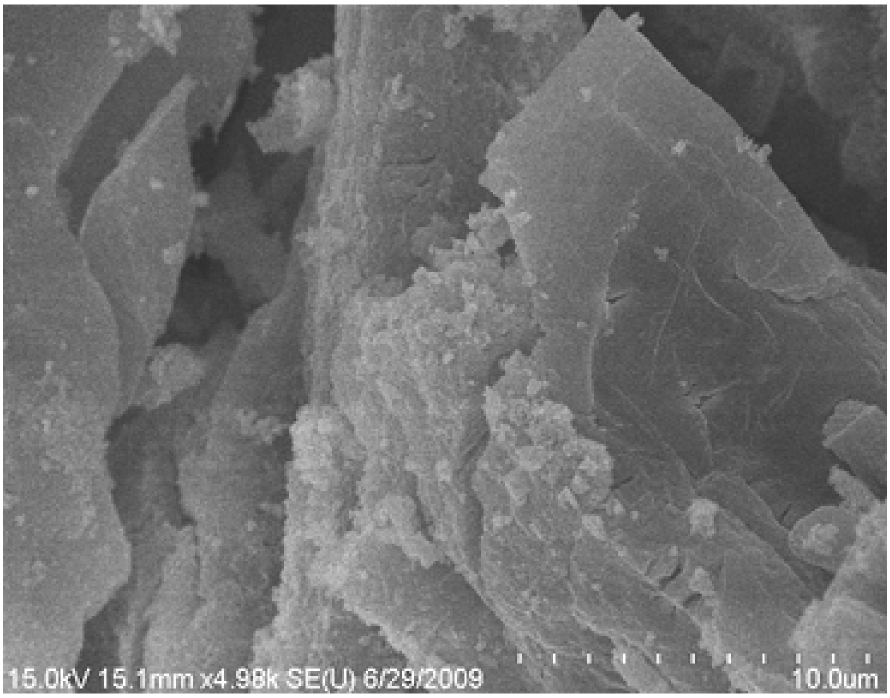

Figure 2.19 SEM Image of struvite obtained by Ye *et al.*,(2010) in his experiments.

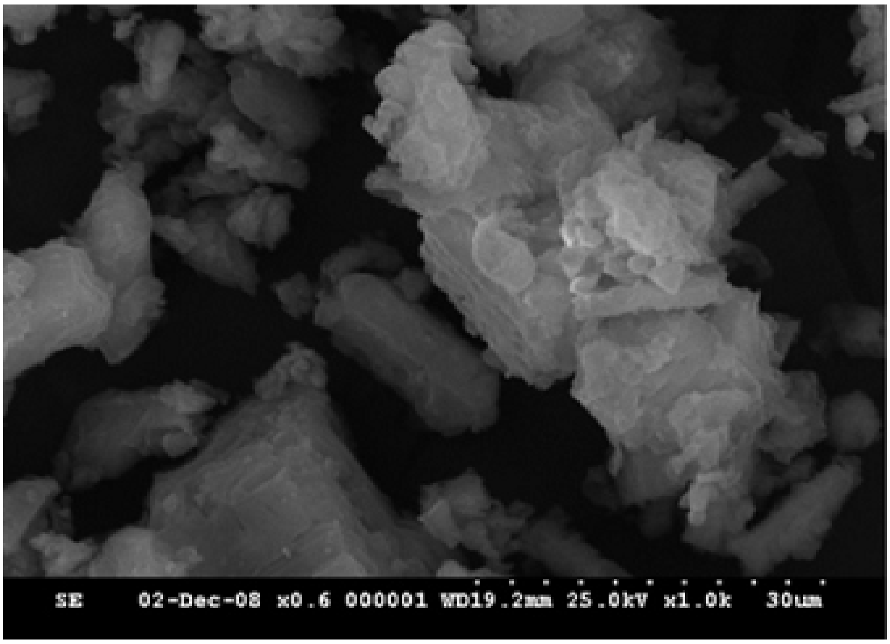

Figure 2.20 SEM Image of struvite recovered from swine wastewater by Rahman *et al.,* (2011)

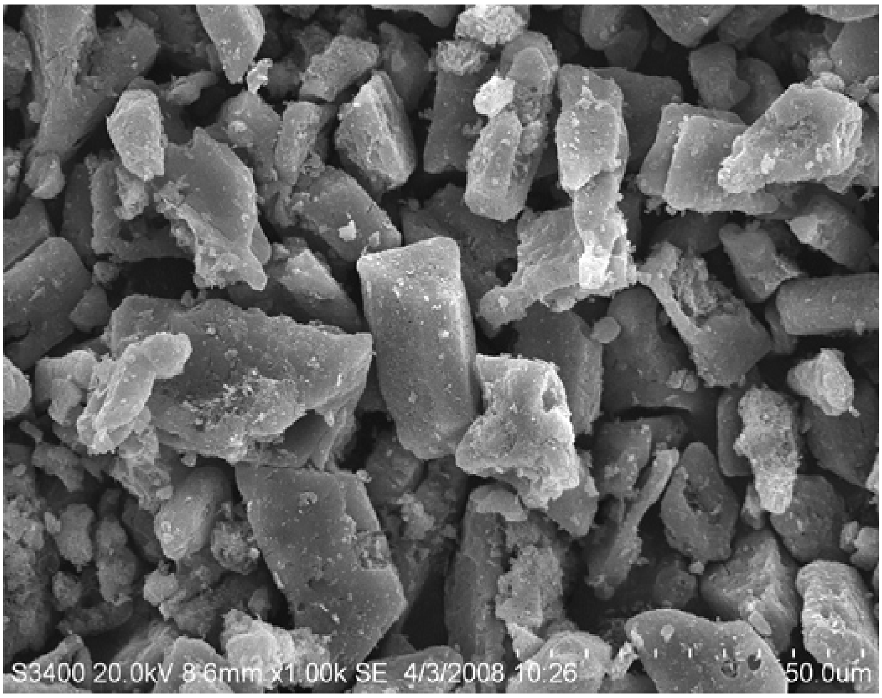

Figure 2.21 SEM Image of struvite recovered from landfill leachates by Zhang *et al.,* (2009)

It can be seen that the morphology and size of struvite obtained from different wastewater could be variable, which are affected by the initial concentration of Mg in solution (Diwani *et al.,* 2007). Le Corre *et al.,* (2005) suggested that the properties of the final products can be monitored by applying optimal conditions, such as pH, concentrations of Mg^{2+}, NH_4^+, and PO_4^{3-}, stirring rate, and feeding rate.

2.6 Economic value of struvite

Struvite is slightly soluble under neutral and/or alkaline conditions. It can be applied as a slow releasing fertilizer with less loss of NH_4^+ and PO_4^{3-} in soil (Yetilmezsoy *et al.*, 2009; Shimamura *et al.*, 2003; deBashan and Bashan *et al.,* 2004). As a nitrogen and phosphorus rich fertilizer, very promising results have been obtained in the field trials to grow plants. Furthermore, the leaching loss after struvite was tested in different kind of soils by Rahman *et al.*, (2011), who designed a reactor, as shown in Figure 2.22. They concluded that the N and P loss were very low, and struvite was a very useful and eco-friendly fertilizer. It also can be applied in flooded areas because it has slow-releasing activities.

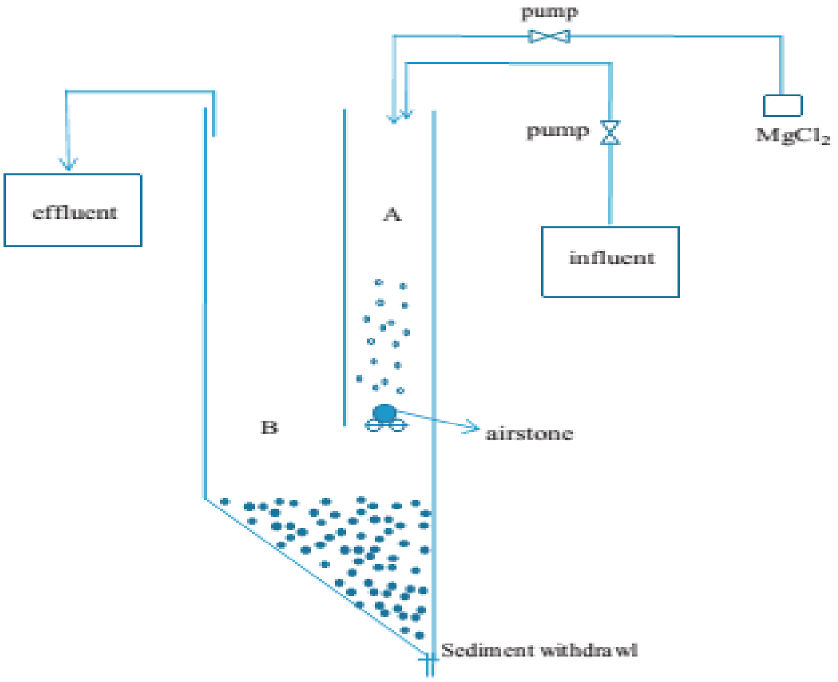

Figure 2.22 Reactor designed by Rahman *et al.*, (2011) to recover NH_4^+ and PO_4^{3-}

From greenhouse studies using struvite and other fertilizers, Massey *et al.*, (2009) also suggested that struvite was the most effective one in different soils at pH levels. Diwani *et al.*, (2007) also conducted greenhouse experiments with three different categories. Their result shows that struvite is fertile, economic and green fertiliser to the environment. In order to apply for this process, the technical feasibility and pilot plant process must be studied and discussed as performed by previous researchers (Elliott and O'Connor *et al.*, 2007; Pastor *et al.*, 2008; Yen *et al.*, 2010).

Currently, MAP has been produced in Unitika, Japan and sold to American company. However, some technical parameters and process costs still need to take into more consideration, including sales forecast, operating cost, sales price of MAP, pricing service and financial outcomes (Münch *et al.*, 2001), before this technology is applied as a large industrial process. Münch *et al.*, (2001) developed his own reactor (Figure

2.16) to analyse the cost of this process. These factors were the economic feasibility which has not been considered widely (Paul *et al.,* 2001; Jeanmaire and Evans *et al.,* 2001; Shu *et al.,* 2006; Berg *et al.,* 2006; Dockhorn *et al.,* 2009).

The major concern in terms of cost, when applying struvite precipitation process for nutrients recovery, should be the foreign Mg resource added to the wastewater, the reagents used to adjust pH of solution, and the maintenance of operations (Li *et al.,* 2008). Struvite can be used as fertilizer and it has very promising value. Hence, it can be considered for recycling to gain value to balance some cost. Based on the additional chemicals only and three assumptions could be made as: 1) the concentration of PO_4^{3-} in the influent is 100mg/L; 2) the molar ratio of Mg^{2+}: PO_4^{3-} was fixed at 1.3:1; 3) pH at 9. Jaffer *et al.,* (2001) estimated that the main cost was the use of sodium hydroxide (Table 2.5), Jaffer *et al.,* (2001)recognised that this could be a challenge which needs to be conquered because the alkalinity of wastewater is normally high.

Schulze-Rettmer *et al.,* (1991) reported that the cost of applying MAP precipitation process was similar to what is needed to treat 1 m^3 wastewater with nitrification and denitrification process. Siegrist *et al.,* (1994) suggested the cost estimation of applying this precipitation process and maintenance must be based on pilot scale study and the overall cost was approximately 20% higher than that of in air stripping process. Moreover, labour cost and electricity cost should also be considered. The benefit of this process is not only the removal and recovery of nitrogen and phosphorous, but also contributes to the environment sustainability.

Table 2.3 Summary of costs for a full-scale plant (Jaffer *et al.*, 2001).

Mg Source	Reactor pH	Cost of NaOH	Cost of Mg	Possible income from struvite	Average P removal (min-max)
mg L^{-1}		£1000 y^{-1}	£ 1000 y^{-1}	£ 1000 y^{-1}	%
$MgCl_2$	9	45	16.4	11.6	95 (94-97)
	8.5	19	16.4	11.2	92 (91-94)
	7.5	0	16.4	9.8	80 (71-88)
$Mg(OH)_2$	8.5	0	8.2	9.5	78 (68-91)

Any processes related to sustainability should not only consider internal impacts, but also the external impacts, such as socio-culture and economic influence (Molinos-Senante *et al.*, 2011). Internal impacts are those factors that can be measured by monetary, such as cost for chemicals, electricity, labour, capital and operation and etc. The external impacts are the economic level benefits, saving phosphorous resource, preventing eutrophication and land contamination, making the earth more sustainable in the long run. Molinos-Senante applied cost-benefit analysis (CBA) methodology, and a series of equations used are as followings:

$$NP=B1+B2 \tag{2.10}$$

NP: Net profit, B1: Benefit 1, B2: Benefit 2

$$B1=\sum_{t=0}^{T}[(APRt*SPPt)+(ASRt*CSMt)+(ARRt*CRt)+(ADRt*CCDt)-(ICt+OMCt+FCt)] \tag{2.11}$$

After consideration of internal and external factors, Molinos-Senante concluded that this process is definitely worth to be promoted. In addition as fertiliser, MAP can also be used as cleaning product and other chemistry materials. The following Table 2.6

was provided from Unitika Japan. Compared the expenses of two processes, it can be seen that MAP process is a promising technology. However, how to make this technology it technically more feasible economical beneficial for an industrial process using waste streams is still a challenge being faced now.

Table 2.4 Economical comparison of phosphorous removal process (Unitika Japan)

		MAP process	Coagulation Addition Activated Sludge Process
Operation cost	1. electricity 2. chemical disposal of sludge	10,100EURO/Y 49,300EURO/Y	900 EURO/Y 102,000 EURO/Y 95,400 EURO/Y
Sales profit of MAP		32,100EURO/Y at 210EURO/ton	
Total		27,300EURO/Y	198,300 EURO/Y

2.7 Modelling of precipitation process of magnesium ammonium phosphate

Models have been useful to provide improved understanding and operation solutions where questions can’t be solved solely by experiments or reduce laborious experiments. In order to estimate the possibility of this chemical process, there are two kinds of basic models have been applied to optimize and predict the precipitation process, which are optimization statistical method and thermodynamic equilibrium computer model. Based on these two basic principles, a number of different models have been developed and applied by researchers, Wu and Zhou *et al.*, (2012) applied response surface methodology to model individual factors and their interaction, predicted the dose optimization by a chemical thermodynamic equilibrium model--Visual MINTEQ, so did Wu *et al.,*(2011) and Mason *et al.*,(2003). Tong and Chen *et al.*, (2009) and Zhang and Chen *et al.*, (2009) employed central composite design (CCD) of response surface methodology (RSM) to design their experiments. RSM helped to measure the interaction of individual factors, reduce laborious experiments, and predict optimal situation.

Thermodynamic equilibrium computer models are based on the dynamic equilibrium of ionic, dissolved and undissolved species in solution. Basically, in order to apply the chemical equilibrium model in synthetic wastewater, NH_4^+, PO_4^{3-}, Mg^{2+}, NH_3, H_3PO_4, $MgNH_4PO_4{\bullet}6H_2O$ must exist in solution (Scott *et al.*, 1991; Wrigley *et al.*, 1992; Musvoto *et al.*, 2000a; Musvoto *et al.*, 2000b). However, other ions such as: HPO_4^{2-}, $H_2PO_4^-$, $MgH_2PO_4^+$, $MgOH^+$, $MgPO_4^-$, dissolved species such as: $MgHPO_4$, H_3PO_4, and undissolved species, such as: $Mg_3(PO_4)_2{\bullet}8H_2O$, $Mg_3(PO_4)_2{\bullet}22H_2O$, $Mg(OH)_2$, $MgHPO_4$, and struvite will also co-exist in solution under equilibrium situation. Using wastewater from WWTP, a complicated model could employ more species, like: $Ca_3(PO_4)_2$, $CaHPO_4$, $Ca(OH)_2$, $CaCO_3$, $CaMg(CO_3)_2$, $Mg_3(PO_4)_2$, $MgCO_3$. Heavy metals and organic matters will also have impact on the equilibrium.

Struvite as the only solid has been considered in a simple model by Loewenthal *et al.*, (1994), in which other species considered were: NH_4^+, PO_4^{3-}, Mg^{2+}, HPO_4^{2-}, $H_2PO_4^-$, NH_3, H_3PO_4, H_2CO_3, CH_3COO^-, and CH_3COOH. Except these species, Ohlinger *et al.*, (1998) applied MINTEQA2 by including $MgH_2PO_4^+$, $MgPO_4^-$, and the impact of ionic strength. Wang *et al.*, (2006) involved $Mg(OH)_2$ in his model [PHREEQC 2.11 (Developed by US Geology survey)] and also those species considered by (Ohlinger *et al.*, 1998). Scott *et al.*, (1991) developed a model considering five undissolved species: $Mg_3(PO_4)_2{\bullet}8H_2O$, $Mg_3(PO_4)_2{\bullet}22H_2O$, $Mg(OH)_2$, $MgHPO_4$, and struvite, and other species which were the same as modelled by Wang *et al.,* (2006). Altogether, eight solids have been considered by different researchers, the more dissolved and undissolved species considered, the more complex of the model is.

METLABORATORY program was introduced by Türker *et al.,*(2010) to calculate species ionic strength based on the following equations, k_{sp} of struvite was also compared with other researchers' shown in Table 2.5:

$$I = \frac{1}{2} \sum {z_i}^2 \mathrm{C}_i \tag{2.12}$$

$$\mathrm{Log}\ \gamma = -0.5Z^2 \frac{\sqrt{\mathrm{I}}}{1+\sqrt{\mathrm{I}}} \tag{2.13}$$

Harada *et al.,* (2006) developed an equilibrium model to predict struvite formation and optimal pH, and then conducted experiments using urine to test this prediction. The model that they developed is shown in Figure 2.20:

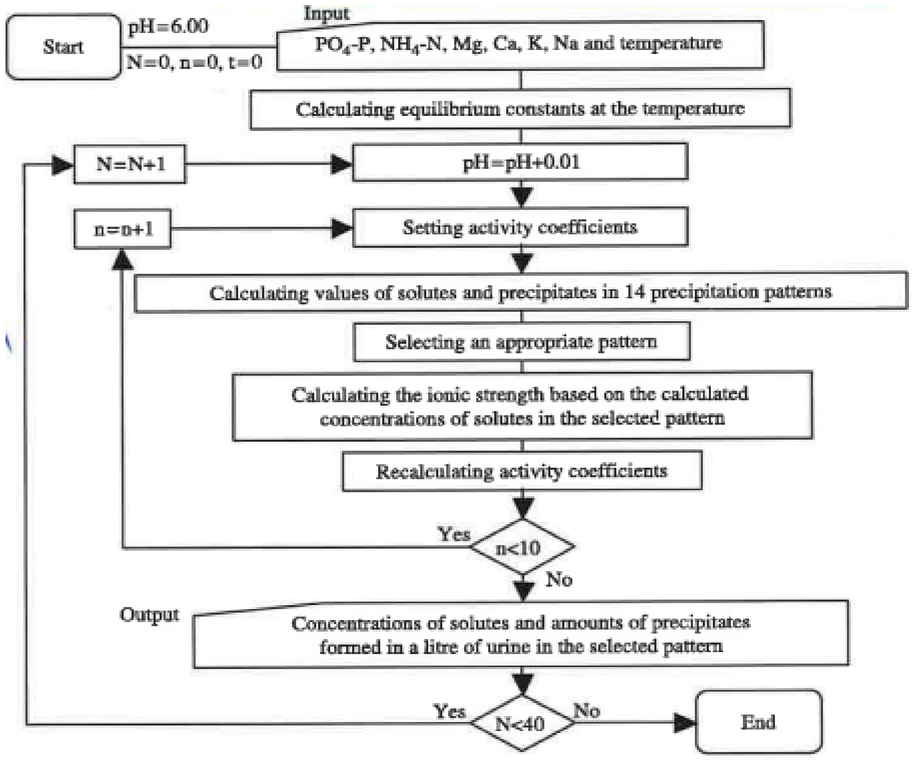

Figure 2.23 A model flow designed by Harada *et al.*, (2006)

A MAPLE 10 program was developed by Gadekar *et al.*, (2010) which was a mathematical model of the precipitation process by using physio-chemical expressions, the output of this model successfully matched most data with experiment result. This model procedure is shown in Figure 2.24:

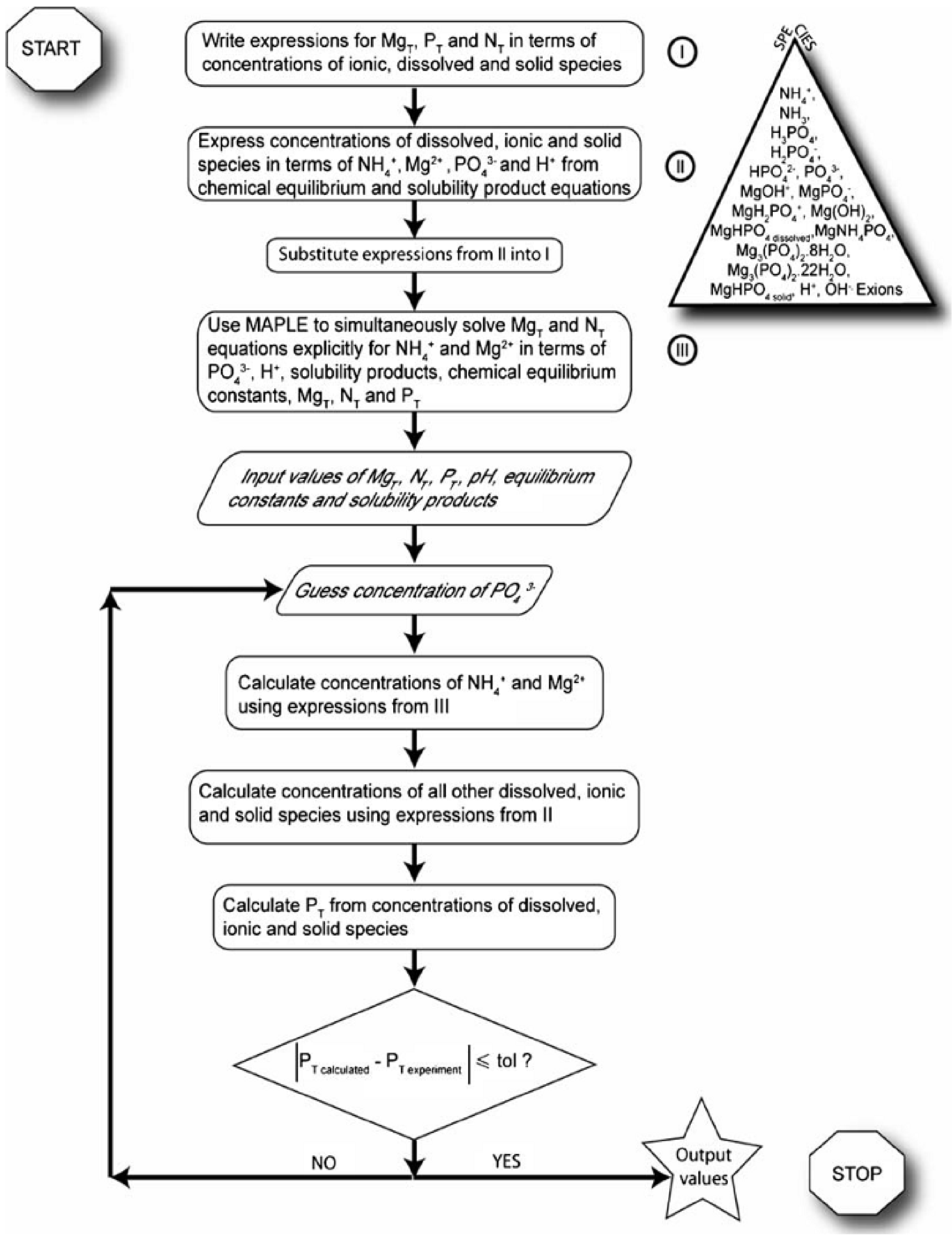

Figure 2.24 Model procedure developed by Gadekar *et al.,* (2010)

Zhang *et al.,* (2011) applied PHREEQC and response surface methodology (RSM) to assess the precipitation recovery from wastewater. Miles *et al.,* (2001) used thermodynamic equilibrium model MINTEQA2 to predict struvite precipitation from anaerobic wastes. The concentration of Mg^{2+}, NH_4^+, and PO_4^{3-}, ionic strength of the solution were computed automatically by models applied. These modelling results were mostly in accordance with laboratory experiments results. Hence these models were successful in predicting the formation of struvite. They can be used to assist the application of this technology.

2.8 Summary

The MAP precipitation technology has received increasing interest recently not because only it can remove ammonium and phosphate, but also recover them in a sustainable manner, turning waste into gold. Based on synthetic wastewater and different kinds of wastewater, factors affecting the precipitation process have been widely determined by many researchers. These include pH, concentration of Mg^{2+}, NH_4^+, and PO_4^{3-}, temperature, feeding sequence, and stirring rate.

This is a physio-chemical process, which is determined by many factors and all the factors can interact with each other. Hence researchers have applied different kinds of models to optimize the process and predict the formation of struvite, models, such as Maple 10, PREEQC2.11, RSM technology, Visual MINTEQ model etc. Some researchers also designed their own models based on the chemical equilibrium expressions. These models output were all proved successful by experiment result.

However, due to the different characteristics of various wastewaters, the concentrations of NH_4^+ and PO_4^{3-} vary significantly. Although factors affecting the MAP formation process has been studied by many researchers, based on synthetic wastewater in this project, the performance of different pH and molar ratio of Mg^{2+} :

NH_4^+ : PO_4^{3-} were investigated further to appraise this process. The main purpose is to remove NH_4^+-N and to reduce the concentration of PO_4^{3-} as possible as it can.

This project aims to apply thermodynamic chemical equilibrium model Visual MINTEQ 3.0 to predict the formation of struvite and estimate the dosage of NaOH needed in this process based on wastewater from Bolivar WWTP, Adelaide. Laboratory scale experiments were carried out and results were compared with model output. Information obtained from this project can provide reference and assist the application of this technology in real world production.

Chapter 3

Materials, Methods and Experiments

3.1 Experiment Setup

As shown in Figure 3.1, the laboratory MAP precipitation system were equipped with a syringe pump (NE-300), a stirrer (IKA Colour SQUID), 500 mL beakers，pH meter (pH/Ion 510, Bench pH/Ion/mV meter), 50ml syringe and timer (Crown Scientific).

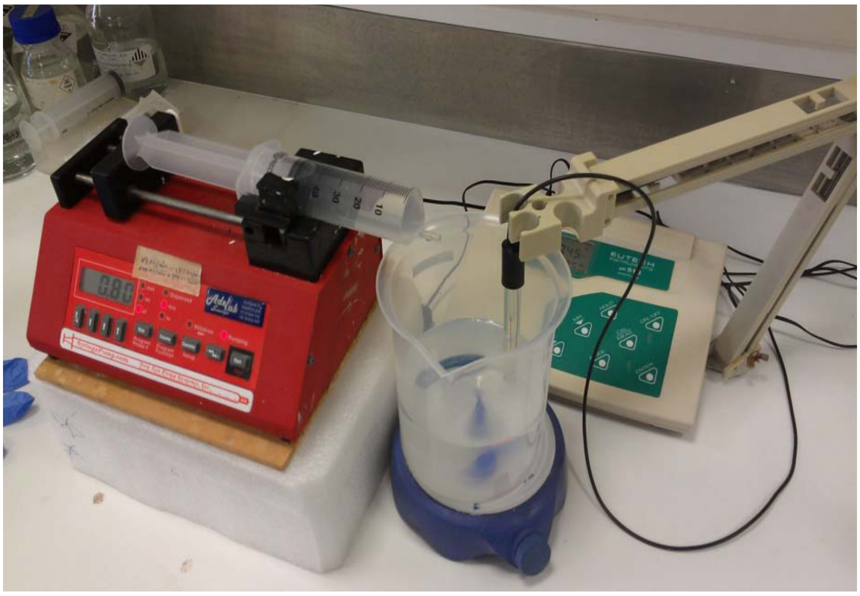

Figure 3.1 Experiment process setup

This work focused on the removal efficiency of nitrogen and phosphate from wastewater. Operation factors that affect the precipitation process were studied, the optimal reaction conditions were determined based on laboratory trial experiments.

3.2 Materials

Chemicals used in this project were: NH_4Cl (Chem Supply SA), $MgCl_2 \bullet 6H_2O$ (Ajax Finechem Pty Ltd), MgO (Chem Supply SA), KH_2PO_4 (Chem Supply SA), H_3PO_4 (85%) (BDH Laboratory Supplies), Sulphuric acid (1.84g/cm^3) (Scharlau Chemie

SA), HCl (32%) (Ajax Finechem Pty Ltd), and NaOH (Chem Supply SA). All chemicals are of analytical grade and used as received. Millipore water (MilliQ water, 18.2 MΩ·cm^{-1}) was used in all experiments, which was obtained from an EASY pure ultra Milli-Q water purification system. pH was adjusted by using 1 N NaOH solution and 1 N HCl solution to the required level.

3.3 Preparation of solutions required

Synthetic wastewater and wastewater from WWTP were used in this study. The synthetic wastewater was used in the first stage to determine optimal operation parameters. The next stage was to carry out experiments using wastewater from Bolivar WWTP, Adelaide to appraise the feasibility of this application.

3.3.1 Ammonium (NH_4^+) preparation

NH_4^+ was gained by adding NH_4Cl into water in this study due to its popularity and easy to obtain. 5.35g NH_4Cl was weighed by Meller AT250 and dissolved into 1L Milli-Q water to get 0.1 mol/L NH_4^+. The weight of crystals was measured by Meller TOLEDO.

3.3.2 Magnesium (Mg^{2+}) preparation

20.3g $MgCl_2 \bullet 6H_2O$ was weighed using Meller AT250 and dissolved into 1L MilliQ water to get 0.1 mol/L Mg^{2+}. The desired dosage of Mg^{2+} is the most important component in this method, because there is little Mg^{2+} existing in wastewater. The cost of this process was mainly contributed by assumption of Mg^{2+} resource. In this study, $MgCl_2•6H_2O$ and MgO were used to obtain Mg^{2+}, because they are used widely in similar project.

3.3.3 Phosphate (PO_4^{3-}) preparation

Phosphate is another important component in the MAP precipitation process. Due to insufficient phosphate available in the wastewater, additional phosphate should be added to maximize nitrogen removal and recovery from wastewater. 13.6g KH_2PO_4 was weighed by Meller AT250 and dissolved into 1L Milli-Q water to get 0.1 mol/L PO_4^{3-}. In this study, KH_2PO_4 and H_3PO_4 were used as phosphate source to acquire the desired concentration in wastewater.

3.4 Wastewater from Bolivar WWTP

The concentration of NH_4^+ was made 1800 mg/L in synthetic wastewater. However, NH_4^+ concentration in the wastewater from Bolivar WWTP, Adelaide was around 1000mg/L (Data from SA Water 2012, laboratory test results), The characteristics of this centrate, as shown in Table 3.1, are NH_4^+–N, PO_4^{3-}-P, pH, total solids (TS), Mg^{2+}, Ca^{2+}, Al^{3+}, Fe^{3+}, K^+, alkalinity, and conductivity,. The main purpose of this project was to remove nitrogen, and then this figure was kept constant when doing experiments.

Table 3.1 Characteristics of centrate from Bolivar WWTP, Adelaide (STDEVA±5.0). pH was 7.5

Items	Concentration (mg/L)
NH_4^+–N	643
PO_4^{3-}--P	235
TS	1973.7
Mg^{2+}	43
Ca^{2+}	38
Al^{3+}	6.5
Fe^{3+}	1.3
K^+	28.6
Alkalinity (as $CaCO_3$)	1153

3.5 Analysis methods and procedure

3.5.1 Analysis methods

All experiments were carried out at ambient temperature in triplicate tests to get the mean experimental results. The reaction time was 30 min, the settling time was 2 hrs; the stirring rate was 200rpm.

Mg^{2+}, Ca^{2+} were tested by Atomic absorption spectrophotometer (SHIMADZU, AA-6300, Figure 3.2) in analytical laboratory of School of Chemical Engineering, The University of Adelaide. PO_4^{3-} was measured by LIUV-201 UV/Vis spectrometer (UV/Vis spectrometer, Figure 3.3); NH_4^+ is measured by DR/890 colorimeter HACH (Figure 3.4). The size and morphology of the crystal was analysed by scanning electron microscopy (SEM) (Philips XL 30) in Adelaide Microscopy, South Australia (Figure 3.6).

3.5.2 Analysis procedure

Prior to any experiments or analysis, the sample was let to settle for 1 hour, then filter the crystals using a 0.45μm filter paper. The filtrated crystal samples were dried at room temperature for 24 hours for further study. The crystal precipitated was divided into two parts. The first part was analysed by X-ray Diffraction (XRD) in School of Chemical Engineering (Figure 3.5), and the second part was analysed by wet analysis, (Dissolved in 1 M HCl). The size and morphology of the crystals were performed by Scanning Electron Microscope (SEM) (Philips XL 30). The characteristics of the crystals were measured by X-ray Diffraction. All experimental results are reported as the mean value of each parameter with standard deviation.

3.5.3 Instruments used

All the instruments used in this study are displayed in the following Figures.

Figure 3.2 SHIMADZU, AA-6300, Atomic absorption spectrophotometer used to measure Mg^{2+}, K^{+} and Ca^{2+}.

Figure 3.3 LIUV-201 UV/Vis spectrometer used to measure PO_4^{3-}

Figure 3.4 Colorimeter HACH used to measure NH_4^+

Figure 3.5 X-ray Diffraction, Miniflex 600 used to identify struvite, magnesite and struvite-(K).

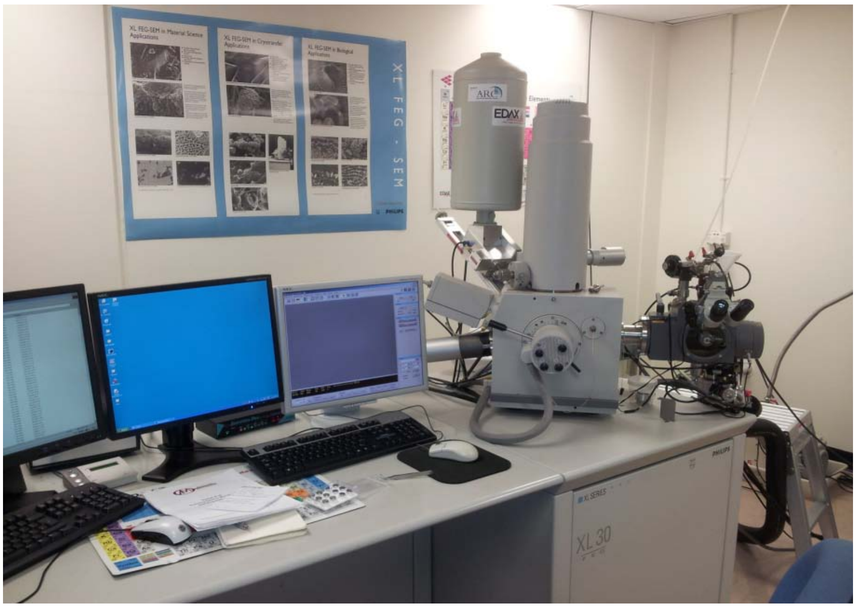

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Figure 3.6 Philips XL 30 Scanning electron microscopy used to measure the morphology and size of struvite.

3.6 Experiments

3.6.1 Sample Preparation

The device used in this experiment was set up as shown in Figure 3.1. The concentration of ammonium was kept constant at 0.1 mol/L, 5.35g NH_4Cl was dissolved in purified water to get ammonium solution, different concentrations of Mg^{2+} and PO_4^{3-} were prepared according to different molar ratios of Mg^{2+} : NH_4^+ : PO_4^{3-}. Sample of different ratio, such as 1:1:1, 1.2:1:1, 1.4:1:1, 1.6:1:1, 2:1:1 were prepared, then the concentration of P was changed to prepare another series of different molar ratio, 1:1:1, 1:1:1.2, 1:1:1.4, 1:1:1.6.

The raw centrate was collected from the Bolivar WWTP, Adelaide and stored in a cool room (4 ºC) prior to the experiment. The basic characteristics of the centrate were summarised in Table 3.1. The concentration of NH_4^+-N was measured as 643 mg/l

3.6.2 Experiments without pH control

Molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-} was prepared at 1:1:1. Theoretically, all ions would be precipitated at appropriate pH. Experiments were done with the variance of pH of the solution from 8 to 11. This experiment was to try to find out the best pH for the formation of struvite. All experiments were done three times at ambient temperature. Overall results will be discussed in Chapter 4.

3.6.3 Experiments with pH control

In this process, synthetic wastewater was first used to perform all experiments at various molar ratio of Mg^{2+} :NH_4^+ :PO_4^{3-}. Each experiment was performed in triplicate and repeated at least three times to observe the reproducibility in order to minimize the deviation and get an average result. The optimal reaction conditions were obtained.

Then thermodynamic chemical equilibrium computer model (Visual MINTEQ 3.0) was introduced to predict and estimate the precipitates from real wastewater, model outcome was recorded. Next, centrate from Bolivar WWTP (Adelaide) was used for laboratory scale experiments under the same conditions as input used in Visual MINTEQ 3.0. However, the centrate was too complicated and mixed industrial wastewater with domestic wastewater, it consists of too many ions, the experimental results showed lots of chemicals included in the precipitated crystals. Finally, the model output and experimental results were compared and discussed.

The molar concentration of NH_4^+ and PO_4^{3-}, in wastewater was 0.036 mol/L and 0.0025mol/L, respectively. In all experiments, the feeding rate was 13.65ml/min, pH was controlled at different value, and stirring rate was 200 rps.

The residual nitrogen was tested by DR/890 colorimeter HACH, Amver^{TM} HACH Test ‘N Tube High Range Ammonium Reagent Set (Figure 3.4). The residual phosphate was tested by LIUV-201 UV/Vis spectrometer (Figure 3.3). The residual magnesium was tested by SHIMADZU, AA-6300, Atomic absorption spectrophotometer (Figure 3.2).

3.6.4 Feeding rate

At pH 9, different feeding rate was tested. The feeding rate was 7.14ml/min, 10ml/min, and 13.3ml/min. The stirring rate was 200rpm.

Chapter 4

Optimisation of Operation Parameters for NH_4^+ and PO_4^{3-} Recovery by Struvite Precipitation

4.1 Introduction

Eutrophication, caused by excessive nutrients like nitrogen and phosphorous discharged from wastewater, is now a worldwide issue which brings nuisance consequence to the environment, such as the death of aquatic lives, contamination of underground water, and loss fertility of land (Ali *et al.,* 2005). On the other hand, nitrogen and phosphorous are the fundamental nutrient elements which are needed by living creatures. Now the only way to obtain phosphorous resource is from mining sources, which are not infinite. Cordell *et al.,* (2009), Gilbert *et al.,* (2009), and Van Kauwenbergh *et al.,* (2010) have reported that rock based phosphorous will be running out in 50-100 years. It is becoming critical to find an alternative resource or recycle nitrogen and phosphorous from resources which are NH_4^+-N and PO_4^{3-}-P rich.

To remove the nitrogen and phosphorous from domestic and industrial wastewater is part of wastewater treatment processes as so called biological nutrient removal (BNR) step. Conventional treatment methods, including A^2/O process, aeration stripping process, ion-exchange process, response surface study process, electrodialysis process, and constructed wet land process, have been widely used to remove NH_4^+-N and PO_4^{3-}-P from wastewater in industrial treatment processes. Thus to reduce the load of NH_4^+ and PO_4^{3-} returning to the process, and to meet the discharge legislation to protect local community environment. Removal of NH_4^+-N and PO_4^{3-}-P by the conventional treatment technologies has been a challenge for water industries worldwide. A chemical process to remove and recover NH_4^+-N and PO_4^{3-}-P has attracted much attention in recent decades, which is called nutrient recovery by the precipitation of magnesium ammonium phosphate (MAP). This process can be applied for nutrient recovery in industrial wastewater (Diwani *et al.,* 2007, Warmadewanthi *et al.,* 2008), municipal landfill leachates (Kim *et al.,* 2007), swine waste (Burns *et al.,* 2001; Jaffer *et al.,* 2001; Çelen *et al.,* 2007), human urine (Ganrot *et al.,* 2007, Etter, B., *et al.,* 2010), leather tanning wastewater (Tunay *et al.,* 1997) and agro-industry wastes (Moerman *et al.,* 2009).

The principle of the precipitation of MAP for recovering ammonium and phosphate is expressed as the following reaction Equation 4.1 (Ali *et al.,* 2005; Nelson *et al.,* 2003; Li *et al.,* 1999; Michalowski *et al.,* 2006). According to Equation 4.1, the magnesium ammonium phosphate (MAP), *i.e.* struvite, normally is produced at a stoichiometric ratio of 1:1:1 under the designable precipitation conditions, while the struvite can be formed as a stable white orthorhombic crystals (Miller *et al.,* 1994; Doyle and Parsons *et al.,* 2002; Yetilmezsoy and Sapci *et al.,* 2009):

$$Mg^{2+} + NH_4^{+} + H_nPO_4^{n-3} + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O \downarrow + n\ H^{+} \qquad (4.1)$$

(*n* = 0, 1, 2. *n* depends on the pH of the solution)

There are a number of systematic parameters which could affect this precipitation reaction and formation of struvite crystals. These parameters consist of chemical composition and concentration of NH_4^+, Mg^{2+}, and PO_4^{3-} sources, pH, and operation conditions of the MAP precipitation process. Many previous studies reported that chemistry of the NH_4^+, Mg^{2+}, and PO_4^{3-} components and their molar ratio, pH and feeding rate of chemical addition are crucial for the operation and optimization of the MAP process. Yetilmezsoy and Sapci *et al.,* (2009) tried three combinations which were $MgCl_2•6H_2O$ + KH_2PO_4, $MgSO_4•7H_2O$ + $NaHPO_4•7H_2O$ and MgO + H_3PO_4 (85%). Kumar *et al.,* (2013) also applied three combinations which were $MgCl_2•6H_2O$ + $NaH_2PO_4•12H_2O$, $MgSO_4•7H_2O$ + $Ca(H_2PO_4)•H_2O$ and MgO +

H_3PO_4(85%). In this project, $MgCl_2 \bullet 6H_2O$ + KH_2PO_4, and MgO + H_3PO_4 (85%) would be used as Mg^{2+} and PO_4^{3-} sources due to their abundance and low cost. Shu *et al.,* (2006) has reported that much of the phosphorous and part of the ammonium of the supernatant obtained from the sludge dewatered effluent that comes from a biological treatment plant can be used for struvite production. However, to make this process happen, additional Mg^{2+} and PO_4^{3-} must be added to maximise the NH_4^+ removal and recovery efficiency (Münch and Bar *et al.,* 2001; Ryu *et al.,* 2008; Stefanowicz *et al.,* 1992; He *et al.,* 2007). The pH is a key parameter that has a great impact on the precipitation reaction for MAP precipitation, and struvite crystallization and stability (Stumm *et al.,* 1996; Le Corre *et al.,* 2009). Previous researchers have studied the effect of pH on the MAP precipitation process. Abbona *et al.,* (1982) measured a critical pH of 5.85, and found that struvite was formed when pH was higher than 5.85, while newberyite can be precipitated if pH is lower than 5.85. While Musvoto *et al.* ,(2000a) found that when pH was higher than 10, brucite is more likely to form rather than MAP. If pH was lower than 7.5, very few crystals were obtained. In this project, the optimal pH would be studied by synthetic wastewater.

This study was to explore if the MAP is a feasible process for recovering ammonium from sludge dewatering effluent in Bolivar wastewater treatment plant, Adelaide, Australia. The concentration of ammonium in sludge dewatering effluent was around 1000 mg/L, which is higher than that of Mg^{2+} and PO_4^{3-} existed in the effluent. Thus, addition of certain level of Mg^{2+} and PO_4^{3-} sources is essential for the recovery of NH_4^+ through the MAP precipitation process. Therefore, the aim of the study associated with this chapter was to identify and optimise the operation conditions for recovering NH_4^+ via MAP precipitation from sludge dewatering effluent. The designed objectives to achieve this aim were to

1) Seek suitable magnesium and phosphorous sources for NH_4^+ removal and recovery;
2) Investigate the impact of pH on the precipitation process;
3) Compare the removal efficiency of ammonium by applying different chemical combinations;
4) Explore the optimal molar ratio of magnesium ammonium and phosphate based on synthetic wastewater;
5) Test the effect of temperature and feeding rate on the removal efficiency and MAP crystal formation.

Synthetic wastewater which has a similar chemical composition in terms of NH_4^+ and PO_4^{3-} in the sludge dewatering effluent will be used in this study. Removal of NH_4^+ and PO_4^{3-}, and formation of struvite mass and crystals will be assessed as key indicators for assessment and optimization of the MAP precipitation for ammonium recovery.

4.2 Materials and Methods

4.2.1 Materials

Chemicals used in this project were: NH_4Cl (Chem Supply SA), $MgCl_2{\bullet}6H_2O$ (Ajax Finechem Pty Ltd), MgO (Chem Supply SA), KH_2PO_4 (Chem Supply SA), H_3PO_4 (85%) (BDH Laboratory Supplies), Sulphuric acid (1.84g/cm^3) (Scharlau Chemie SA), HCl (32%) (Ajax Finechem Pty Ltd), and NaOH (Chem Supply SA). All chemicals are of analytical grade and used as received. Millipore water (MilliQ water, 18.2 MΩ·cm^{-1}) was used in all experiments, which was obtained from an EASY pure Ⅱultra Mill-Q water purification system.

4.2.2 Struvite precipitation system and its operation

The experimental setup for the MAP precipitation consists of a pH meter (pH/Ion 510, Bench pH/Ion/mV meter), syringe pump (NE-300), stirrer (IKA Colour SQUID), three 500 mL beakers， and a timer (Crown Scientific). The pH value was measured by pH meter (pH/Ion 510, Bench pH/Ion/mV meter) and adjusted using 1 N NaOH solution and 1 N HCl solution to the desired level. According to Abbona *et al.*, (1982), the MAP reaction can be completed very fast when it occurs. Hence the reaction time was designed as 20 min, settling time was 1 h. Stirring rate was 200rpm which is the most widely used parameter in laboratory scale experiment. A series of tests were designed to test the effect of pH on the precipitation process.

Based on the results from previous studies in consideration of MAP formation efficiency and cost issue, chemical combinations of $MgCl_2 \bullet 6H_2O+KH_2PO_4$ and $MgO+H_3PO_4$ (85%) were selected and used in this study to test and compare the efficiency of NH_4^+-N. From current experiment results reported in the literature (Buchanan *et al.*, 1994; Song *et al.*, 2007; and Zhang *et al.*, 2009), pH 9 was selected while measuring the performance of different molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-}. The concentration of ammonium was maintained at a constant level during the experiments. A series of experiments were designed and performed in this study. The effect of temperature and reagent addition rate on the precipitation process was also tested. All experiments were done at ambient temperature and 1 atm and repeated triple times for each experiment to get the mean experimental results.

4.2.3 Characterization of crystals precipitated

The size and morphology of the crystals were examined by Scanning Electron Microscope (SEM) (Philips XL 30). The characteristics of the crystals were measured by X-ray Diffraction (MiniFlex 600, Rigaku, Japan).

4.2.4 Analysis of chemicals and data

In this study, the main items monitored were pH, concentrations of Mg^{2+} and PO_4^{3-}-P, and NH_4^+-N, and total mass of the precipitate and/or the crystals. Prior to any analysis, the samples were settled down for 1 hour, then filtered the crystals using a 0.45µm filter paper and dried at room temperature for 24 hours for further study. PO_4^{3-}-P was measured by a spectrophotometer (LIUV-201 UV/Vis spectrometer). NH_4^+-N was measured by (DR/890 colorimeter HACH, Amver^{TM} HACH Test ‘N Tube High Range Ammonium Reagent Set). Mg^{2+} was measured by an atomic absorption spectrophotometer (SHIMADZU, AA-6300).

4.3 Results and Discussion

4.3.1 Optimization of operation pH

pH is a key parameter which affects the precipitation reaction and struvite crystal formation. The effect of pH on precipitation process has been confirmed by previous studies (Stumm and Morgan *et al.,* 1970; Ohlinger *et al.,* 1998; Hoffmann *et al.,* 2004). The pH also varies during the course of MAP precipitation and crystal formation. In this study, a series of experiments without and with pH control were carried out to test the effect of pH on the precipitation process, meanwhile, the optimal pH range was to be identified. The pH values were set up at 8, 8.5, 9, 9.5, 10, 10.5, and 11. The molar ratio of $Mg^{2+}:NH_4^+:PO_4^{3-}$ was applied as the stoichiometric ratio of 1:1:1. Chemical combination of $MgCl_2{\bullet}6H_2O+KH_2PO_4$ was introduced as Mg^{2+} and PO_4^{3-} source to make synthetic wastewater due to its popularity and easy access (Kumar *et al.,*2013; Yetilmezsoy and Sapci *et al.,*2009).

Figure 4.1 shows that there was a sharp drop in each pH curve because more hydrogen ion (H^+) is generated associated with the MAP formation reaction. Equation 4.1 indicates that H^+ can only be generated in the reaction system with the formation of struvite. When the initial pH was 9 and 9.5 as shown in Figure 4.1, pH dropped sharply to 6.3 and 6.7, respectively, till the reaction was finished after 15 mins. This indicates there was intensive reaction between ions and struvite yielded. When the initial pH was 11, pH dropped slightly from 11 to 9.3 till the reaction was finished after 15 mins. This might indicate that struvite is not the only crystals yielded associated with the precipitation.

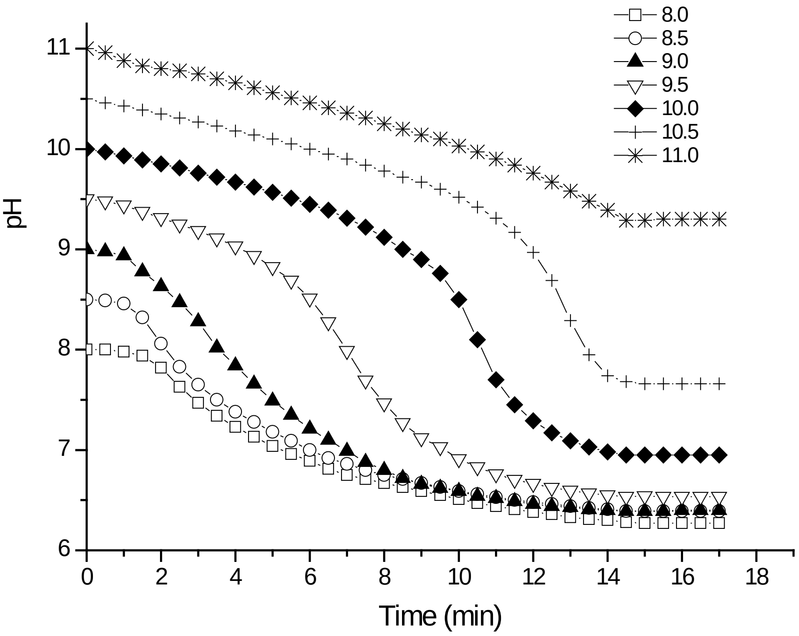

Figure 4.1 pH variations from 8 to 11 during the course of precipitation reaction without pH control. The molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-} was 1:1:1. (STDEVA $_{pH}$ ± 0.02)

Figure 4.2 shows that the total mass of crystals increased with pH raised from 8 to 11, while the removal efficiency NH_4^+ increased to its highest point at pH 9 then decreased to its lowest at pH 11.

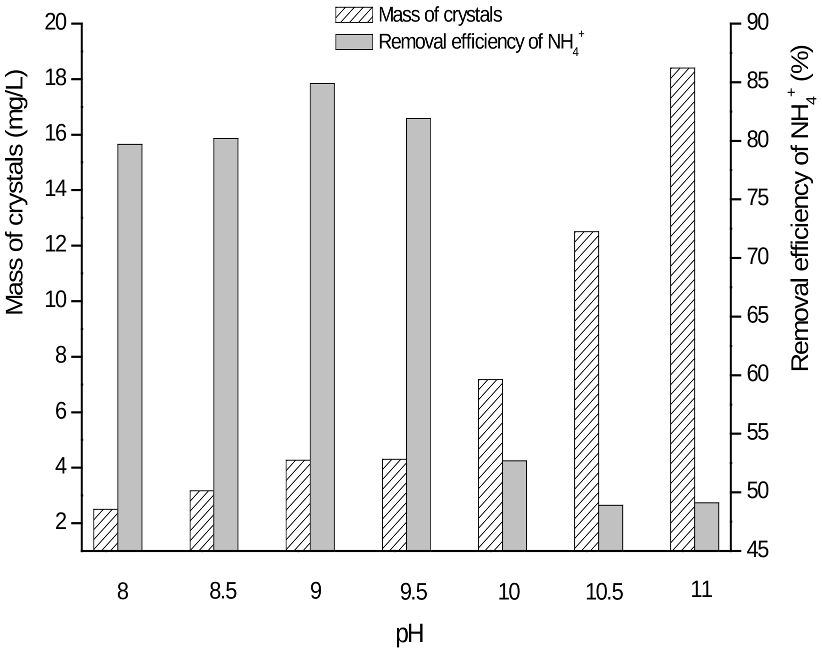

Figure 4.2 Impact of pH on MAP formation and ammonium removal efficiency in laboratory scale experiments without pH control (molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-} was 1:1:1). 1. STDEVA $_{\text{mass}}$ ± 0.5; 2. STDEVA $_{\text{removal efficiency}}$ ± 0.7

The experiments to determine impact of controlled pH on the ammonium removal and MAP formation were carried out under the same conditions. From Figure 4.3, it can be concluded that the particle mass increased with the increase in controlled pH. The highest particle mass peak (7.48 g/L) was reached at pH 9. It is worthwhile to note that the crystal mass decreased when pH was controlled in 9.5 – 10.0, and then increased at the controlled pH raised from 10.0 to 11, reaching a particle mass 7.45 g/L. There might be a few different precipitate particles which could be generated from this reaction, depending on the reaction pH and chemical compositions of Mg^{2+}, NH_4^+, and PO_4^{3-}. These possible particles may include struvite ($MgNH_4PO_4•6H_2O$), newberyite ($MgHPO_4$), bobierrite $Mg_3(PO_4)_2•8H_2O$ and brucite [$Mg(OH)_2$]. As reported in the literature, struvite ($MgNH_4PO_4•6H_2O$) is not the only chemical precipitated during this process. When the concentrations of Mg^{2+} and PO_4^{3-} are high, brucite and $Mg_3(PO_4)_2$ are more likely to be formed at a higher pH (Musvoto *et al.,*2000). Musvoto and co-workers also reported that newberyite would be precipitated when pH is lower than 6. In this work the pH was controlled higher than 8, it was unlikely that newberyite would be formed. Lee *et al.,* (2003) reported that struvite was the dominant crystal in the range of pH 7.5-10. While $Mg_3(PO_4)_2$ was formed in the range of pH 8.5-11, especially when pH is higher than 11 (Tunay *et al.,*1997). Similar result has also been reported by Wu and Zhou *et al.,*(2011).

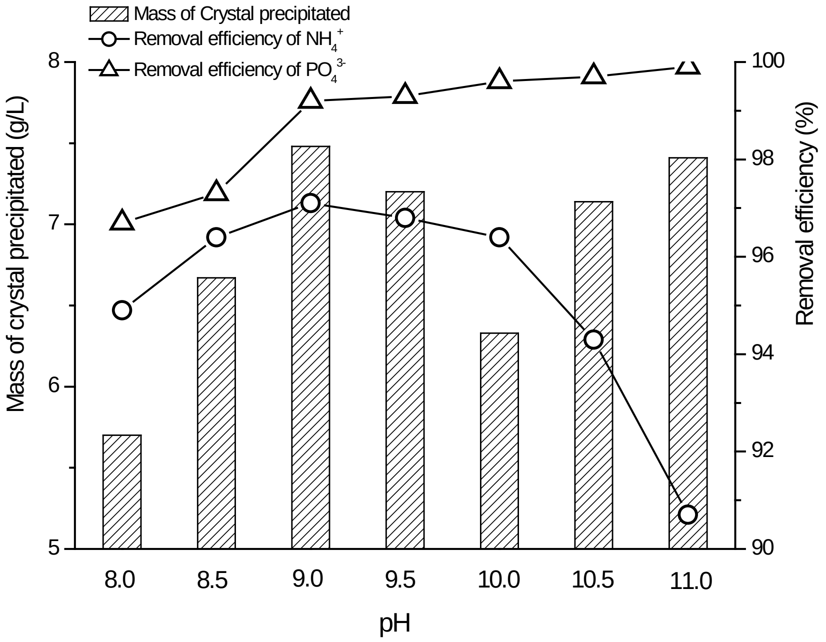

Figure 4.3 Mass profile of crystals and residuals of ammonium and phosphate at a controlled pH rage (8-11) (molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-} was 1:1:1). 1. STDEVA $_{\text{mass}}$ ± 0.09; 2. STDEVA $_{\text{Ammonium removal efficiency}}$ ± 0.02; 3. STDEVA $_{\text{Phosphate removal efficiency}}$ ± 0.09.

In many previous studies, solubility of magnesium ammonium phosphate was not individually controlled by its solubility product constant. Stumm *et al.,* (1996) introduced a concept of conditional solubility product (PS), which shows that the order of the chemicals precipitation could be altered. This PS concept may explain the change of phosphate concentration in Figure 4.3. Higher mass and lowest phosphate removal were obtained at pH 11.

From Figure 4.3, the residual of ammonium in the solution dropped when pH increased from 8 to 9. Obviously, the concentration of ammonium dropped to the lowest level at pH 9, then slightly increased from 9.5 to 10, and increased dramatically to the highest level at pH 11. It could be explained that ammonium is consumed by the reaction to form struvite in the pH range of 9 to 9.5. These results were supportive by those studies as reported in the literature (Huang *et al.*, 2011; Kim *et al.,* 2007).

Based on the data presented in Figure 4.1, 4.2, 4.3, it can be noted that the reaction was intensive while pH was decreased sharply because more hydrogen (H^+) was generated. Once the precipitation reaction is completed the pH became stable after 18 mins, which was similar with the findings from what Zhang *et al.,* (2009) and Nelson *et al.,* (2003). In order to control the reaction to produce struvite as a dominant crystal and maximise the production yield of struvite, pH should be adjusted and maintained at certain level (Zhang *et al.,* 2009; Nelson *et al.,* 2003; and Abbona *et al.,* 1982). There was a slight change of pH if the initial pH was set at 11, resulting in producing more magnesium phosphate [$Mg_3(PO_4)_2$] rather MAP. Overall, the best pH range for struvite precipitation would be between 9 and 9.5 from this study which is well agreed with other researchers' results. Zhang *et al.,* (2009) performed experiments to produce struvite from landfill leachates, when the molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-} was at 1:1:1 and the pH range was 8.5-11, while Zhang optimal pH was found out as 9.5. Buchanan *et al.* (1994) described that the minimum struvite solubility was at pH

9. Tunay *et al.,* (1995) reported that the pH range 8-10 was found to be beneficial for MAP formation. Based on laboratory-scale experiments, a broad pH range between 9.94 and 13.26 also has been confirmed for the precipitation reaction by Shin and Lee *et al.,* (1997). However, these authors did not report chemical compositions of their precipitation particles.

To determine the possible crystal phases of the particles generated from the precipitation reaction, we examined the particle samples with X-ray diffraction (XRD). XRD is the basic technique to determine the bulk structure and composition of materials with crystalline structure. Our XRD measurements showed that the particles were mainly composed of the struvite as the major crystal, followed by a small proportion of magnesium phosphate and brucite, as shown in Figure 4.4. The XRD pattern obtained from synthetic wastewater matched the database model of struvite as shown in Figure 4.4, 4.5 in terms of peak position and intensity. It was confirmed that the majority of crystals formed was struvite after performing XRD (Figure 4.4, 4.5, 4.6, and 4.7). However, different peaks were witnessed as shown in Figure 4.4 and conformed that other chemicals, such as $Mg_3(PO_4)_2$ and brucite, were also formed. The morphology and size were measured by SEM XL30 as shown in Figure 4.6 and 4.7.

From Figure 4.6, we can see that the size of the struvite was about 25 μm with the shape of cuboids at pH 9 without control. Some crystals with smaller size are also witnessed. However, with pH control, as shown in Figure 4.7, the size of the crystal is about 15 μm with the shape of cylinder. It is obvious that the crystal size is more uniform under pH control than that of without control. The result of XRD analysis and SEM images has clearly shown that struvite was formed under both conditions (with and without pH control). However, with pH controlled, the size and shape of the crystals appeared more uniform. Thus, controlled pH should be the preferred reaction condition.

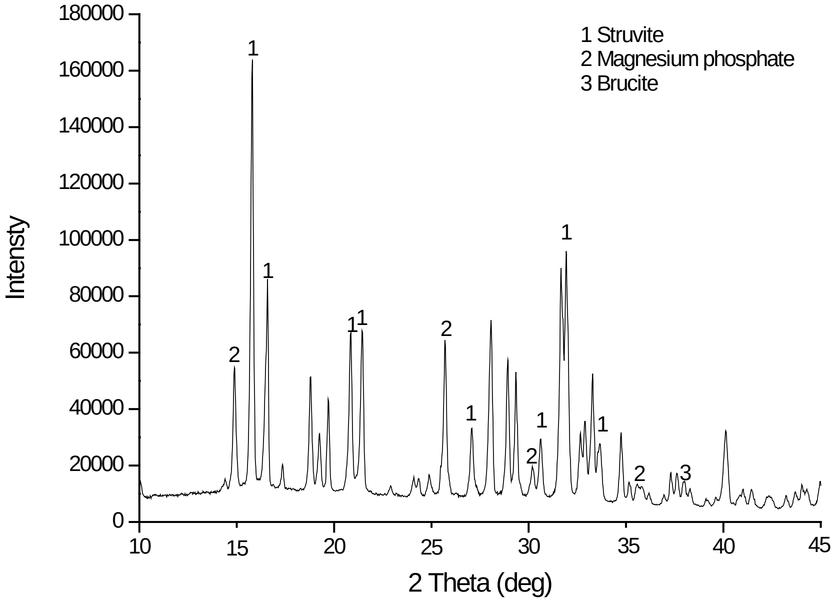

Figure 4.4 XRD pattern of the struvite, magnesium phosphate and brucite precipitated at Mg^{2+}: NH_4^+: PO_4^{3-} molar ratio 1:1:1 at initial pH 9 without pH control. 1. Standard pattern PDF# 15-0762. 2. Standard pattern PDF#35-0134. 3. Standard pattern PDF#44-1482

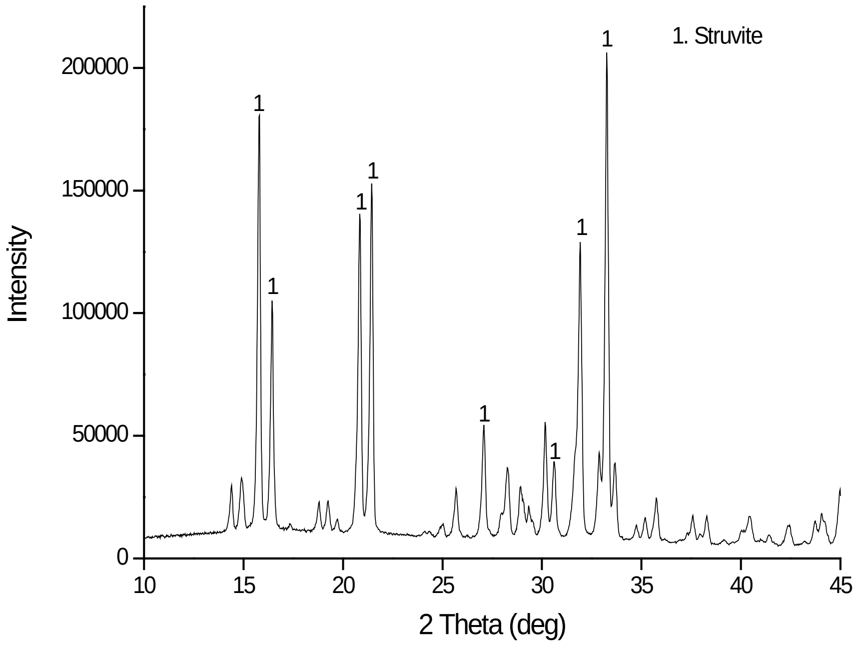

Figure 4.5 XRD pattern of the struvite precipitated at Mg^{2+}: NH_4^+: PO_4^{3-} molar ratio 1:1:1 at initial pH 9 with pH control. 1. Standard pattern PDF# 15-0762.

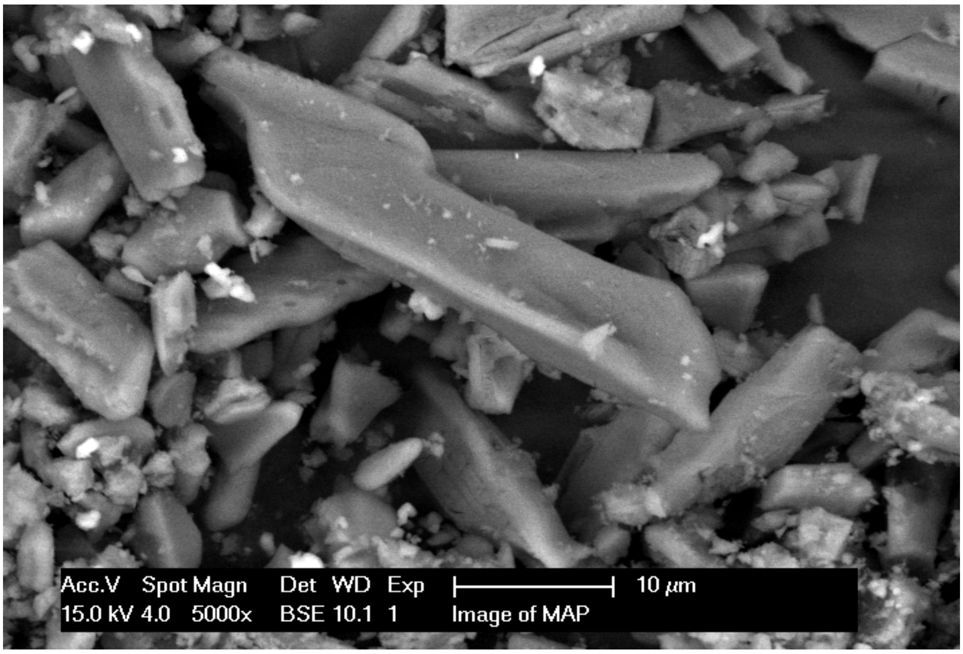

Figure 4.6 SEM image of struvite obtained from synthetic wastewater at initial pH 9 without pH control, the molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-} was 1:1:1.

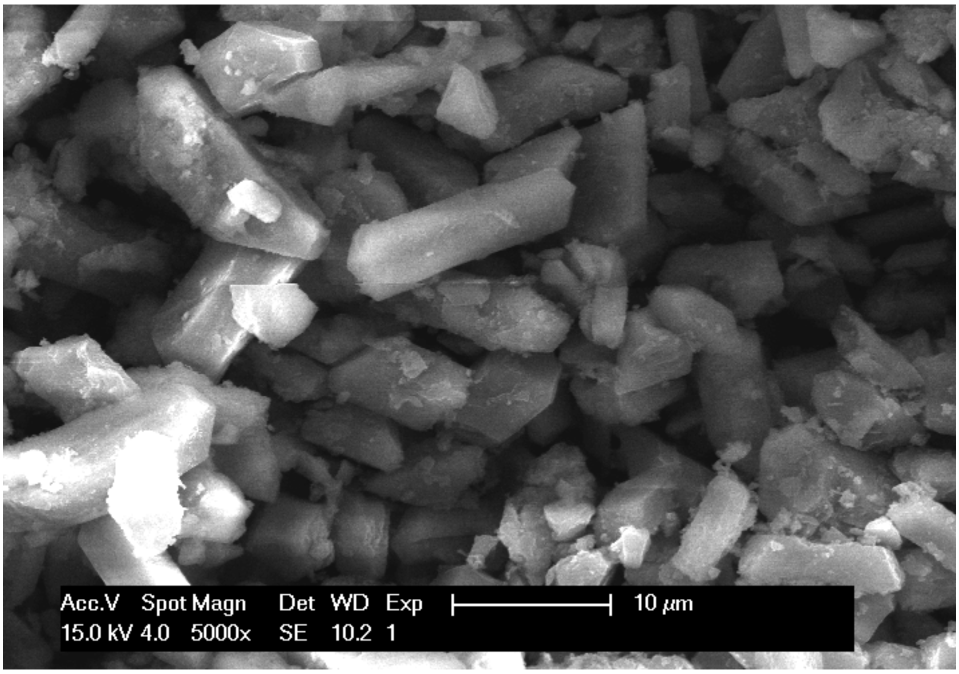

Figure 4.7 SEM image of struvite obtained from synthetic wastewater at initial pH 9 with pH control, the molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-} was 1:1:1.

4.3.2 Magnesium and phosphate sources

The concentration of ammonium in wastewater is normally much higher than that of magnesium and phosphate. In order to remove and recovery ammonium, additional Mg and P sources must be added. The purpose of this was to find out the most suitable Mg and P sources with respect to the productivity and yield of MAP formation, availability and cost of the magnesium and phosphate sources. $MgCl_2{\bullet}6H_2O$, MgO, KH_2PO_4 and H_3PO_4 are the most commonly used chemicals for MAP precipitation process. In consideration of popularity, lower cost, and availability, combination chemicals of $MgCl_2{\bullet}6H_2O$ + KH_2PO_4 and MgO + H_3PO_4 (85%) were used as the supplementary Mg and P sources in this study. The laboratory scale tests were set up at a molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-} of 1:1:1 and pH range of 8.5- 9.5.

Performance of the MAP precipitation was evaluated by the removal efficiency of NH_4^+ and PO_4^{3-}, and production MAP crystals.

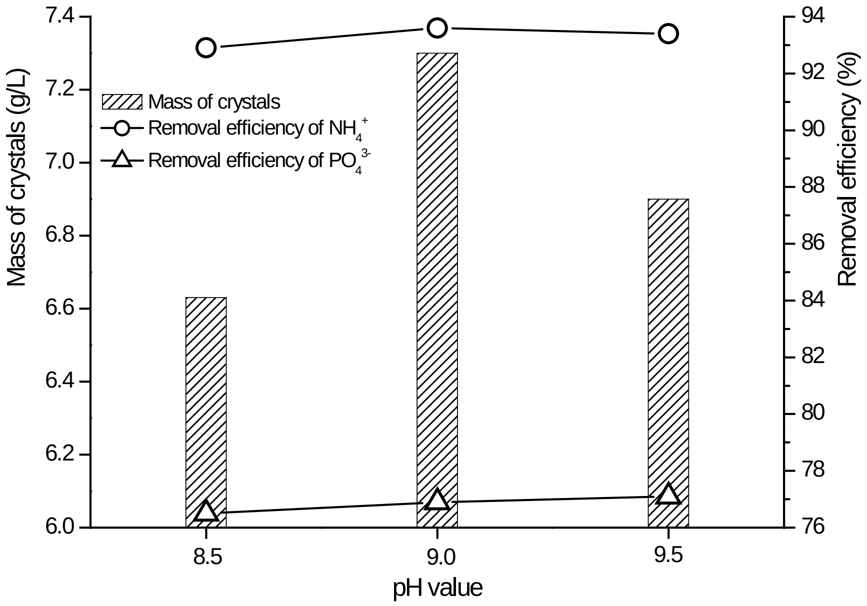

Figure 4.8 Mass of crystals and removal efficiency of ammonium and phosphate at different pH value 8.5, 9 and 9.5 with the molar ratio of Mg^{2+}:NH_4^+:PO_4^{3-} =1:1:1. 1. STDEVA $_{\text{mass}}$ ± 0.04; 2. STDEVA $_{\text{Ammonium removal efficiency}}$ ± 0.05; 3. STDEVA $_{\text{Phosphate removal efficiency}}$ ± 0.40.

When MgO and H_3PO_4 (85%) were used as additional sources, the ammonium removal efficiency and mass of crystals are shown in Figure 4.8. The best ammonium removal efficiency and the highest mass balance were obtained at pH 9, which is similar with the results reported by Kumar *et al.*,(2013).

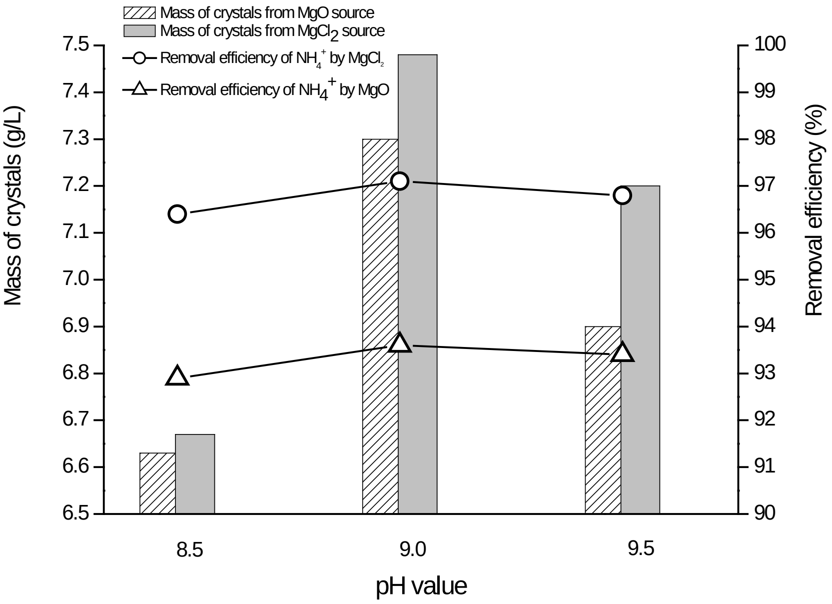

Figure 4.9 System profiles of crystal mass and NH_4^+-N removal efficiency using MgO and H_3PO_4 (85%) and $MgCl_2$•$6H_2O$ +KH_2PO_4 at pH 8.5, 9, and 9.5. 1. STDEVA $_{\text{mass from MgO}}$ ± 0.04; 2. STDEVA $_{\text{mass from MgCl2}}$ ±0.11; 3. STDEVA $_{\text{Ammonium removal efficiency by MgO}}$ ± 0.20; 4. STDEVA $_{\text{Ammonium removal efficiency by MgCl2}}$ ± 0.015.

Figure 4.9 shows that more crystals were precipitated using $MgCl_2$•$6H_2O$ +KH_2PO_4 than the precipitation trial using MgO and H_3PO_4 (85%). The removal efficiency of ammonium when applying $MgCl_2$•$6H_2O$ +KH_2PO_4 was higher than that of MgO and H_3PO_4 (85%). The result in this project well agreed with other researchers' studies. Yetilmezsoy and Sapci *et al.,* (2009) tested three combinations which were $MgCl_2$•$6H_2O$ + KH_2PO_4, $MgSO_4$•$7H_2O$ + $NaHPO_4$•$7H_2O$ and MgO + H_3PO_4 (85%), they concluded that $MgCl_2$•$6H_2O$ + KH_2PO_4 show the best performance in terms of ammonium removal. Kumar *et al.,* (2013) also applied three combinations which were $MgCl_2$•$6H_2O$ + NaH_2PO_4•$12H_2O$, $MgSO_4$•$7H_2O$ + $Ca(H_2PO_4)$•H_2O

and MgO + H_3PO_4(85%), and found that the highest removal efficiency of ammonium was obtained from the combination of $MgCl_2 \bullet 6H_2O$ + $NaH_2PO_4 \bullet 12H_2O$. Hence $MgCl_2 \bullet 6H_2O$ + KH_2PO_4 combination was chosen as additional Mg and P sources when measuring the performance of different molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-} for ammonium recovery.

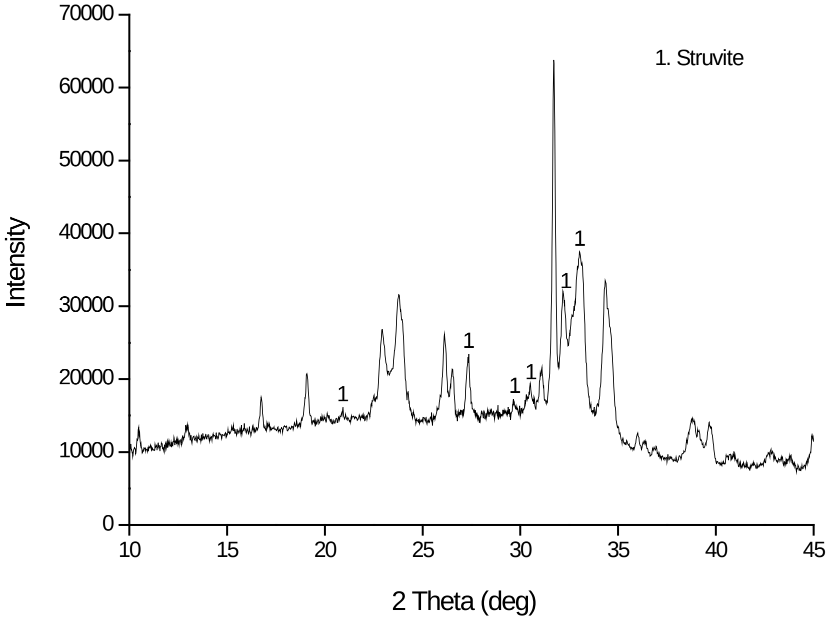

Figure 4.10 XRD shows the struvite precipitated at Mg^{2+}: NH_4^+: PO_4^{3-} molar ratio 1:1:1 at initial pH 9 with MgO as resource. 1. Standard pattern PDF# 15-0762.

Figure 4.10 presents XRD pattern of crystals formed in the precipitation using MgO as source. It is noted that struvite was precipitated crystal which matched well with Standard pattern PDF# 15-0762 from database in terms of peaks position and intensity.

SEM image in Figure 4.11 exhibits that cylinder-like struvite appeared to have fairly uniform size of 15-20 μm and. Du *et al.*, (2010) discovered that the length of crystals precipitated with three chemical combinations was in the range of 15-50 μm with orthorhombic shape. From XRD and SEM analysis, the combination of MgO and H_3PO_4 (85%) can be applied as additional source. However, the pattern is very noisy and there are a lot of other peaks which mean that other chemicals were also precipitated.

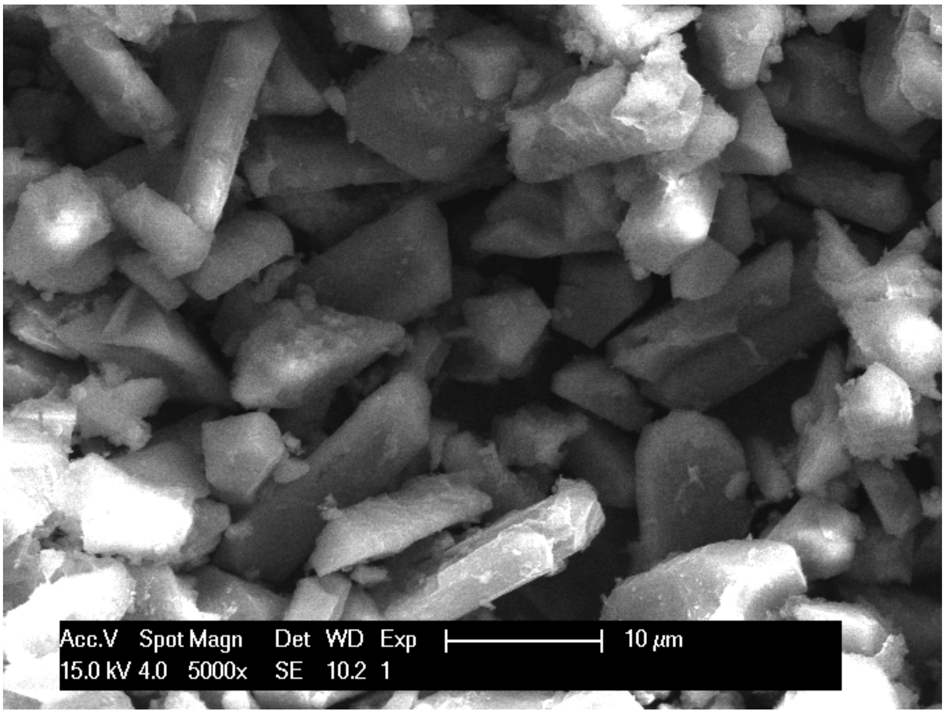

Figure 4.11 SEM image of crystal precipitated by using MgO as resource at pH 9, molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-} =1:1:1.

4.3.3 Effect of Mg^{2+}: NH_4^+: PO_4^{3-} molar ratio

The molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-} has a significant impact on the MAP formation process and removal efficiency of ammonium. A series of tests were designed to measure the performance of MAP precipitation at different Mg^{2+}: NH_4^+: PO_4^{3-} molar ratio on ammonium removal. This study was to find out the best molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-} in terms of ammonium recovery.

When the experiments at molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-} = 1:1:1 and pH 9, were conducted, as shown in Figure 4.12, the removal efficiency of ammonium and phosphate was achieved at 96.4% and 99%, respectively. When increasing the concentration of PO_4^{3-}, the molar ratio of Mg^{2+} : PO_4^{3-} changed from 1:1 to 1:1.6, the removal efficiency of ammonium increased and then decreased to the similar level as at 1:1. These results indicated that the increased concentration of PO_4^{3-} can increase the removal efficiency of ammonium. The same result was obtained by Yetilmezsoy *et al.*, (2009) and Zhang *et al.*, (2011). However, trimagnesium phosphate and magnesium hydroxide could be precipitated if the concentration of Mg^{2+} and PO_4^{3-} is very high, especially if there is plenty of PO_4^{3-}, as reported by Musvoto *et al.,* (2000). They found that when the concentration of PO_4^{3-} was over dosage too much, it will not help much in terms of ammonium removal. Our results supported their findings as shown in Fig 4.12.

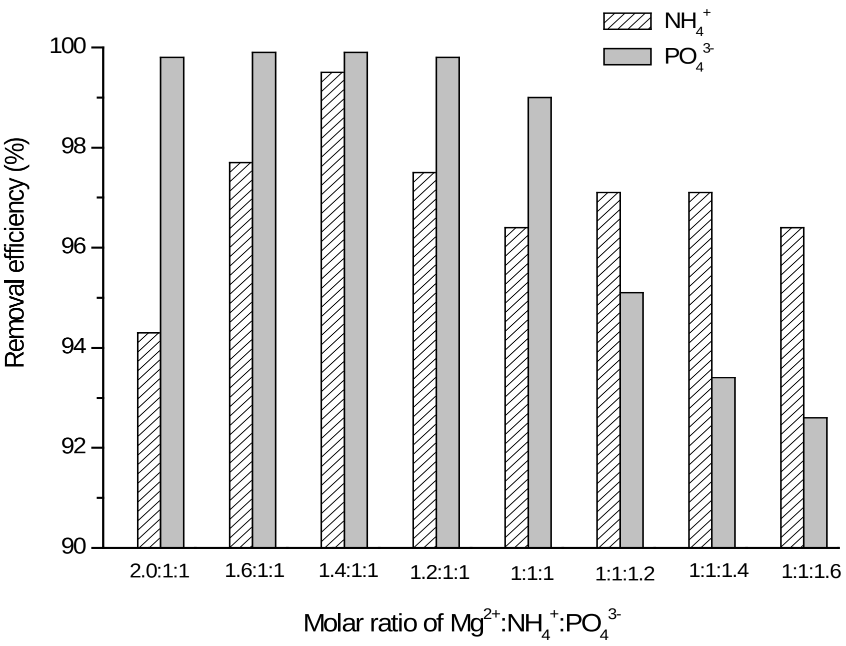

Figure 4.12 Removal efficiency of ammonium and phosphate at different molar ratio of Mg^{2+}:NH_4^+:PO_4^{3-} with pH at 9. 1. STDEVA $_{\text{Ammonium removal efficiency}}$ ± 0.28; 2. STDEVA $_{\text{Phosphate removal efficiency}}$±0.36

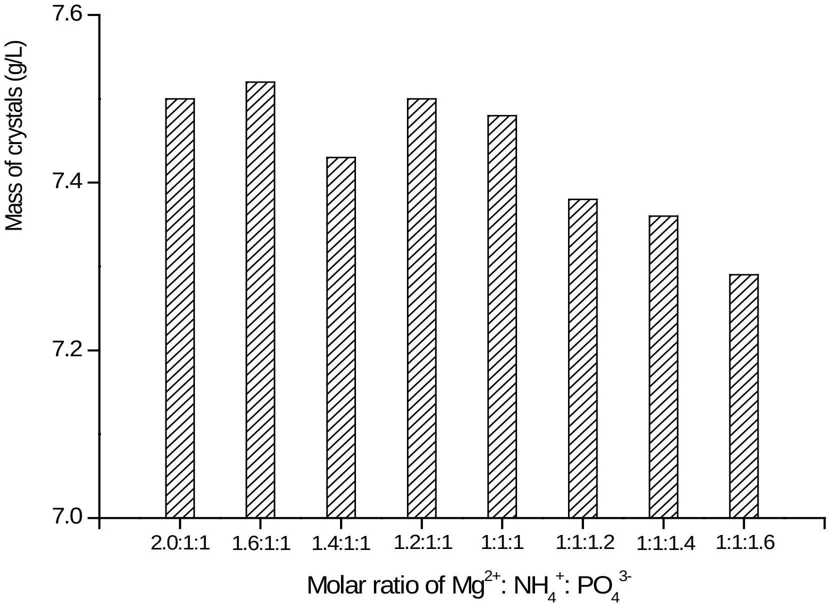

Figure 4.13 Mass of crystals at different molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-} under pH at 9 at stirring rate of 200 rps. (STDEVA $_{\text{mass}}$ ± 0.07).

When the molar ratio of Mg^{2+} :PO_4^{3-} was changed from 1:1 to 2:1, the highest removal efficiency of ammonium 99.5% was reached at 1.4:1, then dropped to 94.3% as the Mg^{2+}: NH_4^+: PO_4^{3-} molar ratio increased from 1.2:1:1 to 1:1:1.6, as indicated Fig 4.12. However, PO_4^{3-} removal appeared to remain at a constantly high level of 99.9% if the Mg^{2+}: NH_4^+ was changed from 2:1 to 1.2:1. Similar results have been reported by Song *et al.*, (2007), who found that the 97% of phosphate has been removed at a molar ratio of Mg^{2+}: PO_4^{3-} = 1.4:1, Uysal *et al.*, (2010) discovered that when the molar ratio of Mg^{2+}: PO_4^{3-} was 1.5:1, 89.35% was the highest removal efficiency for ammonium. Zhang *et al.*, (2009) conducted experiments based on different molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-}. They recognized that increased concentration of magnesium would result in higher removal efficiency of ammonium. However, contradicting result has been reported by Yetilmezsoy and Sapci *et al.*, (2009). They stated that excessive Mg^{2+} has no obvious impact on ammonium removal. In this study, the removal efficiency increased first and then dropped when the molar ratio of Mg^{2+}: PO_4^{3-} increased from 1:1 to 2:1. This can be explained that the excessive Mg^{2+} reacts with phosphate to form $Mg_3(PO_4)_2$, resulting in reducing NH_4^+-N removal efficiency. However, the removal efficiency of phosphate was still very high as shown in Figure 4.12.

The mass of crystals precipitated at different molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-} is shown in Figure 4.13 and Figure 4.15. At a molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-} = 1.4:1:1, the highest removal efficiency of ammonium was obtained. However, the mass appeared to be variable in all trials. Trimagnesium phosphate may be precipitated because the concentration of magnesium and phosphate reached to high levels because $Ksp_{(Mg)3(PO4)2} >> Ksp_{MgNH4PO4\cdot6H2O}$ (Mamais *et al.*,1994). Nelson *et al.*,(2003) also reported that up to 96% of struvite was formed when the molar ratio of

Mg^{2+}:PO_4^{3-} was 1.6:1. Quintana *et al.,* (2005) pointed out that the amount of struvite increased with the increase in magnesium concentration under certain conditions of magnetic stirring and aeration.

Another set of experiments were performed using the molar ratio of Mg^{2+}: NH_4^+ = 1.2:1. Figure 4.14 and 4.15 indicate that the removal efficiency of NH_4^+ increased with the PO_4^{3-} concentration increased. The removal efficiency of ammonium was observed as 99.1% when Mg^{2+}: NH_4^+: PO_4^{3-} was 1.2:1:1.4. However, there was not much difference in terms of NH_4^+ removal between the molar ratio of 1.2:1.4 and 1.2:1.6 as shown in Figure 4.14. A further increase in the PO_4^{3-}concentration would not result in a higher NH_4^+ removal, which was similar with the result obtained by Yetilmezsoy and Sapci *et al.,*(2009). However, the removal of PO_4^{3-} decreased dramatically, which was in accordance with what Capdevielle *et al.,* (2013) reported. The PO_4^{3-} removal was affected by the molar ratio of NH_4^+: PO_4^{3-}. If Mg^{2+}: NH_4^+ was kept constant, an increase in the PO_4^{3-} concentration resulted in lowering the P removal efficiency.

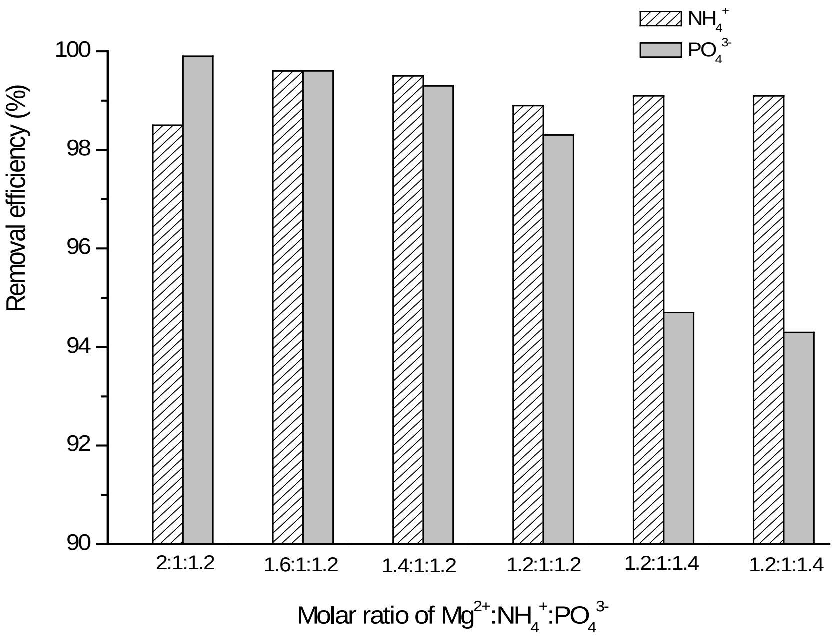

Figure 4.14 Removal efficiency of ammonium and phosphate at different molar ratio of Mg^{2+} : NH_4^+ : PO_4^{3-} with pH at 9 and the stirring rate was 200 rps. 1. STDEVA $_{\text{Ammonium removal efficiency}}$ ±0.19; 2. STDEVA $_{\text{Phosphate removal efficiency}}$ ± 0.29.

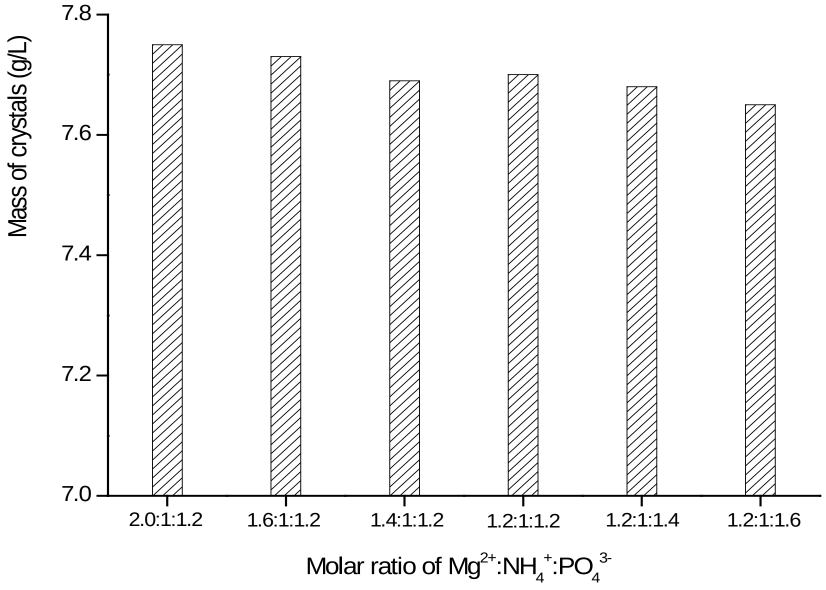

Figure 4.15 Mass of crystals at different molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-} under pH at 9 at stirring rate of 200 rps. (STDEVA $_{\text{mass}}$ ± 0.05).

When the molar ratio of NH_4^+: PO_4^{3-} was fixed at 1:1.2, as the Mg^{2+} concentration increased, the removal efficiency of ammonium raised up to 99.5% at the molar ratio of 1.6:1:1.2, then reduced slightly to 98.5%, as shown in Figure 4.14. The PO_4^{3-} residual in the supernatant became the lowest level at the molar ratio of 2:1:1.2. This conclusion was confirmed again that the increased concentration of Mg^{2+} will lead to higher phosphate removal efficiency (Zhang *et al.,* 2009).

Due to concern of cost, the residual phosphate in the effluent and industrial application of the MAP precipitation process, addition of PO_4^{3-} should be maintained a proper level because it will also contribute to the environment pollution as reported by Basakcilardan-Kabakci *et al.*, (2006); Kabdasli *et al.*, (2003); and Lei *et al.*, (2006). In consideration of the higher NH_4^+ removal efficiency and lower costs, the molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-} = 1.3:1:1.1 will be used in the following experiments.

The highest NH_4^+ removal efficiency was obtained at a molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-} = 1.4:1:1 as the data shown Figure 4.12, and at 1.6:1:1.2 in Figure 4.14. When the most efficient molar ratio was selected from each series of experiments, compared the result showed in Figure 4.16 and 4.17, a conclusion was drawn that molar ratio of 1.3:1:1.1 could be selected as the best a molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-} when considering all factors, such as cost of additional reagents (Mg^{2+} and NaOH), phosphate concentration and removal efficiency of NH_4^+-N. Both ammonium and phosphate could be removed at a high level with the minimum addition of Mg^{2+} and PO_4^{3-}.

The mass profiles of crystals precipitated are presented in Figure 4.17. Other chemicals would be formed in the precipitation system where Mg^{2+} and PO_4^{3-} are rich. This leads to an increasing impurity of the crystals. Hence, the highest removal efficiency of ammonium did not guarantee the highest mass of crystals. After SEM and XRD analysis, the precipitated was MAP as shown in Figure 4.19, Figure 4.20 and Figure 4.21.

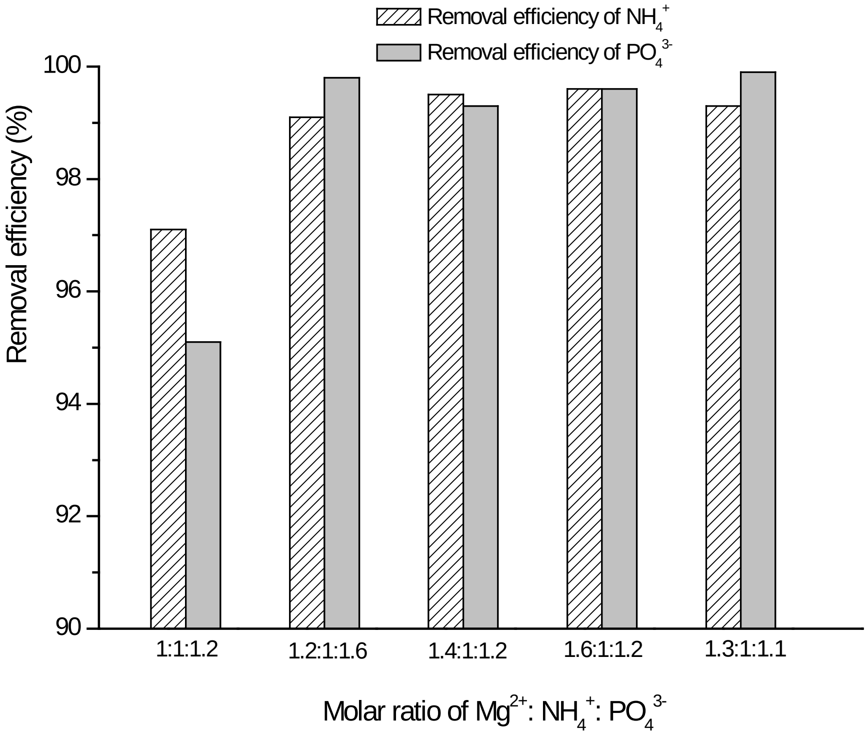

Figure 4.16 Removal efficiency of ammonium and phosphate at different molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-} with pH at 9. 1. STDEVA $_{\text{Ammonium removal efficiency}}$ ±0.09; 2. STDEVA $_{\text{Phosphate removal efficiency}}$ ± 0.35.

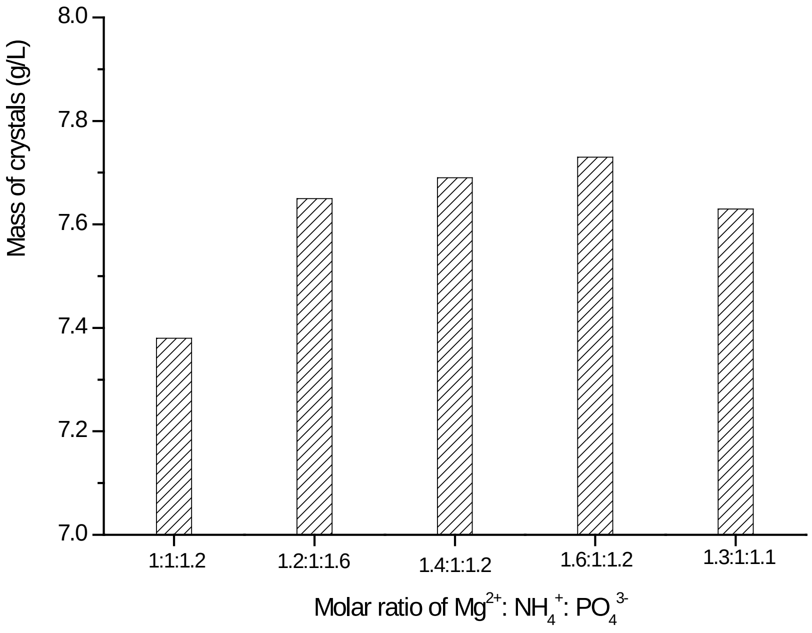

Figure 4.17 Mass of crystals at different molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-} under pH 9. STDEVA±0.12.

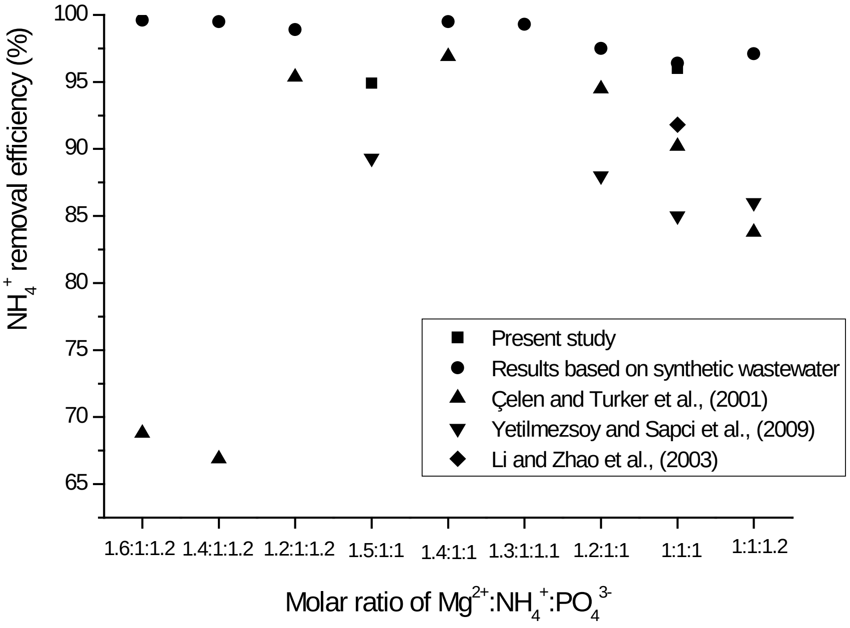

Figure 4.18 Comparison of ammonium removal efficiency obtained by different researchers with different molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-} at pH 9 with $MgCl_2•6H_2O$ as Mg resource.

Based on the present study results, the effect of different molar ratio on the removal of ammonium were evaluated in comparison with other studies. Similar experiment situation has been introduced with the same Mg source ($MgCl_2 \bullet 6H_2O$) and at pH 9, the experimental results in this study were compared with data reported by different researchers (Figure 4.18). Apparently the NH_4^+ removal efficiency obtained in this study was the highest than all those from previous studies. It can be explained that they used real wastewater, while synthetic wastewater was applied in this study. Other chemicals in the wastewater and the operation parameters, such as reagent addition rate and settling time could affect the NH_4^+ removal efficiency. Under the molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-}=1.5:1:1, Uysal *et al.,* (2013) obtained 91.45% removal efficiency of NH_4^+.

The best result was obtained with a molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-}=1.3:1:1.1, the concentration of ammonium and phosphate in effluent was 10.6mg/L and 8mg/L, respectively. This means that the precipitation of MAP can be used to reduce NH_4^+-N significantly before biological treatment (Li and Zhao *et al.,* 1999).

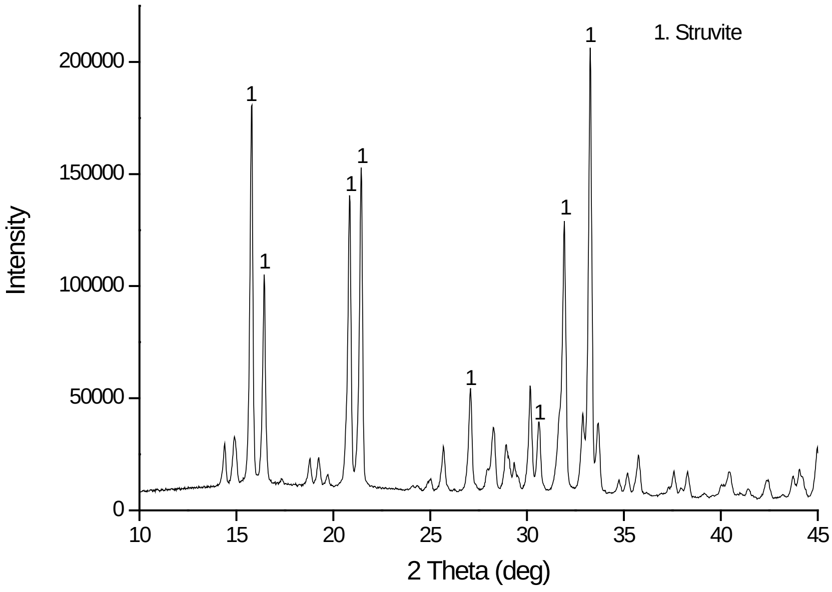

Figure 4.19 XRD pattern of the struvite precipitated at Mg^{2+}: NH_4^+: PO_4^{3-} molar ratio 1:1:1 at initial pH 9 with pH control. 1. Standard pattern PDF# 15-0762.

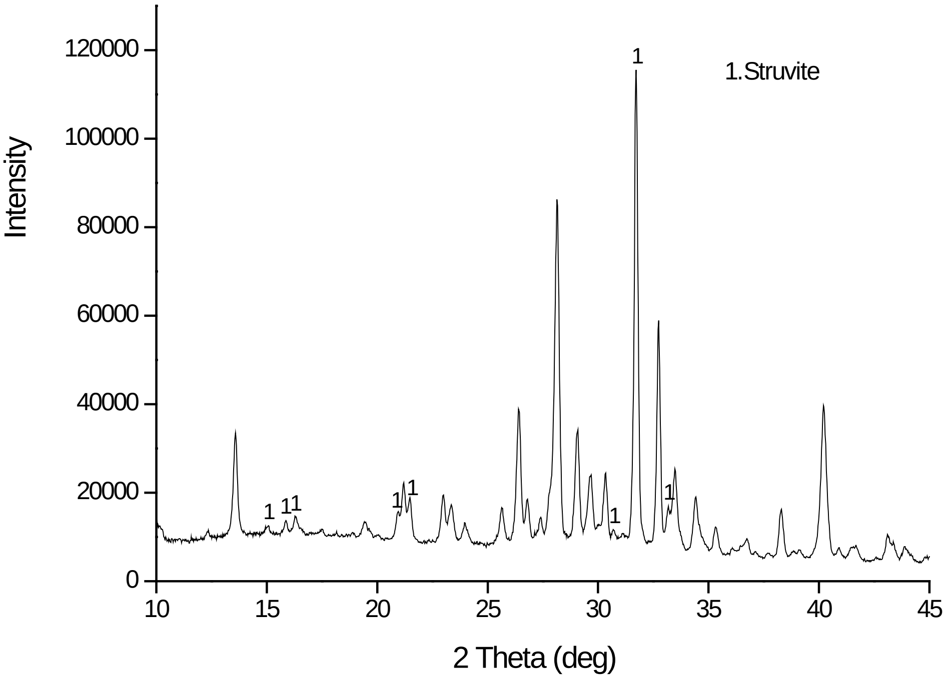

Figure 4.20 XRD of struvite obtained at pH 9 with molar ratio of 1:1:1.2 (Mg^{2+}: NH_4^+: PO_4^{3-}). 1. Standard pattern PDF# 15-0762.

The XRD pattern generated from sample matched well the database model of struvite in terms of peak position and intensity (Figure 4.20), confirmed the existence of struvite (Jaffer *et al.,* 2002).

In this study, at a molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-}=1:1:1.2, the size of struvite obtained was about 15 μm as shown in Figure 4.21. Larger crystals of ~30 μm were found to be dominant in the trail at a molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-}=1.3:1:1.1, The size of crystal obtained by Uysal was about 20 μm with the shape of cuboids with the molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-}=1.5:1:1. Du *et al.,* (2010) discovered that the length of crystals precipitated with three chemical combinations varied in a range of 15-50 μm with orthorhombic shape.

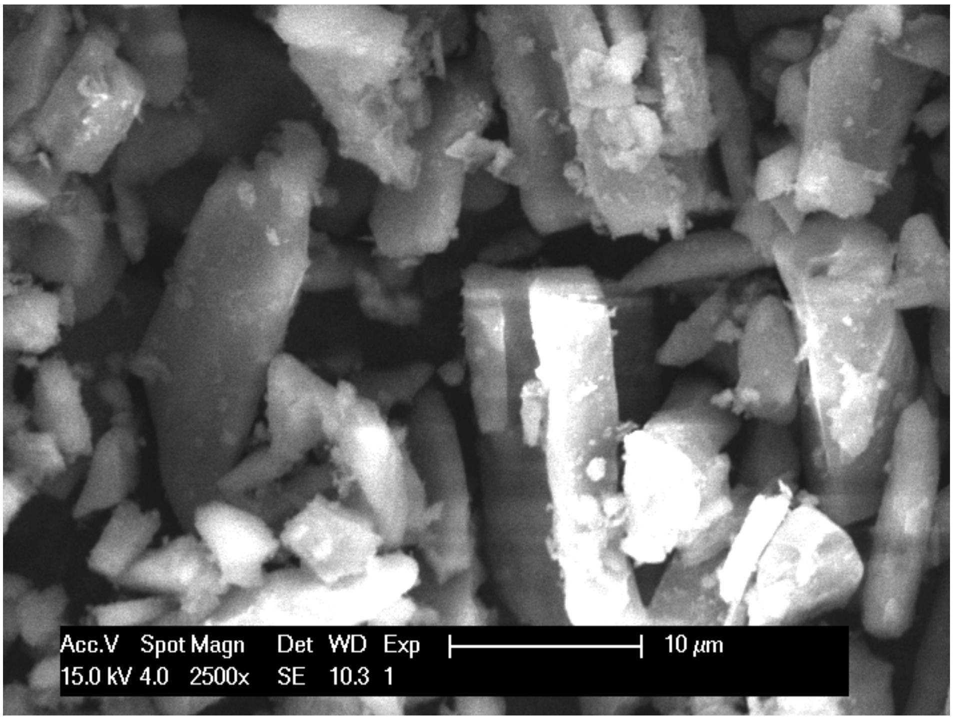

Figure 4.21 SEM image of struvite obtained at room temperature with the molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-} = 1:1:1.2 at pH 9, stirring rate was 200rps.

4.3.4 The effect of feeding rate

Feeding rate is one of the most important operation parameters that influence the formation and crystallization of the MAP crystals and their characteristics. In this study, three feeding rates were introduced to determine the potential effect on the NH_4^+ and PO_4^{3-} removal, size, and morphology of crystals precipitated. Figure 4.22 shows that reagent addition rate appeared to have no significant influence on the removal efficiency of PO_4^{3-} and mass formation, while NH_4^+ removal increased as an increase in feeding rate. Kabdasli *et al.*, (2006) reported that the crystal nucleation process is affected by a number of parameters such as pH, mixing, concentration and presence of foreign ions. In this study, 7.1 mL/min was found to be a favourable reagent addition rate under the stirring rate 200 rps. The best performance in terms of NH_4^+ and PO_4^{3-} removal, and crystal formation was obtained at a reagent addition rate of 7.1 mL/min, as shown in Figure 4.16. In this work, similar mass balance has been obtained (Figure 4.22).

It can be concluded that reagent addition rate had no significant influence on the removal efficiency of ammonium and phosphate as the results shown in this study. The XRD pattern and SEM image are shown in Figure 4.23 and Figure 4.24.

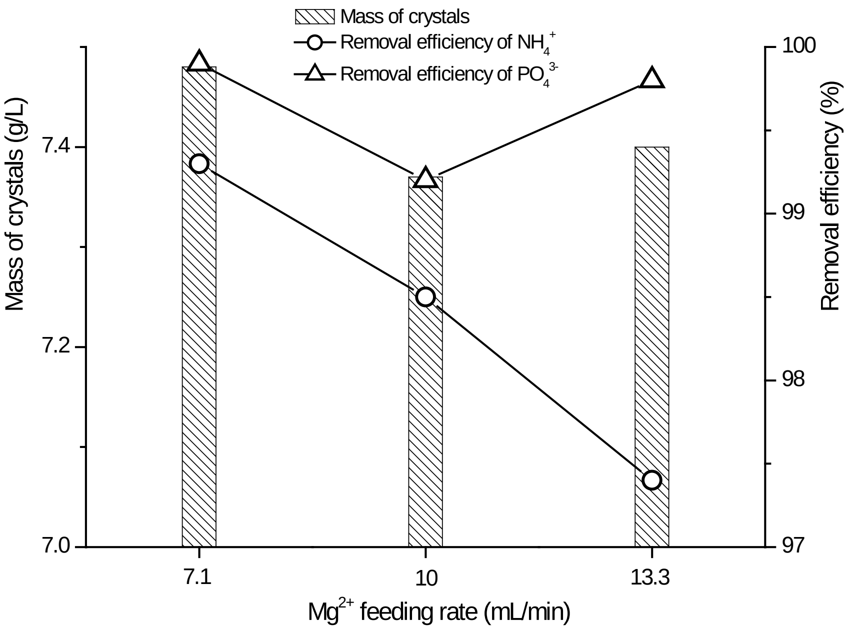

Figure 4.22 Mass of Crystals and removal efficiency of ammonium and phosphate at different feeding rate. 1. STDEVA $_{\text{mass}}$ ±0.07; 2. STDEVA $_{\text{Ammonium removal efficiency}}$ ± 0.04; 3. STDEVA $_{\text{Phosphate removal efficiency}}$ ± 0.06.

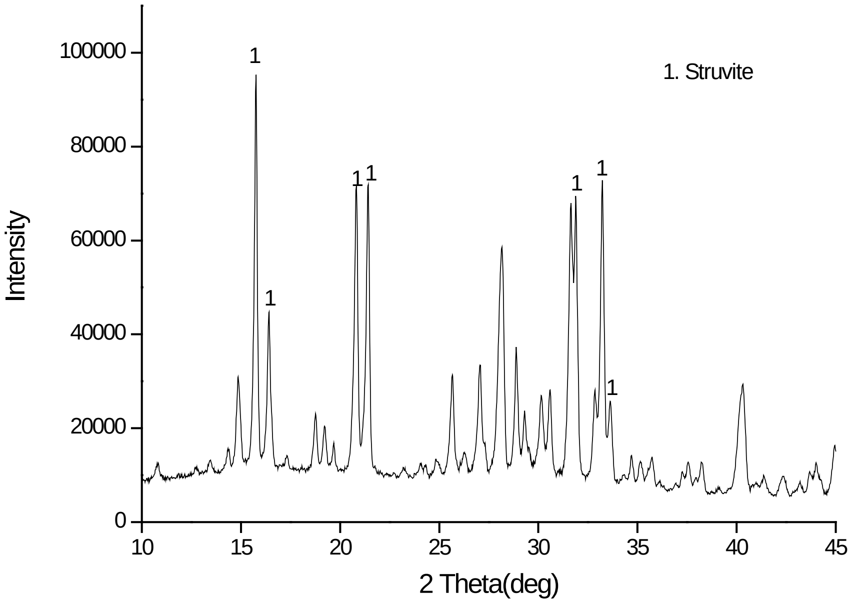

Figure 4.23 XRD of struvite obtained at pH 9 with molar ratio of 1.3:1:1.1 (Mg^{2+}: NH_4^+: PO_4^{3-}) and feeding rate at 7.1 mL/min. 1. Standard pattern PDF# 15-0762.

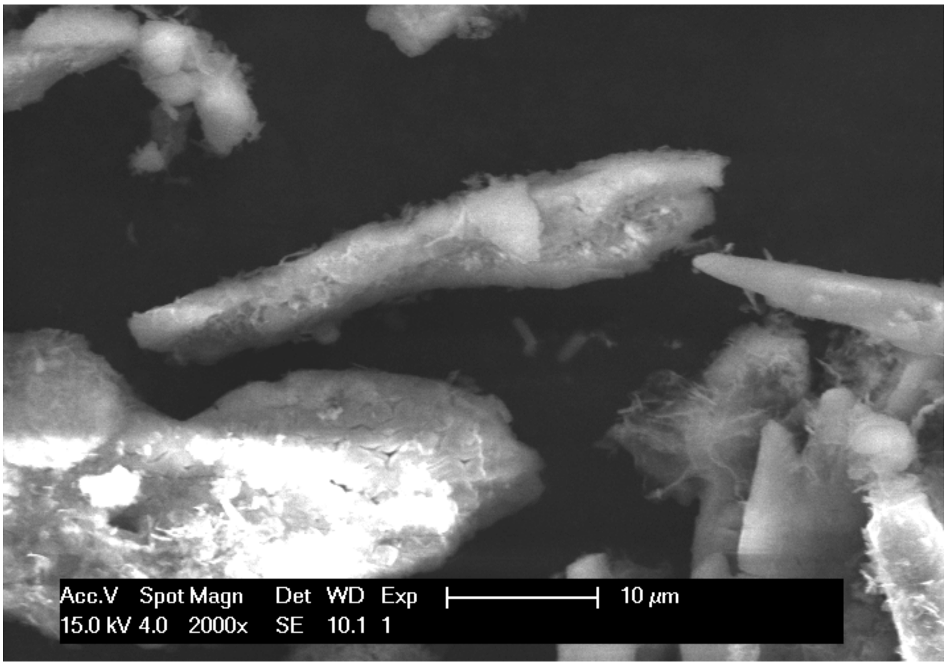

Figure 4.24 SEM image of struvite obtained at 25 ºC with the molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-} = 1.3:1:1.1 at pH 9, reagent addition rate at 7.1 mL/min.

XRD analysis shows (Figure 4.23) that struvite was the dominate precipitate and XRD pattern matches the standard pattern PDF# 15-0762. The size of the crystal obtained was about 30 μm under the reagent addition rate of 7.1 mL/min. The shape of the precipitate was shown in Figure 4.24.

4.3.5 The effect of temperature

Temperature has influence on the ion activity and product solubility (Le Corre *et al.*, 2009), hence it has impact on the MAP process and crystals formation. The purpose of conducting test under different temperatures in this study was to find the possible effect on the removal process in terms of ammonium removal efficiency and size and morphology of crystals precipitated.

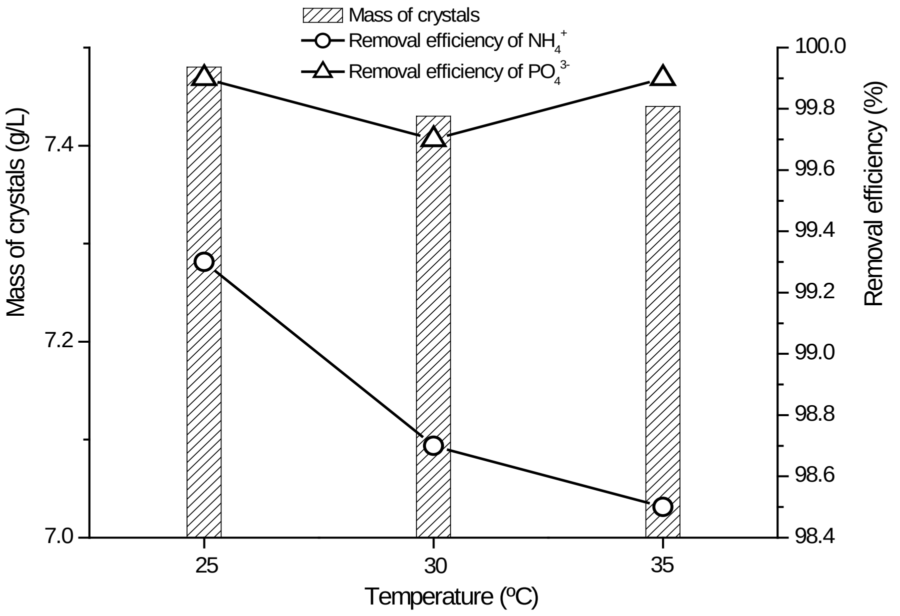

Figure 4.25 Mass of crystals and removal efficiency of ammonium and phosphate at different temperature. 1. STDEVA mass ±0.05; 2. STDEVA $_{\text{Ammonium removal efficiency}}$ ±0.05; 3. STDEVA $_{\text{Phosphate removal efficiency}}$ ± 0.08.

From Figure 4.25, it can be noted that the operation temperature in a range of 25-35 °C had no significant influence on the removal efficiency of NH_4^+-N and PO_4^{3-}-P, as well as crystal mass. This may be because the temperature was not very high and there was no big difference in ions activity except contributing to the volatilization of NH_3. Similar result has been obtained by Çelen and Türker *et al.,* (2001), who did experiments between 25 ºC and 40 ºC at the molar ratio of 1.2:1:1.2. Their result showed that more than 95% ammonium was removed by struvite, which is comparable with 98% ammonium removal in our study as presented in Figure 4.25. This is probably due to different types of wastewater, and parameters, such as: concentrations of ions, stirring rate and feeding rate. Le Corre *et al.,* (2009) has reported that the removal efficiency of phosphate increased with the increase in the reaction temperature and the solubility of struvite was also affected by temperature, With a higher temperature, the significant influence should be the volatility of ammonia from solution.

It is obvious that, as shown in Figure 4.24, 4.26, 4.27, and 4.28, the morphology and size varied with different temperature even only 5 º C differences. Struvite recovered in this study matched with the reference standard pattern from XRD and SEM analysis. When the temperature was raised from 25 ºC to 35 ºC, the size of crystals precipitated were 30 μm, 10 μm, and 14 μm respectively. The shape was shown in Figure 4.27, 4.28, and 4.29. In order to make the crystal settle down easily, the size of the crystal should be a bit larger. Hence, room temperature could be considered as the preferred reaction temperature from industrial application point of view. Rouff *et al.*, (2013) reported that the morphology and size of crystals precipitated were affected by temperature. Their results showed that the size of crystals decreased from 1mm to less than 25 μm when the temperature increased from 25 ºC to 300 ºC. Similar results were also reported by Le Corre *et al.*, (2009) and Aage *et al.*, (1997). Rouff (2013) also reported that 25 ºC was the preferred temperature for the formation of struvite.

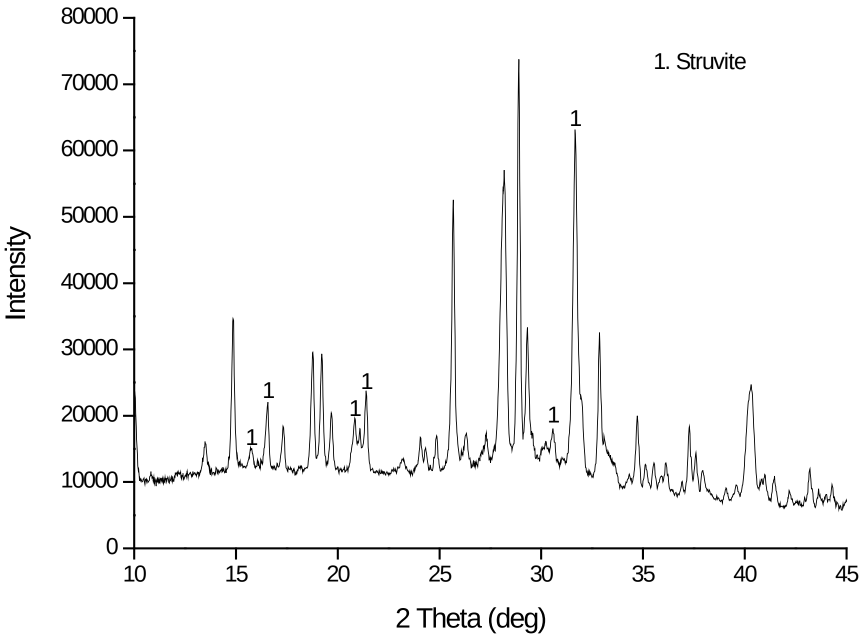

Figure 4.26 XRD of struvite obtained at pH 9 with molar ratio of 1.3:1:1.1 (Mg^{2+}: NH_4^+: PO_4^{3-}) and reagent addition rate at 7.1 mL/min, temperature was 30 degree. 1. Standard pattern PDF# 15-0762.

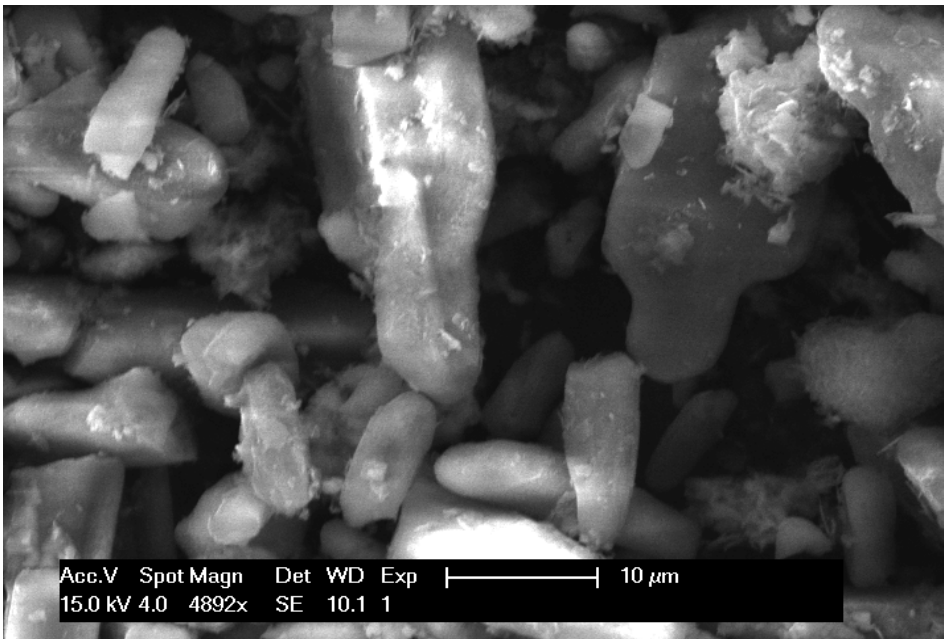

Figure 4.27 SEM image of struvite obtained at 30 ºC with the molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-} = 1.3:1:1.1 at pH 9, stirring rate was 200rps.

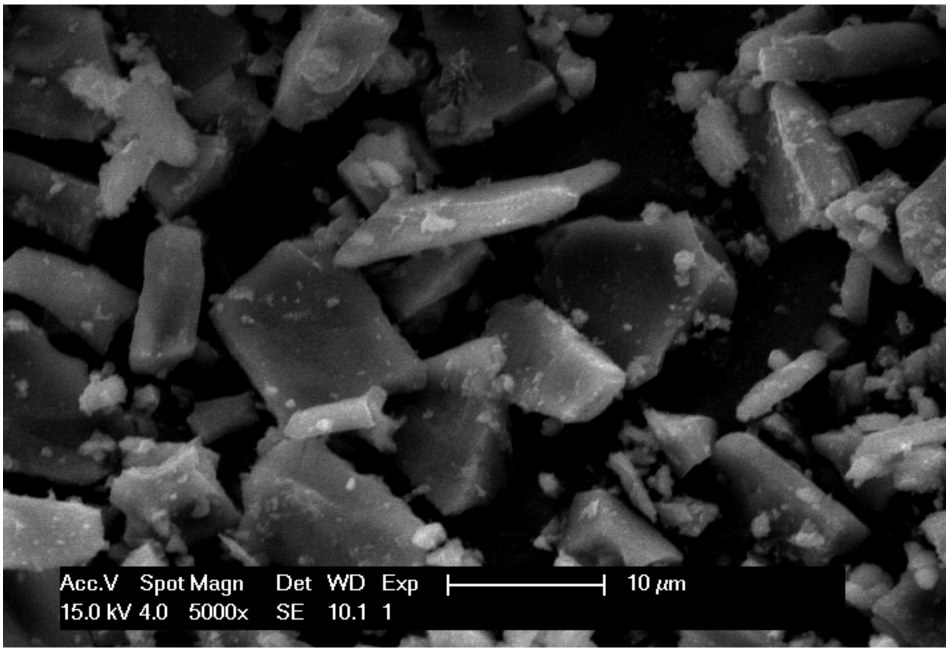

Figure 4.28 SEM image of struvite obtained at 35 ºC with the molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-} = 1.3:1:1.1 at pH 9, stirring rate was 200rps.

4.4 Conclusions

Based on the laboratory scale experiments using synthetic wastewater, following conclusions could be drawn:

1) The best formation pH for struvite precipitation was between 9-9.5. The experimental data obtained in this study appraised pH is the most critical factor for NH_4^+ and PO_4^{3-} removal and recovery through the MAP precipitation process.

2) The combination of $MgCl_2 \bullet 6H_2O$ +KH_2PO_4 resulted in the best performance in terms of removal efficiency when comparing with other combination which was well agreed with the outcome of other researchers.

3) The optimal molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-} was 1.3:1:1.1 based on synthetic wastewater in order to achieve the best yield of struvite.

4) Reagent addition rate and temperature have limited impact on the precipitation process and removal efficiency. However, they can affect the size and morphology of struvite significantly.

5) These operation parameters determined from the artificial wastewater in this study were based on artificial wastewater and may be subjective to further studies using real wastewater from the dewatering effluent from sewage wastewater treatment plant.

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Chapter 5

Modelling of Struvite Precipitation Process

5.1 Introduction

Recently, one technology being widely studied is the NH_4^+-N and PO_4^{3-}-P removal and recovery by the precipitation of magnesium ammonium phosphate (MAP, struvite). This process can retrieve NH_4^+-N and PO_4^{3-}-P simultaneously under supersaturation of these three ions of Mg^{2+}, NH_4 and PO_4^{3-} in solution. The MAP is a valuable fertiliser with rich nutrients of nitrogen and phosphorous beneficial for plants (Çelen and Tüker *et al.*, 2001). In light of this, this method has attracted much attention all over the world. The mechanism of this process is reflected in the following equation (Doyle and Parsons *et al.*, 2002; Yetilmezsoy and Sapci *et al.*, 2009):

$$Mg^{2+} + NH_4^+ + H_nPO_4^{n-3} + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O \downarrow + n\,H^+ \qquad (5.1)$$

(*n=0, 1, 2. n* depends on the pH of the solution)

Different wastewater such as sewage, industrial wastewater, and liquid swine manure has different characteristics in terms of pH and chemical compositions. The changes of pH and other chemicals existed in the wastewater, could significantly affect the MAP precipitation and crystal formation. It is impossible that all these physical and chemical characteristics could be considered and employed in any laboratory scale investigations. The pH is one of the most important factors that affect the precipitation process (Hoffmann *et al.,* 2004). Brooker *et al.*, (1999) indicated that the best pH was between 9-9.4. Nelson *et al.*, (2003) found that the optimum pH for MAP precipitation was 8.9-9.25. Zhang *et al.,* (2011) modelled the effect of pH and found out that the best pH range was between 8.9 and 9.2. By performing laboratory scale experiments based on artificial wastewater, the best pH range obtained in this study was 9-9.5 (Data shown in Chapter 4). In this study, 9 was chosen as fixed reaction pH. However, there are a few crucial questions which need to be answered, when this technology is scaled up and applied for an industrial application, including how to prearrange the reaction situations? And how to predict and determine the dosage of operational parameters?

It is a costing and cumbersome job to determine that how much alkali and Mg sources are needed because the chemical contents of the wastewater can be variable from one wastewater source to others. In this study, a software model of thermodynamic equilibrium Visual MINTEQ 3.0 was applied. It is the aim of this study that this model is used to predict the formation of struvite from sludge dewatering effluent from Bolivar wastewater treatment plant (WWTP) in South Australia. From the results presented in Chapter 4, this study will focus on the most important operation parameters: molar ratio of Mg^{2+}: NH_4^+: PO_4^{3+}, and pH control and their impact on ammonium removal and recovery via the precipitation of struvite. This research will provide reference for the application of this precipitation technique and optimization of the crystallization process for the removal and recovery of nitrogen and phosphorus. The modelling results would be validated by the results obtained in the laboratory scale experiments in this study and those reported in the literature.

5.2 Materials and Methods

5.2.1 Materials

The wastewater was obtained from Bolivar wastewater treatment plant, Adelaide, and stored in cool room (4 ºC) for experiments. The characteristics of the wastewater are shown in Table 5.1. This wastewater is made up of 40% industrial wastewater and 60% municipal wastewater. It is obvious that there is not enough Mg^{2+} and PO_4^{3+} in the wastewater compared to ammonium. In order to maximize the removal of ammonium, additional Mg^{2+} and PO_4^{3+} sources should be applied (Münch and Bar *et al.*,2001; Ryu *et al.*,2008).

Table 5.1 Characteristics of raw wastewater from Bolivar WWTP, ADELAIDE (STDEVA±5.0).

Characteristics (mg/L)	NH_4^+	PO_4^{3-}	Mg^{2+}	K^+	Ca^{2+}	Alkalinity (as $CaCO_3$, mg/L)	pH
	643	235	45	30	42	1153	7.67

Chemicals used in this project were: $MgCl_2 \bullet 6H_2O$ (Ajax Finechem Pty Ltd), KH_2PO_4 (Chem Supply SA), aHCl (32%) (Ajax Finechem Pty Ltd), NaOH (Chem Supply SA). All chemicals are of analytical grade and used as received. 1 N NaOH and 1 N HCl were used for pH control. 1 L flask, 1 L beakers, and glass stirring stick, were used in all experiments. Millipore water (MilliQ water, 18.2 $M\Omega \cdot cm^{-1}$) was obtained from an EASY pure Ⅱ ultra Mill-Q water purification system.

5.2.2 Struvite precipitation test

The laboratory MAP precipitation system was equipped with a pH meter (pH/Ion 510, Bench pH/Ion/mV meter), a syringe pump (NE-300), a stirrer (IKA Colour SQUID), three 1L beakers，and a timer (Crown Scientific). The pH was measured adjusted using 1 N NaOH solution and 1 N HCl solutions to the desired level. The reaction was stirred at 200rpm and was completed in 20 min. The samples were settled for 1 h, according to Abbona *et al.,*(1982), All experiments were carried out at ambient temperature and 1 atm, and were repeated triple times for each experiment to get the mean experimental results.

5.2.3 Characterization of precipitated crystals

The characteristics of the crystals were measured by X-ray Diffraction (MiniFlex 600, Rigaku, Japan). The size and morphology of the crystals were determined and characterised by Scanning Electron Microscope (SEM) (Philips XL 30).

5.2.4 Analytical methods and procedures

The main parameters monitored were pH, concentrations of Mg^{2+}, NH_4^+ and PO_4^{3-}. PO_4^{3-} was measured by a spectrophotometer (LIUV-201 UV/Vis spectrometer). NH_4^+ was measured by a colorimeter (DR/890 HACH) using Amver^{TM} HACH Test ‘N Tube High Range Ammonium Reagent Set. Magnesium was measured by an atomic absorption spectrophotometer (SHIMADZU, AA-6300). Alkalinity was measured by standard titration method (APHA 2005).

5.3 Chemical modelling

In order to study the possibility of this chemical process, a number of models have been developed by previous researchers (Scott *et al.,* 1991; Wrigley *et al.,* 1992; Musvoto *et al.,* 2000a; Musvoto *et al.,* 2000b). Gadekar *et al.,* (2010) applied a MAPLE 10 program which was a mathematical model of the precipitation process using physio-chemical expressions. Harada *et al.*, (2006) designed an equilibrium model to predict struvite formation and optimal pH, and then conducted experiments with urine as ammonium and phosphate sources to test their prediction modelling. Tong and Chen *et al.*, (2009) and Zhang and Chen et al., (2009) employed central composite design (CCD) of response surface methodology (RSM) to design their experiments. PHREEQC 2.11 (Developed by US Geology survey) has been applied by Wang *et al.*, (2006) to study possibility of crystallization of MAP by comparing saturation index (SI) with ΔG. Miles and Ellis *et al.,* (2001) used thermodynamic equilibrium model MINTEQA2 to predict struvite precipitation from anaerobic wastes. Response surface methodology was used to model individual factors and their interactions in a few studies (Mason *et al.,*2003; Wu *et al.,* 2011; Wu and Zhou *et al.,* 2012). In these studies, a chemical thermodynamic equilibrium model--Visual MINTEQ was introduced to predict the dose optimization. Türker *et al.,* (2010) applied METLABORATORY program to calculate the species in the model. Of all models applied by previous researchers, Visual MINTEQ is a powerful database that can be used to calculate the concentration of different ions, solubility and equilibrium of solid and dissolved species in an aqueous solution (Çelen *et al.*, 2007).

All the models are based on the dynamics equilibrium of ionic, dissolved and undissolved species in the solution. Basically, in order to apply the chemical equilibrium model in synthetic wastewater, NH_4^+, PO_4^{3-}, Mg^{2+}, NH_3, H_3PO_4, $MgNH_4PO_4 \bullet 6H_2O$ are the main chemical species existing in the wastewater. While at the same time, ions such as: HPO_4^{2-}, $H_2PO_4^-$, $MgH_2PO_4^+$, $MgOH^+$, $MgPO_4^-$, dissolved species such as: $MgHPO_4$, H_3PO_4, and undissolved species, such as: $Mg_3(PO_4)_2 \bullet 8H_2O$, $Mg_3(PO_4)_2 \bullet 22H_2O$, $Mg(OH)_2$, $MgHPO_4$, and struvite could also possibly co-exist in the solution under the equilibrium situation. As for real wastewater, it will be much complicated which consists of more chemical species, including $Ca_3(PO_4)_2$, $CaHPO_4$, $Ca(OH)_2$, $CaCO_3$, $CaMg(CO_3)_2$, metal phosphate [$\mathbf{M}_3(PO_4)_2$], $MgCO_3$, other heavy metals and organic matters. All these species could have a considerable impact on the chemical equilibrium and its modelling validation.

Loewenthal *et al.,* (1994) and Ohlinger *et al.,* (1998) developed a simple model by considering struvite as the only solid, The chemical species which they employed included NH_4^+, PO_4^{3-}, Mg^{2+}, HPO_4^{2-}, $H_2PO_4^-$, NH_3, H_3PO_4, H_2CO_3, CH_3COO^-, and CH_3COOH. Ohlinger and co-worker's model (1998) also included $MgH_2PO_4^+$, $MgPO_4^-$, and the impact of ionic strength. Wang *et al.,* (2006) involved $Mg(OH)_2$ in their model other than those considered by Ohlinger *et al.,* (1998). Scott *et al.,* (1991) developed a model including five undissolved species: $Mg_3(PO_4)_2 \bullet 8H_2O$, $Mg_3(PO_4)_2 \bullet 22H_2O$, $Mg(OH)_2$, $MgHPO_4$, and struvite, as well as other species involved in the model by Wang *et al.,* (2006). In general, eight solids $Mg_3(PO_4)_2 \bullet 8H_2O$, $Mg_3(PO_4)_2 \bullet 22H_2O$, $Mg(OH)_2$, $MgHPO_4$, struvite, magnesite, monetite, and $Ca(OH)_2$ are main chemical species which have been considered and employed in previous studies. It is likely that the more dissolved and undissolved species are considered, the more complex of the model could be, making the application of the model technically difficult and practically unfeasible for scaling-up and operation of the commercial MAP reactor process.

5.4 Visual MINTEQ 3.0 setup and model revise

5.4.1 Thermodynamic chemical equilibrium

Visual MINTEQ 3.0 is a chemical equilibrium computer program that has thermodynamic data which can be used to estimate species, solubility, and equilibria of dissolved and solid phases in aqueous system (Çelen *et al.,* 2007). This program is the window version of MINTEQA2 and the data for aqueous species include those from MINTEQA2 which was originally developed by the US Environmental Protection Agency in 1999. MINTEQA2 has been exploited by several researchers to predict the precipitation of struvite (Buchanan *et al.*, 1994, Miles and Ellis *et al.*, 2001). Lee *et al.,* (2003) reported that the concentrations of Mg^{2+}, NH_4^+, PO_4^{3-}, and crystals precipitated can be computed by Visual MINTEQ software. In this project, the performance of different molar ratio applied to Bolivar wastewater was investigated and computed under certain pH.

5.4.2 Model revise

It is noticeable that struvite is not included in Visual MINTEQ 3.0. In this study, pK_{sp}=13.26 was used because it was used frequently (Ohlinger *et al.,* 1998), and struvite was added to the database by management tool.

The possible magnesium containing species are: struvite ($NH_4MgPO_4{\bullet}6H_2O$), magnesium hydrogen phosphate trihydrate or newberyite ($MgHPO_4{\bullet}3H_2O$), brucite [$Mg(OH)_2$], bobierrite [$Mg_3(PO_4)_2{\bullet}8H_2O$], and $Mg_3(PO_4)_2{\bullet}22H_2O$, magnesite ($MgCO_3$), nesquehonite ($MgCO_3{\bullet}3H_2O$), dolomite [$CaMg(CO_3)_2$], and huntite [$CaMg_3(CO_3)_4$]. Researchers have found that, at a higher concentration of magnesium and phosphate, the predominant precipitate is newberyite when pH is lower than 6.0 (Musvoto *et al.*, 2000a). At a pH higher than 10.5, brucite is more likely to precipitate (Musvoto *et al.*, 2000b). For trimagnesium phosphate [$Mg_3(PO_4)_2{\bullet}8H_2O$ and $Mg_3(PO_4)_2{\bullet}22H_2O$], Mamais *et al.*,(1994) has indicated that these two chemicals may precipitate eventually, but the crystallization rate is much slower than that of struvite. Thus trimagnesium phosphate was excluded in the model. Dolomite [$CaMg(CO_3)_2$], and huntite [$CaMg_3(CO_3)_4$] exist in nature, while the precipitation conditions of these two chemicals are not well understood, and the process rate is very slow (Mamais *et al.*, 1994). Thus, dolomite and huntite were eliminated from the model.

Species that contain Ca^{2+} considered in this study included monetite (DCP, $CaHPO_4$), dicalcium phosphate dehydrate (Brushite) (DCPD, $CaHPO_4$ $2H_2O$), hydroxyapatite [HAP, $Ca_5(PO_4)_3OH$], tricalcium phosphate (whitelockite) [TCP, $Ca_3(PO_4)_2$], and octacalcium phosphate [OCP, $Ca_8(HPO_4)_2(PO_4)5H_2O$], $Ca(OH)_2$, and calcite ($CaCO_3$). According to Musvoto et al. (2000), if there is sufficient Mg^{2+}, PO_4^{3-}, and Ca^{2+} in wastewater, precursor species would be generated first, then followed to become more thermodynamical stable chemicals, such as HAP, TCP or DCP. While the process to form HAP, precipitation of OCP and TCP is very slow (Ferguson and McCarty *et al.*, 1971) and can be affected severely by the presence of magnesium

(Salimi et al.1985; Abbona *et al.,* 1990). Therefore, HAP, OCP and TCP were removed from the database. Musvoto *et al.,* (2000b) has found out that Mg, phosphate and dissolved organics have great impact on the formation of calcite. Thus, calcite was omitted from database. $Ca(OH)_2$ will be formed at pH higher than 10.5. It was also excluded in the model.

In summary, precipitates considered in the model database are: struvite, newberyite, brucite, magnesite ($MgCO_3$), nesquehonite ($MgCO_3 \bullet 3H_2O$), monetite (DCP, $CaHPO_4$), Brushite (DCPD, $CaHPO_4 \bullet 2H_2O$).

5.4.3 Model operation conditions

The Debye-Huckel method was chosen for activity correction when setting up a model because it is used most widely (Buchanan *et al.,* 1994). The crystals were allowed to precipitate when the ions reach their supersaturation. The model was set up to output the concentration of Mg^{2+}, NH_4^+, PO_4^{3+}, Ca^{2+}, and solids precipitated after reaction.

The main page of Visual MINTEQ 3.0 is shown in Figure 5.1, Figure 5.2 shows the management tool of this model to add or delete possible solids.

pH: Calculated from mass balance

Ionic strength: Fixed at... / To be calculated

Activity: Debye-Hückel

Concentration unit: mg/l / ug/l

Temperature: 25 deg C

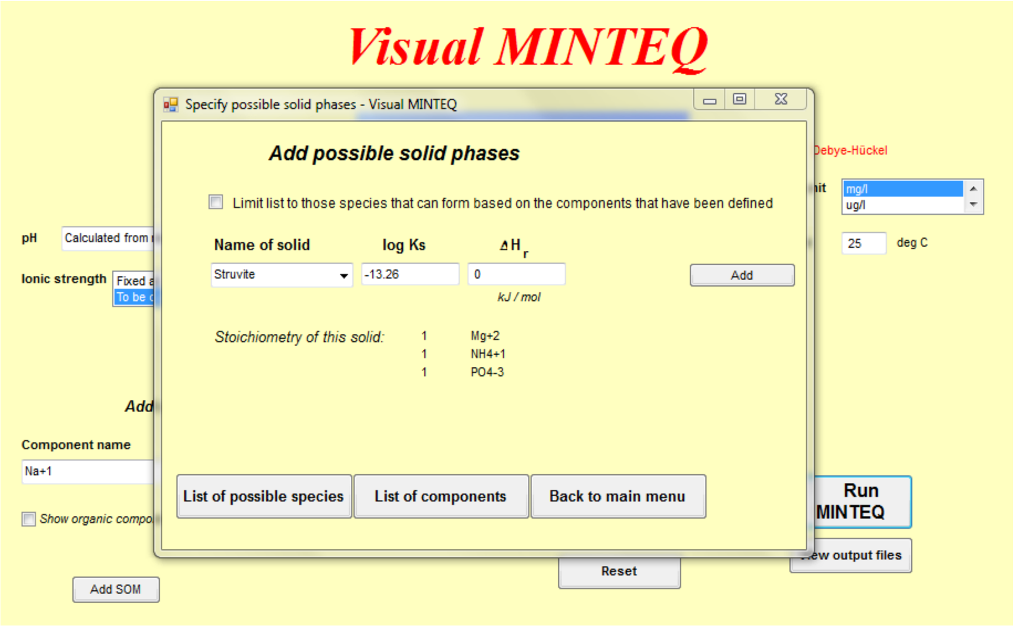
Component name: Select from list

Total concentration: ● 0 mg/l

Fixed activity: ○

☐ Show organic components

Figure 5.1 The main page of Visual MINTEQ 3.0



☐ Limit list to those species that can form based on the components that have been defined

Name of solid: Struvite

log Ks: -13.26

ΔH_r: 0 kJ / mol

Stoichiometry of this solid:
1 Mg+2
1 NH4+1
1 PO4-3

Component name: Na+1

Figure 5.2 Management tool of Visual MINTEQ 3.0 is used to add or delete possible solids to output.

The characteristics of wastewater from Bolivar WWTP, Adelaide are shown in Table 5.1. It is obvious that there is not enough phosphate and magnesium comparing to ammonium. In order to maximise the removal of ammonium, additional phosphate should be applied (Münch and Bar *et al.,* 2001; Ryu *et al.,* 2008; Stefanowicz *et al.,* 1992; He *et al.,* 2007). This modelling process was based on six conditions associated with the relevant assumptions as described in the following statements.

Assumption 1 The original wastewater, pH was adjusted to 9 by 1 M and 5 M NaOH and 1 M HCl to measure the addition of NaOH.

Assumption 2 The molar ratio of ammonium and phosphate is 1:0.8. KH_2PO_4 would be added to adjust to required value. Alkalinity was measured straight away after addition of KH_2PO_4.

Condition 1 The molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-}=1:1:0.8. $MgCl_2{\bullet}6H_2O$ and KH_2PO_4 were added to adjust to the required value. The pH was adjusted to 9 by 1 M and 5 M NaOH and 1 M HCl.

Condition 2 The molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-}=1.5:1:0.8. $MgCl_2{\bullet}6H_2O$ and KH_2PO_4 were added to adjust to the required value. The pH was adjusted to 9 by 1 M and 5 M NaOH and 1 M HCl.

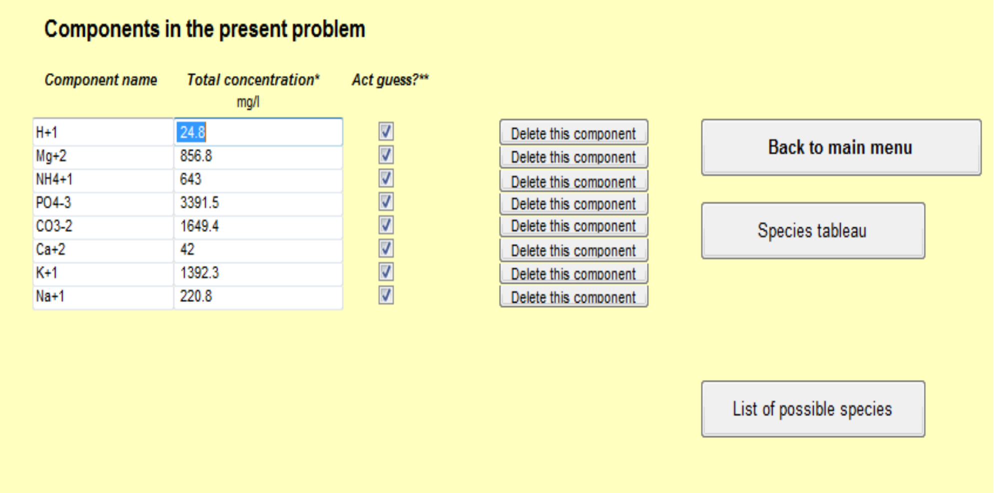
Assumption 3 The molar ratio of ammonium and phosphate is 1:1. KH_2PO_4 would be added to adjust to required value.

Condition 3 The molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-}=1:1:1. The pH was adjusted to 9 by 1 M and 5 M NaOH and 1 M HCl. $MgCl_2{\bullet}6H_2O$ and KH_2PO_4 were added to adjust to the required value.

Condition 4 The molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-}=1.5:1:1. The pH was adjusted to 9 by 1 M and 5 M NaOH and 1 M HCl. $MgCl_2$•$6H_2O$ and KH_2PO_4 were added to adjust to the required value.

Condition 5 The molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-}=2:1:1. The pH will be adjusted to 9 by 1 M and 5 M NaOH and 1 M HCl. $MgCl_2$•$6H_2O$ and KH_2PO_4 were added to adjust to the required value.

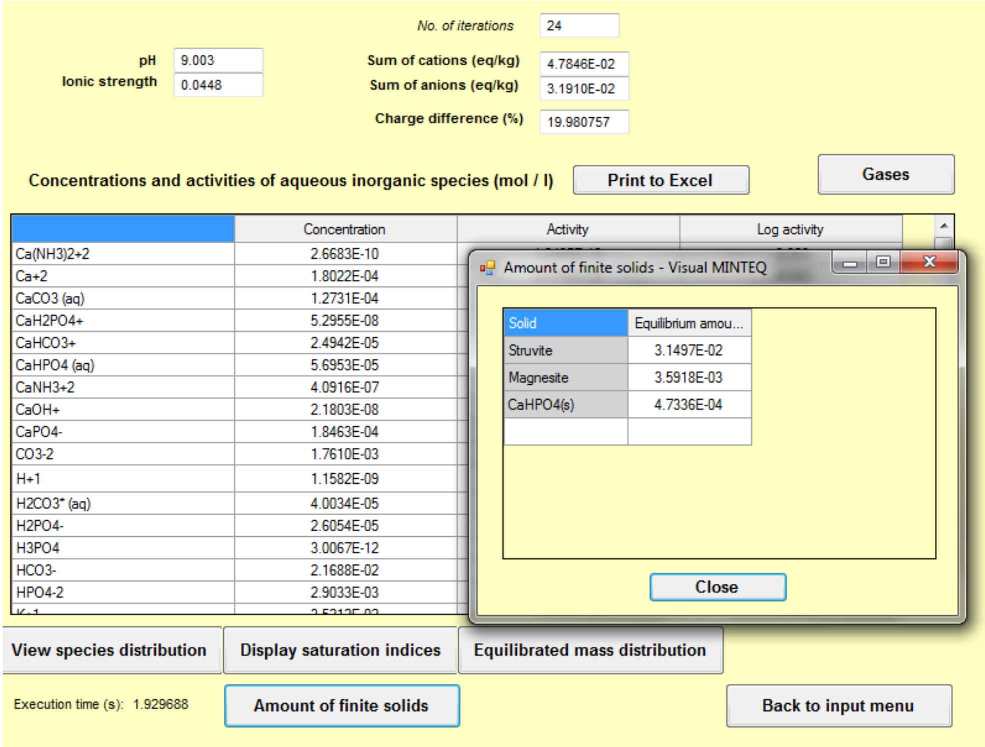
Figure 5.3 shows the page where components concentrations can be added and deleted in Visual MINTEQ 3.0. Figure 5.4 shows the output of pH, possible solids, ionic strength and residual concentrations of different ions.



Components in the present problem

Component name	Total concentration* mg/l	Act guess?**
H+1	24.8	☑
Mg+2	856.8	☑
NH4+1	643	☑
PO4-3	3391.5	☑
CO3-2	1649.4	☑
Ca+2	42	☑
K+1	1392.3	☑
Na+1	220.8	☑

Figure 5.3 The components concentration page to input the different concentrations of ions.


No. of iterations: 24

pH: 9.003

Ionic strength: 0.0448

Sum of cations (eq/kg): 4.7846E-02

Sum of anions (eq/kg): 3.1910E-02

Charge difference (%): 19.980757

Concentrations and activities of aqueous inorganic species (mol / l)

	Concentration	Activity	Log activity
Ca(NH3)2+2	2.6683E-10		
Ca+2	1.8022E-04		
CaCO3 (aq)	1.2731E-04		
CaH2PO4+	5.2955E-08		
CaHCO3+	2.4942E-05		
CaHPO4 (aq)	5.6953E-05		
CaNH3+2	4.0916E-07		
CaOH+	2.1803E-08		
CaPO4-	1.8463E-04		
CO3-2	1.7610E-03		
H+1	1.1582E-09		
H2CO3* (aq)	4.0034E-05		
H2PO4-	2.6054E-05		
H3PO4	3.0067E-12		
HCO3-	2.1688E-02		
HPO4-2	2.9033E-03		

Amount of finite solids - Visual MINTEQ

Solid	Equilibrium amou...
Struvite	3.1497E-02
Magnesite	3.5918E-03
CaHPO4(s)	4.7336E-04

Execution time (s): 1.929688

Figure 5.4 Model outputs of pH, ionic strength, solids and concentration of different ions.

5.5 Results and Discussion

5.5.1 Model output

By doing trial and error addition, 13.3ml of 1 M NaOH was required to increase pH to 9 for the original wastewater, according to the assumption 1. As shown in Table 5.2, an increase in the pH of the solution could only lead to 5.2% NH_4^+ removal, if no additional Mg^{2+} and PO_4^{3-} sources were provided. When $MgCl_2 \bullet 6H_2O$ and KH_2PO_4 was added to raw wastewater, the alkalinity and pH changed, which needed to be measured again and by doing trial and error addition, and H^+ and CO_3^{2-} was measured again.

Table 5.2 Modelling process to measure the dosage of NaOH needed to reach pH 9.

Characteristics (mg/L)	NH_4^+	PO_4^{3-}	Mg^{2+}	K^+	Ca	Na	H^+	CO_3^{2-}	Alkalinity (as $CaCO_{3,}$ mg/L)	pH
Input 1									1153	7.67
Output 1							24.9	1437.4		
Input 2	643	235	45	30	42	305.9	11.6	1437.4		
Output 2	609.7	66.4	1.8	29.9	41.9	306	11.5	1437.2		9
Struvite						434.9mg/L				

Condition 1 The molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-}=1:1:0.8. $MgCl_2 \bullet 6H_2O$ and KH_2PO_4 were added to adjust to the required value. The pH was adjusted to 9 by 1 M and 5 M NaOH and 1 M HCl.

Table 5.3 Model outputs of different ions, removal efficiency of NH_4^+-N and PO_4^{3-}-P, and solid phase predicted under different conditions.

conditions	Input of parameters (mg/L)								N removal (%)	P removal (%)	Output solid phase and mass (mg/L)
	NH_4^+	PO_4^{3-}	Mg^{2+}	Ca^{2+}	K^+	H^+	Na^+	CO_3^{2-}			
1	643	2713.2	856.8	42	1047.9	16.4	409.4	1654.2	75.7	94.5	Magnesite (681.6) Struvite (6609.1) monetite (3.9)
2	643	2713.2	1285.2	42	1047.9	1.0	765.9	1654.2	79.1	98.6	Magnesite (2022.7) Struvite (6903.6)
3	643	3391.5	856.8	42	1392.3	24.8	220.8	1649.4	88.4	89.5	Magnesite (301.7) Struvite (7716.8) monetite (64.4)
4	643	3391.5	1285.2	42	1392.3	8.95	585.35	1649.4	92.8	93.7	Magnesite (1633.5) Struvite (8282.5) monetite (52.1)
5	643	3391.5	1713.6	42	1392.3	0.6	777.2	1649.4	98.4	98.2	Magnesite (2283.3) Struvite (8589.5)

For all conditions, $MgCl_2•6H_2O$ and KH_2PO_4 were added to reach the required molar ratios: 1:1:0.8, 1.5:1:0.8, 1:1:1, 1.5:1:1, 2:1:1, respectively. The dosage of NaOH was also estimated in order to get the output pH 9 as shown in Table 5.3. For Condition 1, 75.7% of ammonium and 94.5% phosphate were removed from wastewater, Wu and Zhou *et al.,* (2012) reported that 74.36% of ammonium removal was computed at pH 8.87 by Visual MINTEQ. Under this condition, 712 mg/L NaOH was estimated in order to get pH 9. The model also indicated that, under this condition, there were three crystals are expected to be formed, including magnesite (681.6 mg/L), struvite (6609.1 mg/L) and $CaHPO_4$(s) (3.9 mg/L). For Condition 2, the removal efficiency of ammonium and phosphate was 79.1% and 98.6%, respectively. The predicted dosage of NaOH was 1332 mg/L. However, there are only two crystals formed: struvite and magnesite. Table 5.3 also depicts that from Condition 1 to Condition 2, the removal efficiency of ammonium and phosphate was increased from 75.7% to 79.1%, and 94.5% to 98.6%, respectively, when the molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-} was raised from 1:1:0.8 to 1.5:1:0.8. These results confirm again that an increase in concentration of Mg^{2+} would result in increasing removal efficiency of ammonium and phosphate (Çelen *et al.,* 2007).

Condition 3 tells us that, in principle, when the molar ratio of NH_4^+ and PO_4^{3-} was 1:1, the removal efficiency of NH_4^+ and PO_4^{3-} were 88.4% and 89.5%, respectively. 384 mg/L NaOH was needed to adjust pH to 9. The precipitated minerals were magnesite and struvite. In Conditions 4 and 5, the removal efficiency of ammonium and phosphate was 92.8% and 93.7%, and 98.4% and 98.2%, respectively. NaOH were needed at 1018 mg/L and 1351.7 mg/L, respectively. The same conclusion can be drawn that the increased concentration of Mg could result in increasing NH_4^+

removal efficiency. An increase in PO_4^{3-} concentration would lead to increased removal NH_4^+ efficiency.

The results show that Visual MINTEQ model can be used to prearrange the concentration of different ions and ammonium removed by struvite precipitation. Once data was input to this model, the additional reagents needed could be estimated (Wu and Zhou *et al.*, 2011).

5.5.2 Experimental results

Table 5.1 shows that there were not enough Mg^{2+} and PO_4^{3-} in wastewater for removing ammonium through MAP precipitation process, Buchanan *et al.,*(1994) and Miles and Ellis *et al.*, (2001) found that additional Mg^{2+} and PO_4^{3-} need to be suppled in order to maximize the removal of ammonium. Liu *et al.,*(2011) confirmed that a large amount of Mg^{2+} and PO_4^{3-} reagents are needed in order to effectively remove NH_4^+. The results of Visual MINTEQ 3.0 were compared with the results from my laboratory experiments which were carried out under the same conditions as modelled. The pH of wastewater was adjusted to pH 9. The MAP process was assessed by determination of the removal efficiency of ammonium and phosphate. By using pH meter and a stirring plate, KH_2PO_4 was first added to amend the required PO_4^{3-} dosage in the solution. It was determined that the dosage of NaOH (1M) was 13.3 ml in Assumption 1. The removal efficiency of NH_4^+ and PO_4^{3-} and other parameters were shown in Table 5.4 and 5.5.

Table 5.4 indicates that the removal efficiency of ammonium and phosphate under Condition 1 was 76.7% and 95.9%, respectively, showing a proportional increase associated with the increase in the Mg^{2+} concentration. Ali *et al.,* (2003) applied Visual MINTEQ and discovered that Mg^{2+} could be an indicator of the formation of struvite by measuring the mass of Mg^{2+} in the flow before and after the precipitation reaction. This was the same result from experiments based on artificial wastewater (Data shown in Chapter 4), which were also confirmed by Zhang *et al.,* (2009) and Song *et al.,* (2007). However, the removal efficiency of ammonium was 96% when the molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-}=1:1:1, decreased to 94.9% at 1:5:1:1 and increased again to 99.5% in Condition 5. Based on laboratory scale experiments, Wu and Zhou *et al.,* (2012) obtained 98.8% removal efficiency of ammonium at pH 9.5 and molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-}=1.26:1:1.11, which corresponded very well to the result obtained in this study.

Table 5.4 Experimental results of different ions, removal efficiency of NH_4^+ and PO_4^{3-}, and crystals confirmed under condition 1, 2, and 3 (STDEVA ±5. 0).

Parameters (mg/L)	Condition 1 (Mg^{2+}: NH_4^+: PO_4^{3-}=1:1:0.8)			Condition 2 (Mg^{2+}: NH_4^+: PO_4^{3-}=1.5:1:0.8)		
	Untreated	Residual	Reduction (%)	Untreated	Residual	Reduction (%)
NH_4^+	643	150	76.7	643	120.9	81.2
PO_4^{3-}	2713.2	111.2	95.9	2713.2	40.7	98.5
Mg^{2+}	856.8	4.1	99.5	1285.2	16.2	98.7
Ca^{2+}	42	39.2	0	42	41.5	0
K^+	1047.9	1043.3	0	1047.9	1038.7	0
pH	6.80	9		6.80	9	
NaOH added (mg/L)		676.4			1198.8	
Alkalinity (mg/L as $CaCO_3$)		1045			1045	
Crystals confirmed by XRD		Magnesite Struvite Struvite-(K)			Magnesite Struvite Struvite-(K)	

Table 5.5 Experimental results of different ions, removal efficiency of NH_4^+ and PO_4^{3-}, and crystals confirmed under condition 4, 5, and 6 (STDEVA ±5.0).

Parameters (mg/L)	Condition 3 (Mg^{2+}: NH_4^+: PO_4^{3-}=1:1:1)			Condition 4 (Mg^{2+}: NH_4^+: PO_4^{3-}=1.5:1:1)			Condition 5 (Mg^{2+}: NH_4^+: PO_4^{3-}=2:1:1)		
	Untreated	Residual	Reduction (%)	Untreated	Residual	Reduction (%)	Untreated	Residual	Reduction (%)
NH_4^+	643	25.7	96.0	643	32.8	94.9	643	3.2	99.5
PO_4^{3-}	3391.5	5.3	99.8	3391.5	13.6	99.6	3391.5	10.2	99.7
Mg^{2+}	856.8	4.0	99.5	1285.2	8.3	99.4	1713.6	200.5	88.3
Ca^{2+}	42	21.2	49.5	42	25.6	39	42	39.8	0
K^+	1392.3	1338.1	3.9	1392.3	1340.6	3.7	1392.3	1355.8	2.6
pH	6.78	9		6.78	9		6.79	9	
NaOH added		372.5			946.7			1135.3	
Alkalinity (mg/L as $CaCO_3$)		1030			1030			1030	
Crystals confirmed by XRD		Magnesite Struvite Struvite-(K) Monetite			Magnesite Struvite Struvite-(K) Monetite			Magnesite Struvite Struvite-(K)	

Sun *et al.,* (2011) studied and compared the precipitation of struvite and struvite-(K) in goats during urolithiasis. Their results showed that the crystals in urine included struvite and struvite-K before stone formation. However, the main crystal was struvite-K after calculi was formed. Crystals formed at different stages are shown in Figure 5.5.

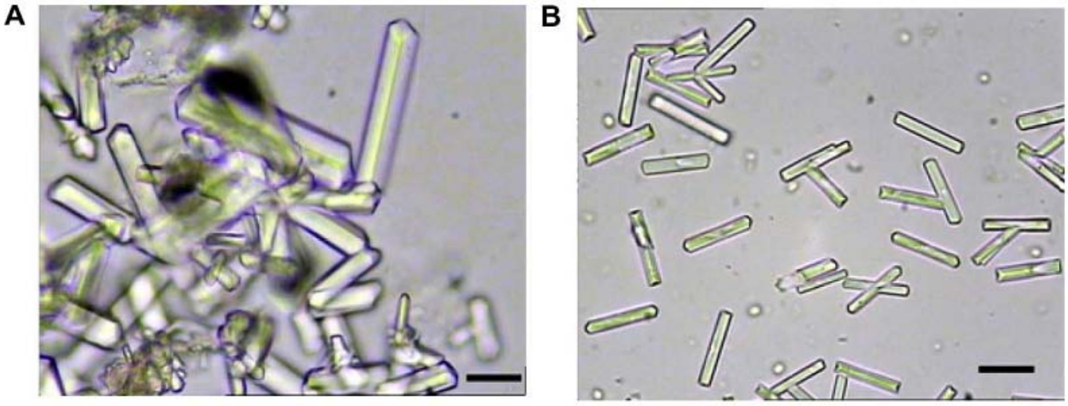


Figure 5.5 Crystals different shape and size in stage A and stage B detected by Sun *et al.,* (2011).

Capdevielle *et al.,* (2013) also detected struvite-(K) from precipitates when the solutions were let to settle for 24h after the reaction. Based on synthesized struvite-K, Zhang *et al.,* (2011) studied the XRD pattern shown in Figure 5.6.

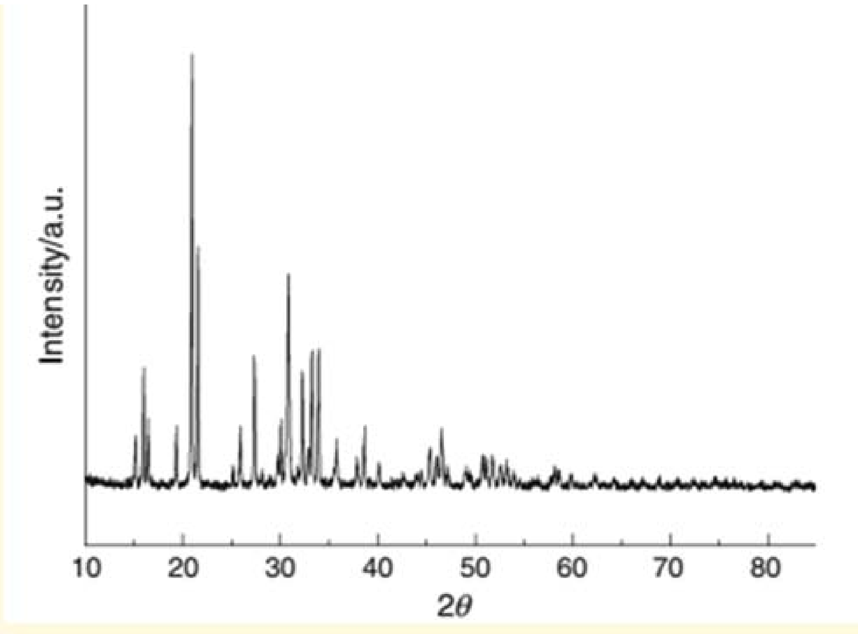


Figure 5.6 XRD of struvite-K studied by Zhang et al (2011)

Many factors included the chemical compositions and concentrations, and operation parameters associated with the MAP precipitation system need to take into consideration. However due to the objective of this project, the factors that affect the formation of struvite-(K) would not be studied and discussed in this project. As struvite-(K) consists of K, Mg, and P, we could assume that this chemical could also be used as fertiliser. The formation of this product also meant that K^+ would affect the struvite precipitation process under certain circumstances. Thus, further detailed tests need to be done to explore the precipitation conditions in this field.

5.5.3 Mass balance analysis

To get a better understanding of the mechanisms of ammonium removal through the MAP formation, the suspended, precipitated and centrate contents were analysed, including NH_4^+ and PO_4^{3-}. Precipitated crystals were dissolved to do further ions analysis. Table 5.7 provides the results from Condition 4. From Table 5.6, there is 7.9% ammonium loss which may not be related to struvite precipitation. This difference was the loss of ammonium by ventilation, mainly because the experiment was conducted in an open beaker and the samples were stirred for 20 min at 200 rps. However, Çelen *et al.,* (2007) reported 35% loss of ammonium was not accounted in crystals and supernatant. 17.9% difference has been recognized by Çelen and Tüker *et al.,* (2001). Wu and Zhou *et al.,* (2012) also experienced 14.83% and 17.35% losses in their experiments using synthetic wastewater with different initial concentrations.

Theoretically, the molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-} is 1:1:1, the molar ratio of these three ions in the precipitate is 0.97:0.89:1 indicating that struvite was formed. The mass difference for PO_4^{3-} and Mg^{2+} was 0.4% and 1.3%, respectively.

Table 5.6 Mass balance analysis from condition 4 (STDEVA ±5.0).

	NH_4^+(mg)	PO_4^{3-}(mg)	Mg^{2+}(mg)	Ca^{2+}(mg)
Untreated centrate (600mL)	64.3	339.2	85.7	4.2
Supernatant(597mL)	2.6	3.2	2.4	4.19
Precipitate (HCl)	56.6	334.5	82.2	0
Mass in (Untreated)	64.3	339.2	85.7	4.2
Mass out (Supernatant + precipitate)	59.2	337.7	84.6	4.19
Difference (%)	7.9%	0.4%	1.3%	0.2%

5.5.4 X-ray diffraction results

Crystals generated from laboratory scale MAP precipitation system were determined by X-ray diffraction. Under condition 1, three minerals were confirmed by X-ray diffraction which were magnesite, struvite and struvite-(K) (Figure 5.1 and 5.2). Under Conditions 3, struvite, magnesite, and monetite were also confirmed in the crystals which well agreed with model prediction except struvite-(K). While Çelen *et al.,* (2007) suggested that brushite should be formed under this operation condition. However, brushite was not detected in this experiment, probably due to its instability at a higher pH or the complexity of the wastewater. The size of struvite was determined in a range of 10 to 25 μm as shown in Figure 5.8.

Despite the crystals confirmed in this study, another interesting chemical was also detected associated with struvite formation, which was $MgKPO_4{\bullet}6H_2O$ [struvite-(K)]. SEM image of struvite-(K) was shown in Figure 5.9. Grasser *et al.,* (2008) has studied the morphology of struvite-(K) based on specimen from Lengenbach, Switzerland and Rossblei, Schladminger Tauern, Styria, Austria. Pictures were shown in figure 5.10 and 5.11. In this work, the size of struvite- (K) was about 15-20 μm.

As shown in the Figure 5.7, there were other peaks present in X-ray diffraction pattern. More detail can be tracked by further analysis of wastewater and XRD software or expert in chemical field.

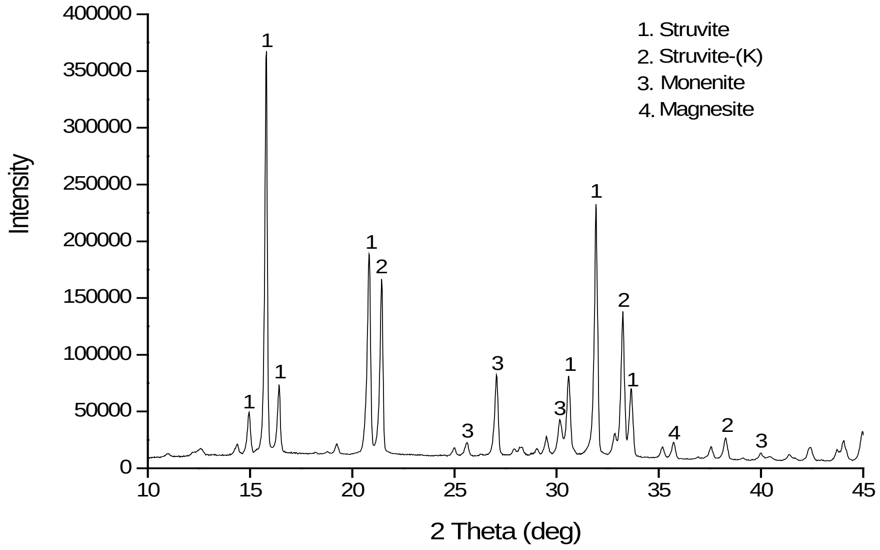


Figure 5.7 XRD pattern of struvite, struvite-(K), monetite, and magnesite confirmed under Condition 3. (1. Struvite, Standard pattern PDF# 15-0762; 2. Struvite-(K), Standard pattern PDF# 35-0812; 3. Monenite, Standard pattern PDF# 09-0080; 4. Magnesite, Standard pattern PDF# 08-0479.)

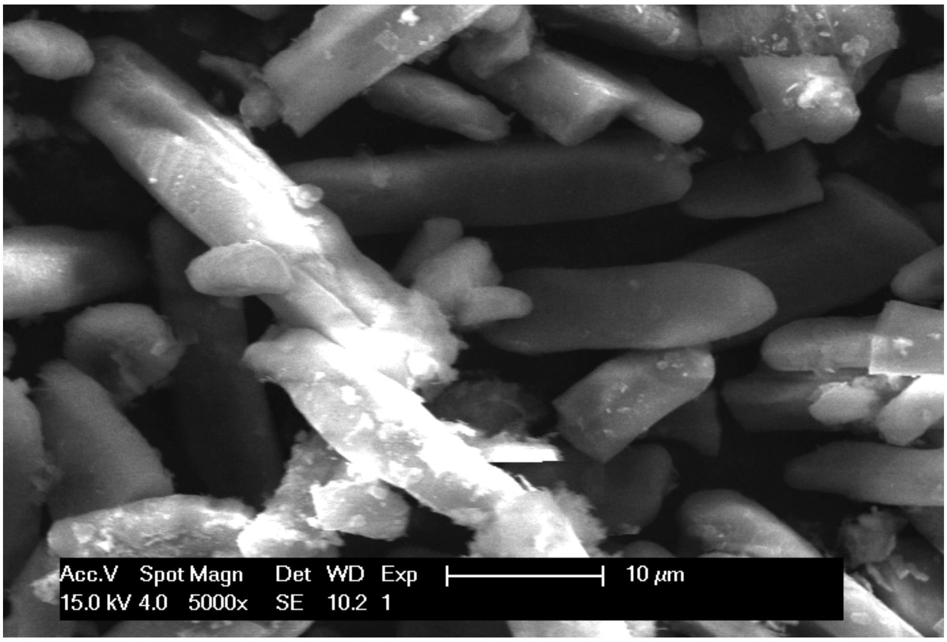


Figure 5.8 SEM image of struvite under Condition 3.

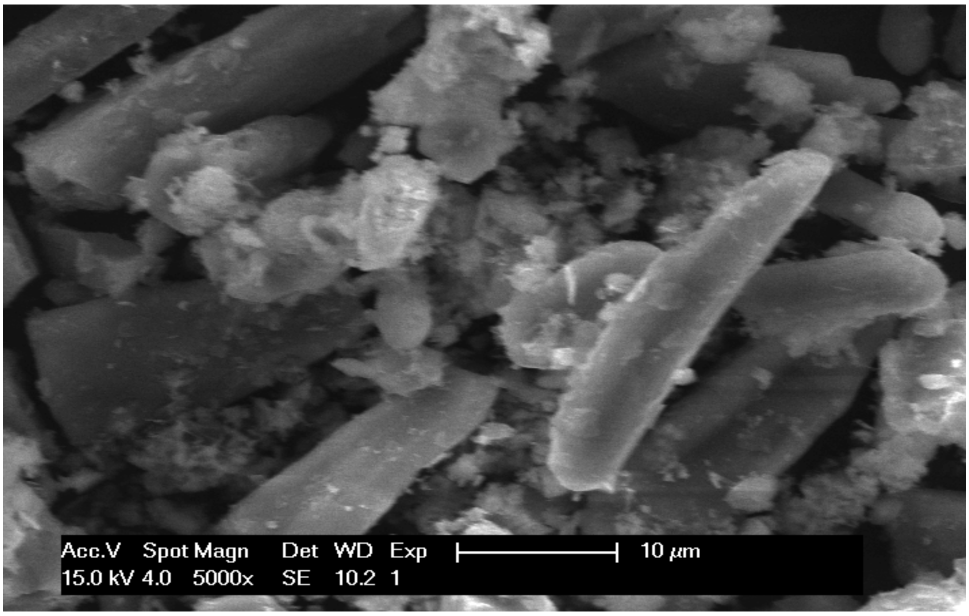


Figure 5.9 SEM image of struvite-(K) under Condition 4.

5.6 Comparison of experimental data with modelling results

Table 5.9 shows the outcomes predicted from the model and the results generated from laboratory scale experiments. Because there were insufficient tests available in literature, hence the comparison was based on data obtained in this work. In general, it could be concluded that the experimental data agreed well with the predicted outcomes.

From Table 5.3, when the centrate pH was increased to 9 without Mg^{2+} addition, the actual removal efficiency of ammonium was only 6.1%, whereas the model result was 5.2%. Çelen *et al,* (2007) obtained 65.9% phosphate removal without any additional chemicals, probably because of difference of contents of the wastewater applied in the experiments.

After the molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-} was adjusted, a conclusion can be made from Table 5.5. In order to maximize the removal efficiency of NH_4^+, additional Mg^{2+} and phosphate are necessary (Stefanowicz *et al.*, 1992; He *et al.*, 2007). When the molar ratio of NH_4^+: PO_4^{3-} was 1:0.8, the Mg^{2+}concentration was increased from Condition 1 to Condition 2, resulting in increasing the NH_4^+: removal efficiency from 75.7% to 79.8% based on model outcome, and from 76.7% to 81.9% according to the experiment results. When the molar ratio of NH_4^+: PO_4^{3-} was 1:1, the NH_4^+ removal efficiency increased from 88.4% to 98.4% from Condition 3 to 5, while the experimental results varied from 96% to 94.9%, and then increased to 99.5%.

It is obvious that the actual removal efficiency appeared slightly higher than the predicted results, probably due to the volatilization of ammonium. The loss of ammonium through volatilization could be monitored by using partial pressure in Visual MINTEQ3.0, while the volatilization is mass transport based rather than equilibrium. Thus, an obvious error could be expected from this model, for example in Condition 4.

The crystals predicted by the model were mostly in accordance with solids precipitated from the experimental tests. However, XRD results revealed that struvite-(K) was detected in the precipitation samples under all operation conditions. The actual dosage of NaOH required was 3%-20% which was lower than the model output, as shown in Table 5.8. This may be because the model was based on $CaCO_3$ alkalinity only, while the actual ions that contributed to alkalinity would include phosphoric acid, dissolved ammonia, and $CaCO_3$. The model input appeared to overestimate NaOH dosage needed to raise pH to 9.

Table 5.7 Comparison of modelling outputs and experimental results under different conditions.

	Predicted NH_4^+ removal (%)	Actual NH_4^+ removal (%)	Predicted dosage of NaOH (mg/L)	Actual dosage of NaOH (mg/L)	Crystals predicted by model	Crystals determined by XRD
Condition 1	75.7	76.7	712	676.4	Magnesite Struvite Monetite	Magnesite Struvite Struvite-(K)
Condition 2	79.1	81.2	1332	1198.8	Magnesite Struvite	Magnesite Struvite Struvite-(K)
Condition 3	88.4	96	384	372.5	Magnesite Struvite Monenite	Magnesite Struvite Struvite-(K) Monetite
Condition 4	92.8	94.9	1018	946.7	Magnesite Struvite Monenite	Magnesite Struvite Struvite-(K) Monetite
Condition 5	98.4	99.5	1351.6	1135.3	Magnesite Struvite	Magnesite Struvite Struvite-(K)

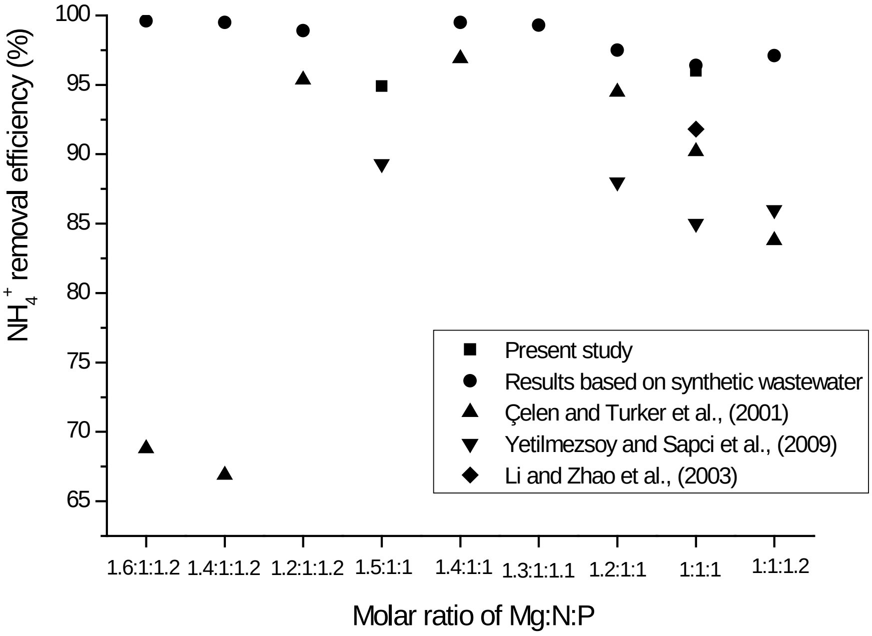


Figure 5.10 Comparison of ammonium removal efficiency obtained by different researchers with different molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-} at pH 9 with $MgCl_2 \bullet 6H_2O$ source.

From the experimental results generated from current work, the effect of different molar ratio on the removal of ammonium at the same pH was compared with the data reported by other studies. The same Mg resource ($MgCl_2 \bullet 6H_2O$) was used in all these studies. Figure 5.8 compares the data which were obtained by different researchers (Yetilmezsoy and Sapci *et al.,* 2009; Çelen and Türker *et al.,* 2001; Li and Zhao *et al.,* 2003) with the results from this study using artificial wastewater (data shown in Chapter 4). It can be seen that the removal efficiency in this study appeared to be comparably higher than those reported data. A similar result has been reported by Wu and Zhao *et al.,* (2012), from which 98.80% ammonium was removed from artificial wastewater at pH 95. The reason can be explained that different wastewater sources were utilised in different studies, as well as operation conditions, such as the feeding rate, phosphate source and settling time could be variable from case to case.

5.7 Summary

In order to maximize ammonium removal efficiency from dewatering centrate, additional reagents must be added including Mg^{2+} and PO_4^{3-} as shown from Modelling output and experimental results. When the molar ratio of NH_4^+: PO_4^{3-} was 1:0.8, under Conditions 1 and 2, 76.7%, 81.2% of NH_4^+ was removed, respectively. When the molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-} was changed under Condition 3, the removal efficiency of $NH_4^+$and PO_4^{3-} was 96% and 99.8%, respectively.

Struvite was generated and confirmed by XRD and SEM analyses. It can be concluded that MINTEQ 3.0 is useful when being applied to predict the dosage of NaOH required with the input of possible struvite precipitation. Under this situation, without adding many agents, the maximum result was obtained in terms of NH_4^+ removal.

Struvite-(K), which was a fairly new chemical named in 2003, was also detected in this study. However the forming condition for this product is not clear at the moment. More work needs to be done in the future in order to well understand this product.

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Chapter 6

Conclusions and Recommendations

6.1 Conclusions

Excessive nutrients such as ammonium and phosphate being discharged to ecosystems have caused increasing eutrophication problems. How to remove and recover these nutrients has been a worldwide issue and a challenge for water industry. This study was aimed at the optimization and modelling of laboratory scale reactor system for precipitation of magnesium ammonium phosphate in terms of ammonium and phosphate removal and recovery. The objectives were to investigate the optimal operational parameters based on synthetic wastewater and to estimate the formation of struvite by applying thermodynamic chemical equilibrium model Visual MINTEQ 3.0.

Comprehensive literature review has been focused on the removal and recovery technologies of NH_4^+ and PO_4^{3-} from wastewater, from conventional biological nutrients removal process to the latest technology—the nutrient recovery by the precipitation of magnesium ammonium phosphate. The influencing factors of this process and details of struvite were also discussed.

Major research of this thesis was to optimise operational parameters of the precipitation process as well as the formation and crystallization of struvite by applying thermodynamic chemical equilibrium Visual MINTEQ3.0. It was proved that this physio-chemical process for ammonium removal and recovery is very promising. Brief conclusions of this research are as followings:

1. A series of experiments for determination of optimum pH and its impact on MAP formation and crystallization were carried out to study the impact on the process. The result shows that there was a preferred pH value during the process and

controlled pH was better than non-controlled pH in terms of struvite yield and ammonium removal efficiency. The best pH range in this study was determined as 9-9.5.

2. The precipitation reaction for formation of MAP and crystallization of MAP particles were significantly affected by the molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-}. The result shows that the best molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-} was found as 1.3:1:1.1 from a series of experiments, where the removal efficiency for ammonium and phosphate was 99.3% and 99.9%, respectively. The supplementation of magnesium and phosphate sources were also investigated in terms of MAP formation , removal efficiency of ammonium and phosphate, and as well as the availability and costs. The result confirmed that $MgCl_2$ + KH_2PO_4 was the most promising and efficient combination for Mg^{2+} and PO_4^{3-} addition.

3. Feeding rate of additional magnesium and temperature were also tested. It was found that they have limited impact on the precipitation process and removal efficiency of ammonium and phosphate. However, feeding rate and temperature can greatly affect the size and morphology of precipitated crystals.

4. In order to better understand the precipitation performance, Visual MINTEQ 3.0 was applied to predict the possible solids formed when relevant ions are present, and also to estimate the dosage of NaOH required in order to reach pH 9. Laboratory scale experiments were carried out using SDE from Bolivar WWTP, Adelaide. Results showed that the model output and experiments were similar based on chemical equilibrium which means this model was applicable when considering the precipitation of struvite except that there was a big error with

ammonium removal. Another interesting result was struvite-(K), which was detected by XRD.

6.2 Recommendations

The predominant goal of this study was to identify the influencing factors for MAP precipitation process, including pH, molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-}, feeding rate and temperature, also the application of thermodynamic model to predict struvite formation and alkaline dosage required. Recommendations for further studies on the development AMP technology can be made based on the research provided in this thesis as the followings:

1. This work is based on laboratory scale study. Future work can focus on the design and operation of a laboratory scale reactor and pilot scale study to observe the performance of this technology. The application of this process to other wastewaters should also be investigated, such as: lagoon, brine wastewater and mining wastewater. The possibility of applying this process to Bolivar WWTP, Adelaide should be considered.

2. The results revealed that size and morphology of the MAP particles could be significantly affected by the reactor configuration and its operation condition, and chemical composition. The size and morphology of the MAP particles, on the other hand, can affect the performance and efficiency of the MAP process. In order to apply this technology in real world, further study could focus on particle size which should be controlled if the relationship between different affecting

parameters and particle size could be calculated. Thus, Struvite generated should be separated easily for the reactor system.

3. As shown in chapter 4 and chapter 5, struvite can be precipitated with other chemicals. How to get struvite as pure as it can has become a challenge for the application of this process. Future research could investigate the purification of struvite to make sure that the yielded product is struvite as possible as it can.

4. This work applied thermodynamic chemical equilibrium database-VISUAL MINTEQ3.0 based on the equilibria of Mg^{2+}, NH_4^+, and PO_4^{3-} in wastewater. Future work can investigate the solution chemistry of different real wastewaters to obtain more data. A complete model could assist in the design of production scale process for nutrient removal and recovery.

5. Struvite-(K) was detected in this study. There were limited papers discussing this product. Further study could be performed to study the conditions of forming it, and the effect of K^+ concentration on the struvite precipitation process.

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Appendix 1 Standard curves for NH_4^+, PO_4^{3-}, and Mg^{2+}

1. Standard curve of PO_4^{3-} :

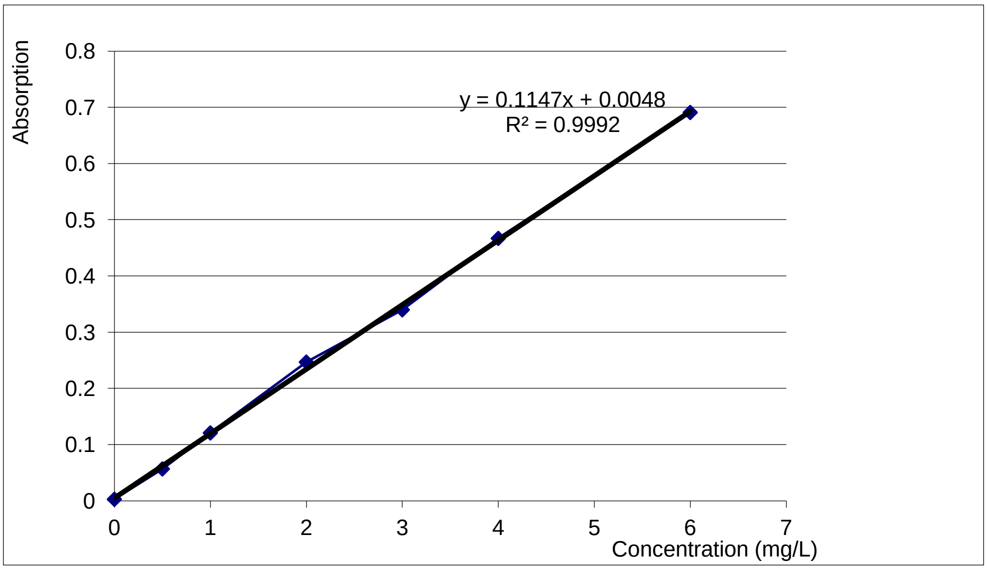

Figure A1.1 Standard curve of PO_4^{3-} by LIUV-201 UV/vis spectrometer

2. Standard curve of NH_4^+:

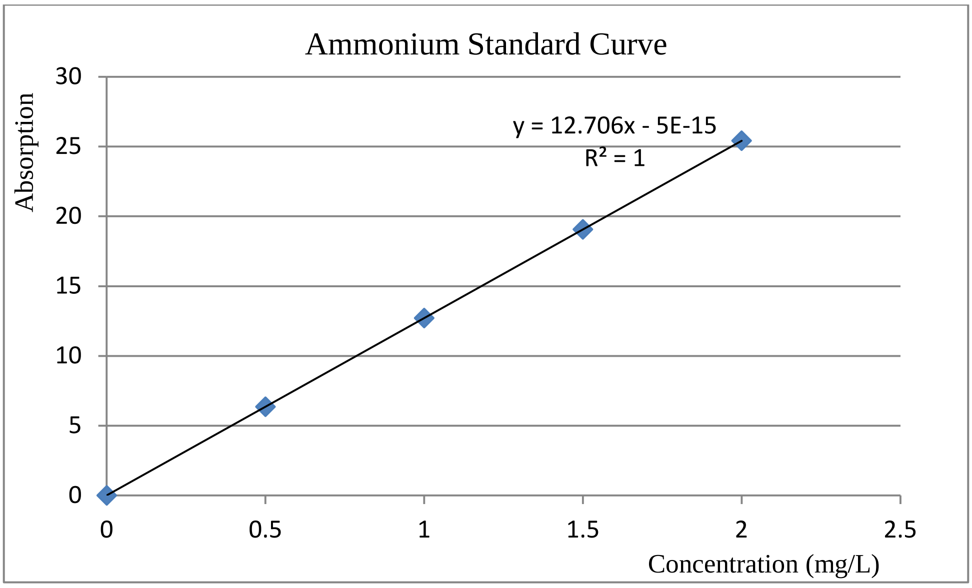

Figure A1.2 Standard curve of NH_4^+ by DR/890 colorimeter HACH, Amver^{TM} HACH Test 'N Tube High Range Ammonium Reagent Set.

3. Standard curve of Mg^{2+}

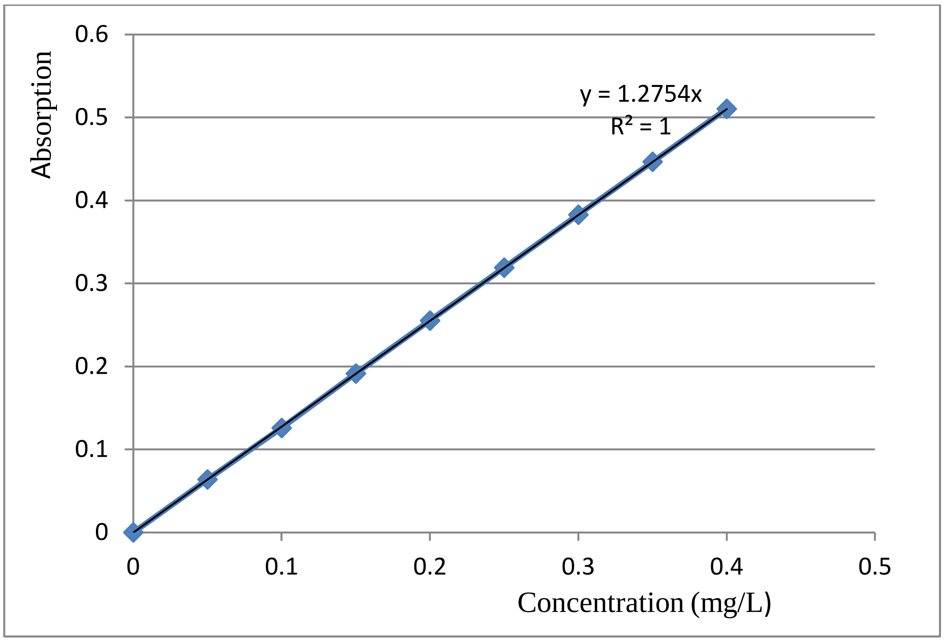

Figure A1.3 Standard curve of Mg^{2+} SHIMADZU, AA-6300, Atomic absorption spectrophotometer (y=1.2754Conc + 0.000).

Appendix 2 SEM images of struvite at different conditions

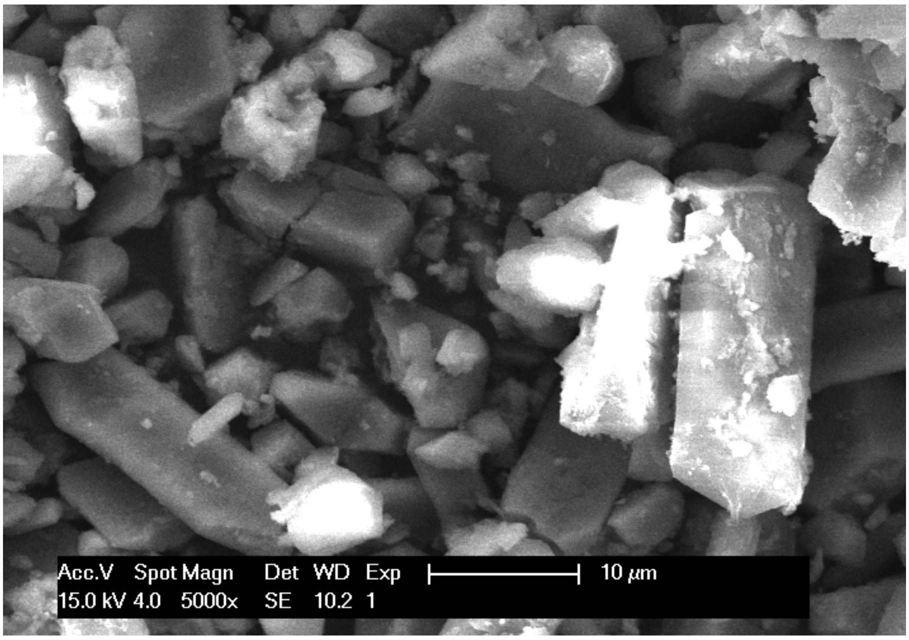

Figure A2.1 SEM image of struvite at pH 8.5 with molar ratio of Mg^{2+} :NH_4^+: PO_4^{3-} =1:1:1

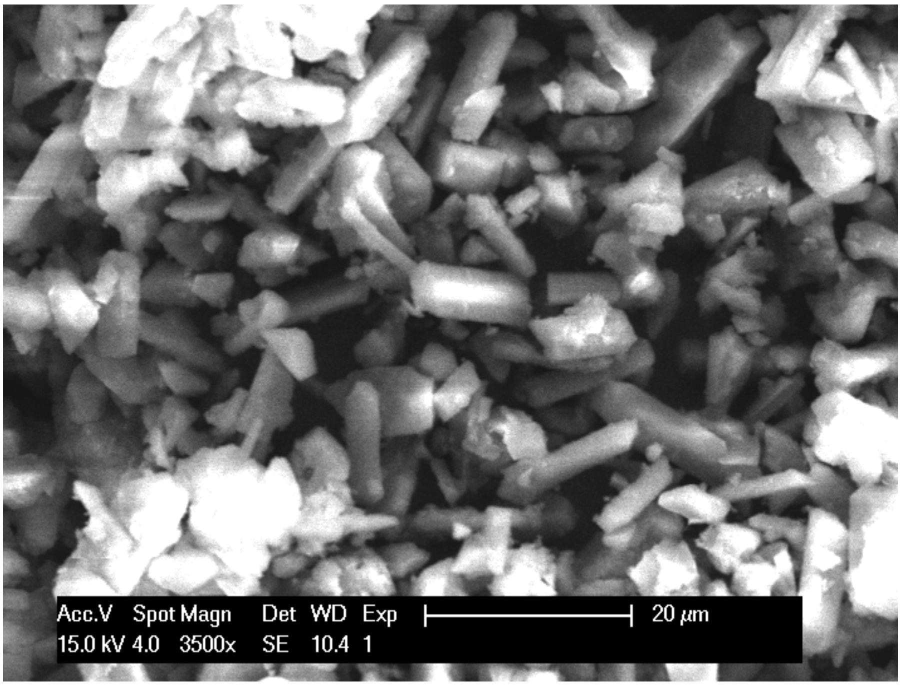

Figure A2.2 SEM image of struvite at pH 9 with molar ratio of Mg^{2+} :NH_4^+: PO_4^{3-} =1.2:1:1

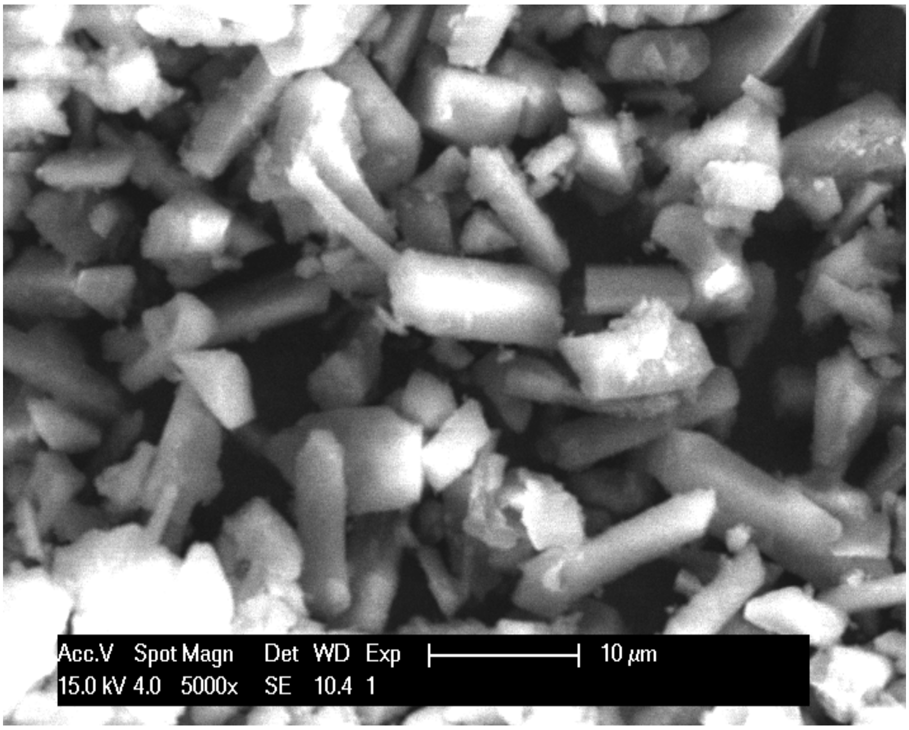

Figure A2.3 SEM image of struvite with molar ratio of Mg^{2+} :NH_4^+: PO_4^{3-} =1.2:1:1.2

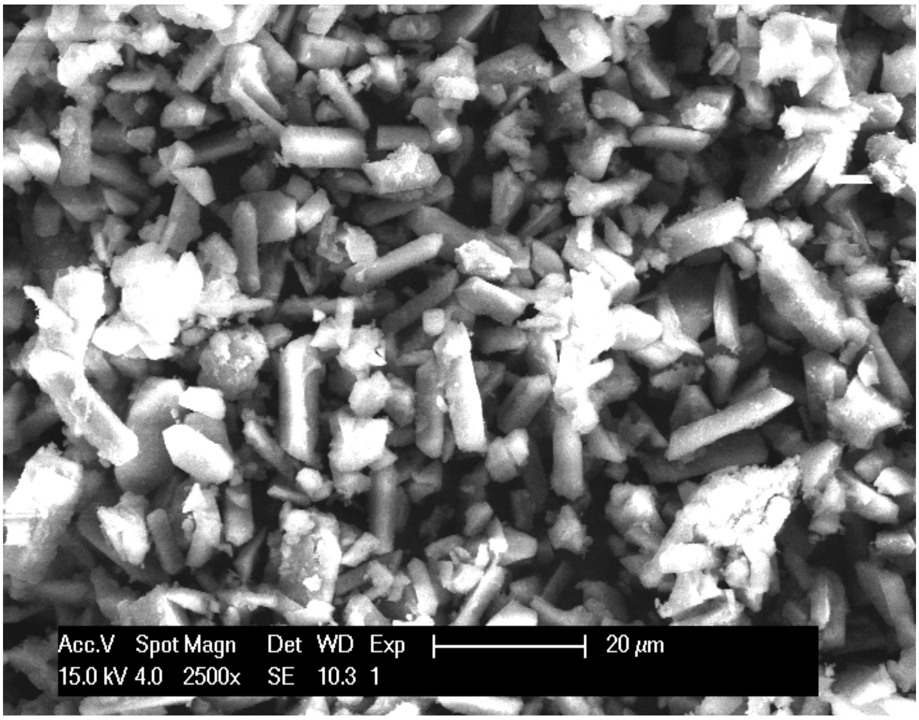

Figure A2.4 SEM image of struvite with molar ratio of Mg^{2+} :NH_4^+: PO_4^{3-} =1.4:1:1.4

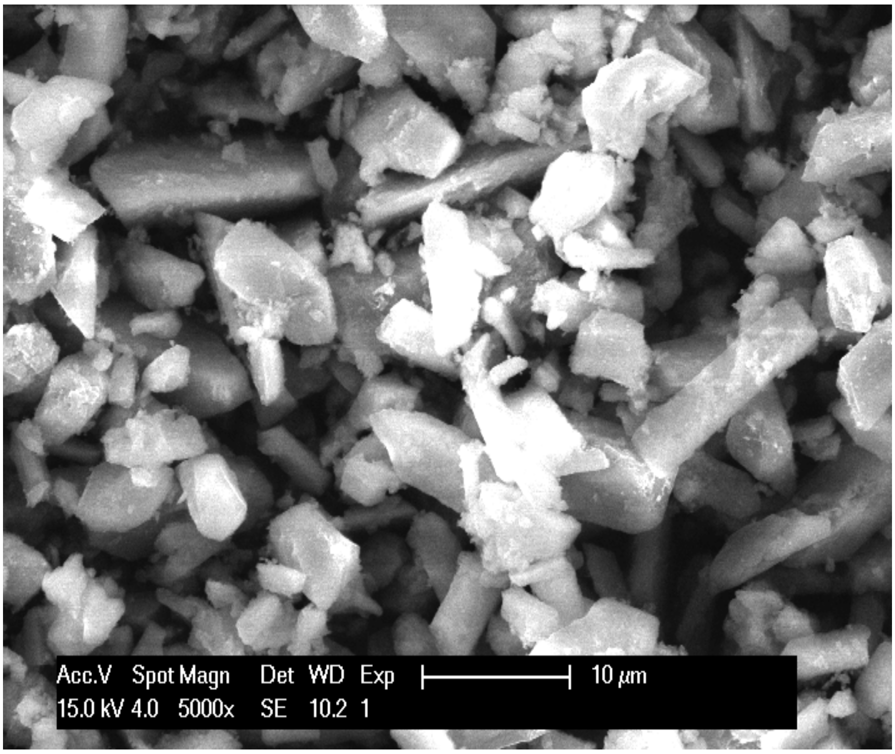

Figure A2.5 SEM image of struvite at pH 9 with molar ratio of Mg^{2+} :NH_4^+: PO_4^{3-} =1.6:1:1

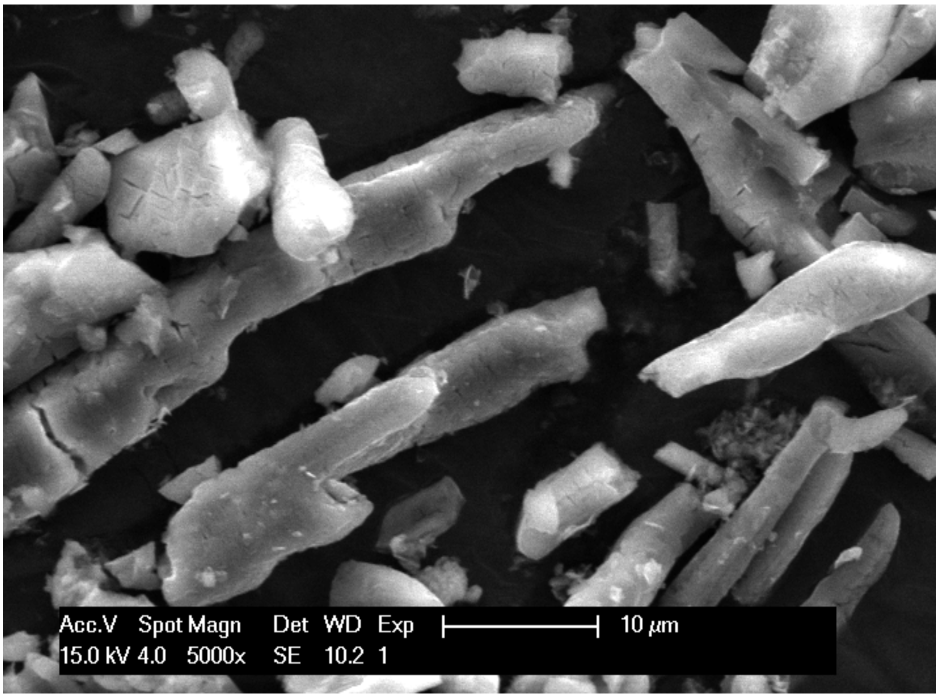

Figure A2.6 SEM image of struvite with molar ratio of Mg^{2+} :NH_4^+: PO_4^{3-} =1.6:1:1.4

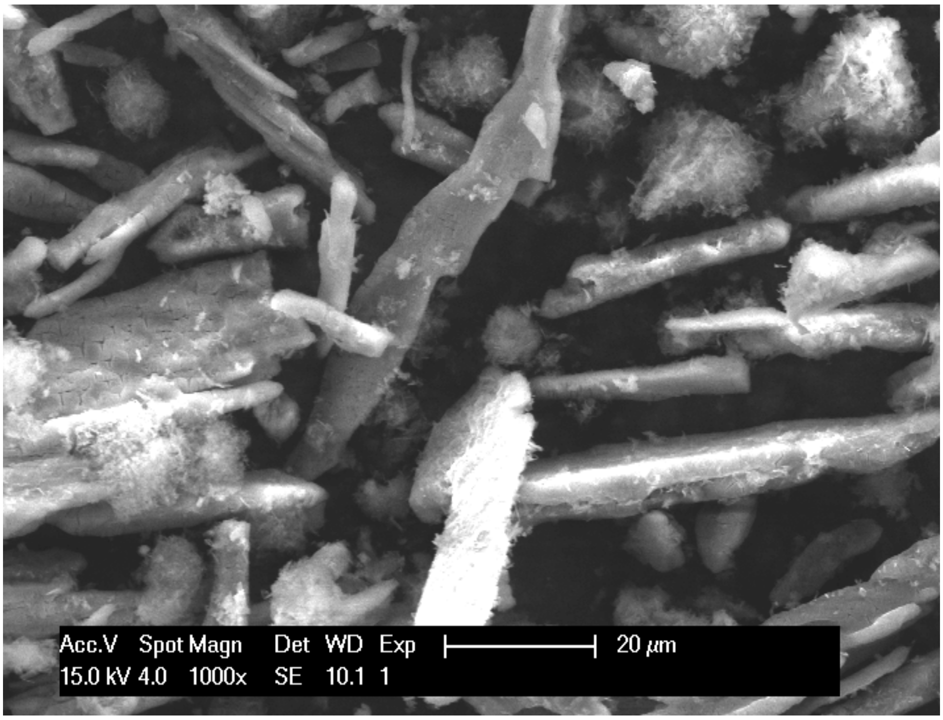

Figure A2.7 SEM image of struvite at pH 9.5 with molar ratio of Mg^{2+} :NH_4^+: PO_4^{3-} =1.3:1:1.