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**POTENTIAL NUTRIENT REMOVAL AND/OR RECOVERY
USING CONTROLLED STRUVITE PRECIPITATION IN
REJECT WATER FROM IVAR GRØDALAND**

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Abstract

The main focus of this study was to investigate the possibilities to control struvite precipitation in IVAR Grødaland, Norway, by determining the optimum conditions for struvite to precipitate. A laboratory scale experiment was conducted using jar testing method. Artificial wastewater and reject water from IVAR Grødaland were used in the test, with similar levels of phosphate and ammonia and variable dosages of magnesium. Struvite precipitation is a pH dependent reaction, and the experiments started with determining the optimum pH by comparing 4 different pH levels from 8 to 11. The result showed that at pH 10, PO₄-P, Mg²⁺, and NH₄-N removal were 5.4 moles, 5.1 moles and 5.2 moles respectively, and 728 mg/l or 5.3 moles TSS assumed to be struvite was formed in the artificial wastewater. In reject water, PO₄-P, Mg²⁺, and NH₄-N were removed 3.9 moles, 2.9 moles and 18.1 moles respectively and 508 mg/l or 3.7 moles TSS assumed to be struvite produced. Using pH 10 as optimum condition, determining optimum Mg²⁺ dosage was conducted using 4 different PO₄-P: Mg²⁺ molar ratios. In artificial wastewater PO₄-P: Mg²⁺ molar ratios were 1:1; 1:2; 1:3; and 1:4. With PO₄-P completely removed and the amount of Mg²⁺ added were low, the optimum dosage was determined to 1:2 PO₄-P: Mg²⁺ molar ratios. Increased Mg²⁺ dosage would increase the TSS but resulting other crystal an addition to struvite. Tests on reject water continued at smaller ranges of Mg²⁺ dosage with PO₄-P: Mg²⁺ molar ratios, which were 1:1; 1:1.5; 1:2; and 1:2.5. The optimum dosage was 1:1.5 PO₄-P: Mg²⁺ molar ratio with PO₄-P completely removed and Mg²⁺ had 60% average removal. Tests with increasing the mixing time to 10 minutes rapid mixing and 20 minutes slow mixing showed no significant improvement. By changing the Mg²⁺ source into sea water, the best dosage was 10% volume of sea water addition with PO₄-P completely removed and Mg²⁺ average removal efficiency at 68% in reject water and 98.2% removal efficiency in artificial wastewater. The tests showed that struvite precipitation can be control at pH 10 and addition of Mg²⁺ between 1 – 1,5 moles that depend on the reject water characteristics. The overall results show that efficient struvite precipitation on reject water is feasible and that seawater appears as a realistic Mg source.

Keywords: *pH, PO₄-P, NH₄-N, Mg²⁺, nutrient removal, struvite precipitation*

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Abbreviations

MAP	Magnesium Amonium Phosphate
HAP	Hydroxylapatite
OCP	Octacalcium phosphate
DCP	Dicalcium phosphate
TCP	Tricalcium phosphate

1. Introduction

Eutrophication, caused by excessive nutrients like nitrogen and phosphorous discharged from wastewater, is now a worldwide issue which brings nuisance consequence to the environment, such as the death of aquatic lives, contamination of underground water, and loss fertility of land[1]. On the other hand, nitrogen and phosphorous are the fundamental nutrient elements which are needed by living creatures. Now the only way to obtain phosphorous resource is from mining sources, which are not infinite. Recent studies have reported that rock based phosphorous will be running out in 50-100 years[2]. It is becoming critical to find an alternative resource or recycle nitrogen and phosphorous from resources which are N and P rich.

Mitigation for phosphorus finite problem cycle can be done by recycling phosphorus from wastewater. Since the implementation of the EC Urban Waste Water Treatment Directive (UWWTD) [1] 97/271/EC (21 May 1991), there are some changes in wastewater treatment. Two of the changes directly impact upon water treatment of sludge produced from wastewater treatment facilities:

- Dumping of sewage sludge at sea is now prohibited.
- Nitrogen and phosphorus limits have been imposed to reduce the potential of eutrophication of sensitive inland and coastal waters.

Because sewage sludge dumping at sea (or any other water body) is now prohibited, sludge treatment and disposal options have been implemented in an attempt to deal with the increased volumes of sludge. The treatment also improved in term of nutrient removal, especially developed to remove compounds containing nitrogen and phosphorous. The result of removing greater concentrations of phosphorus from the wastewater is that the wasted sludge has a greater concentration of phosphorus, nitrogen and magnesium. This combination of ions can result in the formation of a tenacious mineral. This mineral, composed of magnesium ammonium phosphate, is called struvite [3].

In the early 1960s at the Los Angeles Hyperion wastewater treatment plant (WWTP), a white crystalline solid was discovered to have deposited on the underside of the separating screens and in digested sludge lines causing extensive operational problems. Areas of a WWTP affected most by struvite deposition are places where there is an increase in turbulence such as pumps, aerators and pipe bends [4]. Similar instances of pipe blockages due to struvite accumulation have been reported elsewhere (Table 1).

Due to the location and solid, compact manner in which struvite deposits remediation is very difficult. Several remediation methods have been investigated including a mechanical cleaning device, jet washing at 63 kg cm^2 , heat treating (but this destroyed the rubber flanges between pipe sections) and acid washing [4]. Struvite deposits can be removed successfully by acid washing but the process is complex and time consuming and is therefore not considered to be the ideal option.

Preventing struvite deposition in a WWTP can be a formidable and costly task. Some of the methods implemented include the instillation of water “softening” devices before and after sludge digestion [5]. Binding the phosphorus up in an insoluble phase by the addition of ferric

chloride [6]. Diluting digester sludge with secondary effluent [4] and in extreme cases, certain areas of plants have been redesigned [5].

An alternative approach to preventing the problems caused by the formation of struvite in WWTP would be to encourage its precipitation in a dedicated reactor. This would not only avert costly build-up problems but a potentially useful by-product would also be obtained [7].

Table 1.1. Examples of the impact struvite formation has on pipes and associated processes [3].

Process affected	Result
Sludge supernatant system	Struvite accumulation in pipe 5.6 km long. Struvite reported to foul pipes, pumps, aerators and screens
Digested sludge pipeline.	Bore of pipe reduced from 0.3 to 0.15 m.
Pipeline from sludge holding tank to centrifuges.	Bore of pipe reduced from 100 to 50 mm
Vertical PVC pipe (digester effluent)	150 mm diameter reduced by a mean value of 10.65 mm
Horizontal acrylic pipe (digester effluent)	142 mm pipe diameter with negligible struvite build up
90° elbow PVC piping (digester effluent)	150 mm pipe diameter reduced by a mean value of 28.38 mm
Centrate discharge line	150 mm rubber pipe reduced to 60 mm in 12 weeks

This study was to explore the possibilities to prevent struvite scaling and nutrient removal/recovery at IVAR Grødalund, Norway. The concentration of ammonium in sludge dewatering effluent was around 1000 mg/l, which is higher than phosphate, which is around 200 mg/l. Thus, addition of certain level of Mg^{2+} sources is essential for removal/recovery PO_4 -P and NH_4 -N through the struvite precipitation process. Therefore, the aim of the study associated with this chapter was to identify and optimize the operation conditions for remove/recovering PO_4 -P and NH_4 -N via struvite precipitation from sludge dewatering effluent.

1.1. Scope of work

This study was a part of project in cooperation with IVAR and conducted by Environmental Technology Study Program, University of Stavanger. IVAR (*Interkommunalt Vann Avløp og Renovasjon*) is a Norwegian public company that constructs and operates municipal facilities for water, wastewater and general waste. In this study, laboratory scale tests were conducted using jar testing equipment to precipitate struvite in artificial wastewater and reject water from dewatering units at IVAR Grødalund biogas plant.

With the current configuration in IVAR Grødalund biogas plant, scaling in equipment eventually become an issue. This experiment measured parameters that were relevant to struvite precipitation relative to the condition in IVAR Grødalund plant. Parameters controlled were pH and Mg^{2+} dosing. Result would be including PO_4 -P, NH_4 -N, Mg^{2+} and TSS. Based and the result conclusion and suggestion related to the objective will be given.

1.2. Objectives

The main objective of this master thesis was to investigate the optimum condition for struvite to precipitate and also investigate the possibilities for struvite precipitation to be controlled in real scale operation in wastewater treatment. Additional objective is to see the possibilities of using sea water as alternative Mg^{2+} source.

1.3. Thesis outline

This master thesis is entitled: “Potential Nutrient Removal and/or Recovery Using Controlled Struvite Precipitation in Reject Water from IVAR Grødaland” and divided into six chapters.

1. Introduction;
2. Literature Review and Theoretical Background;
3. Materials and Methods;
4. Results;
5. Discussions;
6. Conclusions; and

Appendixes are included to present supporting materials of the whole study.

2. Literature Review and Theoretical Background

Wastewater treatment technologies have been developed and applied for more than 100 years, since the first digester was reported in India in 1859[8]. Other processes, such as, anaerobic digestion, aerobic digestion, composting and incineration, have been developed and designed for treating water. In addition, tertiary treatment was applied in order to recycle water, and to remove/recover nutrients from wastewater.

This chapter describes the theoretical explanation of wastewater treatment technologies in removing phosphate and ammonium in form of struvite. Previous research about struvite formation in municipal wastewater is also described. Furthermore, the factors affecting struvite formation are also presented. Based on this literature review and theoretical background, in the last of this chapter, the knowledge gaps are well defined as specific objectives of this current study.

2.1. Wastewater treatment processes

Most wastewater treatment methods that are applied worldwide consists of three steps in order to make the effluent suitable for discharge or reuse and also to increase the effectivity of the processes. This three steps are physical or primary treatment, biological or secondary treatment and tertiary treatment. A typical wastewater treatment processes is shown in figure 2.1.

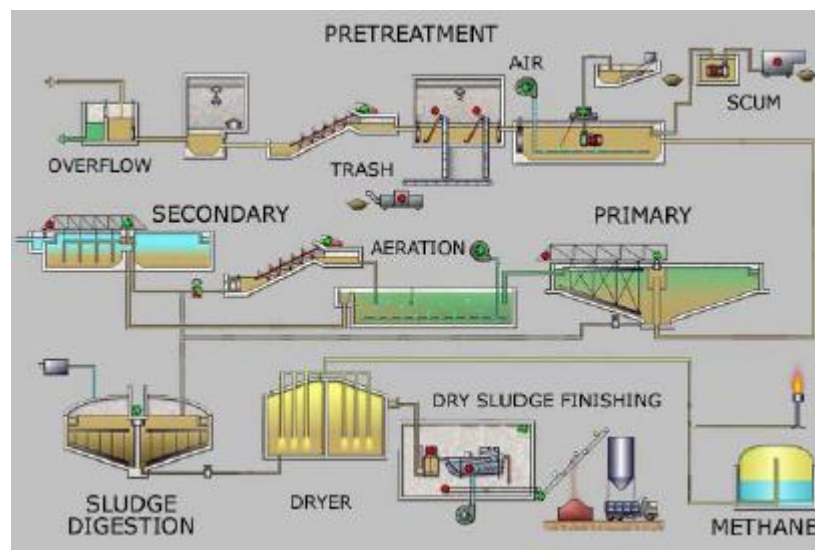


Figure 2.1 Wastewater treatment process [9]

2.1.1. Physical treatment

Physical treatment is conducted by settling or floating process which is applied to separate suspended matters, grit, oil and grease. Physical treatment usually utilizes gravitational force to separate the solid. This process will increase efficiency of the next treatment by removing heavier solids to reduce load on the biological treatment.

2.1.2. Biological treatment

Biological process can be carried out by a single and or combined system of anaerobic or aerobic digestion. The system of this process is the determined by intake nutrient and also the target effluent. Currently, anaerobic digestion and activated sludge are the most widely used process/technologies when treating sludge and municipal wastewater, respectively.

2.1.3. Tertiary treatment

Tertiary treatment includes odor management, disinfection, filtration, nitrogen and phosphorus removal and/or recovery. The removal and recovery of nitrogen and phosphorus has been a critical issue. It is well known that excessive amount of nutrients like NH_4^+ and PO_4^{3-} will result in severe environmental problems, such as, eutrophication, contamination of land and underground water [10]. Many studies have focused on the removal of $\text{NH}_4^+\text{-N}$ and $\text{PO}_4^{3-}\text{-P}$ from wastewater to meet government standard.

Anaerobic digestion

The anaerobic digestion (AD) process has been applied for sludge treatment for more than 100 years. The first digester was built in India in 1859 [8]. It is a well-developed and the most widely used biological process applied in treatment of municipal, industrial and agricultural wastewater. The application of this technology will not be affected by the physical form and composition of the wastes. This process has been applied in many areas, such as municipal wastewater [11], domestic wastewater [12], waste activated sludge [13], animal wastewater [14] and food waste [15].

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

In the first stage of anaerobic digestion, complex and/or insoluble organics, such as carbohydrate, proteins, fats, etc. will be transformed into sugars, amino acids and long chain fatty acids (LCFAs). Basically, the organic waste is broken into a soluble chemical form that can be used by bacteria at this stage. The bacteria which consist of obligate and facultative anaerobes are responsible for hydrolysis and removing a small quantity of oxygen applied into the digester [16]. The second phase is the acidogenesis process. In this process, simpler forms of organic matters are converted into short chain fatty acids by microorganisms, such as propionic acid, Butyric acid, etc. Acetogenesis is the third phase, which changes higher organic acids into acetate, H_2 and CO_2 . Whether the biogas is produced successfully or not is greatly impacted by this intermediate conversion because acids other than acetic acid generated can't be consumed straight away by methanogens. The acetogens bacteria are the driver of biochemical reactions associated with this phase. However, they are sensitive to concentrations of organic and other operating parameters [16]. The last step in this process is methanogenesis, H_2 and CO_2 and acetate produced in the acetogenesis process are utilized by methanogens to

generate methane and CO₂ [16]. Methanogens are also very sensitive to reaction situations and operational parameters [17].

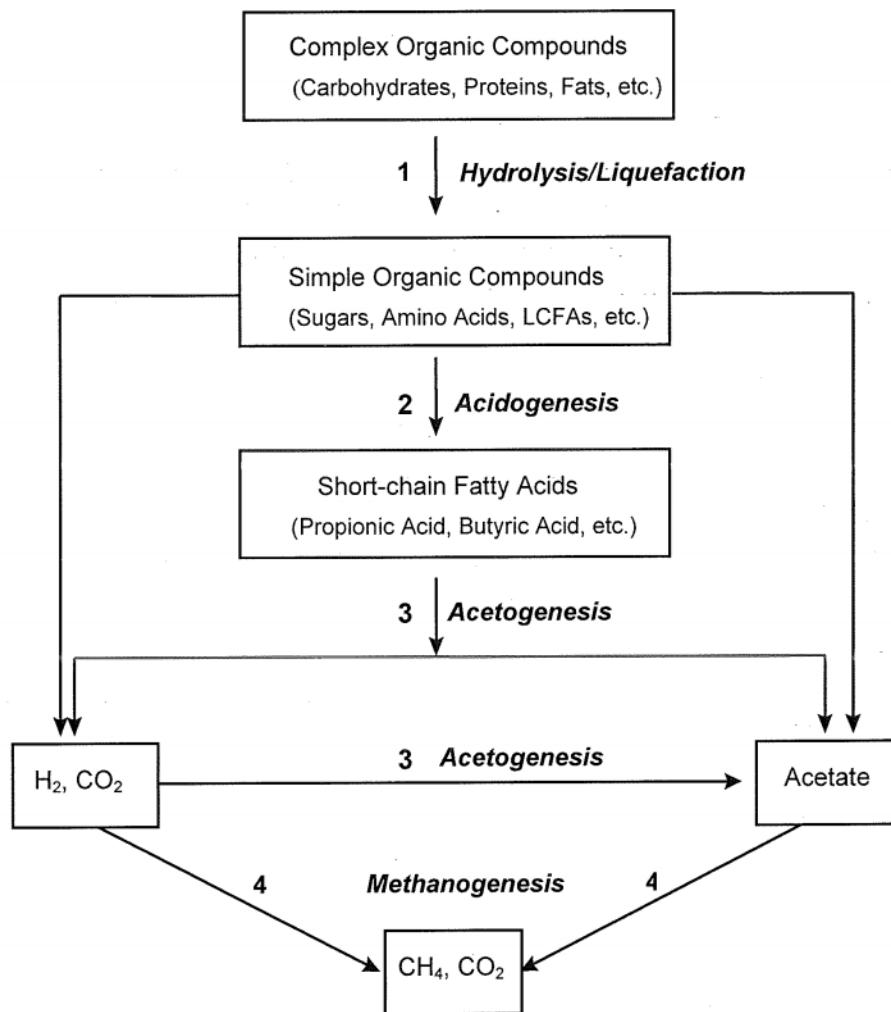


Figure 2.2 Process diagram of anaerobic digestion[18]

The main outcome of AD and aerobic digestion is to degrade organic matters and remove carbon hydrate-based components, while some nitrogen and phosphorus still remain in the sludge and some is released to the liquid phase during degradation of the organic compounds. According to EPA legislation, nitrogen and phosphorus must be removed in order to meet the discharge regulations [19].

Nitrogen removal

Biological and physical/chemical process have been applied to remove nitrogen from wastewater. The main reactions in a biological process are nitrification and denitrification. The nitrification can transform ammonia to nitrite and further to nitrate successfully; however, nitrogen is not significantly removed in this process. In order to remove nitrogen, denitrification is introduced following the nitrification step [9]. In a denitrification process, nitrate is converted to nitrogen gas by bacteria under anoxic conditions. After the denitrification process, the concentration of nitrogen is dramatically reduced.

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

In the aeration and air stripping process, the waste is first treated by air stripping; this process is shown in Figure 2.3.

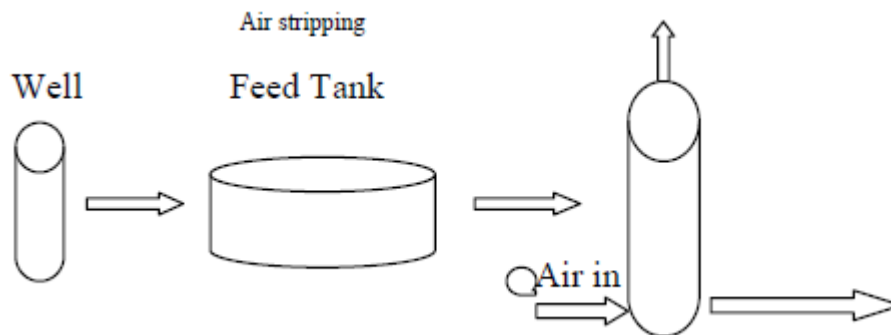


Figure 2.3 Air stripping treatment process [8]

The air stripping process is used to eliminate high concentrations of ammonium from wastewater. If it is operated effectively, the volatile organic matter in wastewater can be removed up to 90 percent [8, 9]. However, this process has some shortcomings. For example, when dissolved oxygen in water is raised to the saturation condition, it will cause the corrosion or air binding in filters. Another common problem is slow removal of hydrogen sulphide and overuse of energy. If NH_3 is not absorbed by hydrogen sulphide or hydrogen chloride, it will be released to air where it acts as a greenhouse gas, contributing climate change and global warming.

Phosphorus removal

There are two processes in removing phosphorus, namely chemical treatment and biological treatment. In biological treatment phosphorus can be removed by an enhanced biological phosphorus removal process. This process depends on phosphorus consumption by aerobic heterotrophs bacteria which can absorb orthophosphate much more than its growth requirements [20]. This process used bacteria called polyphosphate accumulating organisms (PAOs), these bacteria are enriched and will store large amount of phosphorus within their cells. The percentage of PAOs in the solution is proportional to the efficiency of this system. Anaerobic-aerobic-oxic (A-2/O) process and integrated constructed wetlands are very common processes to remove NH_4^+ and PO_4^{3-} . In A2/O process, phosphorus can be up taken by microbial activities in an anaerobic reaction step. A large amount of phosphorus is released in the process. Polyphosphate is synthesized in the bacterial cells in vivo and stored there, finally in the sedimentation tank. The removal of phosphorus and nitrogen is achieved through sludge discharge, A2/O system is viewed with less surplus sludge and stable operation, but with a long sludge aging time. The A2/O system flow chart is shown in Figure 2.4.

Chemical treatment, is based on the precipitation of phosphorus using metal salts. The most widely used salts are ferric and aluminum [9]. Lime as an additional resource has also been applied by many investigators. Foreign reagents are added to the wastewater in this step. These

ions react with $\text{PO}_4^{3-}\text{-P}$ and the reacted products settle out of wastewater. Then P is removed and stored in sludge. In addition, other methods have been developed, such as iron reactive filtration system and enhanced coagulation processes. These processes can achieve as low as 0.03mg/L of phosphate in effluent [9]. The chemical process can be operated in a small and compact reactor and are usually more simple and stable to operate compared to the biological process.

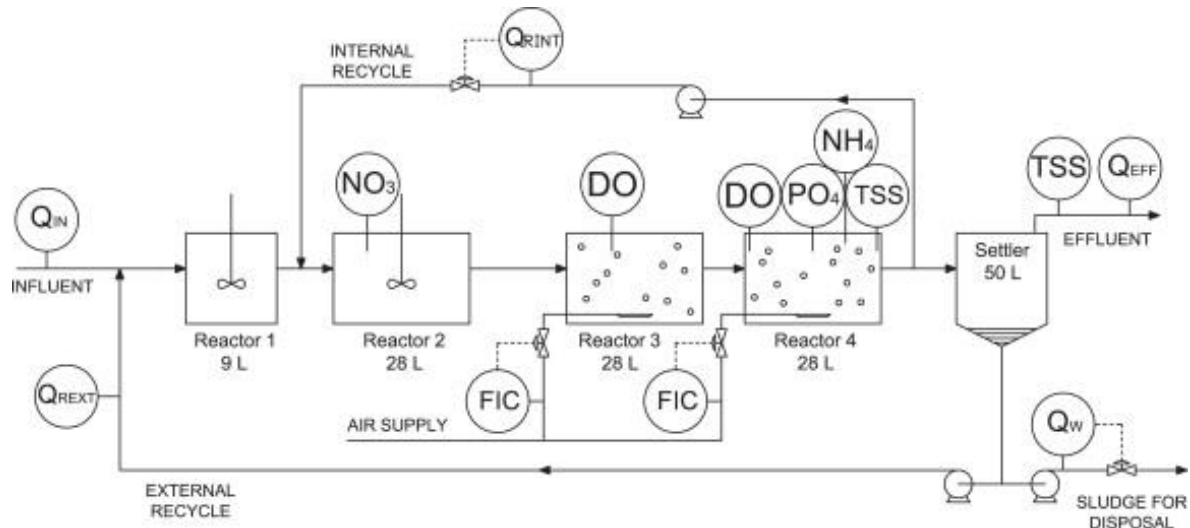


Figure 2.4 Scheme of the A2/O simulated plant for simultaneous C/N/P removal [8]

While integrated constructed wetlands are built to remove $\text{NH}_4^+\text{-N}$ and $\text{PO}_4^{3-}\text{-P}$ from wastewater, this process occupies large amount of land area. However, the removal efficiency of $\text{NH}_4^+\text{-N}$ and $\text{PO}_4^{3-}\text{-P}$ is normally low, and ammonium nitrification in saturated filtration beds is limited [21].

Other processes designed to remove $\text{NH}_4^+\text{-N}$ and $\text{PO}_4^{3-}\text{-P}$ from wastewater are sequencing batch reactors (SBRs), the PhoStrip process, response surface study and electro dialysis process, etc. In this thesis, these processes won't be mentioned in detail.

2.2. NH_4^+ and PO_4^{3-} recovery by the precipitation of magnesium ammonium phosphate

The outcome of wastewater treatment will be treated wastewater and sludge, which need further treatment. The sludge treatment goal is to reduce the volume of sludge as much as possible. The most widely employed method for sludge treatment is anaerobic digestion. In this process, a large fraction of the organic matter (cells) is broken down into carbon dioxide (CO_2) and methane (CH_4), and this is accomplished in the absence of oxygen[22]. About half of the amount is then converted into gases, while the remainder is dried and becomes a residual soil-like material. The treatment of wastewater sludge, from both primary and secondary treatment steps, consists of two main phases[22]:

- In the 1st step, sludge from primary and secondary treatments are combined and heated to a mild temperature (about body temperature) to accelerate biological conversion. The residence time here ranges from 10 to 20 days.

- In the 2nd tank, the mixture is allowed to undergo further digestion. The mixture is no longer mixed to promote separation, and the process already generates its own heat.

Settled sludge is dewatered and thickened to separate as much water as possible to decrease the volume of material. Separation method that used in IVAR Grødaland is centrifuge that can achieve 8% solid fraction. Separated water from the sludge have high N and P concentration which usually called reject water. This reject water that will receive further treatment to recover its high N and P concentration.

Recently, the most intensively studied technology for recovery of ammonium and phosphate is a crystallization process through chemical precipitate reaction among ammonium, phosphate, and magnesium in wastewater. Due to this crystallization reaction, the precipitates addicted to the inner surface of pipes and resulted in blockage. Some wastewater treatment plants have experienced this blockage problem [23]. There are experiments that conducted based on sewage from Slough STW, UK [24]. They designed and operated a precipitation reactor as shown in Figure 2.5. They found that this process was very efficient to remove PO_4^{3-} from the centrifuge liquors.

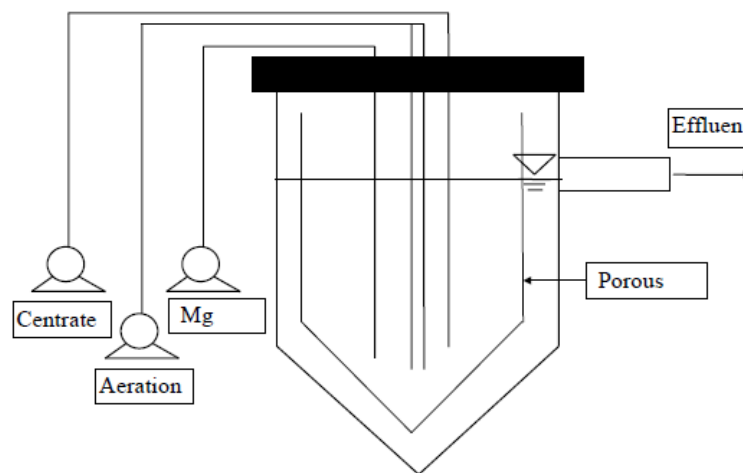


Figure 2.5 Struvite precipitation reactor's design [24]

The chemical species that may be formed in solution are mainly $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ (newberyite), $\text{MgNH}_4\text{PO}_3 \cdot 6\text{H}_2\text{O}$ (MAP, struvite), $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ (bobierrite) and $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$. Ca^{2+} is another most common cation, reacting with PO_4^{3-} to form following compounds: $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ (hydroxyapatite), $\text{Ca}_3(\text{PO}_4)_2$ (whitelockite), $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ (Brushite), CaHPO_4 (monenite), $\text{Ca}(\text{OH})_2$, $\text{Ca}_8(\text{HPO}_4)_2(\text{PO}_4)_4 \cdot 5\text{H}_2\text{O}$ (octacalcium phosphate). Furthermore, MgCO_3 (Magnesite), $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ (nesquehonite), $\text{CaMg}(\text{CO}_3)_2$ (dolomite), $\text{CaMg}_3(\text{CO}_3)_4$ (huntite), and $\text{Mg}(\text{OH})_2$ (brucite) may also be precipitated in the solution under certain conditions [14]. Some of the precipitation products, which contains NH_4^+ and PO_4^{3-} , can be used as fertilizer, such as $\text{MgNH}_4\text{PO}_3 \cdot 6\text{H}_2\text{O}$, $\text{Ca}_3(\text{PO}_4)_2$, especially $\text{MgNH}_4\text{PO}_3 \cdot 6\text{H}_2\text{O}$. Not only can this method remove NH_4^+ -N and PO_4^{3-} -P at the same time, but also recover these two nutrients in a sustainable manner. The study of this process is becoming more and more attractive.

Previous researchers have indicated that the MAP precipitation reaction could occur in different types of wastewaters as long as the concentrations of magnesium, ammonium, and

phosphate reach saturation. Most importantly, this process can be applied in industrial wastewater [25], swine manure [26], landfill leachates [15], sewage [24], and semi-conductor wastewater [27]. One experiment tested and applied MAP cakes obtained from synthetic wastewater and industrial wastewater to fertilize grass in the field [25]. Their results appraised the application of MAP as a fertilizer. Another experiment applied struvite precipitated from effluent of UASB treating poultry manure wastewater to three testing plants [26]. Their results indicated that the struvite recovered from the sludge could be used as a valuable fertilizer for agriculture. Landfill leachates have been applied to precipitate struvite in Hong Kong [15]. They found that large amount of ammonium could be crystallized by adding foreign Mg source with the pH controlled at 8.5 and 9. Another study performed with anaerobic swine lagoon effluent to precipitate struvite has proven that struvite solubility can be minimized by increasing the Mg^{2+}/PO_4^{3-} ratio with the pH value at 9 [28]. By conducting laboratory and field experiments with swine waste, the experiment found that when $MgCl_2$ (64%) was added to the waste pond, the soluble phosphorous was reduced 76% and 90% in laboratory and field experiments respectively[29].

Human urine has been studied by applying freezing-thawing method and MAP precipitation method [30]. The experimental results revealed that freezing-thawing could affect the removal of ammonium, and the removal of NH_4^+ and PO_4^{3-} was affected by the addition of MgO . Another test also worked on human urine in Nepal by fabricating his own reactor, as presented in Figure 2.6, to remove NH_4^+ and PO_4^{3-} [31]. They concluded that a low cost and high efficient reactor could be applied and fabricated in Nepal to remove NH_4^+ and PO_4^{3-} from human urine based on tests on the granulation of struvite at laboratory scale and flocculation based on five different flocculants. It can be drawn that this technology is applicable to remove NH_4^+ -N and PO_4^{3-} -P from urine, leather tanning wastewater [32]and agro-industry wastes [33].

Other reaction process or reactors have also been developed and used in order to remove NH_4^+ and PO_4^{3-} effectively and efficiently. The following reactors are applied by researchers (Shown in Figure 2.7, 2.8, and 2.9).

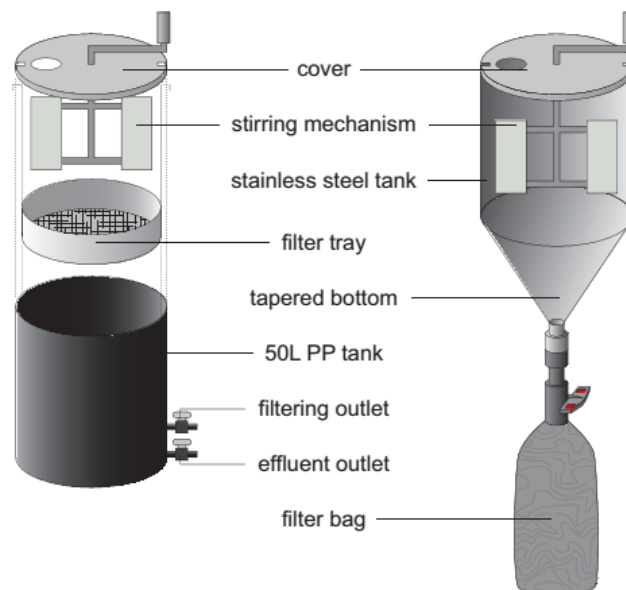


Figure 2.6 Struvite precipitation reactor [31]

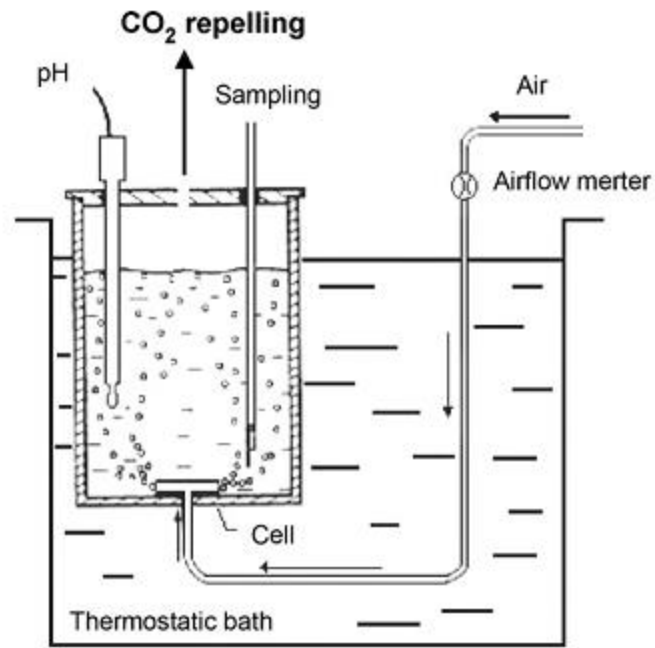


Figure 2.7 Struvite reactor with dissolved carbonate removal technique [34]

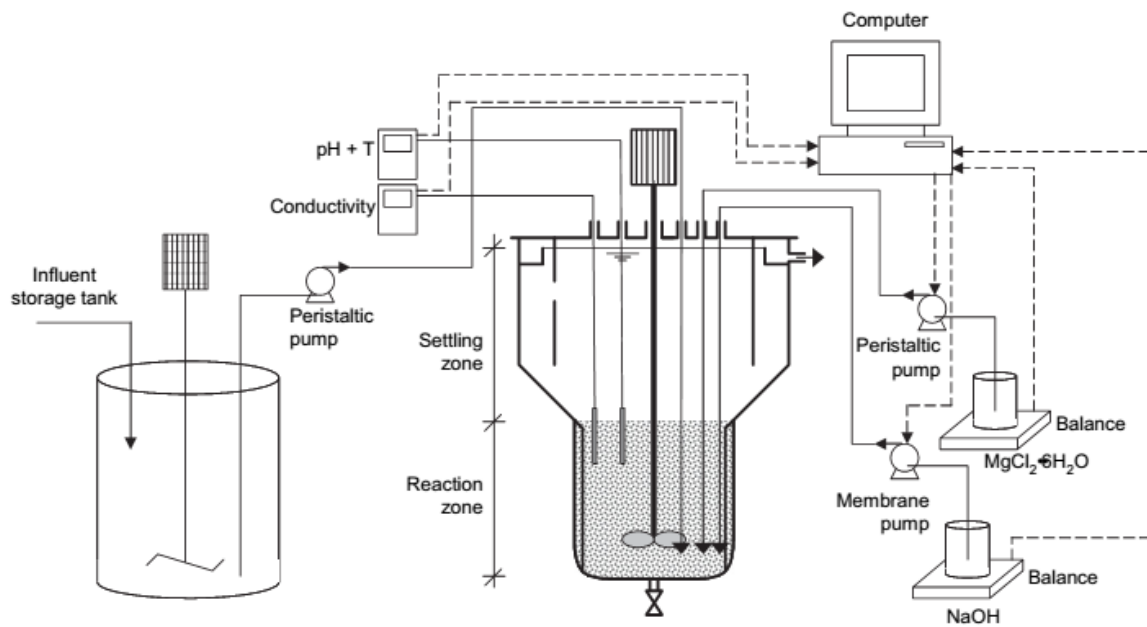


Figure 2.8 Crystallization pilot plant [35]

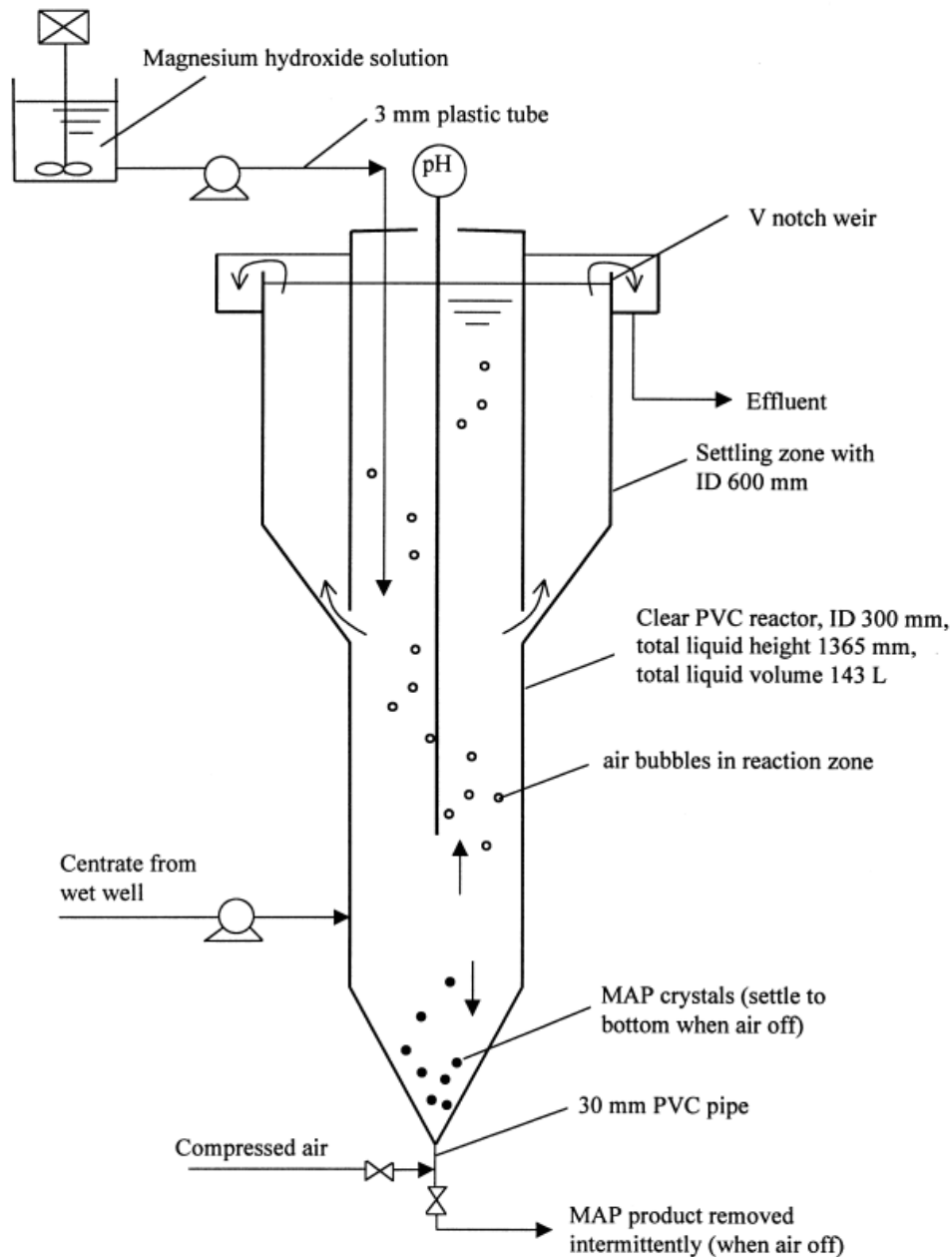


Figure 2.9 Struvite precipitation reactor [36]

2.3. Factors influencing MAP precipitation process

The principle of recovering magnesium ammonium phosphate in precipitation process can be stoichiometrically described as the following reaction equation [37]:



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

Many studies have been done to develop and operate a precipitation process by adding additional reagents at equilibrium conditions [29]. Equation 2.1 shows that the stoichiometric molar ratio of Mg^{2+} : NH_4^+ : PO_4^{3-} is 1:1:1, and this reaction is highly pH dependent. Factors

affecting this formation process are pH of the solution, the concentrations of Mg^{2+} , NH_4^+ -N and $H_nPO_4^{n-3}$

pH (n=0, 1, 2), temperature, reagent addition rate of foreign reagents, and stirring rate.

pH is a predominant operating factor which has significant impact on driving the precipitation reaction, and precipitate formation and crystallization. In order to maximize the struvite formation efficiency and purity, pH must be maintained at certain range. The effect of pH on the crystallization process has been studied by many researchers. Based on laboratory experiments, a critical pH value 5.85 was reported by [38]. At pH lower than 5.85, newberyite was precipitated first, while struvite was formed first when pH was higher than 5.85 [38]. Another experiments with landfill leachates at a molar ratio of $Mg^{2+}: NH_4^+: PO_4^{3-} = 1:1:1$ [39]. They found that the optimal pH was 9.5. NH_4^+ removal efficiency was lower at $pH < 9.5$. However, $Mg_3(PO_4)_2 \cdot 2H_2O$ and $Mg(OH)_2$ rather than struvite were crystallized when pH was higher than 9.5. By comparing results of experiments from two treatment plants, the optimum pH value for struvite precipitation was found at 8.9 and 9.25 respectively [28], they also reported that the optimum pH was not affected by the molar ratio of $Mg^{2+}: PO_4^{3-}$ and the removal was significantly affected by pH.

The optimal pH has been investigated by previous researchers for the precipitates process that the best pH was 9.6 with a range of 9-10 in their experiments[25]. In the experiment, they recognized the pH of the solution dropped immediately once the reaction happened [38]. In order to maintain the precipitation reaction in a continuous process with a stable high yield of struvite, additional alkaline needs to be added to adjust the pH. They also reported other crystals would be precipitated if the pH was too high. This result agreed well with another experiment, that found that the minimum struvite solubility was at pH 9 [40]. However, in consideration of ionic strength, reaction constant (K_{sp}) and magnesium complexes, the minimum solubility for struvite was 10.3 [41]. The optimum pH at 10.7 was also obtained by another researcher [42]. Another experiment found that a suitable pH range was 8-10 [32]. However, based on laboratory-scale experiments, pH between 9.94 and 13.26 has been confirmed by [7]. In general, high removal efficiency of PO_4^{3-} can be achieved in the range of pH between 8 and 13. This is also the benchmark for pH consideration when experiments were performed in this project.

2.3.1. Magnesium source and concentration

The effect of Mg^{2+} concentration in solution has been widely investigated. An experiment was conducted with the fixed molar ratio of NH_4^+ and PO_4^{3-} as 1:1 [39]. When the molar ratio of $Mg^{2+}: NH_4^+: PO_4^{3-}$ was increased from 1:1:1 to 1.25:1:1, the removal efficiency of ammonium increased and then dropped, which indicated that the concentration of Mg^{2+} could affect precipitation reaction, therefore the removal efficiency. This experiment compared different chemical combinations of Mg^{2+} and PO_4^{3-} , and concluded that the combination of $MgCl_2 \cdot 6H_2O + Na_2HPO_4 \cdot 12H_2O$ could lead to the highest ammonium removal [39]. Another test reported that the removal efficiency can be higher than 80% and would be increased further by increasing the $Mg/H_nPO_4^{n-3}$ (n=0, 1, 2) molar ratio [43]. Another study also found that continuous formation of struvite can be obtained when the molar ratio of magnesium and phosphate salts is either more than 0.07 M (Mg^{2+}/PO_4^{3-}) or less than 0.05 M (Mg^{2+}/PO_4^{3-}) [44]. Another result pointed out that the amount of struvite increased with an increase in magnesium

concentration under magnetic stirring and aeration [45]. In light of cost, normally a slight extra Mg^{2+} source can be added to ensure a high removal efficiency of NH_4^+ and PO_4^{3-} .

2.3.2. Ammonium concentration

There are usually sufficient NH_4^+ available in most wastewaters which are used in MAP precipitation. Thus, addition of ammonium sources will not be necessary. However, the concentration of NH_4^+ could be important in terms of struvite formation and crystallization. To investigate the effect of NH_4^+ concentration on the crystallization process for NH_4^+ recovery experiment also used a thermodynamic modelling PHREEQC program [39]. The results showed that the saturation index of MAP is affected by Mg^{2+}/NH_4^+ molar ratio and the initial NH_4^+ concentration. Generally, NH_4^+ removal is slightly complicated under neutral and/or alkaline conditions, if Mg^{2+} concentration is supersaturated. NH_4^+ would be removed in two ways, as shown in Equation 2.2 [34].

(NH_4^+) total removal =

$$(NH_4^+)$$
 removal by MAP + (NH_4^+) removal by volatilization* Equation 2.2

*volatilization of NH_4^+ is affected by increasing of pH

2.3.3. Phosphate concentration

The concentration of phosphate is also a critical parameter which affects the MAP formation process. A high concentration of phosphate would result in increasing removal efficiency of Mg^{2+} and NH_4^+ . The phosphate concentration decreases with the increase in pH and molar ratio of $Mg^{2+}:PO_4^{3-}$ [28]. However, phosphate could react with other metals, which will cause the impurity of MAP. Based on the result, the effect of phosphate concentration on the formation process still needs further study especially when magnesium concentration is kept constant [34].

2.3.4. Temperature and other parameters

In addition to pH and concentrations of Mg^{2+} , NH_4^+-N and $H_nPO_4^{n-3}$, some other operating parameters such as temperature were also studied by previous researchers. The majority of crystallization was newberyite rather than struvite when the temperature was risen from 25 °C to 37 °C [38]. Temperature affects the solubility of chemicals and reaction activities in the solution. Supersaturation [1], nature of materials [46], heavy metals, and other ions including Ca^{2+} and sulphate [15] will also have impact on the precipitation process. All these parameters need to be considered carefully when the MAP precipitation process is conducted with wastewater.

Characteristics of struvite

Struvite is a type of white or light yellow crystal that is sparingly soluble under neutral and/or alkaline conditions. It is a valuable product with slow-releasing activities. An image of a struvite crystal is shown in figure 2.10:



Figure 2.10 Picture of pure struvite crystals [8]

However, further study of MAP particles shows that the morphologies of struvite are quite different under different situations, especially when other ions co-exist. The sizes are different based on different wastewaters and different precipitation conditions. Figures 2.11, 2.12, 2.13, and 2.14 are a few of examples of struvite images presented from different researchers.

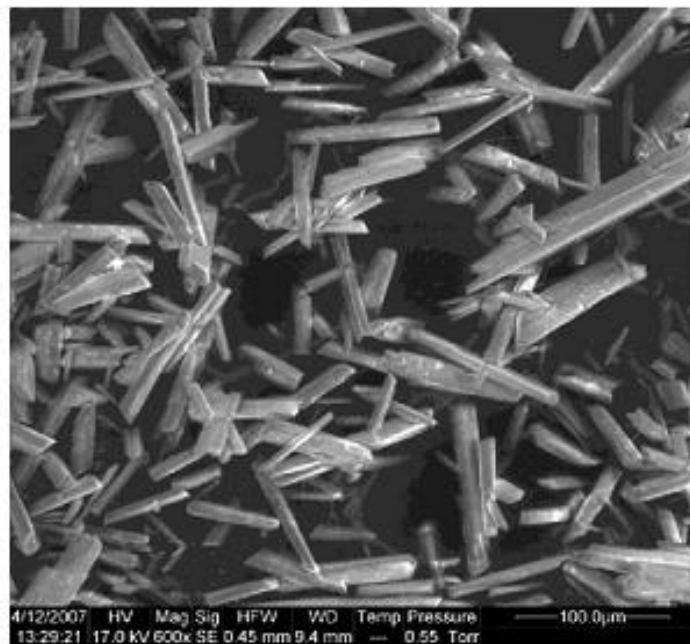


Figure 2.11 SEM Images of struvite obtained in experiment [34]

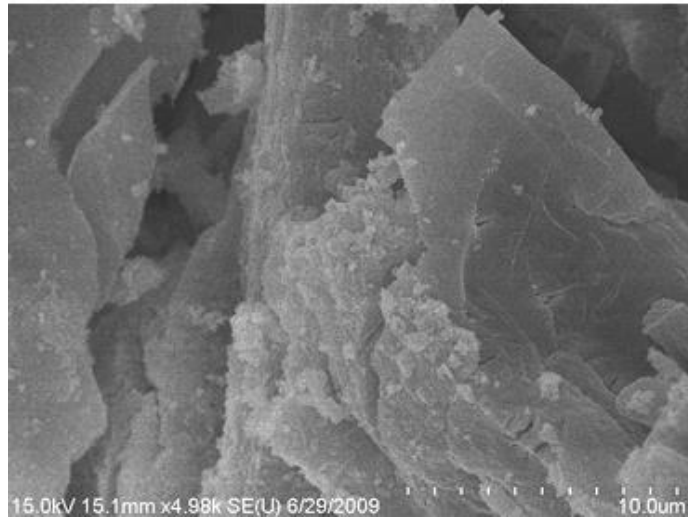


Figure 2.12 SEM Images of struvite obtained in experiment [34]

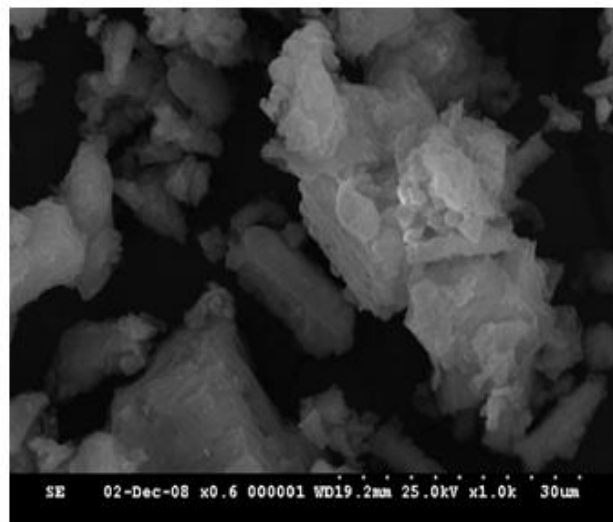


Figure 2.13 SEM Image of struvite recovered from swine wastewater [47]

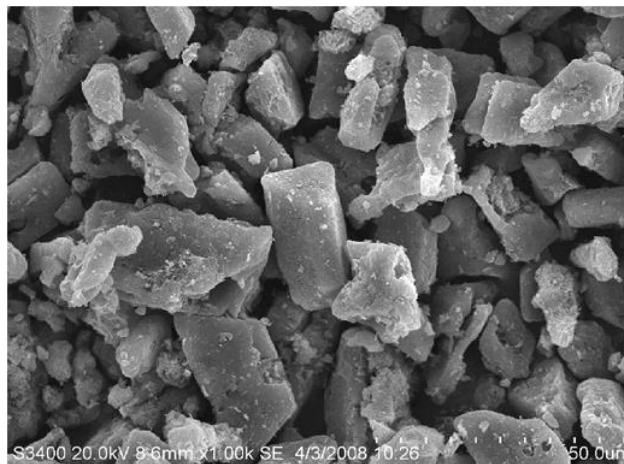


Figure 2.14 SEM Image of struvite recovered from landfill leachates [39]

It can be seen that the morphology and size of struvite obtained from different wastewater could be variable, which are affected by the initial concentration of Mg in solution [25]. An alternative approach to affect the properties of the final products can be achieved by applying optimal conditions, such as pH, concentrations of Mg^{2+} , NH_4^+ and PO_4^{3-} , stirring rate, reaction time and feeding rate [48].

2.4. Economic value of struvite

Struvite is slightly soluble under neutral and/or alkaline conditions. It can be applied as a slow releasing fertilizer with less loss of NH_4^+ and PO_4^{3-} in soil [26]. As a nitrogen and phosphorus rich fertilizer, very promising results have been obtained in the field trials to grow plants. Furthermore, the leaching loss of struvite was tested in different kind of soils in a special designed reactor, shown in Figure 2.15 [47]. They concluded that the N and P loss were very low, and struvite was a very useful and sustainable fertilizer. It also can be applied in flooded areas because it has slow-releasing properties of nutrients.

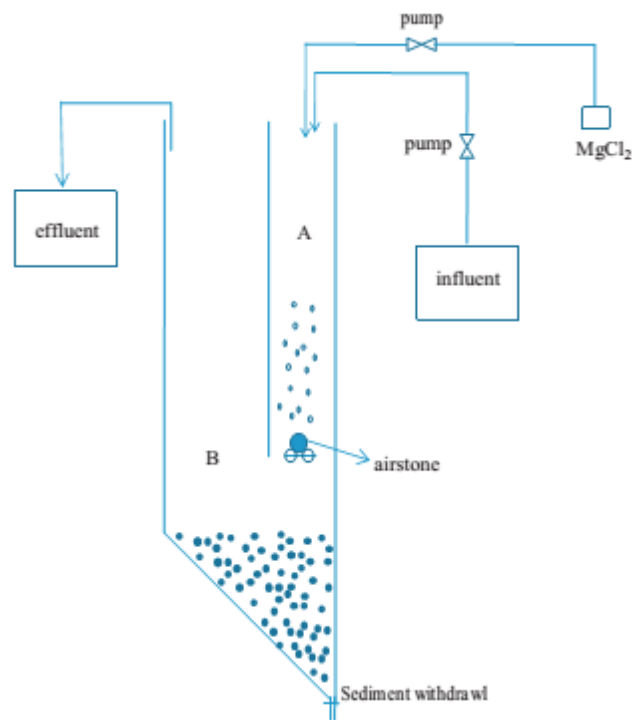


Figure 2.15 Reactor to recover NH_4^+ and PO_4^{3-} [47]

By conducting greenhouse experiments with three different categories, the result shows that struvite is fertile, economic and sustainable fertilizer to the environment [25]. In order to apply for this process, the technical feasibility and pilot plant process must be studied and tested as performed by previous researchers [49].

Currently, MAP has been produced in Unitika, Japan and sold to an American company. However, some technical parameters and process costs still need to take into more test and investigation, including sales forecast, operating cost, sales price of MAP, pricing service and financial [36], before this technology is applied as a large industrial process. [36] developed

his own reactor, as presented in Figure 2.9, to analyses the cost of this process. These factors were the economic feasibility which has not been considered widely.

The major concern in terms of cost, when applying struvite precipitation process for nutrients recovery, should be the type of Mg resource added to the process, the reagents used to adjust pH, and the maintenance of operation [50]. Struvite can be used as fertilizer and it has very promising economic and sustainable value. Hence, it can be considered for recycling to gain value to balance operational cost in struvite production. Based on the additional chemicals only and three assumptions could be made as:

- The concentration of PO_4^{3-} in the influent is 100mg/L;
- the molar ratio of Mg^{2+} : PO_4^{3-} was fixed at 1.3:1;
- pH at 9.

Estimation of the main cost with using of sodium hydroxide is presented in table 2.1. From this estimation, the process could be a challenge which needs to be conquered because the alkalinity of wastewater is normally high [24].

Another experiment reported that the cost of applying MAP precipitation process was similar to what is needed to treat 1 m³ wastewater with nitrification and denitrification process [51]. The cost estimation of applying this precipitation process and maintenance must be based on pilot scale study and the overall cost was approximately 20% higher than that of in air stripping process [52]. Moreover, labor cost and electricity cost should also be considered. The benefit of this process is not only the removal and recovery of nitrogen and phosphorous, but also contributes to the environment sustainability.

Table 2.1 Summary of costs for a full-scale plant [24]

Mg Source (mg/l)	Reactor pH	Cost of NaOH (£1000/y)	Cost of Mg (£1000/y)	Possible Income from Struvite (£1000/y)	Average P removal (min - max) %
MgCl₂	9	45	16.4	11.6	95 (94 -97)
	8.5	19	16.4	11.2	92 (91 -94)
	7.5	0	16.4	9.8	80 (71 -88)
Mg(OH)₂	8.5	0	8.2	9.5	78 (68 -91)

Any processes related to sustainability should not only consider internal impacts, but also the external impacts, such as socio-culture and economic influence [53]. Internal impacts are those factors that can be measured by monetary, such as cost for chemicals, electricity, labor, capital and operation. The external impacts are the economic level benefits, saving phosphorous resource, preventing eutrophication and land contamination, making the earth more sustainable in the long run.

After consideration of internal and external factors, it is concluded that this process is definitely worth to be promoted [53]. In addition, as fertilizer, MAP can also be used as cleaning product and other chemistry materials.

3. Material and Method

This chapter explains the laboratory-scale experiments of struvite precipitation on artificial wastewater and reject water from sludge dewatering, at IVAR Grødalana anaerobic digestion plant. The testing was done with jar tests this experiment consists of 3 parts to determine conditions for struvite formation, using artificial wastewater, reject water and addition of sea water as magnesium source. To determine the optimum procedure, pH and chemical dosage were determined from literature sources and verified in laboratory scale. All laboratory works for this master's thesis project were conducted at University of Stavanger.

3.1. Artificial wastewater

The artificial wastewater was made to have a composition of ions that form struvite at a similar level as the reject water from IVAR Grødalana. The Concentration of this artificial wastewater was not exactly the same as the wastewater, sometimes higher or lower to include the fluctuation of wastewater. The basic information used in determining the composition of the artificial wastewater was that the P: N molar ratio in reject water is around 1:5. For Each experiment 4L of artificial wastewater was made by adding K_2HPO_4 and NH_4Cl to distilled water. Concentrations of artificial wastewaters used in the tests are shown in table 3.1.

Table 3.1 Characteristic of Artificial wastewater

Test	PO ₄ -P (mg/l)	NH ₄ -N (mg/l)
Preliminary	198	503
Preliminary	198	89
Struvite test	205	504
Struvite test	409	1008
Struvite test	205	504
Struvite test	450	2500
Seawater addition	200	500

Magnesium will normally be the limiting factor for this process, and magnesium chloride ($MgCl_2 \cdot 6H_2O$) was added to precipitate struvite. The Concentration of magnesium is depending on the concentration of PO₄-P in the wastewater and the extent of P removal wanted. Addition of $MgCl_2 \cdot 6H_2O$ will be explained in the next sub-chapter.

3.2. Reject water

The Wastewater in this experiment was reject water form anaerobic digestion at IVAR Grødalana. The Concentrations of P and N are shown in table 3.2. 5 liter jars were added, 800 ml each that was used for each experiment. The Wastewater was always homogenized manually each time before used in experiment.

Table 3.2 Characteristic of Reject Water

Test	PO ₄ -P (mg/l)	NH ₄ -N (mg/l)
Preliminary	112.5	1325
Struvite test	112.5	1430
Struvite test	134	1310
Increased mixing time	148	1440
Increased mixing time	133	1440
Seawater addition	146	1580
Seawater addition	125	1340

The concentrations of N and P was used to determine Mg²⁺ dosage in each experiment.

3.3. Jar testing procedure

The Experiment were conducted in a jar testing equipment as shown in figure 3.1. In the test rapid mixing was at maximum speed (> 100 rpm) and slow mixing was at about half speed (50 rpm). Each paddle will mix the sample in 1L beaker.



Figure 3.1 Jar Test Machine

The procedure starts with preparing 4 jar of artificial wastewater, each consists of 80 ml. Before experiment started, the pH of each jar was adjusted as presented in table 3.3, NaOH 5M was used to increased pH. After pH adjustment, Mg-source was added to each jar as presented in table 3.3. Each jar then rapid mixed for 1 minute and then slow mixed for 10 minutes. While mixing proceed, pH will drop slightly, so pH meter need to control every jar so NaOH can be added to maintain designated pH. After mixing finished, sample was taken from each jar while the sample still homogenous to measure TSS, VSS, PO₄-P, NH₄-N, Mg²⁺ and for reject water test will include FSS, TS, and FS.

Table 3.3 Experiment overall plan and experimental variable condition

Date: Analysis	Test No.	Water type	pH	Mg ²⁺ -dosage (mg/l)	Mg ²⁺ -Source	NH ₄ -N (mg/l)	PO ₄ -P (mg/l)
25.01.2017	1	Artificial wastewater	Independent Variable*	124	MgCl ₂ .6H ₂ O	503	198
26.01.2017	2	Artificial wastewater	Independent Variable*	155	MgCl ₂ .6H ₂ O	89	198
01.02.2017	3	Artificial wastewater	10	Independent Variable*	MgCl ₂ .6H ₂ O	504	205
02.02.2017	4	Artificial wastewater	10	Independent Variable*	MgCl ₂ .6H ₂ O	409	1008
14.02.2017	6	Artificial wastewater	10	Independent Variable*	MgCl ₂ .6H ₂ O	504	205
21.02.2017	7	Artificial wastewater	10	Independent Variable*	MgCl ₂ .6H ₂ O	2500	450
27.02.2017	8	Reject water	Independent Variable*	96	MgCl ₂ .6H ₂ O	1325	112.5
28.02.2017	9	Reject water	10	Independent Variable*	MgCl ₂ .6H ₂ O	1430	112.5
01.03.2017	10	Reject water	10	Independent Variable*	MgCl ₂ .6H ₂ O	1310	134
02.03.2017	11	Reject water	10	Independent Variable*	MgCl ₂ .6H ₂ O	1440	148
13.03.2017	12	Reject water	10	Independent Variable*	MgCl ₂ .6H ₂ O	1440	133
15.03.2017	13	Reject water	10	Independent Variable*	Sea water	1580	146
16.03.2017	14	Reject water	10	Independent Variable*	Sea water	1340	125
17.03.2017	15	Artificial wastewater	10	Independent Variable*	Sea water	500	200

* Independent variable is an experimental variable that is being manipulated in this experiment

After the test was carried out, a sample was drawn from the beaker using a syringe for analysis. Sampling from each beaker was conducted when the sample still homogeneous. For each sample, ±50 ml of sample was taken for TS measurement. 20 -50 ml (for reject water) or 100 ml (for artificial wastewater) was draw for TSS and residual nutrient.

3.4. Preliminary test

The Optimum conditions for struvite formation was when the Mg²⁺, NH₄⁺, and PO₄³⁻ exceed the struvite solubility limit at pH around 9-11 as explained in chapter 2.3. This condition will be verified in laboratory scale using artificial wastewater and reject water.

This test conducted with artificial wastewater and reject water, so the result could compare. The test will follow the jar test procedure as explained in chapter 3.3. The independent variable in this tests was pH. which were 8, 9, 10 and 11. The optimum pH would have the highest nutrient removal efficiency.

3.5. Struvite formation test using artificial wastewater

The Results of the preliminary tests were the basis for the following tests. The tests will be conducted at pH 10 for each sample, and 5 M NaOH was used to adjust pH. The test will follow the jar test procedure as explained in chapter 3.3. The independent variable in this tests was Mg^{2+} dosage, by adding $MgCl_2 \cdot 6H_2O$. The quantity of $MgCl_2 \cdot 6H_2O$ addition depends on the PO_4 -P concentration and was added in order to achieve a molar ratio of PO_4 -P: Mg^{2+} to be 1:1; 1:2; 1:3 and 1:4. This addition will conduct after designated pH has been reached.

Several tests were conducted using the same procedure with several different concentration of artificial wastewater, as shown in table 3.1.

3.6. Struvite formation test using reject water

The tests will be conducted at pH 10 for each sample, and 5 M NaOH was used to adjust pH. The test will follow the jar test procedure as explained in chapter 3.3. The independent variable in this tests was Mg^{2+} dosage, by adding $MgCl_2 \cdot 6H_2O$. Additional sample will be needed as a control, this control jar will be treated same as normal sample, but without any addition $MgCl_2 \cdot 6H_2O$. The quantity of $MgCl_2 \cdot 6H_2O$ addition depends on the PO_4 -P concentration and was added in order to achieve a molar ratio of PO_4 -P: Mg^{2+} to be 1:1; 1:1,5; 1:2 and 1:2,5. This addition will conduct after designated pH has been reached.

Further tests were conducted using the same procedure at several different concentrations of artificial wastewater, as shown in table 3.2. Tests with varying mixing times were also performed. In the First test the slow mixing time was increased to 20 minutes, and the second test the mixing time was increased to 10 minutes while maintaining slow mixing at 20 minutes.

3.7. Struvite formation with sea water as Mg^{2+} source

In these tests seawater replaced magnesium chloride as Mg source in the struvite precipitations. The results from the experiments with artificial wastewater and reject water were the base for this experiment. The procedure used in this test is the same as in the previous chapters.

The addition of seawater was based on %-volume. Addition was not by molar comparison to compare the removal effectiveness and sea water volume that added. The Addition of seawater was, 5%, 10%, 15% and 20% of the volume of the respectable jar. Mg in seawater was also determined in order to know approximate Mg addition.

This sample was done 3 times, 2 test using reject water, 1 test using artificial wastewater. The character of the water sample was presented in table 3.2 and table 3.1.

3.8. Analytical Methods

Before analysis, it is important to make sure that the sample to be analyzed was homogenized. Commonly, washing and/or diluting of samples were needed in some of the analytical procedures. In this study, diluting/washing water used was deionized water of 18 M Ω -cm resistances or higher (DI water type 1).

3.8.1.pH and Conductivity Measurement

pH and conductivity were measured using Phenomenal 221 (662-1161). The probe was immersed into the samples until the value was constant. All pH meters were calibrated with buffer standard solutions (4.01 and 7.00) regularly before the experiment started.

3.8.2.TS (Total Solid) and VS (Volatile Solid) measurement

TS measurements were done as a control value for the TSS measurements, according to SM 2540 B. This measurement was done using oven at 105°C for 24 hours minimum. The procedure started with drying the ceramic bowls at 105°C for about 30 minutes to ensure they were completely dry. Then the bowl was weighted at an analytical balance (two decimals) and stored in the desiccator to ensure no moisture on the bowl. Sample was added corresponding to about 2/3 of the volume of the bowl (500 ml), and bowl + sample was weighted. The sample was dried at 105°C for minimum 24 hr, and bowl + solids was weighted.

To determine volatile solids, the bowl + sample was combusted at 550°C for minimum 1 hr. Let the combusted sample cool down in desiccator and weigh. The volatile solids have combusted and the remaining solids are total inorganic solids or total fixed solid (FS). This test following SM 2540 E.

3.8.3.TSS and VSS measurement

TSS measurements were conducted regularly to determine struvite formation, following SM 2540 D. As struvite forming in the solution, the amount of TSS will also increase and the difference of TSS from the beginning and the end is assumed to correspond to the amount of struvite. TSS measurement conducted by filtering the sample and dry the filter at 150°C for minimum 2 hours. TSS value is the amount of solid that stuck in the filter.

The procedure of TSS measurement was started with drying the filters at 105°C for at least 15 minutes prior to weighing to ensure they are completely dry. In TSS measurement we used GF/C glass-fibre filters with 1 µm pore-size, Whatman Glass Microfiber Filter CAT No. 1822-047.

The dried filter was weighted on a balance with 4 decimals (0.0000 g) and kept in the desiccator to ensure no moisture attach to the filter. An appropriate sample volume was measured with a graduated cylinder and left to settle for a while, before filtration. The clarified liquid was filtered first and the concentrated sludge is added at the end. In this way the filtering procedure goes much faster and the result becomes more correct. A small amount of distilled water is used to flush out any solids left in the cylinder. If any analysis is to be done on the filtered sample, then the volume of added distilled water must be noted, in order to calculate the dilution of the filtrate.

After filtration, the filter was dried at 105°C for at least 2 hours and the filtered sample was preserved and stored for further analysis. After drying the filter was cooled in a desiccator, and then weighed. If the filter is exposed to air for a longer period, moisture in the air may change its weight.

For determination of VSS, the filters are combusted in an oven at 550°C for an appropriate period (usually 30 minutes). During this period all organic compounds are burned off and the

remaining solids on the filter paper are inorganic or fix suspended solids (FSS). Weighing the filter will provide the fractions of the organic and inorganic solids, according, respectively. This procedure is according to SM 2540 F.

3.8.4. PO₄-P and NH₄-N measurement

Phosphorus (PO₄-P) and Nitrogen (NH₄-N) measurement were conducted to investigate the remaining concentration after struvite formation. For analysis of PO₄-P and NH₄-N spectroquant test kits were used. The PO₄-P tests kit was Merck Spectroquant® with Product Number 114729 (0.5 – 25.0 mg/l PO₄-P). The NH₄-N kits were Merck Spectroquant® Product Number 114544 (0.5 - 16.0 mg/l NH₄-N). Both PO₄-P and NH₄-N measured in spectrometer (Spectroquant Pharo 300).

The procedures of PO₄-P measurements were started with adding 1 ml filtered sample into the test vial. Then 5 drops of reagent P-2K and 1 dose of reagent P-3K were added to the test vials and mixed vigorously. Then a reaction time of 5 minutes, before reading the vial in a spectrometer to determine the concentration.

The procedures of NH₄-N measurements were started with adding 0.5 ml filtered sample into the test vial. Then 1 drop of reagent N-1K were added to the test vials and mixed vigorously. The reaction time is 15 minutes before placed in a spectrometer to determine the concentration.

3.8.5. Mg²⁺ Measurement

The Mg²⁺ was analyzed on an atomic absorption instrument (AAS), BERGMAN AA-6200 Shimadzu. The samples were preserved with 1 M HNO₃ and stored before analysis. Due to the limited range of the AAS, 0-0.5 ppm, the samples had to be diluted between 100 and 1000 times in order to fit to the range.

The procedure of Mg²⁺ measurement was started with diluting the preserved samples. Before measuring the sample, the AAS was calibrated with standard solutions consisting of 0 M, 0,1 M, 0,25 M, 0,4 M, 0,5 M Mg²⁺ solutions. For every 5 sample measurements the AAS had to be zero calibrated. Operation of this machine had to follow the specific procedure that can be acquired in the laboratory.

4. Result

The Results obtained from the experiments are presented in this chapter. The test was conducted from January 25th to March 17th 2017. This chapter is divided into six sub-chapters: (a) preliminary test on struvite formation in artificial wastewater; (b) struvite formation in artificial wastewater; (c) preliminary test on struvite formation in reject water; (d) struvite formation in reject water; and (e) struvite formation using seawater as Mg²⁺ source (f) Struvite and nutrient removal molar comparison. The presented data and figures have been summarized while the collected raw data are included in the Appendixes. The overall plan and variable conditions for the test are shown in table 4.1.

Table 4.1 Experiment overall plan and experimental conditions

Chapter	Date: Wastewater Sampling	Date: Analysis	Changed Variable(s)	Water sample
4.1	-	25.01.2017	pH	Artificial wastewater
	-	26.01.2017		
4.2	-	01.02.2017	PO ₄ -P: Mg ²⁺	Artificial wastewater
	-	02.02.2017		
	-	14.02.2017		
	-	21.02.2017		
4.3	27.02.2017	27.02.2017	pH	Reject water
4.4	22.02.2017	27.02.2017	PO ₄ -P: Mg ²⁺	Reject water
	28.02.2017	27.02.2017	PO ₄ -P: Mg ²⁺ +mixing time	Reject water
	28.02.2017	02.03.2017		
4.5	08.03.2017	13.03.2017	Seawater	Reject water
	13.03.2017	15.03.2017		Reject water
	13.03.2017	16.03.2017		Artificial wastewater
	-	17.03.2017		

4.1. Preliminary test of struvite formation in artificial wastewater

This preliminary test was conducted to find the optimum pH for struvite formation using artificial wastewater. The characteristics of artificial wastewater, as presented in table 3.1, are based on literature [7] (and expected concentrations in reject water) that stated the minimum concentration of struvite to form are 27 mg/l Mg²⁺, 20 mg/l NH₄⁺ and 106 mg/l PO₄³⁻ which were in the molar ratio of 1: 1: 1 [7]. This was deemed to be the approximate minimum concentration required for precipitation to occur. The struvite formation, PO₄-P, NH₄-N and Mg²⁺ removal efficiency is presented in figure 4.1 below.

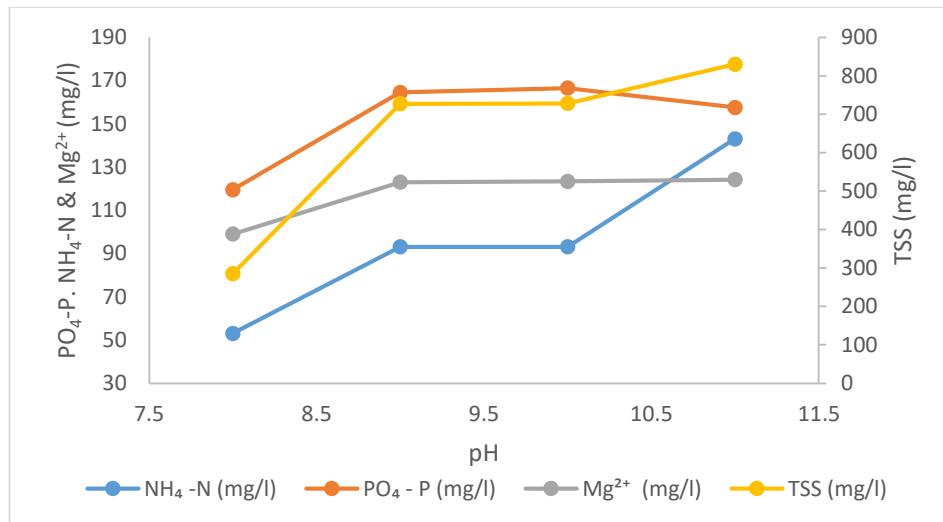


Figure 4.1 TSS production, PO₄-P, NH₄-N and Mg²⁺ removal at different pH in artificial wastewater

Table 4.2 PO₄-P, NH₄-N and Mg²⁺ removal and TSS production at different pH in artificial wastewater

pH	NH ₄ -N (moles)	PO ₄ -P (moles)	Mg ²⁺ (moles)	TSS production (moles)
8	2.9	3.9	4.1	2.1
9	5.2	5.3	5.1	5.3
10	5.2	5.4	5.1	5.3
11	7.9	5.1	5.1	6.0

In this present research, artificial wastewater was used as control for struvite formation in reject water. It was designed that TSS produced in the artificial wastewater test was struvite and assumed there was no competing reaction. Figure 4.1 shows that the highest TSS was at pH 11 by 830 mg/l, besides, 728 mg/l and 727 mg/l in pH 9 and 10 respectively. Table 4.2 shows that there was no more removal of PO₄-P and Mg²⁺ at pH 11, means no more struvite formed. Increased TSS probably occurred because precipitation of carbonates at high pH.

At pH 9 and 10, the amount of TSS or struvite produced in table 4.2, 5.3 moles for pH 9 and 10, positively correspondence with removal PO₄-P which also removed 5.3 moles and 5.4 moles in respective pH. The amount of NH₄-N and Mg²⁺ that reacted with PO₄³⁻ were also close to the amount of removed PO₄-P, which are 5.2 moles of NH₄-N and 5.1 moles Mg²⁺. At pH 11, significant increasing in NH₄-N removal not related to struvite production but probably due to NH₃ degassing.

From the result of this test, the optimum pH for removing the nutrient would be at pH 10, otherwise the highest struvite production occurred at pH 11. To determine the optimum pH, another test was conducted only using pH 10 and 11. The characteristic of this artificial wastewater have been presented in table 3.1 and the results of this test is presented in table 4.3 below. There was slightly increase of Mg²⁺ removal concentration. However, based on the

table 4.3, it shows that PO_4 -P and NH_4 -N removal concentration as well as struvite production were higher at pH 10.

Table 4.3 TSS production, PO_4 -P, NH_4 -N and Mg^{2+} removal at smaller range of pH at artificial wastewater

pH	NH_4 -N (mg/l)	PO_4 -P (mg/l)	Mg^{2+} (mg/l)	TSS (mg/l)
10	43	183	144	837
11	25	125	150	764

From the result, it was considered that the optimum pH to conduct struvite formation test is at pH 10.

4.2. Struvite formation in artificial wastewater

Based on the result of preliminary test, further struvite formation test was conducted at pH 10. The first test was using the same concentration as the preliminary test. This test was conducted to compare the effect of various Mg^{2+} concentrations on struvite formation in artificial wastewater. The amount of added Mg^{2+} was relative to the concentration of PO_4 -P: Mg^{2+} at molar ratios of Mg: P from 1 to 4, corresponding to Mg concentrations from 161 to 644 mg/l. The result is shown in figure 4.2. The initial concentration of artificial wastewater has been presented in table 3.1

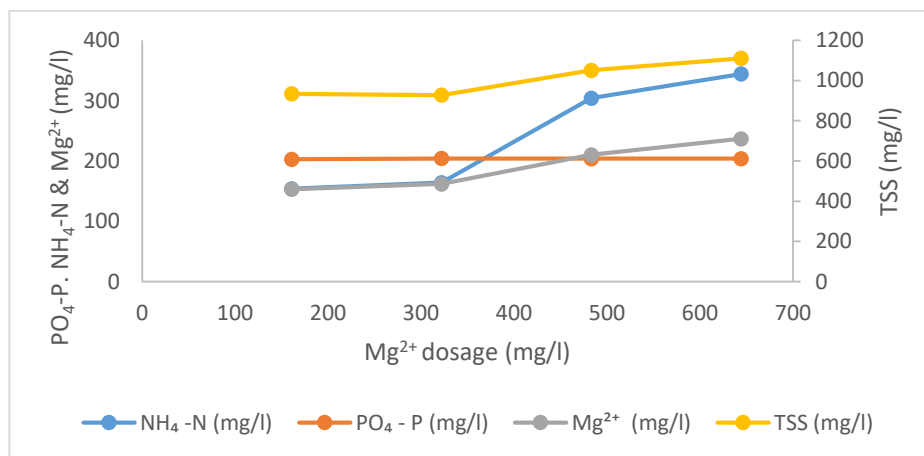


Figure 4.2 TSS production, PO_4 -P, NH_4 -N and Mg^{2+} removal at multiple Mg dosage in artificial wastewater

Table 4.4 PO_4 -P, NH_4 -N and Mg^{2+} removal and TSS production at multiple Mg dosage in artificial wastewater

Mg^{2+} dosage (moles)	NH_4 -N (moles)	PO_4 -P (moles)	Mg^{2+} (moles)	TSS production (moles)
1	8.6	6.5	6.3	6.8
2	9.1	6.6	6.7	6.8
3	16.9	6.6	8.6	7.7
4	19.1	6.6	9.7	8.1

Struvite production, as the figure 4.2 shows, increased as the dosage of Mg^{2+} increased to 3 and 4 moles. The production at 1 and 2 moles added Mg^{2+} showed similar quantities since the

removal of PO_4^{3-} was complete, as shown in table 4.4 that $\text{PO}_4\text{-P}$ removal remain constant after 2 moles Mg^{2+} addition. The removal of $\text{PO}_4\text{-P}$ and Mg^{2+} , which was 6.6 and 6.7 moles respectively, was corresponding to the amount of TSS precipitate as struvite at 2 moles dosage, which was 6.8 moles. Unlike at 1 moles Mg^{2+} dosage, the amount of Mg^{2+} removed, 6.3 moles, was lower compared to $\text{PO}_4\text{-P}$ removal and TSS, which were 6.5 moles and 6.8 moles respectively

The increased TSS at 3 and 4 moles Mg^{2+} dosages, which were 7.7 and 8.1 moles respective to Mg^{2+} dosage, could be consist another crystal besides struvite because there was no more PO_4^{3-} that could react with Mg^{2+} . This TSS could be crystal that consists of Magnesium since the amount of Mg^{2+} removed at 3 and 4 moles dosage were higher compared to $\text{PO}_4\text{-P}$ removal and TSS production.

The test continued with doubling the nutrient concentrations in the artificial wastewater. The characteristic of the artificial wastewater was presented in table 3.1. The variation of Mg^{2+} dosage was the same as in the first test, 1, 2, 3 and 4 moles of Mg^{2+} per mole $\text{PO}_4\text{-P}$. The results of this test is presented in figure 4.3 below. Figure 4.3 shows that the TSS production had different pattern compared to the previous test, as it decreased when the Mg^{2+} dosage increased from 1 to 2 moles. The difference in TSS was, however, so small that it was within the uncertainty of the analytical methods. As the Mg^{2+} dosage continue increased, TSS also increased until reach the highest TSS concentration at highest Mg^{2+} dosage. But TSS at 4 moles Mg^{2+} might not consists of struvite because there was no more PO_4^{3-} to form struvite.

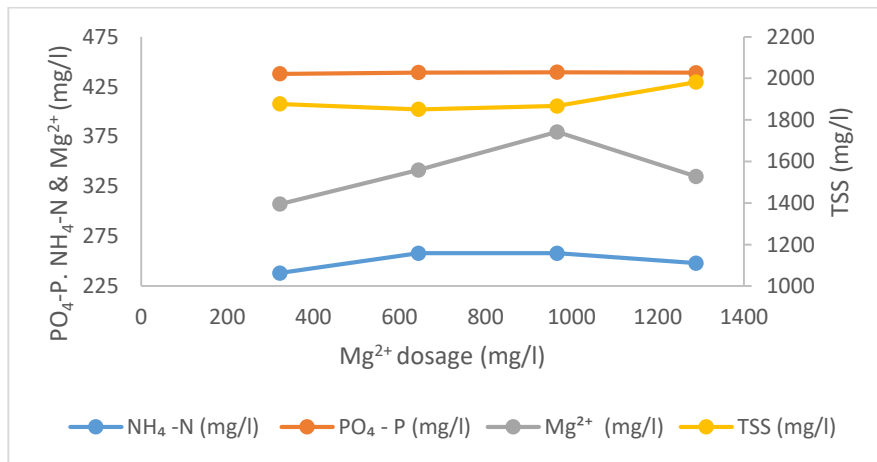


Figure 4.3 TSS production, $\text{PO}_4\text{-P}$, $\text{NH}_4\text{-N}$ and Mg^{2+} removal at multiple Mg dosage in artificial wastewater

Table 4.5 $\text{PO}_4\text{-P}$, $\text{NH}_4\text{-N}$ and Mg^{2+} removal and TSS production at multiple Mg dosage in artificial wastewater

Mg²⁺ dosage (moles)	NH₄-N (moles)	PO₄-P (moles)	Mg²⁺ (moles)	TSS production (moles)
1	13.2	14.1	12.6	13.7
2	14.3	14.2	14.0	13.5
3	14.3	14.2	15.6	13.6
4	13.8	14.2	13.8	14.4

Table 4.5 shows that at 2 moles Mg^{2+} dosage PO_4 -P, NH_4 -N and Mg^{2+} removal had positive corresponding to TSS production that resulting struvite. Moles ratio of each parameter removed have the same value, corresponding to struvite formation theory. The amount TSS itself was 0.7 moles lower than PO_4 -P removal, this could be happened due to analytical error at TSS measurement.

At 4 moles Mg^{2+} dosage, TSS value have increased without any increasing in PO_4 -P and NH_4 -N. TSS at 4 moles Mg^{2+} dosage could be deviate because analytical error in TSS measurement. The amount of Mg^{2+} removal that increased at 3 moles dosage and decreased at 4 moles dosage could be happened due to dilution factor that very high when measured Mg^{2+} in AAS.

To verify the NH_4 -N results of the first test, it was decided to repeat the first test, the same characteristic as presented in table 3.1. The results of this test is presented in figure 4.4. Struvite production in this test showed almost the same result as the first test, although the production at each Mg-dosage was slightly lower than the first test and the increase at the highest dosage was more linear compared to the first test.

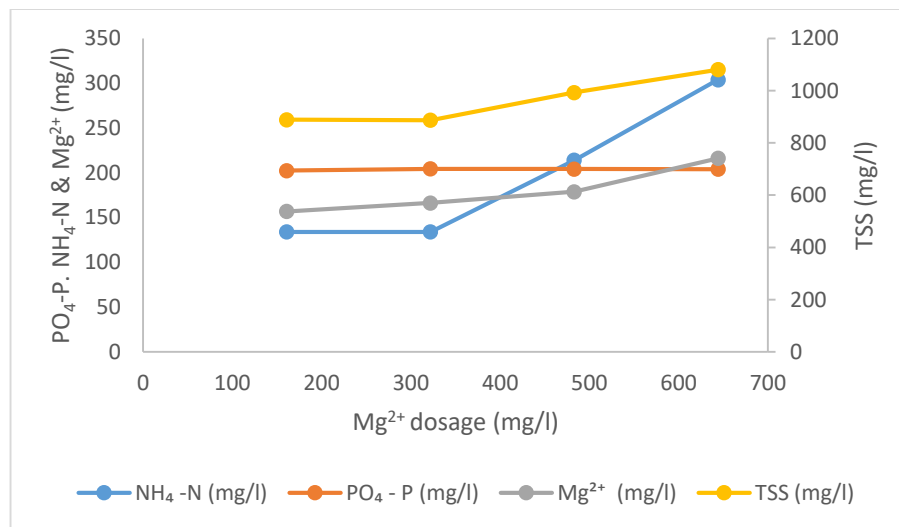


Figure 4.4 TSS production, PO_4 -P, NH_4 -N and Mg^{2+} removal at multiple Mg dosage in artificial wastewater

Table 4.6 PO_4 -P, NH_4 -N and Mg^{2+} removal and TSS production at multiple Mg dosage in artificial wastewater

Mg ²⁺ dosage (moles)	NH ₄ -N (moles)	PO ₄ -P (moles)	Mg ²⁺ (moles)	TSS production (moles)
1	7.4	6.5	6.5	6.5
2	7.4	6.6	6.8	6.5
3	11.9	6.6	7.4	7.2
4	16.9	6.6	8.9	7.9

PO_4 -P removal efficiency has shown the same result as the previous test, as it effectively removed as shown in table 4.6, all Mg^{2+} dosage shows constant 6.6 moles PO_4 -P removal. At 1 moles Mg^{2+} dosage, the PO_4 -P removal, which was 6,5 moles, was slightly lower than other Mg^{2+} dosage. This slight difference means that PO_4 -P already removed completely between 1

to 2 moles Mg^{2+} dosage. Table 4.6 shows that TSS at 1 and 2 moles Mg^{2+} dosage contained struvite because the amount of TSS produced positively correspond with PO_4 -P and Mg^{2+} removal.

As Mg^{2+} removal increased at 3 and 4 moles Mg^{2+} dosage, the amount of TSS also increased, but without any increased PO_4 -P removal. This means that TSS not only consisted of struvite but also other crystal such as magnesium carbonate. Removal of NH_4 -N showed higher molar concentration at every Mg^{2+} dosage, this means some parts of NH_4^+ was removed as struvite and other parts removed as NH_3 because of high pH.

At this point, the result showed that the PO_4 -P was completely removed between 1 and 2 moles and the amount of TSS was corresponding to PO_4 -P removal at 1 and 2 moles Mg^{2+} dosage. TSS became vary as Mg^{2+} dosage increased. To see the effect of high initial concentration of PO_4^{3-} , the test continued with the increasing of all parameter concentration until the same as reject water characteristic as informed, which is 2500 mg/l N and 450 mg/l P as presented in table 3.1.

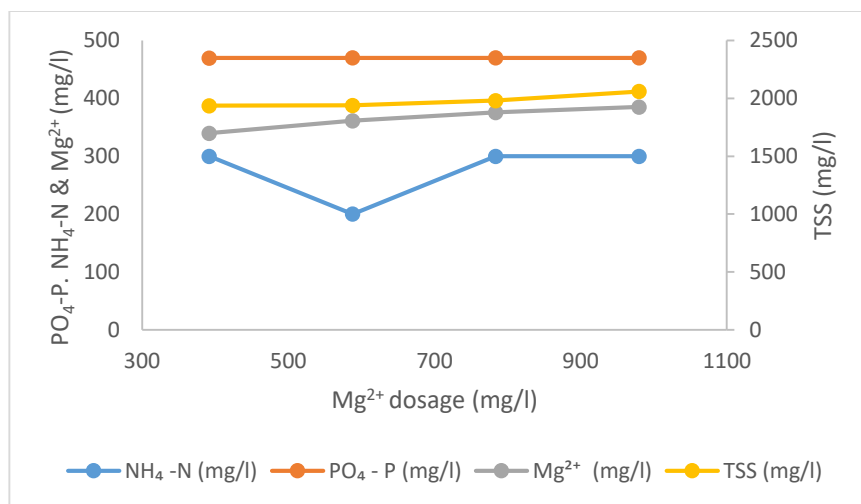


Figure 4.5 TSS production, PO_4 -P, NH_4 -N and Mg^{2+} removal at multiple Mg dosage in artificial wastewater

Table 4.7 PO_4 -P, NH_4 -N and Mg^{2+} removal and TSS production at multiple Mg dosage in artificial wastewater

Mg^{2+} dosage (moles)	NH_4 -N (moles)	PO_4 -P (moles)	Mg^{2+} (moles)	TSS production (moles)
1	16.7	15.2	14.0	14.1
2	11.1	15.2	14.9	14.1
3	16.7	15.2	15.5	14.4
4	16.7	15.2	15.8	15.0

As shown in figure 4.5, TSS production was doubled as expected. This means that the same process in previous test happened in this test. As shown in table 4.7 TSS production at 1 mole had more than twice of value as previous test, which was 14,1 moles, the same as TSS at 2

moles Mg^{2+} dosage, and had positive correspondence as PO_4-P was completely removed and the Mg^{2+} removed had the same amount as TSS.

At 3 and 4 moles Mg dosage, the amount of TSS was still lower than PO_4-P removal, but the amount of Mg^{2+} removed was higher than PO_4-P removal, which were 15,2 and 15.8 moles to respective Mg^{2+} dosage. The difference between Mg^{2+} and PO_4-P molarity might doubt the TSS consists purely struvite. This assumption was also applied at 2 moles Mg^{2+} dosage, as NH_4-N removal had lower concentration compare to other parameter.

Removal of NH_4-N showed higher molar concentration at every Mg^{2+} dosage except at 2 moles Mg^{2+} dosage, this means some parts of NH_4^+ was removed as struvite and other parts removed as NH_3 due to high pH.

Because the inconsistent result of NH_4-N , it was considered to test the spectrophotometer instrument with a series of NH_4-N solution with known concentrations within the range of 0.5 – 16 mg/l NH_4-N concentration. The result of this test is shown in the figure 4.6 below.

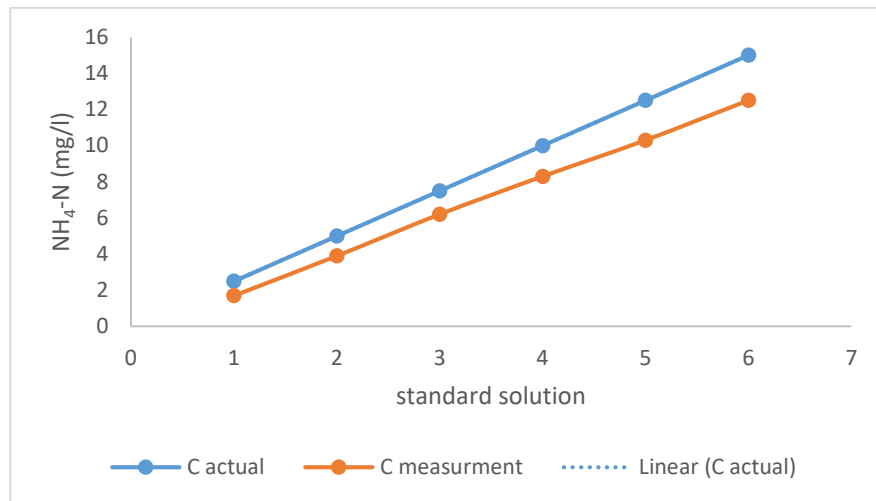


Figure 4.6 Spectrophotometer reading with standard solution

As shown in the figure 4.6, the spectrophotometer reading deviate from the actual concentration by around 20%. And the higher the concentration, the error also was higher, although only a slight increase.

4.3. Preliminary test of struvite formation in reject water

The optimum pH for this test was already known from previous test, pH 10, but in order to verify the data this test was conducted. The test was conducted using reject water from IVAR Grødaland, as shown in overall plan in table 4.1. As the reject water was already at pH 8.5, so the pH variations were 8.5, 9, 10 and 11. Reject water sample already had its original TSS which have been subtracted from the measured TSS resulting the amount of TSS as produced struvite. All results data and calculation are presented in appendix. The initial concentration of reject water already presented in table 3.2 The result of this test is presented in figure 4.8.

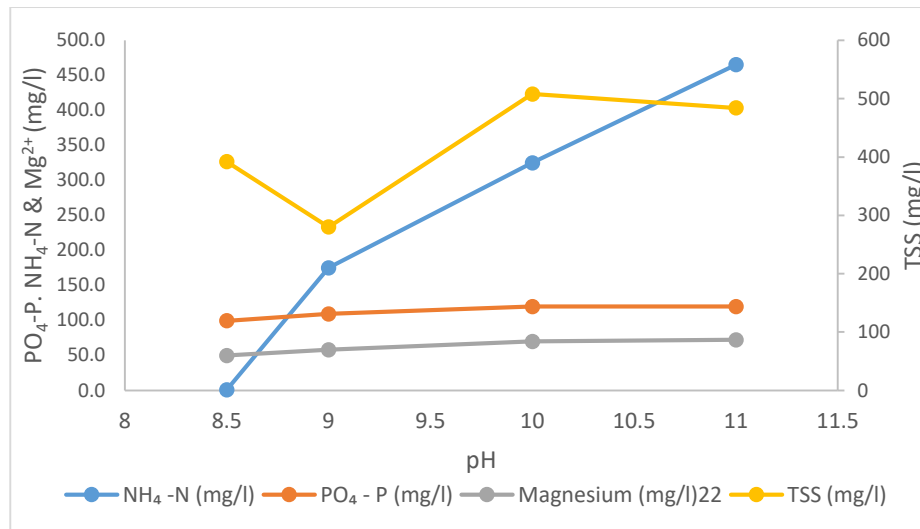


Figure 4.7 TSS production, PO₄-P, NH₄-N and Mg²⁺ removal at different pH in reject water

Table 4.8 PO₄-P, NH₄-N and Mg²⁺ removal and TSS production at different pH in reject water

pH	NH ₄ -N (moles)	PO ₄ -P (moles)	Mg ²⁺ (moles)	TSS production (moles)
8.5	0.0	3.2	2.1	2.9
9	9.7	3.5	2.4	2.0
10	18.1	3.9	2.9	3.7
11	25.8	3.9	3.0	3.5

As shown in figure 4.7, struvite production showed the highest production occurred at pH 10, although there was an odd result at pH 9 (probably analytical error). From the previous tests, struvite production at pH 9 were always higher than pH 8. From a nutrient removal aspect, pH 10 and 11 removed most of the nutrient. Table 4.8 shows that the highest PO₄-P removal was occurred at pH 10 and 11 and the amount of Mg²⁺ removed were not as high as PO₄-P removal, which were 2.9 and 3.0 moles to respected pH. TSS production at pH 10 and 9 also lower than PO₄-P removal but higher compared to Mg²⁺ removal. This means that produced TSS could consist of struvite and another solid consist of P, because there was not enough Mg²⁺ to react with PO₄³⁻ to form struvite.

At 2 moles of Mg²⁺ dosage the amount of TSS was lower compared to PO₄-P and Mg²⁺ dosage. This means that TSS consisted of struvite and PO₄-P removed in another form. NH₄-N removal had much higher removal concentration compared to other parameters. This means small amount of NH₄-N removed would form struvite and the rests were removed as NH₃ due high pH. The 0 value of NH₄-N at pH 8.5 clearly because if error in NH₄-N measurement.

Based from the result it was decided to use pH 10 for the remaining tests.

4.4. Struvite formation in reject water

Based from the preliminary result, the pH for further tests were conducted at pH 10. The first test was conducted with changing the dosage of Mg²⁺. Based on the result of testing with

artificial wastewater, the dosage of Mg^{2+} was focused in a small range, around 1 to 3 moles Mg^{2+} . The test was then conducted at 1, 1.5, 2 and 2.5 moles of Mg^{2+} dosage. Reject water sample already had its original TSS which have been subtracted from the measured TSS resulting the amount of TSS as produced struvite. All results data and calculation are presented in appendix. The characteristic of the initial reject water already presented in table 3.2. The results of this test is shown in figure 4.8.

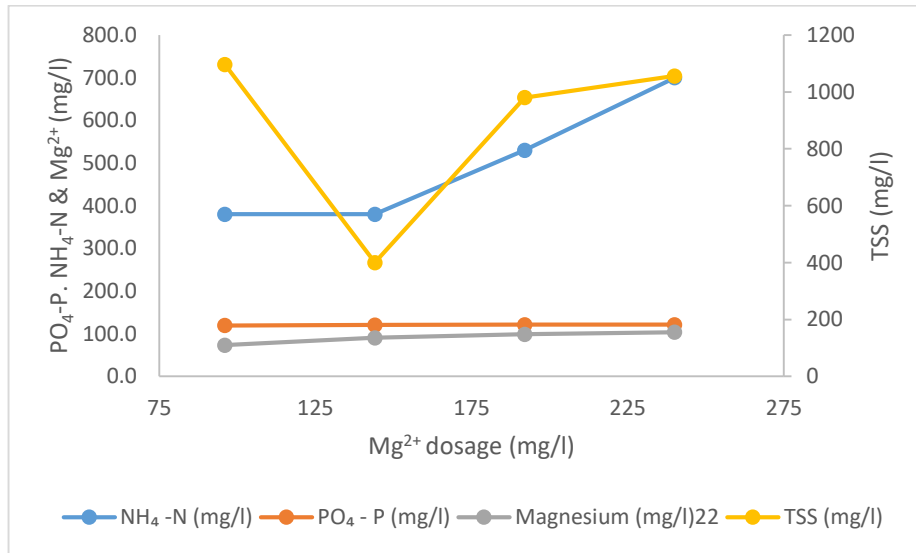


Figure 4.8 TSS production, PO_4 -P, NH_4 -N and Mg^{2+} removal at multiple Mg dosage in reject water

Table 4.9 PO_4 -P, NH_4 -N and Mg^{2+} removal and TSS production at multiple Mg dosage in reject water

Mg²⁺ dosage (moles)	NH₄-N (moles)	PO₄-P (moles)	Mg²⁺ (moles)	TSS production (moles)
1	21.1	3.8	3.0	8.0
1.5	21.1	3.9	3.7	2.9
2	29.4	3.9	4.1	7.1
2.5	38.9	3.9	4.3	7.7

A mistake happened with the TSS measurement in this test. The filter was affected by dust and moisture as the vacuum desiccator suddenly was opened. This mistake gave an odd result for struvite measurement as shown on figure 4.8.

Based on table 4.9, PO_4 -P have been completely removed at all Mg^{2+} dosage. This means the increasing Mg^{2+} removal at 2 and 2.5 moles Mg^{2+} resulting another crystal besides struvite. NH_4 -N removed was much higher compared to other parameters might be removed in 2 ways, 3.9 moles NH_4 -N removed as struvite and the rests were removed as NH_3 due to degassing to stabilize the pH.

To verify the data, the first test was repeated, but with a fresh sample of reject water. The characteristic of the reject water was slightly different as shown in table 3.2. The results are shown in figure 4.9. The struvite production showed the same pattern as the first test. The

difference was, the productions in this test were lower in every variant dosage. The highest production occurred at 2 moles Mg^{2+} dosage and the lowest occurred at 1.5 moles Mg^{2+} dosage. And unlike the first test, the production was slightly decreased at the highest dosage.

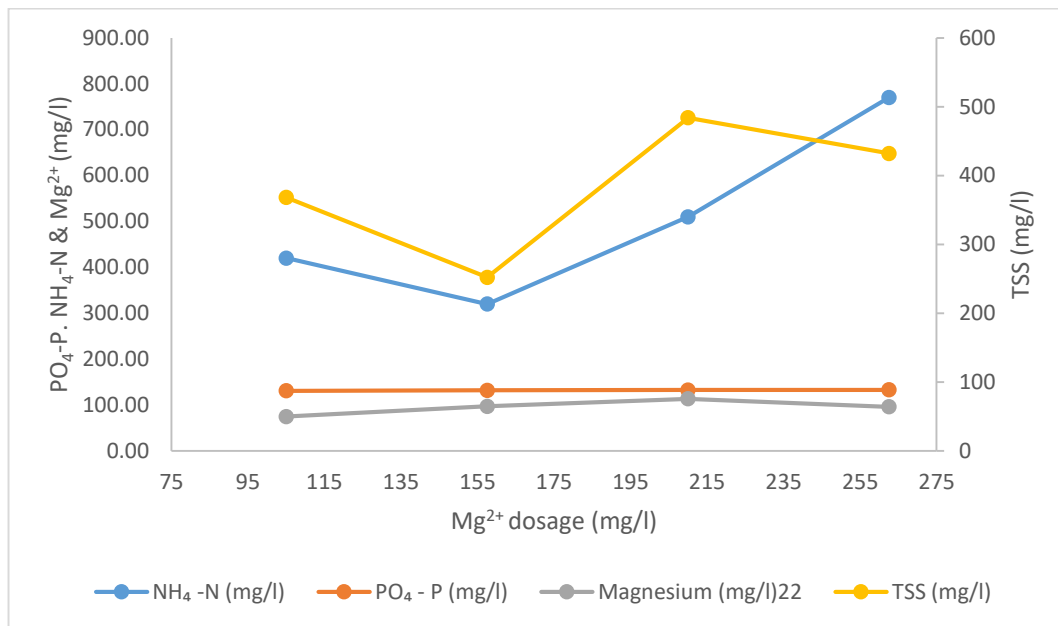


Figure 4.9 TSS production, PO_4 -P, NH_4 -N and Mg^{2+} removal at multiple Mg dosage in reject water

Table 4.10 PO_4 -P, NH_4 -N and Mg^{2+} removal and TSS production at multiple Mg dosage in reject water

Mg²⁺ dosage (moles)	NH₄-N (moles)	PO₄-P (moles)	Mg²⁺ (moles)	TSS production (moles)
1	23.3	4.2	3.1	2.7
1.5	17.8	4.3	4.0	1.8
2	28.3	4.3	4.7	3.5
2.5	42.8	4.3	4.0	3.1

As shown in table 4.10, PO_4 -P already removed in every Mg^{2+} dosage. This means the increasing Mg^{2+} removal at 2 and 2.5 moles Mg^{2+} resulting another crystal besides struvite. NH_4 -N that has been removed was much higher compared to other parameters may remove in 2 ways, 4.3 moles NH_4 -N was removed as struvite and the rests were removed as NH_3 due degassing to stabilize the pH.

Based on all the result until this point, optimum process in struvite formation occurred at 1 and 1,5 moles Mg^{2+} dosage. PO_4 -P was completely removed between 1 to 1.5 Mg^{2+} dosage. To see which dosage was optimum, the test continued by increase the slow mixing time until 20 minutes. The characteristic of reject water was presented in table 3.2 and the results are shown in figure 4.10.

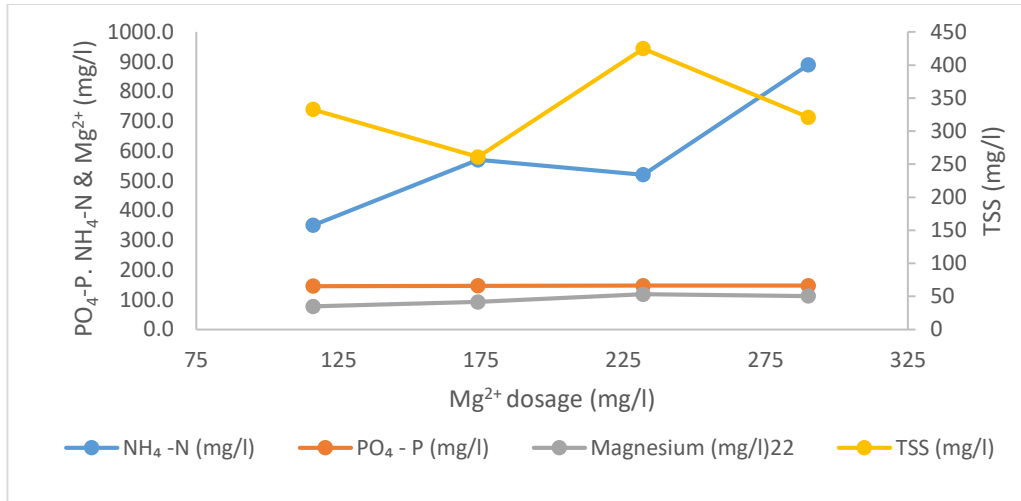


Figure 4.10 TSS production, PO₄-P, NH₄-N and Mg²⁺ removal at multiple Mg dosage and increased mixing time in reject water

Table 4.11 PO₄-P, NH₄-N and Mg²⁺ removal and TSS production at multiple Mg dosage and increased mixing time in reject water

Mg ²⁺ dosage (moles)	NH ₄ -N (moles)	PO ₄ -P (moles)	Mg ²⁺ (moles)	TSS production (moles)
1	19.4	4.7	3.2	1.3
2	31.7	4.7	3.8	0.8
3	28.9	4.7	4.9	2.0
4	49.4	4.8	4.6	1.2

Based on figure 4.10, struvite production has shown the same pattern as the previous test. However, the struvite production was lower than the previous test, since the original reject water had 35 mg/l higher TSS.

Based on table 4.11 the TSS was clearly much lower than previous test due to higher original TSS, 35 mg/l higher. However, the TSS in this case consisted of struvite since the amount of PO₄-P removed as struvite fitted with the amount of NH₄-N and Mg²⁺ removal.

The test was continued with increasing the rapid mixing time to 10 minutes and slow mixing time at 20 minutes. This test was conducted to get sufficient data related to mixing time effect to struvite production. This test was conducted using fresh reject water sample with the characteristic as shown in table 3.2. The results of this test are presented in figure 4.12.

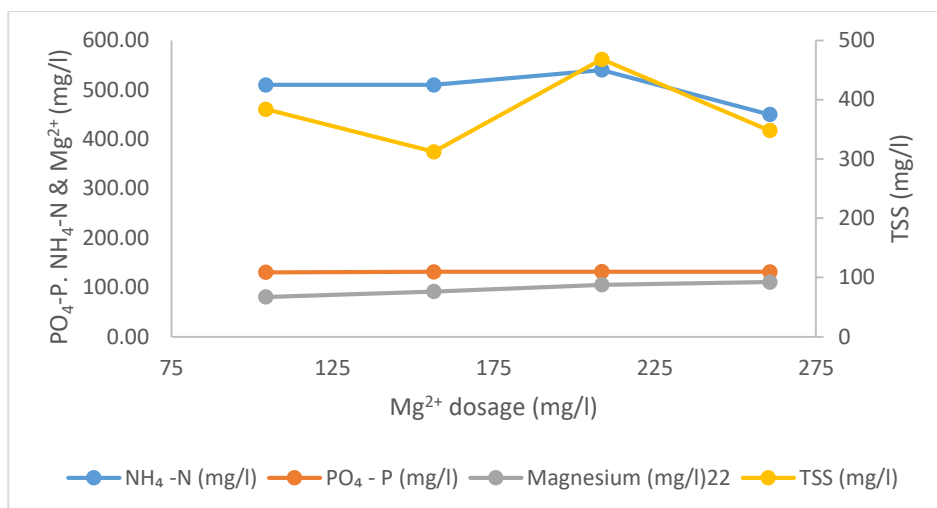


Figure 4.11 TSS production, PO₄-P, NH₄-N and Mg²⁺ removal at multiple Mg dosage and increased mixing time in reject water

Table 4.12 PO₄-P, NH₄-N and Mg²⁺ removal and TSS production at multiple Mg dosage and increased mixing time in reject water

Mg ²⁺ dosage (moles)	NH ₄ -N (moles)	PO ₄ -P (moles)	Mg ²⁺ (moles)	TSS production (moles)
1	28.3	4.2	3.3	2.8
2	28.3	4.2	3.8	2.3
3	30.0	4.3	4.3	3.4
4	25.0	4.2	4.6	2.5

By increasing the rapid mixing time, the amount of struvite that have been produced in this test also increased slightly. Compared to the results of the test with 20 minutes slow mixing, figure 4.10, struvite production at 1 mole dosage increased 51 mg/l, at 1.5 moles dosage, struvite increased 51 mg/l, at 2 moles dosage struvite increased 43 mg/l and at 2.5 moles dosage struvite increase 27 mg/l.

On the contrary, PO₄-P removal slightly decreased. Table 4.12 shows the efficiency decreased by 0.5 moles. All TSS in this test contained struvite since the amount of TSS were lower than other parameters, means that some parts have been removed as struvite and the rests were removed in other way. Reject water consisted of so many ions and material that might inhibit struvite formation, ideal struvite precipitation that happened in artificial wastewater was really hard accomplish in real wastewater with so many unknown variables.

4.5. Struvite formation using seawater as Mg²⁺ source

The last experiment for struvite production was tested using seawater as Mg²⁺ source. The dosage of added seawater was 5%, 10%, 15% and 20% of the sample volume. The dosage was on volume basis, not in concentration, because to simplify the comparison of the amount of seawater needed to get optimum struvite production. This test was conducted in reject water and artificial wastewater as a control. The conditions from previous test conditions were applied for comparison at pH 10, 1 minute of rapid mixing, and 10 minutes of slow mixing.

Due to increased volume by adding sea water, the calculation of $\text{PO}_4\text{-P}$, $\text{NH}_4\text{-N}$ and Mg^{2+} will also accounted dilution factor. All results data and calculation are presented in appendix and the initial characteristic of reject water used in this test was presented in table 3.2.

The result for the reject water test is presented in figure 4.12 below. It shows that TSS production was increased as higher seawater addition until 15% volume addition. The highest TSS production occurred 15% volume seawater. The production was slightly decreased at the highest seawater addition.

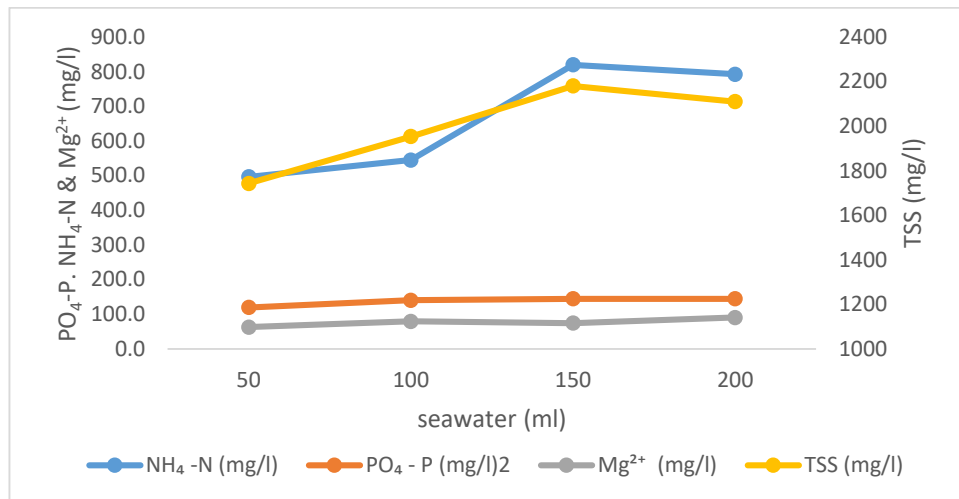


Figure 4.12 TSS production, $\text{PO}_4\text{-P}$, $\text{NH}_4\text{-N}$ and Mg^{2+} removal at multiple sea water addition in reject water

Based on table 4.13, $\text{PO}_4\text{-P}$ was completely removed after 10% sea water addition. At 5% sea water addition, the amount of Mg^{2+} was not enough to form struvite, resulting lower amount of TSS produced compared to TSS production at 10% sea water addition. At 10%, 15% and 20% sea water addition, $\text{PO}_4\text{-P}$ was completely removed and there was still Mg^{2+} residue. All TSS produced in this test contained struvite because the amount of TSS produced was still lower than $\text{PO}_4\text{-P}$, $\text{NH}_4\text{-N}$ and Mg^{2+} removal.

But in order to completely removed $\text{PO}_4\text{-P}$, the optimum sea water additions were between 10% or 15% as presented in table 4.13. Those two volume completely removed $\text{PO}_4\text{-P}$ with minimum volume of seawater. $\text{NH}_4\text{-N}$ removal shows much higher removal as occurred in previous tests, this means some parts of $\text{NH}_4\text{-N}$, proportional with TSS production, were removed as struvite and some more were removed as NH_3 due to high pH.

Table 4.13 $\text{PO}_4\text{-P}$, $\text{NH}_4\text{-N}$ and Mg^{2+} removal and TSS production at multiple sea water addition in reject water

Added sea water (%)	$\text{NH}_4\text{-N}$ (moles)	$\text{PO}_4\text{-P}$ (moles)	Mg^{2+} (moles)	TSS production (moles)
5	60.2	3.9	2.6	2.1
10	57.5	4.5	3.3	2.5
15	42.2	4.7	3.1	3.2
20	43.8	4.7	3.7	3.2

The reject water tests were done twice to verify the data using reject water, which characteristic was presented at table 3.2. The result of this second test is presented in figure 4.13 below. Struvite production showed a slight increase compared to the previous test at 5%, 15% and 20% seawater addition. An average surplus of 200 mg/l struvite production compared to the first test. However, the production pattern was similar to the first test.

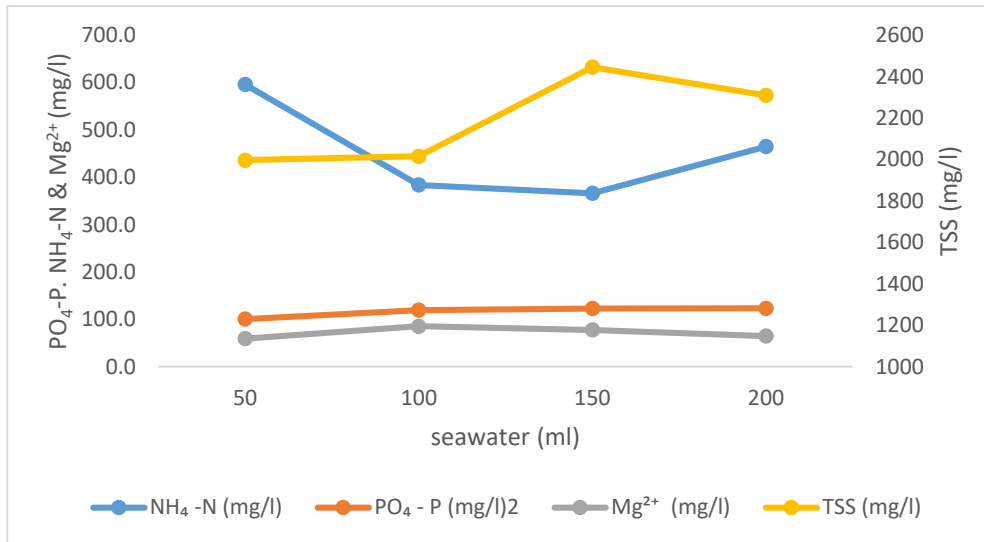


Figure 4.13 TSS production, PO₄-P, NH₄-N and Mg²⁺ removal at multiple sea water addition in reject water

Table 4.14 PO₄-P, NH₄-N and Mg²⁺ removal and TSS production at multiple sea water addition in reject water

Added sea water (%)	NH ₄ -N (moles)	PO ₄ -P (moles)	Mg ²⁺ (moles)	TSS production (moles)
5	41.3	3.2	2.4	2.0
10	53.1	3.9	3.5	2.8
15	54.1	4.0	3.2	3.6
20	48.6	4.0	2.7	3.8

Nutrient removal, on the contrary, has showed lower results compared to the first test. Both PO₄-P and Mg²⁺ had a lower removal. But the removal pattern was the same as the first tests, and the Mg²⁺ dosage that gave significant impact on removal of nutrients were 10% and 15% seawater addition. NH₄-N removal also showed lower removal compare to previous test.

To have a comparison how the seawater effect struvite formation, another test was conducted using artificial wastewater. Condition from the first and second test was applied in this test. Struvite production were similar the first and second tests, the difference was the production increased until that the highest seawater addition. Production was significantly increased at 10% addition and slightly increased at further seawater addition.

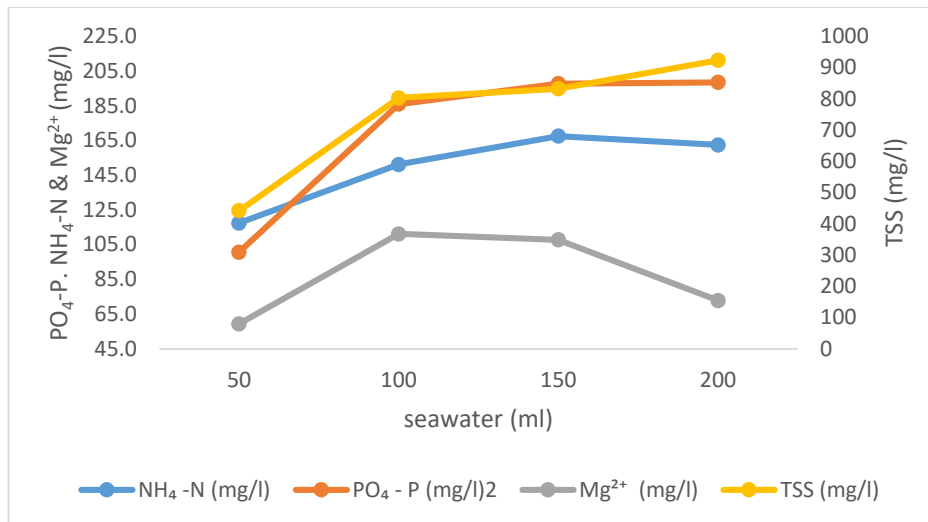


Figure 4.14 TSS production, PO₄-P, NH₄-N and Mg²⁺ removal at multiple sea water addition in artificial wastewater

Figure 4.14 shows a clearer picture about what happened in the process, as the tests were done in the more controlled water, which initial characteristic was presented in table 3.1. All parameters showed similar patterns. All parameters have increased concentration at 10% seawater addition. Only at the highest sea water addition, struvite production increased while the other measured parameters were reduced.

PO₄-P removal efficiency increased by 2,2 moles from 5% to 10% sea water addition as shown in table 4.15, and showed a slight increase at 15% sea water addition. PO₄-P was completely removed after 10% sea water addition. But not all PO₄-P was removed as struvite because the amount of TSS produced was lower than PO₄-P removal. But TSS also consisted of another solid besides struvite due to lower Mg²⁺ removal.

NH₄-N removal showed a relative constant increase as the sea water addition increase. The amount of NH₄-N removed was still much higher compared to TSS produced or PO₄-P removal, means some part of NH₄-N, proportional to TSS production, became struvite and the rests became NH₃ to stabilize pH.

Table 4.15 PO₄-P, NH₄-N and Mg²⁺ removal and TSS production at multiple sea water addition in artificial wastewater

Added sea water (%)	NH ₄ -N (moles)	PO ₄ -P (moles)	Mg ²⁺ (moles)	TSS production (moles)
5	21.3	3.2	2.4	2.6
10	19.4	6.0	4.6	5.3
15	18.5	6.4	4.4	5.5
20	18.8	6.4	3.0	6.2

4.6. Struvite and nutrient removal molar comparison

The composition of struvite represented an equal molar content of Mg²⁺:PO₄³⁻: NH₄⁺ of 1:1:1. The molar consumption of Mg²⁺, PO₄³⁻ and NH₄⁺ in the tests is presented in figure 4.16.

Comparison of the observed struvite production and theoretical calculated production is presented in figure 4.15.

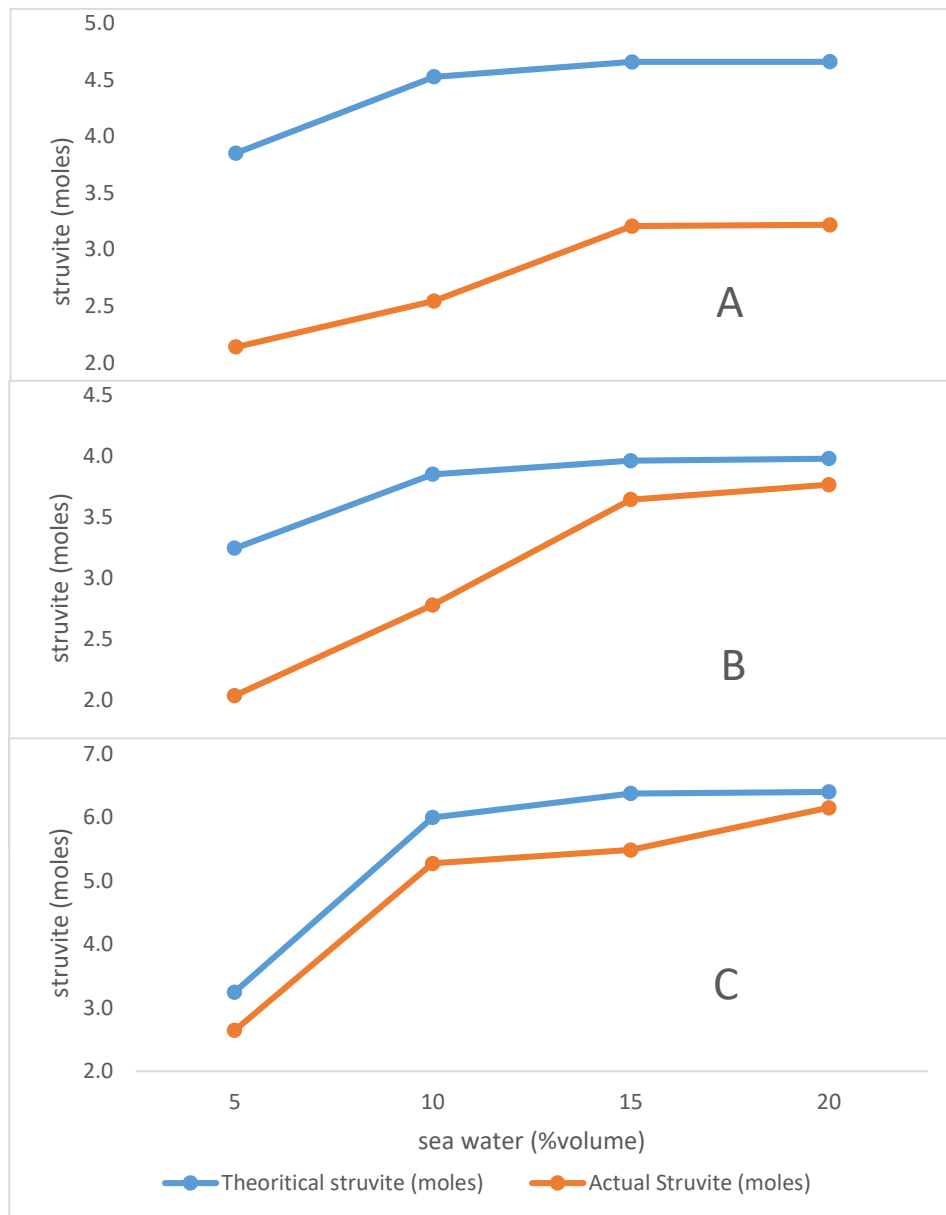


Figure 4.15 Struvite production vs. theoretical calculation in (A) reject water 1; (B) reject water 2; (C) artificial wastewater

As shown in figure 4.16, the observed struvite production was getting closer to the theoretical calculation as the addition of seawater increase. In reject water 1, the average gap between calculation and test result was 1,7 moles. As the test was repeated with the same condition and sample, the average gap became 0,7 moles. A Smaller gap was seen at 15% and 20% sea water addition. Results from the tests using artificial water showed even smaller gaps, with an average gap of 0,6 moles. The results showed proportional correspondence with $\text{PO}_4\text{-P}$ and Mg^{2+} removal in figure 4.16.

Figure 4.16 shows the molar concentration of Mg^{2+} , PO_4^{3-} and NH_4^+ that were removed as struvite by using sea water as Mg^{2+} source. $\text{NH}_4\text{-N}$ removal only showed a relevant result in

reject water 2, as the other samples showed an inconsistent result as shown in previous chapter, probably caused by ammonia stripping. The gap between $\text{PO}_4\text{-P}$ and Mg^{2+} were also very small, 0,4 – 0,7 moles difference. This result showed good correspondence with the struvite production as the average molar gap was only 0,7 moles.

In reject water 1, the gap between $\text{PO}_4\text{-P}$ and Mg^{2+} were 1,3 moles on average and this gap was almost the same as the gap between the observed and calculated struvite production which was 1,7 moles. In the artificial wastewater test, the gap between $\text{PO}_4\text{-P}$ and Mg^{2+} was 1,9 moles in average. This number was quite different from the difference between observed and calculated struvite production in artificial water, which was 0.7 moles on average. The gap was not proportional to the observations in reject water 1 and 2, but somewhat higher. However, the Mg^{2+} removal in reject water 2 and artificial water had similar patterns, while reject water 1 was some different.

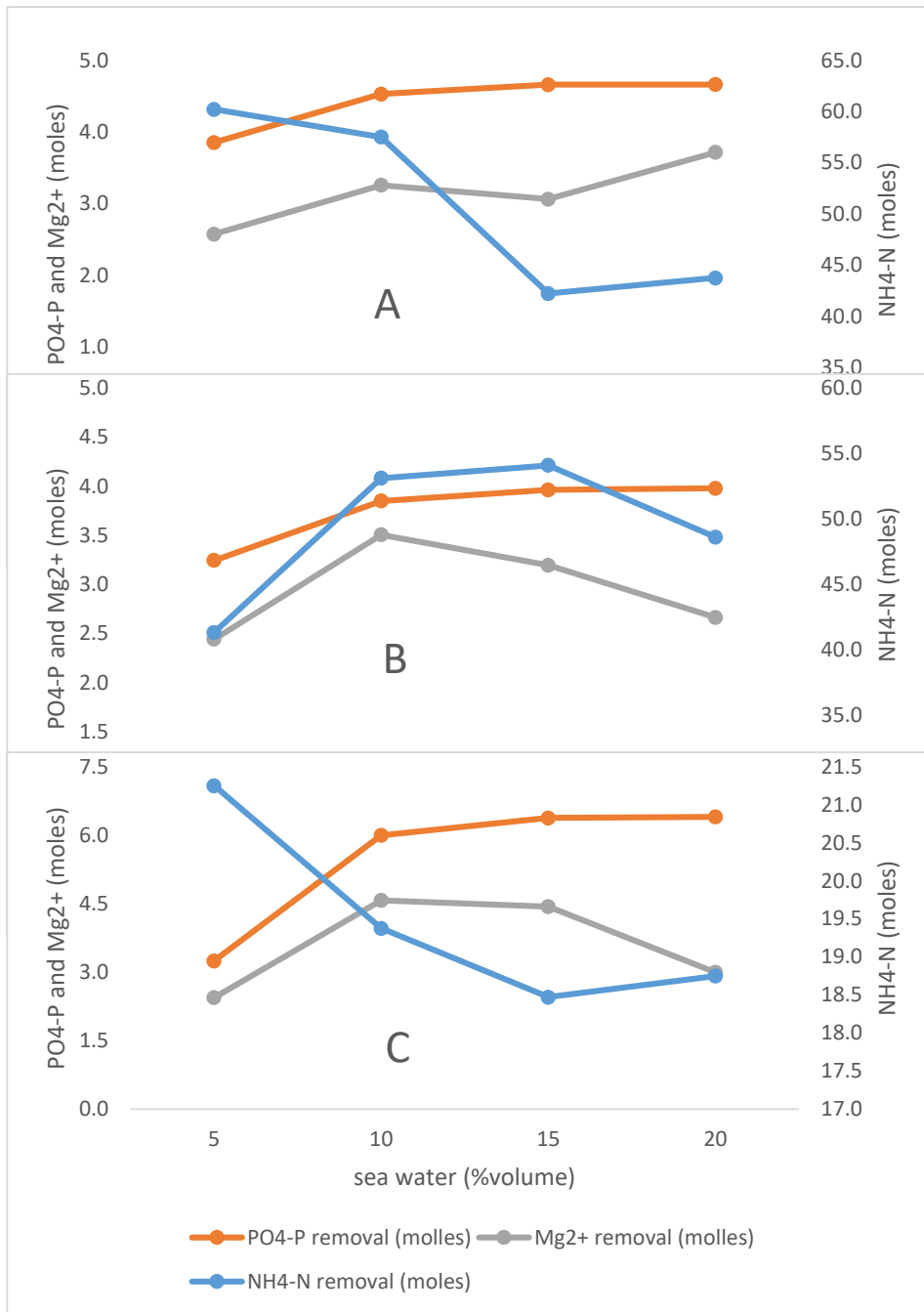


Figure 4.16 Molar comparison of Mg^{2+} , PO_4-P and NH_4-N removal in (A) reject water 1; (B) reject water 2; (C) artificial wastewater

5. Discussion

Results obtained from the experiments are discussed in this chapter. This chapter is divided into 9 sub-chapters: (a) Preliminary test for optimum condition for struvite formation in artificial and reject water; (b) $\text{NH}_4\text{-N}$ loss; (c) Impact of dosing rate on struvite formation; (d) Mole comparison nutrient vs nutrient and nutrient vs struvite; (e) Competing reaction that formed another crystal beside struvite; (f) The effect of reaction time; (g) Seawater potential; (h) Method and procedure improvement; (i) Possible treatment design.

5.1. Preliminary test for optimum condition for struvite formation in artificial and reject water

In struvite formation, pH is a key parameter which affect the precipitation. Effect of pH on struvite formation has been confirmed by previous studies [42]. As the precipitation process proceed, pH would drop because more hydrogen ion (H^+) were generated due to struvite formation. When struvite formation conducted at pH 9 and 9.5, pH dropped sharply to 6.3 and 6.7, until reaction was finished after 15 minutes [54]. The same condition happened to this test, after 1 minutes rapid mixing, the pH was slightly dropped. To stabilize the pH, 5M NaOH was added to the solution. This could indicate that during this rapid mixing time, extensive reaction between ions and struvite yielded.

pH stabilization was conducted during slow mixing and then continued to be stable until the test finished. This indicates that the precipitation reaction was completed when pH became stable [28].

Based from figure 4.1, struvite precipitation was occurred at pH 8 – 11 and intensely precipitated at pH 9 – 11. This result corroborated previous study that pH 8 – 10 was beneficial for struvite formation [32]. Figure 4.1 also shows that the optimum nutrient removal was occurred between pH 9 or 10, similar to result from previous study that found out the optimal pH is 9.5 [39] and 10 [7, 40].

Testing pH 7 was not done as there was no detectable struvite formation and at pH 7.5 only a very small crystal was produced [7]. Table 4.2 shows the $\text{PO}_4\text{-P}$ removal increased as pH increased, only $\text{PO}_4\text{-P}$ removal dropped lightly at the pH 11. This might imply that the highest TSS at pH 11 in figure 4.1 did not only consist of struvite. By repeating the test with only pH 10 and 11, as table 4.3 showed, TSS at pH 10 was higher than TSS at 11. This result was proportional to the nutrient removal, as $\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$ was removed more in pH 10 compared to pH 11.

5.2. $\text{NH}_4\text{-N}$ loss

The results of $\text{NH}_4\text{-N}$ in these tests mostly were inconsistent with the other parameters. Like in figure 4.1, $\text{NH}_4\text{-N}$ removal at pH 11 was increasing while the $\text{PO}_4\text{-P}$ removal was constant. In figure 4.8, where $\text{NH}_4\text{-N}$ removal kept increasing significantly as the other parameters showed a stable removal pattern. This also happened in previous studies as 7.9% ammonium loss was reported which might not be related to struvite precipitation [39]. The difference was the loss of ammonium by stripping, mainly because the experiment was conducted in an open beaker at high pH and the samples were stirred for 20 min at 200 rpm. Another researcher also reported

35% loss of ammonium that was not accounted for in crystals and supernatant [55]. 17.9% difference has also been recognized [56]. Other result showed 14.83% [39] and 17.35% [57] losses in their experiments using synthetic wastewater with different initial concentrations.

In this test, the ammonium concentrations both in artificial wastewater and reject water were higher than phosphate, as shown in table 3.1 and 3.2. This concentration range was normal due to the anaerobic processes prior to the sampling point. Due to its characteristic, ammonia was not stable at high pH, and in experiments with starting pH higher than 8, significant ammonium was lost as a result of degassing of ammonia. Nitrogen concentrations in the fluids decreased by more than 50% in the first two hours, indicating extremely fast diffusion rates of ammonia [50]. According to literature, only 20% of dissolved ammonia-nitrogen will be present as ammonium at pH 10 at temperature of 20 °C [58].

According to Le Chatlier's principle, a chemical equilibrium system that experiences changes in concentration, temperature, volume or total pressure will try to restore equilibrium [59]. When ammonia is removed from the water, this will cause some of the ammonium to be converted to ammonia to restore equilibrium. This process will be repeated when the newly converted ammonia is removed. This theory fitted to the observation of NH₄-N in this experiment.

From the preliminary result, Figure 4.1 and 4.7 show that the higher the pH the more NH₄-N removed. The NH₄-N removal rate was not proportional to removal of the other parameters. This could imply that a part of the removal of NH₄-N became struvite and the rests were degassed as ammonia. The ammonia degassing was proofed by strong ammonia odor that could be smelled from the solution while mixing and parameter measurement

The loss of NH₄-N due to ammonia degassing could also be related to the time the solution was kept at high pH. The rate of ammonia degassing appears to be a function of pH, temperature, time and mixing intensity [50]. This statement corroborated the results, as at the highest pH and Mg dosage, the amount of NH₄-N removed was higher than predicted.

Equipment accuracy also contributed in result deviation. As stated in previous chapter that the spectrophotometer reading was 20% off from the actual result. This error including human error needed to be accounted in loss of NH₄-N.

5.3. Impact of dosing rate on struvite formation

The molar ratio of Mg²⁺: NH₄⁺: PO₄³⁻ has a significant impact on the MAP formation process and nutrient removal. Theoretically, the molar ratio of Mg²⁺: NH₄⁺: PO₄³⁻ is 1:1:1, the molar ratio of these three ions in the precipitate was 0.97:0.89:1 respectively, indicating that struvite was formed. But as the result from the preliminary test, table 4.2, showed that PO₄-P was removed at 5,31 moles and 5,37 moles at pH 9 and 10 as Mg²⁺ was removed 5,29 moles and 5,3 moles at pH 9 and 10. This might imply that to drive all available phosphate from solution, an excess of magnesium might be required.

This experiment has conducted various tests to find the best combination for optimum nutrient removal and struvite formation. The results from the tests using artificial wastewater showed that the optimum nutrient removal occurred at 2 and 3 moles Mg²⁺ (Mg:P) dosage. This conclusion was based from PO₄-P removal, as the NH₄-N always was in excess and the removal

results were not representative as discussed in previous sub chapter 5.2. The difference in PO₄-P removal was not significant, as shown in tables 4.4 until 4.7. As PO₄-P completely removed at 2 moles Mg²⁺ addition, although the difference with 1 moles addition only 0,1 moles at every tests. So based on the data the optimum nutrient removal was occurred when PO₄³⁻: Mg²⁺ molar ratio between 1:1 and 1:2.

Struvite formation as shown in figures 4.2 through 4.5 shows that the maximum production always occurred at 4 moles dosage. This unproportioned result between struvite formation and nutrient removal could happened because there might be another crystal formed beside struvite and analytical error (both possibilities will be explained later). Due to these two possibilities, the optimum dosage for the tests was 2 moles Mg per mole P.

Struvite formation in reject water showed more interesting data, as shown in figures 4.8 until 4.11. with smaller ranges of Mg²⁺ dosage, with ratios of PO₄³⁻: Mg²⁺ at 1:1, 1:1,5, 1:2, 1:2,5, and the results showed that the highest TSS production was at 2 moles Mg²⁺ dosage and the lowest production was at 1,5 moles Mg²⁺ dosage. This result was contradictive since the PO₄-P removal was stable as Mg²⁺ dosage increased, as shown in table 4.9 until 4.12, because it was completely removed at 1.5 moles Mg²⁺ dosage. The relation between struvite formation and PO₄-P removal should be proportional but TSS production increased more than PO₄-P was removed.

Based on table 4.9 until 4.12, PO₄-P was removed over 97% at 1 mole Mg²⁺ per mole PO₄ dosage. But PO₄-P was completely removed at 1,5 moles Mg²⁺ dosage. Similar result also found in the literature, 97% of phosphate has been removed at a molar ratio of PO₄³⁻: Mg²⁺ = 1:1.4 [60].

5.4. Mole comparison of nutrient vs struvite

As the result shown in figures 4.1 until 4.14, struvite production always deviated from the expected result. The deviation itself varied between the tests, some were higher than expected (or calculated), but most of the results had lower production compared to calculated production. Analytical errors might explain some of the observed differences.

From figures 4.1 until 4.14, the TSS produced in the tests was presented as concentration (mg/l). Most of the results gave the same pattern and had a proportional relation with PO₄-P removal. But comparison in moles concentration in figure 4.15, showed that struvite production always were lower compared to the calculated values. The calculated production was based on the PO₄-P removal, that was the limiting nutrient as NH₄⁺ was available in excess and Mg²⁺ addition was controlled.

Based on table 4.15, the removal of PO₄-P was 3.2 moles and Mg²⁺ 2.6 moles (complete removal) at 5% seawater addition, resulting 442 mg/l TSS (struvite). At 10% seawater addition, as the Mg²⁺ concentration increased, PO₄-P removal also increased to 6.0 moles and Mg²⁺ to 5.3 moles (complete removal), resulting in 803 mg/l TSS (struvite). From this data, a proportional relation between struvite, PO₄-P and Mg²⁺ was clearly presented, as PO₄-P removal doubled, struvite production also doubled. Mg²⁺ also showed its function as controlling factor in struvite production. At 5% and 10% sea water addition, the amount of Mg²⁺ was 2.5 moles and 5.3 moles respectively, and the removal was 2.5 moles and 5.3 moles

respectively. This showed that almost all Mg^{2+} was used to produce struvite as long as PO_4^{3-} was still available.

When PO_4^{3-} in solution was used up to form struvite and Mg^{2+} was still abundantly available, Mg^{2+} removal was reduced as Mg^{2+} was not needed any more. This condition was illustrated in table 4.15, at 15% and 20% seawater addition, as Mg^{2+} removal constantly dropped as seawater addition increased. This illustration also explained why Mg^{2+} removal efficiency constantly reduced in the previous tests, Mg^{2+} removal efficiency dropped at 2, 3, 4 moles dosage in the test with artificial wastewater and 1,5, 2, 2,5 moles dosage in the reject water test. As for the reject water, there was already Mg^{2+} available in the reject water, around 6,1 – 6,7 mg/l Mg^{2+} , that's why Mg^{2+} removal efficiency in reject water was never more than 80%.

If we converted the result into moles, the result showed gap that have been stated early in this sub chapter. Based in figure 4.15, the struvite production in artificial water was at average 0,7 moles lower than expected. The production in 10% sea water addition was doubled compared to 5% seawater addition although it was still lower than expected, this shows that the majority of the product was struvite. The gap between struvite production could happen because of analytical error.

When struvite production and Mg^{2+} removal was compared, their molar concentrations were lower than the corresponding PO_4 -P removal, figures 4.15 and 4.16, but struvite concentration, in most tests, had higher molar concentration compared to Mg^{2+} removal. This might happen because the accuracy of AAS that is used to analyze Mg^{2+} was not accurate enough due to the high diluting factor to fit the concentration in the AAS reading range. Most of the samples was diluted between 1000 and 10.000 times, which might affect the deviation from the actual result.

A factor that might explain the production of TSS (suspended solid), there were competing reactions that happened beside struvite formation. The results showed that TSS (suspended solid) produced was not 100% struvite, because the molar consumption of Mg^{2+} was lower than PO_4 -P removal and TSS produced. This competing reaction might result in another crystal that increased the amount of TSS produced. This competing reaction will be explained in the next sub chapter.

From figure 4.15, the molar comparison shows that struvite formation in reject water has always bigger error. This error happened because there were many other ions in the reject water that might inhibit the struvite formation process or create another suspended solid besides struvite. That's why precipitating struvite in reject water could not happen alone as in the tests with artificial wastewater [8].

5.5. Competing reaction that formed other crystals beside struvite

As this experiment conducted at pH 10, there was a possibility that other crystal beside struvite were formed in test with reject water. As the pH value of wastewater increased beyond 10, excess calcium ions reacted with the phosphate to precipitate hydroxyl apatite $Ca_{10}(PO_4)_6(H_2O)_2$ or known as HAP [9]. As the pH adjustment was manually conducted, so there was a possibility that the pH went above 10 and the process precipitated HAP.

This assumption also corroborated by previous research that found that if there is sufficient Mg^{2+} , PO_4^{3-} and Ca^{2+} in wastewater, precursor species would be generated first, then to become

more thermodynamical stable chemicals, such as HAP, TCP or DCP. While the process to form HAP is relative fast, precipitation of OCP and TCP is very slow [61] and can be affected severely by the presence of magnesium [62] [38].

At pH 11 as figure 4.1 shows, there was a possibility that brucite $Mg_3(PO_4)_2$ also was produced in addition to struvite, because this crystal was formed in the range of pH 8.5-11, especially at a pH higher than 10.5 [63]. Another crystal that also was possible to formed was $Ca(OH)_2$ because this crystal tends to be formed at pH 10,5 [9]. Magnesium Carbonate ($MgCO_3$) was also possible to form since the amount of Mg^{2+} added was higher than available PO_4^{3-} , resulting abundant Mg^{2+} available that could react with carbonate in solution.

However, these assumptions could not be proofed in this experiment, because to verify the crystal, the sediment needed to be identified with X-ray diffraction or based on the disappearance of various ions from the liquid phase to the solid phase.

5.6. The effect of reaction time

By increasing the reaction time (mixing time), the test shows slightly improvement in struvite formation and nutrient removal, as shown in figure 4.10 and 4.11 and table 4.11 and 4.12. The increased struvite production and nutrient removal were not as significant as changing pH and Mg dosing, [7] also get similar result as reaction time increased there was a negligible effect on the production of struvite with only 4% more Mg^{2+} and PO_4^{3-} ions being removed between 1 and 180 min.

Examination of the precipitate with a light microscope revealed that the maximum crystal size increased with time [7]. This theory has not confirmed in this experiment as produced TSS was not tested with X-Ray diffraction to identify the size of the crystal produced.

5.7. Seawater potential

Using sea water as Mg^{2+} source will give a huge benefit, as it is economical and sustainabale. Using sea water will reduce the operational costs compared using $MgCl_2 \cdot 6(H_2O)$. Using sea water is also suitable at IVAR Grødaland as it is located at the sea shore. Sea water is an unlimited resource, so the process can continue without any problem regarding input sea water.

When larger volumes of seawater are added, this will result in increased calcium concentration and at the same time dilute the concentration of phosphate. Literature indicates that high Ca^{2+}/PO_4^{3-} concentrations may inhibit struvite crystallization [64]

From the results in figure 4.12 and 4.13, the optimum condition for struvite production and PO_4 -P removal was by adding 10% volume of sea water. As the figures shown, higher seawater additions of 15 and 20 % increased formation of TSS, but not corresponding increase in PO_4 -P removal at it was already close to 100 % at 10 % seawater addition

Using molar comparison in figures, it shows that the amount of struvite that produced was not as high as the theoretical expectation. This might relate to other competing reactions that could occur, since there were many ions in sea water and reject water. This assumption make sense, if the result compared to the result using artificial water, figure 4.14 and. The gap in struvite production was relative constant at 0,5 – 1 mole gap.

Based from this experiment, sea water could become a good alternative as Mg source that can be applied for struvite formation. Although, further research would be needed to optimize the condition and treatment method to be applied

5.8. Method and procedure improvement

Struvite precipitation tests are not new experiments, many studies can be found in literature. This experiment did give a result that can be applied in real conditions, but needs improvement. The first thing need to improve is to determine the composition of the sediment in order to verify the crystal that has been precipitated. X-ray diffraction and light microscope can be used to identify produced crystals and measure their size. Because struvite precipitation is a process depending on time, temperature and pH, changes in those parameters may have affected the precipitation result of the different crystals composition, shape and size.

This type of experiment can also be conducted in 2 parts, laboratory testing and a simulation with computer software. A test using software can be very helpful as the condition and parameter can be controlled to limited unwanted error. Using software, struvite solubility products can be determined, and will be very helpful based on information of the real test in lab. MINTEQA2/PRODEFA2 is an example of software that can be used to simulate struvite precipitation [19].

As stated before, struvite formation is pH dependent. As struvite precipitate, H^+ will be released resulting in decrease of pH. It would be interesting to know how far the struvite would precipitate by continuously monitor the pH. By continuously checking the pH, eventually the pH will stop dropping and this point will be the amount of time of struvite to be precipitated in this specific condition.

Related to NH_4-N loss due to ammonia degassing, it will be better to maintain the pH at neutral or acidic conditions after testing. As stated in chapter 3, this experiment was conducted in pH 10 and then 20% of ammonia-nitrogen will be present as NH_3 at 20 °C [58]. To minimize ammonium loss, it is suggested to lower the pH to neutral or acidic (6 or 7) after the mixing process finished. By adding this step, ammonium loss only occurred during the mixing step.

From literature and this test result, it is known that Mg^{2+} is normally the limiting factor for struvite formation in reject water, and the ammonium concentration is always higher compared to phosphate. In this test, the optimum condition to remove phosphate with adding Mg^{2+} was at a molar ratio of $PO_4-P: Mg^{2+}$ at 1:1.5. It is suggested that further experiments should focus at around 1:1.5 molar ratio and with a range around that.

One have to be aware of the equipment accuracy in this kind of experiment. As stated in previous chapter that there was $\pm 20\%$ lower on the spectrophotometer reading of the NH_4-N measurements. Here it is important of focus on calibration of all equipment before starting the experiments to ensure the results accuracy.

Temperature has influence on the ion activity and product solubility [48], hence it has impact on the MAP process and crystals formation. Temperature in a range of 25- 35 °C had no significant influence on the removal efficiency of NH_4-N and PO_4-P , as well as crystal mass. When the temperature was raised from 25 °C to 35 °C, the size of crystals precipitated were 30 μm , 10 μm , and 14 μm respectively [34]. It was also reported that the morphology and size of

crystals precipitated were affected by temperature. Their results showed that the size of crystals decreased from 1mm to less than 25 μm when the temperature increased from 25 $^{\circ}\text{C}$ to 300 $^{\circ}\text{C}$, similar results with [65]. With all this information, it will be a good decision to control specific temperature as a test variable.

From this test result, further tests can be conducted in continuous flow systems. This type of test will be a good model if struvite formation needs to be applied in a wastewater treatment plant. Continuous flow tests have already been conducted by other researchers and have shown good results. Experiments using a fluidised bed reactor (FBR) will also be an interesting test to conduct.

5.9. Possible treatment design

Based from the test result in this experiment, real scale treatment will be possible to apply, but further and detailed experiment would be a wise approach before designing the treatment. As explained in previous chapter, there are many improvements that can be done to get more comprehensive data for engineering design.

Using the results from this experiment, a rough design of unit processes that may be applied for controlling struvite in real scale treatment is presented in figure 5.1. An example for pilot unit for struvite precipitation reactor is presented in figure 5.2.

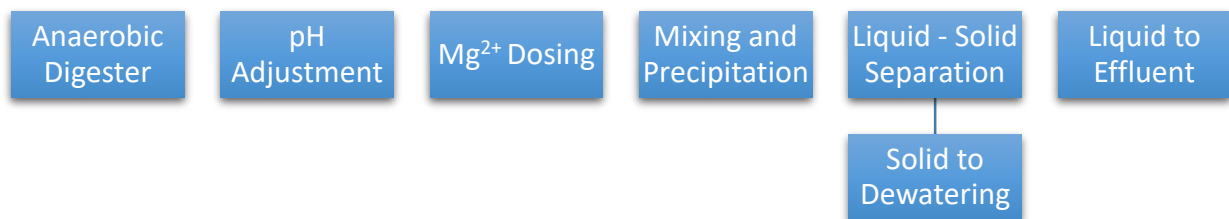


Figure 5.1 Struvite control unit process

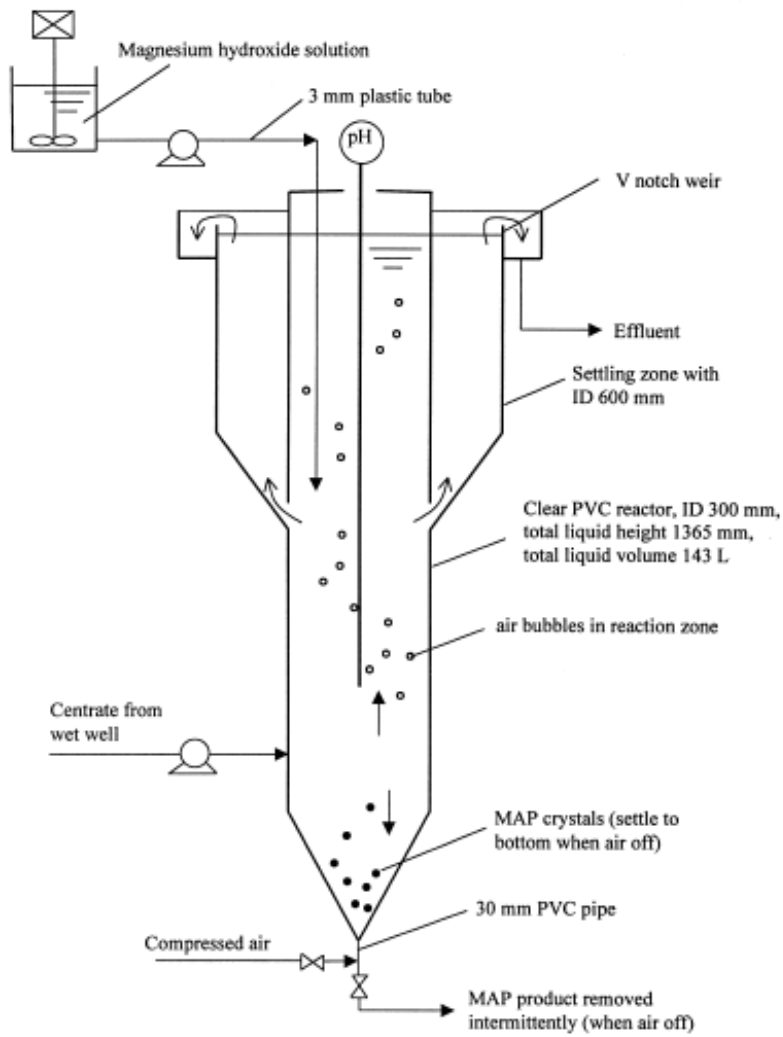


Figure 5.2 Struvite precipitation reactor [36]

6. Conclusion

At preliminary test of struvite precipitation, at 4 different pH levels was applied in artificial and reject water test, at pH levels 8, 9, 10 and 11. The results showed that pH 10 was the optimum pH to remove $\text{PO}_4\text{-P}$ and precipitating struvite. In artificial wastewater $\text{PO}_4\text{-P}$, NH_4^+ and Mg^{2+} removal was 5.4 moles, 5.2 moles and 5.1 moles respectively and 728 mg/l or 5.3 moles TSS, assumed to be struvite. The results showed higher production of struvite at pH 11, but it proved wrong with another test that compared the process at pH 10 and 11, 837 mg/l and 764 mg/l struvite was produced at pH 10 and 11 respectively, and $\text{PO}_4\text{-P}$ was removed 183 mg/l and 125 mg/l respectively. In reject water, $\text{PO}_4\text{-P}$, Mg^{2+} , and $\text{NH}_4\text{-N}$ were removed 3.9 moles, 2.9 moles and 18.1 moles respectively and 508 mg/l or 3.7 moles struvite produced. The test then continued using constant pH 10.

$\text{NH}_4\text{-N}$ removal was inconsistent due to the pH condition that triggered NH_3 degassing. As the test was conducted at pH 10, NH_4^+ attempted to reach equilibrium by releasing ion H^+ to reduce the pH and form ammonia (NH_3) that was stripped out of the liquid.

The optimum Mg^{2+} dosage to precipitated struvite in artificial wastewater was 1:2, $\text{PO}_4\text{-P}$: Mg^{2+} molar ratio. The result showed that $\text{PO}_4\text{-P}$ was always completely removed at 2 moles dosage and had proportional molar ratio with TSS and Mg^{2+} . Increasing TSS as more Mg^{2+} added showed that TSS consisted not only struvite but also magnesium carbonate and other crystal that might precipitated.

The optimum Mg^{2+} dosage to precipitated struvite in reject water was 1:1.5, $\text{PO}_4\text{-P}$: Mg^{2+} molar ratio. The result showed that $\text{PO}_4\text{-P}$ was always completely removed at 1.5 moles Mg^{2+} dosage and had proportional molar ratio with TSS and Mg^{2+} . Further addition of Mg^{2+} dosage did affect the TSS production, as the highest production was always at 2 moles Mg^{2+} dosage.

Using sea water as Mg^{2+} source, the optimum seawater addition was 10% volume if based on $\text{PO}_4\text{-P}$ and Mg^{2+} removal. The result showed that $\text{PO}_4\text{-P}$ was completely removed with Mg^{2+} removal 66% - 71% in reject water. In artificial wastewater, $\text{PO}_4\text{-P}$ removal efficiency was 93% with Mg^{2+} removal 98.2%. This dosage was not the highest $\text{PO}_4\text{-P}$ removal, but if the amount of added sea water and $\text{PO}_4\text{-P}$ removal compared, 10% seawater addition was the most optimum. The other dosage would increase the volume of seawater with very small improvement. But the optimum dosage based on struvite production was 15% sea water addition, as the TSS production always was the highest at this dosage.

The observed struvite production always deviated from the calculated production, usually the actual production was lower than the calculated. The deviation may be because the optimum process conditions were not achieved. Competing reactions might also occur since the reject water and sea water consisted other ions that might inhibit the process.

Based on the result, controlled struvite formation can be applied in IVAR Grødaland, but with more research before design of full scale process. Further test improvements and suggestions have been stated in previous chapter.

7. Reference

1. Ali, M.I. and P.A. Schneider, *Crystallization of struvite from metastable region with different types of seed crystal*. Journal of Non-Equilibrium Thermodynamics, 2005. **30**(2): p. 95-111.
2. Cordell, D., J.O. Drangert, and S. White, *The story of phosphorus: Global food security and food for thought*. Global Environmental Change, 2009. **19**(2): p. 292-305.
3. Doyle, J.D. and S.A. Parsons, *Struvite formation, control and recovery*. Water Research, 2002. **36**(16): p. 3925-3940.
4. Borgerding, J., *Phosphate Deposits in Digestion Systems*. J. Water Pollut. Control Fed., 1972. **44**(5): p. 81-819.
5. Williams, S., *Struvite precipitation in the sludge stream at Slough wastewater treatment plant and opportunities for phosphorus recovery*. Environmental Technology, 1999. **20**(7): p. 743-747.
6. Mamais, D., et al., *Determination of ferric chloride dose to control struvite precipitation in anaerobic sludge digesters*. Water Environment Research, 1994. **66**(7): p. 912-918.
7. Stratful, I., M.D. Scrimshaw, and J.N. Lester, *Conditions influencing the precipitation of magnesium ammonium phosphate*. Water Research, 2001. **35**(17): p. 4191-4199.
8. Amjad, Z., *The Science and technology of industrial water treatment*. 2010, Boca Raton, Fla.: CRC Press IWA Publ.
9. Tchobanoglous, G., et al., *Wastewater engineering : treatment and resource recovery : Volume 1*. 5th international ed. ed. Vol. Volume 1. 2014, New York: McGraw-Hill.
10. Battistoni, P., et al., *Auto-Nucleation and Crystal Growth of Struvite in a Demonstrative Fluidized Bed Reactor (FBR)*. Environmental Technology, 2005. **26**(9): p. 975-982.
11. Dogan, E., et al., *Performance of leaching bed reactor converting the organic fraction of municipal solid waste to organic acids and alcohols*. Chemosphere, 2009. **74**(6): p. 797-803.
12. Ergüder, T.H. and G.N. Demirer, *Low-strength wastewater treatment with combined granular anaerobic and suspended aerobic cultures in upflow sludge blanket reactors*. Journal of Environmental Engineering, 2008. **134**(4): p. 295-303.
13. Romano, R.T. and R. Zhang, *Co-digestion of onion juice and wastewater sludge using an anaerobic mixed biofilm reactor*. Bioresource Technology, 2008. **99**(3): p. 631-637.
14. Uludag-Demirer, S., G.N. Demirer, and S. Chen, *Ammonia removal from anaerobically digested dairy manure by struvite precipitation*. Process Biochemistry, 2005. **40**(12): p. 3667-3674.
15. Kim, D., et al., *Enhancing struvite precipitation potential for ammonia nitrogen removal in municipal landfill leachate*. Journal of Hazardous Materials, 2007. **146**(1-2): p. 81-85.
16. Parawira, W., et al., *Anaerobic batch digestion of solid potato waste alone and in combination with sugar beet leaves*. Renewable Energy, 2004. **29**(11): p. 1811-1823.
17. Parkin, G.F. and W.F. Owen, *Fundamentals of anaerobic digestion of wastewater sludges*. Journal of Environmental Engineering (United States), 1986. **112**(5): p. 867-920.
18. Gerardi, M.H., *The microbiology of anaerobic digesters*. Wastewater microbiology series. 2003, Hoboken, N.J: Wiley-Interscience.
19. EPA, U., *Municipal Nutrient Removal Technologies Reference Document*. 2008.
20. *Large Scale-Chapter 25:Water Quality Management with Solar Energy Capture*. 2007: Elsevier Inc. 465-489.

21. Vymazal, J., *Removal of nutrients in various types of constructed wetlands*. Science of the Total Environment, 2007. **380**(1-3): p. 48-65.
22. *Environmental engineering science*. 2001, Ringgold Inc: Portland. p. n/a.
23. Borgerding, J., *PHOSPHATE DEPOSITS IN DIGESTION SYSTEMS*. Journal of the Water Pollution Control Federation, 1972. **44**(5): p. 813-819.
24. Jaffer, Y., et al., *Potential phosphorus recovery by struvite formation*. Water Research, 2002. **36**(7): p. 1834-1842.
25. El Diwani, G., et al., *Recovery of ammonia nitrogen from industrial wastewater treatment as struvite slow releasing fertilizer*. Desalination, 2007. **214**(1-3): p. 200-214.
26. Yetilmezsoy, K. and Z. Sapci-Zengin, *Recovery of ammonium nitrogen from the effluent of UASB treating poultry manure wastewater by MAP precipitation as a slow release fertilizer*. Journal of Hazardous Materials, 2009. **166**(1): p. 260-269.
27. Warmadewanthi and J.C. Liu, *Recovery of phosphate and ammonium as struvite from semiconductor wastewater*. Separation and Purification Technology, 2009. **64**(3): p. 368-373.
28. Nelson, N.O., R.L. Mikkelsen, and D.L. Hesterberg, *Struvite precipitation in anaerobic swine lagoon liquid: Effect of pH and Mg:P ratio and determination of rate constant*. Bioresource Technology, 2003. **89**(3): p. 229-236.
29. Burns, R.T., et al., *Laboratory and In-Situ Reductions of Soluble Phosphorus in Swine Waste Slurries*. Environmental Technology, 2001. **22**(11): p. 1273-1278.
30. Ganrot, Z., G. Dave, and E. Nilsson, *Recovery of N and P from human urine by freezing, struvite precipitation and adsorption to zeolite and active carbon*. Bioresource Technology, 2007. **98**(16): p. 3112-3121.
31. Etter, B., et al., *Low-cost struvite production using source-separated urine in Nepal*. Water Research, 2011. **45**(2): p. 852-862.
32. Tünay, O., et al., *Ammonia removal by magnesium ammonium phosphate precipitation in industrial wastewaters*. Water Science and Technology, 1997. **36**(2): p. 225-228.
33. Moerman, W., et al., *Phosphate removal in agro-industry: Pilot- and full-scale operational considerations of struvite crystallization*. Water Research, 2009. **43**(7): p. 1887-1892.
34. Korchef, A., H. Saidou, and M.B. Amor, *Phosphate recovery through struvite precipitation by CO₂ removal: Effect of magnesium, phosphate and ammonium concentrations*. Journal of Hazardous Materials, 2011. **186**(1): p. 602-613.
35. Martí, N., et al., *Phosphorus recovery by struvite crystallization in WWTPs: Influence of the sludge treatment line operation*. Water Research, 2010. **44**(7): p. 2371-2379.
36. Münch, E.V. and K. Barr, *Controlled struvite crystallisation for removing phosphorus from anaerobic digester sidestreams*. Water Research, 2001. **35**(1): p. 151-159.
37. Michałowski, T. and A. Pietrzyk, *A thermodynamic study of struvite + water system*. Talanta, 2006. **68**(3): p. 594-601.
38. Abbona, F., H.E. Lundager Madsen, and R. Boistelle, *Crystallization of two magnesium phosphates, struvite and newberyite: Effect of pH and concentration*. Journal of Crystal Growth, 1982. **57**(1): p. 6-14.
39. Zhang, L., et al., *Assessment of the nutrient removal performance in integrated constructed wetlands with the self-organizing map*. Water Research, 2008. **42**(13): p. 3519-3527.
40. Buchanan, J.R., C.R. Mote, and R.B. Robinson, *Thermodynamics of struvite formation*. Transactions of the American Society of Agricultural Engineers, 1994. **37**(2): p. 617-621.

41. Ohlinger, K.N., T.M. Young, and E.D. Schroeder, *Predicting struvite formation in digestion*. Water Research, 1998. **32**(12): p. 3607-3614.
42. Stumm, W. and J.J. Morgan, *Aquatic Chemistry : Chemical Equilibria and Rates in Natural Waters*. 3rd ed. ed. Aquatic Chemistry : Chemical Equilibria and Rates in Natural Waters. 2013, Hoboken: Wiley.
43. Pastor, L., et al., *Struvite formation from the supernatants of an anaerobic digestion pilot plant*. Bioresource Technology, 2010. **101**(1): p. 118-125.
44. Lee, J.E., M.M. Rahman, and C.S. Ra, *Dose effects of Mg and PO 4 sources on the composting of swine manure*. Journal of Hazardous Materials, 2009. **169**(1): p. 801-807.
45. Quintana, M., et al., *Kinetics of phosphorus removal and struvite formation by the utilization of by-product of magnesium oxide production*. Chemical Engineering Journal, 2005. **111**(1): p. 45-52.
46. Parsons, D.W., et al., *An integrated genomic analysis of human glioblastoma multiforme*. Science, 2008. **321**(5897): p. 1807-1812.
47. Rahman, M.M., et al., *Recovery of struvite from animal wastewater and its nutrient leaching loss in soil*. Journal of Hazardous Materials, 2011. **186**(2-3): p. 2026-2030.
48. Le Corre, K.S., et al., *Impact of calcium on struvite crystal size, shape and purity*. Journal of Crystal Growth, 2005. **283**(3): p. 514-522.
49. Elliott, H.A. and G.A. O'Connor, *Phosphorus management for sustainable biosolids recycling in the United States*. Soil Biology and Biochemistry, 2007. **39**(6): p. 1318-1327.
50. Li, L., et al., *Ammonium stability and nitrogen isotope fractionations for NH_4^+ – $NH_3(aq)$ – $NH_3(g_{as})$ systems at 20–70°C and pH of 2–13: Applications to habitability and nitrogen cycling in low-temperature hydrothermal systems*. Ammonium stability and nitrogen isotope fractionations for NH_4^+ – $NH_3(aq)$ – $NH_3(g_{as})$ systems at 20–70°C and pH of 2–13: Applications to habitability and nitrogen cycling in low-temperature hydrothermal systems, 2012. **84**: p. 280-296.
51. Schulze-Rettmer, R., *The simultaneous chemical precipitation of ammonium and phosphate in the form of magnesium-ammonium-phosphate*. Proceedings of the 15th Biennial Conference of the International Association on Water Pollution Research and Control, 1991. **23**(4-6): p. 659-667.
52. Siegrist, H., *Nitrogen removal from digester supernatant - Comparison of chemical and biological methods*, in *Proceedings of the 1996 18th Biennial Conference of the International Association on Water Quality. Part 1*. 1996: Singapore, Singapore. p. 399-406.
53. Molinos-Senante, M., et al., *Economic feasibility study for phosphorus recovery processes*. Ambio, 2011. **40**(4): p. 408-416.
54. Musvoto, E.V., et al., *Integrated chemical-physical processes modelling - I. Development of a kinetic-based model for mixed weak acid/base systems*. Water Research, 2000. **34**(6): p. 1857-1867.
55. Çelen, I., et al., *Using a chemical equilibrium model to predict amendments required to precipitate phosphorus as struvite in liquid swine manure*. Water Research, 2007. **41**(8): p. 1689-1696.
56. Türker, M. and I. Çelen, *Chemical equilibrium model of struvite precipitation from anaerobic digester effluents*. Turkish Journal of Engineering and Environmental Sciences, 2011. **35**(1): p. 39-48.

57. Zhou, S. and Y. Wu, *Improving the prediction of ammonium nitrogen removal through struvite precipitation*. Environmental Science and Pollution Research, 2012. **19**(2): p. 347-360.
58. Capodaglio, A.G., P. Hlavínek, and M. Raboni, *Physico-chemical technologies for nitrogen removal from wastewaters: A review*. Revista Ambiente e Agua, 2015. **10**(3): p. 481-498.
59. Brezonik, P.L. and W.A. Arnold, *Water chemistry : an introduction to the chemistry of natural and engineered aquatic systems*. 2011, Oxford: Oxford University Press.
60. Song, Y., et al., *Nutrients removal and recovery by crystallization of magnesium ammonium phosphate from synthetic swine wastewater*. Chemosphere, 2007. **69**(2): p. 319-324.
61. Ferguson, J.F., D. Jenkins, and W. Stumm, *Calcium phosphate precipitation in wastewater treatment*. Chem Eng Progr Symp Ser, 1971. **67**(107): p. 279-287.
62. Salimi, M.H., J.C. Heughebaert, and G.H. Nancollas, *Crystal Growth of Calcium Phosphates in the Presence of Magnesium Ions*. Langmuir, 1985. **1**(1): p. 119-122.
63. Musvoto, E.V., M.C. Wentzel, and G.A. Ekama, *Integrated chemical-physical processes modelling - II. Simulating aeration treatment of anaerobic digester supernatants*. Water Research, 2000. **34**(6): p. 1868-1880.
64. Martí, N., et al., *Sludge management modeling to enhance P-recovery as struvite in wastewater treatment plants*. Journal of Environmental Management, 2017. **196**: p. 340-346.
65. Rouff, A.A., *Temperature-dependent phosphorus precipitation and chromium removal from struvite-saturated solutions*. Journal of Colloid and Interface Science, 2013. **392**(1): p. 343-348.

Appendix

Test using artificial wastewater

25th January 2017

Beaker	P:Mg	pH	Added Mg ²⁺ (mg/l)	NH ₄ -N (mg/l)	PO ₄ - P (mg/l)	Mg ²⁺ (mg/l)	TSS (mg/l)
1	1:1	8	124	53	120	99.01	285
2	1:1	9	124	93	165	122.99	727
3	1:1	10	124	93	167	123.38	728
4	1:1	11	124	143	158	124.16	830
			124				

26th January 2017

Beaker	pH	P:Mg	Added Mg ²⁺ (mg/l)	NH ₄ -N (mg/l)	PO ₄ - P (mg/l)	Mg ²⁺ (mg/l)	TSS (mg/l)
1	10	1:1	155	46	14.2	11.257	837
2	11	1:1	155	64	73	5.668	764

1st February 2017

Beaker	pH	P:Mg	Added Mg ²⁺ (mg/l)	NH ₄ -N (mg/l)	PO ₄ - P (mg/l)	Mg ²⁺ (mg/l)	TSS (mg/l)	TS (g/l)
1	10	1:1	161	154	202.8	153.14	934	4.008
2	10	1:2	322	164	204.2	161.93	927	5.002
3	10	1:3	483	304	203.9	210.19	1051	5.912
4	10	1:4	644	344	203.9	236.75	1110	6.773
(Artificial water 4 l)								2.836

2nd February 2017

Beaker	pH	P:Mg	Added Mg ²⁺ (mg/l)	NH ₄ -N (mg/l)	PO ₄ - P (mg/l)	Mg ²⁺ (mg/l)	TSS (mg/l)	TS (g/l)
1	10	1:1	322	238	437.8	307.26	1877	7.944
2	10	1:2	644	258	439.2	341.35	1851	9.174
3	10	1:3	966	258	439.4	379.58	1867	11.023
4	10	1:4	1289	248	439	335.01	1982	13.067
(Artificial water 4 l)					440			4.991

14th February 2017

Beaker	pH	P:Mg	Added Mg ²⁺ (mg/l)	NH ₄ -N (mg/l)	PO ₄ - P (mg/l)	Mg ²⁺ (mg/l)	TSS (mg/l)	TS (g/l)
1	10	1:1	161	134	202.46	156.86	889	3.880
2	10	1:2	322	134	204.46	166.23	887	4.810
3	10	1:3	483	214	204.26	178.79	993	5.746
4	10	1:4	644	304	203.96	216.15	1081	6.702
(Artificial water 4 l)								2.706

21st February 2017

Beaker	pH	P:Mg	Added Mg ²⁺ (mg/l)	NH ₄ -N (mg/l)	PO ₄ - P (mg/l)	Mg ²⁺ (mg/l)	TSS (mg/l)	TS (g/l)
1	10	1:1,12	392	300	469.7	339.83	1936	13.678
2	10	1:1,67	588	200	470.0	361.33	1939	15.194
3	10	1:2,23	784	300	470.0	375.80	1981	16.520
4	10	1:2,78	980	300	470.0	385.03	2059	18.342
(Artificial water 4 l)				2200	470.0			12.226

Test using reject water

27th February 2017

Beaker	pH	P:Mg	Added Mg ²⁺ (mg/l)	NH ₄ -N (mg/l)	PO ₄ - P (mg/l)	Mg ²⁺ (mg/l)	Conductivity	TSS (mg/l)	FSS (mg/l)	VSS (mg/l)	TS (mg/l)	FS (mg/l)
1	8.5	1:1	96	1.0	99.5	49.8	11.24	392	-21	413	-698	-1294
2	9	1:1	96	175.0	109.2	58.1	11.34	280	11	269	596	-514
3	10	1:1	96	325.0	119.8	70.0	11.53	508	-81	589	3150	2362
4	11	1:1	96	465.0	119.7	72.1	13.23	484	-109	593	6330	6106
Reject water	8			1325	122.5	5.6	11.40	1104	393	711	3470	1574

28th February 2017

Beaker	pH	P:Mg	Added Mg ²⁺ (mg/l)	NH ₄ -N (mg/l)	PO ₄ - P (mg/l)	Mg ²⁺ (mg/l)	Conductivity	TSS (mg/l)	FSS (mg/l)	VSS (mg/l)	TS (mg/l)	FS (mg/l)
1	10	1:1	96	380.0	119.3	73.0	12.62	1096	207	889	6334	5138
2	10	1:1,5	144	380.0	120.6	90.4	12.80	400	131	269	6116	5352
3	10	1:2	192	530.0	121.2	98.8	12.97	980	7	973	7440	5981
4	10	1:2,5	240	700.0	121.3	103.8	13.33	1056	307	749	7350	6024
Reject water	8.14		96	1430	122.5	5.69	11,40 -> 12,56 (pH10)	1104	393	711	3470	1574

1st March 2017

Beaker	pH	P:Mg	Added Mg ²⁺ (mg/l)	NH ₄ -N (mg/l)	PO ₄ - P (mg/l)	Mg ²⁺ (mg/l)	Conductivity	TSS (mg/l)	FSS (mg/l)	VSS (mg/l)	TS (mg/l)	FS (mg/l)
1	10	1:1	105	420.00	130.8	74.5	12.85	368	296	72	6276	5986
2	10	1:1,5	158	320.00	131.8	97.0	12.90	252	340	-88	6072	5172
3	10	1:2	210	510.00	132.7	113.5	13.11	484	416	68	6978	5750
4	10	1:2,5	263	770.00	132.9	96.0	13.33	432	460	-28	6930	6084
Reject water	7.942			1310	134.0	5.6	11,05 -> 12,73 (pH10)	1060	76	984	3380	1558

2nd March 2017

Beaker	pH	P:Mg	Added Mg ²⁺ (mg/l)	NH ₄ -N (mg/l)	PO ₄ - P (mg/l)	Mg ²⁺ (mg/l)	Conductivity	TSS (mg/l)	FSS (mg/l)	VSS (mg/l)	TS (mg/l)	FS (mg/l)
1	10	1:1	116	350.0	145.5	77.2	12.70	333	128	205	5904	5702
2	10	1:1,5	174	570.0	146.5	92.3	13.02	261	188	73	6188	6126
3	10	1:2	232	520.0	147.1	118.0	13.23	425	264	161	6876	6640
4	10	1:2,5	290	890.0	147.3	112.4	13.55	321	200	121	6824	6450
Reject water	7.942			1440	148.0	5.1	11,98 -> 12,56 (pH10)	1095	240	855	3712	1360

13th March 2017

Beaker	pH	P:Mg	Added Mg ²⁺ (mg/l)	NH ₄ -N (mg/l)	PO ₄ - P (mg/l)	Mg ²⁺ (mg/l)	Conductivity	TSS (mg/l)	FSS (mg/l)	VSS (mg/l)	TS (mg/l)	FS (mg/l)
1	10	1:1	104	510.00	130.4	80.8	12.60	384	380	4	5890	5680
2	10	1:1,5	156	510.00	131.4	91.8	12.78	312	360	-48	6076	5924
3	10	1:2	209	540.00	131.8	105.3	12.88	468	460	8	6768	6376
4	10	1:2,5	261	450.00	131.6	110.8	13.13	348	388	-40	6700	6310
Reject water	7.932			1440	133.0	4.2	10,88 -> 12,08 (pH10)	888	144	744	3200	1292

Test using sea water as Mg²⁺ source

15th March 2017

Beaker	pH	Added seawater (ml)	P:Mg	Dilution factor	NH ₄ -N (mg/l)	PO ₄ - P (mg/l)	Mg ²⁺ (mg/l)	Conductivity (mS/cm)	TSS (mg/l)	ISS (mg/l)	VSS (mg/l)	TS (mg/l)	IS (mg/l)
1	10	50	1:0,44	1.0625	496.3	119.4	62.6	14.00	1743	642	1101	10652	7994
2	10	100	1:0,89	1.1250	545.0	140.4	79.2	15.73	1953	698	1256	11730	9308
3	10	150	1:1,33	1.1875	820.0	144.5	74.4	17.17	2180	789	1392	13172	10764
4	10	200	1:1,77	1.2500	792.5	144.5	90.3	18.40	2110	790	1320	13550	11302
Reject water	7.9				1580	146	6.7	10.86 -> 12,71	1516	348	1168	3972	1526

16th March 2017

Beaker	pH	Added seawater (ml)	P:Mg	Dilution factor	NH ₄ -N (mg/l)	PO ₄ -P (mg/l)	Mg ²⁺ (mg/l)	Conductivity	TSS (mg/l)	ISS (mg/l)	Organic	TS (mg/l)	IS (mg/l)
1	10	50	1:0,52	1.0625	596.3	100.6	59.3	13.99	1998	667	1330	10806	7994
2	10	100	1:1,04	1.1250	383.8	119.4	85.2	15.57	2016	770	1247	11836	9308
3	10	150	1:1,55	1.1875	366.3	122.9	77.6	17.10	2446	888	1558	13194	10764
4	10	200	1:2,07	1.2500	465.0	123.4	64.7	18.49	2310	905	1405	13550	11302
Reject water	8				1340	125	6.1	10,86 -> 12,09	1844	388	1456	4294	1526

17th March 2017

Beaker	pH	Added seawater (ml)	P:Mg	Dilution factor	NH ₄ -N (mg/l)	PO ₄ -P (mg/l)2	Mg ²⁺ (mg/l)	Conductivity	TSS (mg/l)
1	10	50	1:0,32	1.0625	117.5	101	59.4	7.92	442
2	10	100	1:0,65	1.1250	151.3	186	111.2	9.86	803
3	10	150	1:0,97	1.1875	167.5	198	107.8	12.03	832
4	10	200	1:1,29	1.2500	162.5	199	72.9	13.75	924
Reject water	7.8				500	200			0