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Author: Ece Hernes

Programme coordinator: Roald Kommedal

Supervisor(s):

Anders Wold (IVAR), Roald Kommedal (UiS)

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Abstract

This study investigates the struvite crystallization method for phosphorus recovery from IVAR SNJ wastewater treatment plant. The physicochemical properties of struvite, including its crystallization mechanics and the influence of wastewater conditions, are examined.

Different molar ratios of struvite components were tested along with pH with batch reactor and fluidized bed reactor. Additionally, Visual MINTEQ modelling is implemented to examine the effect of molar ratios. The results indicated that a molar ratio of Mg-NH₄-PO₄ of 1,5-1,5-1 for the struvite components yielded optimal performance in terms of struvite crystallization.

The correlation between effluent orthophosphate concentration and pH were examined. Based on the findings, pH 8,5 to 9 is recommended for operation of the struvite reactor.

To implement a potential struvite crystallization reactor at the IVAR SNJ wastewater treatment plant, the plan involves directing all reject water from the secondary treatment's thickening process (BR) into the reactor. Based on this, the other flows that will be directed to the struvite reactor are calculated using average concentrations of struvite components in the centrifuge reject water (SR) and BR. The molar ratio of Mg-NH₄-PO₄ is set to 1,5-1,5-1, and a hydraulic retention time (HRT) of 2 hours is targeted. For a flow rate of 500 m³/d and a phosphate load of 250 mg/l in BR, the optimal quantities determined are 54 m³/d of 1 M magnesium solution and 96 m³/d of centrifuge reject water. Additionally, NaOH adjustments for pH control are estimated to be 9,72 l/d of 1 M NaOH solution. The calculated volume of the full-scale reactor is 55 m³. With these operating parameters, it is anticipated that the harvested struvite from the reactor would amount to 932 kg/d for a wastewater flow rate of 100000 m³/d. Achieving a 90% efficiency in phosphate removal is feasible with the selected operation factors.

The outcomes of this study contribute to the advancement of sustainable wastewater management practices and the promotion of sustainability. By optimizing the struvite crystallization process and understanding its relationship with effluent orthophosphate concentration and pH, this research provides insights for large-scale implementation.

In conclusion, this study highlights the potential of the struvite crystallization method for phosphorus recovery, with strong correlations observed between effluent orthophosphate concentration and pH.

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Abbreviations and terms

Abbreviations

1. EBPR : Enhanced biological phosphorus removal
2. EC : Electrical conductivity
3. I : Ionic strength
4. IAP : Ionic activity product
5. K_s : Solubility product
6. Mg : Magnesium
7. N : Nitrogen
8. $\text{NH}_4\text{-N}$: Ammonium as nitrogen
9. P : Phosphorus
10. PAO : Polyphosphate Accumulating Organisms
11. P_s : Conditional solubility product
12. $\text{PO}_4\text{-P}$: Orthophosphate as phosphorus
13. T : Temperature
14. R : Gas constant
15. WWTP : Wastewater treatment plant
16. z_i : Valence of the ion
17. [M] : Concentration of the chemical in the water
18. {M} : Activity of the chemical in the water
19. α : Ionization fraction of the individual constituents
20. ΔH_r^0 : Reaction enthalpy

Terms used in crystallization process

1. Supersaturation: the thermodynamic situation for the crystallization process.
2. Nucleation: the transformation from the solution phase to solid phase
3. Primary nucleation: the appearance of the first crystal structure
 - 3.1. Homogeneous nucleation: primary nucleation that occurs in the system
 - 3.2. Heterogeneous nucleation: primary nucleation that occurs on the surface
4. Secondary nucleation: the crystal structure building up on a previous structure
5. Nuclei: the centre point where the crystallization started
6. Central driving force: the chemical potential difference between the solution and the solid phases of crystallization
7. Induction time is the time from the supersaturated solution to transforming to nuclei.

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Ece Hernes

1. Introduction

Phosphorus is an essential element for all living organisms and plays a critical role in agricultural production as a key component of fertilizers. However, the reliance on phosphate rocks as the main source of phosphorus is becoming increasingly unsustainable due to their limited availability and the growing demand driven by human activities. Therefore, there is an urgent need to explore alternative resources for phosphorus to ensure long-term sustainability and protect the environment.

Wastewater treatment plants have a major role on environmental protection, aiming to reduce pollution, recover valuable resources such as energy and nutrients, and produce materials suitable for various industries. Phosphorus recovery from wastewater treatment plants offers a promising solution to alleviate phosphorus depletion and minimize the environmental impact of wastewater discharge.

Among the various methods for phosphorus recovery, struvite crystallization has garnered significant attention due to its favourable crystallization process. Struvite, a crystal mineral chemically structured as $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, consists of magnesium, ammonium, and phosphate hexahydrate. It is particularly notable for its composition, as it contains primary macronutrients nitrogen and phosphorus, as well as the secondary macronutrient magnesium. Moreover, struvite exhibits low solubility in water, making it present in only trace amounts in runoff water. Additionally, the crystalline nature of struvite allows for easy handling and transportation in packaged form, making it an ideal compound for nutrient recovery from wastewater (Shaddel et al., 2020).

Given its promising characteristics, the struvite crystallization method has emerged as a key topic in wastewater treatment for effectively recovering the incoming phosphorus load. By harnessing the potential of struvite as a sustainable source of phosphorus, it is possible to address the challenges associated with phosphate rock depletion and contribute to the development of environmentally friendly and resource-efficient wastewater treatment practices.

This study is focused on the phosphorus recovery from wastewater by the struvite crystallization in a fluidized bed reactor. The project is conducted in collaboration with IVAR SNJ wastewater treatment plant located at Mekjarvik. The scope of work includes the following tasks:

- Conducting a literature review of the struvite crystallization method and its application in wastewater treatment.
- Conducting experiments to test the efficiency of the fluidized bed reactor under different conditions, including varying pH, and concentration of chemicals.
- Analysing the results of the experiments and comparing the efficiency of the fluidized bed reactor
- Providing recommendations for the optimization of the fluidized bed reactor to improve its efficiency and sustainability.
- Finding the optimal conditions for struvite crystallization for IVAR SNJ wastewater treatment plant
- Operation of struvite reactor, determination of possible challenges through operation and finding solutions

2. Theory and Background

In this theoretical and background section, the fundamental aspects of struvite are explained, including its structure, crystallization mechanisms, and the impact of wastewater conditions on struvite crystallization.

Phosphorus in the wastewater

Phosphorus is an essential nutrient required by all living organisms, including plants and animals. In the wastewater, it is predominantly sourced from human excreta and cleaning detergents, typically in the form of polyphosphates and phosphonates, which can lead to high levels of phosphorus in wastewater. In addition to domestic wastewater, industrial and commercial wastewater sources also contribute to phosphorus in wastewater. The food processing industry, metal-processing industry, and other industries are significant sources of phosphorus. Farming also contributes to the phosphorus content in wastewater and surface water, originating from manure and fertilizer. (Schaum, 2018)

The disposal of phosphorus to water needs to be regulated as it can induce eutrophication. Eutrophication occurs when excess phosphorus and nitrogen are present in water bodies, leading to the overgrowth of algae and other aquatic plants. This can result in a depletion of dissolved oxygen in the water, leading to the death of aquatic organisms. Additionally, eutrophication can promote a decline in aquatic biodiversity, the loss of potable water sources, and the formation of dead zones in the ocean. (Desmidt et al., 2015)

To address this issue, wastewater treatment plants implement phosphorus removal processes, By reducing the amount of phosphorus in wastewater and recovering it for beneficial use, wastewater treatment plants can help protect the environment and promote sustainable resource management. (Desmidt et al., 2015)

Phosphorus removal from wastewater

Wastewater treatment typically involves the removal of phosphorus by converting it from a soluble to a solid form, which can then be eliminated via sedimentation (Parsons & Smith, 2008). Among the most commonly used methods to accomplish this are chemical precipitation and biological removal, although a variety of other techniques, including crystallization, ion exchange, magnetic separation, and sludge treatment, have also been studied to varying degrees. (Morse et al., 1998; Parsons & Smith, 2008)

Chemical precipitation represents the most common and traditional phosphorus removal process utilized in wastewater treatment. This physicochemical process entails the addition of divalent or trivalent metal salts to the wastewater, resulting in the precipitation of insoluble metal phosphates that settle out by sedimentation. (Morse et al., 1998) Commonly used metal salts for this purpose include alum, sodium aluminate, ferric chloride or sulfate, and lime. (Tchobanoglous et al., 2014)

Alternatively, biological phosphorus removal has been developed as a non-chemical approach. Biological phosphorus removal methods are employed in wastewater treatment processes to reduce phosphorus levels in effluent. These methods utilize specific bacteria called polyphosphate-accumulating organisms (PAOs) that have the ability to take up and store phosphorus under certain conditions. (Bunce et al., 2018).

Enhanced Biological Phosphorus Removal (EBPR) is a biological method used for the removal of phosphorus, which has gained attention as an environmentally sustainable and cost-effective alternative to chemical treatment. This approach, primarily implemented in activated sludge systems, utilizes the metabolic capabilities of microorganisms to facilitate the removal of phosphorus from wastewater. This method is based on the discovery that under certain conditions, activated sludge is capable of taking up phosphorus in excess of the normal levels required for biomass growth. (Bunce et al., 2018)

Phosphorus recovery from wastewater

Phosphorus removal and recovery are typically treated as distinct process steps within wastewater treatment. While phosphorus removal focuses on reducing phosphorus concentrations in wastewater to meet regulatory standards and prevent eutrophication, phosphorus recovery aims to extract and reuse phosphorus as a valuable resource. (Shaddel, 2020)

Crystalline recovery of phosphorus

Phosphorus can be crystalline precipitated from wastewater as struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$). Precipitation has been widely adopted by the wastewater treatment plants that lead the innovations for their advantages as the precipitated product is directly applicable as fertilizer. The products also have low solubility in water and low heavy metals. (Cieřlik & Konieczka, 2017)

Crystallization is a process that involves the transformation of matter from a high free energy, disordered, solvated state to a crystal phase characterized by the regular arrangement of its building units at a low free energy state. This process occurs through a series of steps, including supersaturation of the system, nucleation, and growth.

The first step involves creating a supersaturated solution, where the concentration of solutes in the solution exceeds its saturation point. This results in a state of thermodynamic instability, where the solution is highly reactive and prone to the formation of new phases. The formation of a new phase occurs through nucleation, where small clusters of solute molecules aggregate to form stable nuclei. The nucleation step is highly dependent on factors such as temperature, concentration, and agitation, which can influence the rate and size of nuclei formation.

Once the nuclei are formed, they can undergo growth through the addition of solute molecules to their surface. This results in the formation of a crystal structure with a defined size, shape, and orientation. The growth process is also influenced by external factors such as temperature, concentration, and agitation, which can affect the kinetics of crystal growth and the final crystal properties. (Shaddel, 2020)

Struvite

Struvite is a crystal structured mineral that is chemically structured as $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$. It contains magnesium, ammonium, and phosphate hexahydrate. It has a low solubility in water, therefore

found very low amounts in runoff water. Therefore the struvite is an ideal compound to be used in nutrient recovery from wastewater. (Shaddel et al., 2020)

Struvite forming occurs as large crystals aggregation and has a desired settling and dewatering. It also has low amounts of pathogenic microorganisms and heavy metals which makes the struvite an applicable material for further processes. The studies show that struvite crystallization have a high efficiency of 80% to 90%. (Shaddel et al., 2019)

Struvite, due to its unique and advantageous properties, is a candidate for use as a fertilizer or raw material in the fertilizer industry. It is non-odorous and non-sludgy, and its purity and low tendency for organic micropollutant and pathogen incorporation make it a superior product compared to other fertilizers. Additionally, struvite requires low energy production and has a high capacity for producing a high-quality product. With a P content of 10-12% (28% as P_2O_5), struvite has high plant availability on acidic soils and moderate plant availability on alkaline soils. Struvite performs similarly to commercial fertilizers in terms of plant uptake within one or more growing periods. Its slow-release nature, owing to its low water solubility, makes it a suitable product for turf, horticulture, nurseries, and ornamental procedures. However, it may be less appropriate for agricultural row and grain crops. (Shaddel, 2020)

It is estimated that 100 cubic meters of wastewater can produce 1 kilogram of struvite. If all the wastewater in the world is treated using struvite crystallization technology, 63,000 tons of P_2O_5 could be recovered, which is equal to 16% of the world's phosphate rock production. Struvite can be recovered from wastewater, and up to 171 grams per square meter can be obtained with a purity of 95% without washing. It can be used as a fertilizer for herbages, vegetables, and grain crops, especially for magnesium-dependent crops like sugar beet. Struvite is a long-lasting fertilizer that provides essential crop nutrients such as nitrogen, phosphorus, potassium, calcium, and magnesium. It has slow-release characteristics, which do not burn the seeding or roots, making it more suitable for use in the vast areas of forest. By using struvite, the frequency of fertilization can be reduced, and nutrient loss can be minimized. (T. Zhang et al., 2017)

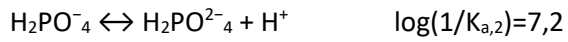
Components of struvite

The components of struvite are pH dependent. Ammonia decreases and magnesium and phosphate ions increase through pH. The solubility of struvite is the lowest where these three components are at the optimal value in the wastewater.

Orthophosphate

Orthophosphates exist in the water in different forms in different pH values. Phosphate ion form of orthophosphate is the component of struvite that participates in crystallization. This form starts to

appear in the water at pH 9,5 and the percentage gets higher with higher pH.



Total phosphate concentration: $C_{T,\text{PO}_4} = [\text{PO}_4^{3-}] + [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}]$

Orthophosphate/total phosphate: $\alpha_{\text{PO}_4^{3-}} = [\text{PO}_4^{3-}] / C_{T,\text{PO}_4}$

$$\alpha_{\text{PO}_4^{3-}} = \frac{1}{[\text{H}^+]^3 / (10^{-2,1} * 10^{-7,2} * 10^{-12,3}) + [\text{H}^+]^2 / (10^{-7,2} * 10^{-12,3}) + [\text{H}^+] / 10^{-12,3} + 1}$$

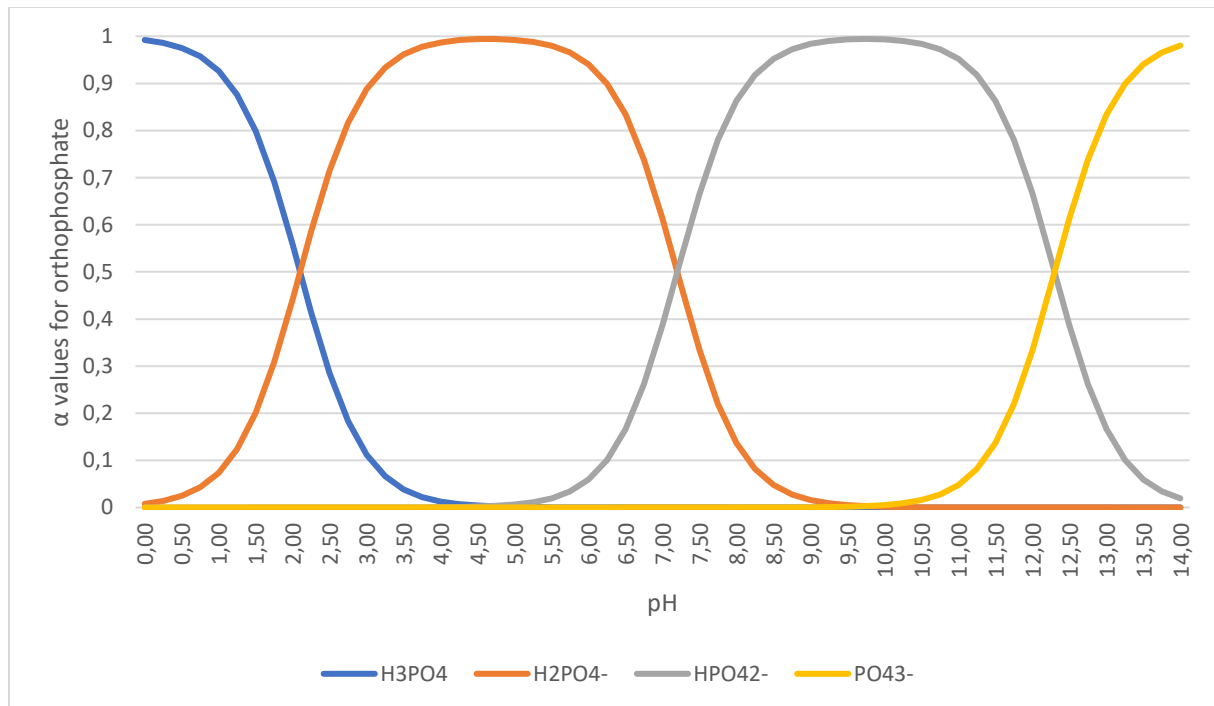
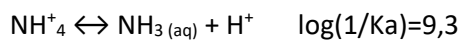


Figure 2-1: Forms of orthophosphate

Ammonia

Inorganic dissolved ammonia exists in two forms in the water.



Total ammonia concentration: $C_{T,\text{N}} = [\text{NH}_4^+] + [\text{NH}_3]$

The percentage of ammonia (NH_4^+) and ammonium (NH_3) in the water is dependent on the pH.

Total ammonium concentration: $C_{T,N} = [\text{NH}_4^+] + [\text{NH}_3]$

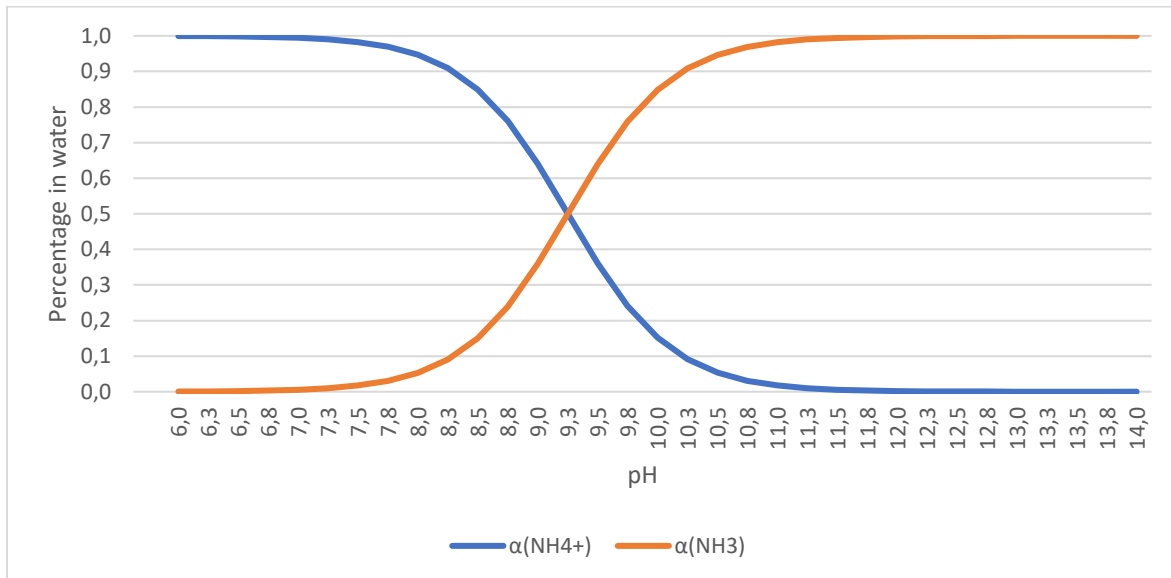
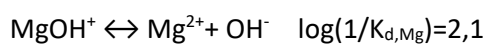


Figure 2-2: Forms of ammonia

Magnesium

Magnesium ions in the water accepted to occur from magnesium hydroxide dissolution to magnesium ions and hydroxide. Other magnesium components also have a similar pH to release the magnesium ions, therefore the α value from the magnesium hydroxide is acceptable to measure the magnesium ions based on the total magnesium measured in the laboratory.



Total magnesium concentration: $C_{T,\text{Mg}} = [\text{Mg}^{2+}] + [\text{MgOH}^+]$

(Snoeyink & Jenkins, 1980)

Theoretical struvite crystallization and pH

The theoretical struvite solubility is calculated based on the $\log(K_s)$ value of 12,60, the temperature is 25°C and the change based on the pH and the percentage of the total concentrations in form of struvite components. Ionic activity is accepted as zero and the concentrations are accepted to be infinitely dilute. And there are not any other components to affect the struvite crystallization.

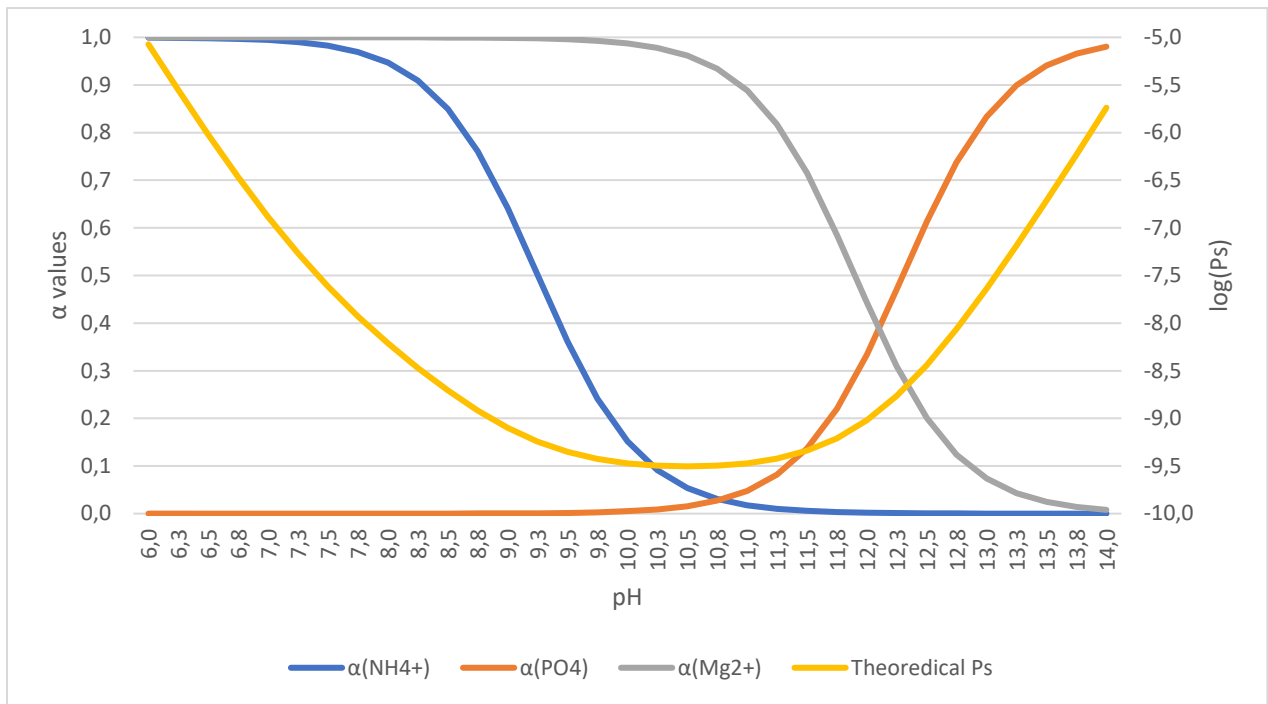


Figure 2-3: Struvite components and solubility product

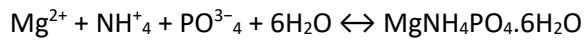
The lowest struvite solubility is at pH 10,50 with the $\log(P_s)$ value of -10,80. The highest efficiency for struvite crystallization occurs at this point.

(Snoeyink & Jenkins, 1980)

Struvite crystallization

Struvite crystallization involves nucleation and then crystal growth. Nucleation is the initial step in the formation of struvite crystals, which occurs when Mg^{2+} , NH_4^+ , and PO_4^{3-} are brought together under the appropriate pH conditions. The time taken for nucleation to occur is known as the nucleation time and is influenced by factors such as pH, mixing energy, coexisting ions, and saturation index. The ion activity in the solution, which is significantly influenced by the pH value, affects the rate of free ion combination. A low ion activity leads to a slower combination speed and a longer nucleation time. The amount and size of struvite crystals are strongly influenced by the mixing energy. The saturation ratio of the solution has the greatest impact on struvite nucleation, as it determines the development of crystals to either a homogeneous or heterogeneous state. (T. Zhang et al., 2017)

The struvite crystal has the chemical structure of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ with the Mg-NH₄-PO₄ ratio of 1-1-1. The concentrations of each component of struvite in the water and pH determines the struvite formation. If the concentrations are higher than the solubility limit for the pH of the water, then struvite crystallization occurs as the chemical reaction showed below.



The solubility of the struvite is,

$$K_{sp} = \{ \text{Mg}^{2+} \} * \{ \text{NH}_4^+ \} * \{ \text{PO}_4^{3-} \} \text{ (Ohlinger et al., 1998)}$$

Or

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

K_{sp} = Struvite solubility product constant in terms of activity

Struvite solubility

Struvite solubility is dependent on the environmental factors and important to consider in calculation the struvite crystallization. Van't Hoff equation gives the equilibrium constant of the struvite in specific conditions using a standard K_{sp} value that is known.

The standard K_{sp} value has been researched and found to be in several values in different research.

Table 2-1: Struvite solubility constant values at 25°C (Bhuiyan, 2007)

Published K_{sp} values for struvite at 25°C from literature			
pK _{sp}	K _{sp}	Origin	Reference
12,36	4,36E-13	Simulation	Buchanan et al., 1994
12,60	2,51E-13	Water	Bube, 1910
12,60	2,51E-13	Simulation	Loewenthal et al., 1994
12,76	1,74E-13	Water	Webb and Ho, 1992
12,93	1,17E-13	Aqueous solution	Age et al., 1997
13,12	7,58E-14	Water	Burn and Finlayson, 1982
13,15	7,08E-14	Aqueous solution	Taylor et al., 1963
13,27	5,37E-14	Synthetic supernatant	Ohlinger et al., 1998
13,36	4,37E-14	Aqueous solution	Babic Ivancic et al., 2002

Conditional solubility product

Conditional solubility product (P_s) is a graphical curve that refers to the change in the value of solubility product (K_s) with effect of pH. Plotting the conditional solubility product to pH provides the optimal conditions for struvite crystallization for reactor design considering the factors of ionic strength and temperature. (Bhuiyan, 2002)

P_s = conditional solubility product

$$P_s = \frac{K_{sp}}{\alpha_{Mg^{2+}} * \gamma_{Mg^{2+}} * \alpha_{NH_4^+} * \gamma_{NH_4^+} * \alpha_{PO_4^{3-}} * \gamma_{PO_4^{3-}}}$$

(Ohlinger et al., 1998)

Where,

$\alpha_{Mg^{2+}}$, $\alpha_{NH_4^+}$, $\alpha_{PO_4^{3-}}$ = ionization fraction of the individual constituents

α = free ion concentration/ total dissolved species concentration

$$\alpha_{Mg^{2+}} = [Mg^{2+}] / C_{T,Mg}$$

$$\alpha_{NH_4^+} = [NH_4^+] / C_{T,NH_3}$$

$$\alpha_{PO_4^{3-}} = [PO_4^{3-}] / C_{T,PO_4^{3-}}$$

$\gamma_{Mg^{2+}}$, $\gamma_{NH_4^+}$, $\gamma_{PO_4^{3-}}$ = Activity coefficient or ionic strength of the individual constituents. Activity coefficient can be calculated through Guntelberg equation.

$$\log \gamma_i = -A * z_i^2 * \frac{\sqrt{I}}{1 + \sqrt{I}}$$

Where,

z_i = Valence of the ion

I = ionic strength

A = constant that equals to 0,5 for water

Electrical conductivity (EC) is a measurement of conductivity in the water, which is determined by ion concentration and the mobility. EC can be used to assess the ionic strength (I) in the water which is used to calculate the conditional solubility product of struvite to predict the crystallization. The relationship between electrical conductivity and ionic strength is complex and not completely straight. Despite to that, electrical conductivity is a good indicator of ionic strength in the water. The EC value is dependent on the temperature and requires to be considerate.

$$EC_t = EC_{25} * (1 + a * (T - 25))$$

Where,

EC_t = electrical conductivity at a specific temperature (°C)

EC_{25} = electrical conductivity at a 25°C ($\mu S * cm^{-1}$)

T = temperature (°C)

a = temperature compensation factor ($^{\circ}C^{-1}$) = 0,0198

Temperature compensation factor is not a constant, it depends on the standard temperature used in the experiment. Therefore, it can only be used for 25°C in this example.

Ionic strength and electrical conductivity relationship was calculated by different researchers and found similar equations. According to research data with using struvite measurements indicate that the relationship between electrical conductivity to ionic strength can be determined with the equation below. EC_t values are converted to EC_{25} value for calculating the ionic strength in the formula.

$$I = 5 * 10^{-6} * EC_{25}$$

Where,

I = ionic strength ($\text{mol} \cdot \text{l}^{-1}$)

EC_{25} = electrical conductivity at a 25°C ($\mu\text{S} \cdot \text{cm}^{-1}$)

(Bhuiyan, 2002)

Temperature effect on solubility product

Struvite solubility in different temperatures can be found with Van't Hoff equation.

$$K_{spT} = K_{spT^0} * e^{\frac{-\Delta H_r^0}{R} * (\frac{1}{T} - \frac{1}{T^0})}$$

Where,

K_{spT^0} = Standard struvite solubility constant

K_{spT} = Struvite solubility constant in specific temperature

T^0 = Temperature at standard condition (°K) = 298 °K

T = Temperature at specific condition (°K)

R = Gas constant = $8,314 \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$

ΔH_r^0 = Reaction enthalpy (at 25°C = $23,62 \text{ kcal} \cdot \text{mol}^{-1} = 98,82 \text{ kJ} \cdot \text{mol}^{-1}$)

Reaction enthalpy has different values in different temperatures. Considering the changes in the reaction enthalpy and the temperature, it is possible to express the struvite solubility constant as a polynomial function of temperature.

Another way to calculate the K_{sp} value is using the experimental data to create a polynomial function. Experiment results in different temperatures were input to the computer program PHREEQC which is designed to model aqueous geochemical calculations. This polynomial function resulted as the analytical expression for the struvite solubility constant. (Bhuiyan, n.d.)

$$\log(K_{sp}) = -1157,45 - 0,784 * T - \frac{63,86}{T} + 556,83 * \log(T) + \frac{19,54}{T^2}$$

(Bhuiyan, 2002)

Where T is temperature in Kelvin (°K).

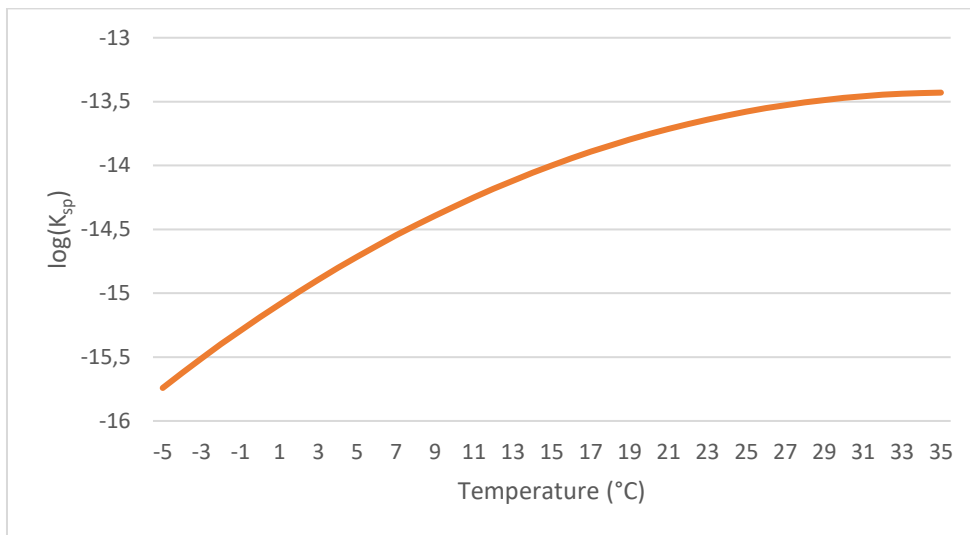


Figure 2-4: Temperature and solubility product correlation

The struvite solubility increases with the temperature. A lower temperature is desired to achieve highest struvite crystallization rate.

Supersaturation ratio

Supersaturation is an essential condition for observing nucleation or growth once the material is in solution. In order for a solution to be supersaturated, the concentration of the solute must exceed its solubility, which is the concentration at which crystals and the solution are at equilibrium.

Supersaturation serves as the driving force for nucleation and growth to occur.

Struvite crystallization occurs when the activity of the components of struvite reaches to the value of the solubility product. To assess whether the wastewater is saturated with respect to struvite, a saturation index is utilized. This is defined by the supersaturation ratio (Ω).

$$\Omega = \frac{IAP}{P_s}$$

Where,

Ω = the supersaturation ratio (the activity based super saturation ratio of struvite) saturation index or

activity based super saturation ratio of struvite

IAP= Ion activity product, calculated with multiplication of struvite component ions' activity values

(Bhuiyan, 2002)

$$IAP = \{Mg^{2+}\} * \{NH_4^+\} * \{PO_4^{3-}\}$$

{Mg⁺²} = magnesium activity

{NH₄⁺} = ammonium activity

{PO₄⁻³} = phosphate activity

K_{sp} or P_s, (solubility product constant) is a constant value for a particular compound that represents the balance point between the dissolved and undissolved forms of the compound. It is determined experimentally under specific conditions (such as temperature and pressure), and its value remains constant under those conditions. On the other hand, IAP (ionic activity product) is calculated using the current ion concentrations in the solution, and it represents the actual thermodynamic driving force for the crystallization or dissolution of the compound. If the IAP is higher than the K_{sp}, the solution is supersaturated, and crystallization will occur until the IAP decreases to the K_{sp}. If the IAP is lower than the K_{sp}, the solution is unsaturated, and dissolution will occur until the IAP increases to the K_{sp}.

if $\Omega > 1$, IAP > P_s, then the ion activity product (IAP) is greater than the solubility product constant (KSP), indicating that the solution is supersaturated, and struvite should crystallize.

If $\Omega = 1$, IAP = P_s, indicating that the solution is at equilibrium conditions and saturated with respect to struvite.

If $\Omega < 1$, IAP < P_s, indicating that the solution is undersaturated and the mineral should dissolve.

$$\Omega = \frac{[Mg^{2+}] * \gamma_{Mg^{2+}} * [NH_4^+] * \gamma_{NH_4^+} * [PO_4^{3-}] * \gamma_{PO_4^{3-}}}{P_s}$$

The effect of impurities on struvite crystallization

In general, the compounds found in wastewater can be divided into those that participate and those that do not participate in the crystallization process. The type and concentration of additional compounds can vary widely among different types of wastewater, and even within the same type of wastewater. Participating compounds can compete with struvite constituent ions for reaction and may coprecipitate, resulting in reduced product purity or inhibition of struvite crystal growth.

Common examples of participating ions found in wastewater include Na⁺, Ca²⁺, Cu²⁺, Zn²⁺, Al³⁺, Cl⁻,

CO_3^{2-} , NO_3^- , and SO_4^{2-} . Participating ions have been shown to cause a reduction in particle size and a change in crystal shape. For instance, the presence of nitrate in the wastewater has been found to favour the formation of struvite crystals with a tubular morphology. (Shaddel, 2020)

Interacting chemicals on struvite crystallization

Suspended solids

Suspended solids may affect the struvite crystallization positively or negatively. In positive way, suspended solids can become a surface for nucleation and lower the required energy for crystallization by making heterogenous nucleation possible. This would enhance the struvite crystallization. In negative way, suspended solids can hinder the crystal growth if it is blocking the active growth sites. When dealing with streams that have a suspended solid concentration above 1000 mgL⁻¹, suspended solids pre-treatment may be necessary. The inhibitory effect of organic matter, such as organic acids and oxalate, on struvite crystallization depends on the molecular weight. High molecular weight compounds can strongly interfere with phosphate removal, whereas low molecular weight organic acids like citric, succinic, and acetic acids have a moderate inhibitory effect. In the anaerobic digestion of sludge, dissolved organic materials such as proteins and humic substances with a strong complexation ability with Mg^{2+} are present. On the other hand, VFAs exhibit weak complexation ability with Mg^{2+} or NH_4^+ . (Shaddel, 2020)

Seed materials

A seed is a suspended solid that affects the crystallization positively by lowering the activation energy barrier. Seeding is a process that facilitates the formation of crystals in a reactor by adding seeds in it. With seeding, the activation energy of nucleation can be reduced, allowing for more efficient crystallization. The availability of either a seed crystal or the creation of a solid interface within the growth medium decreases the energy requirement of nucleation. Homogeneous nucleation necessitates additional energy, thus the use of a seed crystal or a compatible substrate, as in thin film growth, is preferred. (Shaddel, 2020)

Organic matter

Organic matter with high molecular weight such as protein and humic substances strongly interferes with the phosphate removal and have an inhibitory effect on struvite crystallization therefore undesired in the supersaturation. (Shaddel, 2020)

Calcium

Calcium phosphates are another option for recovering phosphorus from wastewater. The type of calcium phosphate formed depends on the supersaturation of Ca: P and pH, with hydroxyapatite being the most stable and least soluble form. Similar to struvite, calcium phosphates have low water solubility but are highly soluble in citric acid, making them more useful under acidic conditions. Recovering calcium phosphates in nanoparticulate form can improve their fertilizer value by increasing their solubility and surface area for crops to grow. Calcium phosphates are generally colourless and pure powder is white but may have slight discoloration due to impurities. (Shaddel, 2020)

Heavy metals and other contaminants

Municipal wastewaters are known to contain a variety of contaminants such as heavy metals, pesticides, pharmaceuticals, personal care products, nanomaterials, per fluorinated compounds (PFCs), hormones, recreational drugs, and pathogens. However, the fate of many of these materials in the struvite recovery process is not well understood. Generally, it is believed that these contaminants will be fixed in the sludge and will have minimal contribution to the final recovered struvite. This is because the struvite recovery process primarily focuses on removing phosphorus and nitrogen from the wastewater and does not target the removal of other contaminants. Therefore, it is important to consider the potential presence of these contaminants when utilizing recovered struvite for agricultural purposes or other applications. (Shaddel, 2020)

Competing reactions

Theoretically, the highest efficiency of struvite crystallization would occur at 1:1:1 ratio for magnesium, ammonium, and phosphate ions. However, wastewater contains various other chemicals and the other reactions that would happen simultaneously during struvite crystallization would compete to consume struvite components and reduce efficiency.

Other reactions that compete with struvite crystallization

Table 2-2: Competing reactions of struvite

Reaction	pKa value
$\text{NH}_4^+ \leftrightarrow \text{NH}_3(\text{aq}) + \text{H}^+$	9,3
$\text{H}_3\text{PO}_4 \leftrightarrow \text{H}_2\text{PO}_4^- + \text{H}^+$	2,1
$\text{H}_2\text{PO}_4^- \leftrightarrow \text{H}_2\text{PO}_4^{2-} + \text{H}^+$	7,2
$\text{HPO}_4^{2-} \leftrightarrow \text{PO}_4^{3-} + \text{H}^+$	12,3

$\text{MgOH}^+ \leftrightarrow \text{Mg}^{2+} + \text{OH}^-$	2,56
$\text{MgH}_2\text{PO}_4^+ \leftrightarrow \text{H}_2\text{PO}_4^- + \text{Mg}^{2+} + \text{OH}^-$	0,45
$\text{MgHPO}_4 \leftrightarrow \text{H}_2\text{PO}_4^{2-} + \text{Mg}^{2+}$	2,91
$\text{MgPO}_4 \leftrightarrow \text{PO}_4^{3-} + \text{Mg}^{2+}$	4,8
$\text{AlPO}_{4(s)} \leftrightarrow \text{Al}^{+3} + \text{PO}_4^{3-}$	21
$\text{FePO}_{4(s)} \leftrightarrow \text{Fe}^{+3} + \text{PO}_4^{3-}$	21,9 to 23

(Tchobanoglous et al., 2014)

IVAR Sentralrenseanlegg Nord-Jæren (SNJ) wastewater treatment plant

IVAR SNJ is a wastewater treatment plant located in Mekjarvik, Rogaland, Norway. It is the largest and most advanced wastewater treatment plant in the region, treating wastewater from Randaberg, Stavanger, Sola, Sandnes, and Gjesdal municipalities. The plant was originally designed to serve 240,000 person equivalents (p.e) and was upgraded in 2017 to serve 400,000 p.e. This upgrade also involved a shift in treatment process from a chemical treatment plant to a mechanical-biological treatment plant with Enhanced Biological Phosphorus Removal (EBPR) to comply with stricter regulations on wastewater quality and to meet the forecasted future demand. A schematic overview of the SNJ treatment plant can be seen in the figure 2-5. (Egeland, 2018, Ramadhania 2021)

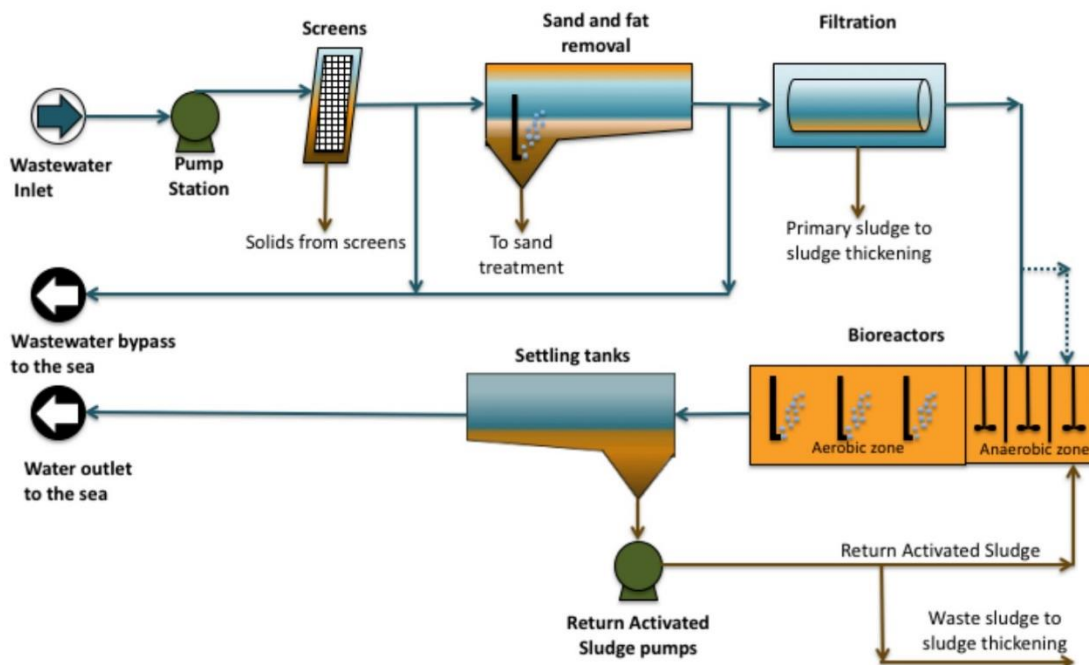


Figure 2-5: Schematic figure of IVAR SNJ WWTP (Egeland, 2018)

The wastewater treatment process begins with the entry of raw wastewater into a pump station, where it is then directed towards the screening unit. The purpose of the screening unit is to effectively separate and remove solid materials present in the wastewater stream. Following the screening process, subsequent treatment steps are initiated, starting with sand and fat removal. These processes aim to eliminate sand, as well as grease and oils that may be present.

Once the pre-treatment is completed, the wastewater undergoes filtration, during which primary sludge is separated and directed towards the sludge thickening unit. This stage helps to concentrate the sludge by removing excess water content, resulting in a more manageable and efficient sludge handling process.

The treated wastewater then proceeds to the bioreactors, where EBPR is implemented. Within these bioreactors, specialized microorganisms facilitate the removal of phosphorus through biological processes. The biological treatment process at IVAR SNJ involves a setup consisting of three parallel process lines, each connected to a bioreactor and four sedimentation basins. The bioreactor is divided into two main parts, with the first part comprising anaerobic chambers. In the other part of the bioreactor, aerobic conditions are maintained by continuously pumping air into the system. This enables polyphosphate-accumulating organisms (PAOs) to access oxygen and effectively remove phosphorus from the wastewater. After biological treatment, the wastewater is directed to the sedimentation basins, where biomass as sludge is removed. A portion of the sludge is recycled back to the anaerobic tank, while the remaining sludge is directed to sludge treatment.

After the bioreactor stage, the wastewater enters settling tanks, where the solid particles and biomass settle at the bottom. A portion of the settled sludge is recycled back to the bioreactors to maintain optimal microbial activity and phosphorus removal efficiency, while the remaining sludge is directed to the sludge thickening unit for further concentration.

Following the settling tanks, the clarified water, free from excessive solids and phosphorus, is discharged into the sea, meeting the regulatory standards for water quality. This comprehensive treatment scheme ensures the effective removal of contaminants and the proper management of sludge, contributing to the overall efficiency and environmental sustainability of the wastewater treatment plant.

EBPR at IVAR SNJ and uncontrolled struvite crystallization

Struvite crystallization is a common operational issue in biological wastewater treatment plants with an Enhanced Biological Phosphorus Removal (EBPR) process. This is due to the increased amount of PO_4^{3-} present in the reject streams from sludge treatment. As the phosphorous is released from the EBPR sludge under anaerobic conditions, the potential for struvite crystallization is highest downstream of the anaerobic phases of sludge treatment. Struvite formation potential in a wastewater treatment plant is dependent on the availability of PO_4^{3-} , NH_4^+ and Mg^{2+} ions.

In the case of SNJ, conductivity testing and ion identification analyses have confirmed that the wastewater is subject to seawater inflow when the tide is high. This results in higher Mg^{2+} concentrations than average wastewater in the region. Combined with the implementation of biological treatment and EBPR, SNJ is experiencing higher levels of uncontrolled struvite crystallization.

Despite the operational issues related to struvite crystallization, the implementation of the EBPR process also provides an opportunity for phosphorous recovery through controlled struvite crystallization. The controlled crystallization of struvite can be a beneficial process, as it can be harvested and used as a fertilizer.

The IVAR SNJ plant exhibits favourable conditions for struvite precipitation in the centrifuge reactor due to the presence of ammonia and orthophosphate in the system, as well as elevated magnesium concentrations originating from seawater intake. As a consequence of the process, the pH of the water increases to approximately 8, further facilitating struvite crystallization. In the current setup, struvite crystallization within the centrifuge reactor is prevented through the addition of iron chloride into the reactor. This measure incurs additional operational costs and detracts from the eco-friendliness of the system. To address this issue, the implementation of a struvite reactor is proposed.

The secondary treatment sludge obtained after thickening contains a high concentration of phosphate resulting from the metabolism of phosphorus-accumulating organisms (PAOs) in the EBPR process. This particular flow, referred to as bio-reject (BR), originates from the reject water derived during the thickening of the biological treatment water. The BR flow serves as a valuable orthophosphate resource for the struvite reactor. Assuming a phosphate removal efficiency of 75% using the EBPR process, the anticipated concentration range of orthophosphate in the BR is projected to be between 200 and 300 mg/L.

After the digested sludge is subjected to dewatering using a centrifuge, the effluent is referred as centrifuge-reject (SR). The concentration of ammonia in the centrifuge reject (SR) is approximately 1000 mg/L. This ammonia serves as the primary ammonia resource for the struvite reactor.

Once the struvite reactor is integrated into the system, the secondary treatment thickening reject stream will be redirected to the struvite reactor, resulting in a reduced concentration of phosphate within the centrifuge reactor and subsequently lowering the rate of struvite production.

The general structure of the IVAR SNJ wastewater treatment plant is illustrated in the figure 2-6, showcasing a potential implementation of a full-scale struvite reactor within the system.

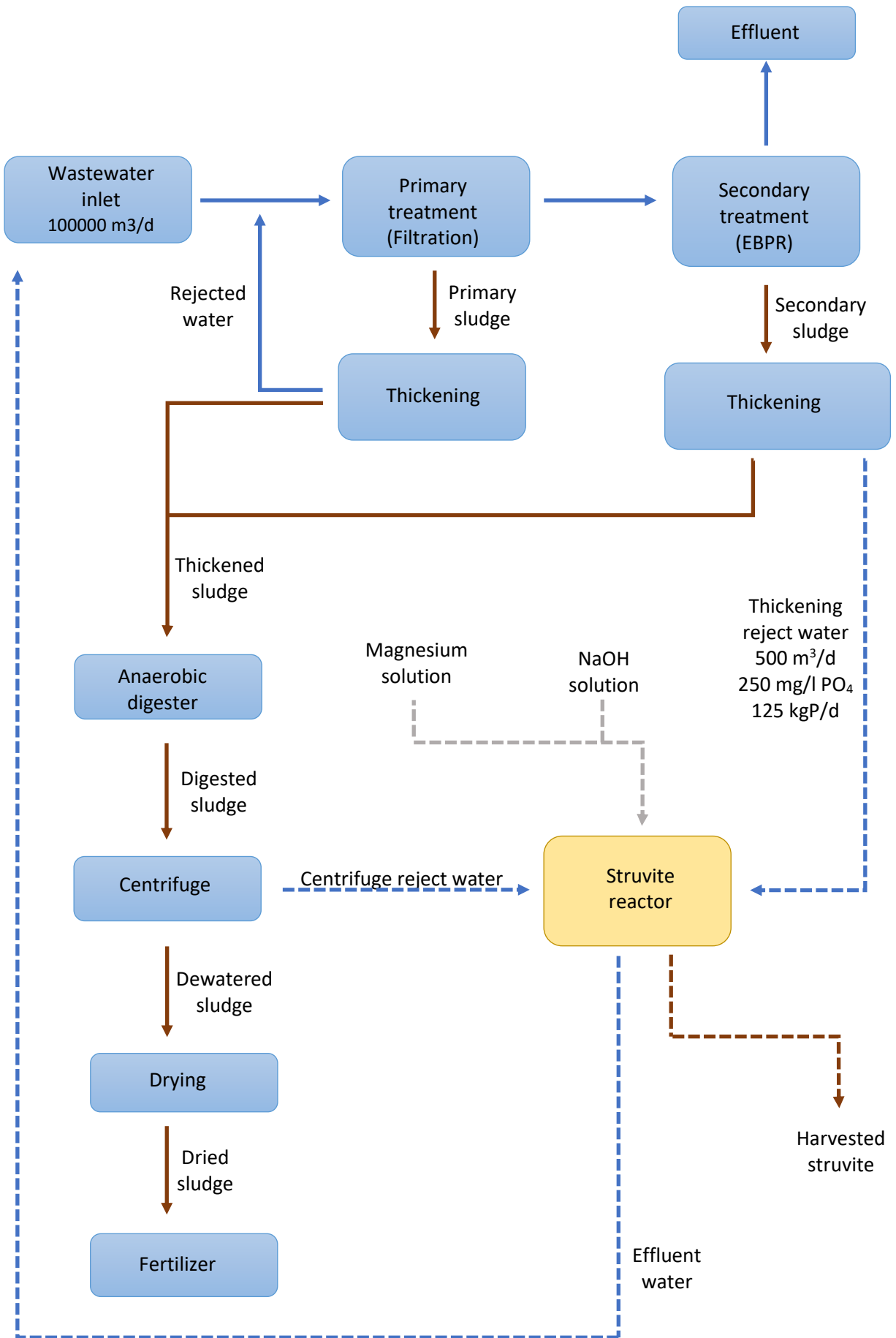


Figure 2-6: IVAR SNJ treatment scheme and potential struvite reactor implementation

Objective

The objective of this study is to investigate the struvite crystallization using a fluidized bed reactor for phosphorus recovery from BR flow of IVAR SNJ WWTP, which has a 125 kgP/d phosphorus load. The primary focus of this research is to gain a comprehensive understanding of the structure and crystallization mechanics of struvite, optimize the struvite crystallization process, and evaluate its potential for large-scale application. These objectives are outlined as follows:

1. Determining the optimal Mg-NH₄-PO₄ molar ratio for the struvite reactor: This objective focuses on finding the ideal ratio of magnesium, ammonia, and orthophosphate components in order to enhance struvite formation and improve phosphorus recovery. The calculation for appropriate flow rates of wastewater that need to be directed to the full-scale struvite reactor for the selected molar ratio is researched.
2. Determining the optimal pH for the struvite reactor: The aim is to identify the pH level that sufficient for an efficient struvite crystallization efficiency and providing an optimal orthophosphate removal while keeping the pH buffer consumption at minimum.
3. Determining the amount of magnesium consumption in the struvite reactor: This objective involves quantifying the magnesium requirements, necessary for efficient struvite crystallization, also researching the possibilities of using sea water as a magnesium resource.
4. Determining potential the struvite production at IVAR SNJ WWTP: This objective involves quantifying the struvite that is produced within the reactor and comparing the value with existing research to observe rationality.
5. Determining the effect of wastewater characteristics on struvite crystallization: This objective focuses on understanding how various wastewater constituents, such as temperature and salinity, influence the process of struvite crystallization based on literary findings and Visual MINTEQ modelling.

The anticipated outcomes of this study include the development of a sustainable and efficient phosphate recover by struvite crystallization for IVAR SNJ WWTP. The findings will contribute to environmental preservation and aid in the protection of valuable resources.

3. Materials and Method

In the Materials and Methods section, the experimental design and measurement methods are explained in detail.

Batch reactor experiments

During the batch reactor experiments, the conditions of the batch reactor were replicated in laboratory beakers. SR and BR samples were taken and analysed. A struvite molar ratio of 1:1:1 was achieved by carefully adjusting the SR and BR volumes in the beakers and addition of sodium dihydrogen phosphate dihydrate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$) to set the concentration of orthophosphate to desired level. Magnesium chloride hexahydrate ($\text{Cl}_2\text{Mg} \cdot 6\text{H}_2\text{O}$) used as the magnesium resource to be added in the sample to obtain the desired magnesium concentration. The pH of the solution was adjusted to the desired level using 1 M of sodium hydroxide (NaOH), and thorough mixing was ensured by utilizing a mixer at a speed of 300 rpm for a duration of 30 minutes.

Following the mixing process, samples were collected from the batch reactor and subjected to analysis. The pH levels of the samples were measured and recorded, along with the concentrations. These data points were then compared to examine any potential correlation between the pH levels and the effluent concentrations.

Pilot reactor experiments

A fluidized bed reactor was utilized for struvite crystallization. The reactor had a volume of 16,4 litres and was operated by pumping air to fluidize the solid particles and to mix the liquid within it. By introducing air, the solid particles were lifted and suspended, creating a fluid-like environment.

Different concentrations of struvite components are tested in different pH levels to observe the optimal crystallization conditions. Worked on wastewater with adjusted concentrations for different ratios of magnesium (Mg), ammonium (NH_4), and orthophosphate (PO_4^{3-}) and different pH values with adjustment using 1 M of sodium hydroxide (NaOH). After operation the concentrations of struvite components were measured, and the efficiency is calculated based on the results. The results were compared with the theoretical struvite crystallization to check the accuracy.

Sodium dihydrogen phosphate dihydrate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$) were added into BR tank to set the concentration of orthophosphate to desired level. Magnesium chloride hexahydrate ($\text{Cl}_2\text{Mg} \cdot 6\text{H}_2\text{O}$) used to make 1 M of magnesium solution as the magnesium resource.

Experiment design

The experimental setup consisted of a fluidized bed reactor with a recycle pump to ensure a uniform concentration distribution throughout the reactor. The feed streams, magnesium, bio-rejekt (BR) and centrifuge-rejekt (SR) waters, were introduced at the bottom of the reactor, while NaOH solution was supplied from the top. To achieve optimal mixing and precipitation, an upward flow direction was employed in the reactor. This arrangement facilitated the dispersion of dissolved concentrations of struvite components throughout the reactor, while allowing the crystallized struvite particles to settle and precipitate at the bottom due to their weight. After that, the effluent water was collected in a separate tank.

In order to reduce the energy required for struvite to begin crystallization, seed crystals were added to the reactor before each experiment was started. The concentrations of the struvite components in the reactor were controlled through the use of pumps. The pumps were routinely monitored to ensure accurate flow rates. Water levels in the feed and the effluent tanks were checked regularly, and flow checks were conducted by measuring the time and volume of water pumped. The pumps were adjusted to different flow rates to achieve various molar ratios of struvite components in the reactor. To determine the impact of different molar ratios and pH values, these conditions were evaluated using a flow reactor. The effluent water was then analysed to observe the effects of the various conditions. The fluidized bed reactor setup is presented in figure 3-1.

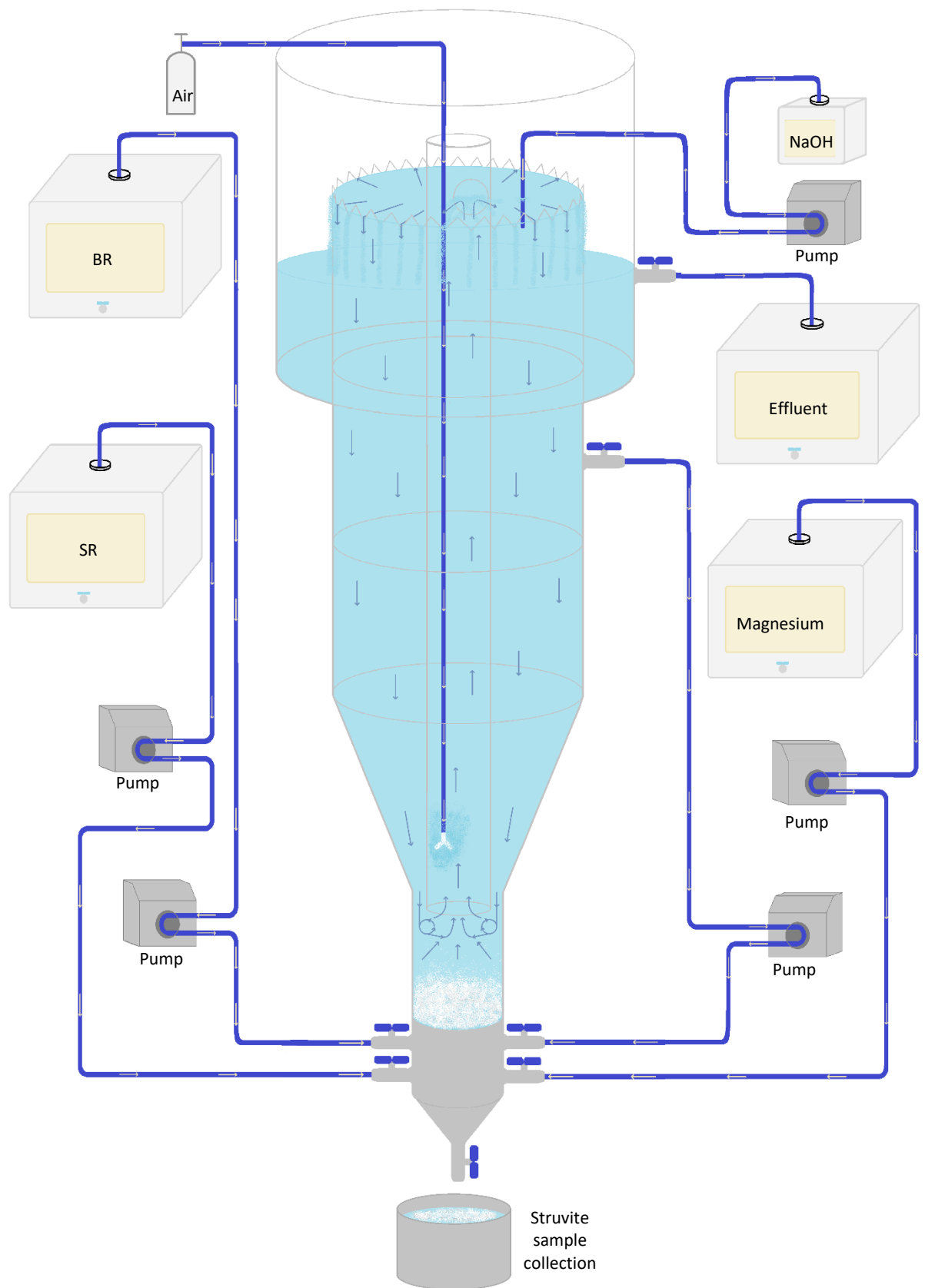


Figure 3-1: Fluidized bed reactor design for struvite reactor

Measurements

Various test kits were utilized for the determination of the concentration of the analytes of interest. The measurements were obtained using a spectrophotometer to read the resultant values.

Total hardness analysis

The total hardness test was used to determine the concentrations of magnesium and calcium in the water tanks prior to entering the reactor. The Spectroquant total hardness cell test was used to measure the total hardness, from which the concentration of Ca^{+2} was determined by subtracting the magnesium hardness value. The test range spanned 0.12 to 5.36 mmol/L Ca, Mg, and the samples were filtered and diluted as necessary prior to analysis.

Magnesium analysis

Magnesium analysis was conducted to determine the concentration of magnesium in the reactor. For this purpose, the Spectroquant magnesium cell test was utilized, which has a range of 5,0 to 75,0 mg/L Mg. Prior to the analysis, samples were filtered and diluted, as required.

Ammonia analysis

To determine the concentration of NH_4^+ in the wastewater samples from SNJ, a Spectroquant Ammonium Cell Test was used. This test utilizes an alkaline solution and $\text{NH}_4\text{-1K}$ reagent to form a blue indophenol derivative in the presence of NH_4^+ . The concentration of NH_4^+ is then determined spectrophotometrically after 15 minutes of reaction time. The range of the test is 4,0 – 80,0 mg/l $\text{NH}_4\text{-N}$, and samples were filtered and diluted, if necessary, before analysis.

Orthophosphate analysis

In low concentrations: To analyse the concentration of $\text{PO}_4\text{-P}$ in the wastewater samples, an ascorbic acid and molybdate reagent was added to the filtered sample in an empty Spectroquant test cell. The molybdate reagent contains ammonium molybdate and antimony tartrate, which react with PO_4^- in the sample to form phosphomolybdic acid. Ascorbic acid reduces the phosphomolybdic acid to molybdenum blue, which is measured spectrophotometrically at a wavelength of 880 nm, 10 minutes after reagent addition.

In high concentrations:

The Spectroquant phosphate cell test was utilized to quantify the orthophosphate concentrations in the sample. The test has a range of 3,0 to 100,0 mg/L $\text{PO}_4\text{-P}$.

pH, Electrical Conductivity, Temperature

For the determination of pH, temperature, and electrical conductivity, a portable WTW 3630 IDS probe was employed. In cases where this specific probe was unavailable, a portable WTW Multi 340i probe was used specifically for pH determination. To ensure accurate measurements, regular calibration of the probes was conducted.

4. Results

In the Results section, the obtained correlations between variables are explained. Additionally, Visual MINTEQ modelling was employed to simulate and understand the precipitation of struvite under various wastewater conditions.

The data collected from the experimental measurements, including struvite component concentrations, pH, temperature, and flow rates, were analysed to identify connections and relationships. Statistical analyses, such as correlation coefficients and regression analyses, were conducted to determine the associations between the variables.

Phosphorus removal in the batch tests

Through this comparative analysis, a notable correlation between the pH levels and the effluent concentrations was observed. This finding suggests that the pH plays a significant role in influencing the final concentrations of the effluent in the struvite precipitation process.

Figure 4-1 and figure 4-2 shows that pH needs to be higher than 8,5 to get sufficient precipitation for the molar ratio of Mg-NH₄-PO₄:1-1-1. These figures also show that there is a low orthophosphate removal at pH around 7.

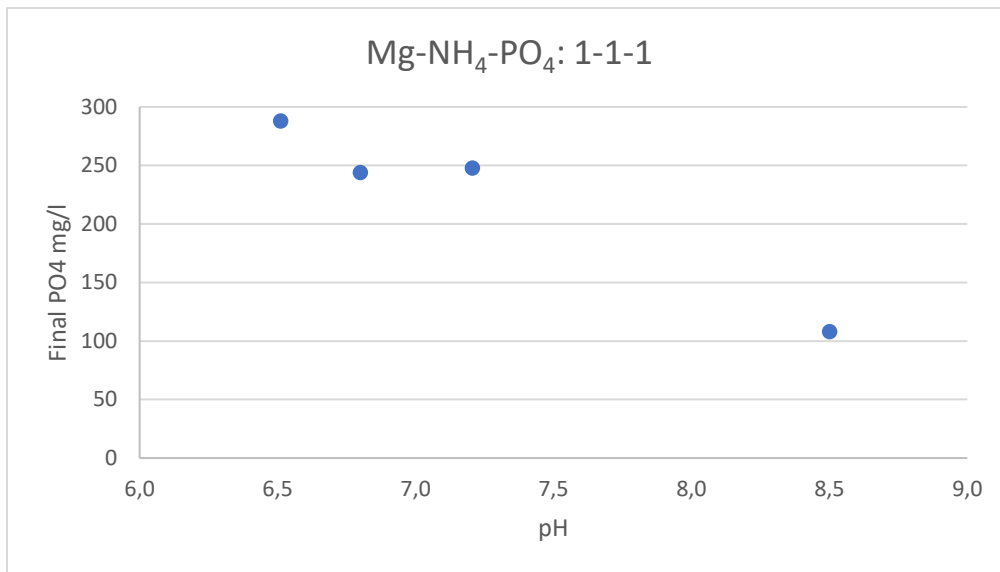


Figure 4-1: Final orthophosphate concentration and pH correlation for molar ratio $Mg-NH_4-PO_4:1-1-1$

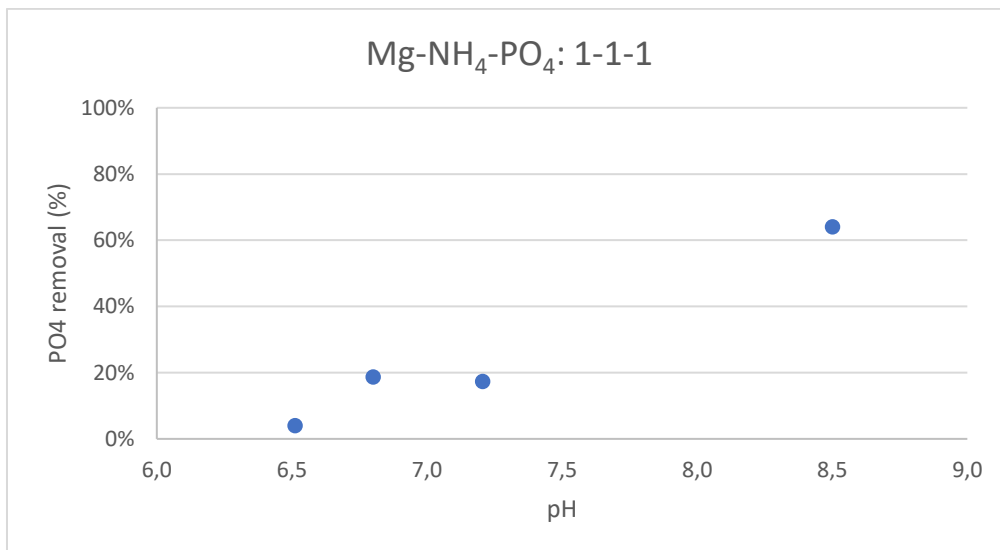


Figure 4-2: Orthophosphate removal and pH correlation for molar ratio $Mg-NH_4-PO_4:1-1-1$

Phosphorus removal in pilot reactor

Different struvite molar ratios were examined at different pH levels to evaluate the impact. The resulting effluent orthophosphate concentrations were compared to pH of the different molar ratios. A correlation between pH levels and the orthophosphate concentrations in the effluent water was observed, indicating a consistent relationship between these variables.

The results from pilot reactor experiments molar ratio of $Mg-NH_4-PO_4:1,5-1,5-1$ at different pH levels is given figure in 4-3 and figure 4-4. The results show that at pH 9,5, the initial concentration of 215 mg/l was reduced to 1,7 mg/l, providing a 99% efficiency of orthophosphate removal. At pH 8,3 the

orthophosphate removal was 91% , while below pH 7, there was not a sufficient orthophosphate removal.

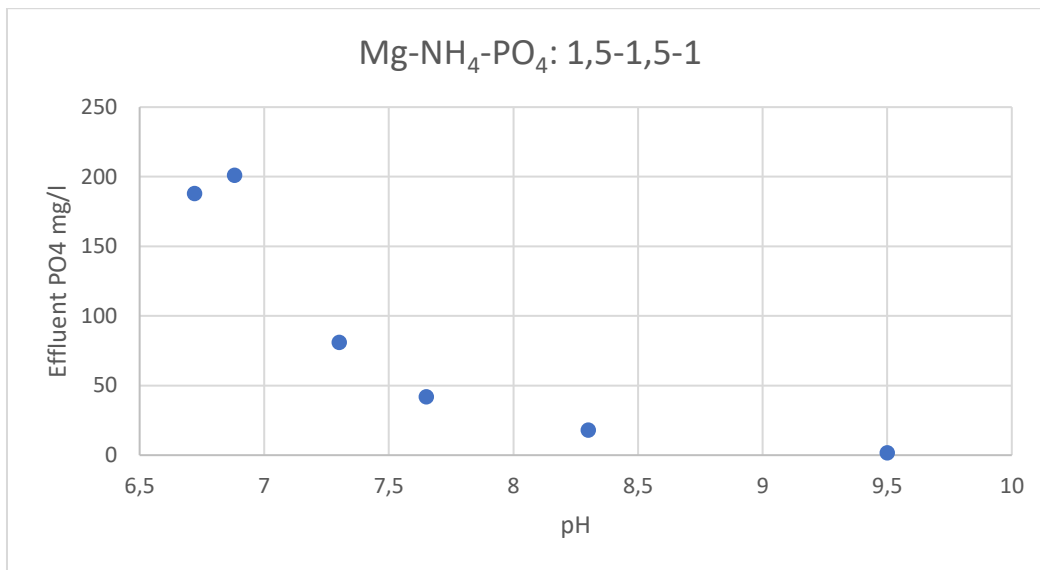


Figure 4-3: Effluent PO4 concentration and pH correlation for molar ratio Mg-NH₄-PO₄:1,5-1,5-1

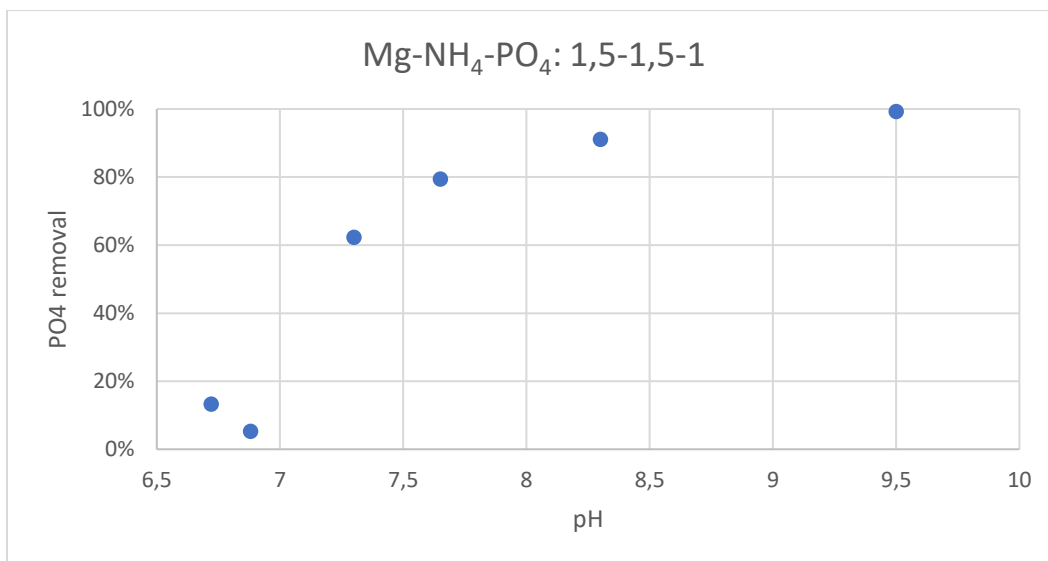


Figure 4-4: Orthophosphate removal and pH correlation for molar ratio Mg-NH₄-PO₄:1,5-1,5-1

The pilot reactor experiments provided results on the effect of different molar ratios of Mg-NH₄-PO₄:3-1,5-1 at various pH levels, as depicted in figure 4-5 and figure 4-6 demonstrates that at pH 8.3, the orthophosphate concentration in the effluent was measured to be 7 mg/l. Comparatively, in Figure 10, the test conducted at the same pH but with a Mg-NH₄-PO₄ molar ratio of 1.5-1,5-1 displayed a higher orthophosphate concentration of 18 mg/l.

The result from molar ratio of $\text{Mg-NH}_4\text{-PO}_4\text{:3-1,5-1}$ show that a low effluent orthophosphate concentration was measured at pH 8,5 with 13 mg/l and the removal efficiency was %93.

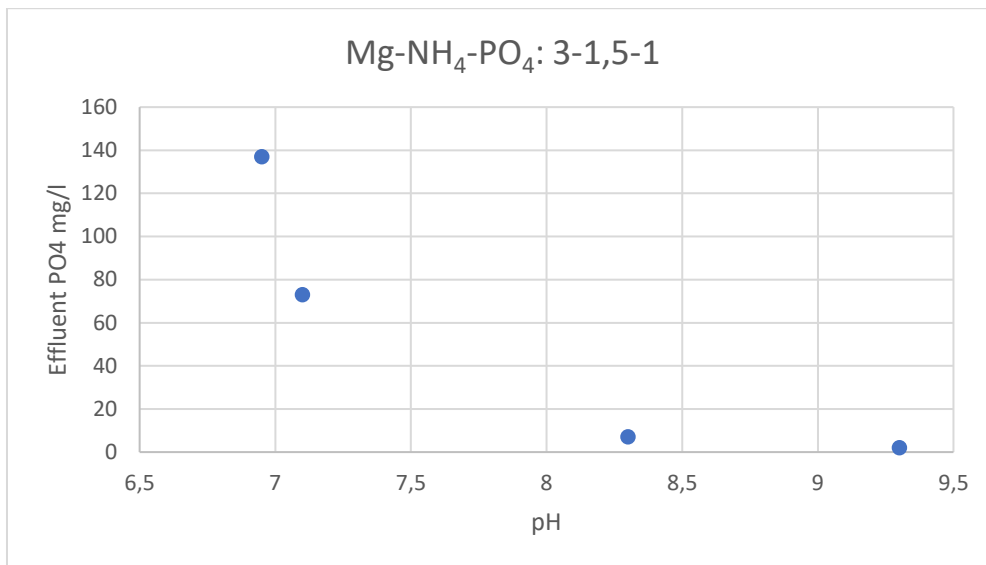


Figure 4-5: Effluent orthophosphate concentration and pH correlation for molar ratio $\text{Mg-NH}_4\text{-PO}_4\text{:3-1,5-1}$

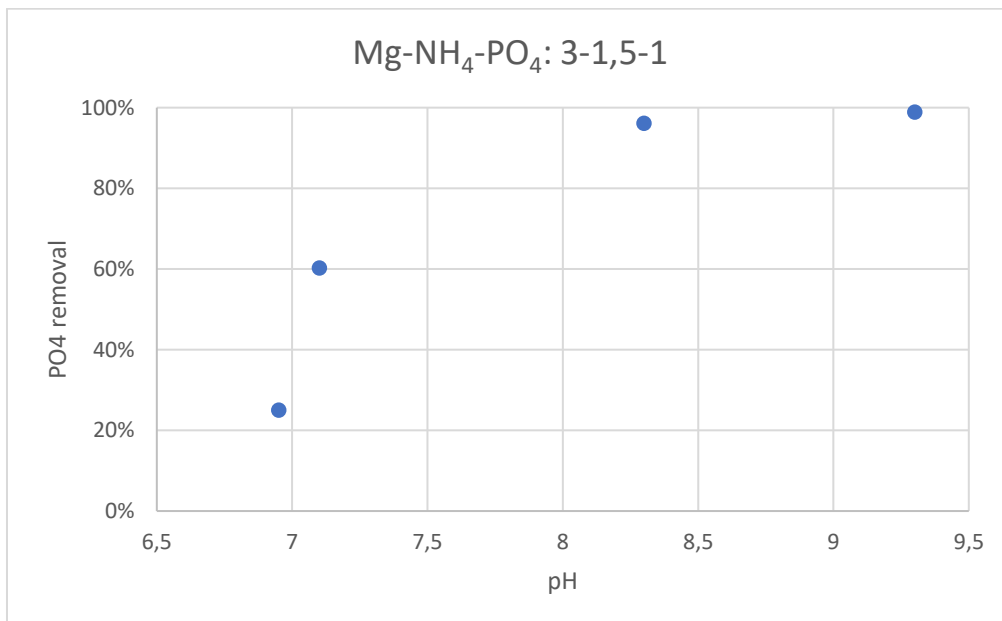


Figure 4-6: Orthophosphate removal and pH correlation for molar ratio $\text{Mg-NH}_4\text{-PO}_4\text{:3-1,5-1}$

The experimental outcomes derived from the application of the molar ratio of $\text{Mg-NH}_4\text{-PO}_4\text{:1,5-3-1}$ demonstrate that a sufficient level of orthophosphate removal can be achievable at pH values of 8,5 and higher.

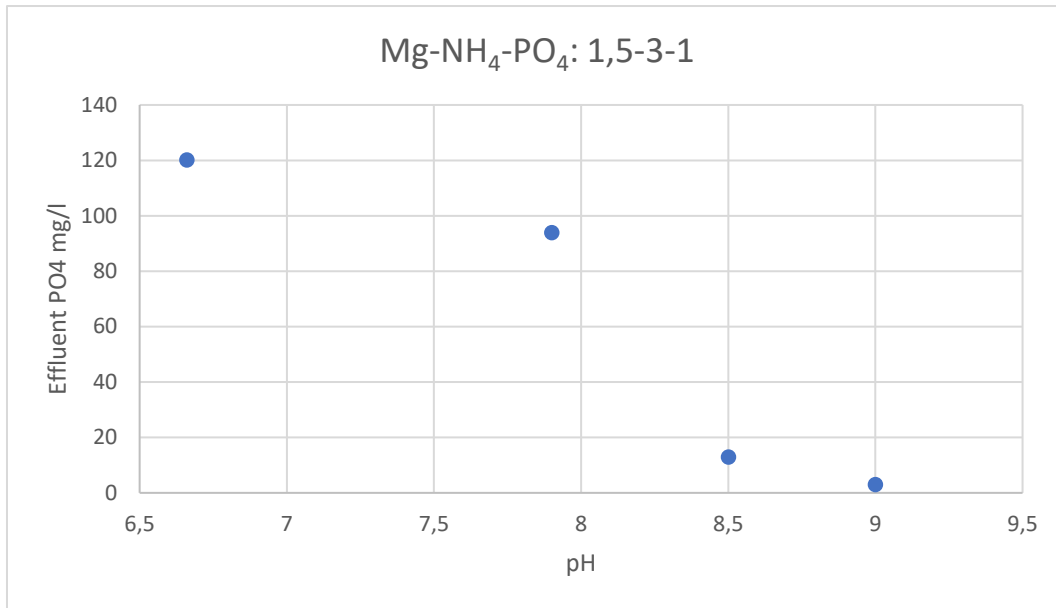


Figure 4-7: Effluent concentration and pH correlation for molar ratio $Mg-NH_4-PO_4:1,5-3-1$

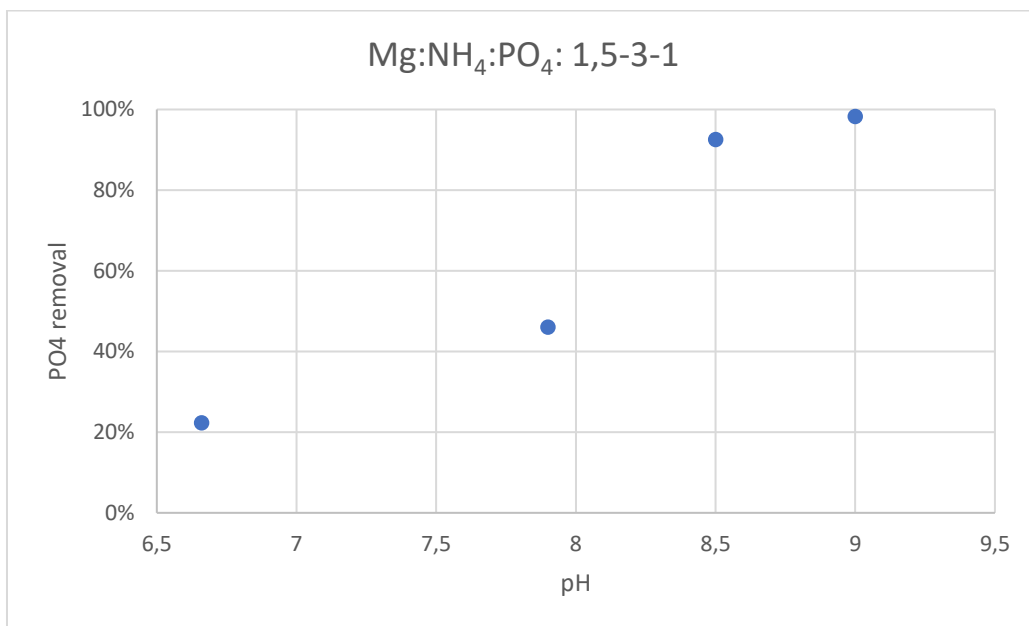


Figure 4-8: Orthophosphate and pH correlation for molar ratio $Mg-NH_4-PO_4:1,5-3-1$

The experimental findings revealed that in all cases where the molar ratio of orthophosphate was lower than that of ammonia and magnesium, a sufficient amount of orthophosphate removal was achieved for a struvite crystallization reactor when the pH was maintained at 8,5 and above.

The effect of molar ratios in the struvite crystallization

The effluent concentrations of the experiments in different molar ratios were compared.

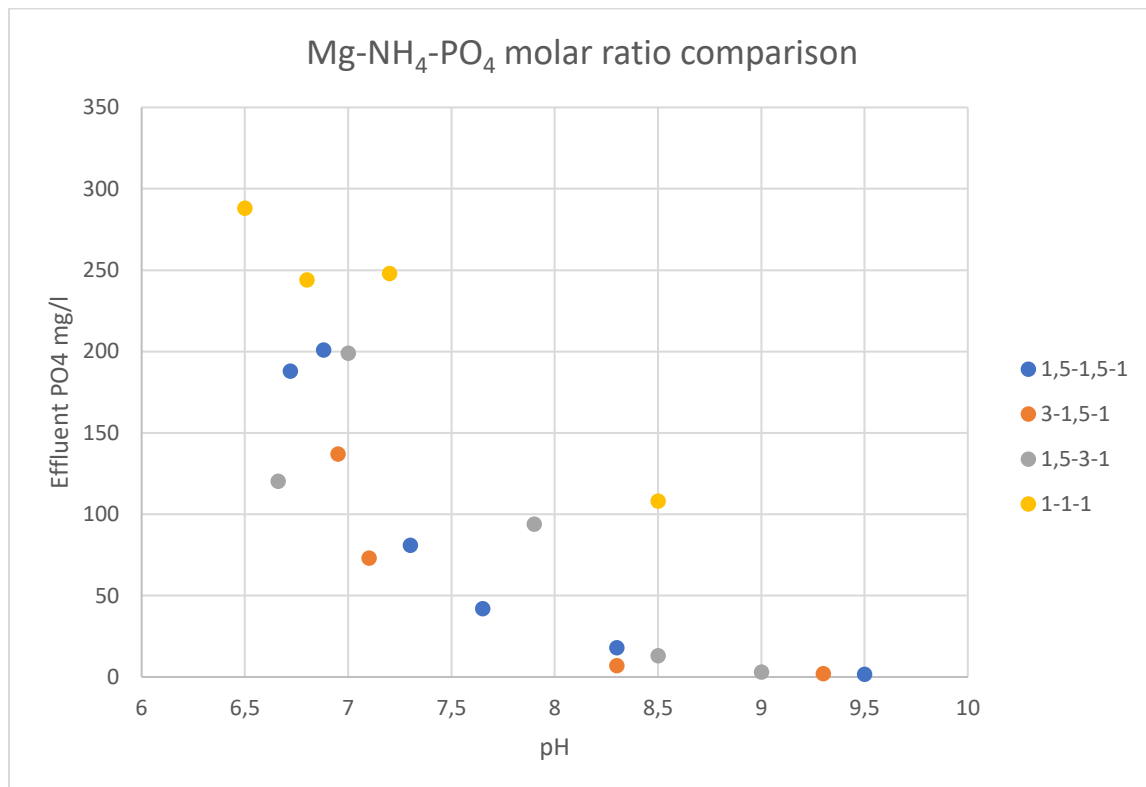


Figure 4-9: Mg-NH₄-PO₄ molar ratio comparison

It was evident that maintaining a lower orthophosphate ratio compared to ammonia and magnesium had an impact on struvite precipitation when the pH was below 8,5. Unfortunately, there is no available data for the molar ratio of 1-1-1 at pH values higher than 8,5. Nevertheless, considering the results of other molar ratios at pH values above 8,5, it is evident that the efficiency of struvite crystallization is remarkably high, with all molar ratios exhibiting similar results of 95% and above efficiency. Hence, it can be concluded that beyond pH 9 and higher, the molar ratio of struvite components becomes insignificant. However, it is still recommended to maintain a lower orthophosphate ratio compared to other struvite components to ensure complete utilization of orthophosphate.

Saturation ratio and orthophosphate efficiency

The supersaturation ratio represents the thermodynamic state of a solution in relation to its equilibrium point. It considers all the variables influencing struvite crystallization, including temperature, electrical conductivity, struvite concentrations, and pH. The relationship between the supersaturation ratio and phosphorus removal was then examined.

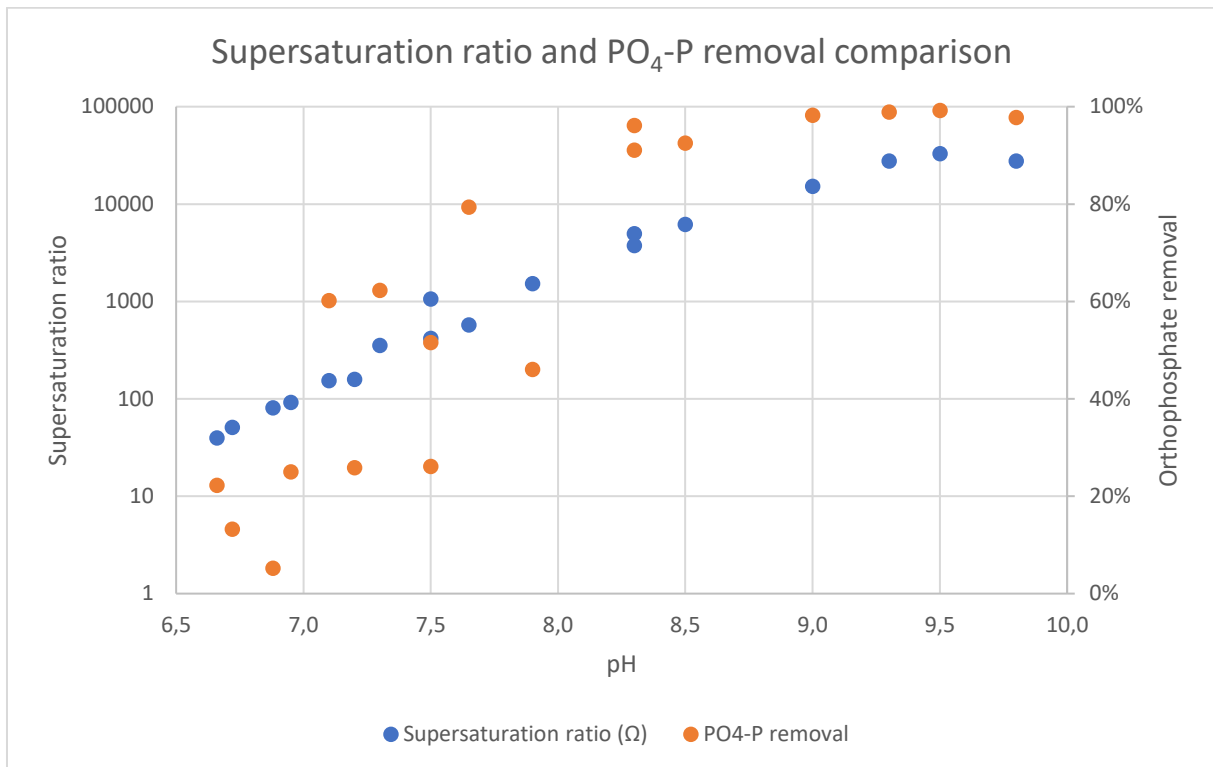


Figure 4-10: Supersaturation ratio and PO₄-P removal comparison

The analysis revealed a notable correlation between the logarithmic scale of the supersaturation ratio and orthophosphate removal. The calculation of the supersaturation ratio involves multiple steps and considers various variables to quantify the level of supersaturation, and the resulting curve resembles the trends observed for pH and orthophosphate removal. Based on these findings, it can be concluded that pH is a sufficient parameter to consider when assessing orthophosphate removal, and there is no need to specifically consider the supersaturation ratio. The supersaturation ratio exhibited a close correlation with pH in terms of orthophosphate removal efficiency.

Potential struvite production rate at IVAR SNJ treatment plant

Ammonia removal from the solution occurs solely during the formation of struvite and does not participate in any reactions that compete for struvite (Enyemadze et al., 2021). As a result, the amount of struvite production can be determined using the ammonia removal.

$$\text{Struvite production} = (NH_{4-in} - NH_{4-out}) * MW_{struvite} * Q$$

Where:

NH_{4in}-NH_{4out} = the amount of removed ammonia (mol)

MW_{struvite} = molecular weight of struvite (245,3 g/mol)

Q = flow rate of fluidized bed reactor (l/h)

At pH 7 and above, some of nitrogen exists in the form of ammonium (NH_3). As pH levels increase, a greater proportion of nitrogen is present as ammonium ions. It is important to note that ammonium is a volatile compound, and a portion of it can be lost through volatilization. However, the extent of this ammonium loss was not determined or considered in this study.

Struvite recovered by pilot reactor

When the hydraulic retention time was set to approximately two hours, the flow rate of the pilot reactor was measured to be approximately 9,5 L/h. The average concentration of ammonia in the fluidized bed reactor was determined to be 203 mg/L, equivalent to 0,119 mol/L. By utilizing the pilot reactor and establishing the conditions for a minimum of 85% removal efficiency, approximately 0,101 mol/L of ammonia would be removed. Consequently, the estimated struvite removal rate would amount to $9,5 \text{ l/h} * 0,101 \text{ mol/l} * 245,3 \text{ g/mol} = 235.4 \text{ g/h}$. It was determined that approximately 2062 kilograms of struvite can be produced annually by using the pilot scale struvite reactor.

Visual MINTEQ modelling

Visual MINTEQ, a freely available chemical equilibrium modelling software, was utilized in this study. Specifically, version 3.1, which was updated on 4 September 2022, was used to calculate metal speciation, solubility equilibria, and sorption in water. The software utilizes advanced descriptions of complexation and sorption reactions

Visual MINTEQ calculates the saturation index of various minerals based on the input data. The saturation index is calculated by subtracting the logarithm of the ion activity product (IAP) from the logarithm of the solubility product constant (K_s). A negative saturation index indicates that the mineral is undersaturated and will not precipitate in the water, while a positive saturation index indicates that the water is oversaturated and will precipitate. Visual MINTEQ provides a list of possible minerals that may precipitate from the existing chemicals in the water based on their calculated saturation indices.

Modelling with different molar ratios of struvite

One of the challenges encountered in this study was the difficulty in achieving the desired molar ratios of the struvite components due to the complex nature of the wastewater. Additionally, it was challenging to maintain accurate flow rates for the pumps due to changes in flow rate over time after calibration. To overcome these challenges, Visual MINTEQ modelling was employed to investigate

the effect of varying the molar ratio of each component of struvite. This approach allowed for a more thorough understanding of the process involved and provided insight into how to optimize the struvite crystallization process.

Table 4-1: Visual Minteq models of different molar ratios

pH	6,5	7	7,5	8	8,5	9	9,5	10	10,5	11
1:1:1	-2,681	-1,89	-1,234	-0,679	-0,186	0,236	0,539	0,683	0,674	0,514
5:1:1	-2,173	-1,436	-0,823	-0,288	0,197	0,617	0,917	1,049	1,008	0,793
1:5:1	-2,022	-1,231	-0,575	-0,019	0,476	0,905	1,218	1,373	1,37	1,212

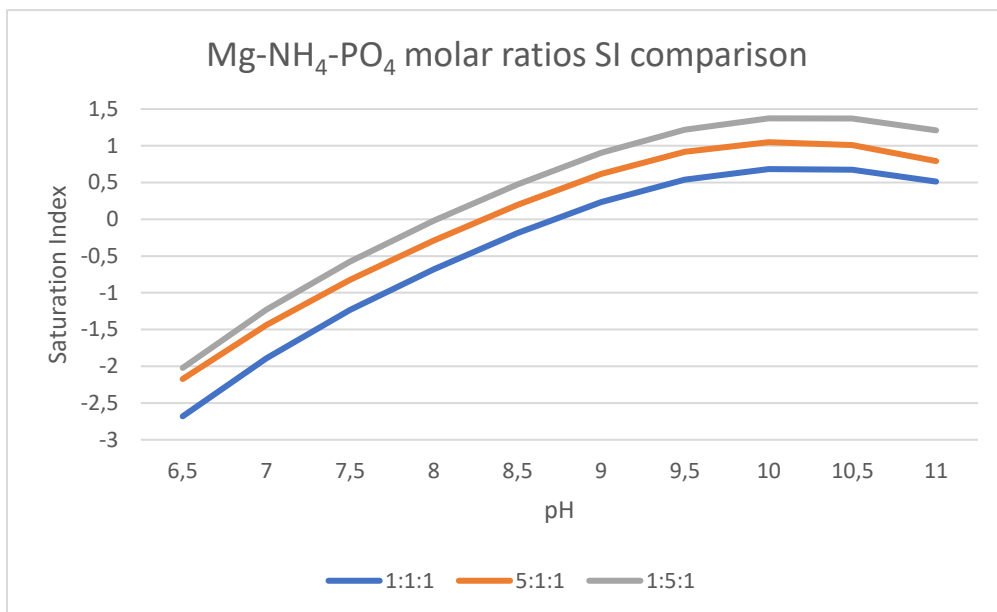


Figure 4-11: Saturation index for different molar ratios in Visual Minteq

The results obtained from the Visual MINTEQ model indicate that increasing the concentration of ammonia has a more pronounced effect on the struvite crystallization process compared to magnesium. This observation can potentially be attributed to the fact that ammonia does not participate in the formation of other mineral components, while magnesium is involved in multiple mineral reactions. Consequently, the availability of ammonia in the system may contribute more significantly to the formation of struvite crystals, as it remains readily accessible for the crystallization process. On the other hand, magnesium, being consumed by multiple minerals, may have a relatively lower impact on struvite crystallization compared to ammonia.

The comparison of the experiments between the molar ratios of Mg-NH₄-PO₄ at 3-1,5-1 and 1,5-3-1 reveals that the latter ratio tends to exhibit higher efficiency in terms of struvite crystallization compared to the former. These findings align with the results obtained from the Visual MINTEQ model, providing validation for its predictive capabilities.

Modelling with competing reactions

The program was run with the pilot reactor data were used to provide input values for average expected concentrations. The concentration values used were as follows: magnesium (315 mg/L), ammonium (200 mg/L), and orthophosphate (190 mg/L). Temperature was set to 19 °C. The results obtained from the program were analysed for different pH values.

- Model 1: Modelling with struvite components only
- Model 2: Modelling with addition of calcium and metals: The presence of different chemical species in wastewater can affect the efficiency of struvite crystallization. While the exact concentrations of these chemicals are often unknown, they are typically expected to be present in small values, with the exception of calcium, which is known to interrupt struvite crystallization. In the model, an exaggerated calcium concentration of 350 mg/l was intentionally utilized, which exceeds the typical levels found in average wastewater. This elevated calcium concentration was chosen to provide a more distinct and observable effect of calcium on the struvite precipitation process. By using higher amounts of calcium, the influence and significance of calcium in the precipitation of struvite could be more effectively examined and evaluated. To represent the presence of metals in the wastewater, 1 milimolal Fe²⁺, 0,5 milimolal Fe³⁺, and 0,5 milimolal Al were added.
- Model 3: Modelling with calcium, metals, and addition of salt: An alternative magnesium resource that has gained attention in recent years is seawater, as magnesium is the second most abundant cation in seawater. However, the use of seawater would introduce other ions into the struvite crystallization system, which may affect the efficiency of the process. Visual MINTEQ model was run to examine the impact of salinity on the performance of the struvite reactor. To simulate the salinity conditions, 5 milimolal Na⁺ and 5 milimolal Cl⁻ were added into the model. Same amount of calcium was added as in model 2.

Comparison of Visual MINTEQ models

The results of the Visual MINTEQ models were compared. The model without impurities showed that the highest efficiency of struvite crystallization occurred at pH 10, while the theoretical calculation showed the highest efficiency at pH 10.5. However, when impurities were involved in the reactor, as would be the case in a real reactor using wastewater, the highest struvite crystallization was found at

pH 9,5. Model 2 and Model 3 showed almost identical results, indicating that salinity did not have a significant effect on struvite crystallization. In the impurity models, the other minerals that precipitated besides struvite also generally had a higher precipitation rate with pH, which suggests that the precipitated material would have approximately the same number of impurities at every pH value. It should be noted that these models were based on the same concentration values, and therefore the comparison was made only in terms of pH and impurities. Different concentration values could result differently.

Table 4-2: Comparison of Visual Minteq models in different pH levels

pH	6,5	7	7,5	8	8,5	9	9,5	10	10,5	11
Model 1	-0,2	0,48	1,06	1,58	2,07	2,49	2,8	2,93	2,88	2,64
Model 2	-0,41	0,29	0,87	1,38	1,82	2,16	2,33	2,26	1,98	1,55
Model 3	-0,42	0,27	0,86	1,36	1,81	2,15	2,31	2,25	1,97	1,55

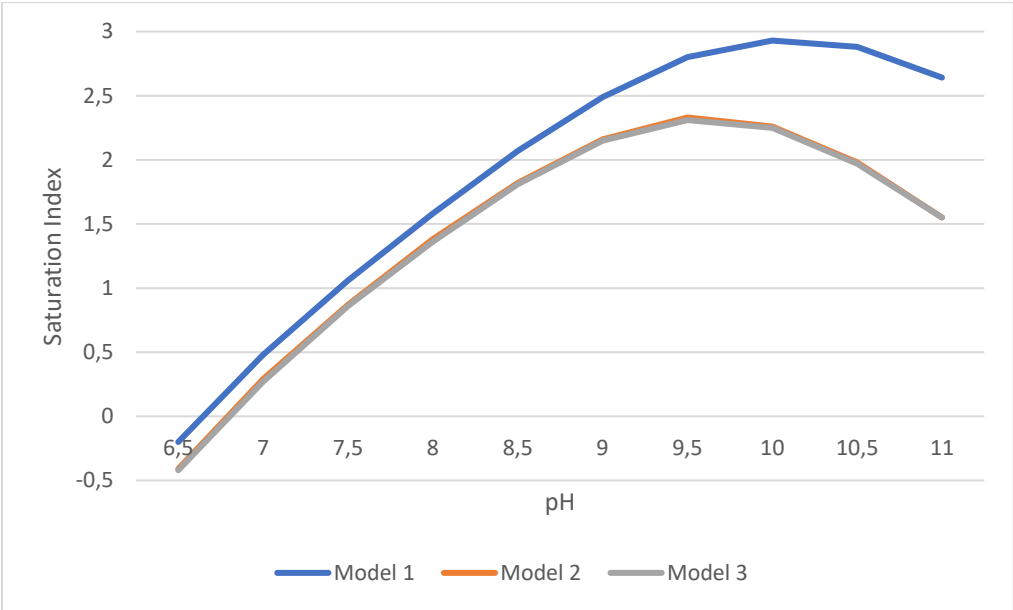


Figure 4-12: Saturation index for different models

According to Visual MINTEQ modelling, the highest efficiency of struvite crystallization occurs at pH 10 in the absence of impurities in the water. However, when calcium is present, the saturation index decreases, and the optimal pH for struvite crystallization shifts to 9,5. Batch and pilot reactor experiments have demonstrated that a pH range of 8,5 to 9 is sufficient for achieving effective struvite crystallization. Going beyond this pH range would incur additional costs for operating the struvite reactor without significant benefits.

Furthermore, the Visual MINTEQ model indicates that the impact of calcium on the struvite reactor is negligible within the operational pH range. It is important to note that the model employed exaggerated calcium concentrations, suggesting that under typical wastewater conditions, the effect of calcium would be much less and can be considered negligible.

The model also suggests that the presence of salts and metals in average wastewater concentrations has minimal effect on struvite crystallization. The influence of metals is negligible. The information about salt opens up the possibility of utilizing sea salt as a magnesium resource for the struvite reactor, which could offer potential advantages in terms of cost and resource utilization.

5. Discussion

In the Discussion section, the observed correlations between variables are discussed in the context of the experiments and theoretical knowledge. The identified correlations between variables, such as pH, temperature, concentrations of struvite components, and removal rates, are interpreted. Theoretical concepts and models related to struvite precipitation and wastewater treatment are introduced to provide a theoretical framework for interpreting the observed correlations.

Molar ratio of struvite components

The main reason for processing a struvite crystallization reactor is the phosphorus removal. It is possible to enhance the phosphate removal with increasing the other concentrations of the struvite components. The lower concentrated struvite component will be more depleted, and the increased concentration will more exist in the effluent water. In terms of phosphorus removal, orthophosphate is the aimed component to be depleted.

Below pH 8,5, there is a discernible improvement in orthophosphate removal when increasing the molar ratios of ammonia and magnesium. However, the overall efficiency of struvite crystallization remains low at this pH range, regardless of the molar ratios used.

There is insufficient data available between pH 8,5 and 9 to draw definitive conclusions. Nonetheless, it is reasonable to anticipate that both pH and molar ratios play a role in influencing struvite crystallization within this range.

Once the pH reaches 9 and above, the efficiency of struvite crystallization significantly improves,

exceeding 95%. At this point, the impact of molar ratios becomes negligible, with pH emerging as the primary parameter influencing struvite crystallization.

The Visual MINTEQ models showed that, increased the molar ratio of ammonia and magnesium compared to orthophosphate, could improve orthophosphate removal from the wastewater. The models consistently demonstrated that increasing the concentration of ammonia has a greater impact on struvite crystallization compared to increasing the concentration of magnesium. This finding was corroborated by experimental results. However, both the experimental data and the models indicated that the difference between increased ammonia and increased magnesium in the reactor had a similar effect on struvite crystallization, as long as the orthophosphate concentration was maintained at a depletion level. This suggests that achieving efficient orthophosphate removal primarily relies on ensuring the depletion of orthophosphate in the wastewater.

Struvite recovery by full scale reactor

If the struvite crystallization reactor is integrated into the IVAR SNJ wastewater treatment plant, the entirety of the reject water from the secondary treatment's thickening process (BR) will be directed to the struvite crystallization reactor. The quantity of reject water from the centrifuge reactor (SR) will be determined by considering the available centrifuge reactor capacity and the desired ratio of struvite components.

The average concentrations of struvite components in SR and BR are as used in the calculation. Molar ratio of Mg-NH₄-PO₄:1,5-1,5-1, and HRT of 2 hours are aimed. Magnesium solution is 1 M. BR flow is 500 m³/d ≈ 20833 l/h. Considering BR flow and the molar ratio, the flows of magnesium solution and SR is calculated.

Table 5-1: Concentrations and flows of full-scale struvite reactor

SR concentrations			BR concentrations			Mg	SR	BR	Mg
Mg (mg/l)	NH ₄ -N (mg/l)	PO ₄ -P (mg/l)	Mg (mg/l)	NH ₄ (mg/l)	PO ₄ (mg/l)	(mg/l)	flow (l/h)	flow (l/h)	flow (l/h)
45	1000	35	30	25	250	2431	4000	20833	2400

SR is found 96 m³/d and magnesium solution 57,6 m³/d. These flows provide Mg-NH₄-PO₄:1,58-1,54-1. Total flow of the reactor is 653,6 m³/d.

HRT $\approx 2 \text{ h} = V / (4000+20833+2400) \text{ l/h}$, if volume is selected $V=55000$ litres, then HRT equals to 2,02 hours.

Magnesium solution of 1 M contains 24,31 g/l of magnesium. For 57,6 m³/d flow of magnesium solution, 1400 kilograms of magnesium is needed per day. If the magnesium resource is magnesium chloride, then approximately 5483 kilograms of the chemical needed per day.

2 ml/min of 1 M NaOH was used for adjusting the pH to 8,3 for 16,4 litres of reactor. For a 55 m³ of reactor, 9,72 l/d of NaOH solution is required.

Based on the average orthophosphate concentration of 200 mg/l inside the struvite reactor, achieving a 90% removal efficiency would result in an effluent concentration of 20 mg/l.

$$(200-20) \text{ g/m}^3 * 653,6 \text{ m}^3/\text{d} = 117648 \text{ g/d} = 118 \text{ kg/d P removal}$$

$$117648 \text{ g/d} / 30,97 \text{ g/mol} = 3799 \text{ mol/d P removal}$$

$$3799 \text{ mol/d} * 245,3 \text{ g/mol} = 931895 \text{ gStruvite/d} = 932 \text{ kg/d struvite production}$$

[Struvite crystallization reactor at IVAR SNJ](#)

Based on the obtained findings and results, the full-scale reactor implemented at IVAR SNJ WWTP has been designed with the data as illustrated in the figure 5-1.

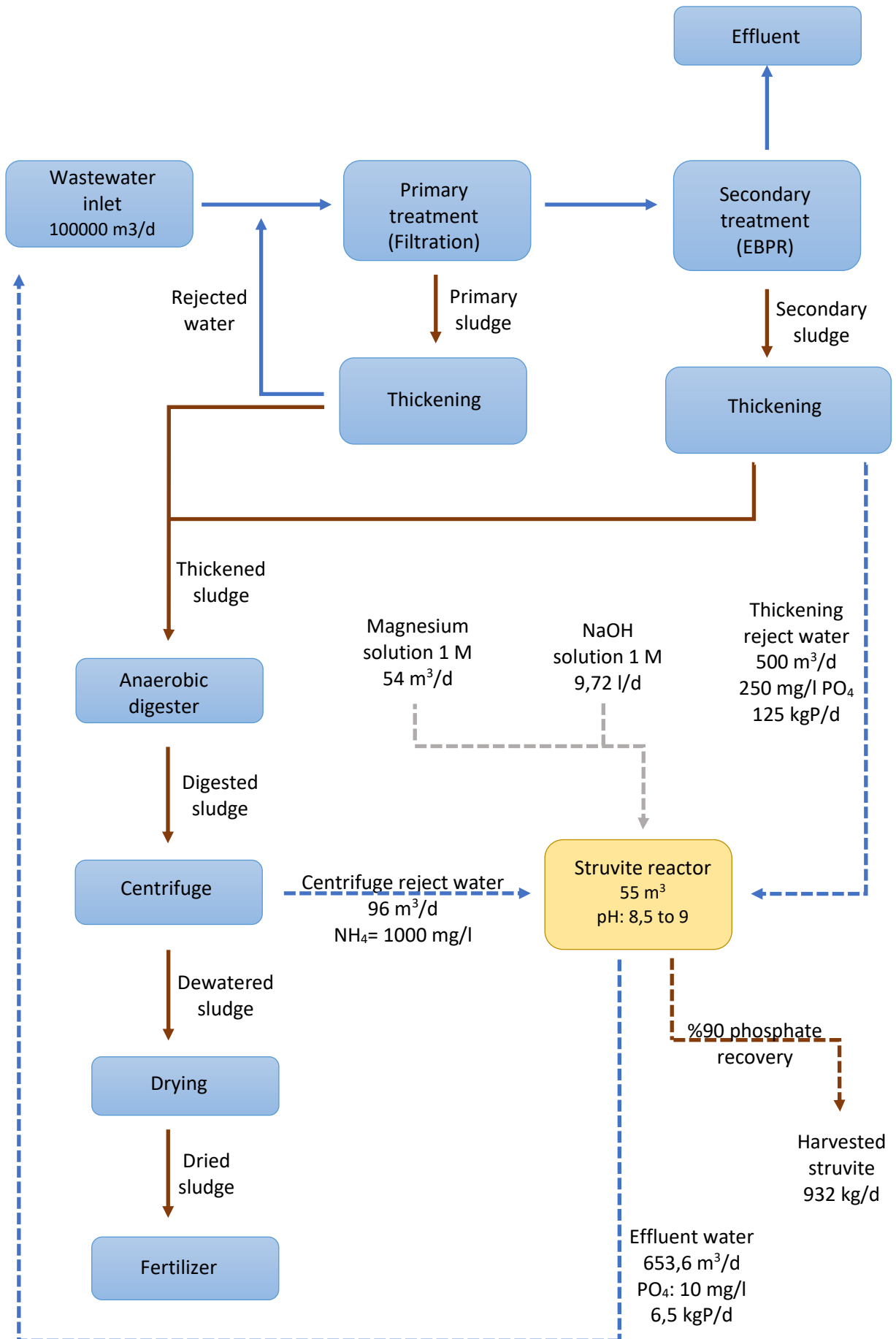


Figure 5-1: IVAR SNJ treatment scheme and potential struvite reactor implementation

Struvite production

The total of 100,000 m³/d of wastewater is treated at IVAR SNJ WWTP, the calculation indicates a potential recovery of 932 kg/d of struvite from the wastewater. This translates to 0.932 kg of struvite production per 100 m³ of wastewater. The findings of this study align with existing research estimates, which suggest that 1 kilogram of struvite can be produced from every 100 m³ of wastewater. (T. Zhang et al., 2017)

6. Conclusion

The conclusions derived from the study are as follows:

1. Super saturation is the parameter in determining struvite crystallization within the system. It is primarily influenced by pH, while the impact of other factors is considered insignificant. Consequently, emphasizing the role of pH in the process is deemed appropriate. This study suggests a pH of 8,5 or higher for an orthophosphate removal for an efficiency of 85% or greater.
2. Regarding the molar ratio of the struvite components, it is recommended to maintain a lower concentration of orthophosphate compared to magnesium and ammonia in order to enhance phosphate removal as keeping the orthophosphate as the depleting material in the chemical reaction. A Mg-NH₄-PO₄ ratio of 1,5-1,5-1 would suffice to ensure an adequate supply of ammonia and magnesium for efficient orthophosphate recovery as struvite.
3. Calcium has a suppressing effect on struvite precipitation. Nonetheless, for this effect to become discernible, the concentration of calcium needs to surpass the typical levels found in wastewater treatment plants. Therefore, concerns regarding the decreasing effect of calcium can be disregarded. Salinity and metal concentrations within average wastewater levels have negligible impacts on struvite crystallization.

Suggestions for further research

Increasing particle size

During the experiments, the crystallization of struvite was successfully achieved. However, the produced struvite was in the form of fine dust particles. This particle size is not appropriate for a real-size reactor due to several operational problems. The fine dust particles tend to swim up in the water under turbulence and may reach undesired locations in the reactor, causing clogging in the pipes and taps, as well as undesired struvite growth on the walls. Additionally, the effluent water may contain

struvite particles, which can result in the discharge of phosphorus in the outlet. These were the main operational challenges encountered during the pilot-scale operation of the struvite reactor. It is necessary to have bigger sized struvite particles to prevent these challenges. Struvite is required to settle in the bottom part of the reactor using their weight. Therefore, further research focused on long term operation at different recirculation rates is strongly recommended.

Sustainable magnesium resource

Magnesium chloride hexahydrate ($\text{Cl}_2\text{Mg}\cdot 6\text{H}_2\text{O}$) used for making 1 M of magnesium solution and used as the magnesium resource for struvite. The use of magnesium chloride as the magnesium resource for struvite formation in the system has a negative impact on its eco-friendliness and sustainability, as well as adding to the overall cost by requiring an additional chemical from industry. An alternative magnesium resource that has gained attention in recent years is seawater, as magnesium is the second most abundant cation in seawater. According to the results of the Visual MINTEQ modelling, the effect of salinity on struvite crystallization was found to be insignificant. As a result, using seawater as a source of magnesium in future studies is highly recommended.

Vivianite precipitation

The results of the Visual MINTEQ modelling indicated a high saturation index for the crystallization of vivianite in the presence of iron in the water. Vivianite precipitation, due to its cheaper production cost compared to struvite, is a promising avenue for future research. Vivianite can be used in various applications, including the production of LiFePO_4 , a key component of Li-ion batteries, and as a fertilizer in agriculture. Despite these potential benefits, vivianite crystallization is not as widely used as struvite crystallization. (C. Zhang et al., 2021). This method may be a viable alternative in wastewater treatment plants where a magnesium source is not readily available. However, further research and detailed assessments are necessary to determine the applicability, effectiveness, and operational conditions of vivianite crystallization.

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8. Appendix

In the Appendix section, detailed information related to the study is provided, including extensive lists of analysed data and calculated values.

Batch reactor experiment data

The orthophosphate concentration in the batch was set to 300 mg/l by adding Sodium dihydrogen phosphate dihydrate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$) into the beaker. The concentration after the crystallization is analysed.

Table 8-1: Batch reactor experiment data

pH	Mg-NH ₄ -PO ₄			PO ₄ (mg/l)
8,5	0,98	1,03	1	108
6,8	0,98	1,03	1	244
7,2	0,98	1,03	1	248
6,5	0,98	1,03	1	288

Influent measurements for pilot reactor

The struvite components' concentrations in all tanks were analysed and recorded, along with the recording of the pH, temperature, and electrical conductivity values of the reactor tank. The measurement of pump flows was conducted regularly by recording the passing time and the filled-up volume. Additionally, the pump flow values were verified with the tank volume levels to ensure the reliability of the results. The hydraulic retention time was calculated based on the fluidized reactor volume of 16.4 litres.

Table 8-2: Influent concentrations, flows and HRT

SR concentrations			BR concentrations			Mg	SR	BR	Mg	HRT (h)
Mg (mg/l)	NH ₄ -N (mg/l)	PO ₄ -P (mg/l)	Mg (mg/l)	NH ₄ -N (mg/l)	PO ₄ -P (mg/l)	(mg/l)	flow (l/h)	flow (l/h)	flow (l/h)	
45	1012	36	27	24	248	2550	2,88	5,46	1,10	1,7
48	1004	13,4	52	35	288	2431	1,27	6,22	0,86	2,0
48	1004	13,4	52	35	288	2431	1,20	5,50	0,84	2,2
41	986	30	20	24	256	2431	1,26	6,72	1,64	1,7
41	986	30	20	24	256	2431	1,15	6,64	1,66	1,7
45	1012	36	27	24	248	2550	0,28	1,41	0,16	8,8

48	1004	13,4	52	35	288	2431	1,07	5,45	0,85	2,2
45	1012	36	27	24	248	2550	0,28	1,41	0,16	8,8
45	1012	36	27	24	248	2550	0,21	0,40	0,14	21,8
41	986	30	20	24	256	2431	1,26	6,72	0,64	1,9
45	1012	36	27	24	248	2550	2,46	6,00	0,60	1,8
45	992	42	20	24	256	2431	1,26	6,37	0,71	2,0
41	986	30	20	24	256	2431	1,39	6,94	1,73	1,6
45	1012	36	27	24	248	2550	2,46	6,00	0,60	1,8
45	1012	36	27	24	248	2550	2,46	6,00	0,60	1,8
41	986	30	20	24	256	2431	1,37	6,04	1,48	1,8
48	1004	13,4	52	35	288	2431	1,07	5,45	0,85	2,2
45	1012	36	27	24	248	2550	0,28	1,41	0,16	8,8

The concentration values of the fluidized bed reactor were calculated based on the influent tank concentrations and flow rates. The molar ratio of struvite components in the reactor was determined based on the reactor tank concentrations. Temperature, pH, and electrical conductivity values were measured and recorded.

Table 8-3: Reactor tank concentrations, molar ratio, pH, T and ECt data

Reactor tank						Mg-NH ₄ -PO ₄ ratio			pH	T	ECt
Mg		NH ₄ -N		PO ₄ -P							
mg/l	M	mg/l	M	mg/l	M						
326	0,0134	323	0,0190	155	0,0050	2,68	3,80	1,00	6,7	19	6,7
296	0,0122	179	0,0128	217	0,0070	1,74	1,82	1,00	6,7	17,5	6,77
317	0,0130	186	0,0109	212	0,0068	1,90	1,59	1,00	6,9	18	6,7
435	0,0179	146	0,0086	183	0,0059	3,03	1,46	1,00	7,0	18,6	6,14
446	0,0183	137	0,0081	183	0,0059	3,10	1,36	1,00	7,1	18,7	6,7
253	0,0104	172	0,0101	194	0,0063	1,66	1,61	1,00	7,2	19	6,7
328	0,0135	171	0,0101	215	0,0069	1,94	1,45	1,00	7,3	18	6,7
253	0,0104	172	0,0101	194	0,0063	1,66	1,61	1,00	7,5	19	6,7
504	0,0207	301	0,0177	141	0,0046	4,54	3,88	1,00	7,5	19	6,7
202	0,0083	163	0,0096	204	0,0066	1,26	1,46	1,00	7,7	18	6,7
199	0,0082	291	0,0171	174	0,0056	1,46	3,04	1,00	7,9	19	6,7
229	0,0094	168	0,0099	202	0,0065	1,45	1,52	1,00	8,3	17,2	4,81

439	0,0180	153	0,0090	181	0,0058	3,09	1,54	1,00	8,3	18,7	6,7
199	0,0082	291	0,0171	174	0,0056	1,46	3,04	1,00	8,5	19	6,7
199	0,0082	291	0,0171	174	0,0056	1,46	3,04	1,00	9,0	19	6,7
425	0,0175	169	0,0099	178	0,0058	3,03	1,72	1,00	9,3	19,3	6,07
328	0,0135	171	0,0101	215	0,0069	1,94	1,45	1,00	9,5	18,9	6,81
253	0,0104	172	0,0101	194	0,0063	1,66	1,61	1,00	9,8	19	6,7

The reactor was operated for a period exceeding the three times of hydraulic retention time, after which the effluent from the reactor was collected and analysed.

During the experiments, some data of temperature and electrical conductivity was lost. These missing values were approximated using known values and were denoted with a distinctive colour in the result list. It is expected that the difference between the actual and assumed values would be inconsequential and would not have any significant impact on the results.

Calculation of supersaturation ratio

To accurately calculate the supersaturation ratio of a solution, the temperature-dependent equilibrium constant (K_{sp}) was taken into consideration. The electrical conductivity values were measured and used to calculate the ionic strength of the solution. The ion activity product (IAP) and the conditional solubility product (P_s) can then be calculated using the concentrations. The supersaturation ratio can then be calculated as the ratio of the IAP to the P_s .

Table 8-4: Calculation of supersaturation ratio

Mg-NH ₄ -PO ₄ ratio			pH	K_{sp}	P_s	IAP	Ω	Mg removal	NH ₄ removal	PO ₄ removal
2,68	3,80	1,00	6,7	2E-14	3E-08	1,25E-06	8E+07	27%	2%	22%
1,74	1,82	1,00	6,7	1E-14	2E-08	1,07E-06	8E+07	11%	15%	13%
1,90	1,59	1,00	6,9	1E-14	1E-08	9,62E-07	7E+07	4%	10%	5%
3,03	1,46	1,00	7,0	2E-14	1E-08	8,93E-07	6E+07	13%	8%	25%
3,10	1,36	1,00	7,1	2E-14	6E-09	8,66E-07	6E+07	25%	25%	60%
1,66	1,61	1,00	7,2	2E-14	4E-09	6,5E-07	4E+07	27%	26%	26%
1,94	1,45	1,00	7,3	1E-14	3E-09	9,3E-07	6E+07	41%	29%	62%
1,66	1,61	1,00	7,5	2E-14	2E-09	6,5E-07	4E+07	45%	39%	52%

4,54	3,88	1,00	7,5	2E-14	2E-09	1,66E-06	1E+08	87%	72%	26%
1,26	1,46	1,00	7,7	1E-14	9E-10	5,17E-07	4E+07	35%	40%	79%
1,46	3,04	1,00	7,9	2E-14	5E-10	7,77E-07	5E+07	38%	15%	46%
1,45	1,52	1,00	8,3	1E-14	2E-10	5,99E-07	5E+07	56%	59%	91%
3,09	1,54	1,00	8,3	2E-14	2E-10	9,33E-07	6E+07	31%	46%	96%
1,46	3,04	1,00	8,5	2E-14	1E-10	7,77E-07	5E+07	78%	36%	93%
1,46	3,04	1,00	9,0	2E-14	5E-11	7,77E-07	5E+07	73%	46%	98%
3,03	1,72	1,00	9,3	2E-14	4E-11	9,85E-07	6E+07	33%	57%	99%
1,94	1,45	1,00	9,5	2E-14	3E-11	9,3E-07	6E+07	58%	50%	99%
1,66	1,61	1,00	9,8	2E-14	2E-11	6,5E-07	4E+07	79%	64%	98%