SIMULTANEOUS MANAGEMENT OF NITROGEN AND PHOSPHORUS IN DEWATERED SLUDGE LIQUOR BY COMBINING ANAMMOX PROCESS WITH STRUVITE CRYSTALLIZATION

by

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Abstract

A process combination of anaerobic ammonium oxidation (ANAMMOX), followed by struvite crystallization, was examined for simultaneous removal of nutrients (nitrogen and phosphorus) from dewatered sludge liquor or centrate. Phosphorus recovery as struvite can recover more than 90% P from centrate; however, the effluent after struvite crystallization still contains high concentrations of ammonium nitrogen (NH_4-N). ANAMMOX is a cost effective alternative process for NH_4-N removal and this process can remove 85% - 90% of NH_4-N from centrate, but leaves high concentration of phosphorus phosphate (PO_4-P) in the treated effluent. Combining ANAMMOX and struvite recovery can offer a sustainable solution for managing phosphorus and nitrogen at wastewater treatment plants. The ANAMMOX process, followed by a struvite crystallization process, was selected as the combination sequence for this first study. Synthetic feed was prepared with different molar ratios of Mg: NH_4-N: PO_4-P to mimic centrate, partially nitrified centrate and centrate treated by ANAMMOX process (ANAMMOX effluent). To determine the molar ratio of Mg: NH_4-N: PO_4-P, centrate was obtained from Lulu Island Wastewater Treatment Plant and partial nitrification, followed by ANNAMOX process, was conducted on this batch of centrate. Jar tests were conducted to determine the struvite formation potential from synthetic ANAMMOX effluent, as it has a very low N: P ratio. Pure struvite formed successfully in the jar tests with P-removal efficiency up to 88%. The process combination was upgraded to bench-scale, fluidized bed reactors for further investigation on the nutrient recovery efficiencies and associated chemical costs. The process combination successfully reduced NH_4-N concentration to 70 mg/L from an initial value of 800 mg/L. The concentration of PO_4-P was reduced to 15 mg/L in the final treated effluent, from a starting value of 119 mg/L. Overall, the combination resulted in phosphorus-phosphate (PO_4-P) removal rate as

high as 87% and ammonium-nitrogen (NH_4-N) as high as 92%. The mean particle size for struvite from ANAMMOX effluent ranged between 90 - 160 μm, and was larger than struvite particle formed from centrate. However, chemical costs associated with caustic and magnesium consumption, were found to be higher for the process combination, compared to just struvite formation using centrate.

Preface

This thesis is an original, unpublished, and independent work of the author, Parssa Hassan. The experimental setup configurations used in this research, described in Chapter 2, were based on previous designs developed by the Civil and Environmental Engineering Department, UBC, and were modified by myself to best suit the outcomes of this research. All data presented in this study were generated at the Environmental Laboratories, Civil Engineering Department, The University of British Columbia, Vancouver (Point Grey Campus), Canada.

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List of Abbreviations

AA	Atomic Absorption
AAS	Atomic Absorption Spectrophotometer
ANAMMOX	Anaerobic Ammonium Oxidation
BC	British Columbia
BNR	Biological Nutrient Removal
°C	Degree Celsius
Calc.	Calculated
EBPR	Enhanced Biological Phosphorus Removal
Efl.	Effluent
gm	Grams
hrs	Hours
HRT	Hydraulic Retention Time
Inf.	Influent
L	Litre
LIWWTP	Lulu Island Wastewater Treatment Plant
MAP	Magnesium Ammonium Phosphate
Max.	Maximum
Mg	Magnesium
mg/L	Milligram per Litre
Min.	Minimum
Mins	Minutes
mL/min	Millilitre per Minute
mm	Millimetre
N	Nitrogen
NH_4-N	Ammonium-nitrogen
NO_x	Nitrites and Nitrates
NO_2	Nitrites
NO_3	Nitrates
N_2O	Nitrous Oxide

P	Phosphorus
PO_4-P	Phosphate-phosphorus
PAO	Phosphate Accumulating Organism
PNC	Partially Nitrified Centrate
Q_{inf}	Total Influent Flow Rate
Q_{RR}	Recycle Flow Rate
RR	Recycle Ratio
SSR	Supersaturation Ratio
Theo.	Theoretical
UBC	University of British Columbia
WWPT	Wastewater Treatment Plant
WWPTs	Wastewater Treatment Plants
XRD	X-ray Diffraction
μm	Micro meter or microns

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Dedication

To my parents

1. Introduction

1.1. Background

Nitrogen (N) and phosphorus (P) are fundamental elements for living organisms. However, the presence of these nutrients in excess creates adverse effect in the environment. Wastewater is significantly rich in these nutrients due to human activities. Therefore, nitrogen and phosphorus should be removed from wastewater before discharge to water bodies, to prevent adverse effects in the environment. Typically, in wastewater treatments plants (WWTPs), significant volumes of sludge are produced during the wastewater treatment. The produced sludge is often further processed for mass reduction in anaerobic digesters before the final reuse or disposal. During sludge digestion, dewatered sludge liquor or centrate is released in the digester, which contains very high amount of soluble ammonia and soluble phosphorus. The literature indicates that up to 90% of phosphate-phosphorus (PO_4-P) is re-released from sludge into the sludge liquor (Mavinic *et al*., 1998). The concentration of ammonium-nitrogen (NH_4-N) ranges from 500 mg/L to 1500 mg/L in centrate. Hence, centrate is highly nutrient rich and should not be discharged of directly to receiving water bodies. An extensive study conducted by Schindler (2006) in Ontario, Canada proved that both phosphorus and nitrogen were equally responsible for causing eutrophication in natural water bodies. Eutrophication causes excessive algae growth, which causes a toxic effect in water bodies, killing fish and other living organism, and ultimately reduces the availability of water resources. As a result, centrate has to be recycled back to WWTPs, combining it with raw influent for the treatment process. This adds additional nutrient loading to the plant, which affects process efficiencies and increases operating costs. It has been reported that in WWTPs, 15 – 20% of influent NH_4-N concentration and 8% of influent PO_4-P is contributed by centrate (Fux *et al*., 2002; Wild *et al*. 1997). To reduce this additional nutrient loading in wastewater, the

removal of the nutrients from centrate through interception becomes desirable (Forrest *et al*., 2007).

Struvite crystallization and anaerobic ammonium oxidation (ANAMMOX) are two established technologies now applied for removal of phosphorus and nitrogen from wastewater, respectively. Phosphorus removal and recovery from wastewater in the form of struvite, a white crystalline compound ($MgNH_4PO_4.6H_20$), has successfully removed and recovered more than 90% phosphorus from centrate (Adnan *et al*., 2003b; Fattah *et al*., 2008a; Fattah *et al*., 2008b). Phosphorus recovery as struvite has gained interest since its composition makes it a potentially beneficial product in the fertilizer industry. The fertilizer recovered as struvite also provides an alternative source of phosphorus to mined mineral rock. Struvite recovery can reduce maintenance costs in WWTPs by preventing undesirable struvite deposition in pipes, elbows, valves, pumps, etc. However, the struvite recovery process leaves a significant amount of NH_4-N in the treated effluent, as struvite chemistry requires equimolar N to P molar ratios (the molar ratio of N : P is around 20 : 1, in centrate).

Alternatively, the ANAMMOX process is a relatively cost effective microbial process that can be effectively applied on centrate for removing the high nitrogen loading. This process can successfully remove up to 90% of NH_4-N from centrate (Fux *et al*., 2002), but, leaves a significant amount of soluble phosphorus in the final effluent (Fux *et al*., 2006).

1.2. Research Objectives

The current technologies applied for nutrient removal from centrate only offer us a solution for either phosphorus recovery or nitrogen removal. To effectively manage nutrient loadings at treatment plants, a unified solution is highly required. The successful combination of

ANAMMOX and struvite recovery could offer us a sustainable solution for managing phosphorus and nitrogen simultaneously, at wastewater treatment plants.

ANAMMOX and struvite crystallization process can be combined in two feasible ways, as demonstrated in Figure 1.1 and Figure 1.2.

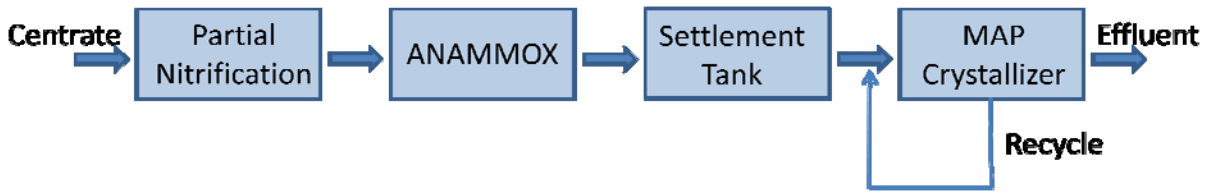


Figure 1.1. Combination 1: ANAMMOX followed by struvite crystallization

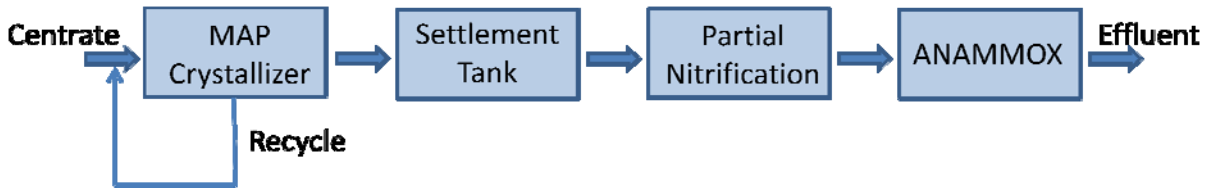


Figure 1.2. Combination 2: Struvite crystallization followed by ANAMMOX

Combination 1, that is, ANAMMOX followed by struvite crystallization process was selected as the combination sequence for the study in phase 1 of this work. The flow diagram of the process combination is shown in Figure 1.3 with the expected outcomes of each step inside the parenthesis.

Centrate → Partial Nitrification → ANAMMOX → Struvite Crystallization → Effluent

↓ (high N&P) ↓ (low N, high P) ↓ ($Mg.NH_4.PO_4.6H_2O$) ↓ (low N, low P)

Figure 1.3. Flow diagram of the process combination selected for phase 1

The objectives of this study were designed for the following outcomes:

- To find a solution for simultaneous nutrient (nitrogen and phosphorus) removal from wastewater (dewatered sludge liquor or centrate).
- To investigate if struvite crystallization was possible for a low N : P molar ratio feed (ANAMMOX effluent).
- To determine the maximum nitrogen and phosphorus removal efficiencies in the final effluent resulting from the process combination.
- To compare the chemical costs associated with struvite production from ANAMMOX effluent with struvite produced from centrate.

2. Literature Review

2.1 Nutrient Removal and Recovery Methods

2.1.1 Nitrogen Recovery

Nitrogen exists in the form of Ammonium-nitrogen (NH_4-N), nitrite-nitrogen (NO_2) and nitrate-nitrogen (NO_3) in wastewater. If wastewater effluent containing ammonia higher that regulatory limits is discharged in water bodies like lakes, river etc., it causes eutrophication and creates toxic environment for aquatic life (Robert and Russo, 1981). Therefore, the removal of ammonia from wastewater is essential for the protection of many receiving waters. Two methods of ammonia removal from wastewater are discussed in the following sections.

2.1.1.1 Nitrification-Denitrification

Biological nitrification-nitrafication-denitrification is the most widely used treatment process for nitrogen removal from wastewater. The process removes nitrogen in two separate steps. The first step is two phase biological nitrification and nitrification process, where ammonia is first oxidized to nitrites, and, then to nitrates, under aerobic conditions (Sliekers *et al*., 2002). The dissolved oxygen (D.O.) of the system needs to be maintained 2.0 mg/L or above for the healthy growth of the nitrifying bacteria. This is also an alkalinity consuming step. The second step of the process is biological denitrification, where the nitrates are converted to nitrogen gas under anoxic conditions (Sliekers *et al*., 2002). The simplified reaction steps of nitrification, nitrafication and denitrification are given in Equation 2.1 to 2.3 below (Metcalf and Eddy, 2003):

$$NH_3 + CO_2 + 1.5O_2 + \text{Ammonia Oxidizing Bacteria} \rightarrow NO_2^- + H_2O + H^+ \quad (2.1)$$

$$NO_2^- + H_2O + H^+ + \text{Nitrite Oxidizing Bacteria} \rightarrow NO_3^- \quad (2.2)$$

$$5CH_3COOH + 8NO_3^- \rightarrow 4N_2 + 10CO_2 + 6H_2O + 8OH^- \quad (2.3)$$

The major drawback of the process is the addition of external carbon source in the denitrification process. The denitrifying bacteria required electron donors for completing the denitrification process and, thus, addition of extra carbon source makes the whole system expensive. Among the carbon sources, methanol is relatively (currently) cheap and is most commonly used in the denitrification process.

2.1.1.2 Anaerobic Ammonium Oxidation (ANAMMOX)

Anaerobic Ammonium Oxidation (ANAMMOX) is a novel microbial process for removing nitrogen from wastewater (dewatered sludge liquor) (Strous *et al*., 1998). There is no requirement for an external carbon source addition in this process (like conventional nitrification denitrification). The operational cost savings can be up to 90%, by opting for the ANAMMOX process over the conventional processes (Jetten *et al*., 2001). The conventional nitrification–denitrification process is also unsuitable for dewatered sludge liquor of centrate as high amount of CO_2 is released. The advantages mentioned have made ANAMMOX process a novel nitrogen removal technology for replacing traditional nitrification denitrification for wastewater treatment. Further, since only half of the ammonia to be treated is oxidized to nitrite, nitrous oxide production is anticipated to be half than that produced in the traditional nitrification-denitrification process. Details on ANAMMOX process are discussed in Section 2.2.

2.1.2 Phosphorus Recovery

Phosphorus (P) is one of key element required for all living organisms for growth and biological productivity. However, excess amount of phosphorus is one of the major elements contributing to eutrophication in water bodies. The major source of P is from phosphates commonly used in

pesticides, detergents and fertilizers, generally washed out with wastewater. Thus, severe regulations have been imposed on the discharge limits of P concentrations in wastewater. The most common processes of P removal are by phosphorus fixation in activated sludge, either by biological or by chemical methods. These methods are discussed in the following sections.

2.1.2.1 Biological Processes

Biological (BNR, EBPR) process removes phosphorus by using phosphorus accumulating organisms (PAOs). These organisms use their own metabolism to accumulate phosphorus (phosphates) as polyphosphates under certain conditions. An overall 80 – 90% of phosphorus removal has been reported to be achieved by this method. Biological processes have the advantages of avoiding chemical usage and prevention of chemical sludge production. However, the process requires complex plant design and operating conditions (Morse *et al*., 1998). Detailed literature and reviews on biological P removal processes can be found in Bowker and Stensel (1990).

2.1.2.2 Chemical Processes

Chemical precipitation using various metal salts, are one of the most common techniques applied for P removal processes. Metal salts include aluminum and iron precipitation, calcium phosphate precipitation, struvite precipitation, membrane/ion exchange with precipitation etc. Phosphorus recovery (as calcium phosphate) has been described to be very promising as the recovered forms were close to that of mined phosphorus and use in the P-industry (Driver *et al.,* 1999).

Precipitation of P as magnesium ammonium phosphate, commonly known as struvite, has gained popularity as a process of P recovery (Doyle *et al*., 2003). The composition of struvite (N, P and Mg) makes it a potentially useful product that can be directly used as fertilizer (Booker *et al*.,

1999). This method has already reduced the demand of mined phosphorus in the P-industry, by giving an alternative solution. Detailed discussion on struvite chemistry and recovery is provided in Section 2.3 to Section 2.9.

2.2 ANAMMOX Process and Benefits

The first recognition of the ANAMMOX process started in the 1970's when Broda (1977) predicted that micro-organisms oxidized ammonia to nitrite and nitrate, based on thermodynamics calculations. After numerous studies conducted by several researchers, in 1999, Strous *et al.* described ANAMMOX process bacteria for the first time, by illustrating the removal of ammonia and nitrite and into nitrogen gas under anaerobic conditions, by bacteria cells.

Strous *et al*. (1998) estimated that ANAMMOX stoichiometry requires 1 mole ammonia to 1.32 moles nitrite and converts into 1.02 mole nitrogen gas and 0.26 mole nitrate for the process to complete. The resultant ANAMMOX process reaction is given as Equation 2.4.

$$NH_4^+ + 1.32\ NO_2^- + 0.066\ HCO_3^- + 0.13\ H^+ \rightarrow 1.02\ N_2 + 0.26\ NO_3^- + CO_2 + 0.066CH_2O_{0.5}N_{0.15} + 2.03\ H_2O \quad (2.4)$$

In most types of wastewater, nitrite is not available in a molar ratio of 1.32 for 1 mole of ammonium. Therefore, an external source of nitrite is required for completion of the ANAMMOX process (Zhang *et al*., 2008). This can be achieved by combining other accompanying processes, like partial nitrification, for generating nitrites and fulfilling the requirements of additional nitrites.

In nitrification, ammonia is oxidized by aerobic ammonium oxidizing bacteria under aerobic conditions. In this step, ammonia is partially oxidized to nitrite by nitrifying organisms, thus producing an effluent which contains a mixture of ammonia and nitrite. The simplified partial nitrification reaction is given below at Equation 2.5 and Equation 2.6:

$$NH_4^+ + 1.5\ O_2 \rightarrow NO_2^- + 2H^+ + H_2O \qquad (2.5)$$

$$NH_4^+ + HCO_3^- + 0.75\ O_2 \rightarrow 0.5\ NH_4^+ + 0.5\ NO_2^- + CO_2 + 1.5\ H_2O \qquad (2.6)$$

Partial nitrification by ammonium oxidation to form nitrites (up to 53%) was achieved in a lab scaled continuous stirred tank (CSTR) using dewatered sludge liquor (centrate), by van Dongen *et al*. (2001). Similarly, partial nitrification of up to 58% was achieved in a pilot scale CSTR reactor by Fux *et al*. (2002). Partial nitrification required a temperature of around 30°C to achieve successful conversion of ammonium to nitrites in the studies mentioned.

The effluent produced after partial nitrification is processed in the second step, the ANAMMOX reactor, where ammonium works as the electron donor for denitrification and nitrite serves as the electron acceptor. The formed nitrite and the remaining ammonium in the effluent is converted to nitrogen gas in the ANAMMOX reactor and complete nitrogen removal process from wastewater. This step is anoxic; the presence of oxygen causes inhibition of the anaerobic ammonium conversion (Strous *et al*., 1997). A complete ANAMMOX process has achieved stable nitrogen removal of more than 90% from wastewater in many studies (Third *et al*., 2001; van Kempen *et al*., 2001).

There are major advantages of using an ANAMMOX process over a conventional nitrification- -denitrification process. The ANAMMOX process requires less oxygen during the partial nitrification step. There is no requirement of adding organic carbon in the second denitrification

step. The autotrophic bacteria consumes dissolved carbon dioxide as the source of carbon, thus no carbon dioxide gas is released in this process, and reduces the potential for production of nitrous oxide (N_2O) by half, making it friendlier to the environment.

However, the ANAMMOX process also carries some important disadvantages. The major drawback of the system is the slow growth ANAMMOX bacteria. It has been suggested that the doubling time for these bacteria are between 9 to 14 days, they are very hard to grow (especially in vitro), and, they tend to wash out from continuously operated reactors (Waki *et al.,* 2013; Gao *et al*., 2012; Yapsakli, 2010; Strous *et al*., 1998). The success rate of the process is dependent on balanced reactor conditions. The nitrite in the ammonium/nitrite ratio should be available at 50% for the good development of the process (Galí *et al*., 2007; van de Graaf *et al*., 1995). Nitrous oxide (N_2O), a green house gas, can also be produced in by ammonium oxidizing bacteria and nitrite oxidizing bacteria in the process (Lipschultz *et al*., 1981; Freitag & Bock, 1990). Studies show that N_2O emission of the nitrogen load to the reactor was 2.3% from full scale two-stage ANAMMOX reactor (Kampschreur *et al*., 2008), 1.2% from full scale single-stage reactor (Kampschreur *et al*., 2009a), and, 0.1% from lab-scaled single stage ANAMMOX reactor (Sliekers *et al*., 2002). Even though N_2O emission is monitored in ANAMMOX process, the percentages are still lower than conventional nitrification - denitrification process. Nitrous oxide (N_2O) emission from various WWTPs can be found in details in Kampschreur *et al*. (2009b).

2.3 Struvite Recovery and Benefits

Struvite (magnesium ammonium phosphate, MAP) scale deposition occurs spontaneously in wastewater treatments plants under favourable conditions. When the appropriate ions are present, the problem associated with struvite (or other mineral) scaling is nothing new at treatment plants.

In 1937 struvite scaling was noticed for the first time in a multiple stage sludge digestion system (Rawn *et al*., 1939). The deposition causes a severe nuisance by affecting treatment process efficiencies in plants and causing maintenance issues. Therefore, struvite depositions are of significant concern in wastewater treatment plants (WWTPs) (Doyle *et al.*, 2003). The causes of struvite deposition have been widely investigated. Various techniques have been applied for struvite deposition control, such as prevention by chemical dosing with iron salts (Mamais *et al.*, 1994), dilution of struvite crystals with water effluent (Borgerding, 1972), chemical inhibitors addition (Doyle *et al.*, 2003; Snoeyink and Jenkins, 1980) etc. Recovering phosphorus from wastewater can prevent scaling problems in WWTPs, saving huge maintenance costs and reduces pollution caused by excessive discharge of nutrients (P and N) in the effluent.

Phosphorus recovery, in the form of struvite, gained a lot of interest in the past decade as it offers economical and environmental benefits with its fertilizer qualities in agriculture sector (Doyle *et al.*, 2003; Owen *et al.,* 2009). The low solubility property of struvite allows prolonged release of nutrients in the fertilizer during the agriculture season, making fertilizer application less frequent, without the danger of burning crop roots (Bridger *et al*., 1961; Gatterell *et al*., 2000; Ries *et al*., 1969). Struvite recovery also provides a sustainable alternative solution to mined phosphorus in the fertilizer industry (Jaffer *et al*., 2002; Berg, 1982). A study by Sterling and Ashley, (2003) indicated that slow release fertilizers, like struvite, can be added to increase the level of nutrients in nutrient deficit streams, to increase salmonid production and fish fertility, and, will last up to four months, in situ.

Heavy metal contamination is present in fertilizers produced from phosphate rock as degradation in phosphate rock increases metal contamination in it (von Horn and Sartorius, 2009). Struvite recovery as fertilizer eliminates the possibility of such heavy metal contamination, which is a

major advantage (Fattah *et al.,* 2008b). Struvite recovery also reduces the amount of sludge produced during wastewater treatment. Sludge mass reduction up to 49% was reported by implementing struvite recovery, instead of phosphorus accumulation in biosolids (Woods *et al*., 1999).

2.4 Struvite Chemistry

Struvite ($Mg.NH_4.PO_4.6H_20$) is an orthophosphate containing equimolar concentrations of magnesium, ammonium and phosphate, bound by six moles of water. The most general equation used to describe struvite formation is given below at Equation 2.7 (where n = 0, 1, or 2).

$$Mg^{+2} + NH_4^{+} + H_nPO_4^{3-n} + 6H_20 \leftrightarrow Mg.NH_4.PO_4.6H_20 + nH^{+} \qquad (2.7)$$

The struvite crystallization occurs in two stages: nucleation (crystal birth) and crystal growth (Jones, 2002). The reaction between magnesium, ammonium and phosphate ions releases hydrogen ions in the solution. Therefore, a drop in the pH value is monitored when struvite crystals spontaneously precipitate out of solution. Precipitation of struvite is always evident at WWTPs in areas with high turbulence (pumps, elbows, propellers, valves) and areas with high phosphate, high magnesium, and high pH, like digested sludge liquor pipelines.

The prediction and formation chemistry is complex and dynamic and depends on many factors, which are discussed in Section 2.5.

2.5 Factors Affecting Struvite Formation

Struvite nucleation and growth is complex and depends on many combinations of factors. The key factors will be discussed in the following section.

2.5.1 pH

The hydrogen ion concentration (measured by pH) is one the most important factors that influence struvite crystallization process, as it is linked to the concepts of saturation and solubility. A low hydrogen ion concentration (high pH) causes increases the rate of struvite crystallisation and a higher concentration (lower pH value) increases solubility. Struvite scaling in WWTPs occurs mostly due to reduced hydrogen ion concentration coincident with a pH increase, caused by CO_2 stripping ($HCO_3^- \rightarrow CO_2 + OH^-$) in wastewater (Neethling and Benisch, 2004). A specific range of pH has been found to be suitable for optimum struvite precipitation (Booker *et al*., 1999; Stratful *et al*., 2001). Experiments conducted by Booker *et al*., (1999) by analyzing molar removal of NH_4^+, PO_4^{-3} and Mg^{2+}demonstrated maximum struvite precipitation at a pH range of 8.8 and 9.4. Stratful *et al*., (2001) recommended operation at a pH value > 8.5 for effective struvite removal.

However, conditions where pH > 9 shows inhibition to struvite formation, as ammonium ion (NH_4^+) is transferred in gaseous free ammonia (NH_3). Thus, ionic nitrogen concentration is reduced affecting the required molar ratio (Mg : N : P = 1 : 1 : 1) for struvite formation (Booker *et al*., 1999; Buchanan *et al*., 1994).

The optimum range of operational pH for maximum phosphorus recovery is highly variable with the characteristics of wastewater (Stratful *et al*., 2001). In most literature, the recommended operational pH range to achieve more than 80% phosphorus recovery is suggested to be between 8.0 and 9.0 (Münch and Barr, 2001; Jaffer *et al*., 2002). However, other literature has demonstrated more than 90% phosphorus recovery for a pH ranging from 7.3 to 7.5 (Adnan *et al*., 2003a; Fattah, 2004; Fattah *et al*., 2008b).

2.5.2 Supersaturation Ratio (SSR)

Supersaturation ratio (SSR) of a solution indicates it's potential to form struvite. The pH value controls the SSR ratio of the solution. When SSR > 1, the solution is supersaturated and struvite precipitation occurs. When SSR < 1, the solution remains under saturated and thus struvite precipitation is not possible. SSR = 1 indicates the solution to be at equilibrium state. The SSR of a system needs to be maintained between 1 and 5 to achieve the highest amount of phosphorus recovery as struvite. SSR can be calculated from Equation 2.8.

$$SSR = P_s/P_{s\text{-}eq} \tag{2.8}$$

P_s = Conditional solubility product of struvite in a solution

$P_{s\text{-}eq}$ = P_s under equilibrium condition

To maintain a constant SSR > 1 in solution, pH value needs to be consistently maintained in the optimum range (section 2.5.1). Struvite growth rate also depends on the supersaturation level of centrate. Doyle *et al.* (2002) demonstrated that at a constant SSR value, struvite growth rate reached up to seven times the initial value, after 40 hours precipitation.

2.5.3 Temperature

Temperature has a lower impact on the chemistry of struvite formation compared to pH and SSR value. The solubility and struvite crystal morphology is mainly affected due to temperature variation (Durrant *et al*., 1999). Temperature affects the struvite solubility product, which is linked to the supersaturation state of the solution where a crystal grows. Aage *et al*. (1997) demonstrated that struvite solubility increased as temperature changed from 10°C to 50°C, and Burns and Finlayson (1982) demonstrated a similar trend when the temperature increased from

25°C to 45°C. This explains why a temperature between 25°C to 35°C is considered to be the best conditions for struvite formation. Lower temperatures also favour phosphorus recovery more efficiently (Adnan *et al*., 2004). Studies conducted by Boistelle *et al.* (1983) and Babić-Ivanĉić *et al*. (2002) demonstrated that for identical feed concentrations, struvite crystals formed at 37°C were thick and square, compared to the crystals formed at 25°C, which were rectangular and prismatic.

2.5.4 Turbulence or Mixing Energy

Turbulence or mixing energy also influences struvite formation. In WWTPs, high turbulence areas liberate CO_2 from wastewater, reducing acidity causing increase in pH value and subsequent precipitation of struvite. In struvite crystallizers, turbulence is also required during operation for allowing particles to collide with each other, resulting in struvite formation. Struvite particle shapes depend on the shear gradient or the amount of turbulence in the reactor. Studies show that high turbulence creates compact crystals and low turbulence creates elongated crystals (Ohlinger *et al*., 1999). However, too much turbulence affects crystal size as nucleation is accelerated but crystal growth is limited, which eventually causes crystal breakage (Durrant *et al*., 1999).

2.5.5 Ammonium to Phosphorus Molar Ratio

Wastewater like dewatered sludge liquor or centrate, generally carries a higher molar ammonium concentration than phosphorus. Studies showed that phosphorus removal as struvite was sharper with the increase in ammonium concentration (Münch and Barr, 2001). Higher ammonium concentration forms relatively pure struvite (Stratful *et al*., 2001).

2.5.6 Magnesium to Phosphorus Molar Ratio

The molar ratio of Mg : P influences the amount of phosphorus recovered as struvite during crystallization process. Studies indicated that a molar ratio of 1.05 : 1.00 for Mg : P was required to achieve 95% P recovery from centrate (Jaffer *et al*., 2002; Fujimoto *et al*., 1991) . Other studies indicated that a higher molar ratio of 1.30 : 1.00 was required to guarantee high P recovery as struvite (Shimamura *et al*., 2003; Münch and Barr, 2001). However, the presence of excessive Mg during operation decreases struvite purity by transforming into newberyite ($MgHPO_4.3H_2O$) (Babić-Ivanĉić *et al*., 2002; Demeestere *et al*., 2001).

2.5.7 Presence of Foreign Ions

Impurities in solution can inhibit struvite crystal growth rate by blocking sites where crystal could be produced (Jones, 2002). The presence of relatively high levels of calcium in sludge liquor interacts with phosphate and forms calcium phosphate (Le Corre *et al*., 2005).

2.6 Chemicals for Struvite Formation

2.6.1 Caustic

Struvite formation in wastewater is highly dependent on the balance of alkalinity and acidity measured as pH of the system. In wastewater treatment plants, unintentional struvite precipitation occurs inside pipes whenever the pH is high. This is because pH helps to preserve the supersaturation ratio of the solution. Therefore, for intentional phosphorus recovery as struvite, the pH of the system has to be maintained within a certain range to ensure the SSR is greater than 1. The most common chemical use to control and maintain the pH is by adding caustic (NaOH) externally (Fattah *et al*., 2008a; Jaffer *et al*., 2002; Münch and Barr, 2001; Ohlinger *et al*., 1999). Another alternative of raising the pH instead of using NaOH solution is by

stripping CO_2 from wastewater (Jordaan *et al*., 2013; Zhang, 2006). This method avoids the use of chemicals and saves cost for struvite production. The recommended value of pH value in a system is between 7.5 and 9.0 for the best phosphorus recovery as struvite (Fattah *et al*., 2008a; Fattah *et al*., 2008b; Jaffer *et al*., 2002; Celen and Türker, 2001).

2.6.2 Magnesium

Theoretically, equimolar amount phosphate, ammonium and magnesium are required to form struvite. In most wastewater, the limiting factor for struvite formation is the inadequate amount of magnesium in the system. As a result, magnesium needs to be added externally to the system to initiate struvite formation and phosphorus recovery. Two common sources used for external magnesium addition are magnesium hydroxide {$Mg(OH)_2$} and magnesium chloride ($MgCl_2$). $Mg(OH)_2$ is the cheaper chemical of the two and it also helps to raise the pH in the system. However, as it functions as a base, it becomes hard to control the external caustic dose during operation and the pH is a desired range (Jaffer *et al*., 2002; Münch and Barr 2001). For these reasons, $MgCl_2$ is preferred mostly as the external source. This chemical is easy to transport and dissociates in water faster than $Mg(OH)_2$ (Jaffer *et al*., 2002).

Although theory suggests a molar ratio of Mg : P to be 1 : 1, in practice excess amount of magnesium is required in the system to achieve higher phosphorus recovery. Suggested molar ratio ranges between 1.3 and 2.0 (Fattah *et al*., 2008b; Adnan *et al*., 2003a; Jaffer *et al*., 2002; Münch and Barr, 2001).

2.7 Operating Cost for Struvite Production

The production cost of struvite is mainly dependant on the cost of chemicals and the energy required to pump the feed in the reactors. Studies shows cost associated with energy

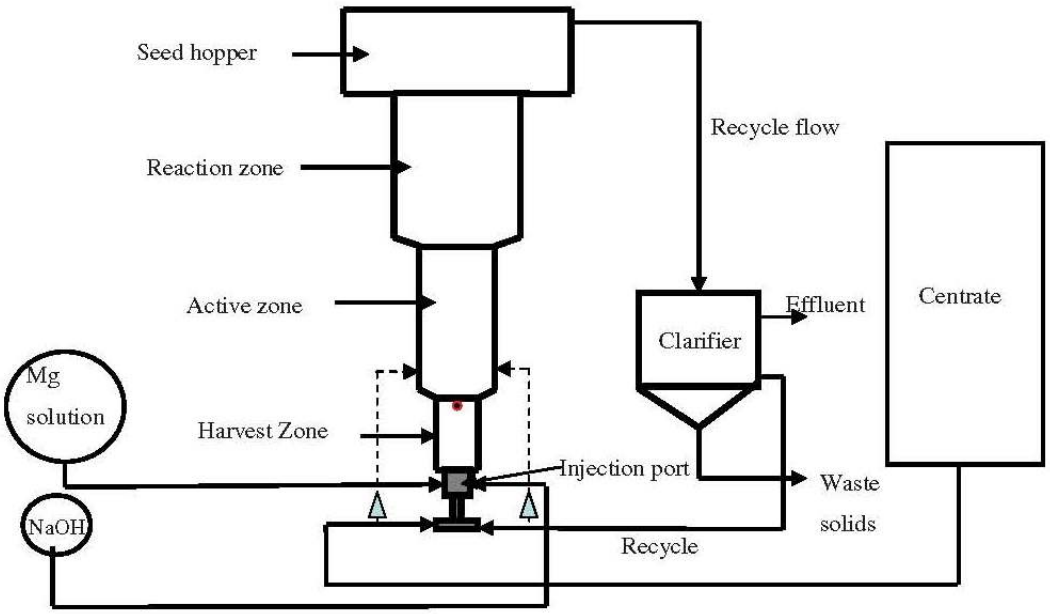
consumption were insignificant when compared to the cost of chemicals (Jaffer *et al*., 2002). The two main chemicals used for the struvite crystallization process are a magnesium source (generally $MgCl_2$) and caustic (NaOH) to maintain the desired pH inside the reactor. Caustic addition alone caused 97% of the total chemical cost in this process (Jaffer *et al*., 2002). Caustic usage can be reduced by choosing air/CO_2 stripping method to increase the pH in the system (Zhang, 2006; Battistoni *et al*., 2001).

2.8 Fluidized Bed Reactors for Struvite Crystallization

Fluidized bed reactors are the most common process used for struvite crystallization from wastewater. In this process, the particles responsible for struvite formation participate spontaneously inside the reactor. Once the molar ratio of Mg:N:P reaches 1:1:1, struvite nucleation starts. Struvite growth occurs over time either by seeding materials (sand or struvite) or by interaction between by the smaller struvite particles. The particles are kept into continuous motion either by controlling the solution flow rate (Fattah *et al.,* 2012; Fattah *et al*., 2008a; Fattah *et al*., 2008b; Adnan *et al.*, 2003a) or by up-flow circulation of air (Suzuki *et al*., 2002).

In fluidized bed reactors, the feed is typically centrate and anaerobically digested sludge liquors and it enters from the bottom of the reactor in the reacting zone. NaOH solution is more commonly used to adjust the pH of the solution (Fattah *et al.,* 2012; Fattah *et al*., 2008a; Fattah *et al*., 2008b; Adnan *et al.*, 2003a). The flow velocity of wastewater is greater in the bottom column sections and decreases gradually to the upper sections, allowing treated effluent discharge from the reactor top (outflow). The struvite particles remain fluidized and grow inside the column section. The pilot-scale, fluidized reactor used for struvite crystallization and P recovery from centrate at Lulu Island Wastewater Treatment Plant (LIWWTP) in Richmond,

B.C., Canada is shown in Figure 2.1. The operating parameters of this reactor can be found in details in Fattah *et al*., (2008b).



Adopted from Fattah *et al*., (2012)

Figure 2.1. Fluidized bed reactor for struvite crystallisation

Phosphorus recovery over 90%, as struvite, from centrate has been successfully achieved by using fluidized bed reactors processes (Fattah *et al*., 2008b; Adnan *et al*., 2003a).

2.9 Struvite Morphology

Struvite is a crystalline substance with a unique orthorhombic structure that can be identified by X-ray diffraction (XRD). The technology matches peaks and intensities produced by the crystals to its database of crystal structures for identification (Doyle and Parsons, 2002). XRD technology does not provide any composition details of struvite particles. Dissolution of struvite

particles in acidic solution is commonly practiced for measuring the ionic constituents of crystal binding elements.

Studies on struvite pellet sizes indicated that the Mg : P molar ratio and Mg concentration has strong influence on crystal size (Fattah *et al*., 2008b; Le Corre *et al*., 2007). A study conducted by Hirasawa *et al*. (1997) demonstrated that large crystals were produced by crystal agglomeration, when Mg : P molar ratio was 2. By increasing the molar ratio to 4, the crystals shape became needle like crystals. However, Le Corre *et al.* (2007) indicated in their study that no correlation existed between struvite particle size and magnesium dosage. Their study also indicated that pH was the most influential parameter that controlled struvite quality (like morphology, purity), struvite quantity and nutrient removal.

3. Materials and Methods

3.1 Process Description

The study was divided into three processes for the determination of simultaneous nutrient removal from wastewater by combining ANAMMOX treatment process with struvite crystallization. The first step of the process was conducted to verify if the ANAMMOX effluent contained significant soluble phosphorus and to confirm the molar of N : P (1 : 1) for struvite production. The second step of the process was conducted to establish struvite formation potential using ANAMMOX effluent, which has very low N : P molar ratio. The third step of the process combination (using bench scaled fluidized bed reactors), was operated to quantify nitrogen and phosphorus removal and recovery efficiencies.

3.1.1 Part 1: Feed Characteristics Determination

Centrate obtained from Lulu Island Wastewater treatment plant was partially nitrified and then characterised for the ANAMMOX process to determine the effluent characteristics. Nitrifying sludge seed of 150 mL was added in a jar and centrate was pumped at 0.5 mL/min flow rate into the jar. The DO was maintained between 2 mg/L to 4mg/L and a magnetic stir bar was used to keep the centrate and the sludge seeds well mixed. The process temperature was maintained at 30°C. Influent pumping was stopped when the total feed volume reached 1000 mL. The process indicated that partial nitrification on centrate was complete when the feed solution reached a pH value of 6. The changes of constituents in centrate by partial nitrification were measured to prepare synthetic partially nitrified centrate. Literature values from Kosari (2011) for effluent constituents after ANAMMOX were used to prepare synthetic ANAMMOX effluent feed.

Detailed process description for partial nitrification and ANAMMOX process is given in Kosari, (2011).

3.1.2 Part 2: Struvite Formation Potential Tests

Jar tests were performed to determine the struvite formation potential of synthetic centrate, partially nitrified centrate and ANAMMOX effluent. Grab samples of 1L from each feed were taken into jars and magnesium and caustic solution was added externally using graduated burettes. The mixing was kept at 80 rpm for all the jars. Once the reactions were complete, the precipitated struvite was collected by filtration through 0.20 micron filter papers. Pictures of jar test by two different methods are shown in Figure 3.1 and Figure 3.2.

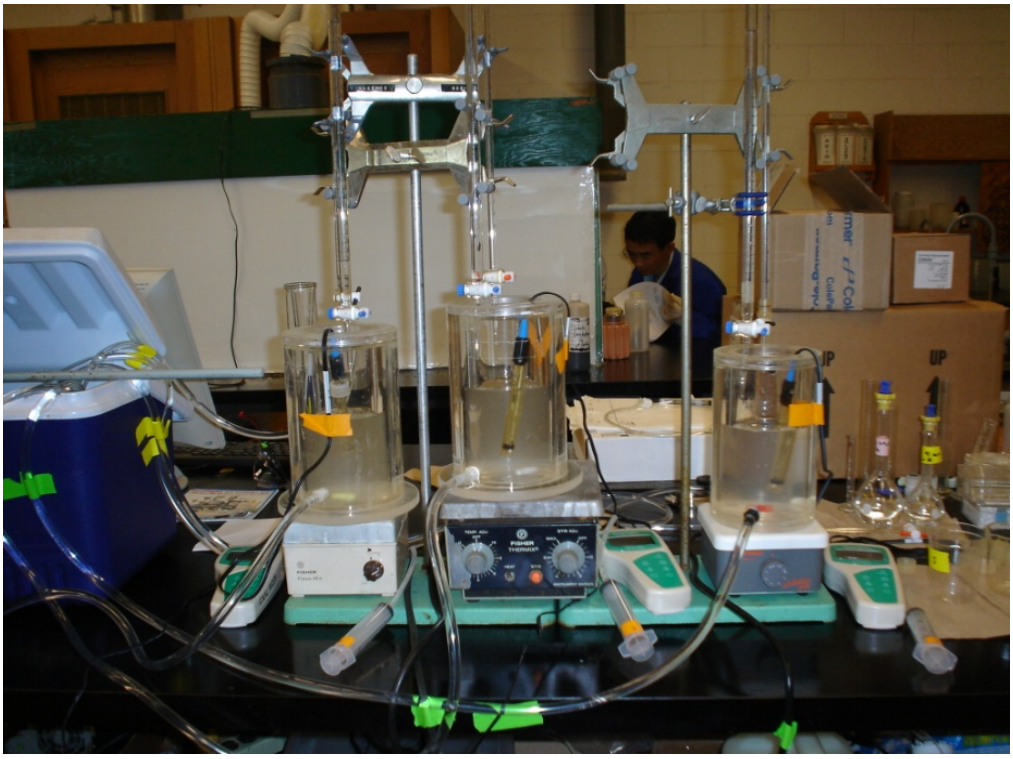


Figure 3.1. Jar test on feeds under controlled temperature.

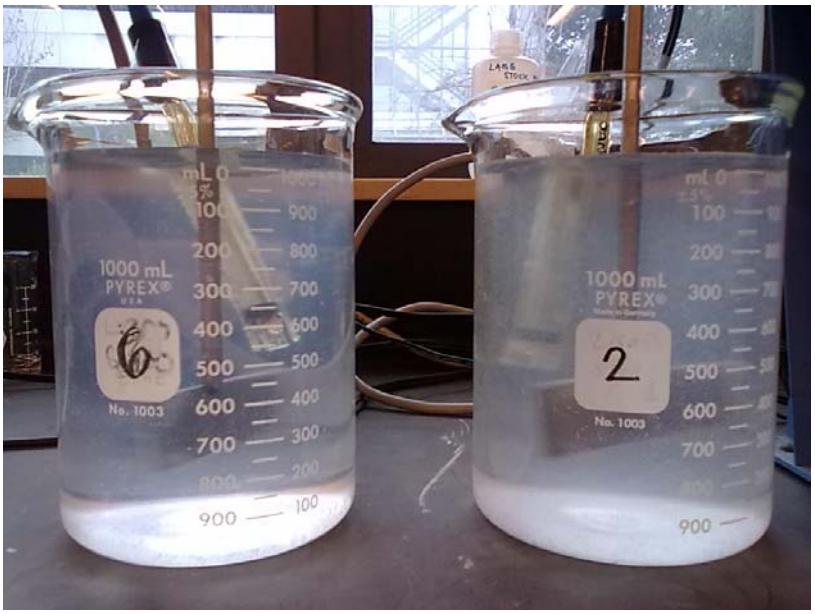


Figure 3.2. Jar test of feeds using Phipps and Bird stirrer instrument at room temperature

3.1.3 Part 3: Continuous Process with Fluidized Bed Reactors

Three identical lab scale reactors were designed and built using transparent polyvinyl chloride plastic. Each crystallizer (reactor) was connected to a feed tank, an external clarifier, a pH controller, magnesium and caustic storage containers, and pumps for feed, magnesium, caustic and recycle stream. The reactor design is shown in Figure 3.3 and the dimensions are given in Table 3.1.

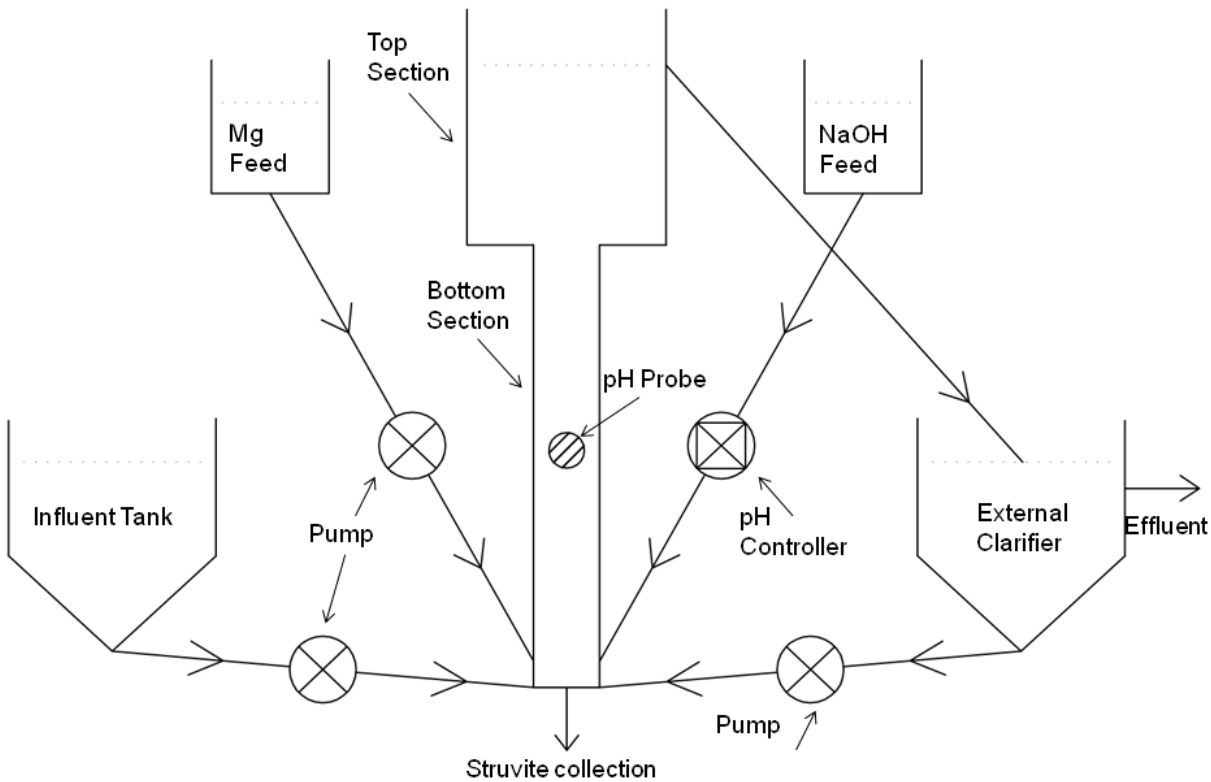


Figure 3.3. Lab scaled struvite crystallizer flow diagram.

Table 3.1. Dimensions of fluidized bed reactor

Dimension	Length, mm (in)	Inner Diameter, mm (in)	Area, mm^2 (sq. in)	Volume, mm^3 (cu. in)
Bottom section	609.6 (24)	40.44 (1.592)	1284.5 (1.991)	$7.64*10^5$ (47.774)
Top Section	406.4 (16)	77.27 (3.042)	4689.0 (7.268)	$1.861*10^6$ (116.286)
Total Volume mm^3 (cu. in)				$2.625*10^6$ (160.20)

The concept of a fluidized bed reactor (based on previous work at UBC) was used for the design of the reactors. Two different cross sectional areas were used. The bottom part of the reactor had

a smaller cross-sectional area than the top section and acted as the mixing zone. The top section acted as the settling zone for the struvite particles. For a given upflow velocity, the top section of the reactor had a lower upflow velocity than the bottom section, allowing struvite particles to stay inside the reactor and prevent washout. External clarifiers were equipped for recycling effluent and capturing fine struvite particles washed out from the reactors. Wastewater and the recycle streams were fed from the reactor bottom. Caustic and magnesium feed were connected 150 mm (6 inches) above the influent and recycle line. The amount of magnesium to be added into the reactors was calculated from known concentrations of PO_4-P and NH_4-N, the total flow rates inside the reactors, and experiment run time. A pH probe was installed 300 mm (12 inches) above the feed and recycle streams in each reactor and one in each external clarifier, to monitor the pH during continuous operation. The process was operated continuously until sufficient struvite growth was achieved inside the reactors. Once a significant amount of particles gathered at the bottom section, the process was stopped and struvite particles were collected from a collection port attached to the bottom section of the reactors.

3.2 Chemicals, Storage and Pumps

3.2.1 Influent Feed

Synthetic feed of ANAMMOX treated centrate, partially nitrified centrate and centrate containing key struvite forming constituents were used as influents in this study. The chemical compositions are shown in Chapter 4, Tables 4.1 to 4.3. The chemicals used to make the synthetic feeds were commercial grade ammonium chloride (NH_4-N), sodium bicarbonate ($NaHCO_3$), sodium nitrite ($NaNO_2$), sodium nitrate ($NaNO_3$), sodium dihydrogen phosphate ($NaPO_4H_2.2H_2O$), calcium chloride dihydrate ($CaCl_22H_2O$) and magnesium chloride hexahydrate ($MgCl_2.6H_2O$). During continuous tests, each type of feed was stored in a 60L

capacity holding tank and was pumped inside the reactors by 1-100 rpm Masterflex™ laboratory-scaled pumps. Masterflex™ laboratory-scaled 6-600 rpm pump was used for recycling effluent back in the reactor.

3.2.2 Magnesium (Mg) Feed

Magnesium feed was made using commercial grade magnesium chloride hexahydrate pellets ($MgCl_2.6H_2O$). The solution was stored in a 2L graduated cylinder and pumped into the reactors using Zellweger Analytics Inc.'s reagent pump. The Mg solution was made in such a way that the molar ratio of Mg : PO_4-P was always 1.1 inside the reactors during the whole operation.

3.2.3 Caustic (NaOH) Feed

Commercial grade sodium hydroxide or caustic (NaOH) was used to prepare a base solution for the study. The pellets were dissolved in distilled water to the desired normality and pumped into the reactors using pH controllers.

3.2.4 pH Controllers

The caustic solution pump was connected to pH controllers by Eutech Instruments (Model: alpha pH-800) and by the Environmental Laboratory, University of British Columbia to keep the pH inside the reactors under a certain range by controlling the amount of caustic pumped in the reactors. The pH inside the reactors and external clarifiers were monitored continuously with Oakton gel filled, epoxy body pH probes connected to the pH controllers and Oakton pH meters. The pH probes were calibrated by using standard buffer solution of pH 4, pH 7 and pH 10.

3.3 Sample Collection and Preservation

Grab samples of influent and effluent were collected during each experiment. Magnesium and caustic samples were collected for the storages jars before and after each experiment were performed. The pH of feed inside the reactors were monitored and controlled by an inbuilt pH probe connected to a pH controller. The sample pH and temperature were measured using Oakton gel filled, epoxy body pH probes connected to Oakton pH meters.

3.4 Analytical Methods

3.4.1 Magnesium

Analysis of magnesium was performed by flame atomic absorption spectrophotometry using a Varian Inc. SpectrAA220 Fast Sequential Atomic Absorption Spectrophotometer (AAS).

With real wastewater where soluble organics are present in the samples, 1mL of concentrated nitric acid was added to 10mL of sample and digested. This prevented the organics from interfering during analysis. Samples collected for magnesium test were first preserved in plastic containers using few drops of concentrated nitric acid (HNO_3). To prevent interference by carbonate ion in AAS, 2 mL of 100,000 mg/L lanthanum solution was added to each 100 mL of magnesium sample before testing in the AAS. Samples were diluted when necessary.

3.4.2 Ortho-Phosphate (PO_4-P)

Analysis for ortho-phosphate samples were performed by using flow injection analysis on Lachat QuickChem 8000 instrument. Samples were diluted before testing when necessary.

3.4.3 Ammonium (NH_4-N)

Analysis for ammonia samples were performed by using flow injection analysis on Lachat QuickChem 8000 instrument. Dilution of samples was performed before testing.

3.4.4 Nitrite and Nitrate (NO_x-N)

Analyses for nitrite and nitrate samples were performed by using flow injection analysis on Lachat QuickChem 8000 instrument.

3.4.5 Calcium

Analysis of calcium was performed to check the composition of struvite precipitates. The tests were performed by atomic absorption spectrophotometry using the AAS.

3.4.6 Caustic

Caustic (NaOH) solutions were dissolved in distilled water to make caustic solutions. Caustic samples were collected during each run of experiment and sodium ion in the solution was analyzed. Measured sodium ion concentration gave the molar strength of the caustic solution used in the experiment. The volume of caustic used in the experiment by each reactor during each run was recorded. The mass of caustic was calculated then from the consumed volume and caustic concentration.

3.4.7 Alkalinity

Alkalinity of the influent and effluent was measured during the study. A pH probe was used to measure the alkalinity. Sulfuric acid (0.2N or 0.02N) was added to the influent and effluents samples till pH of the sample reached 4.5. Alkalinity calculations are provided in Section 3.7.

3.4.8 Filtration

All samples were filtered before analysing using cellulose nitrate membranes (filter papers) having a nominal pore size of 0.20 microns. These removed all the suspended particles from the samples giving more accuracy in obtained results.

3.5 Struvite Collection, Drying, Analysis and Quality Determination

Struvite precipitates were collected for each reactor after completion of an experimental run. The collected particles were first filtered using nylon membranes with nominal pore size of 0.20 microns. The collected precipitates in the filter paper were first washed with distilled water, and then washed with reagent alcohol, to evaporate the water trapped in the precipitates quickly, thus, reducing the crystal drying time.

The dried struvite crystals were then analysed for magnesium, ortho-phosphate, ammonium and calcium. For analysing these constituents, 0.25 gm of precipitate was first dissolved in 50mL of 5% nitrite acid. Once dissolved, the sample was filtered by 0.20 µm cellulose membrane and diluted 50 times. The molar ratio of each constituent present in the precipitate gave the purity of the crystals formed during the experiments. The molar ratio of water in struvite was determined by oven drying a measured amount of struvite for 24 hours and then re-measuring the remaining weight. Struvite particles were also analysed in XRD to check the purity of the substance.

3.6 Particle Size Distribution

Particle size distribution of struvite particles was obtained using a Malvern Mastersizer 2000 particle size analyzer model Hydro 2000S. A particle size distribution image was captured by B3-Series Motic Microscope.

3.7 Terminology

3.7.1 Removal Efficiency

X-removal efficiency (%) = $(X_{influent} - X_{effluent})*100/X_{influent}$

$X_{influent}$ = Concentration of X of influent at reactor inlet in mg/L.

$X_{effluent}$ = Concentration of X of effluent collected from external clarifier in mg/L.

3.7.2 Recycle Ratio

Recycle Ratio (RR) = Q_{RR} / Q_{inf}

Q_{RR} = Recycle flow rate; Q_{inf} = Total influent flow rate.

3.7.3 Alkalinity

Alkalinity, mg/L $CaCO_3$ = (A x N x 50000) / (mL of sample)

Where, A = mL standard acid used to reach pH 4.5; N = normality of standard.

4. Results and Discussions

4.1 Part 1: Determination of Soluble PO_4-P in Feed after the ANAMMOX Process

Key constituents having direct influence on struvite formation were measured using centrate collected from Lulu Island Wastewater Treatment Plant. The centrate batch was assumed to be completely well mixed while determining the concentrations, given in Table 4.1 below.

Table 4.1. Concentrations of key constituents in centrate

Descriptions	Unit	Centrate		
		Maximum	Minimum	Average
pH	-	8.1	7.9	8.1
Alkalinity	mg/L	2840	2660	2750
NH_4-N	mg/L	800	765	775
NO_2-N	mg/L	-	-	-
NO_3-N	mg/L	-	-	-
PO_4-P	mg/L	95	92	93
Mg	mg/L	10	8.5	9
Ca	mg/L	23	22.5	22.5

The molar ratio of NH_4-N: PO_4-P in centrate was found to be around 18.00 : 1.00 which complies with the values suggested in the literature. Partial Nitrification, followed by ANAMMOX was performed on this batch of centrate to determine the changes in the constituents mentioned in the above table and monitor the reduction in N value, in comparison to

the change in P value due to the biological process. The results obtained from the two step N removal process are given below in Table 4.2 and Table 4.3.

Table 4.2. Concentrations of key compounds in feed after partial nitrification

Descriptions	Unit	Partially Nitrified Centrate		
		Maximum	Minimum	Average
pH	-	7.5	5.7	6
Alkalinity	mg/L	45	25	35
NH_4-N	mg/L	420	400	410
NO_2-N	mg/L	400	365	375
NO_3-N	mg/L	-	-	-
PO_4-P	mg/L	118	110	115.5
Mg	mg/L	5.5	3.5	4.5
Ca	mg/L	26	25	25.5

Partial nitrification on centrate was able to reduce approximately, 47 % NH_4-N from centrate by converting the NH_4-N into nitrite (NO_2). The alkalinity of the centrate was reduced to 35 mg/L from an initial value of 2750 mg/L. However, the PO_4-P concentration increased to 115.5 mg/L from an initial concentration of 93mg/L in the partial nitrification process. The significant increase in the soluble PO_4-P concentration monitored in the partial nitrification phase could be explained by the fact that a huge reduction in the alkalinity of centrate (low pH) induced acidic conditions in the feed, resulting in an increased solubility of the nutrients in the wastewater. Study has indicated that solubility can be increased by lowering pH of buffered solutions (Vemula *et al*., 2010).

Table 4.3. Concentrations of key constituents in feed after ANAMMOX process

Descriptions	Unit	ANAMMOX		
		Maximum	Minimum	Average
pH	-	6.4	5.7	6
Alkalinity	mg/L	40	30	35
NH_4-N	mg/L	120.5	100.5	115
NO_2-N	mg/L	76	70	72
NO_3-N	mg/L	182	175	179
PO_4-P	mg/L	118	110	115
Mg	mg/L	5	4	4.5
Ca	mg/L	26	25	25.5

The ANAMMOX process was able to remove 85% of NH_4-N from the centrate. The N : P molar ratio in the effluent after ANAMMOX process was calculated to be 2.25 : 1.00, which is greater than the required molar ratio of 1 for N. Thus, struvite formation was possible, theoretically, as struvite formation requires equimolar ratio's of N : P.

The constituents measured in this phase of the experiment were used to make synthetic feed for proceeding into the next phases of the research.

4.2 Part 2: Struvite Formation Potential in Feed after ANAMMOX Process

Struvite formation tests were carried out using synthetic feeds of centrate, partially nitrified centrate and ANAMMOX effluent. Struvite formation test was carried out on treated effluent from ANAMMOX process (referred as ANAMMOX effluent in the study). Struvite formation

with centrate was also conducted to compare struvite formation potential and efficiency of nutrient recovery with ANAMMOX effluent. As ANAMMOX effluent has very low N : P ratio, struvite formation tests were also carried out on partially nitrified centrate feed, to verify if N :P ration has any impact on the struvite formation process.

The average concentrations of the compound in Table 4.1, 4.2 and 4.3 were used to make the feed. As Mg was the limiting element in the feeds for struvite formation, it was added externally. Caustic solution was added externally to control the pH in the system, so that the SSR in all three feeds remained greater than 1.

The struvite formation tests for the feeds were carried out at three different temperatures. The selected temperatures were 20°C, 25°C and 30°C and two pH end points, 8.30 and 8.50. The maximum temperature was chosen to be 30°C as ANAMMOX process requires a relatively high temperature, to operate successfully. The jar tests were also performed using two different methods. In method 1, the variations of temperatures were maintained. Caustic was added gradually in the all three feeds with corresponding sampling over time. In method 2 of the jar tests, Phipps and Birds stirrer instrument was used to maintain the same mixing feed for all three feeds at room temperature. Samples were taken only for the influent and the final effluent, once struvite formation reactions were assumed to be complete.

The results on the phosphorus recovery from the two jar test methods are discussed below.

4.2.1 Jar Test Method 1: P and N Recovery at Variable Temperature

Jar test Method 1 was conducted to verify if ANAMMOX effluent was suitable for producing struvite crystals, as the N : P ratio was very low (≈ 2 : 1), in comparison to centrate. The N : P molar ratio of centrate is typically very high (approximately 20 : 1), and, this has proved to be

favourable for the quick formation of struvite crystals in the process. Theoretically, the requirements are equimolar amounts of N : P for struvite formation. Therefore, it was expected that ANAMMOX effluent will have the same struvite formation potential as centrate, as the availability of N was greater than the required molar amount in the solution.

The detailed summary of the influent and effluent values obtained in Method 1 of jar tests is given in details in Appendix A. In this method, 20°C, 25°C and 30°C temperatures were maintained in the feed solutions of ANAMMOX effluent to determine the struvite formation potential and maximum percentage of phosphorus recovery. Centrate and partially nitrified centrate were tested to perform a comparative study on the phosphorus recovery as struvite. Caustic (NaOH) was added gradually in the feed to increase the pH of the solution and maintain the SSR > 1 in the system. Thus, the struvite formation was initiated and, over time, the soluble PO_4-P and NH_4-N decreased in the solution as struvite precipitated out. Magnesium was added in such a way that the molar ratio of Mg : P remained 1.1 : 1.0 in all the solutions during the jar tests.

Samples were taken from the effluent after certain time increments to monitor the reduction rate of soluble P and soluble N in the feeds. The reduction of soluble P, and soluble N in centrate, partially nitrified centrate and ANAMMOX effluent at different temperatures over time are given in Figures 4.1 to 4.6. The left side of the graph indicates the influent concentration of PO_4-P and NH_4-N for centrate, partially nitrified centrate and ANAMMOX effluent.

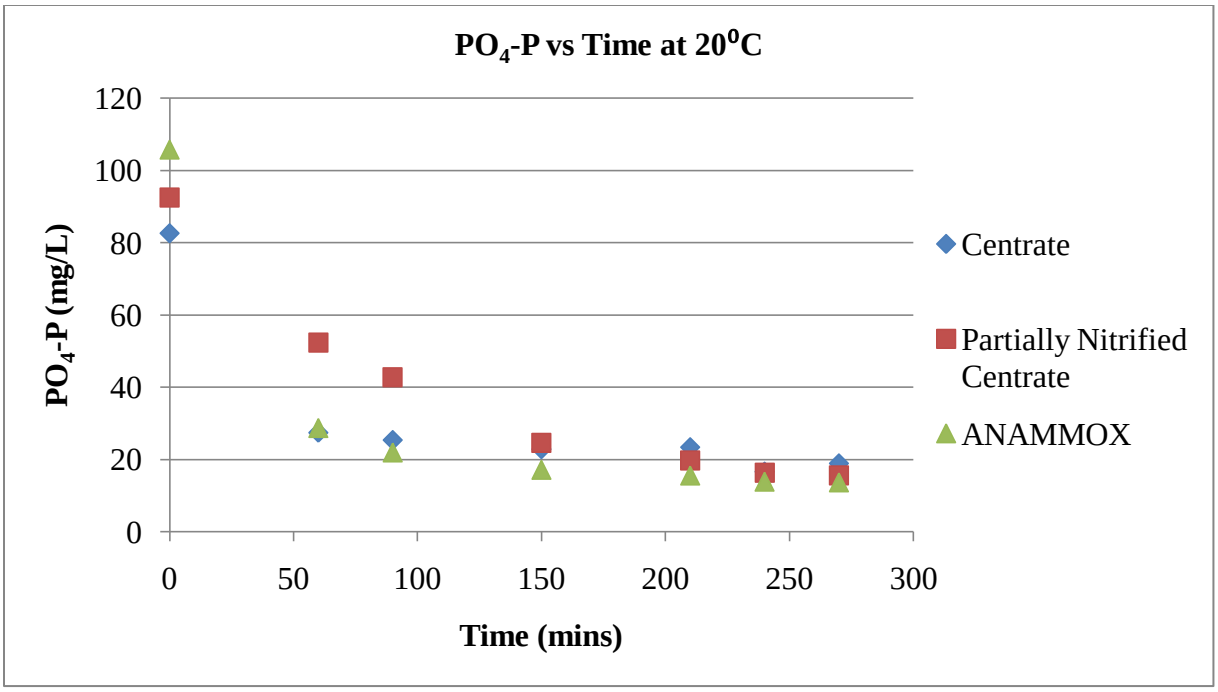


Figure 4.1. Phosphorus removal as struvite over time by addition of caustic at 20°C

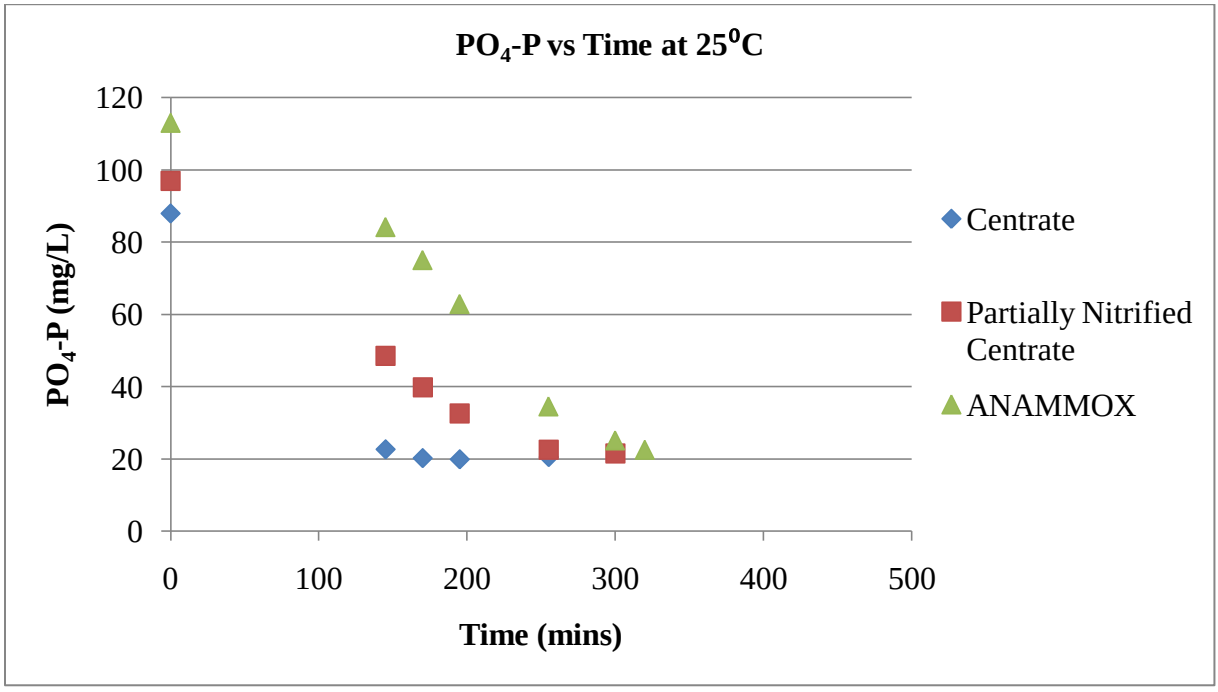


Figure 4.2. Phosphorus removal as struvite over time by addition of caustic at 25°C

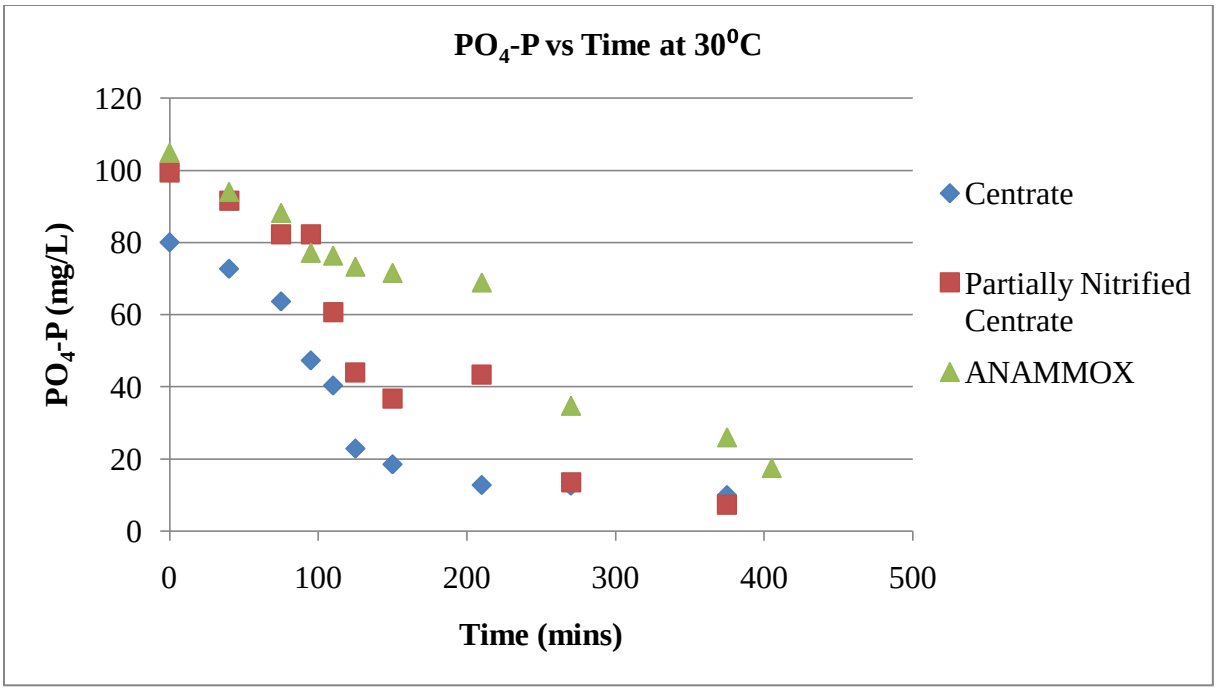


Figure 4.3. Phosphorus removal as struvite over time by addition of caustic at 30°C

From Figures 4.1 to 4.3, gradual reductions in soluble phosphorus in the form of struvite were observed at all temperatures, in all feed types. Struvite precipitation from ANAMMOX effluent reduced soluble P concentration from a maximum value of 113 mg/L to a minimum concentration of 13mg/L. For the maximum temperature 30ºC, soluble PO_4-P was reduced from an initial value of 105mg/L to 17.5mg/L, in the ANAMMOX effluent. Therefore, struvite recovery of more than 80% was possible for even the highest temperature in this feed. Also from the figures, it can be observed that the reaction rate of struvite formation and P removal was slower in most cases in the ANAMMOX effluent in comparison to centrate and partially nitrified centrate. The reason was assumed to be the low N:P ratio in ANAMMOX feed in comparison to the other two feeds, as the rest of the constituent concentrations were of similar value. Also, improved removal efficiency was noted as the temperatures dropped in the jar tests.

The removal of nitrogen for the feeds in this process is given from Figure 4.4 to Figure 4.6.

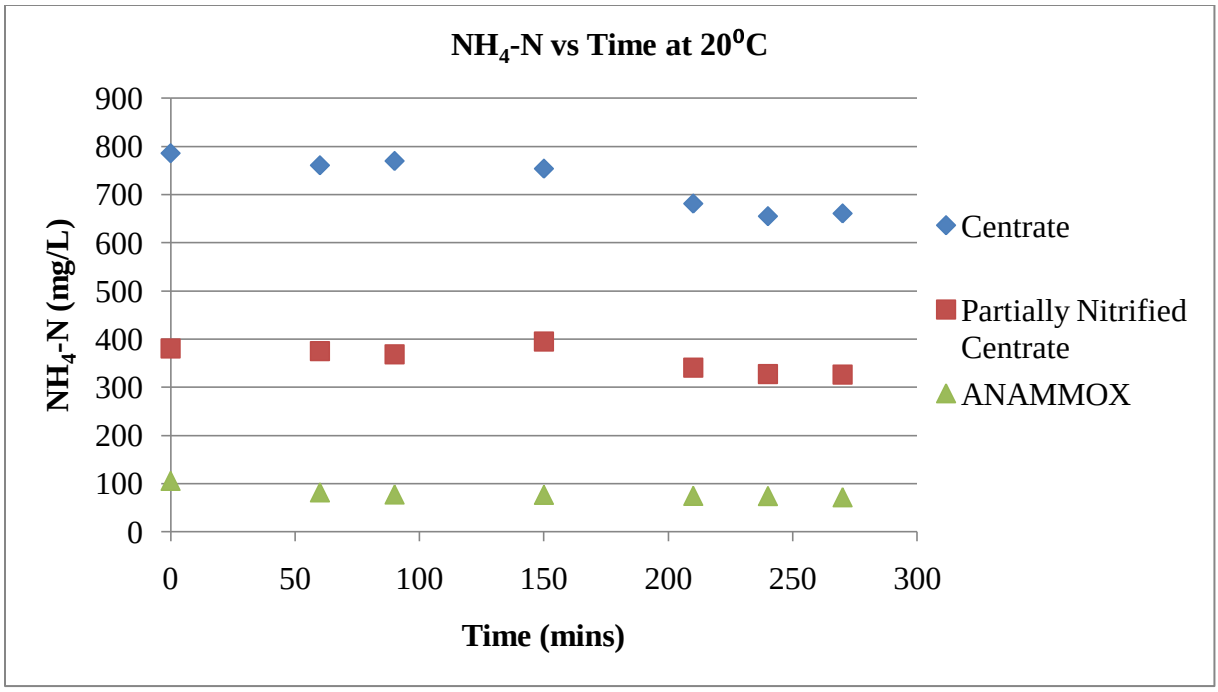


Figure 4.4. Nitrogen removal over time by addition of caustic at 20°C

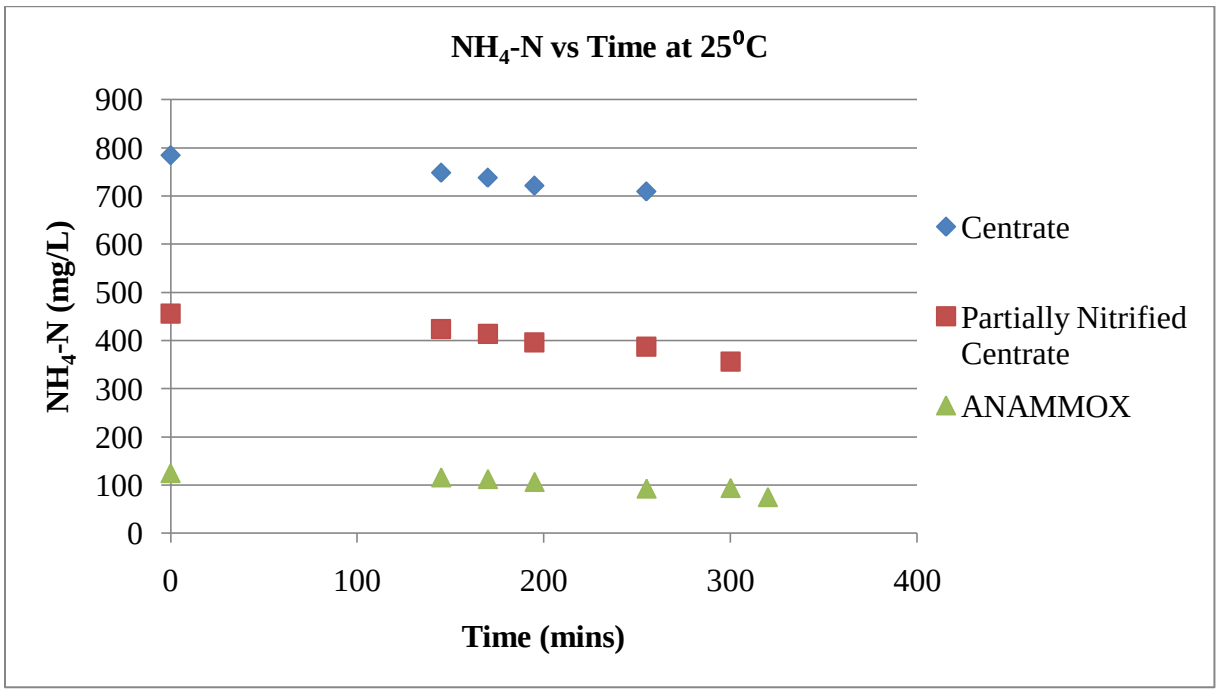


Figure 4.5. Nitrogen removal over time by addition of caustic as at 25°C

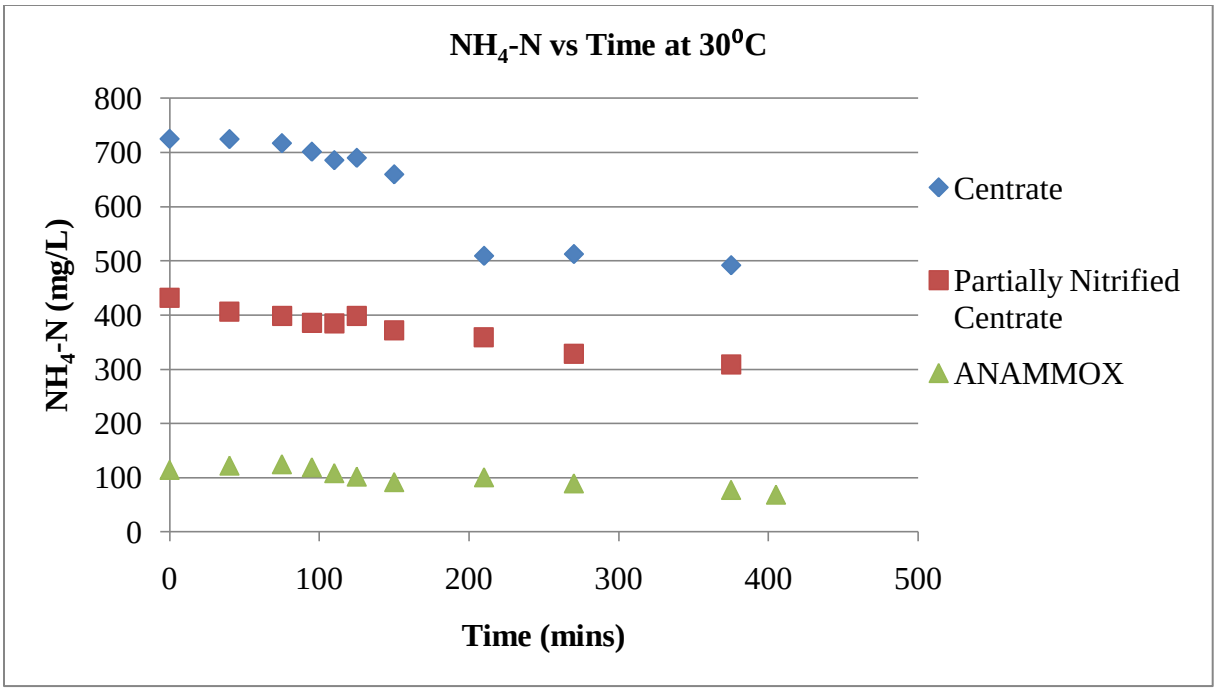


Figure 4.6. Nitrogen removal over time by addition of caustic at 30°C

In Figures 4.4 to 4.6, the diamonds represent centrate, the squares represent centrate that has been partially nitrified and the triangles represent feed that was treated by complete ANAMMOX process. The NH_4-N values in the y-axis, starting at the initial point (0,0) represents the N values of feed at each step of the process combination, before struvite crystallization was performed on the solutions.

It can be observed from the figures that struvite crystallisation process using pure centrate showed reduction of NH_4-N concentration to 600 mg/L from maximum initial values ranging between 725 mg/L to 785 mg/L. Whereas, struvite crystallisation process using ANAMMOX effluent reduced NH_4-N concentrations to a minimum value of 68mg/L from 115 mg/L. The molecular weight of N and P are 14 gm/mol and 31 gm/mol, respectively. As a result, for equimolar removals of these nutrients, the removal rate for P during the jar tests are steeper (Figure 4.1 to 4.3) compared to the N removal rates (Figures 4.4 to 4.6).

The struvite formation rate was always found to the faster for centrate (Figures 4.1 to 4.6) in comparison to partially nitrified centrate and ANAMMOX feed. This complies with the literature that, a higher N : P ratio accelerates struvite formation in wastewater.

Although, PO_4-P recovery as struvite was approximately 80% in all three sets of temperature, lower temperatures were found to be favourable for struvite formation in the tests. The average PO_4-P recovery for ANAMMOX effluent was 88% at 20°C, whereas, the recovery was 81% and 79%, on average, for 25°C and 30°C, respectively. Therefore, for the next steps of the experiments, room temperature (around 20°C) was maintained with a focus to achieve maximum nutrient recovery efficiencies from the process combination.

In this method of jar test, the gradual increments of caustic (NaOH) were added into the feed solutions, based on the reading from the pH meter connected inside each jar. Caustic (NaOH) was only added to the solutions when a decrease in the pH value due to struvite precipitation was observed. Addition of NaOH was done until the pH set point reached a stable value of 8.3 or 8.5 in the solution.

The fluctuation in pH value observed in the feeds, during the jar tests at 20ºC, is shown in Figure 4.7.

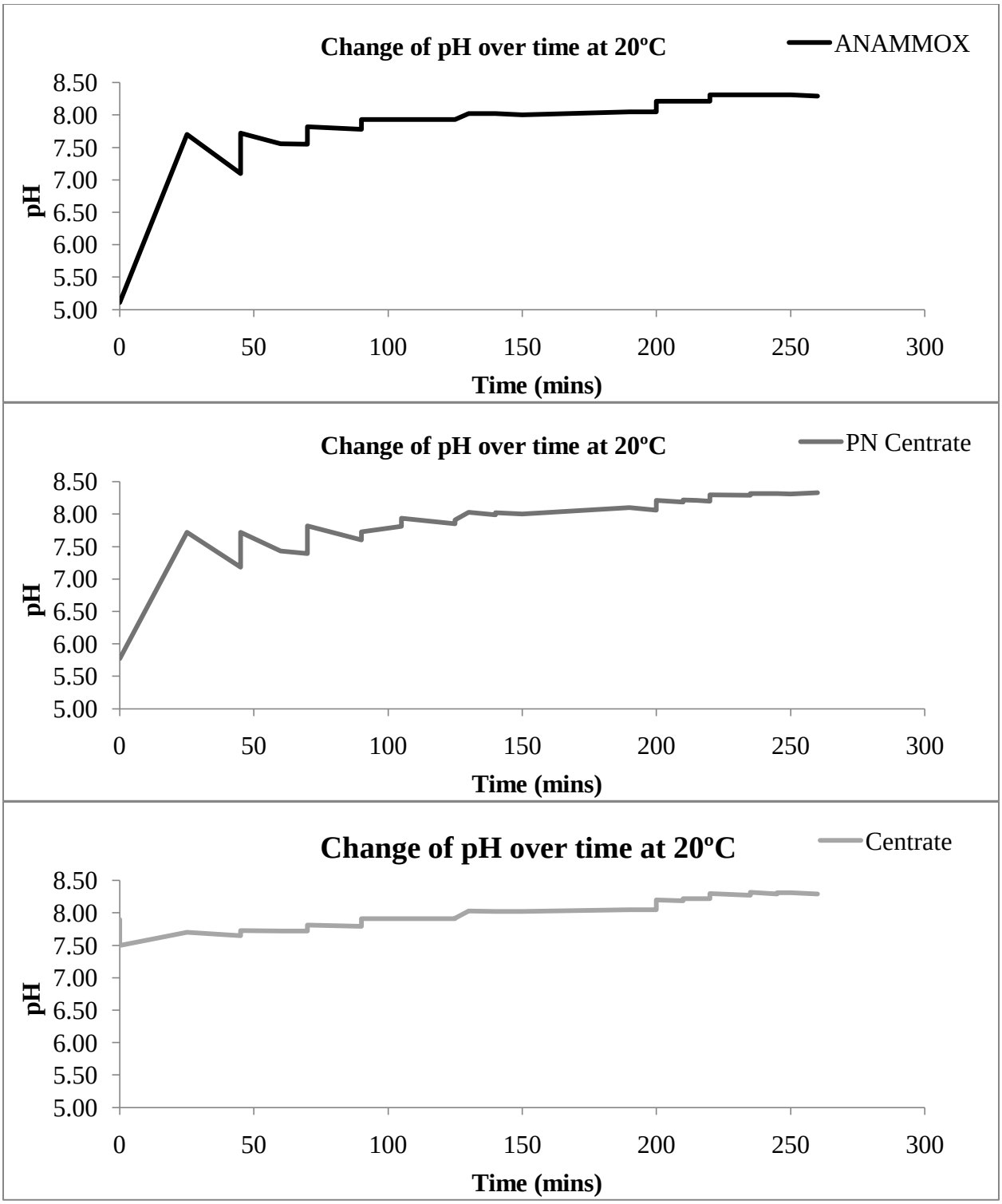


Figure 4.7. Change of pH over time in feeds during jar test at 20ºC

From Figure 4.7, it can be observed that the fluctuation in pH for ANAMMOX and partially nitrified feed was significant, compared to centrate. The phenomena observed could be explained by the soluble alkalinity of the solutions. From Tables 4.1 to 4.3, it can be seen that centrate has a very high soluble alkalinity in the system, which acts as a buffer; whereas, ANAMMOX and partially nitrified feed has a very low soluble alkalinity. For centrate, it took a significant amount of caustic addition to raise the pH initially for initializing struvite precipitation. However, the system was able to maintain the high pH for a prolonged period of time and precipitate out a majority of the soluble phosphorus as struvite. These conditions allowed the reaction rate to be faster in comparison to ANAMMOX and partially nitrified feed, as observed in Figures 4.1 to 4.3. For ANAMMOX and partially nitrified feed, less caustic solution was required to increase the solution's pH, but the addition was more frequent to maintain SSR>1 for struvite precipitation.

Therefore, to determine if alkalinity had any influence on struvite formation in centrate, and, to have an estimate on the amount of chemical grade caustic requirement for struvite formation, method 2 jar tests were performed.

4.2.2 Jar Test Method 2: Influence of Alkalinity and NaOH Requirement

Jar test method 2 was conducted to determine if alkalinity had any influence on struvite formation in centrate feed. The tests were conducted by sampling effluent samples only after complete struvite crystallization in the feed. This eliminated errors that resulted due to multiple effluent samplings from feed volume in jar test method 1. This method also provided an estimate on the amount of chemical grade caustic required for struvite formation. The mass balance

calculations in this step were very accurate due to use of simple equipment configurations, small feed volumes, and small extraction of effluent sample volumes for analysis.

In jar test method 2, a Phipps and Bird Stirrer instrument was used for uniform mixing of solutions. This experiment was conducted at room temperature (20°C) only. Influent samples from all three feeds were taken before adding magnesium (Mg) to the required molar ratio. Magnesium was added such that the molar ratio of Mg : P was 1.1 : 1.0 in the feed. Influent samples were again taken after Mg addition, to verify if alkalinity initiated any spontaneous struvite precipitation. After influent samples were taken, NaOH was added externally to the feed untill a stable pH end point of 8.3 and 8.5 was reached, indicating experiment completion. The results obtained on PO_4-P and NH_4-N reduction are given in Tables 4.4to 4.6.

Table 4.4. Concentration changes in centrate during struvite crystallization

Centrate						
Description	Influent (Before Mg)	Influent (After Mg)	Effluent 1 (pH = 8.3)	Reduction Effluent 1 (%)	Effluent 2 (pH = 8.5)	Reduction Effluent 2 (%)
Column 1	Column 2	Column3	Column 4	Column 5	Column 6	Column 7
Alkalinity (mg/L, $CaCO_3$)	3000	2640	2420	19.3	2450	18.3
NH_4-N (mg/L)	825.5	780	770	6.7	762.5	7.6
PO_4-P (mg/L)	100	21	11.5	88.5	11.5	88.5
Mg (mg/L)	100	69	27	73	26	74

From Table 4.4, it can be observed that the alkalinity, PO_4-P, NH_4-N and Mg concentrations of centrate feed were higher before Mg was added. After Mg was added to the feed, PO_4-P concentration reduced from 100 mg/L to 21 mg/L (79%) without the requirement of external caustic. The alkalinity of the solution was reduced from 3000 mg/L to 2640mg/L. A reduction in NH_4-N and Mg concentration was also observed in this step. After experiment completion by caustic addition, an overall 88% PO_4-P was removed and recovered as struvite. The alkalinity further reduced from 2640 mg/L to 2420 mg/L in the final effluent. This indicates that the high alkalinity in centrate promoted spontaneous struvite formation when magnesium was available to the required molar ratio, as per struvite stoichiometry.

Table 4.5. Concentration changes in partially nitrified centrate during struvite crystallization

Partially Nitrified Centrate						
Description	Influent (Before Mg)	Influent (After Mg)	Effluent 1 (pH = 8.3)	Reduction Effluent 1 (%)	Effluent 2 (pH = 8.5)	Reduction Effluent 2 (%)
Column 1	Column 2	Column 3	Column 4	Column 5	Column 6	Column 7
Alkalinity (mg/L, $CaCO_3$)	147.5	147	177	-20.5	225	-53.1
NH_4-N (mg/L)	431	430	369	14	360	16.3
PO_4-P (mg/L)	107	100.5	12	88	5	95
Mg (mg/L)	127.5	125.5	41	67.5	34	73

The NH_4-N concentration reduced to 431 mg/L after partial nitrification on centrate from an initial concentration of 825.5 mg/L, which is indicated in column 2 in Table 4.5. Struvite crystallization was performed on partially nitrified centrate, and, the reduced concentrations of the nutrients are given in the columns 4 and 7 in Table 4.5.

Table 4.6. Concentration changes in ANAMMOX effluent during struvite crystallisation

ANAMMOX Effluent						
Description	Influent (Before Mg)	Influent (After Mg)	Effluent 1 (pH = 8.3)	Reduction Effluent 1 (%)	Effluent 2 (pH = 8.5)	Reduction Effluent 2 (%)
Column 1	Column 2	Column3	Column 4	Column 5	Column 6	Column 7
Alkalinity (mg/L, $CaCO_3$)	76	76	165	-117.1	97	-27.6
NH_4-N (mg/L)	138	137.5	113.5	17.5	94.3	31.5
PO_4-P (mg/L)	125.5	124.5	55.5	55.5	24	80.8
Mg (mg/L)	136.5	136.5	90	34	52.5	61.5

The NH_4-N concentration reduced to 138 mg/L from an initial concentration of 825.5 mg/L, after complete ANAMMOX process was performed on centrate, which is indicated in column 2 in Table 4.6. Struvite crystallization was performed on ANAMMOX treated effluent, and, the reduced concentrations of the nutrients are given in the columns 4 and 7 in Table 4.6.

From Table 4.5 and Table 4.6, it was observed that the low soluble alkalinity did not have any influence on soluble PO_4-P, NH_4-N and Mg concentrations, after adding Mg in the feeds. Struvite formation only initiated when NaOH solution was added to the feed, to raise the pH. After NaOH addition, PO_4-P concentration was reduced by a maximum of 94% and 80% in

partially nitrified feed and ANAMMOX feed, respectively. Higher pH end point yielded more struvite recovery in case of both feeds, unlike centrate, which achieved maximum P recovery efficiency at pH 8.3. An increase in the concentration of alkalinity in the final effluent was also monitored for ANAMMOX and partially nitrified feed. This indicated that alkalinity did not influence struvite formation in these two feeds, like it had for centrate.

The amount of NaOH required in grams for experimental completion was recorded for each feed. The total amount of struvite formed was filtered and dried before being weighed. The amount of struvite collected was divided by the amount of caustic used to determine NaOH consumed per gram struvite. The struvite particles collected were also tested into its molar constituents of Mg : NH_4-N : PO_4-P for purity check. Details are mentioned in Tables 4.7 to 4.9.

Table 4.7. Caustic consumed for struvite production in centrate

	Centrate					
Description	Struvite theoritical (gms)	NaOH theo. (gm/gm)	Struvite calculated (gms)	NaOH consumed (gms)	NaOH calculated (gm/gm)	Mg:NH_4:PO_4
Influent	0.6258	-	-	-	0.0000	-
Effluent1 pH 8.3	0.7030	0.4723	0.6982	0.3320	0.4755	0.99 : 0.99 : 1
Effluent2 pH 8.5	0.7026	0.4128	0.6755	0.2900	0.4293	0.99 : 0.99 : 1

Table 4.8. Caustic consumed for struvite production in partially nitrified centrate

Partially Nitrified Centrate						
	Struvite theoritical (gms)	NaOH theoretical (gm/gm)	Struvite calculated (gms)	NaOH consumed (gms)	NaOH calculated (gm/gm)	$Mg:NH_4:PO_4$
Influent	-	-	-	-	-	-
Effluent1 pH 8.3	0.6977	0.4658	0.7893	0.3250	0.4118	1.03 : 0.97 : 1
Effluent2 pH 8.5	0.7537	0.4644	0.8693	0.3500	0.4026	0.94 : 0.95 : 1

Table 4.9. Caustic consumed for struvite production in ANAMMOX effluent

ANAMMOX						
	Struvite theoritical (gms)	NaOH theoritical (gm/gm)	Struvite Calculated (gms)	NaOH consumed (gms)	NaOH calculted (gm/gm)	$Mg:NH_4:PO_4$
Influent	-	-	-	-	-	-
Effluent1 pH 8.3	0.5460	0.4487	0.5210	0.2450	0.4702	1.05 : 0.89 : 1
Effluent2 pH 8.5	0.7957	0.3871	0.8204	0.3080	0.3754	1.00 : 0.91 : 1

The theoretical amount of struvite produced in the feed was calculated based on the amount of phosphorus removed during the process. It can be noticed that the struvite amount in theory, and in actual, falls within ±5% discrepancy for ANAMMOX effluent and centrate. Therefore, the

values obtained theoretically can be considered as accurate, and can be used for future calculations. It can also be noted that the NaOH consumed for struvite production was also in the same range and comparable for all the feeds. However, as the jar tests were performed only on 1L grab samples, the results obtained cannot be considered representative for a full scale process combination. Therefore, further study was conducted to determine the NaOH consumption for struvite production in ANAMMOX feed, using bench scale, fluidized bed reactors and is discussed in Section 4.3.

4.2.3 Summary of Jar Test Method 1 and Method 2

The combined results obtained from both methods of jar tests are summarized in Table 4.10.

Table 4.10. Summary of jar test results after struvite crystallization

Description	ANAMMOX treated Centrate (min.-max.)	Partially Nitrified Centrate (min.-max.)	Centrate (min.-max.)
Influent PO_4-P conc. (mg/L)	104.89 ~121.00	92.56 ~100.50	80.13 ~ 95.50
Effluent PO_4-P conc. (mg/L)	13.75 ~ 23.95	5.25 ~ 21.56	11.45 ~ 20.58
P-removal efficiency (%)	79 ~ 88	78 ~ 94	80 ~ 89
Influent NH_4-N conc. (mg/L)	105.84 ~137.50	380.33 ~ 456.18	725.12 ~ 771.35
Effluent NH_4-N conc. (mg/L)	68.42 ~ 94.30	308.47 ~ 360.00	660.50 ~ 709.55
N-removal efficiency from the jar test (%)	17 ~ 40	14 ~ 28	8 ~ 32
N-removal efficiency from process combination (%)	88 ~ 91	53 ~ 60	8 ~ 32
Influent pH	5.80 ~ 5.90	5.80 ~ 5.90	7.80 ~ 7.90
Effluent pH	8.30 ~ 8.50	8.30 ~ 8.50	8.30 ~ 8.50

In the jar tests, it was possible to recover PO_4-P (as struvite) as high as 88% from ANAMMOX effluent. In comparison, up to 88% PO_4-P was recovered as struvite from centrate feed, in this study. Partially nitrified centrate had the highest PO_4-P removal of 94% in the jar tests. Overall, the process combination of ANAMMOX, followed by struvite crystallization, was able to reduce in excess of 85% PO_4-P and 85% NH_4-N from centrate in the final effluent. Lower temperatures were also found to be favourable for nutrient recovery as struvite. Also, higher pH resulted in higher struvite formation, thus, higher P and N recovery from ANAMMOX effluent.

4.3 Part 3: Continuous Operation with Bench-Scaled Fluidized Bed Reactors

In treatment plants, the process combination of ANAMMOX followed by struvite crystallization will be operating continuously in reactors if applied to pilot or full scale. The jar tests provided a positive indication that the processes could be combined successfully for simultaneous nutrient recovery. However, the results were not representative to real treatment plant process conditions. Therefore, a bench scale continuous operation using fluidized bed reactors were opted for the next step of the study, so that the results obtained in this step can be considered representative to pilot or full scale treatment plants. This study was conducted to determine the nutrient removal efficiencies resulting from the process combination under continuous reactor operation for a significant period.

Synthetic feeds of centrate, partially nitrified centrate and ANAMMOX treated centrate were prepared and were fed into three identical reactors, under the similar conditions for process operation. Magnesium (Mg) feed and caustic (NaOH) feed were added externally to balance the stoichiometry inside the reactors and to keep the pH under control to maintain SSR greater than unity respectively. Influent samples and effluent samples were taken at random times, to check

whether the reactors attained steady state conditions once the whole process was under operation. The results on the removal of NH_4-N and PO_4-P in the form of struvite inside the reactors, under different operating conditions, are discussed in the later sections.

4.3.1 Operating Condition 1: Low Influent Flow Rate

4.3.1.1 Phosphorus and Nitrogen Removal and Recovery

The first operating condition was chosen at a low influent flow rate (Q_{inf} = 40 mL/min; HRT = 70 mins when RR = 0) in each reactor. All three reactors had recycle lines and the RR ratio was maintained between 2 and 5 to obtain the best results. The control pH was kept between 7.5 and 8.1 to achieve the best possible recovery of N and P as struvite. A picture of the whole process under operation is shown below in Figure 4.8. Struvite particles forming inside the reactors, during operation, can be clearly observed in the picture.

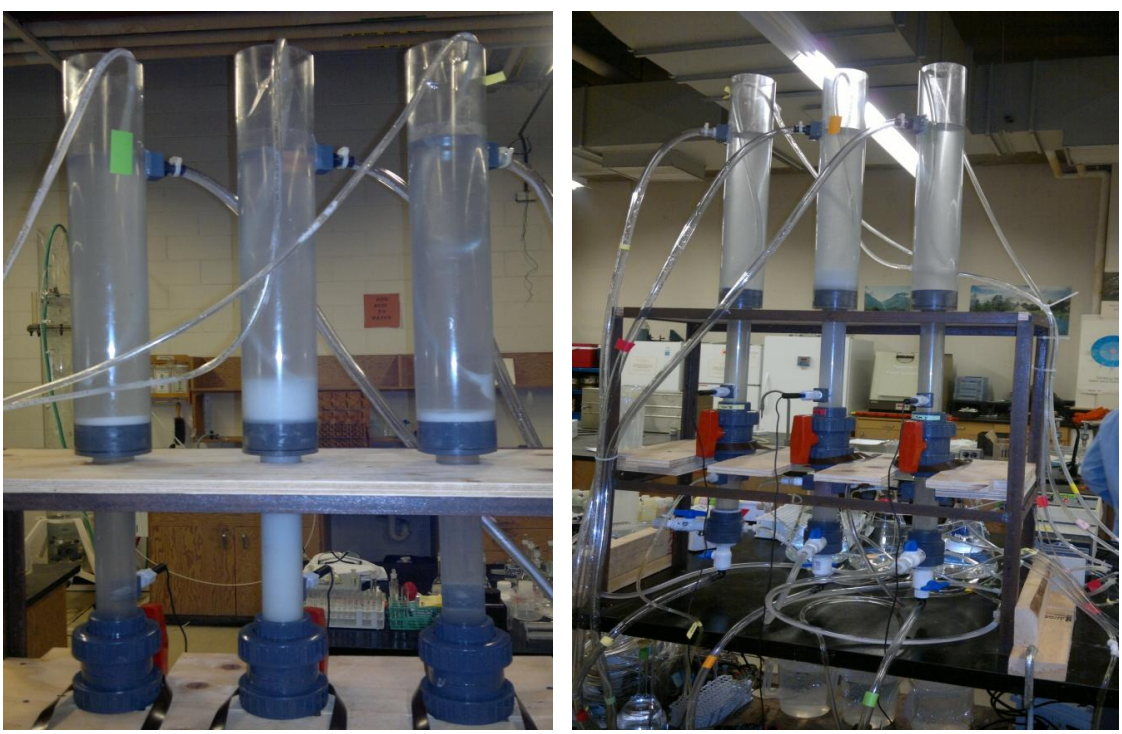


Figure 4.8. Reactors under operation for struvite crystallization

Once the process was under operation, the reactions attained steady state conditions depending on the recycle ratio (RR). A higher RR initiated steady state condition sooner than at a lower ratio.

The tests were carried out under different upflow velocities (by changing the recycle ratio) and different control pH, given in Table 4.11, to determine the best operating condition for struvite recovery using all three feeds. The process was able to maintain steady state conditions and constant P removal and recovery, by parameter optimization. Details of each operation, with influent and effluent values, are given in Appendix B.

Table 4.11. Key operating conditions for struvite crystallization in low flow rate

Operation No.	Influent Flow Rate, Q_{inf} (mL/min)	Recycle Ratio	Control pH		
			ANAMMOX	Partially Nitrified Centrate	Centrate
Run 1	40.00	2.00	7.90	7.90	7.90
Run 2	40.00	2.00	7.80	7.80	8.00
Run 3	40.00	2.00	7.70	7.70	8.10
Run 4	40.00	5.00	7.60	7.60	7.80

As centrate influent always maintained a high pH of 7.8 or more due to high alkalinity, the pH controller set point had to be maintained slightly more than the influent pH value, to initiate struvite formation. Once the process was under operation with addition of magnesium and caustic feed externally, reduction in the soluble concentration of PO_4-P and NH_4-N was expected due to struvite precipitation. The process was assumed to be under steady state conditions once the solutions in the reactor were completely well mixed.

Figures 4.9 to 4.14 shows the average effluent concentrations of PO_4-P and NH_4-N in all three feeds obtained when the operation was under steady state conditions.

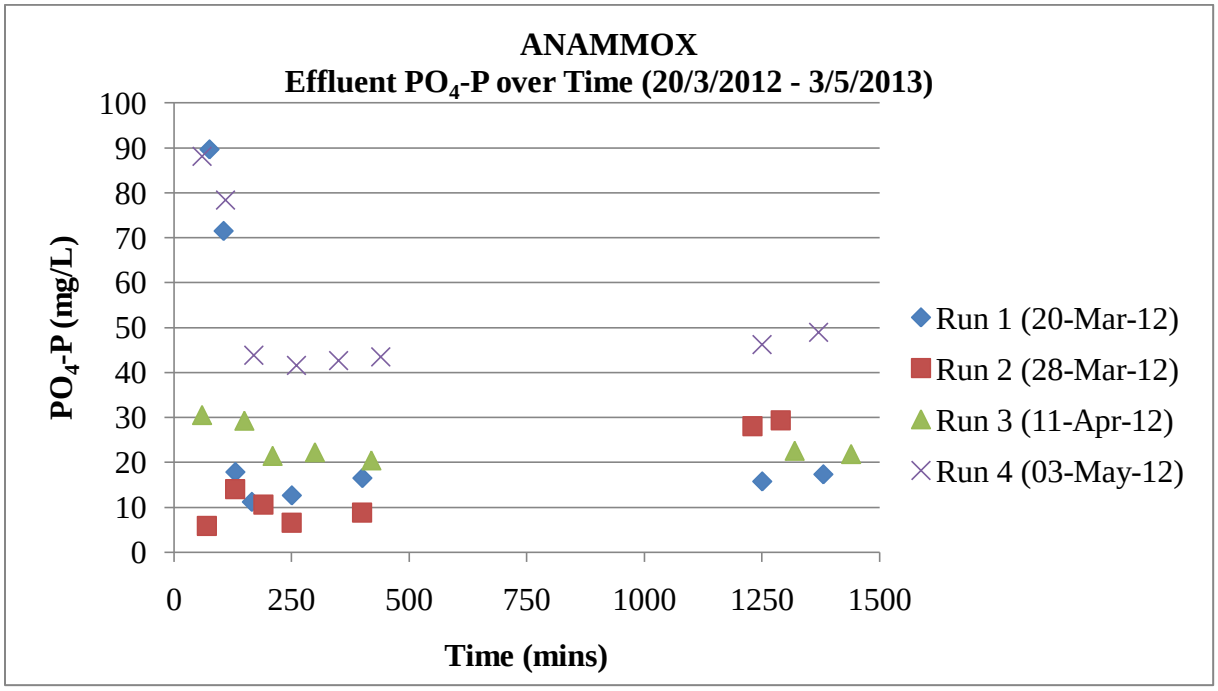


Figure 4.9. Soluble PO_4-P concentration in ANAMMOX effluent over time

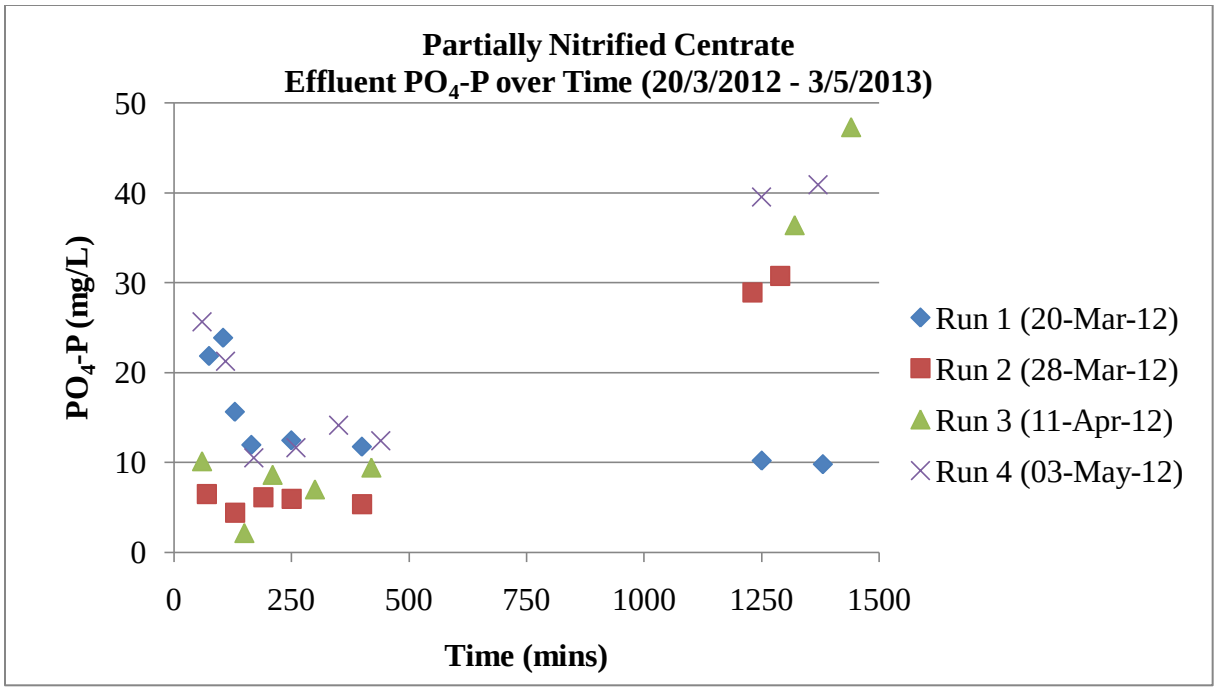


Figure 4.10. Soluble PO_4-P concentration in partially nitrified centrate over time

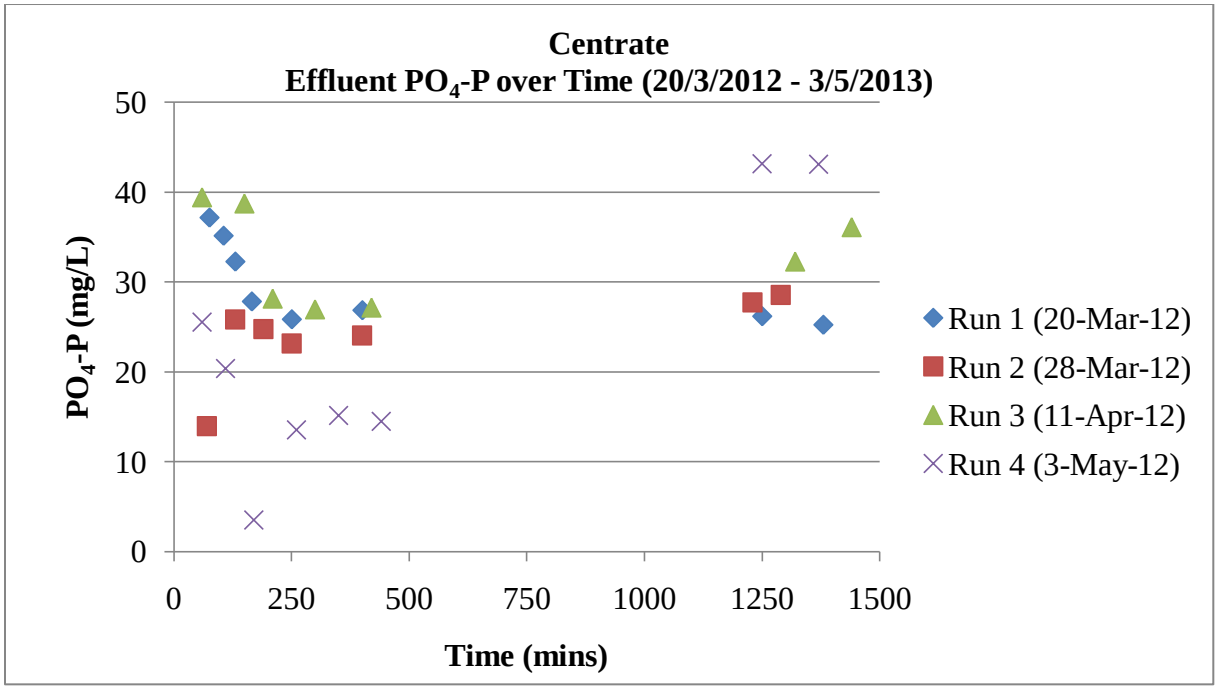


Figure 4.11. Soluble PO_4-P concentration in centrate over time

The reactions achieved steady state condition sometime before 100 minutes, as it took 70 minutes for the feed to fill the reactor for the first time before the recycle line could be opened. It can be seen from Figure 4.9 that ANAMMOX feed was able to maintain the same stability as centrate, in spite of having a very low N : P molar ratio. Effluent samples were collected from the external clarifiers connected with the reactors for the first 8 hours (480 minutes) during operation. As manual sampling was performed, overnight sampling was not conducted during process operation, which explains the blank sections in Figures 4.9 to 4.14. Effluent samples were again collected the following day to confirm that struvite formation reaction was under steady state during continuous operation. In case of run 3 and run 4, it was observed that phosphorus recovery as struvite lowered over time. This resulted due to struvite scaling the recycle line of the reactors, reducing the total flow rate inside the reactors, and, the probability of particle collision to form struvite crystals.

The PO_4-P concentrations of ANAMMOX effluent ranged between 117 mg/L to 94 mg/L, before struvite crystallization. After recovering struvite from ANAMMOX effluent, the soluble PO_4-P concentration was reduced to an average value of 15mg/L in Run 1 and Run 2, under steady state conditions. In comparison, centrate PO_4-P concentration reduced to an average value of 22 mg/L in Run 4, from a maximum value of 109 mg/L. In partially nitrified centrate, struvite crystallization reduced the PO_4-P concentration to 13 mg/L, on average, in Run 2 from an initial value of 119 mg/L, as shown in Figure 4.10.

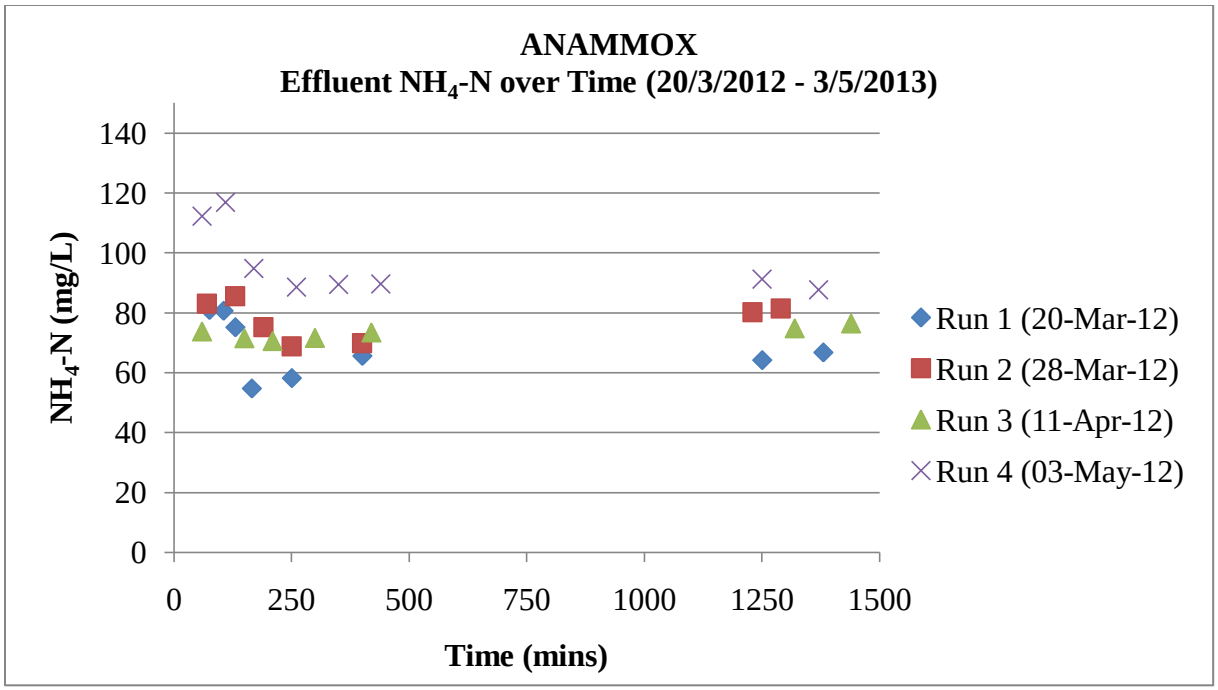


Figure 4.12. Soluble NH_4-N concentration in ANAMMOX effluent over time

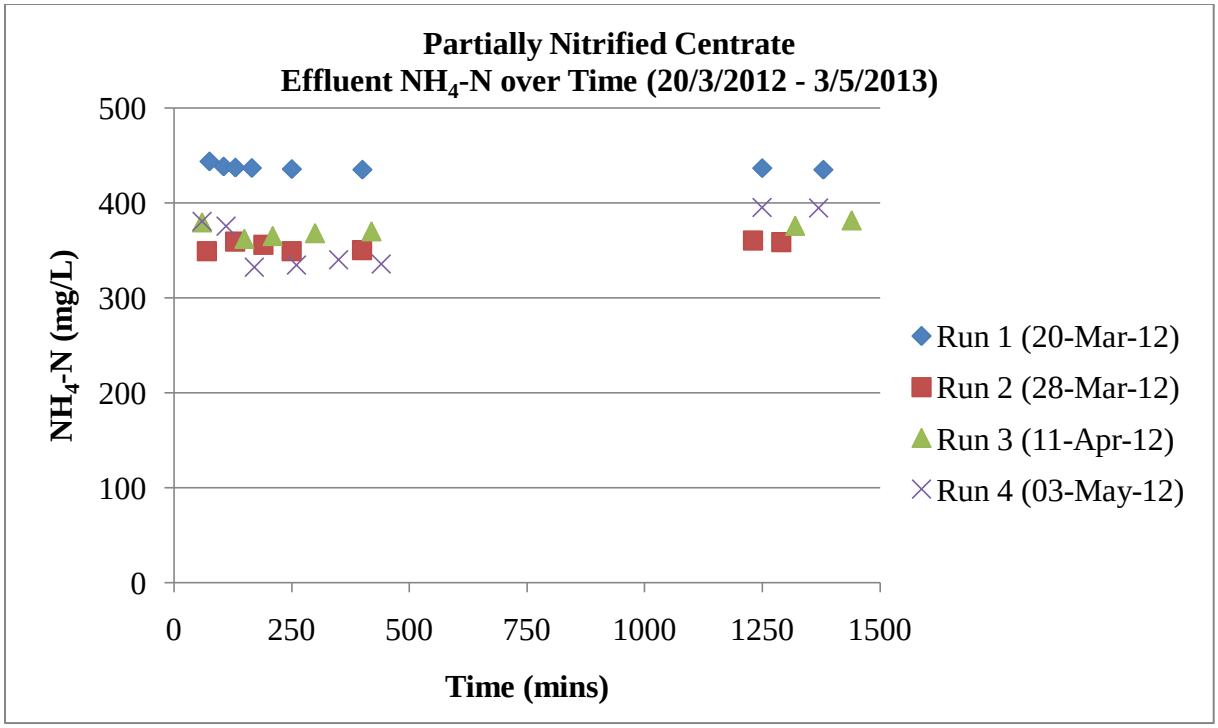


Figure 4.13. Soluble NH_4-N concentration in partially nitrified centrate over time

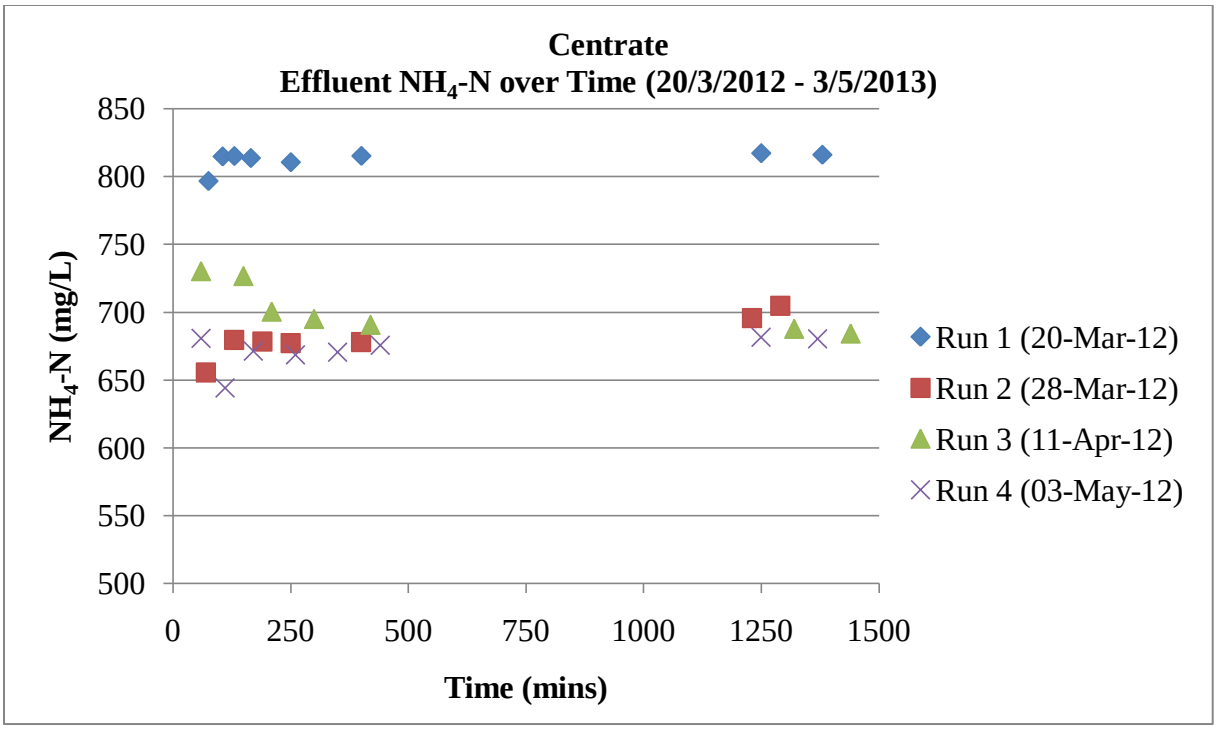


Figure 4.14. Soluble NH_4-N concentration in centrate over time

The concentrations of NH_4-N ranged between 128 mg/L to 113 mg/L in treated feed after completing the ANAMMOX process on centrate. Struvite crystallization on ANAMMOX effluent resulted in a minimum NH_4-N concentration of 68 mg/L, to a maximum value of 128 mg/L.

In case of ANAMMOX, run 4 had the least amount of phosphorus and nitrogen removal in the form of struvite. The difference in run 4 was the recycle ratio was 5, whereas the rest were only 2. This indicated that less turbulence was more favourable for struvite formation in ANAMMOX feed.

Each operation was maintained for a maximum period of 24 hours (1440 minutes), as long as the plugs and ports did not get clogged due to struvite deposition over time. Once the ports were clogged, an increase in the concentration of soluble PO_4-P and NH_4-N was observed and

operation had to be stopped for maintenance purposes. The sharp increase in soluble PO_4-P and NH_4-N concentration was monitored in the effluent samples taken after 22 hours (1320 minutes) of operation and can be observed in Figures 4.9 to 4.14. Increasing the recycle ratio resulted in more plugging inside the reactors and consequently lowering the mixing turbulence in the reactors. A difference in pH value to ± 0.5 was also monitored between the effluent samples and the reactor solution. Therefore, to increase the mixing energy of the solution for the same pH value between the reactor feed and the effluent, and, to prevent particle deposition into the ports of the reactors, the influent flow rate was increased to 140 mL/min; this is discussed later in Section 4.3.2.

4.3.1.2 Phosphorus and Nitrogen Removal Efficiency

For operating condition Q_{inf} = 40 mL/min, the overall process performance, using ANAMMOX effluent as the feed for struvite crystallization in comparison with partially nitrified centrate, and centrate is given in Figure 4.15 and Figure 4.16. Each group of values represented in the figures are the average P and N removal percentage, when the feeds were operated under conditions mentioned in Table 4.11. For ANAMMOX treated centrate, the best values where found under certain operating conditions which were not the best case for centrate and/or partially nitrified centrate. However, partially nitrified centrate maintained an overall steady and high P and N recovery efficiency as struvite, under all operating conditions.

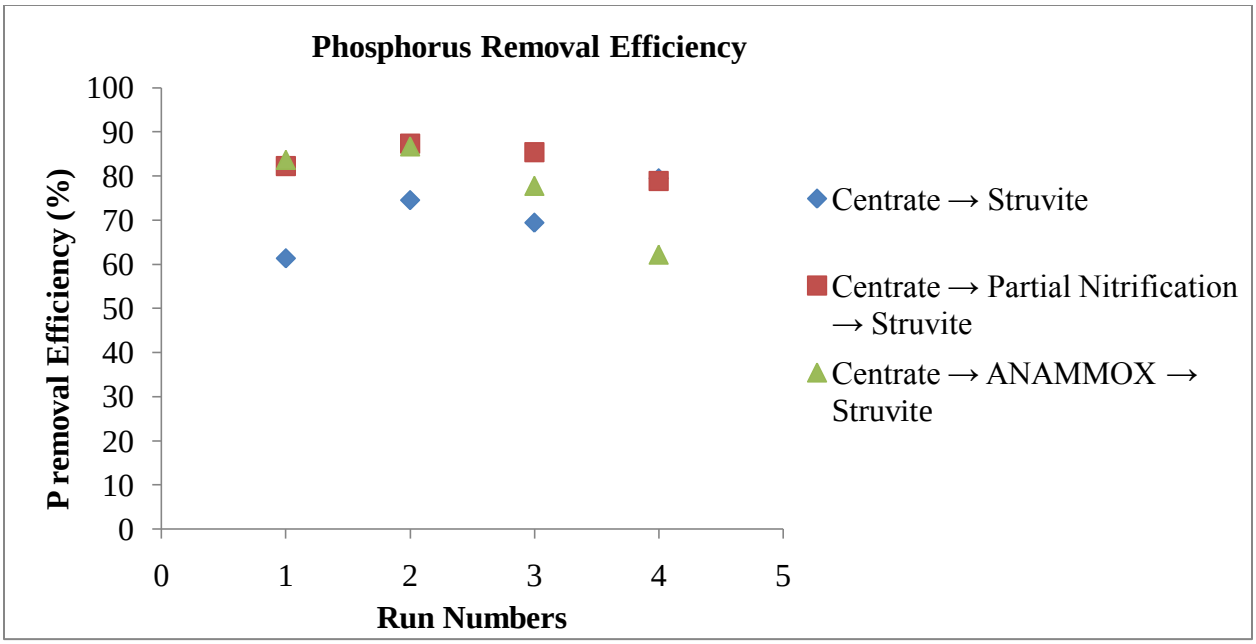


Figure 4.15. Average percentage of PO_4-P removal from feeds during operation

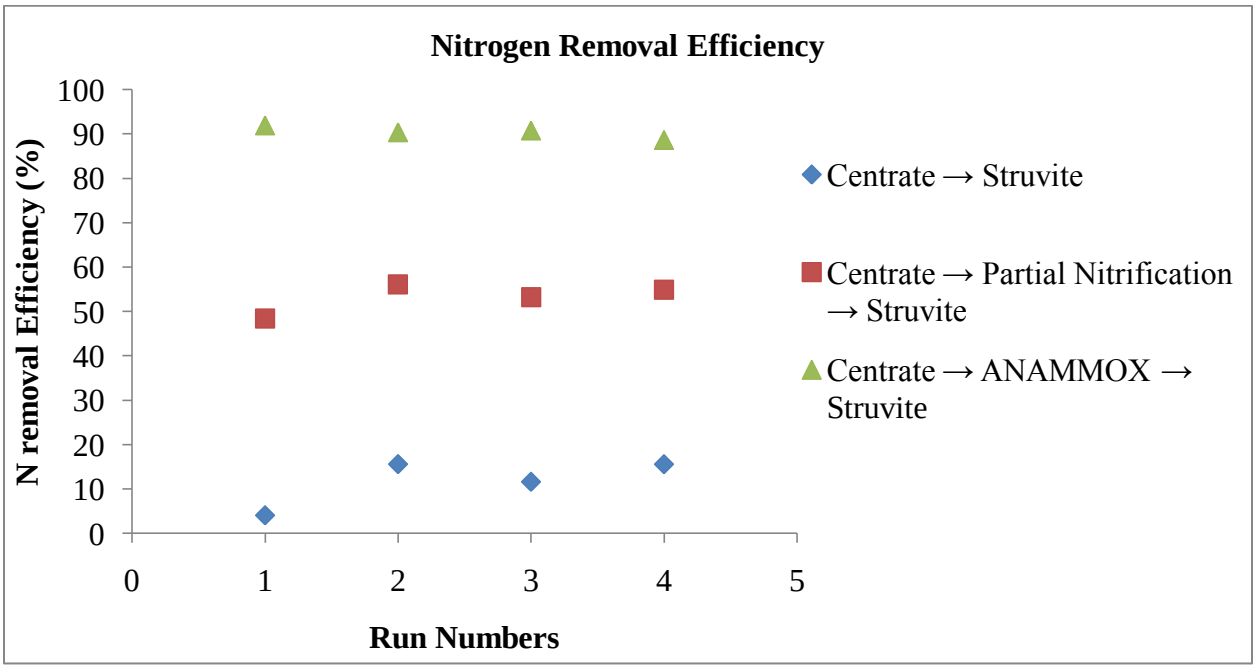


Figure 4.16. Average percentage of NH_4-N removal from feeds during operation

The process combination of ANAMMOX, followed by struvite precipitation, successfully removed up to 86% of PO_4-P from the influent. In comparison, centrate and partially nitrified centrate removed up to 80% and 87% PO_4-P, respectively.

In terms of N recovery, a maximum 92% of NH_4-N was removed by using ANAMMOX effluent for struvite crystallization, with the average removal being around 90%. The final effluent produced from the process combination of ANAMMOX, followed by struvite crystallization, was able to reduce PO_4-P concentration from 110 mg/L to 15 mg/L and NH_4-N concentration from 800 mg/L to 70 mg/L, on average from centrate. This performance exceeded that of the other two feeds.

4.3.2 Operating Condition 2: High Influent Flow Rate

4.3.2.1 Phosphorus and Nitrogen Removal and Recovery

To prevent struvite deposition in the reactor ports and to induce more mixing energy between the struvite forming elements, the influent flow rate was increased to 140 mL/min (HRT = 18 when RR = 0). The process was operated for approximately 8 hrs, instead of 24 hrs, due to lack of synthetic feed storage space in the lab, and, associated high chemical cost for preparing synthetic feed (the process required 200 L/day of solution for each type of feed).

The tests were carried out under different upflow velocities and different control pH's in the crystallizers, just like the previous condition, to determine the best operating condition for struvite recovery using ANAMMOX effluent. The process was able to maintain steady state conditions and constant P removal and recovery, by parameter optimization. Details of each operation with influent and effluent values are given in Appendix B and the operating conditions for these runs are given in Table 4.12.

Table 4.12. Key operating conditions for struvite crystallization in high flow rate.

Operation No.	Influent Flow Rate, Q_{inf} (mL/min)	Recycle Ratio	Control pH		
			ANAMMOX	Partially Nitrified Centrate	Centrate
Run 5	132.00	1.5	7.50	7.50	7.80
Run 6	140.00	5.0	7.50	7.60	7.90
Run 7	140.00	5.0	7.50	7.80	8.00
Run 8	140.00	5.0	7.50	-	-
Run 9	140.00	5.0	7.60	-	-
Run 10	140.00	5.0	7.80	-	-

Once the process was under operation with addition of magnesium and caustic feed externally, the process was under steady state conditions and the solutions in the reactor were completely well mixed, due to the higher upflow velocities. The upflow velocities resulting from different influent flow rates and recycle ratios are given in Appendix C.

Figures 4.17 to 4.22 shows the average effluent concentrations of PO_4-P and NH_4-N in all three feeds obtained when the operation was under steady state conditions.

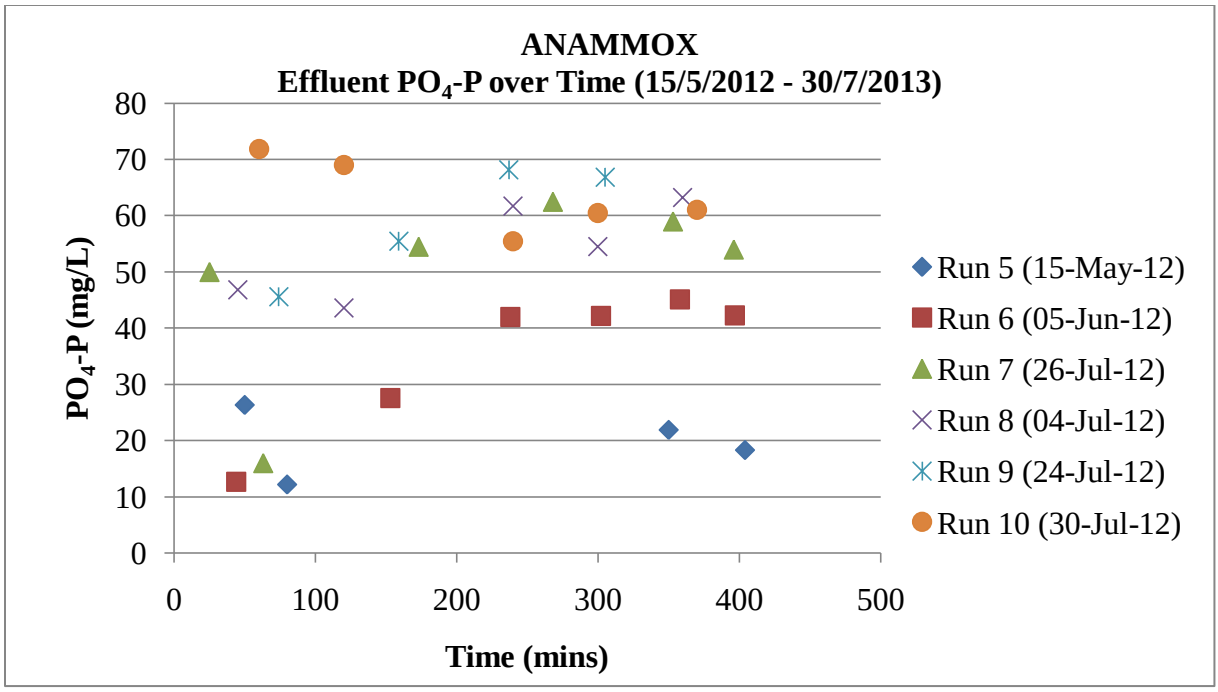


Figure 4.17. Soluble PO_4-P concentration in ANAMMOX effluent over time

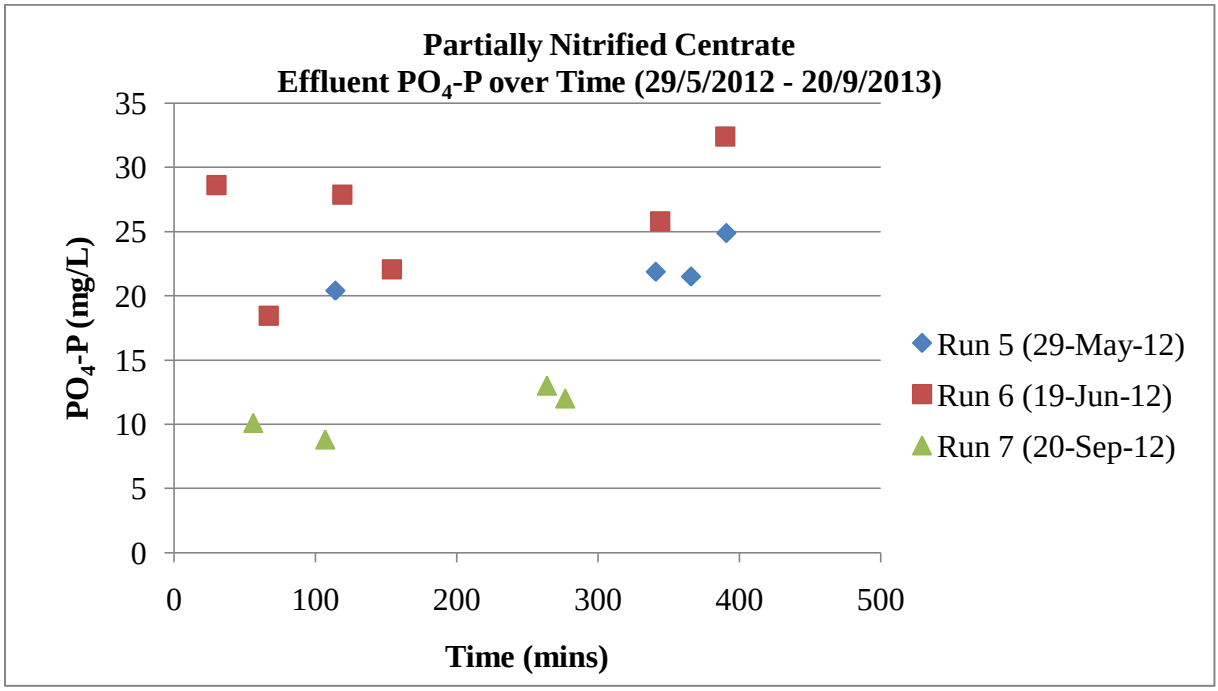


Figure 4.18. Soluble PO_4-P concentration in partially nitrified centrate over time

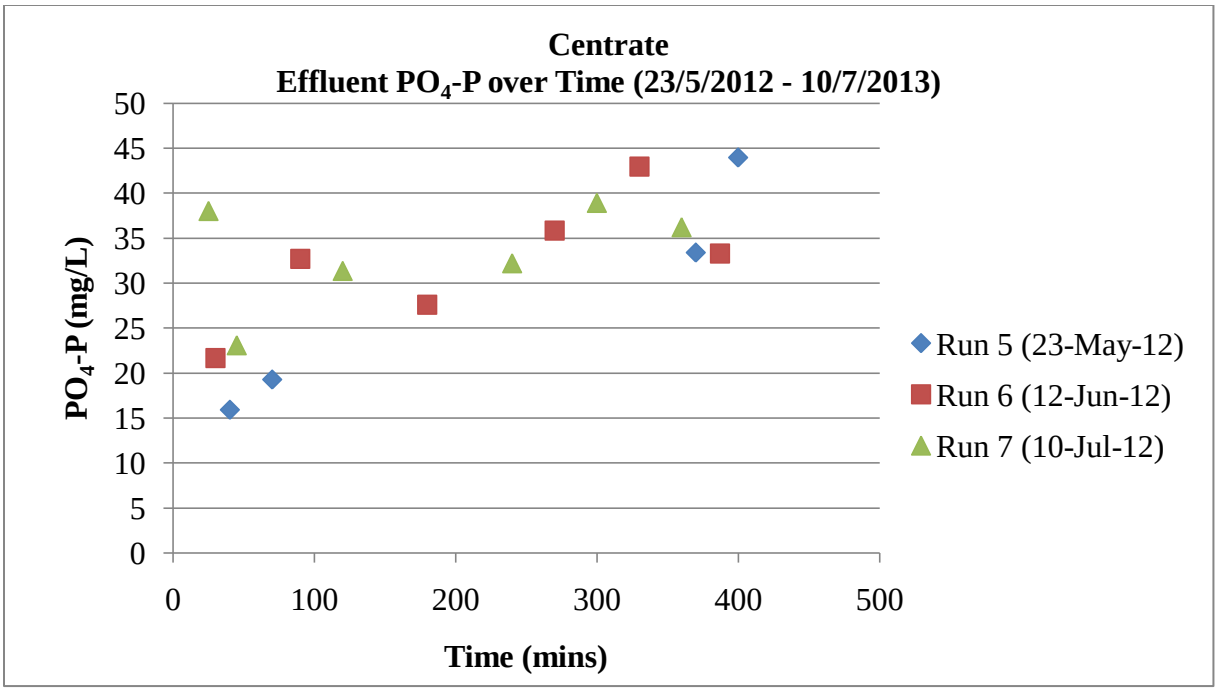


Figure 4.19. Soluble PO_4-P concentration in centrate over time

The reactions achieved steady state conditions sometime before 30 minutes, as the HRT in the reactors was 18 minutes, before the recycle line could be opened. It can be seen from Figure 4.17 that ANAMMOX feed was able to maintain fairly stable steady state conditions in the reactor.

The PO_4-P concentrations of ANAMMOX effluent (Figure 4.17) ranged between 94 mg/L and 119 mg/L. An average minimum PO_4-P concentration of 19.5 mg/L was achieved in Run 5 under steady state conditions by recovering struvite from ANAMMOX effluent. In comparison, centrate PO_4-P concentration (Figure 4.19) was reduced to an average minimum of 28 mg/L in Run 5 from a maximum concentration of 108 mg/L after struvite crystallization. In partially nitrified centrate (Figure 4.18), the PO_4-P concentration was reduced to 11mg/L, on average, in Run 7, after struvite crystallization from an initial maximum value of 120 mg/L.

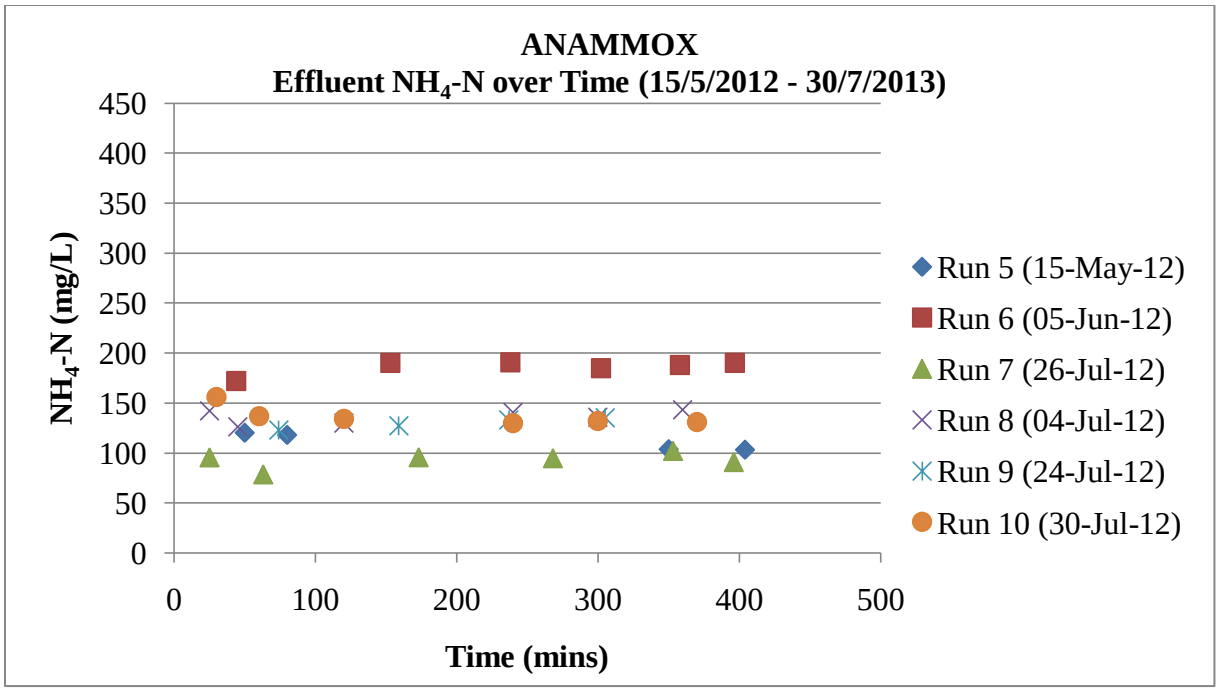


Figure 4.20. Soluble NH_4-N concentration in ANAMMOX effluent over time

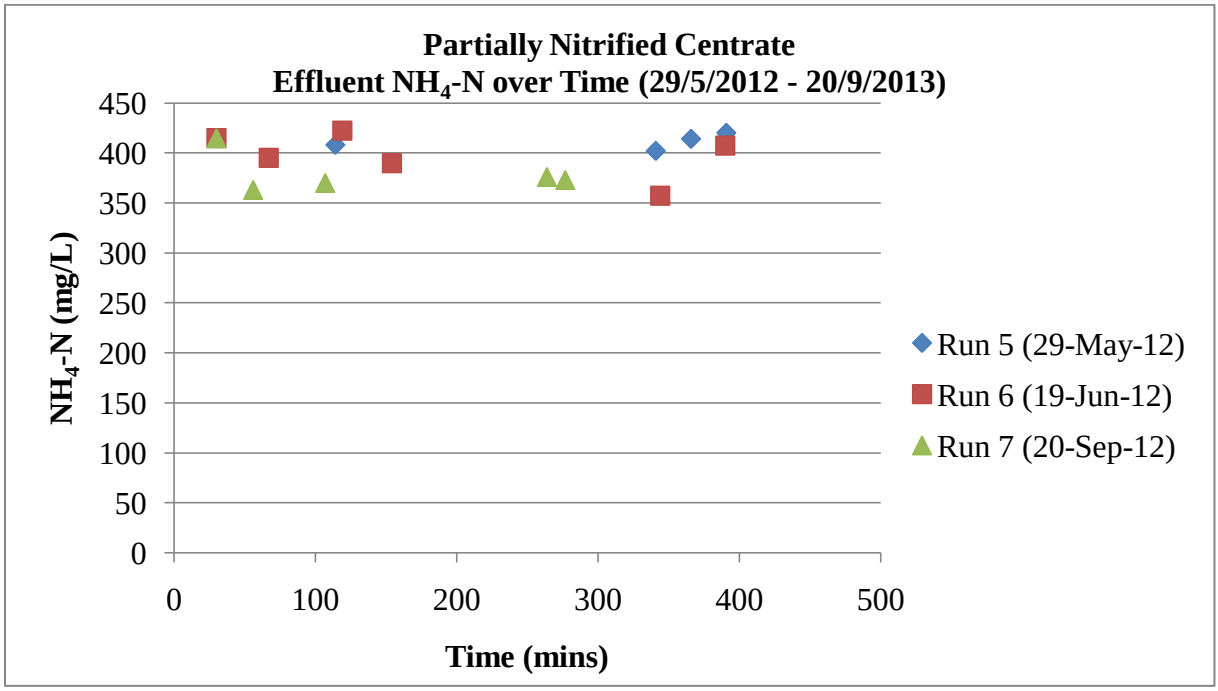


Figure 4.21. Soluble NH_4-N concentration in partially nitrified centrate over time

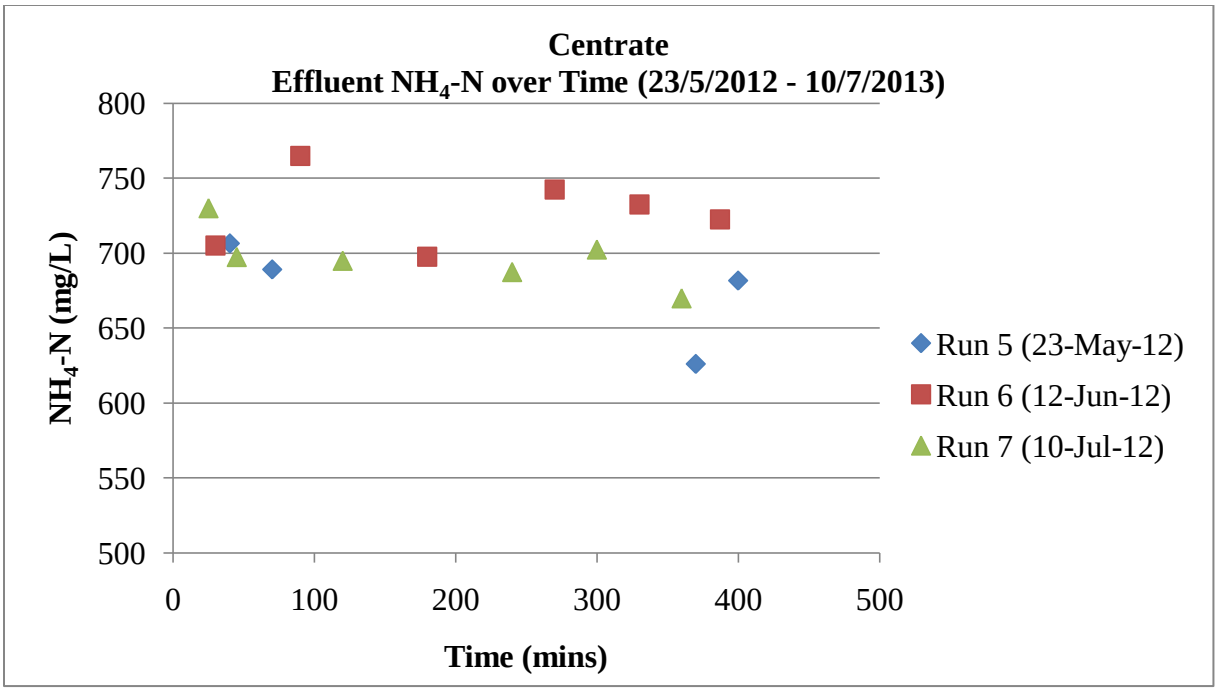


Figure 4.22. Soluble NH_4-N concentration in centrate over time

For NH_4-N, ANAMMOX treated effluent (Figure 4.20) resulted in a minimum concentration of 92 mg/L in Run 7 after struvite recovery from initial concentrations ranging between 200 mg/L to 117 mg/L.

In the case of ANAMMOX, Run 5 had the maximum phosphorus and nitrogen removal in the form of struvite. The difference in run 5 from the other operations was the recycle ratio. This indicated, again, that less turbulence was favourable for struvite formation in ANAMMOX feed.

As the PO_4-P and NH_4-N concentrations were repetitive, even by parameter optimization, for centrate and partially nitrified centrate effluent, more operations (run 8 to run 10) were performed only on ANAMMOX treated feed to further investigate its struvite forming ability, nutrient removal efficiency and chemical caustic and magnesium consumption, alone.

4.3.2.2 Phosphorus and Nitrogen Removal Efficiency

For operating condition Q_{inf} = 140 mL/min, the overall process performance, using ANAMMOX effluent as the feed for struvite crystallization in comparison to partially nitrified centrate, and centrate, is shown in Figure 4.23 and Figure 4.24. For efficiency calculation of ANAMMOX feed for Runs 8 to 10, the average influent and effluent concentration of PO_4-P and NH_4-N in centrate and partially nitrified centrate obtained in Run 7 was used. Thus, the P and N removal efficiency indicated in Figure 4.23 and Figure 4.24, for Runs 8 to 10 for centrate and partially nitrified centrate feed, are the results obtained from Run 7.

Each group of values represented in the graph are the average P and N removal percentage when the feeds were operated under conditions mentioned in Table 4.12. However, partially nitrified centrate maintained an overall steady and high P and N recovery efficiency as struvite, in this case as well, under all operating conditions.

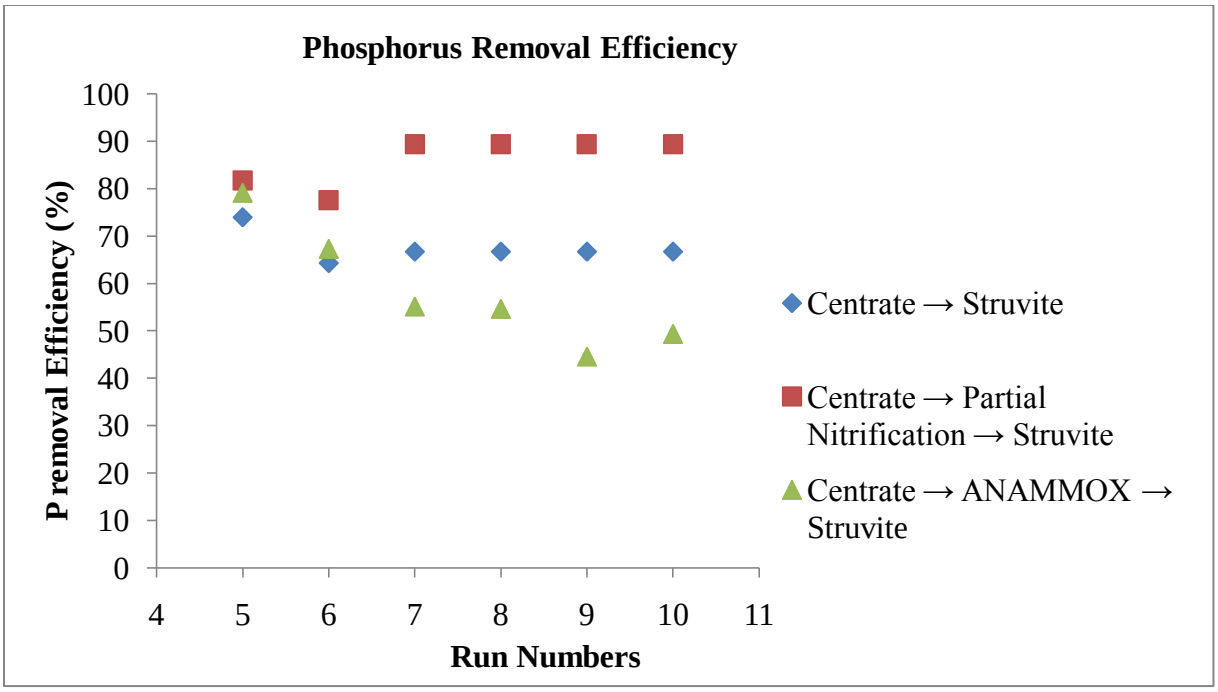


Figure 4.23. Average percentage of PO_4-P removal from feeds during operation

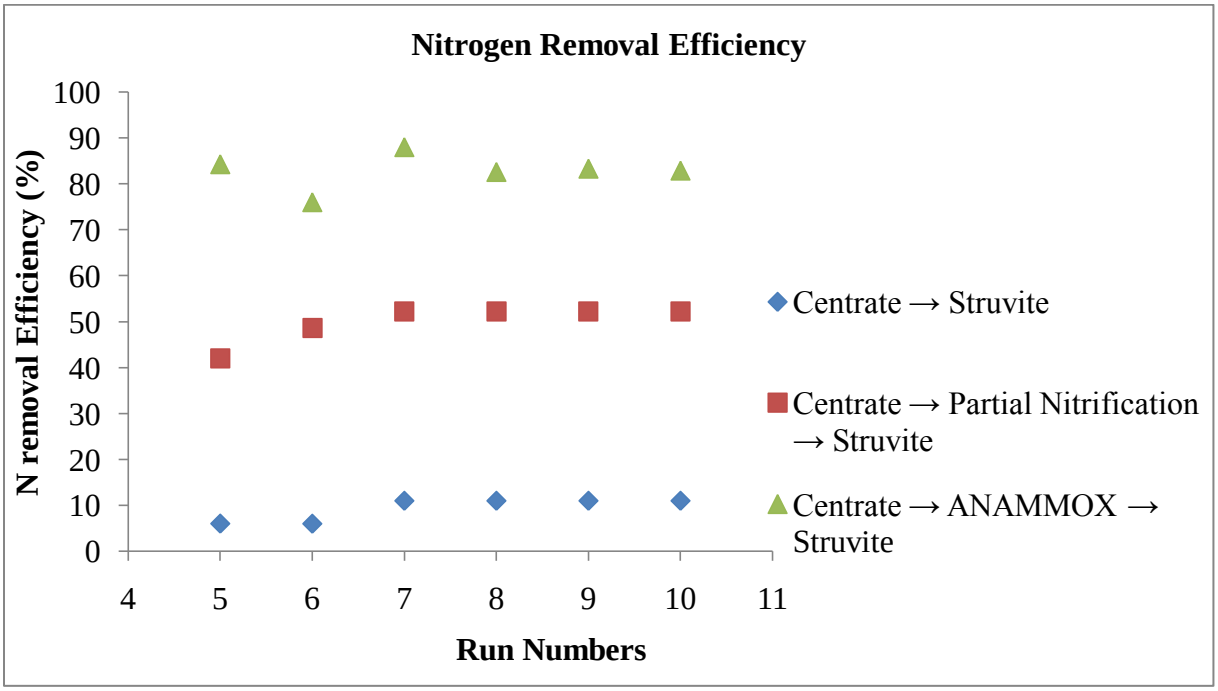


Figure 4.24. Average percentage of NH_4-N removal from feeds during operation

The process combination of ANAMMOX, followed by struvite precipitation, successfully removed up to 79% of PO_4-P from the influent. In comparison, centrate and partially nitrified centrate removed up to 73% and 89% PO_4-P, respectively.

In terms of N recovery, a maximum 88% of NH_4-N was removed using ANAMMOX effluent followed by struvite crystallization, with the average removal being around 82%. The final effluent produced from the process combination of ANAMMOX, followed by struvite crystallization, was able to reduce PO_4-P concentration from 119 mg/L to 19.5 mg/L and NH_4-N concentration from 775 mg/L to 92 mg/L, on average, from centrate.

From previous figures, it can be noticed that the PO_4-P recovery efficiency was stable for partially nitrified feed, achieving more than 80% in each run. In case of ANAMMOX and centrate, the increase in the recycle ratio resulted in a much lower removal efficiencies. The PO_4-P recovery efficiency for ANAMMOX effluent dropped from 79% to 55% (Figure 4.23), with the increase of RR from 1.5 to 5. This phenomenon was also evident when the operation was performed at low a flow rate, and, the RR was increased from 2 to 5. This may have resulted due to availability of low N : P molar ratio in ANAMMOX effluent. Literature also suggests that high N concentration in feeds increase struvite formation rates (Münch and Barr, 2001). For ANAMMOX effluent, the particles needed more time to bind as struvite crystals. Thus, a lower upflow velocity was found favourable for the process combination of ANAMMOX followed by struvite crystallization for higher nutrient recovery. Further study needs to be conducted to determine favourable flow conditions for the maximum nutrient recovery in this process combination.

4.3.3 Chemical Costs

After the completion of each operation, the struvite collected from all the reactors was filtered, dried and weighed. The theoretical weight of struvite produced in the reactors was also calculated by using the mass of average PO_4-P removed during operation. The calculations are given in details in Appendix D. It was observed that there was a significant difference between the measured and theoretical struvite weights for both high flow rate and low flow rate during operation. The differences in the theoretical and actual values were assumed to be for the following reasons;

- During low flow rate, a significant amount of struvite scaling on the reactor walls and struvite clogging in effluent/recycle ports and pipes were observed. These made the mass of struvite collected after process completion less than the actual mass formed in the operation.
- For high flow rates, struvite scaling on reactor walls evident. There was less clogging in the ports, but, high flow rate with a high recycle ratio, caused much of particle wash out at the starting hours of the process. Thus, the mass of struvite collected after the process was less than the mass actually formed in the operation.

Therefore, the theoretical struvite mass was used for the calculation of chemical cost associated with caustic and magnesium.

4.3.3.1 Caustic (NaOH) Consumption

Caustic is one of the two major chemical expenses for struvite production. As the continuous process combinations were bench scaled, the consumption was calculated in as a smaller mass value, which are grams required per gram struvite being produced.

For low flow rate continuous process (Q_{inf} = 40 mL/min), the amount of NaOH required for producing one gram of struvite varied significantly in case of the ANAMMOX feed and partially nitrified centrate feed, compared to centrate feed. However, the calculations indicated that both ANAMMOX feed and partially nitrified feed required more caustic for struvite production than centrate feed. A comparative bar chart with standard deviation is shown in Figure 4.25.

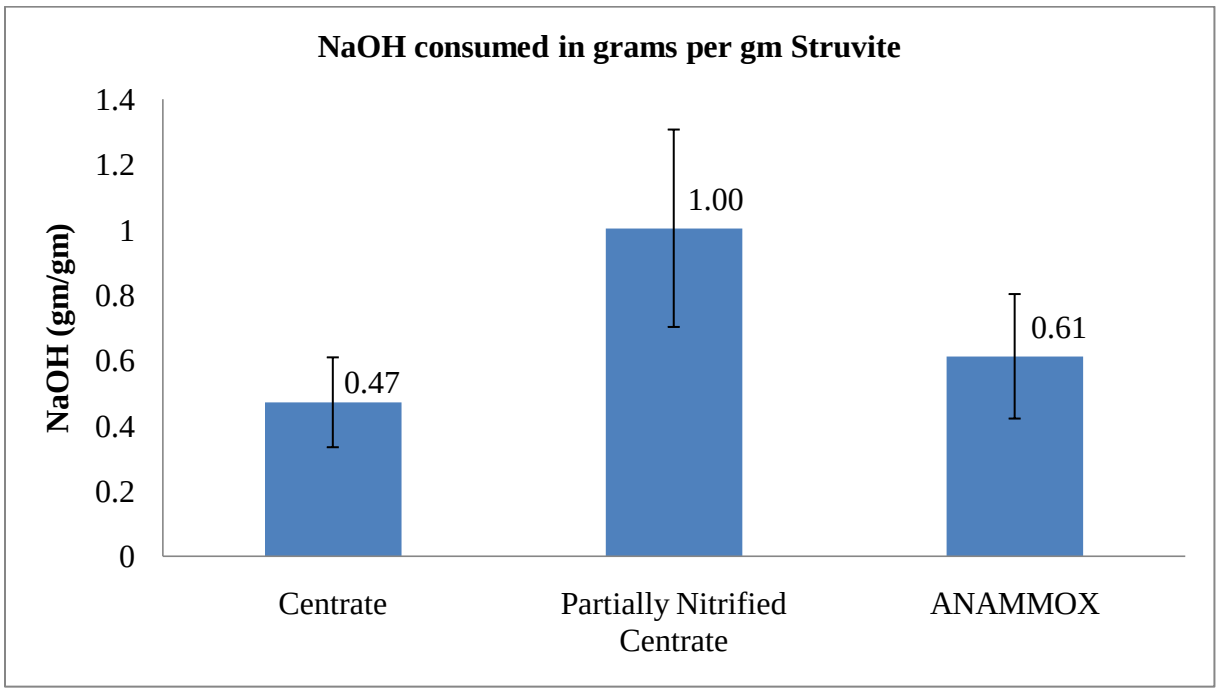


Figure 4.25. NaOH consumed in grams per gram struvite for Q_{inf} = 40 mL/min

The amount of caustic requited for producing 1 gm struvite from ANAMMOX treated centrate varied between 0.89 gm and 0.49 gm, with an average of 0.61 gm. For partially nitrified centrate, the values were between 1.25 gm and 0.56 gm, with an average of 1.0 gm; whereas, for centrate, the value remained between 0.62 gm and 0.31 gm, with an average of 0.47 gm.

The major reason for the fluctuation in the caustic consumption value was due to low upflow velocity. The low flow rate did not allow enough mixing inside the reactors; as a result, the pH

value in the bottom section of the reactor was different from the top clarifier of the reactor. Also, the time lag for the caustic injection point to the pH probe was also high. Therefore, there was a possibility of more caustic injection in the solution than was actually required.

Therefore, to determine a stable caustic requirement for struvite production in ANAMMOX and partially nitrified feed, the flow rate was increased to 140 mL/min from 40 mL/min.

Caustic consumed to produce struvite per gram was fairly consistent for the high flow rate condition in the reactors. The amount of caustic consumed in each feed during this operation is shown in Figure 4.26

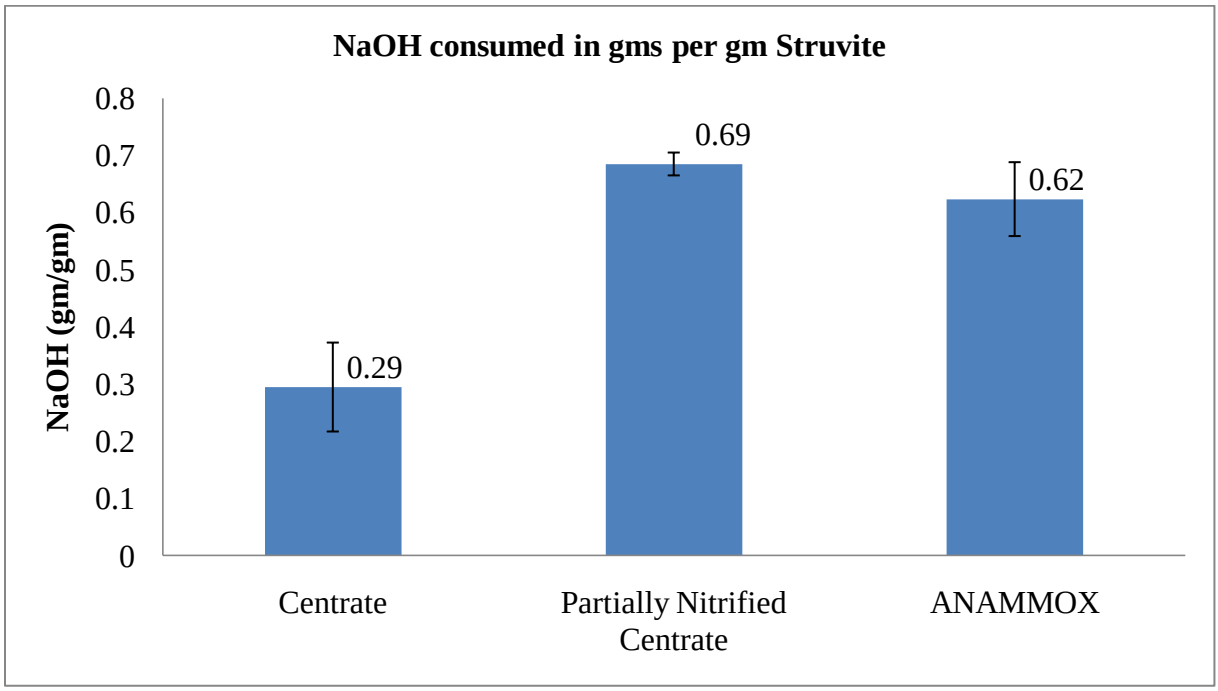


Figure 4.26. NaOH consumed in grams per gram struvite for Q_{inf} = 140 mL/min

The average amount of caustic required for producing 1 gram struvite from ANAMMOX feed and partially nitrified feed was 0.62 ± 0.06 grams and 0.69 ± 0.02 grams, respectively in this process. Caustic requirement for struvite production, using centrate as feed, was only 0.29 ± 0.08

grams per gram struvite. Therefore, from the overall process using different mixing energies, it was found that caustic consumption was higher in ANAMMOX effluent and partially nitrified centrate feed for making struvite particles, than centrate. This helped to maintain an SSR > 1 for centrate feed, and a continuous supply of centrate influent (pH > 8) from reactor bottom also aided the pH of the solution remain high inside the reactor.

The alkalinity in the system was found to be the controlling factor for the caustic consumption for the struvite formation chemistry. Centrate had a dissolved alkalinity of 2700 mg/L, which worked as a buffer for the feed and allowed the system to maintain a highly stable pH, for a prolonged time during operation. The continuous supply of centrate feed (pH >8) from reactor bottom also helped to keep the pH high inside the reactor.

The alkalinity in ANAMMOX treated centrate and partially nitrified centrate ranged between 50 mg/L and 150 mg/L, only and the influent pH was about 6. The solution had no buffering capacity like centrate. As a result, the feeds are prone to constants demand of caustic to maintain a high pH inside the system (to maintain SSR > 1 for struvite formation). The pH fluctuation in the solutions was frequent and the control pH dropped rapidly, once the particles formed. As a result, caustic pumping was frequent and a continuous supply of a low pH feed from the influent tanks aided in the caustic consumption, by constantly lowering the overall pH of the solution.

4.3.3.2 Magnesium Consumption

The amount of chemical magnesium feed used the process of producing struvite was found to be fairly close for all three feeds. ANAMMOX feed required slightly higher Mg than partially nitrified centrate and centrate. A bar chart is given, with the standard deviation in Figure 4.27.

Operations at both flow rates are included in the graph. The mass of magnesium required for struvite formation is given in Appendix D.

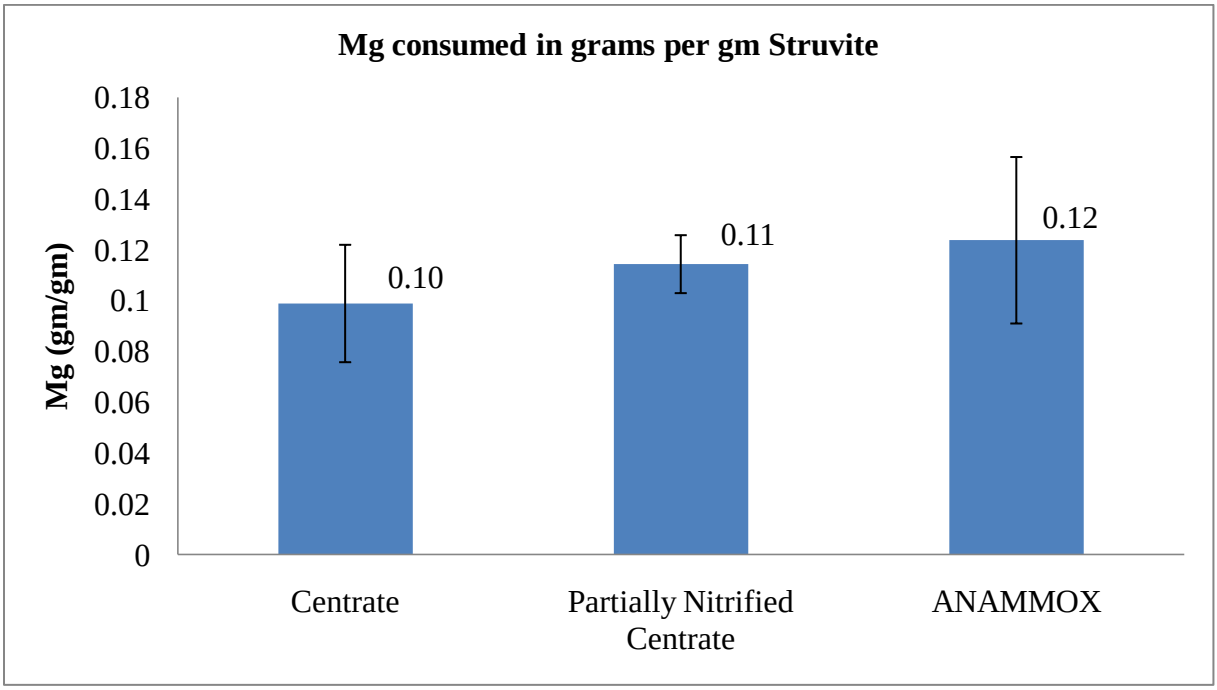


Figure 4.27. Magnesium consumed in grams per gram struvite from overall operation.

The average amount of magnesium required for producing 1 gram struvite from ANAMMOX feed and partially nitrified feed was 0.12 ± 0.03 grams and 0.11 ± 0.01 grams, respectively in this process. Caustic requirement for struvite production, using centrate as feed, was only 0.10 ± 0.02 grams per gram struvite. Therefore, magnesium usage was not significantly higher for producing struvite from ANAMMOX feed, in comparison to centrate struvite.

4.4 Struvite Purity

X-ray Diffraction (XRD) was performed on struvite particles to check its purity. The process confirmed that the particles where pure struvite in the cases for centrate, partially nitrified centrate and ANAMMOX. An X-ray Diffraction (XRD) image conducted on struvite particles

from ANAMMOX effluent in given in Figure 4.28. The image illustrates the peaks and intensities of the particles being matched with the peaks and intensities of struvite particles in the XRD database.

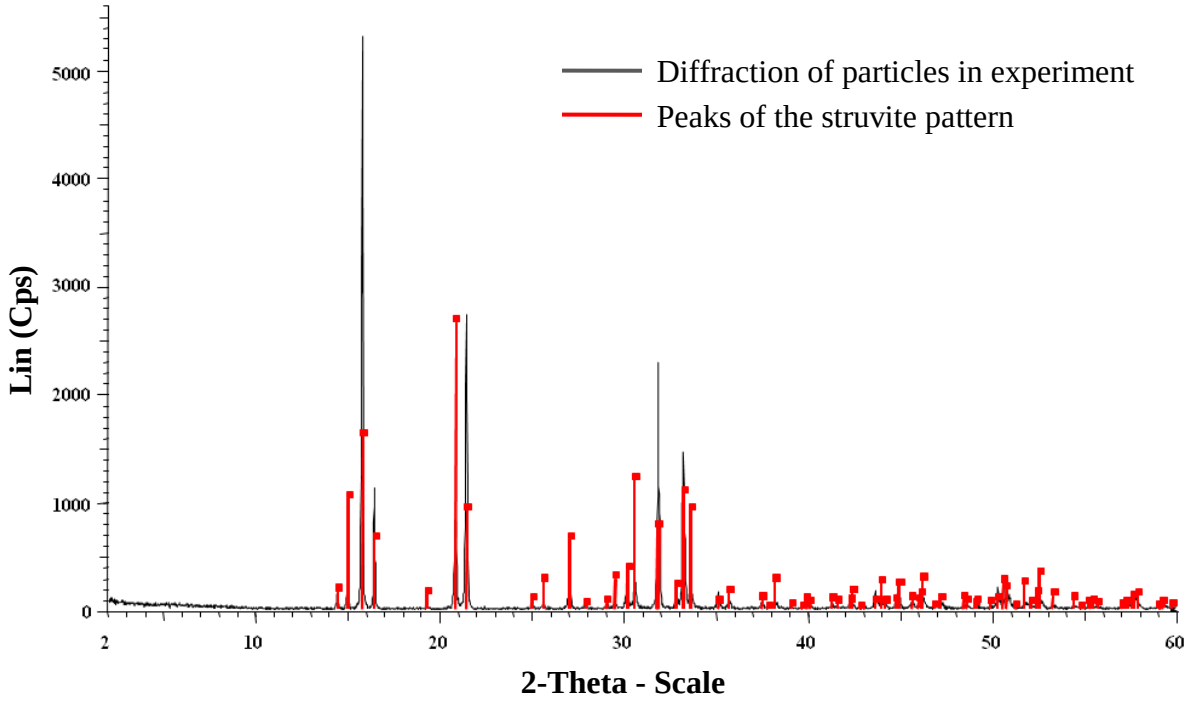


Figure 4.28. XRD image of struvite recovered from ANAMMOX effluent

The struvite particle collected from each run for each feed type was dried and weighted. A certain amount was taken from each type of feed, solubilised in acid and tested for Mg : NH_4-N : PO_4-P molar ratio. Pure struvite contains equimolar Mg : NH_4-N : PO_4-P and 6 moles of water. The actual molar ratios of the crystals are available in Appendix E.

4.5 Struvite Particle Size Distribution and Morphology

A particle size distribution showed that ANAMMOX effluent and partially nitrified centrate feed produced overall larger particles than centrate. A particle size distribution graph is shown below in Figure 4.29. The actual particle size distribution values are given in Appendix F.

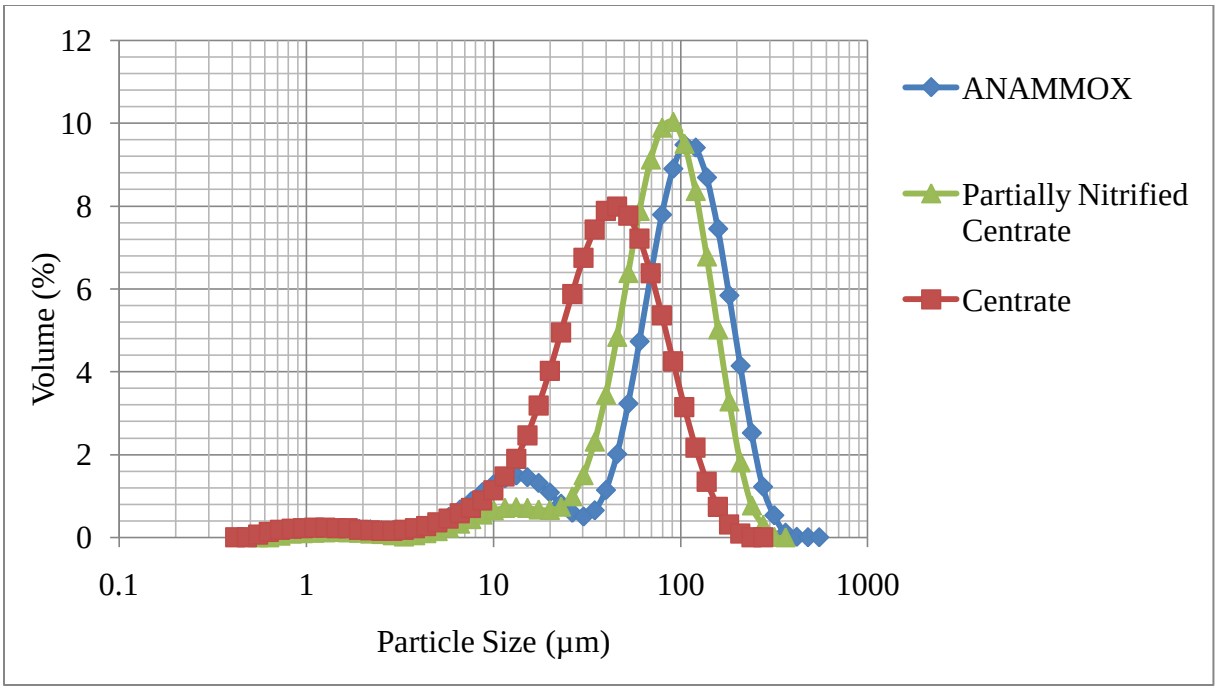


Figure 4.29. Particle size distribution of struvite crystals

The mean particle size of struvite crystals from the ANAMMOX feed ranged between 90 µm - 160 µm. The mean size of struvite particles from centrate and partially nitrified centrate feed ranged between 30 µm - 69 µm and 60 µm - 110 µm, respectively. A detailed study performed elsewhere on struvite particle size, also demonstrated that the mean particle size of struvite from real dewatered sludge liquor, ranged between 48.73 ± 0.58 µm to 69.36 ± 10.24 µm. (Le Corre *et al*., 2007).

Microscopic images for struvite particles showed that struvite from centrate and partially nitrified centrate has similar morphology of rectangular, prismatic-shape, whereas, ANAMMOX effluent produced elongated, prismatic shaped struvite. The difference is attributed to the varying N : P molar ratio in the feeds; it can be predicted that partially nitrified centrate will have the same potential for pelletisation of struvite crystals like as centrate struvite pellets. The struvite

crystals collected during the continuous bench scale operation, in given Figure 4.30. The microscopic images of the struvite particles are given in Figure 4.31 to Figure 4.33

a.) Centrate b.) PN Centrate c.) ANAMMOX

Figure 4.30. Image of struvite crystals collected from all feeds.

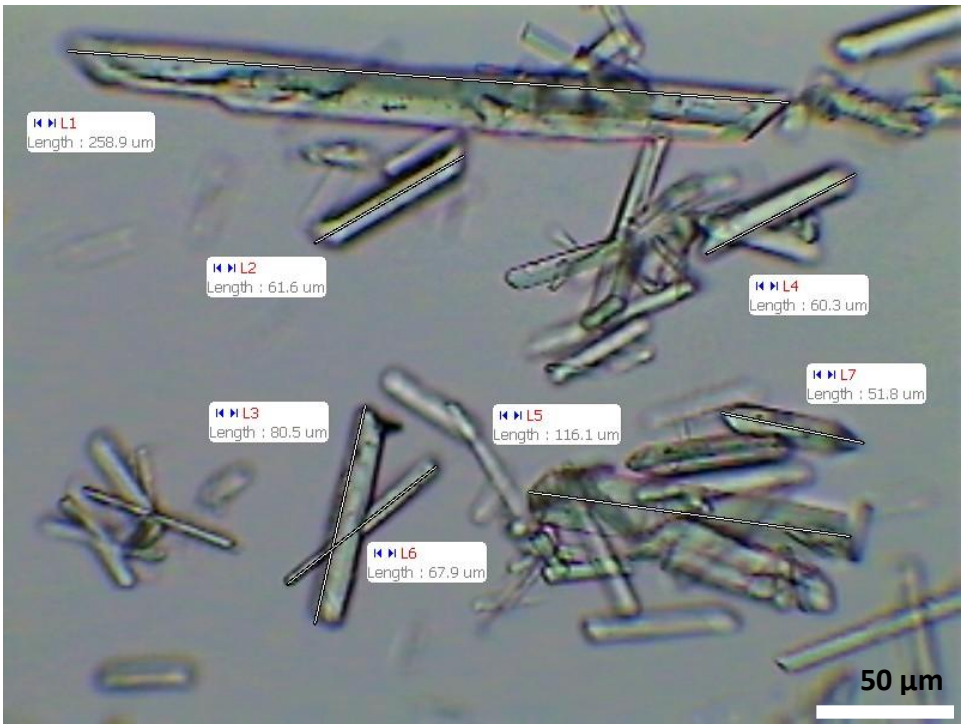


Figure 4.31. Microscopic image of struvite crystals from ANAMMOX effluent

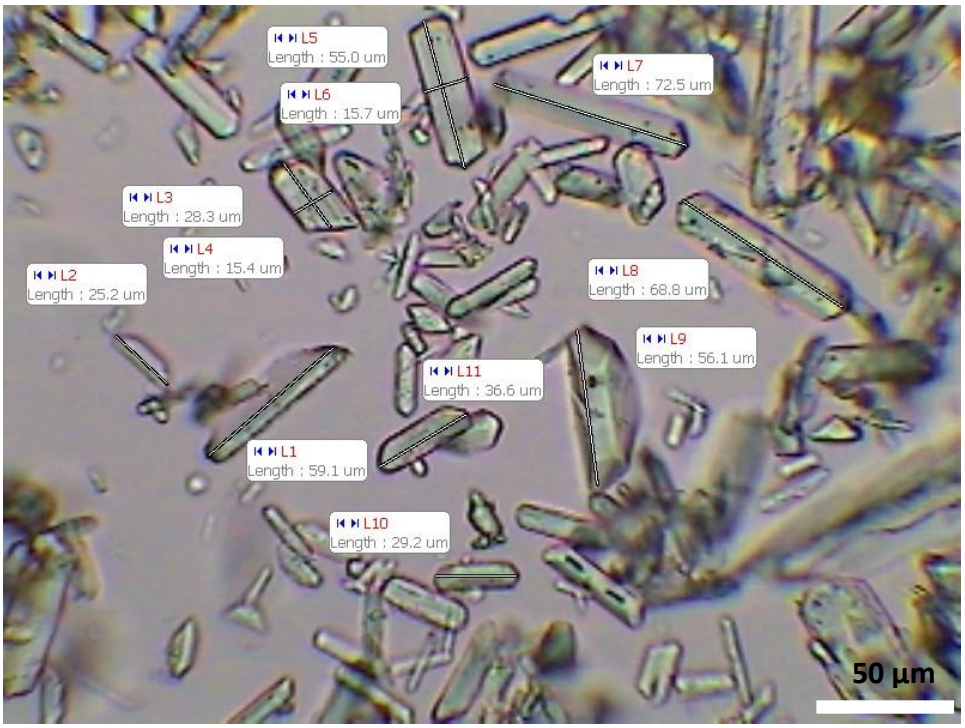


Figure 4.32. Microscopic image of struvite crystals from partially nitrified centrate

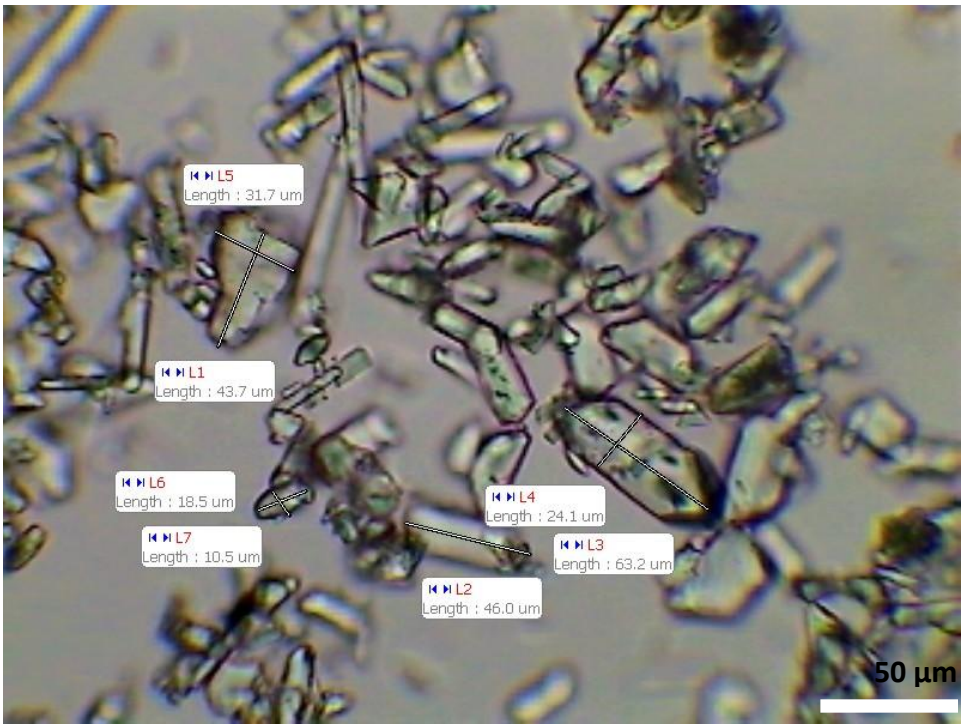


Figure 4.33. Microscopic image of struvite crystals from centrate

ANAMMOX effluent struvite particles were, overall, larger in size and had more surface area. This might be beneficial in adhering more particles and aiding in agglomeration to form pellets.

Further study is required to examine the pellet forming potential of struvite particles formed from the process combination of ANAMMOX, followed by struvite crystallization.

5. Conclusions and Recommendations

5.1 Conclusions

The objective of the study was to establish a solution for simultaneous removal of nitrogen (N) and phosphorus (P) from dewatered sludge liquor or centrate. The ANAMMOX process was combined with struvite precipitation where centrate first goes through a complete ANAMMOX treatment process, followed by struvite crystallization of the effluent from the ANAMMOX process. The process combination was able to successfully remove P and N simultaneously from centrate and produce an effluent significantly low in N and P concentrations. The nutrients were recovered as a potentially useful fertilizer, called struvite or MAP (Magnesium Ammonium Phosphate). The major findings from this study are summarized below:

- Partial nitrification and ANAMMOX process reduced NH_4-N up to 85% from centrate. However, an increase in PO_4-P concentration was monitored in the effluent from 93 mg/L to 115 mg/L.
- The effluent resulting from ANAMMOX process on centrate contained NH_4:N : PO_4-P molar ratio of approximately 2.25 : 1.00, which was more than the theoretical requirement of 1 : 1 for struvite production.
- Jar tests conducted on the effluent from the ANAMMOX process at various temperatures demonstrated simultaneous P and N removal in the form of struvite, under optimised conditions. P removal efficiency was higher for a pH end point 8.5 than pH 8.3 for ANAMMOX effluent unlike centrate, which achieved maximum removal efficiency at pH 8.3.

- Jar tests also illustrated that high alkalinity promoted spontaneous struvite formation in centrate, when magnesium was available at stoichiometric requirements, without addition of base solution.
- The process combination of ANAMMOX, followed by struvite crystallization in the jar tests, was able to reduce PO_4-P from a maximum 120 mg/L to a minimum 14 mg/L, in the final effluent. The NH_4-N concentration was reduced to a minimum of 68 mg/L from 770 mg/L, in the final effluent. Overall, the process combination achieved 91% NH_4-N and 88% PO_4-P, from centrate.
- A continuous process using bench scaled fluidized bed reactors were operated at two sets of influent flow rates, of 40 mL/min and 140 mL/min. The recycle ratio and control pH was varied to different values for determining the best P and N removal efficiency in the process combination. The continuous process was able to reduce PO_4-P from a maximum 119 mg/L to a minimum 15 mg/L, in the final effluent. The NH_4-N concentration was reduced to a minimum of 70 mg/L from 800 mg/L, in the final effluent. The low influent flow rate of 40 mL/min, with a recycle ratio of 2.0, was found as the best conditions for struvite formation from the process combination.
- The process combination in the continuous process achieved PO_4-P and NH_4-N removal and recovery up to 87% and 92%, respectively, in the final effluent. The final effluent resulted in a very low PO_4-P and NH_4-N concentration and a unified solution for nutrient recovery was obtained.
- Caustic consumption was higher for producing struvite from the process combination, compared to struvite produced directly from centrate. ANAMMOX and partially nitrified feed required 0.62 ± 0.06 and 0.69 ± 0.02 grams of commercial grade NaOH,

respectively, to produce 1 gram pure struvite. Caustic (NaOH) requirement for struvite production, using centrate as feed, was less at 0.29 ± 0.08 gram per gram struvite.

- Magnesium consumption was also higher in the process combination compared to struvite produced only from centrate. ANAMMOX and partially nitrified feed required approximately 0.12 ± 0.03 grams and 0.11 ± 0.01 grams of Mg, respectively, to produce 1 gram pure struvite. Magnesium (Mg) requirement for struvite production, using centrate as feed, was less at 0.10 ± 0.02 gram per gram struvite.
- ANAMMOX effluent produced pure struvite particles with a larger mean particle size, compared to struvite particles produced from centrate. The mean particle size of struvite crystals from the ANAMMOX feed ranged between 90 - 160 μm. The mean size of struvite particles from centrate and partially nitrified centrate feed ranged between 40 - 69 μm and 60 - 120 μm, respectively.

5.2 Recommendation for Future Research

Based on the study conducted on the process combination of ANAMMOX, followed by struvite crystallization, for simultaneous removal and recovery of nutrients from synthetic feed, the author makes the following recommendations for further study.

- The study on process combination of ANAMMOX followed by struvite crystallization was conducted using synthetic feed of centrate, partially nitrified centrate and ANAMMOX effluent. Synthetic feed gives the flexibility to understand a process in depth, as it contains only the key constituents that influence the process. However, the influence of different parameters present in real wastewater is not considered in this study, which may have a significant role in the process combination. Therefore, the study

should be conducted using real wastewater (side streams), to verify the results obtained from synthetic wastewater.

- The continuous process was conducted on bench scaled fluidized reactors. The scale should be upgraded to pilot scale, so that it can be comparable to full scale wastewater treatment plants. Also, the pelletisation property of struvite crystals from ANAMMOX effluent should be studied.
- The chemical costs associated with struvite production from the process combination of ANAMMOX and struvite crystallization was higher than struvite produced directly from centrate. This will increase the overall process cost associated with struvite production. Further study is underway to see the scope of minimizing caustic usage for struvite production, using real wastewater. Stripping of CO_2 from the feed could alleviate the need for additional caustic, hence reduce the chemical costs. Pelletisation of struvite particles using real ANAMMOX effluent is recommended and underway.
- Similarly, research on reversing these two processes, that is struvite crystallisation followed by ANAMMOX treatment process, is recommended and underway.

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Appendix A

A.1 P and N removal from ANAMMOX effluent by jar test - method 1

ANAMMOX Effluent Temp: 20±1°C; Initial pH: 5.70; NaOH: 1N						
Sample No.	**Time (mins)**	**NaOH (mls)**	**pH of sample**	**NH_4-N (mg/L)**	**PO_4-P (mg/L)**	**Mg (mg/L)**
1	0	0.00	5.11	105.85	105.84	54.4892
2	60	5.55	7.55	82.17	28.78	20.912
3	90	0.35	7.80	77.82	22.02	16.2662
4	150	0.35	8.00	77.05	17.22	13.2753
5	210	0.30	8.21	74.99	15.64	11.9316
6	240	0.15	8.31	74.55	13.94	11.1295
7	270	0.00	8.29	72.06	13.74	11.8357

ANAMMOX Effluent Temp: 25±0.2°C; Initial pH: 5.70; NaOH: 1N						
Sample No.	**Time (mins)**	**NaOH (mls)**	**pH of sample**	**NH_4-N (mg/L)**	**PO_4-P (mg/L)**	**Mg (mg/L)**
1	0	0.00	5.70	125.11	113.07	40.9688
2	145	3.00	7.48	116.11	84.20	36.9592
3	170	0.35	7.61	112.61	75.06	33.0212
4	195	0.55	7.75	106.61	62.89	30.1264
5	255	1.00	8.18	92.81	34.54	17.1056
6	300	0.30	8.39	94.04	25.12	16.2834
7	320	0.20	8.52	75.05	22.53	13.8596

ANAMMOX Temp: 30±1°C; Initial pH: 5.86; NaOH: 1N							
Sample No.	**Time (mins)**	**NaOH (mls)**	**pH of sample**	**NH_4-N (mg/L)**	**PO_4-P (mg/L)**	**$MgCl_2.6H_2O$ (mls)**	**Mg (mg/L)**
1	0	2.35	8.02	114.09	104.89	2.00	5.5387
2	40	0.30	8.19	121.98	94.05	2.00	8.8246
3	75	0.00	7.99	124.47	88.23	2.00	8.6403
4	95	0.00	7.85	118.82	77.15	4.00	16.1727
5	110	0.00	7.70	108.06	76.38	5.00	27.601
6	125	0.00	7.57	101.72	73.32	5.00	34.2632
7	150	0.00	7.49	91.51	71.60	5.50	55.6688
8	210	0.35	7.44	100.41	68.94	0.00	56.9648
9	270	0.55	7.89	89.20	34.76	0.00	37.8884
10	375	0.20	8.20	77.10	26.01	0.00	71.8036
11	405	0.20	8.53	68.42	17.52	0.00	30.1364

A.2 P and N removal from partially nitrified centrate by jar test - method 1

Partially Nitrified Centrate Temp: 20±1°C; Initial pH: 5.76; NaOH: 1N						
Sample No.	**Time (mins)**	**NaOH (mls)**	**pH of sample**	**NH_4-N (mg/L)**	**PO_4-P (mg/L)**	**Mg (mg/L)**
1	0	0.00	5.77	380.325	92.56	56.5456
2	60	3.65	7.39	374.95	52.41	41.7836
3	90	0.75	7.60	368.7	42.80	32.1098
4	150	1.13	8.00	394.85	24.69	17.5608
5	210	0.63	8.21	340.95	19.78	14.3652
6	240	0.35	8.31	327.175	16.35	12.8528
7	270	0.00	8.33	326.75	15.59	13.1037

Partially Nitrified Centrate Temp: 25±0.2°C; Initial pH: 5.76; NaOH: 1N						
Sample No.	**Time (mins)**	**NaOH (mls)**	**pH of sample**	**NH_4-N (mg/L)**	**PO_4-P (mg/L)**	**Mg (mg/L)**
1	0	0.00	5.76	456.175	96.95	47.0416
2	145	4.00	7.42	423.9	48.54	28.1368
3	170	0.50	7.65	413.675	39.85	24.5466
4	195	0.40	7.80	395.775	32.55	21.5770
5	255	1.20	8.19	387.55	22.64	12.6033
6	300	0.40	8.27	356.55	21.56	11.5375

Partially Nitrified Centrate Temp: 30±1°C; Initial pH: 5.94; NaOH: 1N							
Sample No.	**Time (mins)**	**NaOH (mls)**	**pH of sample**	**NH_4-N (mg/L)**	**PO_4-P (mg/L)**	**$MgCl_2.6H_2O$ (mls)**	**Mg (mg/L)**
1	0	2.56	8.12	431.88	99.47	2.00	5.5463
2	40	0.00	8.04	406.5	91.55	2.00	3.7835
3	75	0.00	7.99	398.5	82.34	2.00	4.4250
4	95	0.00	7.86	385.47	82.28	4.00	8.7222
5	110	0.00	7.71	384.94	60.66	5.00	16.4187
6	125	0.00	7.58	397.92	43.93	5.00	23.9506
7	150	0.00	7.47	371.35	36.76	5.50	37.8684
8	210	0.60	7.37	358.74	43.43	0.00	38.8772
9	270	1.10	8.14	328.33	13.54	0.00	23.8136
10	375	0.70	8.57	308.47	7.26	0.00	20.8660

A.3 P and N removal from centrate by jar test - method 1

Centrate Temp: 20±1°C; Initial pH: 7.80; NaOH: 1N						
Sample No.	**Time (mins)**	**NaOH (mls)**	**pH of sample**	**NH_4-N (mg/L)**	**PO_4-P (mg/L)**	**Mg (mg/L)**
1	0	0.00	7.50	785.7	82.64	49.0256
2	60	1.76	7.72	760.6	27.44	27.256
3	90	0.32	7.79	769.6	25.40	24.94
4	150	0.93	8.02	753.65	22.87	16.3662
5	210	0.90	8.22	680.95	23.41	13.8174
6	240	0.90	8.31	654.75	16.65	12.4352
7	270	0.00	8.29	660.5	18.94	11.9305

Centrate Temp: 25±0.2°C; Initial pH: 7.80; NaOH: 1N						
Sample No.	**Time (mins)**	**NaOH (mls)**	**pH of sample**	**NH_4-N (mg/L)**	**PO_4-P (mg/L)**	**Mg (mg/L)**
1	0	0.00	7.80	784.5	87.90	38.1604
2	145	2.45	7.87	748.35	22.72	18.4404
3	170	1.35	8.10	738.05	20.29	15.3343
4	195	0.60	8.20	721.6	19.96	12.2635
5	255	0.15	8.21	709.55	20.58	11.9077

Centrate Temp: 30±1°C; Initial pH: 7.80; NaOH: 1N							
Sample No.	**Time (mins)**	**NaOH (mls)**	**pH of sample**	**NH_4-N (mg/L)**	**PO_4-P (mg/L)**	**$MgCl_2.6H_2O$ (mls)**	**Mg (mg/L)**
1	0	0.91	8.09	725.12	80.13	2.00	6.9076
2	40	0.00	8.05	724.7	72.80	2.00	4.0361
3	75	0.00	8.04	717.16	63.75	2.00	4.7036
4	95	0.00	7.99	701.46	47.39	4.00	7.4509
5	110	0.00	7.97	685.78	40.44	3.00	10.9479
6	125	0.00	7.94	690.14	22.96	3.00	15.8376
7	150	0.00	7.91	659.7	18.59	3.00	22.087
8	210	0.84	8.32	509.45	12.85	0.00	17.5586
9	270	0.20	8.41	512.77	12.65	0.50	20.2328
10	375	0.20	8.42	492.14	10.05	0.00	18.7486

Appendix B

B.1 Continuous operation of ANAMMOX effluent at Q_{inf} = 40 mL/mins

ANAMMOX								
Date	**Time (mins)**	**Sample No.**	**Remarks**	**pH of solution**	**Mg_{in} (gm/L)**	**Mg_{out} (mg/L)**	**NH_4-N (mg/L)**	**PO_4-P (mg/L)**
20-Mar-12	0	1	Influent	6.60	24.00	1.48	128.64	93.24
20-Mar-12	75	2	1st reactor effluent	12.00	24.00	0.47	80.95	89.61
20-Mar-12	105	3	Effluent	10.60	24.00	2.29	80.68	71.48
20-Mar-12	130	4	Effluent	9.45	24.00	6.95	75.16	17.88
20-Mar-12	165	5	Effluent	9.12	24.00	4.52	54.65	11.24
20-Mar-12	250	6	Effluent	8.88	24.00	5.31	58.13	12.69
20-Mar-12	400	7	Effluent	8.71	24.00	7.16	65.56	16.54
21-Mar-12	1250	8	Effluent	8.64	24.00	6.94	64.15	15.79
21-Mar-12	1380	9	Effluent	8.56	24.00	8.57	66.73	17.37

ANAMMOX								
Date	**Time (mins)**	**Sample No.**	**Remarks**	**pH of solution**	**Mg_{in} (gm/L)**	**Mg_{out} (mg/L)**	**NH_4-N (mg/L)**	**PO_4-P (mg/L)**
28-Mar-12	0	1	Influent	5.75	25.00	2.66	113.32	111.02
28-Mar-12	70	2	1st reactor effluent	9.53	25.00	20.98	83.06	5.81
28-Mar-12	130	3	Effluent	10.16	25.00	11.03	85.60	14.08

ANAMMOX								
Date	**Time (mins)**	**Sample No.**	**Remarks**	**pH of solution**	**Mg_{in} (gm/L)**	**Mg_{out} (mg/L)**	**NH_4-N (mg/L)**	**PO_4-P (mg/L)**
28-Mar-12	190	4	Effluent	9.15	25.00	16.52	75.15	10.65
28-Mar-12	250	5	Effluent	8.89	25.00	41.16	68.75	6.59
28-Mar-12	400	6	Effluent	8.75	25.00	26.56	69.85	8.83
29-Mar-12	1230	7	Effluent	8.30	25.00	35.15	80.15	28.11
29-Mar-12	1290	8	Effluent	8.23	25.00	33.97	81.51	29.42

ANAMMOX								
Date	**Time (mins)**	**Sample No.**	**Remarks**	**pH of solution**	**Mg_{in} (gm/L)**	**Mg_{out} (mg/L)**	**NH_4-N (mg/L)**	**PO_4-P (mg/L)**
11-Apr-12	0	1	Influent	6.01	26.85	3.55	114.42	108.25
11-Apr-12	60	2	1st reactor effluent	9.13	26.85	35.65	73.85	30.55
11-Apr-12	150	3	Effluent	8.89	26.85	42.54	71.58	29.29
11-Apr-12	210	4	Effluent	8.65	26.85	29.45	70.64	21.45
11-Apr-12	300	5	Effluent	8.78	26.85	22.63	71.69	22.26
11-Apr-12	420	6	Effluent	8.85	26.85	19.27	73.52	20.45
12-Apr-12	1320	7	Effluent	8.91	26.85	21.10	74.90	22.59
12-Apr-12	1440	8	Effluent	9.01	26.85	18.97	76.51	21.86

ANAMMOX								
Date	**Time (mins)**	**Sample No.**	**Remarks**	**pH of solution**	**Mg_{in} (gm/L)**	**Mg_{out} (mg/L)**	**NH_4-N (mg/L)**	**PO_4-P (mg/L)**
3-May-12	0	1	Influent	5.77	29.62	3.81	114.68	117.67
3-May-12	60	2	1st reactor effluent	10.90	29.62	3.18	112.26	88.15
3-May-12	110	3	Effluent	11.55	29.62	2.69	116.93	78.44
3-May-12	170	4	Effluent	11.12	29.62	3.40	94.75	43.83
3-May-12	260	5	Effluent	9.15	29.62	7.95	88.61	41.56
3-May-12	350	6	Effluent	8.95	29.62	6.98	89.45	42.65
3-May-12	440	7	Effluent	8.88	29.62	8.11	89.70	43.54
4-May-12	1250	8	Effluent	8.70	29.62	20.56	91.15	46.25
04-May-12	1370	9	Effluent	8.62	29.62	22.01	87.72	48.91

B.2 Continuous operation of partially nitrified centrate at Q_{inf} = 40 mL/mins

Partially Nitrified Centrate								
Date	**Time (mins)**	**Sample No.**	**Remarks**	**pH of solution**	**Mg_{in} (gm/L)**	**Mg_{out} (mg/L)**	**NH_4-N (mg/L)**	**PO_4-P (mg/L)**
20-Mar-12	0	1	Influent	6.70	-	1.48	511.63	82.85
20-Mar-12	75	2	1st reactor effluent	8.00	25.00	2.76	443.77	21.87
20-Mar-12	105	3	Effluent	10.40	25.00	9.26	438.32	23.90
20-Mar-12	130	4	Effluent	8.80	25.00	4.76	437.16	15.65
20-Mar-12	165	5	Effluent	8.62	25.00	3.36	436.71	11.97
20-Mar-12	250	6	Effluent	8.35	25.00	3.58	435.56	12.47
20-Mar-12	400	7	Effluent	8.29	25.00	3.40	434.95	11.76
21-Mar-12	1250	8	Effluent	7.96	25.00	3.34	436.54	10.21
21-Mar-12	1380	9	Effluent	7.92	25.00	2.79	434.85	9.81

Partially Nitrified Centrate								
Date	**Time (mins)**	**Sample No.**	**Remarks**	**pH of solution**	**Mg_{in} (gm/L)**	**Mg_{out} (mg/L)**	**NH_4-N (mg/L)**	**PO_4-P (mg/L)**
28-Mar-12	0	1	Influent	5.84	24.00	3.37	422.58	99.31
28-Mar-12	70	2	1st reactor effluent	9.18	24.00	13.56	349.28	6.50
28-Mar-12	130	3	Effluent	8.84	24.00	21.82	359.43	4.42
28-Mar-12	190	4	Effluent	8.81	24.00	20.56	355.83	6.15
28-Mar-12	250	5	Effluent	8.76	24.00	22.25	349.40	5.97
28-Mar-12	400	6	Effluent	8.70	24.00	21.85	350.15	5.35
29-Mar-12	1230	7	Effluent	8.61	24.00	10.85	360.45	28.94
29-Mar-12	1290	8	Effluent	8.53	24.00	7.11	358.85	30.76

Partially Nitrified Centrate								
Date	**Time (mins)**	**Sample No.**	**Remarks**	**pH of solution**	**Mg_{in} (gm/L)**	**Mg_{out} (mg/L)**	**NH_4-N (mg/L)**	**PO_4-P (mg/L)**
11-Apr-12	0	1	Influent	5.92	25.00	3.31	417.43	118.78
11-Apr-12	60	2	1st reactor effluent	9.18	25.00	20.15	379.51	10.15
11-Apr-12	150	3	Effluent	9.61	25.00	23.33	362.15	2.16
11-Apr-12	210	4	Effluent	8.81	25.00	6.52	365.19	8.64
11-Apr-12	300	5	Effluent	8.64	25.00	8.29	368.21	7.02
11-Apr-12	420	6	Effluent	8.82	25.00	7.63	370.11	9.45
12/04/2012	1320	7	Effluent	8.77	25.00	5.41	375.90	36.43
12/04/2012	1440	8	Effluent	8.53	25.00	10.18	381.58	47.34

Partially Nitrified Centrate								
Date	**Time (mins)**	**Sample No.**	**Remarks**	**pH of solution**	**Mg_{in} (gm/L)**	**Mg_{out} (mg/L)**	**NH_4-N (mg/L)**	**PO_4-P (mg/L)**
3-May-12	0	1	Influent	5.89	28.80	3.30	428.93	104.41
3-May-12	60	2	1st reactor effluent	9.10	28.80	15.23	380.59	25.67
3-May-12	110	3	Effluent	8.70	28.80	19.44	375.50	21.27
3-May-12	170	4	Effluent	9.48	28.80	22.79	332.33	10.54
3-May-12	260	5	Effluent	8.74	28.80	23.45	334.68	11.65
3-May-12	350	6	Effluent	8.62	28.80	24.34	340.15	14.14
3-May-12	440	7	Effluent	8.48	28.80	23.61	335.55	12.45
4-May-12	1250	8	Effluent	8.37	28.80	15.65	395.12	39.57
4-May-12	1370	9	Effluent	8.35	28.80	10.27	394.83	40.91

B.3 Continuous operation of centrate at Q_{inf} = 40 mL/mins

Centrate								
Date	**Time (mins)**	**Sample No.**	**Remarks**	**pH of solution**	**Mg_{in} (gm/L)**	**Mg_{out} (mg/L)**	**NH_4-N (mg/L)**	**PO_4-P (mg/L)**
20-Mar-12	0	1	Influent	7.60	21.00	2.34	847.30	70.83
20-Mar-12	75	2	1st reactor effluent	8.88	21.00	1.74	796.60	37.19
20-Mar-12	105	3	Effluent	8.44	21.00	8.04	814.85	35.17
20-Mar-12	130	4	Effluent	8.10	21.00	7.65	815.12	32.29
20-Mar-12	165	5	Effluent	7.92	21.00	7.11	813.65	27.86
20-Mar-12	250	6	Effluent	7.95	21.00	9.89	810.57	25.87
20-Mar-12	400	7	Effluent	7.93	21.00	12.68	815.26	26.88
21-Mar-12	1250	8	Effluent	7.89	21.00	11.56	817.25	26.21
21-Mar-12	1380	9	Effluent	7.90	21.00	19.32	816.10	25.26

Centrate								
Date	**Time (mins)**	**Sample No.**	**Remarks**	**pH of solution**	**Mg_{in} (gm/L)**	**Mg_{out} (mg/L)**	**NH_4-N (mg/L)**	**PO_4-P (mg/L)**
28-Mar-12	0	1	Influent	7.40	21.00	6.59	807.60	94.17
28-Mar-12	70	2	1st reactor effluent	9.25	21.00	6.57	655.70	13.97
28-Mar-12	130	3	Effluent	8.06	21.00	22.15	679.70	25.85
28-Mar-12	190	4	Effluent	8.05	21.00	22.55	678.45	24.75
28-Mar-12	250	5	Effluent	8.06	21.00	23.08	677.05	23.15
28-Mar-12	400	6	Effluent	8.03	21.00	22.65	677.95	24.07
29-Mar-12	1230	7	Effluent	7.91	21.00	27.84	695.73	27.76
29-Mar-12	1290	8	Effluent	7.92	21.00	28.13	704.55	28.59

Centrate								
Date	**Time (mins)**	**Sample No.**	**Remarks**	**pH of solution**	**Mg_{in} (gm/L)**	**Mg_{out} (mg/L)**	**NH_4-N (mg/L)**	**PO_4-P (mg/L)**
11-Apr-12	0	1	Influent	7.75	20.00	6.47	794.80	98.45
11-Apr-12	60	2	1st reactor effluent	8.30	20.00	8.96	730.15	39.45
11-Apr-12	150	3	Effluent	8.38	20.00	7.66	726.60	38.76
11-Apr-12	210	4	Effluent	8.01	20.00	8.15	700.36	28.15
11-Apr-12	300	5	Effluent	8.10	20.00	7.45	695.00	26.95
11-Apr-12	420	6	Effluent	8.07	20.00	10.60	690.68	27.15
12-Apr-12	1320	7	Effluent	8.05	20.00	21.02	687.75	32.29
12-Apr-12	1440	8	Effluent	8.13	20.00	17.13	684.25	36.12

Centrate								
Date	**Time (mins)**	**Sample No.**	**Remarks**	**pH of solution**	**Mg_{in} (gm/L)**	**Mg_{out} (mg/L)**	**NH_4-N (mg/L)**	**PO_4-P (mg/L)**
3-May-12	0	1	Influent	7.75	29.86	5.08	794.30	108.77
3-May-12	60	2	1st reactor effluent	8.90	29.86	10.65	680.65	25.54
3-May-12	110	3	Effluent	9.10	29.86	13.84	644.05	20.40
3-May-12	170	4	Effluent	8.76	29.86	25.76	671.20	3.55
3-May-12	260	5	Effluent	8.03	29.86	26.45	668.54	13.56
3-May-12	350	6	Effluent	8.01	29.86	24.65	670.59	15.15
3-May-12	440	7	Effluent	8.04	29.86	24.69	675.48	14.52
4-May-12	1250	8	Effluent	7.90	29.86	38.15	681.65	43.15
4-May-12	1370	9	Effluent	7.88	29.86	37.50	680.45	43.11

B.4 Continuous operation of ANAMMOX effluent at Q_{inf} = 140 mL/mins

ANAMMOX								
Date	**Time (mins)**	**Sample No.**	**Remarks**	**pH of solution**	**Mg_{in} (gm/L)**	**Mg_{out} (mg/L)**	**NH_4-N (mg/L)**	**PO_4-P (mg/L)**
15-May-12	0	1	Influent	5.61	10.45	5.21	144.01	94.33
15-May-12	50	2	1st reactor effluent	10.44	10.45	9.62	120.17	26.36
15-May-12	80	3	Effluent	10.05	10.45	11.46	118.03	12.14
15-May-12	350	4	Effluent	8.67	10.45	21.96	103.79	21.90
15-May-12	404	5	Effluent	8.86	10.45	19.75	103.30	18.29

ANAMMOX								
Date	**Time (mins)**	**Sample No.**	**Remarks**	**pH of solution**	**Mg_{in} (gm/L)**	**Mg_{out} (mg/L)**	**NH_4-N (mg/L)**	**PO_4-P (mg/L)**
05-Jun-12	0	1	Influent	5.83	9.64	2.97	221.00	108.00
05-Jun-12	44	2	1st reactor effluent	10.30	9.64	4.76	172.00	12.70
05-Jun-12	153	3	Effluent	8.05	9.64	27.68	190.00	27.55
05-Jun-12	238	4	Effluent	7.78	9.64	32.97	191.00	41.95
05-Jun-12	302	5	Effluent	7.75	9.64	28.27	185.00	42.20
05-Jun-12	358	6	Effluent	7.72	9.64	9.76	188.00	45.10
05-Jun-12	397	7	Effluent	7.71	9.64	34.09	190.00	42.30

ANAMMOX								
Date	**Time (mins)**	**Sample No.**	**Remarks**	**pH of solution**	**Mg_{in} (gm/L)**	**Mg_{out} (mg/L)**	**NH_4-N (mg/L)**	**PO_4-P (mg/L)**
26-Jun-12	0	1	Influent	5.88	8.86	2.94	117.00	110.00
26-Jun-12	25	2	1st reactor effluent	9.50	8.86	7.90	95.60	50.00
26-Jun-12	63	3	Effluent	8.52	8.86	12.14	78.60	15.98
26-Jun-12	173	4	Effluent	7.34	8.86	48.44	95.70	54.50
26-Jun-12	268	5	Effluent	7.28	8.86	54.89	94.70	62.50
26-Jun-12	353	6	Effluent	7.47	8.86	48.62	102.00	59.00
26-Jun-12	396	7	Effluent	7.43	8.86	25.85	90.90	54.00

ANAMMOX								
Date	**Time (mins)**	**Sample No.**	**Remarks**	**pH of solution**	**Mg_{in} (gm/L)**	**Mg_{out} (mg/L)**	**NH_4-N (mg/L)**	**PO_4-P (mg/L)**
04-Jul-12	0	1	Influent	5.90	8.79	2.45	145.00	119.00
04-Jul-12	25	2	1st reactor effluent	6.93	8.79	72.36	142.00	110.00
04-Jul-12	45	3	Effluent	7.49	8.79	36.46	126.00	46.80
04-Jul-12	120	4	Effluent	8.11	8.79	35.09	130.00	43.60
04-Jul-12	240	5	Effluent	7.71	8.79	54.86	140.50	61.70
04-Jul-12	300	6	Effluent	7.17	8.79	45.40	136.00	54.50
04-Jul-12	360	7	Effluent	7.36	8.79	42.22	143.00	63.20

ANAMMOX								
Date	**Time (mins)**	**Sample No.**	**Remarks**	**pH of solution**	**Mg_{in} (gm/L)**	**Mg_{out} (mg/L)**	**NH_4-N (mg/L)**	**PO_4-P (mg/L)**
24-Jul-12	0	1	Influent	5.71	10.40	3.29	151.50	106.50
24-Jul-12	74	2	1st reactor effluent	7.48	10.40	52.64	123.00	45.60
24-Jul-12	159	3	Effluent	7.61	10.40	53.11	127.00	55.40
24-Jul-12	237	4	Effluent	7.56	10.40	57.65	133.00	68.20
24-Jul-12	305	5	Effluent	7.23	10.40	55.17	135.00	66.80

ANAMMOX								
Date	**Time (mins)**	**Sample No.**	**Remarks**	**pH of solution**	**Mg_{in} (gm/L)**	**Mg_{out} (mg/L)**	**NH_4-N (mg/L)**	**PO_4-P (mg/L)**
30-Jul-12	0	1	Influent	5.90	10.43	3.71	167.00	116.50
30-Jul-12	30	2	1st reactor effluent	7.60	10.43	73.77	156.00	111.00
30-Jul-12	60	3	Effluent	7.20	10.43	54.83	137.00	71.90
30-Jul-12	120	4	Effluent	7.51	10.43	50.69	134.00	69.00
30-Jul-12	240	5	Effluent	7.70	10.43	41.91	130.00	55.45
30-Jul-12	300	6	Effluent	7.58	10.43	42.80	132.00	60.45
30-Jul-12	370	7	Effluent	7.52	10.43	43.87	131.00	61.05

B.5 Continuous operation of partially nitrified centrate at Q_{inf} = 140 mL/mins

Partially Nitrified Centrate								
Date	**Time (mins)**	**Sample No.**	**Remarks**	**pH of solution**	**Mg_{in} (gm/L)**	**Mg_{out} (mg/L)**	**NH_4-N (mg/L)**	**PO_4-P (mg/L)**
29-May-12	0	1	Influent	5.80	8.22	3.11	454.00	121.52
29-May-12	114	2	1st reactor effluent	8.34	8.22	7.57	408.00	20.39
29-May-12	341	3	Effluent	8.62	8.22	6.93	402.00	21.86
29-May-12	366	4	Effluent	8.64	8.22	7.05	414.00	21.49
29-May-12	391	5	Effluent	7.90	8.22	8.73	420.00	24.87

Partially Nitrified Centrate								
Date	**Time (mins)**	**Sample No.**	**Remarks**	**pH of solution**	**Mg_{in} (gm/L)**	**Mg_{out} (mg/L)**	**NH_4-N (mg/L)**	**PO_4-P (mg/L)**
19-Jun-12	0	1	Influent	5.85	8.61	2.92	470.00	115.00
19-Jun-12	30	2	1st reactor effluent	8.92	8.61	8.89	415.00	28.60
19-Jun-12	67	3	Effluent	8.62	8.61	3.02	395.00	18.45
19-Jun-12	119	4	Effluent	7.96	8.61	8.74	422.50	27.85
19-Jun-12	154	5	Effluent	8.34	8.61	4.30	390.00	22.05
19-Jun-12	344	6	Effluent	8.43	8.61	4.33	357.50	25.80
19-Jun-12	390	7	Effluent	8.22	8.61	6.21	407.50	32.40

Partially Nitrified Centrate								
Date	**Time (mins)**	**Sample No.**	**Remarks**	**pH of solution**	**Mg_{in} (gm/L)**	**Mg_{out} (mg/L)**	**NH_4-N (mg/L)**	**PO_4-P (mg/L)**
20-Sep-12	0	1	Influent	5.86	10.54	3.84	434.00	103.00
20-Sep-12	30	2	1st reactor effluent	8.30	10.54	85.86	415.00	74.90
20-Sep-12	56	3	Effluent	9.08	10.54	22.86	363.00	10.10
20-Sep-12	107	4	Effluent	9.60	10.54	19.93	370.00	8.81
20-Sep-12	264	5	Effluent	9.48	10.54	14.54	376.00	13.00
20-Sep-12	277	6	Effluent	9.65	10.54	12.43	373.00	12.00

B.6 Continuous operation of centrate at Q_{inf} = 140 mL/mins

Centrate								
Date	**Time (mins)**	**Sample No.**	**Remarks**	**pH of solution**	**Mg_{in} (gm/L)**	**Mg_{out} (mg/L)**	**NH_4-N (mg/L)**	**PO_4-P (mg/L)**
23-May-12	0	1	Influent	7.70	7.24	5.47	708.15	108.00
23-May-12	40	2	1st reactor effluent	8.50	7.24	20.59	706.58	15.92
23-May-12	70	3	Effluent	8.09	7.24	22.20	689.18	19.29
23-May-12	370	4	Effluent	7.90	7.24	23.54	626.08	33.41
23-May-12	400	5	Effluent	7.77	7.24	28.24	681.73	43.98

Centrate								
Date	**Time (mins)**	**Sample No.**	**Remarks**	**pH of solution**	**Mg_{in} (gm/L)**	**Mg_{out} (mg/L)**	**NH_4-N (mg/L)**	**PO_4-P (mg/L)**
12-Jun-12	0	1	Influent	7.84	7.16	4.39	773.75	90.60
12-Jun-12	30	2	1st reactor effluent	8.13	7.16	36.78	705.00	21.65
12-Jun-12	90	3	Effluent	7.55	7.16	44.32	765.00	32.70
12-Jun-12	180	4	Effluent	7.44	7.16	46.87	697.50	27.60
12-Jun-12	270	5	Effluent	7.45	7.16	46.90	742.50	35.85
12-Jun-12	330	6	Effluent	7.48	7.16	35.72	732.50	42.95
12-Jun-12	387	7	Effluent	7.55	7.16	31.44	722.50	33.30

Centrate								
Date	**Time (mins)**	**Sample No.**	**Remarks**	**pH of solution**	**Mg_{in} (gm/L)**	**Mg_{out} (mg/L)**	**NH_4-N (mg/L)**	**PO_4-P (mg/L)**
10-Jul-12	0	1	Influent	7.66		4.54	775.60	100.00
10-Jul-12	25	2	1st reactor effluent	7.65	8.58	22.61	730.00	38.00
10-Jul-12	45	3	Effluent	7.90		17.32	697.50	23.10
10-Jul-12	120	4	Effluent	7.70		21.74	695.00	31.35
10-Jul-12	240	5	Effluent	7.63		22.08	687.50	32.20
10-Jul-12	300	6	Effluent	7.60		10.84	702.50	38.90
10-Jul-12	360	7	Effluent	7.64		9.05	670.00	36.20

Appendix C

C.1 Upflow velocities during operation for various flow conditions.

Reactor Sections	Length mm	Inner Dia. mm	Area mm^2	Volume mm^3	Flow rate mL/min	Flow rate mm^3/min	Recycle Ratio	Total Flow mm^3/min	Upflow velocity mm/min
Bottom	609.6	40.44	1284.44	782991.66	40	40000	0	40000	31.14
Top	406.4	77.27	4689.34	1905747.70	40	40000	0	40000	8.53
Bottom	609.6	40.44	1284.44	782991.66	40	40000	2	120000	93.43
Top	406.4	77.27	4689.34	1905747.70	40	40000	2	120000	25.59
Bottom	609.6	40.44	1284.44	782991.66	40	40000	5	240000	186.85
Top	406.4	77.27	4689.34	1905747.70	40	40000	5	240000	51.18

Reactor Sections	Length mm	Inner Dia. mm	Area mm^2	Volume mm^3	Flow rate mL/min	Flow rate mm^3/min	Recycle Ratio	Total Flow mm^3/min	Upflow velocity mm/min
Bottom	609.6	40.44	1284.44	782991.66	132	132000	0	132000	102.77
Top	406.4	77.27	4689.34	1905747.70	132	132000	0	132000	28.15
Bottom	609.6	40.44	1284.44	782991.66	132	132000	1.5	330000	256.92
Top	406.4	77.27	4689.34	1905747.70	132	132000	1.5	330000	70.37

Reactor Sections	Length mm	Inner Dia. mm	Area mm^2	Volume mm^3	Flow rate mL/min	Flow rate mm^3/min	Recycle Ratio	Total Flow mm^3/min	Upflow velocity mm/min
Bottom	609.6	40.44	1284.44	782991.66	140	140000	0	140000	109.00
Top	406.4	77.27	4689.34	1905747.70	140	140000	0	140000	29.85
Bottom	609.6	40.44	1284.44	782991.66	140	140000	5	840000	653.98
Top	406.4	77.27	4689.34	1905747.70	140	140000	5	840000	179.13

Appendix D

D.1 Caustic and magnesium consumption for struvite production

ANAMMOX Effluent										
Date	20-Mar-12	28-Mar-12	11-Apr-12	3-May-12	15-May-12	5-Jun-12	26-Jun-12	4-Jul-12	24-Jul-12	30-Jul-12
Operation No.	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10
Avg. Influent PO4-P (mg/L)	93.24	111.02	108.25	117.67	94.33	108.00	110.00	119.00	106.50	116.50
Avg. Effluent PO_4-P (mg/L)	15.25	14.78	24.06	44.44	19.67	35.30	49.33	53.96	59.00	58.98
PO_4-P Reduced (%)	83.64	86.68	77.77	62.23	79.15	67.31	55.15	54.66	44.60	49.37
Flow Rate (mL/min)	37.14	41.86	41.86	41.86	132	140	140	140	140	140
Run Time (mins)	1380	1290	1440	1402	414	400	396	360	305	305
PO_4-P (gms)	4.00	5.20	5.07	4.30	4.08	4.07	3.36	3.28	2.03	2.46
Struvite (95% of $P_{insolube}$) (gms)	29.21	37.98	37.08	31.41	29.81	29.75	24.58	23.95	14.82	17.95
NaOH consumed (gms)	26.00	18.60	18.00	18.40	20.80	17.60	14.00	13.20	9.33	12.60
NaOH (gm/gm struvite)	0.89	0.49	0.49	0.59	0.70	0.59	0.57	0.55	0.63	0.70
Mg consumed (gms)	-	-	-	2.89	5.05	3.86	2.88	1.81	1.91	2.76
Mg (gm/gm struvite)	-	-	-	0.09	0.17	0.13	0.12	0.08	0.13	0.15

Partially Nitrified Centrate							
Date	20-Mar-12	28-Mar-12	11-Apr-12	3-May-12	29-May-12	19-Jun-12	19-Jun-12
Operation No.	Run1	Run2	Run3	Run4	Run5	Run6	Run7
Avg. Influent PO4-P (mg/L)	82.85	99.31	118.78	104.41	121.52	115.00	103.00
Avg. Effluent PO_4-P (mg/L)	14.70	12.58	17.31	22.02	22.15	25.86	10.98
PO_4-P Reduced (%)	82.25	87.33	85.42	78.91	81.77	77.51	89.34
Flow Rate (mL/min)	41.86	37.14	37.14	37.14	132.00	140.00	140.00
Run Time (mins)	1380	1290	1440	1402	391	390	270
PO_4-P (gms)	3.94	4.16	5.43	4.29	5.13	4.87	3.48
Struvite (95% of $P_{insolube}$) (gms)	28.77	30.36	39.66	31.35	37.48	35.57	25.42
NaOH consumed (gms)	31.00	34.20	22.40	39.20	25.20	24.00	18.00
NaOH (gm/gm struvite)	1.08	1.13	0.56	1.25	0.67	0.67	0.71
Mg consumed (gms)	-	-	-	3.28	3.95	4.23	3.26
Mg (gm/gm struvite)	-	-	-	0.10	0.11	0.12	0.13

Centrate							
Date	20-Mar-12	28-Mar-12	11-Apr-12	3-May-12	23-May-12	12-Jun-12	10-Jul-12
Operation No.	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7
Avg. Influent PO4-P (mg/L)	70.83	94.17	98.45	108.77	108.00	90.60	100.00
Avg. Effluent PO_4-P (mg/L)	27.39	24.02	30.13	22.37	28.15	32.34	33.29
PO_4-P Reduced (%)	61.32	74.49	69.39	79.43	73.94	64.30	66.71
Flow Rate (mL/min)	38.40	38.40	38.40	38.40	132.00	140.00	140.00
Run Time (mins)	1380	1290	1440	1402	370	387	387
PO_4-P (gms)	2.30	3.47	3.78	4.65	3.90	3.16	3.61
Struvite (95% of $P_{insolube}$) (gms)	16.82	25.39	27.61	33.99	28.50	23.07	26.41
NaOH consumed (gms)	10.40	13.80	11.60	10.40	10.80	5.20	7.40
NaOH (gm/gm struvite)	0.62	0.54	0.42	0.31	0.38	0.23	0.28
Mg consumed (gms)	-	-	-	3.37	2.80	1.64	3.36
Mg (gm/gm struvite)	-	-	-	0.10	0.10	0.07	0.13

Appendix E

E.1 Molar ratio of struvite constituents

ANAMMOX							
Date	**Run No.**	**Mg (mg/L)**	**NH_4-N (mg/L)**	**PO_4-P (mg/L)**	**Mg (Moles)**	**NH_4-N (Moles)**	**PO_4-P (Moles)**
20-Mar-12	1	438.24	318.89	683.70	0.82	1.03	1.00
28-Mar-12	2	968.85	468.70	1684.80	0.73	0.60	1.00
11-Apr-12	3	469.63	284.95	658.05	0.91	0.96	1.00
03-May-12	4	456.89	320.55	652.30	0.89	1.09	1.00
15-May-12	5	456.10	326.80	654.50	0.91	1.11	1.00
05-Jun-12	6	471.39	277.00	650.00	0.92	0.94	1.00
26-Jun-12	7	476.62	244.50	644.50	0.94	0.84	1.00
04-Jul-12	8	468.47	263.00	683.67	0.87	0.85	1.00
24-Jul-12	9	448.73	269.00	604.00	0.95	0.99	1.00
30-Jul-12	10	464.98	291.00	645.00	0.92	1.00	1.00

Partially Nitrified Centrate							
Date	**Run No.**	**Mg (mg/L)**	**NH_4-N (mg/L)**	**PO_4-P (mg/L)**	**Mg (Moles)**	**NH_4-N (Moles)**	**PO_4-P (Moles)**
20-Mar-12	1	457.86	330.39	720.10	0.81	1.02	1.00
28-Mar-12	2	1068.50	641.35	2074.90	0.66	0.68	1.00
11-Apr-12	3	481.65	309.15	648.20	0.95	1.06	1.00
03-May-12	4	451.77	307.10	641.90	0.90	1.04	1.00
29-May-12	5	472.13	300.85	641.60	0.94	1.04	1.00
19-Jun-12	6	462.37	301.00	657.50	0.90	1.01	1.00
20-Sept-12	7	494.14	244.67	652.67	0.97	0.83	1.00

Centrate							
Date	**Run No.**	**Mg (mg/L)**	**NH_4-N (mg/L)**	**PO_4-P (mg/L)**	**Mg (Moles)**	**NH_4-N (Moles)**	**PO_4-P (Moles)**
20-Mar-12	1	420.74	311.88	643.40	0.83	1.07	1.00
28-Mar-12	2	1040.50	577.35	1097.80	0.70	0.67	1.00
11-Apr-12	3	461.74	317.45	635.20	0.93	1.11	1.00
03-May-12	4	457.12	317.25	646.55	0.90	1.09	1.00
23-May-12	5	457.03	302.15	671.05	0.87	1.00	1.00
12-Jun-12	6	465.29	297.00	650.00	0.91	1.01	1.00
10-Jul-12	7	479.25	281.00	643.50	0.95	1.00	1.00

Appendix F

F.1 Particle size distribution of struvite particles

Centrate		Partially Nitrified Centrate		ANAMMOX	
Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %
0.55	0.07	0.55	0	0.55	0
0.631	0.13	0.631	0	0.631	0.02
0.724	0.18	0.724	0.04	0.724	0.06
0.832	0.21	0.832	0.09	0.832	0.09
0.955	0.23	0.955	0.1	0.955	0.14
1.096	0.24	1.096	0.11	1.096	0.16
1.259	0.24	1.259	0.12	1.259	0.19
1.445	0.23	1.445	0.13	1.445	0.2
1.66	0.22	1.66	0.12	1.66	0.2
1.905	0.19	1.905	0.11	1.905	0.2
2.188	0.17	2.188	0.09	2.188	0.19
2.512	0.16	2.512	0.08	2.512	0.17
2.884	0.16	2.884	0.05	2.884	0.17
3.311	0.18	3.311	0.02	3.311	0.17
3.802	0.22	3.802	0.05	3.802	0.2
4.365	0.28	4.365	0.1	4.365	0.26
5.012	0.36	5.012	0.15	5.012	0.35
5.754	0.46	5.754	0.23	5.754	0.49
6.607	0.58	6.607	0.33	6.607	0.67
7.586	0.72	7.586	0.44	7.586	0.87
8.71	0.9	8.71	0.55	8.71	1.09
10	1.14	10	0.65	10	1.28
11.482	1.47	11.482	0.71	11.482	1.42
13.183	1.9	13.183	0.73	13.183	1.49
15.136	2.47	15.136	0.71	15.136	1.45
17.378	3.19	17.378	0.67	17.378	1.31
19.953	4.02	19.953	0.66	19.953	1.08
22.909	4.95	22.909	0.74	22.909	0.81
26.303	5.88	26.303	0.99	26.303	0.59
30.2	6.75	30.2	1.5	30.2	0.5
34.674	7.44	34.674	2.31	34.674	0.65
39.811	7.88	39.811	3.44	39.811	1.14

Centrate		Partially Nitrified Centrate		ANAMMOX	
Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %
45.709	7.99	45.709	4.84	45.709	2.01
52.481	7.77	52.481	6.38	52.481	3.23
60.256	7.21	60.256	7.88	60.256	4.73
69.183	6.38	69.183	9.12	69.183	6.32
79.433	5.36	79.433	9.89	79.433	7.79
91.201	4.25	91.201	10.03	91.201	8.9
104.713	3.15	104.713	9.5	104.713	9.48
120.226	2.17	120.226	8.36	120.226	9.41
138.038	1.35	138.038	6.78	138.038	8.69
158.489	0.74	158.489	5.02	158.489	7.45
181.97	0.31	181.97	3.28	181.97	5.84
208.93	0.1	208.93	1.81	208.93	4.14
239.883	0	239.883	0.77	239.883	2.52
275.423	0	275.423	0.3	275.423	1.22
316.228	0	316.228	0.01	316.228	0.53
363.078	0	363.078	0	363.078	0.11
416.869	0	416.869	0	416.869	0.01
478.63	0	478.63	0	478.63	0
549.541	0	549.541	0	549.541	0