AFRICA CENTER OF EXCELLENCE FOR WATER MANAGEMENT

ADDIS ABABA UNIVERSITY

Recovery and Removal of Phosphorus via Struvite ($MgNH_4PO_4. 6H_2O$) Crystallization in Fluidized Bed Reactor from Domestic Wastewater

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MSc. Thesis

By

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A thesis submitted to the Department of Water Supply and Sanitation, School of Graduate Studies, African Center of Excellence for Water Management (ACEWM)/Addis Ababa university (AAU) in partial fulfillment of the requirements for the degree of Master of Science in Water Management specialization of hydrology and water resources.

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This is to certify that the thesis entitled "**Recovery and Removal of Phosphorus via Struvite** ($MgNH_4PO_4 . 6H_2O$) **Crystallization in Fluidized Bed Reactor from Domestic Wastewater**'' submitted in partial fulfillment of the requirements for the degree of Master's with specialization in Water Supply and Sanitation, the Graduate Program of the Water management and has been carried out by Mr. Eskinder Tamru Belachew under our supervision. Therefore, we confirm that the student has fulfilled the requirements and hence hereby can submit the thesis to the department for defense.

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Dr. Shimelis Kebede

(Main Advisor)

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Dr. Adey Feleke

(Co - Advisor)

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Date

DECLARATION

I, Eskinder Tamru declare that the content of this thesis is my original work with the exception of such quotations or references which have been credited to their authors or sources and this thesis has not been previously submitted to this or any other University for a degree award.

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ABSTRACT

Phosphorus is a vital nutrient for food production which is produced from limited, non-renewable resource called phosphate fossil. At the present rate of utilization, the world's reserve of phosphate fossil will be exhausted soon. However, wastewater contain huge amount of phosphorus which can be recycled to reduce depletion of phosphate fossil. Beside this fact, phosphorus should be removed from wastewater before discharging it into water bodies, to avoid eutrophication. One of the promising methods of phosphorus recovery in to useful end product is struvite crystallization.

The present study focuses on recovery of phosphorus via struvite crystallization from domestic wastewater in fluidized bed reactor. Response surface experimental design was implemented to optimize process parameters such as pH (8 – 12), ammonium to phosphate molar ratio (1 - 4), magnesium to phosphate molar ratio (0.5 – 2.5) and reaction time (1hr. – 5 hr.) using model solution. The optimized value for pH, ammonium to phosphate molar ratio, magnesium to phosphate molar ratio and reaction time were found to be 10, 2.9, 1 and 4 hr. respectively. Under this optimized value 81% and 74% phosphorus removal efficiency was achieved from model solution and domestic wastewater respectively. Similarly, 1.29 and 2.9 gram of struvite yield was obtained from 10 litter of model solution and domestic wastewater respectively. Although higher amount of struvite yield (2.9 gram) was obtained from domestic wastewater, struvite crystal purity was lower (68.7%). Elemental composition of crystals precipitated under optimized condition indicate that octahedral struvite crystals was the dominant compound which was further identified by scanning electron microscope, Fourier transform infrared spectroscopy and X-ray diffraction.

This study also investigated the potential of Basaka Lake water as locally available magnesium source for struvite crystallization. Seventy nine percent (79%) and sixty eight percent (68%) phosphate removal efficiency were achieved from model solution and domestic wastewater respectively by employing Basaka Lake water as a source of magnesium. Overall, struvite crystallization from domestic wastewater is a sustainable eco-friendly approach for removal of phosphorus via struvite which can be used as fertilizer in agricultural sector.

Key word/ phrase: - Fluidized bed reactor, Crystallization, Struvite, Response surface, Phosphorus recovery

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ACRONYMS AND ABBREVIATIONS

AAiT - Addis Ababa institute of Technology

AAS - Atomic absorption spectroscopy

AASTU - Addis Ababa science and technology university

AAWSA - Addis Ababa city water supply and sewerage authority

ANOVA - Analysis of variance

ATP - Adenosine triphosphate

Ca - Calcium

$Ca_{10}(PO_4)_6(OH)_2$ - Hydroxyapatite

CCD - Central Composite Design

Cd - Cadmium

CNCS - Collage of natural and computational sciences

CO_2 - Carbon di oxide

CO_3 - Carbonate

COD - Chemical oxygen demand

COD - Crystallography open database

Cr - Chromium

FBR - Fluidized bed reactor

FTIR - Fourier transformation Infrared

GDP - Gross domestic product

H - Hydrogen

HCO_3 - Bicarbonate

HPO_4 - Hydrogen phosphate

KH_2PO_4 - Potassium di hydrogen phosphate

Ksp - Solubility constant

Mg - Magnesium

$MgCl_2$ - Magnesium chloride

$MgCl_2$ $6H_2O$ - Magnesium chloride hex hydrate

$MgCO_3$ - Magnesium carbonate

$MgHPO_4$ $3H_2O$ - Newberyite

$MgNH_4PO_4$. $6H_2O$ - Struvite

MgO - Magnesium oxide

Mg $(OH)_2$ - Magnesium hydro oxide (Brucite)

MoWIE - Ministry of water, Irrigation and Energy

Mn - Manganese

N - Nitrogen

$NaNH_4HPO_4$ $4H_2O$ - Stercorite

NH_3 - Ammonia

NH_4 - Ammonium

NH_4Cl - Ammonium chloride

O_2 - Oxygen

OH - Hydro oxide

P - Phosphorus

Pb - Lead

PO_4 - Phosphate

RSM - Response Surface Method

RT - Retention time

SEM - Scanning electron microscope

STR - Stirred tank reactor

UK - United Kingdom

USD - United states dollar

UV - Ultra Violate

WWTP - Wastewater treatment plant

XRD - X- ray diffraction

Zn - Zink

1 INTRODUCTION

1.1 Background

Phosphorus is an essential nutrient for production of food in agriculture. Large quantity of phosphors containing fertilizer are used to enhance crop production in order to feed ever growing global population. However, most of these fertilizers are produced from phosphate fossil which is finite, non-renewable resource. At the present rate of utilization, the world's reserve of phosphate fossil will be exhausted within decades (Hallas et al., 2019). Moreover, more than 85% of phosphate fossils are located in few countries making other agrarian countries such as Ethiopia to be dependent on them for food production (Kumari et al., 2020). Therefore, it is important to recover phosphorus from various source through sustainable technology.

On the other hand, it is well known that wastewater from households and selected industries contain large quantity of phosphorus. According to Parsons & Smith, (2008) an average of 0.6 kg phosphorus per capital enter into domestic wastewater from human waste every year. Based on a few studies conducted on phosphorus which enter into domestic wastewater treatment plants in Ethiopia, the amount of phosphorus varies between the dry and rainy seasons with an average of 18 mg/L (Mahlet Melaku, 2017), thus making it worthy of recovery.

Different technologies such as chemical precipitation, biological degradation, crystallization, tertiary filtration and ion exchange are applied for removal and recovery phosphorus from wastewater (Guadie et al., 2014). Among them crystallization gained a lot attention in recent years due to its useful end product called struvite. Struvite is a crystal formed from magnesium, ammonium and phosphate with six molecules of water ($MgNH_4PO_4.\ 6H_2O$). It can be used as phosphorus containing fertilizer in agriculture. Moreover, as compared to other commercially available fertilizer, struvite is preferable due to its prolonged and simultaneous release of nutrients such as phosphorus, ammonium and magnesium. (Bhuiyan et al., 2008a)

Additionally, without any specific phosphorus removal technology, excess load of phosphorus in wastewater brings eutrophication of water bodies. It can also cause clogging of pipelines and pumps in wastewater treatment plants due to spontaneous precipitation of struvite. Borgerding, (2016) discovered the existence of white crystalline solid (struvite) causing operational problem in wastewater treatment plant.

Fluidized bed reactors (FBR) and Stirred tank reactors (STR) can be used for crystallization of struvite from wastewater. The crystals produced from stirred tank reactors are very fine due to excessive turbulence which eventually make crystal harvesting process more difficult. However bigger crystals can be produced in fluidized bed reactors due to an increased reaction surface area by fluidizing the crystals (Hiroyuki & Katsutoshi, 2019).

Although plenty phosphate and ammonium ions exist in domestic wastewater, it lacks magnesium ion for struvite crystallization. As a result, additional magnesium source is required to enhance the crystallization process. In most cases commercially available water-soluble magnesium salts such as $MgCl_2$, MgO and Mg $(OH)_2$ are used as magnesium source for struvite crystallization. However, the use of this salts increases the cost needed for crystallization process (Guadie et al., 2020). Therefore, it is important to search locally available magnesium source although previous studies suggest see water and brine as economical magnesium source for struvite crystallization (Liu et al., 2013).

Struvite crystallization from wastewater can produce phosphorus containing fertilizer called struvite, reduce eutrophication of water bodies and avoid operational problems in wastewater treatment plants due to clogging of pipe lines by unwanted struvite deposition. Despite these facts, little attention is given to produce struvite in controlled way in developing countries like Ethiopia. Although struvite crystallization is proven from nutrient rich domestic wastewater in developed countries resulted from their life style, investigating the potential of domestic wastewater for struvite crystallization in developing countries with lower gross domestic product (GDP) is a critical gap to be filled. Beside this, finding more economical and locally available magnesium source for struvite crystallization is also a challenging task to investigate. Further most technologies for struvite crystallization also require detail optimization to reduce process loss.

This study aims to recover phosphorus in the form of struvite from domestic wastewater and to check the possibility of Basaka Lake water for struvite crystallization as economical and locally available magnesium source.

1.2 Statement of the problem

Phosphorus is an essential nutrient used to improve agricultural production. It is derived from finite source called phosphate rock which takes 10-100 millennium to be formed through weathering and sedimentation (Suh & Yee, 2011). On the other side mobilization of phosphate rock for agricultural purpose has increased dramatically through time in order to feed ever growing global population. These unbalanced rates of phosphate rock formation and mobilization creates big problem on both input and output ends.

On the input side, the available phosphorus in the world may be exhausted due to increased utilization of phosphate rock since it is finite, non-renewable resource (Saerens et al., 2021).As a result, there will be a critical challenge on food supply if there is no mechanism to recover the available phosphorus.

On the output side, Excessive utilization of phosphate rock result excess load of phosphorus in wastewater which flow into the river and wastewater treatment plants through dense network of streams and open channels. Excess load of phosphorus in rivers brings eutrophication which can reduce the quality of water. Beside eutrophication, it can also cause clogging of pipelines and pumps in wastewater treatment plants due to deposition of spontaneously formed struvite crystals.

Additionally, the supply of phosphorus containing fertilizer is very low in developing countries like Ethiopia. According to national bank of Ethiopia annual report (2018/2019), Total fertilizer import bill reached 500 million USD in 2018/2019. Yet fertilizer use in the country is very low. Only 30-40% of farmers in the country use fertilizer on recommended rate (Rashid et al., 2014). Low level application of fertilizer in agricultural industry causes low productivity leading to negatively affect the overall economy of the country. However, recovery of phosphorus through crystallization process can produce struvite which can be used as a fertilizer.

Although the importance of phosphorus recovery in the form of struvite is well known, little consideration is given in developing countries. Further there is little research on optimization of process parameters for struvite crystallization. Therefore, this research optimizes process parameters and investigate the potential of domestic wastewater for struvite crystallization. Further It also search economical and locally available magnesium source for struvite crystallization in order to reduce the cost needed for external magnesium.

1.3 Objective of the study

1.4 General objective

The general objective of this research is to recover phosphorus through struvite crystallization in fluidized bed reactor from domestic wastewater.

1.4.1 Specific objectives

- To optimize process parameters such as pH, Mg/PO_4, NH_4/PO_4 and reaction time (RT) on both removal efficiency of phosphorus and struvite yield by employing response surface methodology using model solution.
- To investigate struvite crystallization potential of domestic wastewater from Tuludimtu condominium wastewater treatment plant.
- To characterize and compare synthesized struvite crystals from model solution and domestic wastewater.
- To check struvite crystallization potential of Basaka Lake water as locally available external magnesium source.

1.5 Research questions

1. What are the optimum values of process parameters such as pH, Mg/PO4, NH4/PO4 and RT in order to achieve maximum struvite yield and phosphate removal efficiency?
2. What are the characteristics of synthesized crystals from both model solution and domestic wastewater?
3. What is the difference between synthesized crystals from model solution and domestic wastewater?
4. Is it possible to use Basaka Lake water as economical and locally available external magnesium source for struvite crystallization?

1.6 Significance of the study

This study demonstrates the potential of domestic wastewater for recovery of phosphorus in the form of struvite instead of being a cause for water pollution. It also contributes something for the development of phosphorus recovery technologies at industry scale by providing important information about various factors that affect crystallization process. Further it gives basic information about struvite crystals produced from domestic wastewater in order to use it as phosphorus containing fertilize in agriculture. Moreover, it also gives an insight for specific removal mechanism of phosphorus and nitrogen from wastewater in order to avoid eutrophication of water bodies.

Policy makers can also use it in order to known what are the resource at our hand, how the recourses at our hand can be used, how eutrophication of water bodies can be reduced and how operational problems due to unwanted struvite deposition can be solved in wastewater treatment plants.

1.7 Scope and limitation of the study

This research was conducted using laboratory scale fluidized bed reactor to precipitate struvite from synthetic and domestic wastewater. The domestic wastewater sample were collected from tuludimtu sewage treatment plant in Addis Ababa. Additionally, process optimization was caried out using synthetic wastewater focusing on reaction parameters such as pH, NH_4/PO_4, Mg/PO_4 and reaction time (RT). Basaka Lake water sample which was collected from the central part of the lake employed as economical and locally available magnesium source for struvite crystallization.

Due to limitation of time the characterization of domestic wastewater and Basaka Lake water did not include seasonal variation. Further for the same reason, it was not possible to characterize struvite produced from domestic wastewater by employing Basaka Lake water as locally available magnesium source.

2 LITERATURE REVIEW

2.1 Wastewater

Any activities that use a water can produce a wastewater as a byproduct. A water is changed into wastewater after its characteristics affected by domestic, commercial and industrial use. Although there is no universally accepted definition for the term wastewater, most literatures define it as a 'used water'. (Connor et al., 2017; Brogowski & Renman, 2004; Tchobanoglous et al., 2011) However, this definition does not separate treated wastewater from untreated one which is important information in many contexts. In general, it is a combination of domestic, commercial, institutional, industrial and agricultural effluent which contain organic matter, nutrients and hazardous material.

Nutrient such as phosphorus and nitrogen enter into wastewater from domestic, industrial and agricultural sources. Domestic contribution of nutrient load in wastewater comes from blackwater (excreta, urine and fecal sludge) and grey water (used water from washing and bathing) (Aiyuk et al., 2004). Due to the composition wastewater, it is considered as major cause for environmental pollution. Without any specific nutrient removal mechanism more than seventy percent of nutrients in wastewater would end up in waterbodies leading to eutrophication which negatively affect water quality and aquatic biodiversity (Simon & J.Smith, 2008). Moreover, in low-income countries, 92% of wastewater are released to the environment without any kind of treatment and consequently cause serious deteriorations of water quality (Sato et al., 2013).

On the other hand, wastewater is a critical component for energy and nutrient recovery. Energy can be recovered in the form of biogas, heating/cooling and electricity. Since 1896 biogas was produced from organic waste such as sewage sludge, manure and municipal solid waste by anaerobic digestion technology (Demirbas et al., 2016). Now a days wastewater is also used to produce electricity through microorganism activities in microbial fuel cell (Pandey et al., 2011).

Wastewater contain huge concentration of phosphors and nitrogen which are essential nutrient for plant growth. According to Cahill et al., (2003) more than 60 % of urine is nitrogen. Due to the existence of large quantity of nutrients in wastewater, it is also considered as a resource instated of water pollution causing agent. Nutrients including phosphorus and nitrogen can be recovered from wastewater in the form of organic fertilizer for agricultural application. Hallas et al., (2019) can produce phosphorus containing fertilizer called struvite form anaerobically treated municipal wastewater in USA.

2.2 Domestic wastewater

Domestic wastewater is a water produced from various human activities at home including food preparation, restroom usage and laundry. It is a combination of yellow, brown, gray and black water. Wastewater from toilet mostly called black water is a mixture of urine (yellow water) and human feces combined with flushed water (brown water). It is a main component of domestic wastewater which contain high organic matter and nutrients. More than 70% of domestic wastewater originate from toilet (Boehler et al., 2007). Another component of domestic wastewater is gray water which includes water used in shower, laundry and kitchen. Generally gray water is a water used in home except wastewater from toilet. Figure 2.1 shows the component of domestic wastewater.

Figure 2.1 Components of domestic wastewater.

The composition and strength of domestic wastewater varies seasonally, daily and even hourly basis due to variation of water usage at home. However, the average composition and strength of domestic wastewater is dependent on living standard, habits, diets, life style and per capital water usage. Wastewater from developed countries contain huge amount of nutrients as compared to developing countries as a result of the difference in living standard and life style. The main composition of domestic wastewater are nutrients, microorganisms, metals, suspended solid particles, organic and inorganic materials which can adversely affect the environment. According to Huang et al., (2010) domestic wastewater is composed of 70% dissolved and 30% suspended solid. Suspended solids include food particles, feces, grits and toilet paper which can lead to increase biological oxygen demand of receiving water bodies. Further suspended solids can form sludge in wastewater treatment plant. Dissolved solids can also form a precipitate by chemical and biological means depending on desired purpose. Most of the time domestic wastewater is physically characterized by grey in color and musty odor with suspended solids.

The chemical components of domestic wastewater include 70% of organic and 30% of inorganic compounds as well as various gasses (Hossein et al., 2004). Major organic compounds in domestic wastewater are proteins, carbohydrates and fats which reflect the diet of the people. In organic compound such as nitrogen, phosphorus, sulfide chlorides and heavy metals are also common in domestic wastewater. Additionally, gasses such as hydrogen sulfides, methane and ammonia are present in domestic wastewater due to decomposition of organic matter. On the other hand, biological components of domestic wastewater are different microorganisms including protozoa, bacteria, fungi, algae, ferns, mosses and plant seeds. Most of microorganisms in domestic wastewater originates from human feces who is infected by disease.

2.2.1 The occurrence of phosphorus in domestic wastewater

The main source of phosphorus in domestic wastewater is black water which is a mixture of human feces and urine. According to Johnny, (2018) an average of 1.28 g of phosphorus exist in urine although the concentration phosphorus depends on the diet of the person excreting the urine. Additionally, an average of 0.2 kg of phosphorus per capital per year enter in to domestic wastewater as a result of human feces. Further Harder et al., (2019) demonstrate the occurrence of 0.2 – 0.37 kg/cap/year of phosphorus in urine. Similarly, this author also indicates that human feces per capital per year contain 0.1- 0.21 kg of phosphorus. Based on a few studies conducted on phosphorus which enter into domestic wastewater treatment plants in Ethiopia, the amount of phosphorus an average of 18 mg/L (Mahlet Melaku, 2017), thus making it worthy of recovery.

2.2.2 Impacts of excessive phosphorus in domestic wastewater

Discharge of phosphorus rich wastewater causes a series water quality deterioration which has negative impact of water supply. Extreme loading of phosphorus in water bodies cause eutrophication which can lead to loss of aquatic organism. Although nutrients such as carbon, nitrogen and phosphorus can cause eutrophication of water bodies, phosphorus is the most concern when the problem of eutrophication arises due to the existence of very small amount of phosphorus in fresh water bodies under natural condition (Walter et al., 2017). Further biological oxygen demand of water bodies also increased after aquatic organisms consume dead algae.

Beside water quality degradation, Excessive phosphorus in wastewater also cause a serious problem in wastewater treatment plant due to deposition spontaneously precipitated white crystals called struvite (Kecskésová et al., 2020). Deposition of struvite in pipes can increase the pressure and lead to breakage of pipe in wastewater treatment plant. Although different techniques such as dilution of struvite crystals with water effluents, addition of chemical inhibitors and chemical dosing of iron salts are applied to control spontaneous precipitation of struvite in wastewater treatment plants, most of them are very costly and not effective (K. S. Le Corre et al., 2009).

2.3 Removal and recovery of phosphorus from domestic wastewater

Phosphorus is essential element for agricultural production and industrial development. Despite of its use, it released to water bodies in wastewater and cause eutrophication. So, legislation designed to remove phosphorus from wastewater. Since 1950 different phosphorus removal technologies are developed to reduce the amount of phosphorus enring in to waterbodies. Previously chemical precipitation was the most applied technology to remove phosphorus from wastewater (Morse et al., 1998). However, biological phosphorus removal and crystallization technologies has become firmly established now a days. Further the development of phosphorus removal technologies offers the opportunity for recovery of phosphorus since it is finite resource on the earth crust.

2.3.1 Chemical precipitation

The use of chemical precipitation technology for phosphorus removal from wastewater started in Switzerland in order to reduce the growing problem of eutrophication (Morse et al., 1998). But now adays it is widespread in many countries. Chemical precipitation is a physio chemical process in which phosphorus is removed from wastewater by addition of metal salts in order to form insoluble metal phosphate precipitations that can be easily removed by sedimentation. During wastewater treatment, chemical precipitation can be applied before primary sedimentation, at aeration tank and after secondary treatment. Although phosphorus is effectively removed through chemical precipitation, it is not recommended in most cases as a result of high chemical cost and production of harm full sludge (Yeoman et al., 1988).

Further when the sludge produced by chemical precipitation is disposed to agricultural plots, it can cause human health risk through food chain. So, this negative impact of chemical precipitation leads to the development of substitute phosphorus removal technology that can produce use full end product for agricultural application.

2.3.2 Biological phosphorus removal

Biological phosphorus removal technology based on the phenomena called luxury uptake in which activated sludge can up take phosphorus excess to that required for biomass growth under certain condition (Srinath et al., 1959). It was achieved by introducing an anerobic zone a head of aerobic zone in activated sludge process. In anerobic zone phosphorus accumulating organisms such as *Acinetobacter* uses adenosine triphosphate (ATP) as energy source and release phosphorus in to solution in the absence of oxygen (Bowker & Stensel, 1990). However, when they move to aerobic zone, they up take excess phosphorus from the solution. Through repeated cycle of phosphors accumulation organisms in anaerobic and aerobic environment, they can store excess phosphorus. So, phosphorus can be easily removed from the system by removing this phosphorus accumulating organisms.

As compared to chemical precipitation, biological phosphorus is advantageous by avoiding excess sludge production and the cost needed for chemical. However, it requires complicated treatment plant configuration. Further phosphate removal efficiency of this technology is very low and variable in practice. As a result, complimentary chemical precipitation may require in order to achieve effluent standard.

2.3.3 Crystallization technologies

Since 1970 crystallization technologies has been developed in order to produce marketable end product beside removal of phosphorus from wastewater (Morse et al., 1998). Crystallization is a process used to form solid crystals from supersaturated solution. It is solid liquid separation process in which mass transfer of solute occurs from the liquid to solid phase. Although different useful end products can be produced trough crystallization technologies, struvite and calcium phosphate are the most common end products which can be used for improvement of agricultural productions and industrial application.

Calcium phosphate crystallization technologies can be applied in most type wastewater treatment plants. It takes placed by adding milk of lime or caustic soda in fluidized bed reactor. Further the process also requires pre-degasification and post filtration (Tran et al., 2014). The first is used to reduce carbonate ions in wastewater that may react with calcium and form calcium carbonate which is problematic for some application. Whereas the second is used to ensure very low amount of phosphate in final effluent. The main advantage of phosphors removal by calcium phosphate crystallization is that the process did not produce any additional sludge. Further the end product can be used as fertilizer in agricultural plots (Bhuiyan et al., 2008).

Struvite crystallization is another technology used for removal and recovery of phosphorus from wastewater. This crystallization process is based on the principle of struvite crystal nucleation and growth in reactor. Most of the time struvite crystallization require different seeding materials to initiate the process. Beside seeding materials, alkaline solution and magnesium salts are also used to create suitable reaction condition for the process.

Table 2.1 Crystallization technologies for phosphorus recovery

Reference	Process/Technology	Source of wastewater	Recovered form of P	P removal
Brett et al. (1997)	Fluidized bed crystallization	Anaerobic supernatant	Struvite	90%
Fujimoto et al. (1991)	Stirred reactor	Anaerobic supernatant	Struvite	60%-70%
Giesen (1999)	DHV Crystal actor	Anaerobic sludge	$CaPO_4$	70%
Ishikawa et al. (2004)	FBR seeded with struvite	Dewatering sludge	Struvite	>90%
Jaffer and Pearce (2004)	Air-agitated reactor	Centrifuge liquors	Struvite	60%-80%
Suzuki et al. (2002)	Aeration column	Swine wastewater	Struvite	65%
Cecchi et al. (2003)	FBR seeded with silica	Anaerobic supernatant	Struvite	62%

2.4 Physical and chemical property of struvite

Struvite is a white crystal formed from with an equal molar concentration of magnesium, ammonium and phosphate combined with six water molecules (MgNH4PO4.6H2O). Theoretically it is composed of 38.7 % phosphate, 7.3 % ammonia and 10% magnesium. Its molar wight and solubility constant are 245.43 g/mol and 10-13.26 respectively (Rehman et al., 2019). The solubility constant of struvite (Ksp) is $10^{-13.26}$ (Ohlinger et al., 1999). It is also readily soluble in acidic solution but less soluble in neutral and alkaline condition. Struvite crystals has orthorhombic shape formed by regular PO4 octahedral, distorted MgO (H2O)6 octahedral, and NH4 groups in which all groups held together by hydrogen bonding (Abbona & Boistelle, 1979). Figure 2.2 shows the molecular structure of struvite.

According to Rahman et al., (2014) its crystal size varied from 15 micro meter to 3.5 millimeter depending on different production conditions. Further boiling of struvite crystals resulted in loss of five water molecules and form monohydrate compound called dittmarite which has higher concentration of phosphate than struvite (Bhuiyan et al., 2008b).

In most cases struvite is considered as phosphorus containing fertilizer. But it is also an effective source of nitrogen for growth of plants. Additionally, it is preferable fertilizer in flooded area due to its low specific gravity around 1.7 in which it is not fleshed away by rainfall (K. S. Le Corre et al., 2009). Furthermore, it has a capacity to increase the soil pH which make struvite crystals suitable for acidic soil (Bhuiyan et al., 2008).

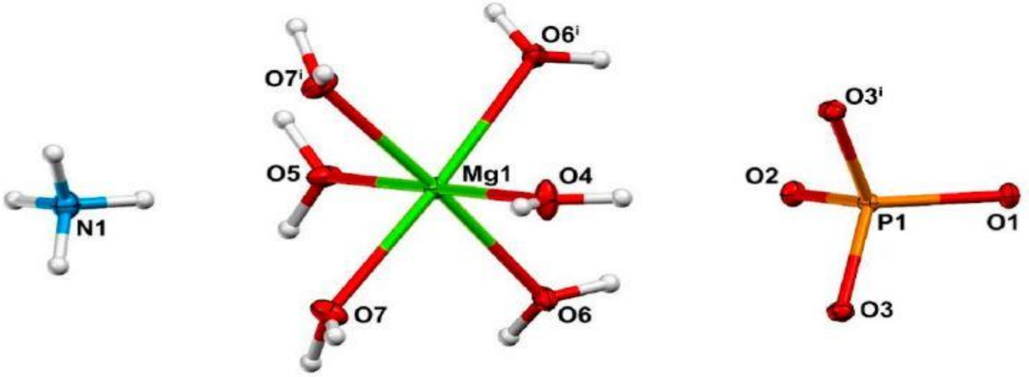


Figure 2.2 Molecular structure of struvite (source: Prywer et al., 2019).

2.5 Fertilizer quality of struvite

Struvite is effective fertilizer as compared to other fertilizers due to its low solubility in water which prolongs the release of nutrients and reduce burning of plant root (Johnston & Richards, 2003). Thus, it is preferable in flooded and coastal agriculture. It also contains magnesium ion which make it suitable fertilizer for crops such as sugar beet that require magnesium additional to phosphorus and nitrogen (Gaterell et al., 2000). Further as compared to conventional fertilizer, it is desirable in forests and grasslands where fertilizers are applied once a year. According to (Escobar et al., 2004) struvite can reduce nitrogen loss by leaching and evaporation. As a result, it is eco-friendly fertilizer in agricultural.

2.6 Struvite formation

Crystallization is a process that used to separate desired solid phase from liquid for different industrial applications. It is a complex process leading to formation of solid particles with regular structures called crystal. Supersaturation ratio is the driving force for the crystallization process in which initiate the occurrence of first crystal (Le Corre et al., 2009). Crystallization of any solid particle consists of two main processes i.e., nucleation and crystal growth. Nucleation corresponds to the birth crystal in a liquid or gaseous media. During nucleation stage ions combine together to form crystal embryos, which is the first state of crystals. Mostly it is governed by kinetics of reaction. Whereas crystal growth corresponds to the development of crystals until the equilibrium is reached. It determines the final size of crystal according to the crystallization kinetics (rate of growth).

Similarly, struvite nucleation occurs in solution when components of struvite forming ions combine together to form embryos (Mullin, 2001). There are two types of struvite nucleation exist i.e., homogeneous nucleation and heterogeneous nucleation. Homogeneous nucleation related to the occurrence of crystals spontaneously in highly purified solution such as syntactic wastewater. Whereas heterogeneous nucleation is the occurrence of crystal in the presence of foreign particles or impurities. Due to the existence of impurities in wastewaters, struvite formation from wastewater is likely to be heterogeneous nucleation. Predicting the mechanism of struvite nucleation is very difficult and complex as it is controlled by a combination of factors such as the crystal state of initial compounds, thermodynamic of liquid solid equilibrium, phenomena of mass transfer between solid and liquid phases and kinetics of reaction (Jones, 2002). Further several physic-chemical parameters can also influence struvite nucleation mechanisms such as pH of the solution, supersaturation, mixing energy, temperature, and presence of foreign ions (Le Corre et al., 2009).

After nucleation, the next step is crystal growth. In this stage, crystals embryos increase in size until they reach maximum detectable crystal size. The growth rate of crystals is essentially controlled by processes of mass transfer and surface integration mechanisms. The mass transfer process corresponds to the transport of solutes from the solution to the crystal surface by diffusion and convection while the surface integration process corresponds to the incorporation of material into the crystal lattice through mechanisms of surface integration (Le Corre et al., 2009).Theoretically the rate of crystal growth is expressed as the change in size of crystals with respect to time (Jones, 2002).

Although nucleation seems to be the most important step in struvite crystallization process, crystal growth is responsible for the final size and structure of crystals which are essential parameters in order to harvest struvite crystals (Abbona & Boistelle, 1979).

2.7 Parameters affecting struvite crystallization

Struvite crystallization process is very complex and dependent on different factors such as pH, supersaturation level, aeration rate, mixing energy, temperature, molar ratio between struvite constitutes ions and the presence of foreign ions in the precipitating solution. Moreover, reaction kinetics, thermodynamics and a phenomena of mass transfer between solid and liquid phases also affect the process of crystal formation which in turn influence the size and purity of harvested struvite crystals.

2.7.1 pH

The pH is one of the main factors which can influence the process of crystallization. It directly related to supersaturation index of the solution which is the driving force for nucleation of struvite crystals. It also controls the rate of crystal growth. In most cases, supersaturation index of the solution increases with pH which fevers formation of struvite crystals. However, continuous increase in pH leads to vaporization of ammonium which in turn reduce struvite formation. Booker et al., (1999) identify the specific pH range from 8.5 to 9.5 in order to get maximum yield of struvite. Further pH affects the solubility of struvite. According to (Borgerding, 2016) the solubility of struvite decrease from $3000\ \text{mg. L}^{-1}$ to less than $100\ \text{mg. L}^{-1}$ for pH an increase of pH from 5 to 7.5 . Most literatures who investigate the effect of pH on struvite formation found higher phosphorus removal efficiency by increasing the pH of the solution (Stratful et al., 2001; Guadie et al., 2014). This may be due to the fact that increasing the pH of the solution decreases struvite solubility facilitating formation of struvite crystals.

Struvite precipitation is associated with the release of proton in the solution which leads to lower the pH of the solution ($Mg^{2+} + NH_4^+ + HPO_4^{3-} = MgNH_4PO_4.6H_2O + H^+$) (Kumar & Pal, 2013). The rate at which the pH of the solution decrease reflects the speed of struvite formation. Thus, it can be used as an indicator of struvite nucleation (Rahman et al., 2014).

2.7.2 Molar ratio between struvite constitutes ions

Molar ratio between struvite constitute ions can affect the quantity and purity of harvested struvite crystals. Theoretically the molar ratio between NH4+, Mg2+ and PO43- is one to one as it is shown in chemical formula of struvite ($MgNH_4PO_4.\ 6H_2O$). However, in order to improve formation of struvite, NH4+ and Mg2+ need to be excess.(Le Corre et al., 2009).

Different literatures apply wide range of molar ratio for struvite crystallization, but in most cases, lower struvite yield was harvested when molar ratio between constitute ions less than one. Yetilmezsoy & Zengin, (2009) found lower struvite yield when the molar ratio between PO4 and Mg is 0.8. Zhang et al., (2009) also indicate that phosphate removal efficiency increased by increasing the mola ratio between constitute ions. However, the author found insignificant increase of phosphate removal efficiency when the molar ratio increases beyond one. Similarly, (Zheng et al., 2004) suggest 1.15:1:1 molar ratio for optimum struvite crystallization.

Further the molar ratio also affects the average size of harvested struvite crystals. According to Hutnik et al., (2019) the average size of struvite crystals increases from 42 to 58 micro meter when the molar ratio between Mg and PO4 increase from 1 to 1.2. Matynia et al., (2006) also found larger crystal size with higher molar ratio between Mg and PO4.

2.7.3 Supersaturation ratio

At a fixed pH, supersaturation index of the solution affects crystallization process in terms of induction time. Induction time is a time required to grow measurable struvite crystal size. In other word it is the sum of nucleation time and crystal growth time (time necessary to grow to detectable crystal size) (Jones, 2002). It is highly dependent on supersaturation index. Bouropoulos & Koutsoukos, (2000) shows 20-fold times reduction of induction time by increasing supersaturation ratio from 1.13 to 3.33 which in turn fever struvite formation.

Bhuiyan et al., (2008) also conduct a serious of experiment using synthetic wastewater in order to see the effect of supersaturation ratio on crystallization process. Their result indicate that struvite precipitation potential of the solution is directly proportional to super saturation ratio. Additionally, supersaturation ratio of the solution also affects the rate of crystal growth. Kofina & Koutsoukos, (2005) proven that rate of crystal growth increased by increasing supersaturation ratio of the solution which leads improve surface diffusion of particles.

2.7.4 The presence of foreign ions

The presence of foreign ions such as calcium, sodium, sulfate and carbonate ions in the solution can affect struvite crystallization process by blocking the site for crystal growth. According to Liu & Wang, (2019) the presence of calcium and carbonate in the solution negatively affect crystal growth by increasing induction time. Furthe calcium can react with phosphate as shown in chemical equation 1 leading to reduce the amount of phosphate required for struvite crystallization. (Le Corre et al., 2009) states that the formation of struvite crystals might be limited and even inhibited by amorphous calcium phosphate when there is plenty of calcium ion in the solution.

$$5Ca_2+ + 3PO_3^{-\,4} + H_2O \rightarrow Ca_5(PO_4)_3OH + H^+ \qquad 1$$

The presence of sulfate ion also negatively affects struvite formation by increasing induction time. Kabdasli et al., (2006) states that induction time required for struvite crystallization increases from 1 min 59s to 4 min 25s by increasing sulfate concentration from 12.5 to 25 milli mole. The effect of zinc and copper on struvite formation was investigated by Muryanto & Bayuseno, (2014) . There finding suggested that zinc and copper can adversely affect struvite formation even in very low concentration (1-5 ppm).

2.7.5 Aeration

Aeration might increase the pH value of the solution by liberating carbon dioxide gas from the solution which in turn fevers the formation of struvite crystals. According to Liu et al., (2011) struvite formation increases with aeration rate and reached a plateau at around 0.73 L min^{-1}. On the other hand, aeration might also negatively affect struvite formation by volatilizing ammonia gas from the solution (Yetilmezsoy & Zengin, 2009). Further high aeration may produce foam in the reactor during crystallization process which adversely affect struvite formation. (Rahman et al., 2014).

2.7.6 Temperature

Temperature affect struvite crystallization in terms of solubility product and crystal morphology (Durrant et al., 1999). According to Burns & Finlayson, (1982) struvite solubility increase $0.7.10^{-14}$ to $1.45.10^{-14}$ by increasing the temperature from 25^{o}C to 45^{o}C. Since the solubility product is linked to supersaturation state of the solution, the precipitation of struvite is more difficult at high temperatures. This is the reason why most authors use room temperature to study struvite precipitation.

Temperature affects the mechanism of crystal growth. At higher temperature crystal growth is based on diffusion whereas at low temperature it is controlled by surface integration (Jones, 2002). The rate of crystal growth is also dependent on the temperature which directly affect the final size of crystals. Furthermore, temperature can also affect the shape of crystal. Boistelle et al., (1983) effectively noticed a change between struvite crystals obtained at 25◦C and crystals obtained at 37◦C. At 25^{o}C the author found rectangular and prismatic shape of crystals whereas at 37^{o}C the shape of crystals changed in to square.

2.7.7 Turbulence or mixing energy

Mixing energy (Turbulence) is one of the factors which can affect struvite crystallization. Hight turbulence liberate carbon di oxide from the solution which fever the formation of struvite by increasing the pH of the solution (Le Corre et al., 2009). It can also affect the growth rate of crystals (Warmadewanthi et al., 2020). observe lowest growth rate of crystals in low mixing zone of the reactor as compared to higher mixing zone. Moreover, low mixing energy could result elongated shape of crystals than high mixing energy which in turn adversely affect growth rate of crystals by limiting agglomeration of struvite particles (Ohlinger et al., 1999). On the other hand, high mixing energy may adversely affect the final size of crystals by increasing crystal breakage (Durrant et al., 1999).

2.8 Magnesium source used for struvite crystallization

Crystallization of struvite from wastewater has gained attention of the scientific community due to its potential for recovery of phosphorus as fertilizer. It also used to manage the impact of phosphorus and nitrogen on receiving waterbodies in the country that already facing critical challenge with regard to water pollution. Struvite crystallization has proven to be economically and environmentally feasible method to reduce and recover phosphorus from wastewater (Mamakoa et al., 2019). However, the use of water-soluble magnesium salts for struvite crystallization significantly reduces the cost effectiveness of the process.

Environmental impact, cost, availability and struvite quality are some of the criteria to select magnesium source for struvite crystallization from wastewater. But in most cases, water soluble magnesium salts such as $MgCl_2$, $MgCO_3$, $Mg(OH)_2$ and MgO are used as magnesium source for struvite crystallization. Although these commercially available water-soluble magnesium salts increase the of quality struvite, they are very expensive. Even the production of this salts is not environmentally viable. $MgCl_2$ is produced from sea water or brine which require a lot of energy (Mamakoa et al., 2019). Similarly, MgO is also produced thorough energy requiring process (Li et al., 2019). Further the cost required for these salts reduce the cost effectiveness of crystallization process. As a result, it is important to find a low cost and easily accessible Mg source to make the process of struvite synthesis commercially attractive. Sakthivel et al., (2012) suggest wood ash as cheap and available magnesium source for struvite crystallization. Table 2.1 shows the cost and environmental impact of water-soluble magnesium salts for struvite crystallization.

Table 2.2 The cost, availability and environmental impact of water-soluble magnesium salts.

Magnesium source	Cost	Availability	Environmental impact
$MgCl_2$	USD 0.04kg	Easily available	Energy intensive
MgO	USD 0.08kg	Available	Requires energy
$MgCO_3$	Naturally available	Easily available	Carbon footprint due to transportation

Source: (Mamakoa et al., 2019)

2.8.1 Sustainable magnesium source for struvite crystallization

Sea water is a promising and cheap alternative to conventional magnesium sources. Kumari et al., (2020) investigate the potential of sea water for struvite crystallization using synthetic sea water which is formulated by dissolving sodium chloride (24 g/L), magnesium chloride (4.6 g/L), magnesium sulphate (6.2 g/L), calcium chloride (1.16 g/L), potassium chloride (0.695 g/L) and sodium hydrogen carbonate (0.201 g/L) in deionized water. However, real sea water composed of different chemical compounds and biological organisms. As a result, it is better to dilute in order to minimize the effect of different chemicals and microorganisms in sea water as well as wastewater used for struvite crystallization.

Evangel, (2017) did a series of experiment using sea water for struvite crystallization from distillery wastewater. His result demonstrates that around 97 % phosphate removal efficiency is obtained by employing sea water as magnesium source. Beside the source of magnesium, the author use sea water in order to dilute harmful distillery wastewater. Guadie et al., (2020) also uses Afdera lake water as a source of magnesium to recover phosphorus from urine. Although urine contain large amount of phosphorus and nitrogen, its magnesium concentration is low for struvite crystallization under a normal condition. As a result, addition of an external magnesium ion is essential to enhance the formation of struvite from urine.

Previously different studies use locally available magnesium sources such as brine (Liu et al., 2013), bittern (Etter et al., 2011), seawater (Evangel, 2017;Kumari et al., 2020), wood ash (Sakthivel et al., 2012) and seawater nano-filtration concentrate (Birnhack et al., 2015) to recover phosphorus via struvite crystallization.

3 MATERIALS AND METHODS

3.1 Preparation of model solution

Model solution creates a controlled environment by avoiding the fluctuation of various characteristics in domestic wastewater. It also allows the flexibility to study the effect of each parameter in great detail. Model solution formulation of aerobically treated domestic wastewater was designed as per the characteristic given by Addis Ababa city water supply and sewerage authority (AAWSA) (Appendix 15). The characteristic of model solution employed in this study is provided in Table 3.3. It was prepared by mixing various salts with distilled water in order to achieve desired concentration. The reason behind using distilled water is, to avoid the potential effect of ionic specious in tap water.

Table 3.1 The characteristics of model solution.

	pH	PO_4	Mg	NH_4
Model solution	6.8	60 mg/l	Negligible	Varied depending on experiment

Salts used to prepare the influent were commercial grade potassium di hydrogen phosphate (KH_2PO_4) as phosphate source, ammonium chloride (NH_4Cl) as ammonium source and magnesium chloride hexahydrate ($MgCl_2$-$6H_2O$) as magnesium source. Depending on desired experimental conditions different concertation of potassium di hydrogen phosphate (0.632 mmol/L), ammonium chloride (0.632 mmol/L – 3.16 mmol/L) and magnesium chloride hexahydrate (0.316 mmol/L – 1.58 mmol/L) were prepared and feed to the reactor from ten litter influent holding tank. Detail procedure of model solution formulation was presented in Appendix 15.

3.2 Construction of reactor and its operation

Lab scale fluidized bed reactor (FBR) were installed at Addis Ababa institute of Technology (AAiT) in Environmental research laboratory. The reactor was designed and developed similar to the one reported in literature Guadie et al., (2014) with little modifications. Cross-sectional area of the bottom part of reactor was modified to avoid any breakage of precipitated crystal due to high turbulence. Furthermore, it has air pump at the bottom to fluidize precipitated crystals.

The reactor was made up of stainless steel to avoid any corrosion and resist high temperature. Additionally, the surface of stainless-steel materials has higher struvite accumulation rate due to their surface roughness.

The total volume and height of the reactor is 12 liter and 1.5 meter respectively. The reactor had three distinct parts, bottom (volume 930 mL, diameter 65 mm), middle (volume 4130 mL, diameter 110 mm), and top (volume 4950 mL, diameter 180 mm), in which the volume and diameter increased towards the top while the up-flow velocity decreased (Figure 3.1).

The upper part of the reactor called the top clarifier was used to delay very fine crystals and provide continuous reseeding of the reactor by recycling the effluent whereas the lower and middle parts of the reactor were designed for nucleation and crystal growth respectively. Additionally, the lower part of the reactor was also used for crystal removal if the system is not connected with external sedimentation tank.

Each part of the reactor was connected by cone-shape structures at an angle of 45°. The strategy of inserting cone-shaped structures between the parts was aimed at reducing unwanted crystal loss and accumulation of struvite at each junction. Additionally, the top of the reactor is covered by lid in order to reduce ammonia stripping.

The diameter changes caused turbulent eddies above each transition, ensuring sufficient mixing in the reactor, and also helped to classify the fluidized particles by size. The larger crystals accumulated at the bottom end were harvested periodically. Generally, such type of reactor creates high turbulence at the lower end which used to increase the mechanical strength of formed crystals.

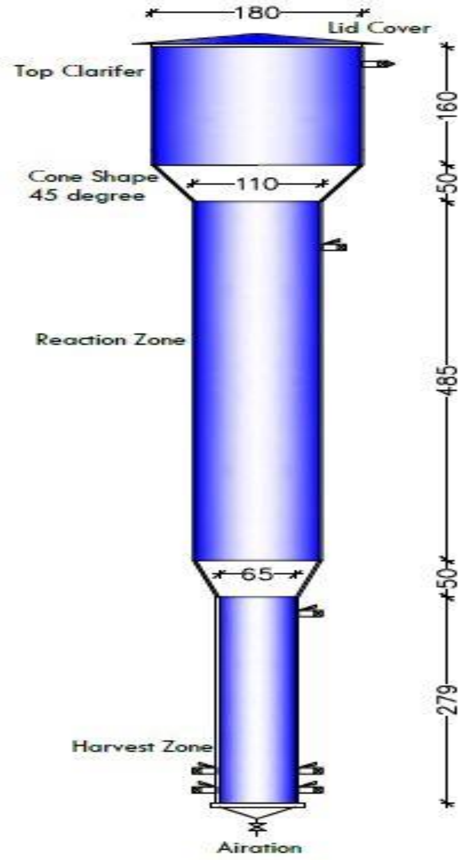


Figure 3.1 Fluidized bed reactor deign.

The total crystallization system including reactor and accessories were shown in Figure 3.2 & 3.3. The crystallization system contains a reactor with eight valves: five of them at the bottom section for influent supply, pH control and product recovery, one valve at the middle section for pH control and one valve at the top for effluent recycle and pH control. Beside the reactor, the system contains an external recycler (volume = 13,000 mL, height = 840), peristaltic pumps (YZ1515XLonger Pump Co., Ltd., China), air pump (AMAZON pet power air pump SH-A5, China), influent holding thermoplastic tank (volume = 10,000 mL) and effluent holding tank (volume 15,000 mL).

Before, a continuous mode of operation was functional, the flow rate capacity of each peristaltic pump was checked by pumping water into measuring cylinder for one minute. Accordingly, the pump has a capacity to inject 10 ml of solution in 1 minute under 1 revolution (1rpm=10ml. min^{-1}).

The entire system was continuously operated, influent and alkaline solutions were continuously supplied to the FBR at the bottom ports using peristaltic pumps while the solution was mixed by using air pump at bottom part of the reactor. The influent was divided into two individual flows: model solution and prepared magnesium chloride solution as shown in Figure 3.3. Prior to mixing in to the reactor, each solution was adjusted to the desired pH using pH meter (iSTEK.inc, Korea, pH N-25). Additionally, the level of pH was also monitored continuously in the lower, middle and top parts of the reactor after mixed in the reactor. Whenever pH deviation was observed, 0.05 mol/L of Sodium hydroxide / Hydrochloric acid solution were pumped into the reactor by adjusting pump head rpm to raise or lower the pH value.

As the waste containing constitute of struvite ions pumped to the reactor and mixed due to aeration at the bottom of the reactor, struvite plates were formed and moved upward (fluidized) on different cross-sectional areas. While the waste moved upward continuously, its velocity decreased leading to segregation of formed crystals. Larger crystals were eventually accumulated in the lower and middle part of the reactor. At this stage, the fine crystals were channeled out with the effluent via the upper part of the reactor to the external tank and are recycled back to the reactor.

After sufficient reaction time, the effluent was removed from the reactor to the effluent tank through bottom valve. Finally, the precipitated crystals were settled down for two hours in effluent tank and filtered through 0.45 mm filter paper (Whatman filter paper, UK). The crystal obtained after filtration was dried at room temperature for 48 h for further analysis whereas the spent was used for phosphate (PO_4) and ammonium (NH_4) analysis.

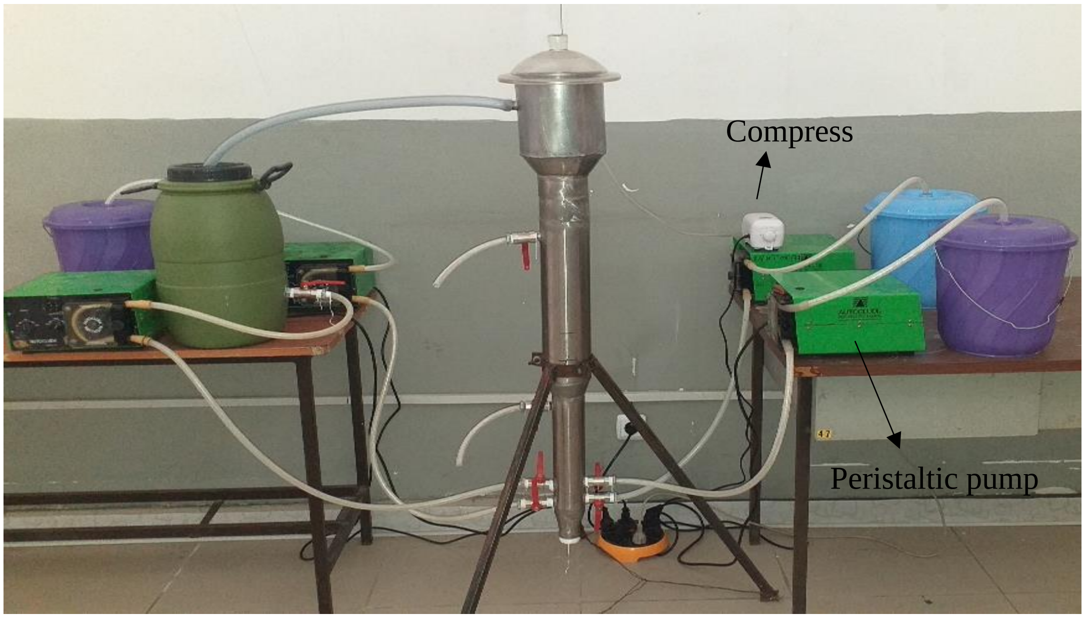


Figure 3.2 Laboratory scale struvite crystallization system.

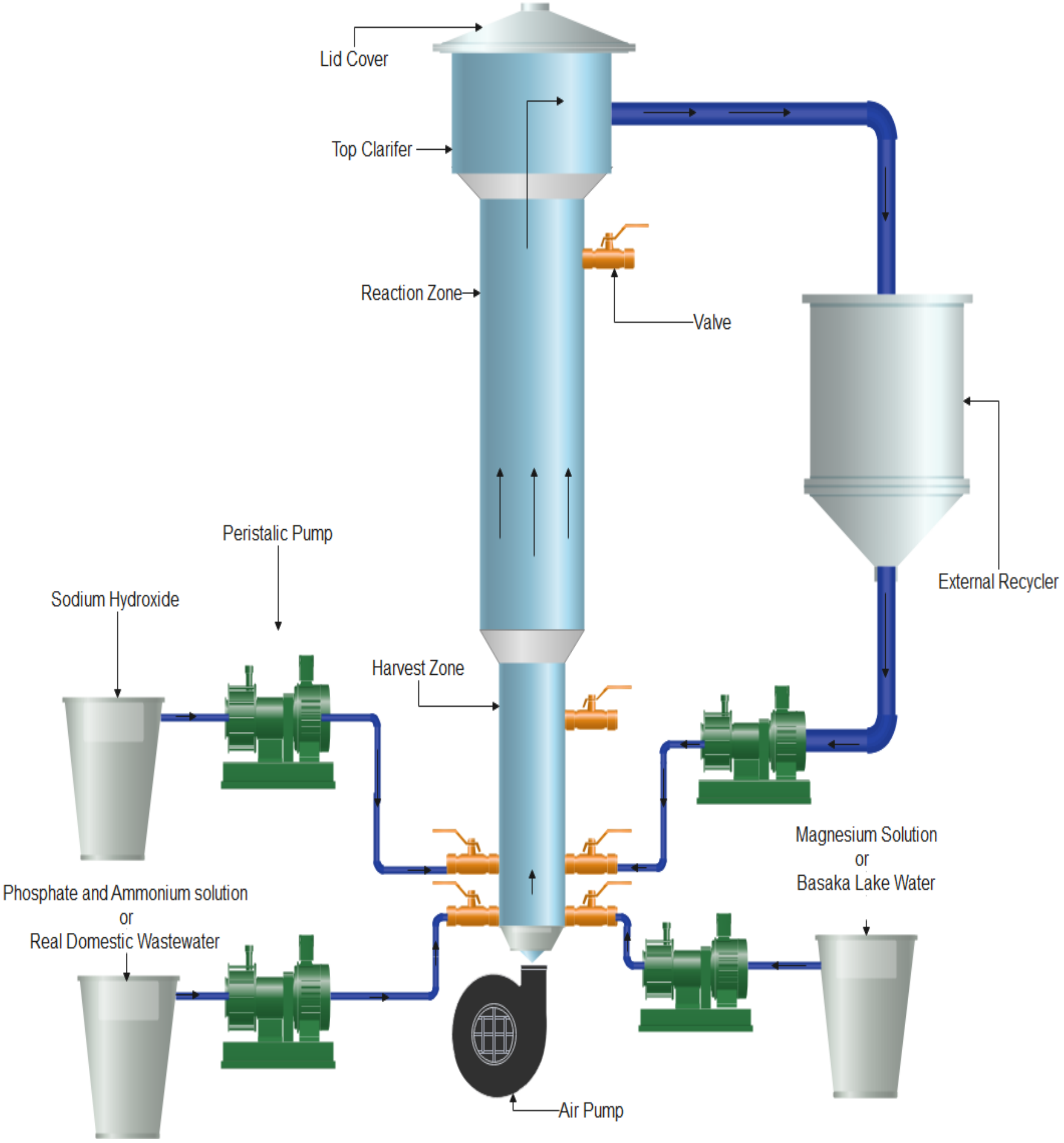


Figure 3.3 Crystallization system flow sheet.

3.3 Experimental procedures and data analysis

The effect of process parameters on removal and recovery of phosphorus by struvite crystallization process was evaluated by a multiple factor optimization (parallel processing of two and more parameters).

A multivariate mathematical model approach called Response Surface Method (RSM) was used for the study. The Central Composite Design (CCD) is one of the major RSM which used to evaluate the effect of the selected independent parameters, their interaction identifies the optimum response in the least number of experimental runs.

The CCD was designed using Design Expert Software package (version 13, Stat-Ease, Inc., U.S.). The number of experiments was calculated as follows:

$$\text{Number of experiment (N)} = 2^k + 2K + K_c \qquad 2$$

Where K represents number of independent parameters and K_c denotes the central point replicates. Accordingly, the required number of experiments with four variables (k = 4) and six central point (kc = 6) was 30 as mentioned in equation (Eq. 2).

A five-level, four-variable Central Composite Design (CCD) of the RSM, composed of 16 factorial points (coded as ±1), 8 axial points (coded as ±2), and 6 replications of center points (coded as 0), was employed to evaluate the effects of pH (A), Ammonium to phosphate ratio (B), Magnesium to phosphate ratio (C) and Retention time (D) on the response parameters such as phosphate removal efficiency (Y1) and struvite yield (Y2).

Table 3.1 shows the experimental ranges of independent parameters employed in the present study, which were fixed on the basis of preliminary experiments and previous studies. The reason behind selecting basic pH region is, in order to produce adequate amount of struvite crystals with bigger size for harvest.

Table 3.2 Experimental factors with their levels in central composite design.

Symbol	**Parameter**	**Level**				
		-α	**-1**	**0**	**+1**	**+α**
A	pH	8	9	10	11	12
B	$NH_4:PO_4$	1	2	3	4	5
C	$Mg:PO_4$	0.5	1	1.5	2	2.5
D	RT	1	2	3	4	5

After conducting 30 experiments as presented in Table 3.2, the coefficient of the polynomial of the mathematical model were calculated using the following quadratic equation (Eq. 3)

$$Y = \beta_o + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i<j} \sum \beta_{ij} X_i X_j + \varepsilon \qquad 3$$

where Y is experimental response; Xi and Xj are experimental variables or factors; βo is a constant; βi, βii, and βij are the regression coefficients for linear interaction effect, quadratic interaction effects, and cross-products interaction effects, respectively; and ε is the random error.

Analysis of variance (ANOVA) was used to evaluate regression coefficient and significance of the model. Quality of fit of the model equations and their statistical significance were expressed using F-test, coefficient of determination (R^2), prediction coefficients of determination (Pred R^2) and adjusted coefficients of determination (Adj-R^2). Linear variables and interaction amongst them were then analyzed using response surface plots (3D) respectively.

Optimization was carried out using design expert software by employing model solution with phosphate concentration close to aerobically digested domestic wastewater. Since domestic wastewater contain sufficient amount of phosphate and ammonium concentration for struvite crystallization, their concentration was not included as factor. However, their molar ratio which affect struvite crystallization process, size and quality of struvite was tested on different values. All the experiments were independent and run sequentially at an ambient temperature of approximately 25 °C.

3.4 Sampling and analyses

The effluent samples were collected from effluent holding tank after every experiment and subsequently filtered by Whatman filter pepper with 0.45 micro meter pore size in order to remove fine crystals before chemical analysis. The ionic concentration of phosphate (PO_4), ammonium (NH_4), magnesium (Mg), calcium (Ca), carbonate (CO_3) and bicarbonate (HCO_3) and nitrogen (N) were analyzed by using UV- spectrometer as per instrumental protocol (Palin test photometer 7100). Heavy metals which are excreted in human urine and feces (i.e., Zn, Mn, Cr, Cd, Pb) in precipitated struvite was quantify using flame atomic absorption spectroscopy (AAS) through acid digestion method (3g of precipitate in 50ml) as recommended by Environmental Protection Agency. All the analysis were done in triplicate and the result are presented as average.

3.5 Phosphate removal efficiency calculation

After the influent and effluent phosphate concentration was measured, the removal efficiency of phosphate was calculated using Eq. 4.

$$\text{Phosphate removal efficiency (\%)} = \frac{\text{PO4 in influent} - \text{PO4 in effluent}}{\text{PO4 in influent}} * 100\% \qquad 4$$

3.6 Compositional characterization of the struvite

The crystal formed from model solution and domestic wastewater under optimized condition were examined by X- ray diffraction (XRD), Fourier transformation Infrared (FTIR) and Scanning electron microscope (SEM) to confirm the presence of struvite. Further the chemical composition of crystals was determined by dissolving 0.5 g of crystal sample in 250ml of 3M hydro chloric acid solution as reported Ping et al., (2016). Then solution was stirred and allowed to stay overnight in order to accelerate and ensure complete dissociation. At last, the solution was diluted by adding 750ml of distilled water and analyzed for phosphate, ammonium and magnesium concentration.

Texture and surface morphology of precipitated crystals was examined using a scanning electron microscope at Addis Ababa science and technology university (AASTU). Whereas, crystalline nature of crystals and functional groups present in the crystals were determined in Addis Ababa university, collage of natural and computational sciences (CNCS) using X- Ray diffractometer using monochromatized Cu-Kα radiation from 2θ = 10° to 60° and FTIR on wavelength range 400- 4000cm^{-1} respectively.

After analyzing FTIR and XRD data using origin pro software package (Origin Pro 2021), identification of phase peaks and functional groups were accomplished by comparing the observed XRD and FTIR patterns to that of standard pure struvite from crystallography open database (COD). The quantitative phase determination of precipitated crystals was done through automatic Rietveld refinement technic using Match!3 software package (Version 3, 2021).

3.6.1 Assessment of struvite purity

The purity of struvite obtained under optimized condition were evaluated by dissolution method as described in section 3.6. Although the molar ratio of Mg, P and N in struvite is 1:1:1, Mg and P tend to be bound into some impure compounds rather than struvite. As a result, N is the only reference ion to calculate struvite purity (struvite in precipitates). In this study, struvite purity was calculated according to Eq.5.

$$P_{struvite} = \frac{nN * Mstruvite}{mp} * 100\% \quad 5$$

Where - $P_{struvite}$ is the purity of struvite

- $M_{struvite}$ is the molecular weight of struvite,
- mp is the mass of dissolved precipitates,
- nN is the mole of N in the dissolved precipitates.

3.7 Recovery of phosphate from domestic wastewater

After completion of the response surface experimental design optimization, domestic wastewater from tuludimtu wastewater treatment plant was used to produce struvite under optimized condition. An aerobically digested domestic wastewater was collected from aeration tank using 20-liter containers then transported to laboratory. The reason behind collecting the sample from aeration tank is, aeration tank is the best please to get high amount of phosphorus before phosphorus is removed from wastewater by bacterial activity in membrane filter. Further aeration is used to increase the pH of the solution in order to fever crystallization process. The collected wastewater was kept undisturbed till settled at room temperature (20-25°C) for about 24hrs in the laboratory. Then the supernatants were collected for analysis of PO_4, NH_4 and Mg before crystallization experiment. Struvite crystallization procedure was identical to crystallization process from model solution except model solution was replaced by domestic wastewater.

Tuludimtu wastewater treatment plant is decentralized wastewater treatment plant located at 979642N latitude and 481103E longitude. It started operation in 2018 under management of Addis Ababa Water and Sewerage Authority (AAWSA). The treatment plant treats 20000m^3/day of domestic wastewater from nearby condominiums by using membrane bioreactor technology.

The treatment system consists of rectangular basket screen (gap width 40mm), combined pretreatment unit, rectangular equalization and mixing tank (length 16.7m, width 6.5m depth 4.7m), fine screening (remove particles greater than 2 mm), two rectangular primary clarifier tank (length 10.5m, width 3.5m, depth 4.7m), two rectangular aeration tank (length 20.2m, width 4.4m, depth 4.9m), containerized membrane filter treatment unit and circular storage tank (diameter 3.82m and depth 3.85m). Schematic diagram of the treatment plant is shown in Figure 3.4.

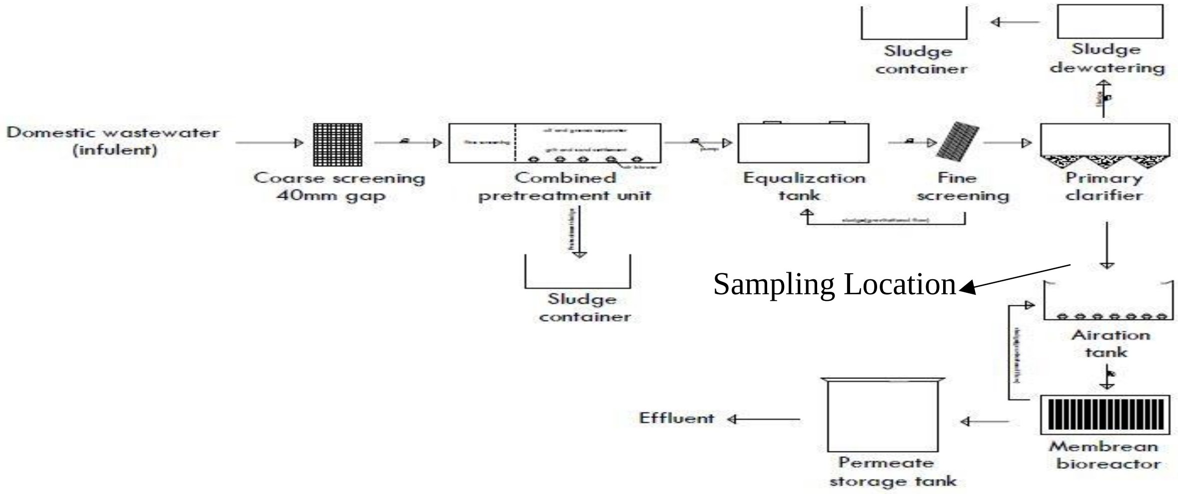


Figure 3.4 Schematic diagram of Tulu Dimtu 3 sewage treatment plant and sampling location.

3.8 Lake Basaka water as an alternate source of magnesium

In this study, Lake Beseka which is located in Fantale Woreda East Shoa Zone Oromia Regional State, was assessed for its potential use as alternative magnesium source for struvite crystallization. It is geographically located at latitude 8° 51.5′ N and longitude of 51.5′ E; the altitude is 950 m (Umer et al., 2020). The water was collected from the central part of the lake and transported to laboratory through ice box. Before any experiment, the lake water is characterized as reported in section 3.4 in Ethiopian ministry of water and irrigation laboratory (MoWIE).

The last triplicate experiments were conducted by using Basaka Lake water as low-cost alternative source of magnesium. Both model solution and domestic wastewater were mixed with Basaka Lake water as described in section 3.1 to know it's potential for struvite crystallization. Crystallization procedure is similar to other experiments except magnesium solution is replaced by Basaka Lake water. The volume of lake water mixed to the wastewater was determined based on the molar ratio between Mg and PO_4 which is one from theoretical molar ratio in struvite ($Mg:PO_4=1$) (Appendix 15).

4 RESULT AND DISCUSSION

4.1 Process optimization of struvite crystallization

Relationship between independent process parameters (pH, NH_4/PO_4, Mg/PO_4 and RT) and their responses on phosphate removal efficiency of fluidized bed reactor (FBR) and struvite yield was evaluated by applying response surface experimental design methodology. Table 4.1 shows experimental design and their response on phosphate removal efficiency and struvite yield. Phosphate removal efficiency in the FBR varied between 20.1% and 88.9% while struvite yield ranged from 0.23 to 1.45 gram per ten liters of model solution. The lowest yield (0.23g/10L) was recovered at pH 8. Parsons & Doyle, (2002) also confirm the production of very small amount of struvite pallets in neutral and acidic pH.

Table 4.1 Experimental design matrix and their responses for phosphate removal efficiency and yield of struvite

Run	Factors				Response			
	A	B	C	D	Phosphate removal (%)		Struvite yield (mg/l)	
	pH	NH_4:PO_4	Mg:PO_4	HRT (hr.)	Actual	Predicted	Actual	Predicted
1	9	4	2	4	62.1	77.16	0.98	1.68
2	10	3	1.5	3	84.5	82.97	1.38	1.91
3	10	3	1.5	3	84.1	82.97	1.38	1.91
4	10	3	1.5	3	83.6	82.97	1.37	1.91
5	11	2	1	4	74.8	71.23	1.22	1.66
6	9	4	2	2	50.1	51.61	0.78	1.21
7	10	3	0.5	3	62.6	63.08	0.98	1.49
8	11	2	2	4	85.8	86.06	1.4	1.97
9	12	3	1.5	3	70.2	68.01	1.12	1.56
10	9	4	1	2	40.7	51.46	0.59	1.15
11	9	2	2	2	46.9	44.16	0.7	1.06
12	10	3	2.5	3	83.5	78.06	1.35	1.86
13	10	3	1.5	3	82.6	82.97	1.35	1.91
14	11	4	1	2	68.9	67.86	1.1	1.57
15	8	3	1.5	3	20.1	33.33	0.23	0.6650
16	11	2	1	2	62.5	62.06	0.99	1.42
17	9	4	1	4	45.3	74.13	0.67	1.58
18	9	2	1	2	38.1	39.08	0.55	0.8975
19	9	2	1	4	51.2	59.83	0.79	1.30
20	11	4	2	4	88.9	88.86	1.45	2.05
21	10	3	1.5	5	79.5	88.48	1.28	1.93
22	11	2	2	2	65.9	74.01	1.05	1.70
23	11	4	2	2	76.6	74.89	1.24	1.74
24	10	3	1.5	3	83.4	82.97	1.36	1.91
25	11	4	1	4	76.2	78.96	1.22	1.83
26	10	5	1.5	3	72.3	82.51	1.15	1.88
27	10	1	1.5	3	67.5	67.33	1.07	1.56
28	10	3	1.5	1	54.5	53.76	0.84	1.22
29	9	2	2	4	63.9	67.78	1.01	1.50
30	10	3	1.5	3	82.6	82.97	1.35	1.91

Based on the result obtained from experiments, regression analysis indicate that quadratic model was the most appropriate model for both experimental response (phosphate removal efficiency and struvite yield) due to high determination coefficient (R^2 = 0.9926 for phosphorus removal efficiency and R^2 = 0.9911 for struvite yield) as shown in Table 4.2 and 4.3. In addition, the difference between pred R^2 and Adj $R^2$is also less than 0.2 showing a good agreement between them. (Saadat et al., 2018).

Table 4.2 Fit summary of the model for phosphate removal efficiency.

Source	Sequential p-value	Lack of Fit p-value	R^2	Adjusted R^2	Predicted R^2	
Linear	< 0.0001	0.0004	-	0.5979	0.5346	
2FI	0.8638	0.0003	-	0.5315	0.4846	
Quadratic	**< 0.0001**	**0.5133**	**0.9926**	**0.9857**	**0.9678**	**Suggested**
Cubic	0.3670	0.5882	-	0.9878	0.9153	Aliased

Table 4.3 Fit summary of the model for yield of struvite.

Source	Sequential p-value	Lack of Fit p-value	R^2	Adjusted R^2	Predicted R^2	
Linear	< 0.0001	0.0005	-	0.5865	0.5224	
2FI	0.9813	0.0003	-	0.4839	0.4335	
Quadratic	**< 0.0001**	**0.4565**	**0.9911**	**0.9828**	**0.9602**	**Suggested**
Cubic	0.2265	0.7984	-	0.9879	0.9601	Aliased

Similarly, the graphical representations of actual verses predicted values of both phosphate removal efficiency and struvite yield (Figure 4.1) indicate that the mathematically calculated values are close to the experimental ones.

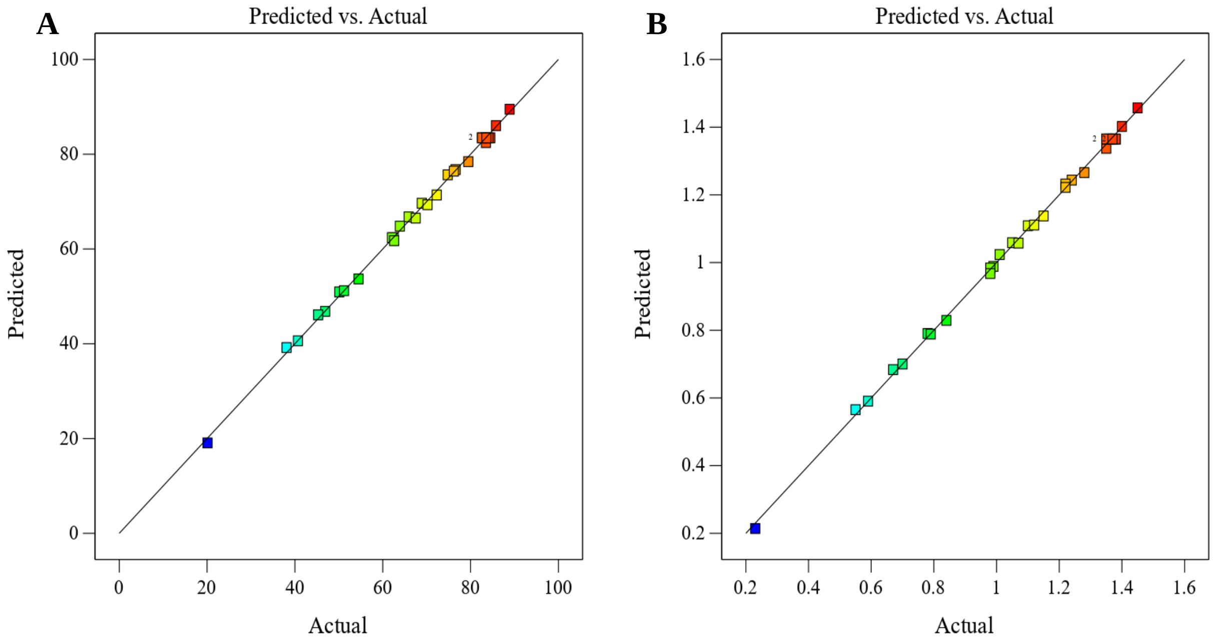


Figure 4.1 Experimental and predicted values of (A) phosphate removal efficiency and (B) struvite yield.

The significance of the model and its parameters were investigated by using analysis of variance (ANOVA) (Appendix 5). A reliable regression model should have fisher test value (F-value) greater than 4 and probability value (P-values) less than 0.05 (Gebregziabher et al., 2021). The F-value of the model was 144.21 and 119.31 for phosphate removal efficiency and struvite yield respectively. This indicate that the developed regression model is significant and can predict accurately. Similarly, the p-value of the models were < 0.0001 for both responses implying that the probability of error occurrence is less than 0.01%. Moreover, insignificant lack of fit P value of both responses (0.5133 for phosphate removal efficiency and 0.4565 for struvite yield) shows that the models fit experimental date properly.

Beside the model which correlate the study parameter with their response, all linear model terms such as pH, NH_4/PO_4, Mg/PO_4 and RT are significant model terms with P-value less than 0.0001 for both responses. Additionally, some interaction model terms such as pH * Mg, pH* NH_4, and NH_4 * Mg are also significant model terms with P-value less than 0.005 for both responses.

Based on the P value, among interaction model terms pH * RT (AD) with P value < 0.0001 for phosphate removal efficiency and 0.0022 for struvite yield was the most significant model term followed by pH * Mg (AC), pH* NH_4 (AB), and NH_4 * Mg (BC) respectively. However, RT*NH_4/PO_4 (BD) and RT*Mg/PO_4 (CD) with P-value of 0.3012 and 0.1306 respectively were not significant interaction model terms for phosphate removal efficiency. Similarly, these two interactions were also not significant interaction model terms for struvite yield with P value of 0.596 and 0.345 respectively. This indicate that the effect of RT on molar ratio of NH_4/PO_4 and Mg/PO_4 is very little over the tested range for both responses.

Based on the results obtained from experimental design, the evolved model equation for phosphate removal efficiency and struvite yield excluding the insignificant terms are presented in Eq. 6 and 7 respectively.

$$\text{Phosphate removal efficiency} = 82.97 + 8.677A + 3.8B + 3.75C + 8.68D - 1.64AB + 1.72AC - 2.89AD - 1.23BC - 8.07A^2 - 2.01B^2 - 3.1C^2 - 2.96D^2 \qquad 6$$

$$\text{Struvite yield} = 1.91 + 0.2225A + 0.0817B + 0.0942C + 0.1767D - 0.0262AB + 0.0288AC - 0.0425AD - 0.025BC - 0.1987A^2 - 0.0462B^2 - 0.0575C^2 - 0.0825D^2 \qquad 7$$

Where A, B, C and D represent values of pH, molar ratio $NH_4:PO_4$, molar ratio $Mg:PO_4$ and reaction time respectively.

These two equations show the combined effect of variables on both phosphorus removal efficiency and struvite yield. As shown in Eq. 6 and 7, the positive values in all linear model terms shows that both responses rise by increasing linear variables. On the other hand, second order effects of all linear model terms were negative on both responses due to the fact that all linier model terms negatively affect the responses when extremely increased.

Furthermore, the normal plot of residuals in diagnostic plots ensures the normality assumption. The data set has normal distribution if normal probability of experimental residuals is a straight line. Experimental points follow a straight line for both responses showing normal data distribution (Appendix 7).

The Residuals Vs runs plot also shows the experimental data are within allowable range (±3) as shown in Figure 4.2, indicating that the developed model fits experimental data properly and can predict accurately.

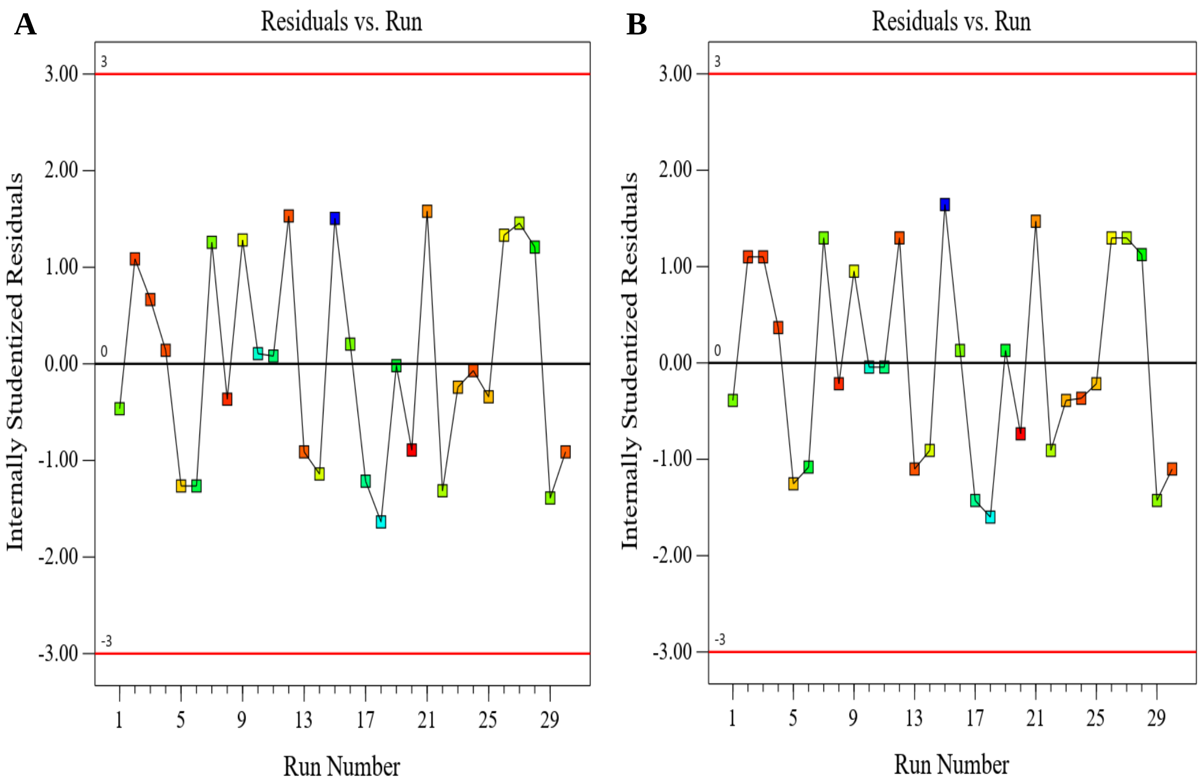


Figure 4.2 Residual vs run plot for (A) phosphate removal efficiency and (B) struvite yield.

4.2 Linear effect of parameters

Although the linear effect of one parameter was affected by multiple interaction of various parameters in one factor at a time plots, the linear effect of each parameter clearly identified on these plots.

4.2.1 Effect of reaction time (RT) on struvite crystallization

Reaction time (RT) is an important parameter which affected the struvite crystallization prosses. Reaction time refers to the time after addition of magnesium during which air is supplied to mix the solution. As shown in Fig.4.3, phosphate removal efficiency and struvite yield rose from 58% to 90% and 1.3g to 2 g respectively by increasing the RT from 1hr to 4 hr. This is due to the existence of sufficient time for initiating crystallization process. However, when the reaction time increase beyond 4 hr., There is a little decrease in both percentage removal of phosphate and struvite yield due to dispersal of formed struvite crystals.

According to K. S. Le Corre et al., (2007) maximum percentage phosphorus removal was detected when RT is 3hr. Above this point, the author noticed no further increase in removal efficiency.

Further the result of this study was in agreement with X. Liu et al., (2014) who reported that removal efficiency of fluidized bed reactor increase to 90% with an increase of reaction time until 4 hr.

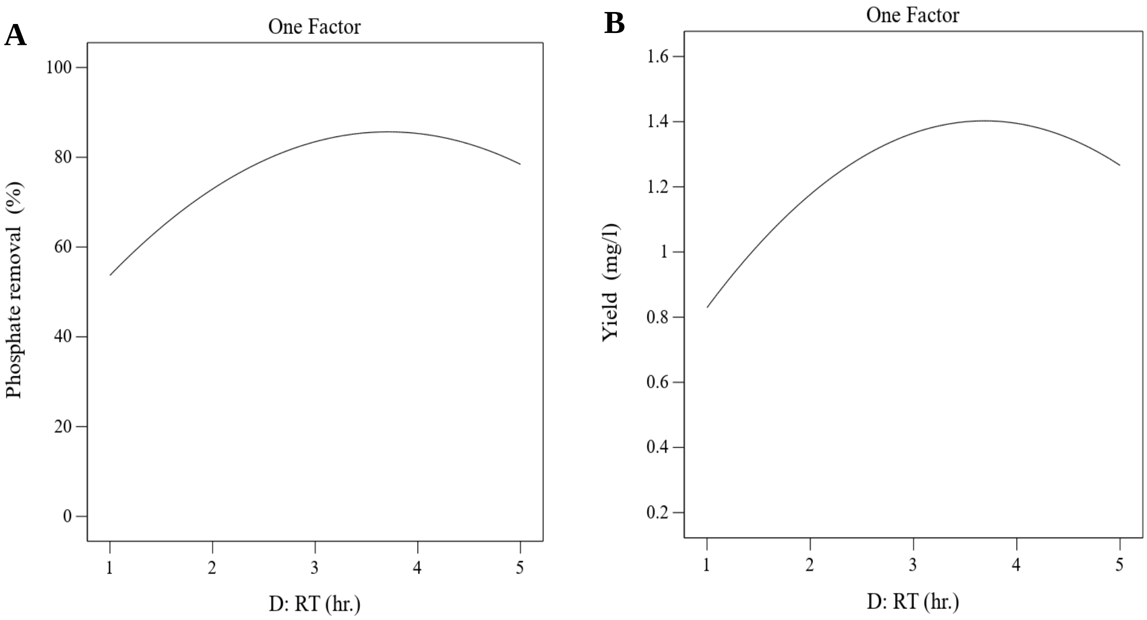


Figure 4.3 Effect of reaction time on (A) phosphate removal efficiency and (B) struvite yield.

4.2.2 Effect of NH_4: PO_4 ratio on struvite crystallization

Phosphate removal efficiency and struvite yield greatly affected by the molar ratio between NH4 and PO4. In this study, when the molar ratio between NH4 and PO4 increased from 1 up to 4, the removal efficiency of phosphate and struvite yield were increased gradually from 67% to 85% and 1.5 g to 1.9 g respectively. The reason for this increase in both response is, due to the fact that supersaturation is favored by increasing the molar ratio between NH4 and PO4 which accelerate nucleation rate of precipitate formation (K. Le Corre et al., 2009). However, as shown in Fig.4.4, for the molar ratio above 3.25, the change in both responses were not significant due to little amount of PO4 and Mg remained in the solution which can react with NH4 to form struvite.

The positive effect of increasing molar ratio between NH4 and PO4 for struvite crystallization was consistence with other studies (Kumari et al., 2020). Additionally, Guadie et al., (2014) found a gradual increase of phosphors removal efficiency from 65% to 88% when the molar ratio rises from 1 to 10.

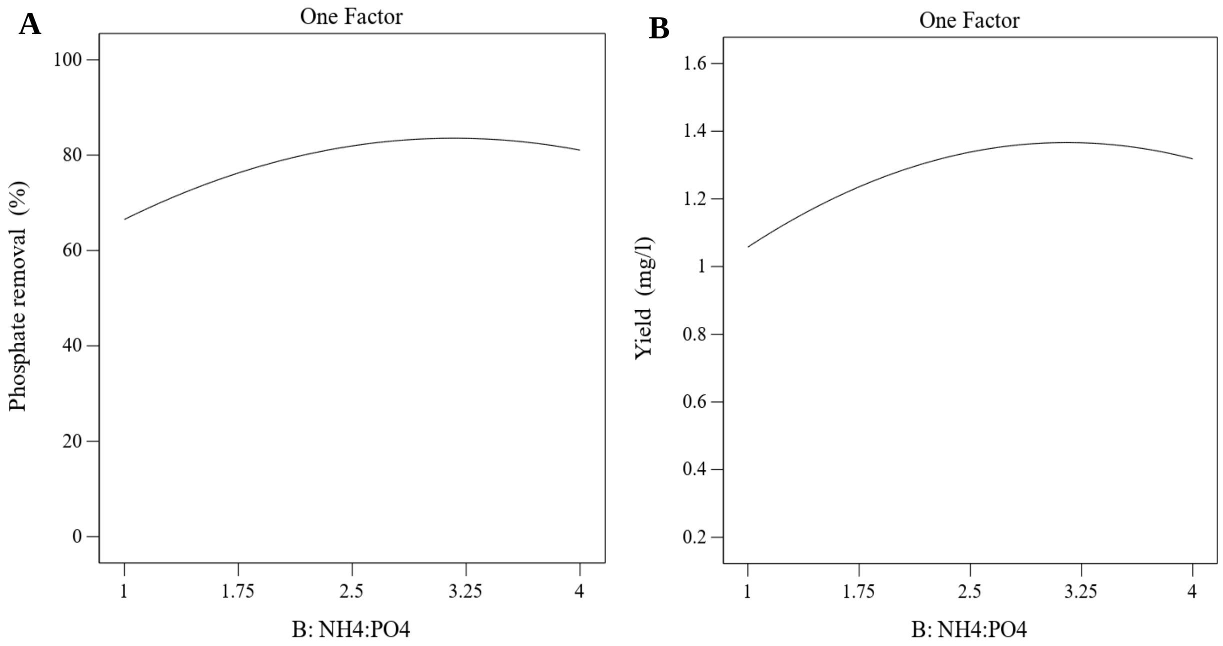


Figure 4.4 Effect of NH_4:PO_4 on (A) phosphate removal efficiency and (B) struvite yield

4.2.3 Effect of pH on struvite crystallization

pH is the most important parameter which affect struvite crystallization. This may be due to its influence on existing species in the solution and ionic activity of each struvite constituent ions. Higher pH negatively affects struvite crystallization due to the conversation of ammonium (NH_4) and magnesium (Mg) into ammonia gas (NH_3) and magnesium hydroxide Mg $(OH)_2$ respectively according to chemical equation 8 and 9 (Ye et al., 2010). On the other hand, at lower pH hydrogen phosphate (HPO_4) which has less ionic activity may take part in the reaction rather than phosphate ion (PO_4) as shown in reaction equation 10. (Kumar & Pal, 2013). Thus, both extremely high and low pH negatively affect struvite crystallization.

$$NH_4^+ = NH_3 + H^+ \tag{8}$$

$$Mg + 2H_2O = Mg\,(OH)_2 + 2H^+ \tag{9}$$

$$Mg + NH_4 + HPO_4^{-2} + 6H_2O = MgNH_4PO_4.\ 6H_2O + H^+ \tag{10}$$

The solubility product of struvite was also affected by the pH of the solution although hydrogen concentration does not directly involve in solubility product equation (Eq. 11). Struvite solubility decreased with increasing pH, leading to increase struvite precipitation potential (Guadie et al., 2014).

Ksp = $[Mg^{+2}]\ [NH_4^{+}]\ [PO_4^{-3}]$ 11

As shown in Figure 4.5, at any magnesium to phosphate ratio (Mg: PO_4) over the range of pH tested from 8 - 12, higher phosphate removal efficiency and struvite yield were achieved with the highest value of 87% and 1.3g respectively at pH = 10.5. However, at pH > 10.5 both phosphate removal efficiency and struvite yield gradually decreased to 60% and 1.5g due to conversion of ammonium and magnesium into ammonia gas and magnesium hydroxide respectively. On the other hand, the lowest phosphate removal efficiency (20%) and struvite yield (0.45g) were achieved at pH = 8. This is due to the fact that hydrogen phosphate with low ionic activity take part in the reaction than phosphate ion at low pH value. The result of this study is also supported by finding of Hutagalung, (2017) who reported maximum phosphate removal efficiency at pH = 10.

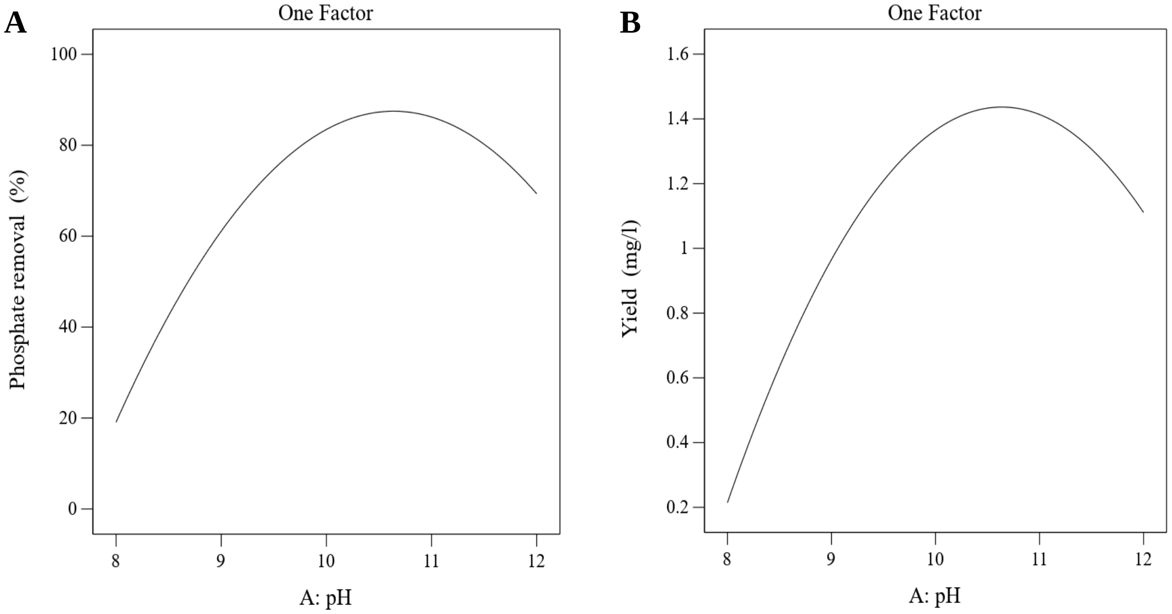


Figure 4.5 Effect of pH on (A) phosphate removal efficiency and (B) struvite yield.

4.2.4 Effect of Mg: PO_4 ratio on struvite crystallization

The molar ratio between Mg and PO_4 is another critical parameter for struvite crystallization. Although this ratio is one theoretically as shown in chemical formula ($MgNH_4PO_4.6H_2O$), in practice greater molar ratio is commonly employed to increase supersaturation ratio (Eq. 12) which is the driving force for crystallization process (Sun et al., 2020).

Super saturation ratio = $\gamma_{Mg}[Mg^{+2}] * \gamma_{NH4}[NH_4^{+}] * \gamma_{PO4}[PO_4^{-3}]$ / Ksp 12

Where [ ] and γ the concentration and activity of ionic species respectively.

As shown in the Figure 4.6, for any NH_4:PO_4 ratio when the molar ratio between Mg and PO_4 increases from 0.5 to 1.7, phosphate removal efficiency and struvite yield gradually increased from 56% to 83% and 0.7g to 1.9g respectively. However, beyond this point both phosphate removal efficiency and struvite yield remain almost constant. This may be due to less amount of NH_4 remained in the solution to react with magnesium and phosphate leading to lower struvite crystallization process. The finding of this study is in agreement with Liu et al., (2008) who reported that phosphorus removal efficiency rises to 86% by increasing the molar ratio between Mg and PO_4 up to 1.6. Furthermore, Bhuiyan et al., (2008) also found 85% phosphate removal when the molar ratio between Mg:PO_4 was 2.

Generally, struvite crystallization increased by adding Mg in excess to NH_4. However, addition of higher excess of Mg^{+2} is not advantageous in particular when constant phosphate removal efficiency and struvite yield is observed due to the cost needed for magnesium supply.

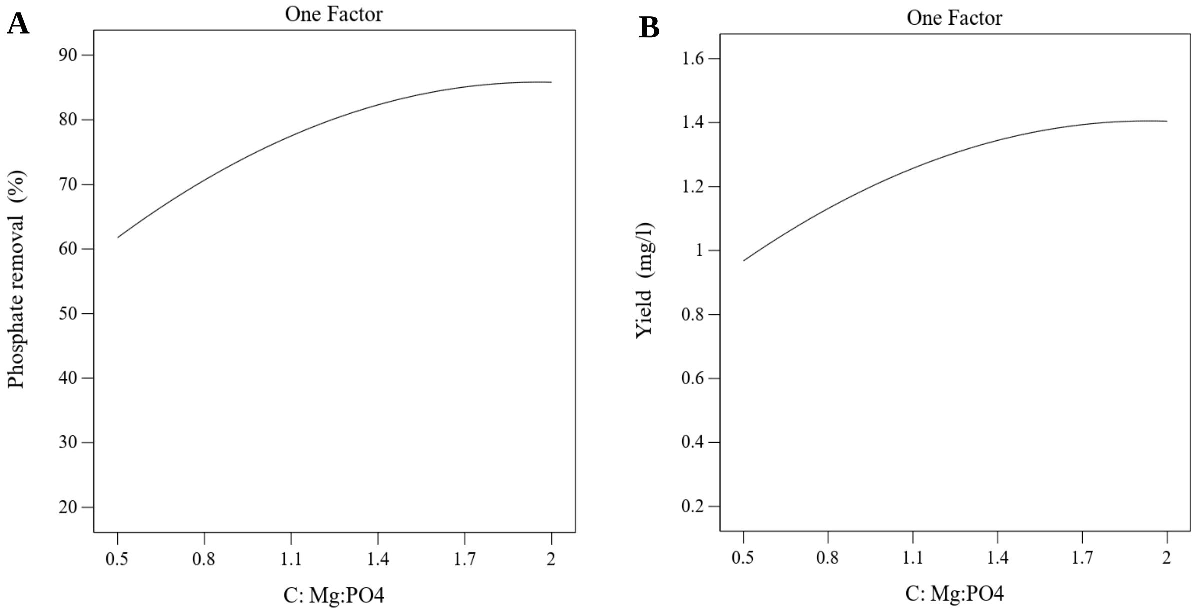


Figure 4.6 Effect of Mg:PO_4 on (A) phosphate removal efficiency and (B) struvite yield.

4.3 Interaction effects of parameters

4.3.1 Interaction effect between pH and reaction time (RT)

As it shown in Figure 4.7, the interaction effect of pH and RT on phosphate removal efficiency and struvite yield, is due to the aeration time. Prolonged RT gives sufficient time for stripping of carbon dioxide by aeration leading to pH increment of the solution according to chemical equation 13. Thus, the pH value increased with RT in addition to sodium hydroxide solution. Suzuki et al., (2005) who crystalize struvite through aeration from swine wastewater confirmed that the increase of pH from 7 to 8.6 due to striping of carbon di oxide by aeration. Ohlinger et al., (1999) also reported the increase of pH by prolonged aeration time in struvite crystallizer.

$$HCO_3^- = CO_2\uparrow + OH^- \qquad 13$$

As it is shown in Figure 4.7, as both RT and pH increases, the phosphate removal efficiency and struvite yield reached around 90% and 1.8 g respectively. However, beyond RT=4, phosphate removal efficiency and struvite yield decreased due to dispersal of formed struvite crystals by extended aeration. Similarly, beyond pH = 10.5, both responses decreased due to formation of ammonia gas and magnesium hydroxide according to chemical equation 8 and 9 respectively. This finding is in agreement with Ye et al (2010) who find lower struvite yield when the pH of the solution increases beyond 10.7.

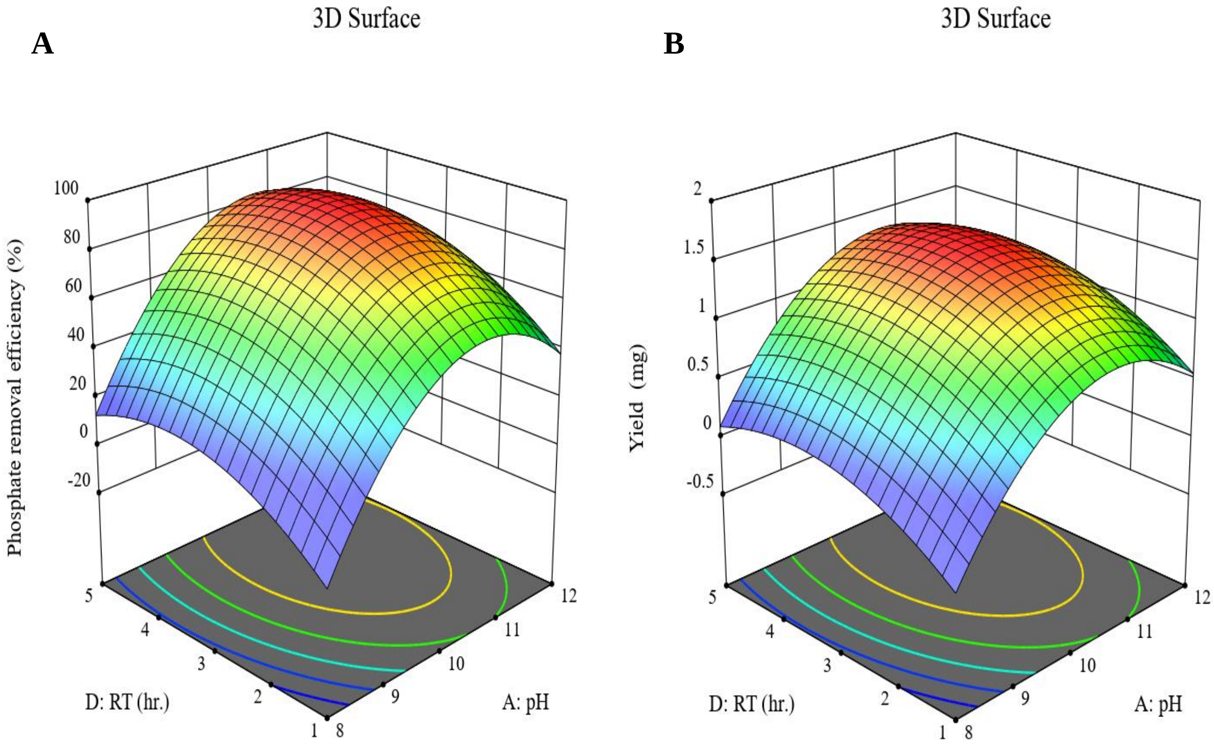


Figure 4.7 Interaction effect between pH and RT on (A) phosphate removal efficiency and (B) struvite yield.

4.3.2 Interaction effect between pH and NH_4

The interaction effect of pH and molar ratio between NH_4 and PO_4 on both phosphate removal efficiency and struvite yield is clearly demonstrated in Figure 4.8. Phosphate removal efficiency and struvite yield rise up to around 85% and 1.8 g respectively when both pH and the molar ratio between NH_4 and PO_4 increases. However, at pH above 10, there is lower phosphate removal efficiency and struvite yield which is attributed to deprotonation of ammonium according to chemical equation 8.

Kumari et al., (2020) also reported deprotonation of ammonium (NH_4) in to ammonia (NH_3) gas at a pH above 10. Thus, struvite crystallization process negatively affected by vaporization of ammonia gas (NH_3) at higher pH.

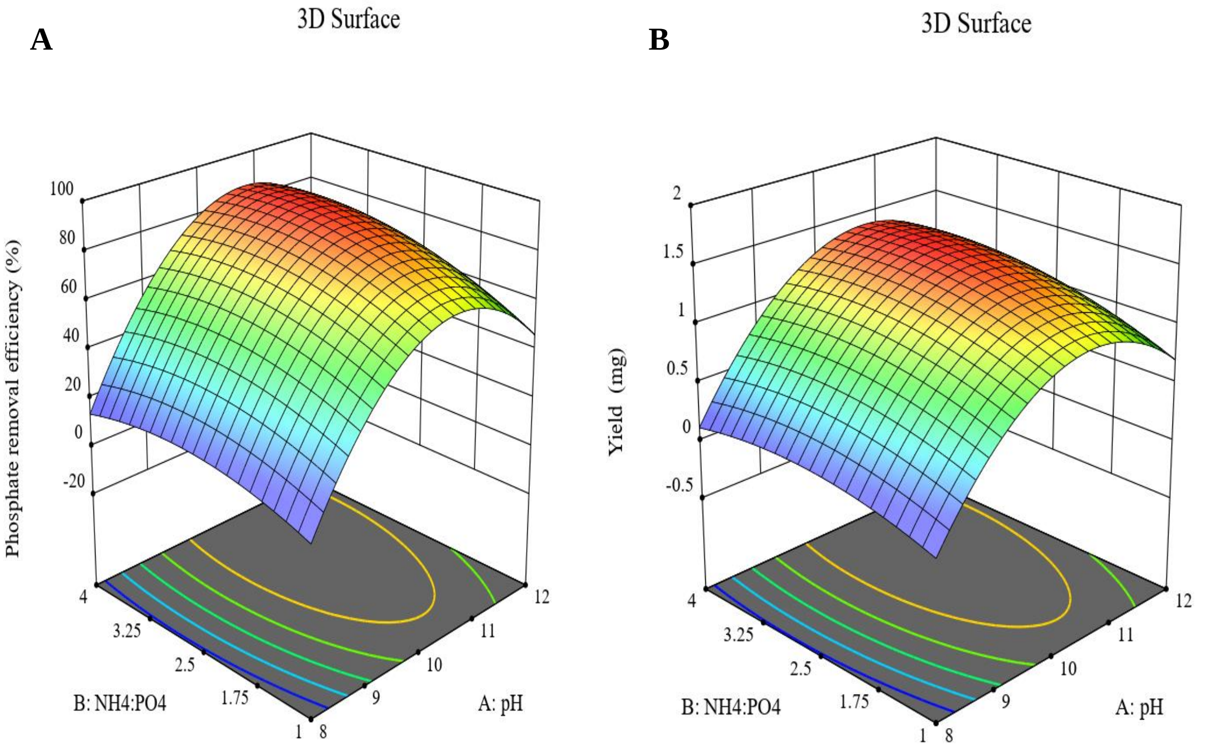


Figure 4.8 Interaction effect between pH and NH_4:PO_4 on (A) phosphate removal efficiency and (B) struvite yield.

4.3.3 Interaction effect between pH and Mg

Significant interaction existed between pH and molar ratio between Mg and PO_4 as shown in Figure 4.9. When the pH and molar ratio between Mg and PO_4 increased, the removal efficiency of phosphate and struvite yield rose up to around 89%. However, at pH above 11 the removal efficiency of phosphate and struvite yield was shown to drop due to formation of Mg $(OH)_2$ according to chemical equation 9.

Kumar & Pal, (2013) also found lower phosphorus removal efficiency of stirred tank reactors at a pH above 11 due to formation of sticky precipitate such as Mg $(OH)_2$ which may reduce the chance for struvite crystallization.

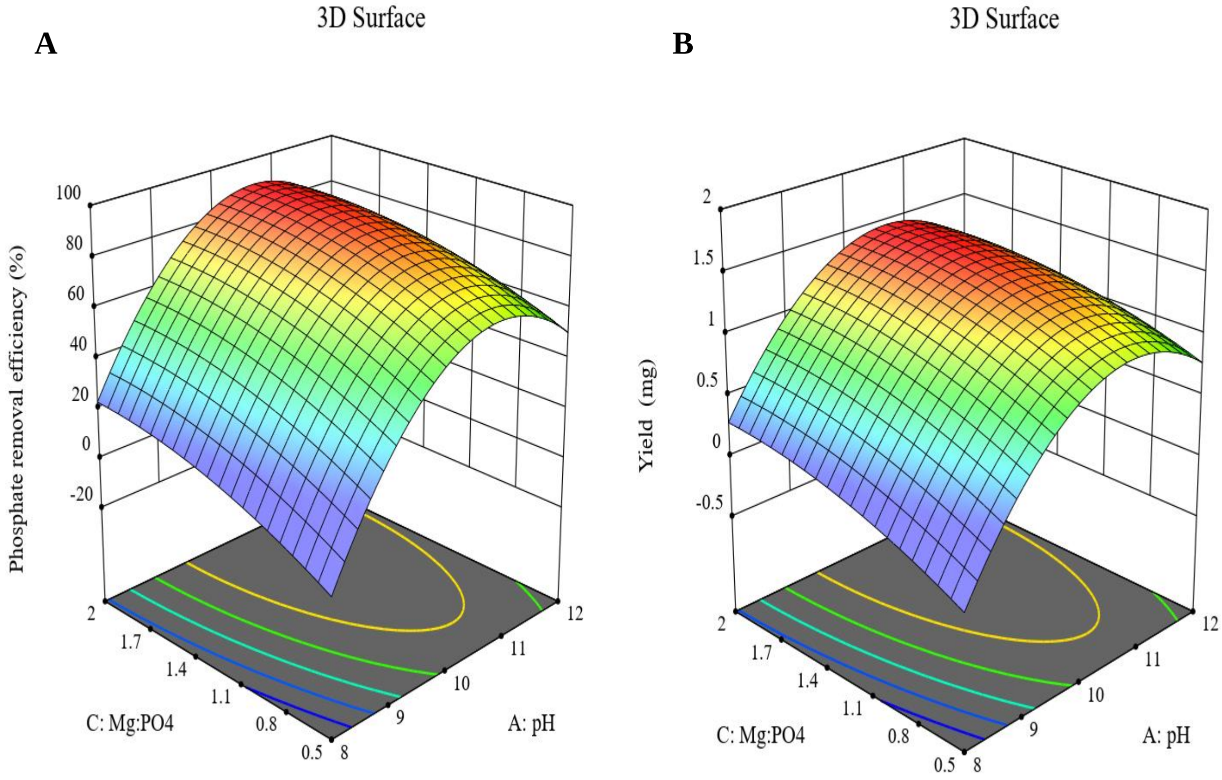


Figure 4.9 Interaction effect between pH and Mg:PO_4 on (A) phosphate removal efficiency and (B) struvite yield.

4.3.4 Interaction effect between NH_4 and Mg

The combined effect of NH_4:PO_4 and Mg:PO_4 on phosphate removal efficiency and struvite yield is shown in Figure 4.10. When both NH_4:PO_4 and Mg:PO_4 increased, the removal efficiency of phosphate and struvite yield was shown to increase up to 87% and 1.9g respectively. This may be due to an increase in supersaturation ratio of the solution which positively affect nucleation rate precipitate formation and crystal growth. As shown in chemical equation 12, higher concentration of NH_4 and Mg in the solution leads to increase supersaturation ratio which increases the chance of struvite formation. However, the yield increment does not significant after the Mg:PO_4 is 1.6

and NH_4:PO_4 is 2.5. Such findings coincide with other studies (Kumari et al., 2020; Liu et al., 2011).

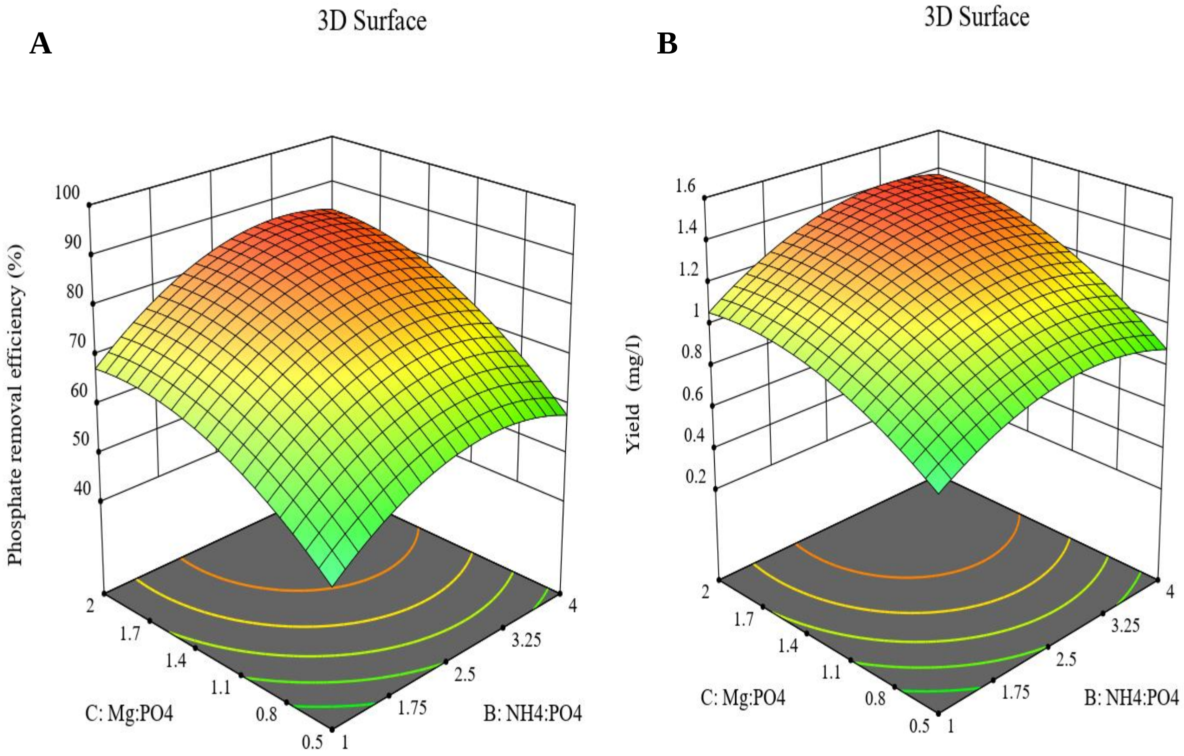


Figure 4.10 Interaction effect between Mg:PO_4 and NH_4:PO_4 on (A) phosphate removal efficiency and (B) struvite yield.

4.4 Optimization of operational parameters

In this study optimization was carried out accordingly numerical optimization techniques on the given correlation model with the given constraint. The operating parameters were chosen so as to maximize struvite crystallization in order to achieve highest phosphate removal efficiency and struvite yield.

For optimization of operational variables, the pH of the solution was put in target pH =10 in order to eliminate the formation of other sticky precipitate such as $Mg(OH)_2$ which affect the purity of precipitated struvite. Furthermore, targeted pH value (pH = 10) is also used to reduce formation of ammonia gas that negatively affect crystallization process. On the other hand, molar ratio between NH_4 and PO_4 were left in range to reflect the variation of ammonium in domestic wastewater while the molar ratio between magnesium and phosphate were put as minimum in order to reduce the cost of magnesium needed for struvite crystallization. Reaction time was also put in target (RT =4 hr.) for optimization process to remove dispersal of any formed struvite crystals due to prolonged reaction time.

After optimization analysis, several sets of experiments were suggested by the model and one of them were selected for validation (Table 4.4). To validate the selected optimum condition, triplicate experiments were conducted using optimum process parameters which is suggested by the model. Accordingly, 81±1.3% phosphate removal efficiency and 1.29±0.6g of struvite yield were obtained. This result is in agreement with the predicted data from optimization analysis (Table 4.4). The small percentages of error of 3.11% for phosphate removal efficiency and 4.4% for struvite yield, between the optimization and the validation results, further confirm that the models are suitable and sufficient to predict the responses. The struvite produced at optimal conditions was then characterized and its purity checked in as demonstrated in section 3.6 and 3.6.1 respectively.

Additionally, based on the experiment conducted at optimum condition, Phosphate concentration of synthetic wastewater reduced from 60 mg/l to 11.4 mg/l leading to reduce eutrophication of water bodies significantly.

Table 4.4 Optimized value of operational parameters.

No	pH	NH_4:PO_4	Mg:PO_4	RT (hr.)	Phosphate removal efficiency (%)	Struvite yield (g)	Desirability
1	10	2.9	1	4	83.6%	1.36	0.883

4.5 Recovery of phosphate from domestic wastewater

In order to verify the production of struvite from domestic wastewater with more complex matrix, triplicate experiments were conducted using wastewater from aeration tank of Tulu Dimtu wastewater treatment plant (WWTP) at optimum conditions which was determined by using synthetic wastewater. The characteristic of the domestic wastewater at the time of study is shown in Table 4.5.

Table 4.5 The characteristic of domestic wastewater at the time of study.

Parameters	**Values**
pH	8
PO_4	93.6 mg/l

NH_4	53.2 mg/l
Mg	0.5 mg/l

As shown in Table 4.5, the concentration of phosphate (93.6mg/l) and ammonium (43.2 mg/l) in the domestic wastewater at the time of study was higher than formulated synthetic wastewater leading to enhanced struvite crystallization process (Ye et al., 2016). Phosphate and ammonium concentrations of incoming wastewater vary due to fluctuation in the volume of water used for flush in toilet, for washing and variation of the organic matter used at household level. Additionally, the molar ratio of ammonium and phosphate was nearly 3, indicating sufficient amount of ammonium existed in domestic wastewater for struvite crystallization. Slightly alkaline pH = 8 of domestic wastewater is also fever struvite crystallization. De-Bashan & Bashan, (2004) demonstrate that a pH value higher than 7.5 is requirement for struvite crystallization.

Although chemical oxygen demand (COD) was not measured in this study it was anticipated that the chemical oxygen demand of domestic wastewater is higher due to the presence of organic matter which can inhabit struvite crystallization (Barnes et al., 2007). Further the existence of calcium, carbonate and bicarbonate in real domestic wastewater negatively affect struvite crystallization process (Corre et al., 2009).

As shown in Table 4.5, the concentration of magnesium in domestic wastewater is not sufficient for struvite crystallization. As a result, magnesium chloride solution was mixed with domestic wastewater in fluidized bed reactor.

Seventy four percent (74±1.5%) phosphate removal efficiency and two-point nine gram (2.9±0.6g) of precipitate were obtained from experiment using domestic wastewater at optimum condition. As compared to removal efficiency of phosphate from synthetic wastewater, slightly lower phosphate removal efficiency was achieved due to the presence of various organic and inorganic compound in domestic wastewater that can inhabit struvite crystallization. However higher amount of precipitate was obtained from experiments using domestic wastewater. This may be due to the precipitation of other compounds with struvite in fluidized bed reactor although the concentration of phosphate is higher. The struvite obtained from domestic wastewater is also characterized and its purity checked in as presented in section 3.6 and 3.6.1 respectively.

4.6 Characterization of the product struvite

4.6.1 Appearance and color

Color of the struvite crystals formed from domestic wastewater were grey, whereas color of crystals produced from model solution was white (Figure 4.11). The domestic wastewater in Tulu Dimtu is sourced mainly form residential areas and condominium housings and a mixture of brown, yellow and grey water get to the treatment plant thus affecting the color of the product.

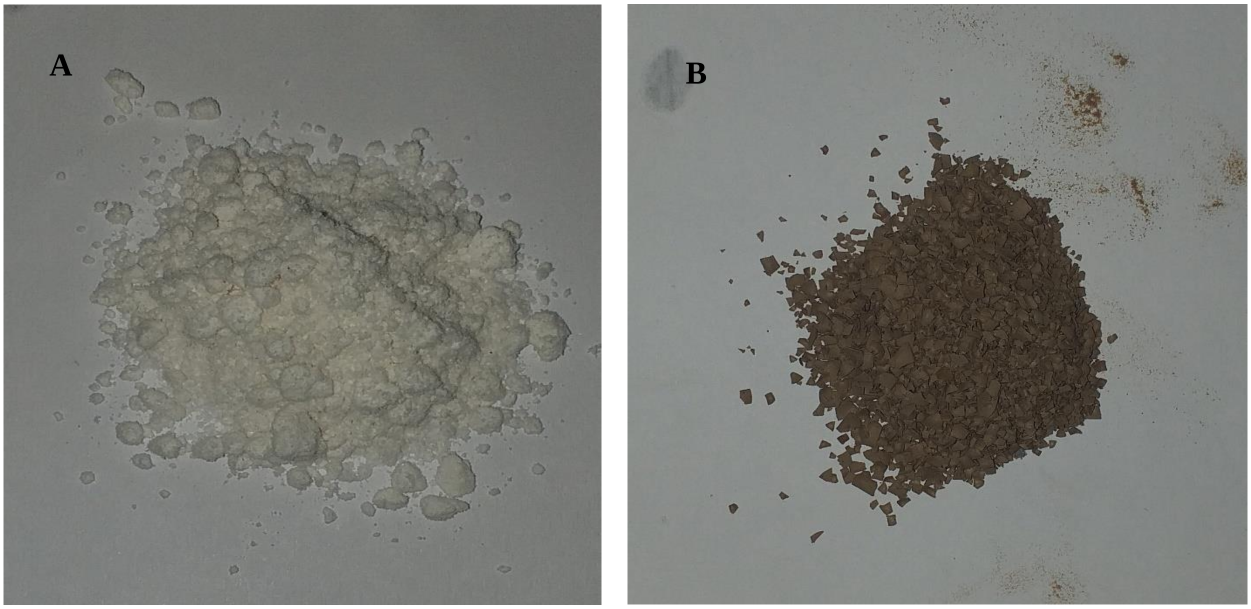


Figure 4.11 The color of precipitates from (A) synthetic wastewater (B) domestic wastewater.

4.6.2 Composition and purity analysis

Elemental composition of precipitated crystals was shown in Table 4.6. The composition of crystals precipitated from model solution was very close to theoretical composition of pure struvite. However elemental composition of precipitated crystals from domestic wastewater was affected by the presence of impurities such as suspended solids, organic and inorganic maters in domestic wastewater. During struvite crystallization process suspended solids attached to the surface of struvite crystals implying that there are unknown solids or ions present in the final product. Consequently, the amount of struvite constituent ions in these crystals was significantly decreased.

Huang et al., (2006) found ten percent impure compounds from the total mass of crystals precipitated from domestic wastewater with higher suspended solid concentration which suggest that suspended solids in domestic wastewater adversely affect compositional characteristics of struvite.

In this study eight nine percent pure struvite was precipitated from model solution, whereas the purity of precipitated crystals from domestic wastewater was decreased to seventy two percent (Table 4.6). This may be due to the cross reaction of phosphate and magnesium with other ions which exist in domestic wastewater (Hao et al., 2008). Detail struvite purity calculation is presented in Appendix 15.

Table 4.6 Crystal composition and purity of struvite.

Struvite constituent ions	Measured value		Theoretical value in 0.5g of struvite (mg/l)	Theoretical value (%)
	Precipitated crystals from synthetic wastewater (mg/l)	Precipitated crystals from domestic wastewater (mg/l)		
PO_4	179.2	130.1	193.4	38.7%
NH_4	31.9	23.5	36.76	7.4%
Mg	44.5	34.17	49.52	9.9%
Struvite purity	89.1%	68.7%	-	100%

4.6.3 Scanning electron microscope (SEM) analysis

The surface of the struvite crystal was smooth orthorhombic shape with fine stripes. Under 1659 X magnification (Figure 4.12), tightly-aggregated smooth orthorhombic, brick-like and rod-like crystals was observed in the struvite produced using model solution. Increasing the magnification from 3317 X to 6083 X, revealed the orthorhombic shape crystals clearly (Appendix 1).

As it is reported by Kumari et al., (2020) struvite can occur in various morphologies such as, orthorhombic type, pyramidal type, needle type, feather shaped, star type, prismatic type, rectangular platelet type and dendritic type depending on their growth conditions.

The abrasion caused by surrounding up flow fluid in fluidized bed reactor rounds off the tips of fine crystals, so that the entire crystal surface looks smooth. Additionally, the existence of fine stripes on the surface of the crystals was resulted from higher abrasion in the reactor. (Huang et al., 2006)

Although the crystal hardness was not measured using specific test in this study, they did not easily break in the process of harvesting and drying. The hardness of the crystals was resulted from tight aggregation as shown in Figure 4.8 (Huang, 2003).

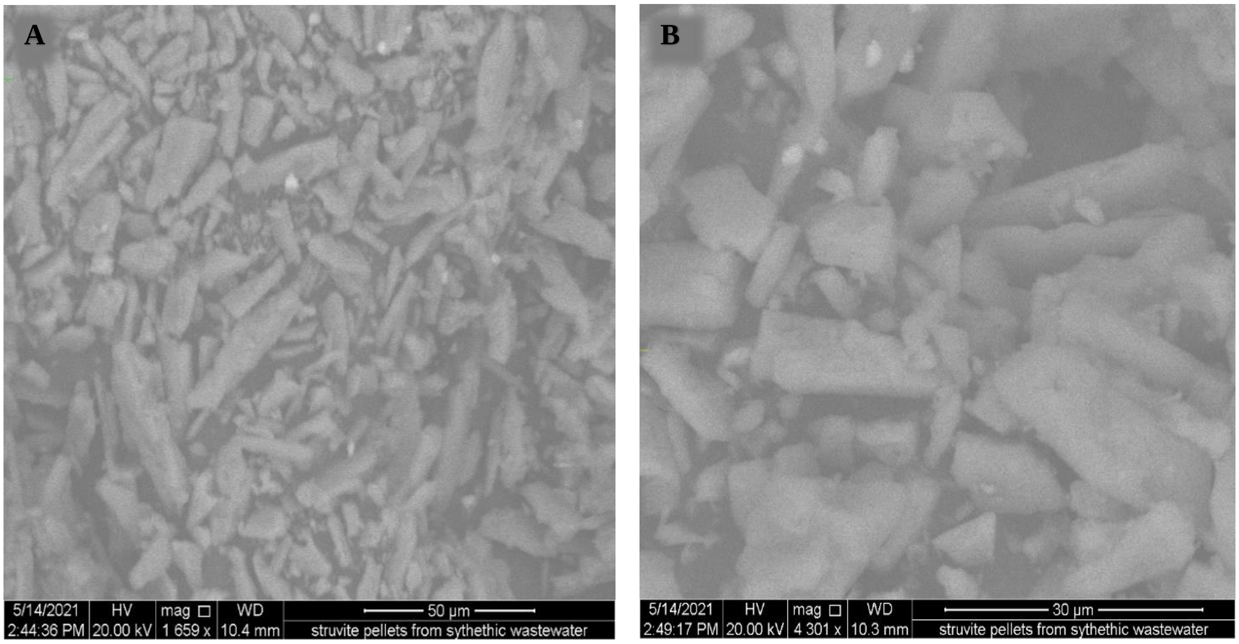


Figure 4.12 SEM image of crystals harvested from synthetic wastewater under (A) 1659X magnification (B) 4301X magnification.

On the other hand, the morphology of crystals which was produced from the domestic wastewater was different from crystals of model solution in size, shape and texture. The crystal surface was irregular dendritic shape with fine stripes. Moreover, the crystals were monolithic and courser in size (Figure 4.13). This may be due to the difference in the matrix and the presence of additional substances in domestic wastewater which affect the formation and growth of struvite crystals. Higher magnification (3000X) revealed the presence of small particles on the surface of the crystal (Appendix 2). This may be due to the formation of various compounds during struvite crystallization which can deposit on the surface of the struvite crystals.(Yan & Shih, 2016)

A very interesting image under magnification 3000X (Appendix 2) showed that uneven appearance of struvite particles with obvious cracks indicating the influence of absorbed foreign ions on the surface (Yan & Shih, 2016) thus affecting the growth of struvite crystals. Irregular dendritic shape of crystals as shown under magnification 3000X confirms the existence of struvite particles although orthorhombic shape is dominant in crystals of synthetic wastewater. Further the hardness of precipitates from domestic wastewater was lower than the precipitate of model solution. The reason could be due to the aggregated nature of the precipitates of model solution in the absence of coexisting salts (Shih et al., 2017).

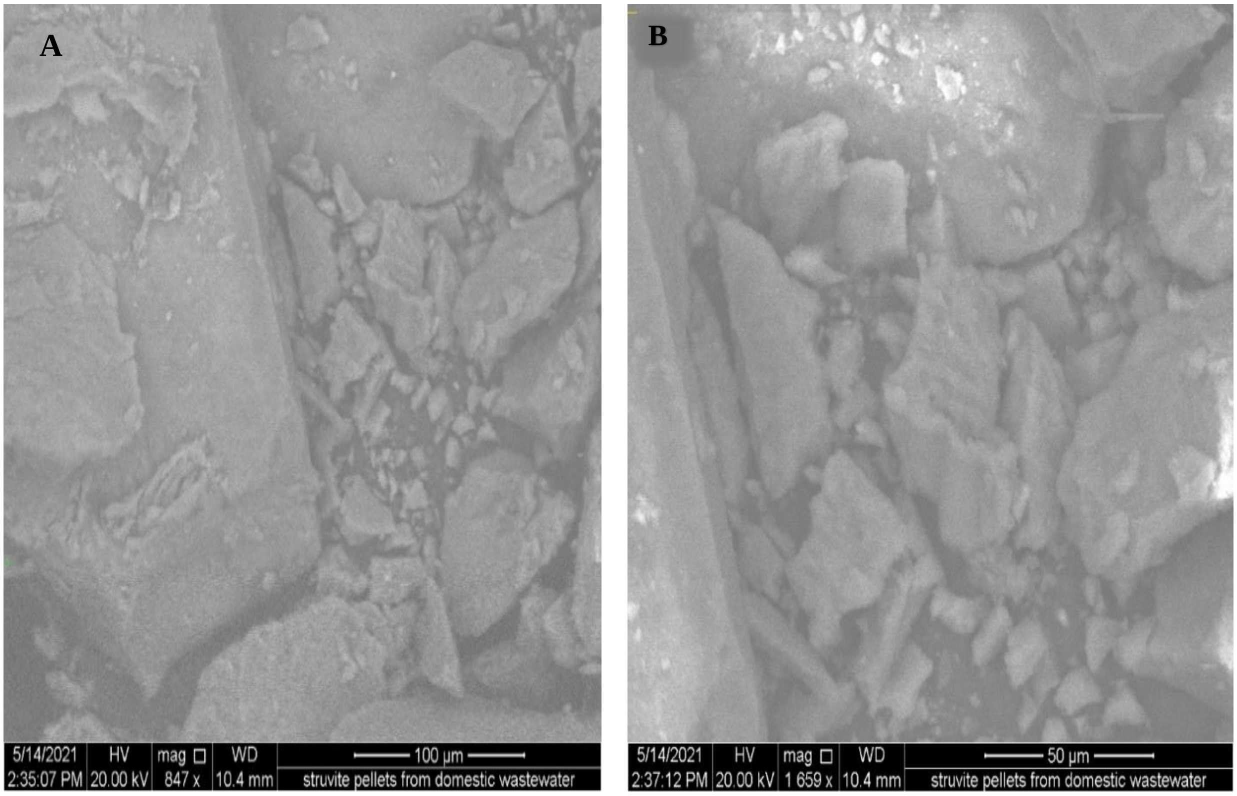


Figure 4.13 SEM image of crystals harvested from domestic wastewater under (A) 847X magnification (B) 1659X magnification.

4.6.4 Fourier transform infrared spectroscopy (FTIR) analysis

The infrared spectra of crystals which is produced from model solution showed the presence of absorption related to water vibration in three regions. The band located between 1600cm^{-1}-1700cm^{-1} is due to bending of water molecules. In this study the plateau at 1649cm^{-1} is attributed to bending vibration of water molecules (Figure 4.14). Another band occurred between 600cm^{-1} to 1000cm^{-1} is associated with liberation of water molecules (Sidorczuk et al., 2020). According to Stefov et al., (2004) six bands related to water liberation were identified at 897, 862, 783, 766, 722 and 710 cm^{-1}. Although most of these bands are not visible in our crystals which might be as a result of overlaps with each other and with lines assigned to phosphate tetrahedra, the absorbance at 887 cm^{-1} may be inferred to be associated with liberation of water molecules (Figure 4.10).

The broad band occurred between 2000cm^{-1} up to 4000cm^{-1} is related to water stretching. As compared to bulk water stretching (2700-3800cm^{-1}), its position is shifted to lower wavenumber due to strong interaction with neighborhood (Novak, 1976). The main components of this band are occurred at 2398cm^{-1},2920cm^{-1},3263cm^{-1} and 3401cm^{-1} as it is shown in Figure 4.14. The discrete structure of these band confirms various water states in struvite (Sidorczuk et al., 2020).

The band at 1016 cm^{-1} and 1076 cm^{-1} are related to symmetric and asymmetric stretching mode of phosphate respectively (Figure 4.14). These modes are used to analyze the coordination environment of phosphate ions. Phosphate anion interacts directly only with hydrogens of water or ammonium by forming hydrogen bonds (Richard K, 2000). In this study the plateau at 1076 cm^{-1} resulted from the fact that phosphate tetrahedrons in struvite are surrounded by counter ions (NH_4^+ and Mg $(H_2O)_6{}^{2+}$) with delocalized positive charge. Additionally, strong narrow band located at 558 and low intensity pack at 423 are related to bending mode of phosphate group. This assignment is confirmed by Stefov et al., (2004).

In most solids, ammonium gives a band at 1399-1402 and 1630-163cm^{-1} (Berg et al., 1977). However, in struvite these bands are shifted toward higher frequency due to strong hydrogen bond between ammonia and the neighborhood water molecules as well as phosphate tetrahedron. In this study the plateau at 1461cm^{-1} may be attributed to H – N – H bending mode.

According to De Oliveira & Hase, (2001) the band maximum at 298,360 and 460cm^{-1} are assigned to Mg -- O modes resulted from variation of water molecules with respect to Mg atom. In our case low intensity mode appeared at 453cm^{-1} is related to the Mg — O mode. This result is supported by Buchanan et al., (1963) who found that the plateau at 460cm^{-1} attributed to Mg — O mode.

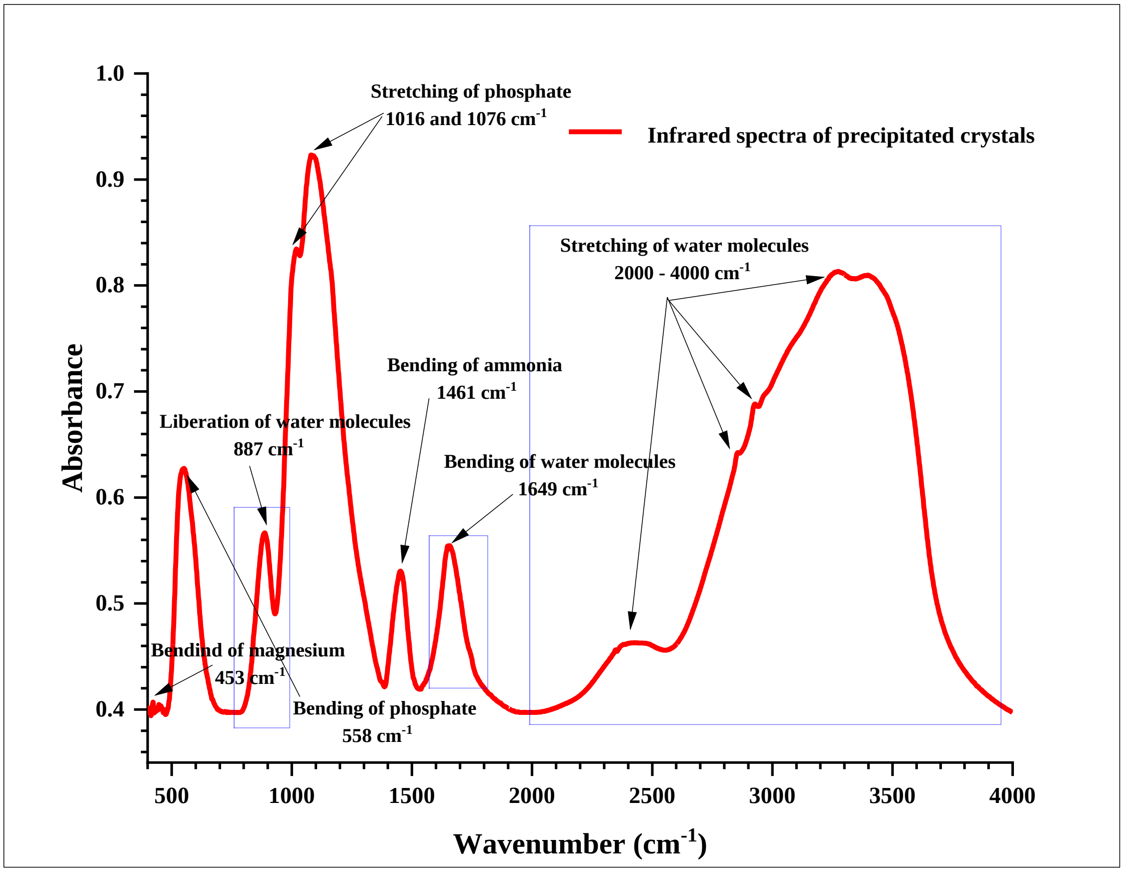


Figure 4.14 FTIR analysis of harvested crystals from synthetic wastewater.

On the other hand, the infrared spectra of the harvested precipitate from the domestic wastewater are similar to that of model solution with little difference. As shown in the Figure 4.15, the peaks at 2853, 2920 and 3399 are related to water stretching. However, the sharp peak at 3701 cm^{-1} indicates the existence of non-hydrogen bonded or free OH group of alcohol and phenols in the precipitation (Silverstein et al., 2005). This may be due to the existence of alcohols and phenols in domestic wastewater. The intensity band at 874 and 1661 are attributed to liberation and bending vibration of water molecules respectively.

The plateau at 1062 and 582 are associated with bending and stretching of phosphate group respectively. The band appearing at 1464 is assigned to N—H bending vibration in ammonia ion. Further the intensity observed at 450 cm^{-1} is associated with vibration of water molecules with respect to Mg.

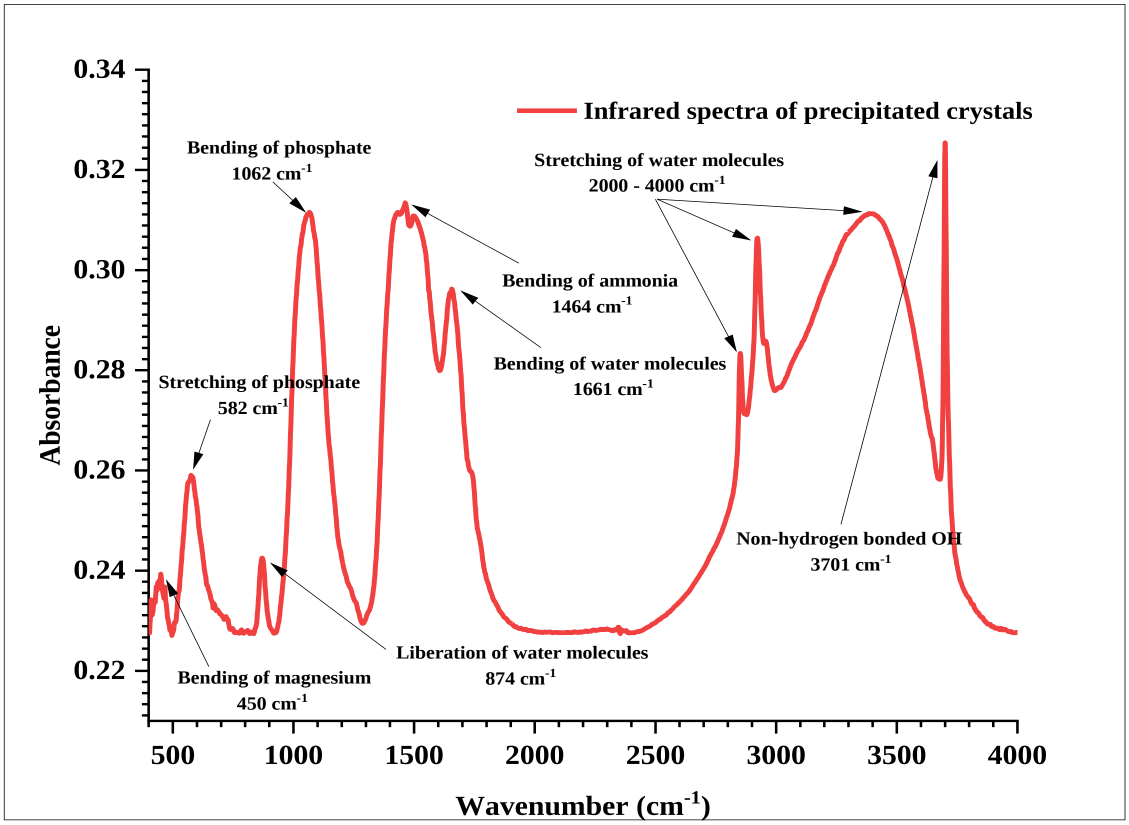


Figure 4.15 FTIR analysis of harvested crystals from domestic wastewater.

4.6.5 X-ray diffraction (XRD) analysis

The qualitative and quantitative phase of precipitated crystals were examined using X-Ray Diffraction (XRD) combined with Rietveld refinement method. The obtained XRD pattern were compared to reference diffraction file of pure struvite from crystallography open database (COD 96-900-7675). Figure 4.16 represents the diffraction pattern of crystals from model solution.

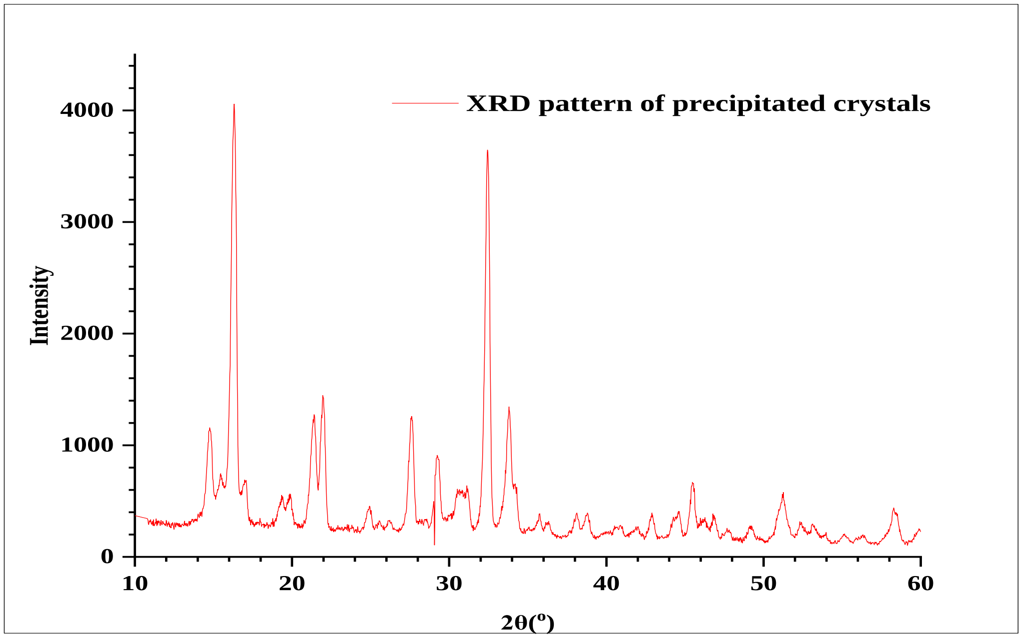


Figure 4.16 X-Ray Diffraction analysis of precipitated crystals from model solution.

The peaks of crystals precipitated from model solution matched well with the reference struvite peaks (Figure 4.17). Most of characteristic peaks of pure struvite were identified in diffraction of experimentally precipitated crystals. Their miller indices were also labeled in Fig 19. Major peaks obtained at 2θ value of 15.12, 15.95, 17.23, 21.53, 22.79, 27.19, 31.41, 32.82, 33.12, 33.82 and 34.53 corresponding to miller indices of 101, 002, 011, 111, 012, 103, 211, 004, 022 and 212 respectively which typically belong to struvite crystals (Lu et al., 2016). Additionally, green straight line at bottom indicates that the peaks difference between experimentally precipitated crystals and reference pure struvite was very small.

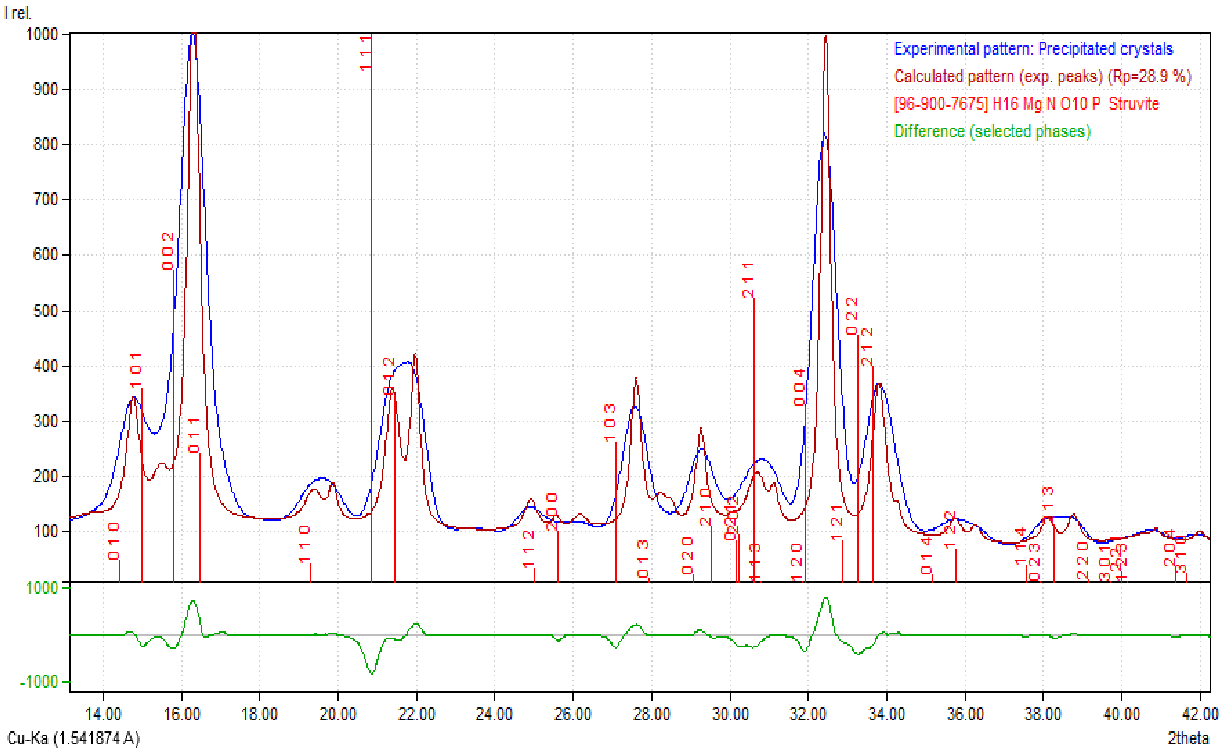


Figure 4.17 X-Ray Diffraction analysis of precipitated crystals from synthetic wastewater matched with reference struvite peaks.

Rietveld refinement of XRD pattern was used to quantitatively determine the phase of the precipitate. Rietveld refinement is a technique in which the height, width and position of measured reflections was matched with theoretical diffraction profile of the substance. In this study refinement of precipitated XRD pattern was matched with diffractions peaks corresponding to Newberyite ($MgHPO_4$ $3H_2O$) and Brucite ($Mg(OH)_2$) in addition to diffraction pattern of pure struvite. Kumari et al., (2020) indicate the formation of brucite at higher pH and Pi et al., (2010) also illustrate the formation of Newberyite when there is little ammonia present in the solution.

As shown in Figure 4.18, Rietveld refinement of XRD pattern demonstrated that the precipitated crystals have 92.2% struvite, 7.2% Newberyite and 0.5% brucite. Therefore, XRD data confirms that orthorhombic struvite is the dominant crystal phase exist in precipitated crystals which was synthesized under optimized value of pH and nitrogen to phosphate ratio.

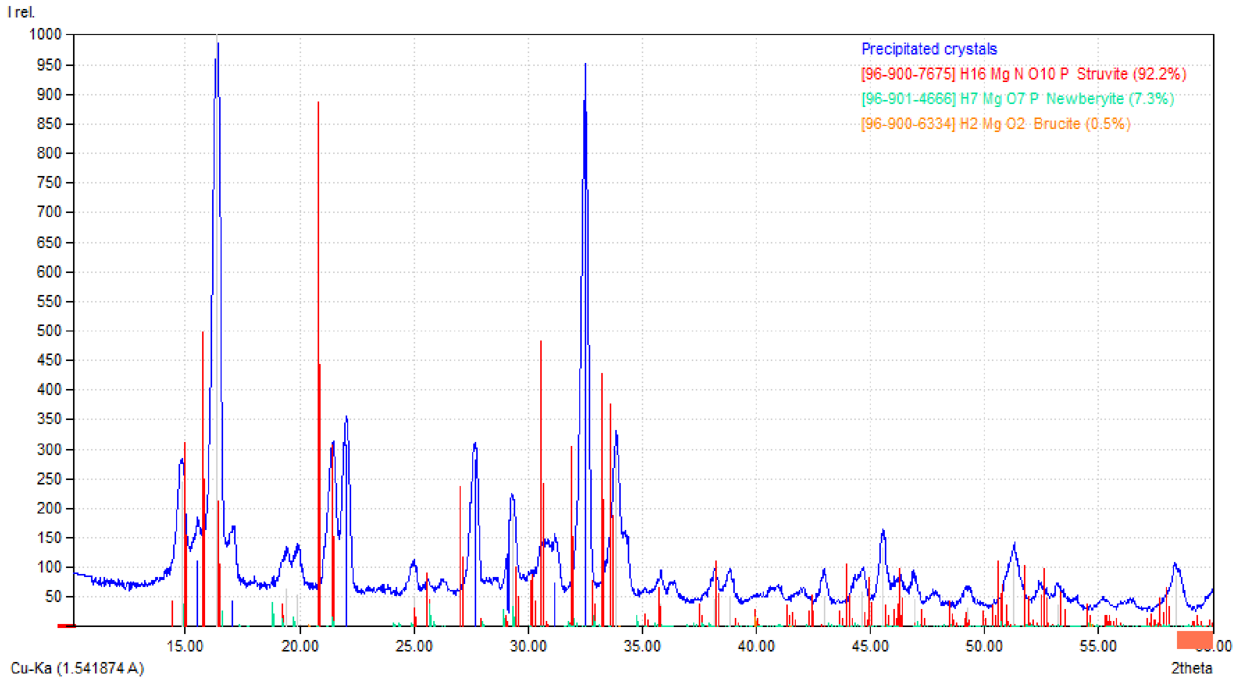


Figure 4.18 X-Ray Diffraction analysis of precipitated crystals and its comparison with standard patterns of struvite, Newberyite and Brucite.

The quantitative phase of precipitate obtained from the domestic wastewater was different from the precipitate of model solution due to the existence of different ions which can combine with constitute of struvite ions leading to reduce the crystallization process. Specifically, the presence of calcium and sodium ions in domestic wastewater resulted in the formation of amorphous impurities such as hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) and stercorite ($NaNH_4HPO_4$ $4H_2O$) which can probably emerge in precipitation (Kane et al., 2016). Due to this, the XRD spectra of these precipitate tend to have amorphous form as shown in Figure 4.19. Additionally, characteristic peaks of the struvite were also disappeared, indicating that struvite crystallization was inhibited by coexisting ions such as calcium, sodium, bicarbonate and carbonate.

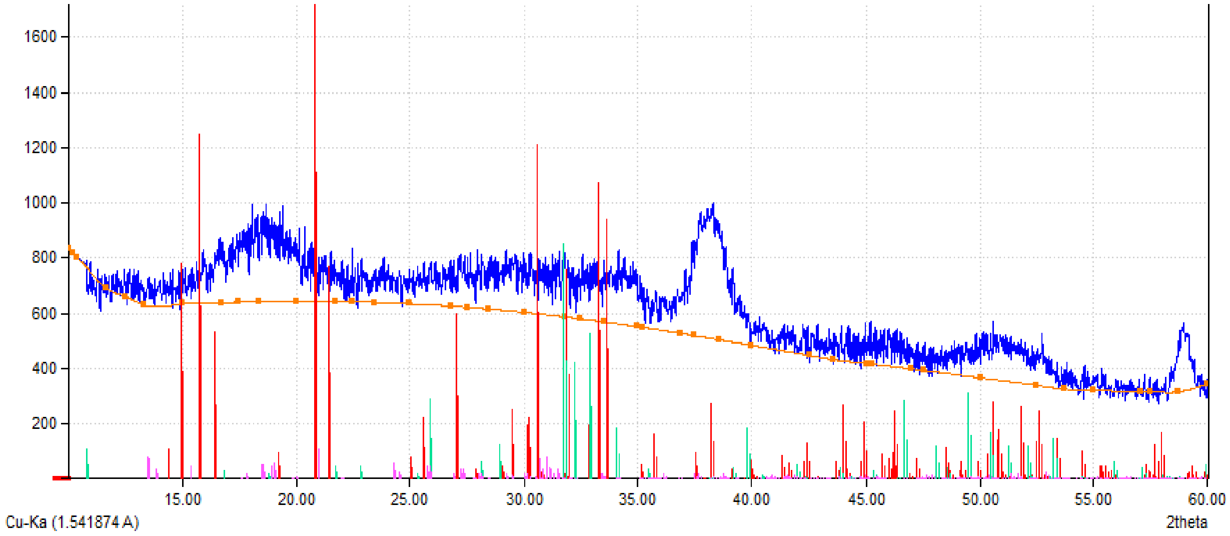


Figure 4.19 X-Ray Diffraction analysis of precipitated crystals from domestic wastewater and its comparison with standard patterns of Struvite, Hydroxyapatite and Stercorite.

4.7 Heavy metal concentration in the precipitated struvite

The presence of heavy metals in domestic wastewater affects the quality of recovered struvite when it is utilized as fertilizer. Heavy metals in the precipitated struvite imposes human health risk via their incorporation into the food chain. However, there is no legislative standard for heavy metal concentration in struvite precipitated from wastewater currently. Tabel 4.7 summarizes heavy metal concentration in struvite recovered from domestic wastewater in this study and different literatures. Hevey metals concentration in precipitated struvite was relatively very low ensuring possible use as fertilizer. This might be due to the presence of very small amount of heavy metals in domestic wastewater. Li et al., (2019) showed heavy metal concentration in recovered struvite varies depending on their initial abundance in wastewater. As compared to other heavy metals, higher Zink and Manganese amount in the precipitate resulted from their relative high concentration in domestic wastewater. Furthermore, higher manganese concentration in the precipitate might be caused by strong interaction between manganese and struvite (Forrest et al., 2008).

Table 4.7 Heavy metal concentration in precipitated struvite and other struvite in literature.

Type of struvite	Heavy metal concentration in mg Kg^{-1} struvite					Reference
	Zn	Cr	Cd	Pb	Mn	
This study	200	2	4	12	68	-
Urine struvite	841	< 6	< 6	< 81	-	(Gell et al., 2011)
Blackwater struvite	< 59	< 4	< 4	< 59	-	(Gell et al., 2011)
Sewage struvite	< 338	< 677	0.2	< 0.17	-	(Ueno & Fujii, 2001)
Source diverted black water struvite	22.9	-	> DL	> DL	52.1	(Mohammed, et al., 2020)

4.8 Basaka Lake water as an alternate source of magnesium for struvite crystallization

Although the characteristics of Basaka Lake water varies spatially and temporarily, it's characteristics at the time of study was presented in Table 4.8. It's magnesium concentration (31mg/l) and basic pH value (9) make the lake water suitable for struvite crystallization. However Alemayehu et al., (2006) who found 9.5 pH value and 17 mg/l magnesium ion concentration in Basaka Lake water in summer season did not support the result of this study. This may be due to special and temporal variability of the lake water characteristics.

Table 4.8 Characteristics of Basaka Lake water.

Parameter	pH	Mg^{2+}	NH_4	PO_4	Ca^{2+}	HCO_3^-	CO_3^{2-}
Values(mg/l)	9	31	0.14	2.44	18	2430	1215

By employing Basaka Lake water as convectional magnesium source for struvite crystallization from model solution, seventy-nine percent (79±2%) phosphate removal efficiency was obtained (Table 4.9). The efficiency was comparable to removal efficiency of phosphate which was achieved using magnesium chloride solution. Although there are different ions present in Basaka Lake water which can inhabit struvite crystallization, higher phosphate removal efficiency was obtained due to the fact that phosphate can combine with other ions such as calcium, sodium and bicarbonates and form other precipitate leading to increase phosphate removal efficiency (Le Corre et al., 2009).

The result of this study indicates the potential of Basaka Lake water for use as alternative source of magnesium for struvite crystallizations. Guadie et al., (2020) reported 81% of phosphorus removal via struvite crystallization from urine by employing Afdera lake water as alternative source of magnesium. Similarly Ravn & Simonsen, (2007) also found up to 87% phosphors removal efficiency by using sea water for struvite crystallization.

Similarly, sixty-eight percent (68%±1.6) of phosphate was removed from domestic wastewater via struvite crystallization by employing Basaka Lake water as a magnesium source. As compared to the removal efficiency of phosphate from model solution, the efficiency was lowered due to the existence of different organic and inorganic compounds in domestic wastewater which can inhabit struvite crystallization.

Table 4.9 The potential of magnesium chloride solution and Basaka Lake water for struvite crystallization from synthetic and domestic wastewater.

Source of magnesium for struvite crystallization		Phosphate removal efficiency (%)
Magnesium chloride ($MgCl_2$)	Model solution	81%
	Domestic wastewater	74%
Basaka Lake water	Model solution	79%
	Domestic wastewater	68%

Despite the existence of new compounds in Basaka Lake water, the infrared spectra, X- ray diffraction pattern and scanning electron microscope image of the precipitated crystals from model solution by employing Basaka Lake water as magnesium source was similar with that of crystals precipitated using magnesium chloride solution. (Appendix 3 & 4). This implies that struvite was the dominant compound in both cases.

5 CONCLUSION AND RECOMMENDATION

5.1 Conclusion

This study investigated the optimum parameters required for wastewater-based struvite recovery using model solution and used the parameters to understand struvite production from aerobically treated domestic wastewater from Tulu Dimtu WWTP. Linear and interaction effects of process parameters such as pH, NH4/PO4, Mg/PO4 and RT were evaluated and optimized using model solution by employing response surface methodology. The optimum conditions, pH = 10, NH4/PO4 = 2.9, Mg/PO4 = 1 and RT = 4 can remove 81% phosphate and produce 1.29g of struvite from 10-liter synthetic wastewater.

The optimum parameters were further used to evaluate the potential of domestic wastewater for phosphorus recovery in the form of struvite. Accordingly, 74% phosphate removal efficiency and 2.9 g of precipitate crystals were obtained from domestic wastewater under optimum condition.

The precipitated crystals from model solution and domestic wastewater under optimum condition were also characterized in order to confirm existence of struvite crystals. The purity of model solution -based struvite yield was 89.1% while domestic wastewater-based struvite production was 68.7%.

This study investigated the potential of Basaka Lake water as a local magnesium source for struvite crystallization. Experimental results shows that 79% and 68% phosphate removal efficiency were obtained from model solution and domestic wastewater respectively by employing Basaka lake water as magnesium source for struvite crystallization.

Generally, this study demonstrated the potential of domestic wastewater for production of struvite which can be used as phosphorus containing fertilizer in agriculture. Beside the production of struvite, recovery of phosphorus via struvite crystallization can also be used as effective phosphorous removal mechanism from wastewater in order to control eutrophication and invasive effect of plants on water bodies.

5.2 Recommendation

Struvite crystallization is found to be eco-friendly and promising phosphorus removal and recovery mechanism from domestic wastewater. Scientific researches and investigations are recommended to continue in order to fill the knowledge gap in the area. Even though this study checks the possibility of Basaka lake water as alternative magnesium source, other researchers can extend it by characterizing the produced precipitates. Hopefully Basaka lake water can be used as cheap and locally available magnesium source for struvite crystallization after further investigation. Generally further studies are recommended in the following areas.

- To conduct similar investigation at pilot and field scale.
- To evaluate and optimize the effect of other operational parameters such as temperature, aeriation rate and up flow velocity on the quality and yield of struvite.
- To assess the influence of co-existing ions such as calcium, sulfate, carbonate, sodium, heavy metals and organic compounds on struvite crystallization.
- To evaluate fertilizer potential of struvite through plant study and compare it with other conventional fertilizers.
- To characterize domestic wastewater-based precipitates produced using Basaka lake water as magnesium source.
- To conduct detail economic analysis of struvite crystallization.

6 REFERENCE

Abbona, F., & Boistelle, R. (1979). Growth morphology and crystal habit of struvite crystals (MgNH 4 PO 4 6 H 2 O). *Journal of Crystal Growth*, *46*(3), 339–354.

Aiyuk, S., Amoako, J., Raskin, L., Van Haandel, A., & Verstraete, W. (2004). Removal of carbon and nutrients from domestic wastewater using a low investment, integrated treatment concept. *Water Research*, *38*(13), 3031–3042. https://doi.org/10.1016/j.watres.2004.04.040

Alemayehu, T., Ayenew, T., & Kebede, S. (2006). Hydrogeochemical and lake level changes in the Ethiopian Rift. *Journal of Hydrology*, *316*(1–4), 290–300. https://doi.org/10.1016/j.jhydrol.2005.04.024

Barnes, D., Li, X., & Chen, J. (2007). Determination of suitable pretreatment method for old-intermediate landfill leachate. *Environmental Technology*, *28*(2), 195–203. https://doi.org/10.1080/09593332808618782

Berg, R. W., Poulsen, F. W., & Bjerrum, N. J. (1977). Low temperature vibrational spectroscopy. I. Hexachlorotellurates. *The Journal of Chemical Physics*, *67*(5), 1829–1837. https://doi.org/10.1063/1.435139

Bhuiyan, M. I. H., Mavinic, D. S., & Koch, F. A. (2008a). *Phosphorus recovery from wastewater through struvite formation in fluidized bed reactors : a sustainable approach*. 175–181. https://doi.org/10.2166/wst.2008.002

Bhuiyan, Mavinic, D. S., & Koch, F. A. (2008b). Thermal decomposition of struvite and its phase transition. *Chemosphere*, *70*(8), 1347–1356. https://doi.org/10.1016/j.chemosphere.2007.09.056

Birnhack, L., Nir, O., Telzhenski, M., & Lahav, O. (2015). A new algorithm for design, operation and cost assessment of struvite (MgNH4PO4) precipitation processes. *Environmental Technology (United Kingdom)*, *36*(15), 1892–1901. https://doi.org/10.1080/09593330.2015.1015455

Boehler, M., Joss, A., Buetzer, S., Holzapfel, M., Mooser, H., & Siegrist, H. (2007). Treatment of toilet wastewater for reuse in a membrane bioreactor. *Water Science and Technology*, *56*(5), 63–70. https://doi.org/10.2166/wst.2007.557

Boistelle, R., Abbona, F., & Lundager Madsen, H. E. (1983). On the transformation of struvite into newberyite in aqueous systems. *Physics and Chemistry of Minerals*, *9*(5), 216–222. https://doi.org/10.1007/BF00311958

Booker, N. A., Priestley, A. J., & Fraser, I. H. (1999). Struvite formation in wastewater treatment plants: Opportunities for nutrient recovery. *Environmental Technology (United Kingdom)*, *20*(7), 777–782. https://doi.org/10.1080/09593332008616874

Borgerding, J. (2016). *Phosphate deposits in digestion systems*. *44*(5), 813–819.

Bouropoulos, N. C., & Koutsoukos, P. G. (2000). Spontaneous precipitation of struvite from aqueous solutions. *Journal of Crystal Growth*, *213*(3–4), 381–388. https://doi.org/10.1016/S0022-0248(00)00351-1

Bowker, G., & Stensel, D. (1990). *Phosphorus Removal from Wastewater*. 585–586.

Brogowski, Z., & Renman, G. (2004). Characterization of Opoka as a basis for its use in wastewater treatment. *Polish Journal of Environmental Studies*, *13*(1), 15–20.

Buchanan, R. A., Caspers, H. H., & Murphy, J. (1963). Lattice Vibration Spectra of Mg(OH)_2 and Ca(OH)_2. *Applied Optics*, *2*(11), 1147. https://doi.org/10.1364/ao.2.001147

Burns, J. R., & Finlayson, B. (1982). Solubility product of magnesium ammonium phosphate hexahydrate at various temperatures. *Journal of Urology*, *128*(2), 426–428. https://doi.org/10.1016/S0022-5347(17)52952-3

Cahill, D. J., Fry, C. H., & Foxall, P. J. D. (2003). Variation in urine composition in the human urinary tract: Evidence of urothelial function in situ? *Journal of Urology*, *169*(3), 871–874. https://doi.org/10.1097/01.ju.0000052404.42651.55

Connor, Fay, & Lenox, D. (2017). The united Nation world water development report. In *Angewandte Chemie International Edition, 6(11), 951–952.*

De-Bashan, L. E., & Bashan, Y. (2004). Recent advances in removing phosphorus from wastewater and its future use as fertilizer (1997-2003). *Water Research*, *38*(19), 4222–4246. https://doi.org/10.1016/j.watres.2004.07.014

De Oliveira, E. F., & Hase, Y. (2001). Infrared study and isotopic effect of magnesium hydroxide. *Vibrational Spectroscopy*, *25*(1), 53–56. https://doi.org/10.1016/S0924-2031(00)00107-7

Demirbas, A., Taylan, O., & Kaya, D. (2016). Biogas production from municipal sewage sludge (MSS). *Energy Sources, Part A: Recovery, Utilization and Environmental Effects*, *38*(20), 3027–3033. https://doi.org/10.1080/15567036.2015.1124944

Durrant, A. E., Scrimshaw, M. D., Stratful, I., & Lester, J. N. (1999). Review of the feasibility of recovering phosphate from wastewater for use as a raw material by the phosphate industry. *Environmental Technology (United Kingdom)*, *20*(7), 749–758. https://doi.org/10.1080/09593332008616870

Etter, B., Tilley, E., Khadka, R., & Udert, K. M. (2011). Low-cost struvite production using source-separated urine in Nepal. *Water Research*, *45*(2), 852–862. https://doi.org/10.1016/j.watres.2010.10.007

Evangel, S. A. (2017). Potential Nutrient Removal and/or Recovery Using Controlled Struvite Precipitation in Reject Water from IVAR Grødaland. *Master's thesis*, *University of Stavanger*, *49*(89), 15242.

Fernández-Escobar, R., Benlloch, M., Herrera, E., & García-Novelo, J. M. (2004). Effect of traditional and slow-release N fertilizers on growth of olive nursery plants and N losses by leaching. *Scientia Horticulturae*, *101*(1–2), 39–49. https://doi.org/10.1016/j.scienta.2003.09.008

Gaterell, M. R., Gay, R., Wilson, R., Gochin, R. J., & Lester, J. N. (2000). An economic and environmental evaluation of the opportunities for substituting phosphorus recovered from wastewater treatment works in existing uk fertiliser markets. *Environmental Technology (United Kingdom)*, *21*(9), 1067–1084. https://doi.org/10.1080/09593332108618050

Gebregziabher, B., Kassahun, S. K., & Kiflie, Z. (2021). Statistical optimization of mixed peanut shell and Khat (Catha edulis) stem carbonization process for molasses enhanced cold and low-pressure pelletization. *Biomass Conversion and Biorefinery*. https://doi.org/10.1007/s13399-021-01446-5

Guadie, A., Belay, A., Liu, W., Yesigat, A., Hao, X., & Wang, A. (2020). Rift Valley Lake as a potential magnesium source to recover phosphorus from urine. *Environmental Research*, *184*(January). https://doi.org/10.1016/j.envres.2020.109363

Guadie, A., Xia, S., Jiang, W., Zhou, L., Zhang, Z., Hermanowicz, S. W., Xu, X., & Shen, S. (2014). Enhanced struvite recovery from wastewater using a novel cone-inserted fluidized bed reactor. *Journal of Environmental Sciences (China)*, *26*(4), 765–774. https://doi.org/10.1016/S1001-0742(13)60469-6

Hallas, J. F., Mackowiak, C. L., Wilkie, A. C., & Harris, W. G. (2019). Struvite phosphorus recovery from aerobically digested municipal wastewater. *Sustainability (Switzerland)*, *11*(2), 1–12. https://doi.org/10.3390/su11020376

Hao, X. D., Wang, C. C., Lan, L., & Van Loosdrecht, M. C. M. (2008). Struvite formation, analytical methods and effects of pH and Ca 2+. *Water Science and Technology*, *58*(8), 1687–1692. https://doi.org/10.2166/wst.2008.557

Harder, R., Wielemaker, R., Larsen, T. A., Zeeman, G., & Oberg, G. (2019). Recycling nutrients contained in human excreta to agriculture: Pathways, processes, and products. *Critical Reviews in Environmental Science and Technology*, *49*(8), 695–743. https://doi.org/10.1080/10643389.2018.1558889

Hiroyuki, H., & Katsutoshi, I. (2019). Phosphorus Recovery by Crystallization. *Phosphorus - Recovery and Recycling*. https://doi.org/10.5772/intechopen.81549

Hossein Ma, A., . P. B., . F. V., & . F. K. (2004). Feasibility of Continuous Flow Sequencing Batch Reactor in Synthetic Wastewater Treatment. *Journal of Applied Sciences*, *5*(1), 172–176. https://doi.org/10.3923/jas.2005.172.176

Huang, H., Mavinic, D. S., Lo, K. V., & Koch, F. A. (2006). Production and basic morphology of struvite crystals from a pilot-scale crystallization process. *Environmental Technology*, *27*(3), 233–245. https://doi.org/10.1080/09593332708618637

Huang, Hui. (2003). *Pilot Scale Phosphorus Recovery from Anaerobic Digester Supernatant*. *December*, 231.

Huang, M. H., Li, Y. M., & Gu, G. W. (2010). Chemical composition of organic matters in domestic wastewater. *Desalination*, *262*(1–3), 36–42. https://doi.org/10.1016/j.desal.2010.05.037

Hutagalung, S. A. E. (2017). *Potential Nutrient Removal And/Or Recovery Using Controlled Struvite Precipitation In Reject Water From Ivar Grødaland*. *June*.

Hutnik, N., Stanclik, A., Piotrowski, K., & Matynia, A. (2019). Recovery of phosphates(V) from wastewaters of different chemical composition. *Open Chemistry*, *17*(1), 1071–1079. https://doi.org/10.1515/chem-2019-0114

Johnny, G. T. (2018). *Recovery of Phosphorus and Nitrogen from source-separated urine: process optimization in bench-scale*. *Master's thesis*, *Addis Ababa University*.

Johnston A.E.*, & Richards, I. R. (2003). Effectiveness of different precipitated phosphates as phosphorus sources for plants. *Soil Use and Management*, *19*(1), 45–49. https://doi.org/10.1079/sum2002162

Jones. (2002). Crystallization Process Systems.*University collage London*.

Kabdaşli, I., Parsons, S. A., & Tünay, O. (2006). Effect of major ions on induction time of struvite precipitation. *Croatica Chemica Acta*, *79*(2), 243–251.

Kane, S. N., Mishra, A., & Dutta, A. K. (2016). International Conference on Recent Trends in Physics (ICRTP 2016). *Journal of Physics: Conference Series*, *755*(1). https://doi.org/10.1088/1742-6596/755/1/011001

Kecskésová, S., Imreová, Z., Martonka, M., & Drtil, M. (2020). Chemical dissolution of struvite precipitates in pipes from anaerobic sludge digestion. *Chemical Papers*, *74*(8), 2545–2552. https://doi.org/10.1007/s11696-020-01096-3

Kofina, A. N., & Koutsoukos, P. G. (2005). Spontaneous precipitation of struvite from synthetic wastewater solutions. *Crystal Growth and Design*, *5*(2), 489–496. https://doi.org/10.1021/cg049803e

Kumar, R., & Pal, P. (2013). Turning hazardous waste into value-added products: Production and characterization of struvite from ammoniacal waste with new approaches. *Journal of Cleaner Production*, *43*, 59–70. https://doi.org/10.1016/j.jclepro.2013.01.001

Kumari, S., Jose, S., Tyagi, M., & Jagadevan, S. (2020). A holistic and sustainable approach for recovery of phosphorus via struvite crystallization from synthetic distillery wastewater. *Journal of Cleaner Production*, *254*. https://doi.org/10.1016/j.jclepro.2020.120037

Le Corre, K. S., Valsami-Jones, E., Hobbs, P., & Parsons, S. A. (2007). Impact of reactor operation on success of struvite precipitation from synthetic liquors. *Environmental Technology*, *28*(11), 1245–1256. https://doi.org/10.1080/09593332808618885

Le Corre, K. S., Valsami-Jones, E., Hobbs, P., & Parsons, S. A. (2009). Phosphorus recovery from wastewater by struvite crystallization: A review. In *Critical Reviews in Environmental Science and Technology* (Vol. 39, Issue 6). https://doi.org/10.1080/10643380701640573

Li, B., Boiarkina, I., Yu, W., Huang, H. M., Munir, T., Wang, G. Q., & Young, B. R. (2019). Phosphorous recovery through struvite crystallization: Challenges for future design. *Science of the Total Environment*, *648*, 1244–1256. https://doi.org/10.1016/j.scitotenv.2018.07.166

Liu, B., Giannis, A., Zhang, J., Chang, V. W. C., & Wang, J. Y. (2013). Characterization of induced struvite formation from source-separated urine using seawater and brine as magnesium sources. *Chemosphere*, *93*(11), 2738–2747. https://doi.org/10.1016/j.chemosphere.2013.09.025

Liu, X., Hu, Z., Wang, J., & Wen, G. (2014). Effect of hydraulic retention time and seed material on phosphorus recovery and crystal size from urine in an air-agitated reactor. *Water Science and Technology*, *69*(7), 1462–1468. https://doi.org/10.2166/wst.2014.044

Liu, X., Hu, Z., Zhu, C., Wen, G., Meng, X., & Lu, J. (2013). Influence of process parameters on phosphorus recovery by struvite formation from urine. *Water Science and Technology*, *68*(11), 2434–2440. https://doi.org/10.2166/wst.2013.514

Liu, X., & Wang, J. (2019). Impact of calcium on struvite crystallization in the wastewater and its competition with magnesium. *Chemical Engineering Journal*, *378*(May), 122121. https://doi.org/10.1016/j.cej.2019.122121

Liu, Y. H., Kwag, J. H., Kim, J. H., & Ra, C. S. (2011). Recovery of nitrogen and phosphorus by struvite crystallization from swine wastewater. *Desalination*, *277*(1–3), 364–369. https://doi.org/10.1016/j.desal.2011.04.056

Liu, Y. H., Rahman, M. M., Kwag, J. H., Kim, J. H., & Ra, C. S. (2011). Eco-friendly production of maize using struvite recovered from swine wastewater as a sustainable fertilizer source. *Asian-Australasian Journal of Animal Sciences*, *24*(12), 1699–1705. https://doi.org/10.5713/ajas.2011.11107

Liu, Z., Zhao, Q., Lee, D. J., & Yang, N. (2008). Enhancing phosphorus recovery by a new internal recycle seeding MAP reactor. *Bioresource Technology*, *99*(14), 6488–6493. https://doi.org/10.1016/j.biortech.2007.11.039

Lu, X., Shih, K., Li, X. Y., Liu, G., Zeng, E. Y., & Wang, F. (2016). Accuracy and application of quantitative X-ray diffraction on the precipitation of struvite product. *Water Research*, *90*, 9–14. https://doi.org/10.1016/j.watres.2015.12.014

Mahlet Melaku (2017). Performance Evaluation and Model-Based Optimization of Membrane Bioreactors: The Case of Addis Ababa Package Treatment Plant. MSC Thesis. http://etd.aau.edu.et/handle/123456789/24825

Mamakoa, E., Masindi, V., & Neomagus, H. (2019). *Sources of Magnesium used in the Synthesis of Struvite from Wastewater: A Review*. https://doi.org/10.17758/eares8.eap1119260

Matynia, A., Koralewska, J., Wierzbowska, B., & Piotrowski, K. (2006). The influence of process parameters on struvite continuous crystallization kinetics. *Chemical Engineering Communications*, *193*(2), 160–176. https://doi.org/10.1080/009864490949008

Morse, G. K., Brett, S. W., Guy, J. A., & Lester, J. N. (1998). Review: Phosphorus removal and recovery technologies. *Science of the Total Environment*, *212*(1), 69–81. https://doi.org/10.1016/S0048-9697(97)00332-X

Mullin. (2001). Crystallization. *American Chemical Society*..

Muryanto, S., & Bayuseno, A. P. (2014). Influence of Cu2+ and Zn2+ as additives on crystallization kinetics and morphology of struvite. *Powder Technology*, *253*, 602–607. https://doi.org/10.1016/j.powtec.2013.12.027

Novak, A. (1976). Hydrogen Bonding in Solids. Correlation of Spectroscopic and Crystallographic Data*. *Physiology and Behavior*, *17*(2), 337–344. https://doi.org/10.1016/0031-9384(76)90084-6

Ohlinger, K. N., Young, T. M., & Schroeder, D. E. (1999). *Kinetics effects on preferential struvite accumulation in wastewater*. *August*, 730–737.

Pandey, B., Mishra, V., & Agrawal, S. (2011). Production of bio-electricity during wastewater treatment using a single chamber microbial fuel cell. *International Journal of Engineering, Science and Technology*, *3*(4), 42–47. https://doi.org/10.4314/ijest.v3i4.68540

Parsons, S. A., & Doyle, J. D. (2002). Struvite formation, control and recovery. *Water Research*, *36*(16), 3925–3940.

Parsons, S. A., & Smith, J. A. (2008). Phosphorus removal and recovery from municipal wastewaters. *Elements*, *4*(2), 109–112. https://doi.org/10.2113/GSELEMENTS.4.2.109

Pi, T., Lozano-García, S., Caballero-Miranda, M., Ortega-Guerrero, B., & Roy, P. (2010). Discovery and characterization of a struvite layer in the Chalco paleolake, Mexico. *Revista Mexicana de Ciencias Geológicas*, *27*(3), 573–580.

Ping, Q., Li, Y., Wu, X., Yang, L., & Wang, L. (2016). Characterization of morphology and component of struvite pellets crystallized from sludge dewatering liquor: Effects of total suspended solid and phosphate concentrations. *Journal of Hazardous Materials*, *310*, 261–269. https://doi.org/10.1016/j.jhazmat.2016.02.047

Prywer, J., Sieroń, L., & Czylkowska, A. (2019). Struvite grown in gel, its crystal structure at 90 k and thermoanalytical study. *Crystals*, *9*(2). https://doi.org/10.3390/cryst9020089

Rahman, M. M., Salleh, M. A. M., Rashid, U., Ahsan, A., Hossain, M. M., & Ra, C. S. (2014). Production of slow release crystal fertilizer from wastewaters through struvite crystallization - A review. *Arabian Journal of Chemistry*, *7*(1), 139–155. https://doi.org/10.1016/j.arabjc.2013.10.007

Rashid, S., Tefera, N., Minot, N., & Ayele, G. (2014). Fertilizer in Ethiopia: An Assessment of Policies, Value Chain, and Profitability. *SSRN Electronic Journal*, *December*. https://doi.org/10.2139/ssrn.2373214

Rehman, S., Jilani, G., Hussain, Q., & Ijaz, S. S. (2019). *Journal of Environmental & Separation of Struvite from Sewerage Water and its Evaluation as*. *9*(2).

Richard K, B. (2000). Review: the structure of simple phosphate glasses. *Journal of Non-Crystalline Solids*, *263–264*(0), 1–28. http://www.sciencedirect.com/science/article/pii/S0022309399006201

Ryu, H. D., & Lee, S. I. (2016). Struvite recovery from swine wastewater and its assessment as a fertilizer. *Environmental Engineering Research*, *21*(1), 29–35. https://doi.org/10.4491/eer.2015.066

Saadat, S., Raei, E., & Talebbeydokhti, N. (2018). Enhanced removal of phosphate from aqueous solutions using a modified sludge derived biochar: Comparative study of various modifying cations and RSM based optimization of pyrolysis parameters. *Journal of Environmental Management*, *225*(April), 75–83. https://doi.org/10.1016/j.jenvman.2018.07.037

Saerens, B., Geerts, S., & Weemaes, M. (2021). Phosphorus recovery as struvite from digested sludge – experience from the full scale. *Journal of Environmental Management*, *280*(August). https://doi.org/10.1016/j.jenvman.2020.111743

Sakthivel, S. R., Tilley, E., & Udert, K. M. (2012). Wood ash as a magnesium source for phosphorus recovery from source-separated urine. *Science of the Total Environment*, *419*, 68–75. https://doi.org/10.1016/j.scitotenv.2011.12.065

Sato, T., Qadir, M., Yamamoto, S., Endo, T., & Zahoor, A. (2013). Global, regional, and country level need for data on wastewater generation, treatment, and use. *Agricultural Water Management*, *130*, 1–13. https://doi.org/10.1016/j.agwat.2013.08.007

Shih, Y. J., Abarca, R. R. M., de Luna, M. D. G., Huang, Y. H., & Lu, M. C. (2017). Recovery of phosphorus from synthetic wastewaters by struvite crystallization in a fluidized-bed reactor: Effects of pH, phosphate concentration and coexisting ions. *Chemosphere*, *173*, 466–473. https://doi.org/10.1016/j.chemosphere.2017.01.088

Sidorczuk, D., Kozanecki, M., Civalleri, B., Pernal, K., & Prywer, J. (2020). Structural and Optical Properties of Struvite. Elucidating Structure of Infrared Spectrum in High Frequency Range. *Journal of Physical Chemistry A*, *124*(42), 8668–8678. https://doi.org/10.1021/acs.jpca.0c04707

Silverstein, R. M., Webster, F. X., & Kiemle, D. J. (2005). Spectrometer identification of organic compounds. In *State university of New York* (Vol. 61, Issue 5).

Simon, & Smith. (2008). Phosphorus Removal and Recovery from Municipal Wastewaters. *Centre for Water Science, Cranfield University* 109–112.

Srinath, E. G., Sastry, C. A., & Pillai, S. C. (1959). Rapid removal of phosphorus from sewage by activated sludge. *Experientia, 15*(9), 339–340. https://doi.org/10.1007/BF02159818

Stefov, V., Šoptrajanov, B., Spirovski, F., Kuzmanovski, I., Lutz, H. D., & Engelen, B. (2004). Infrared and Raman spectra of magnesium ammonium phosphate hexahydrate (struvite) and its isomorphous analogues. I. Spectra of protiated and partially deuterated magnesium potassium phosphate hexahydrate. *Journal of Molecular Structure*, *689*(1–2), 1–10. https://doi.org/10.1016/j.molstruc.2003.08.019

Stratful, I., Scrimshaw, M. D., & Lester, J. N. (2001). Conditions influencing the precipitation of magnesium ammonium phosphate. *Water Research*, *35*(17), 4191–4199. https://doi.org/10.1016/S0043-1354(01)00143-9

Suh, S., & Yee, S. (2011). Phosphorus use-efficiency of agriculture and food system in the US. *Chemosphere, 84*(6), 806–813. https://doi.org/10.1016/j.chemosphere.2011.01.051

Sun, H., Nayeem, A., & Liu, Y. (2020). Phosphorus recovery from source-diverted blackwater through struvite precipitation. *Science of the Total Environment*. *743*.

Suzuki, K., Tanaka, Y., Kuroda, K., Hanajima, D., & Fukumoto, Y. (2005). Recovery of phosphorous from swine wastewater through crystallization. *Bioresource Technology*, *96*(14), 1544–1550. https://doi.org/10.1016/j.biortech.2004.12.017

Tchobanoglous, G., Franklin, L., Burton, E. C., & Stensel, H. D. (2011). *Wastewater Engineering Treatment and Reuse (Fourth Edition), 2011*.

Tran, A. T. K., Zhang, Y., De Corte, D., Hannes, J. B., Ye, W., Mondal, P., Jullok, N., Meesschaert, B., Pinoy, L., & Van Der Bruggen, B. (2014). P-recovery as calcium phosphate from wastewater using an integrated selectrodialysis/crystallization process. *Journal of Cleaner Production*, *77*, 140–151. https://doi.org/10.1016/j.jclepro.2014.01.069

Umer, A., Assefa, B., & Fito, J. (2020). Spatial and seasonal variation of lake water quality: Beseka in the Rift Valley of Oromia region, Ethiopia. *International Journal of Energy and Water Resources, 4*(1), 47–54. https://doi.org/10.1007/s42108-019-00050-8

Walter, A., Finger, R., Huber, R., & Buchmann, N. (2017). *Smart farming is key to developing sustainable agriculture*. *114*(24), 6148–6150. https://doi.org/10.1073/pnas.1707462114

Warmadewanthi, Rodlia, A., Ikhlas, N., Pandebesie, E. S., Bagastyo, A. Y., & Herumurti, W. (2020). The Effect of Mixing Rate on Struvite Recovery from the Fertilizer Industry. *IOP Conference Series: Earth and Environmental Science*, *506*(1). https://doi.org/10.1088/1755-1315/506/1/012013

Yan, H., & Shih, K. (2016). Effects of calcium and ferric ions on struvite precipitation: A new assessment based on quantitative X-ray diffraction analysis. *Water Research*, *95*, 310–318. https://doi.org/10.1016/j.watres.2016.03.032

Ye, X., Ye, Z. L., Lou, Y., Pan, S., Wang, X., Wang, M. K., & Chen, S. (2016). A comprehensive understanding of saturation index and upflow velocity in a pilot-scale fluidized bed reactor for struvite recovery from swine wastewater. *Powder Technology*, *295*, 16–26. https://doi.org/10.1016/j.powtec.2016.03.022

Ye, Z. L., Chen, S. H., Wang, S. M., Lin, L. F., Yan, Y. J., Zhang, Z. J., & Chen, J. S. (2010). Phosphorus recovery from synthetic swine wastewater by chemical precipitation using response surface methodology. *Journal of Hazardous Materials*, *176*(1–3), 1083–1088. https://doi.org/10.1016/j.jhazmat.2009.10.129

Yeoman, S., Stephenson, T., Lester, J. N., & Perry, R. (1988). The removal of phosphorus during wastewater treatment: A review. *Environmental Pollution*, *49*(3), 183–233. https://doi.org/10.1016/0269-7491(88)90209-6

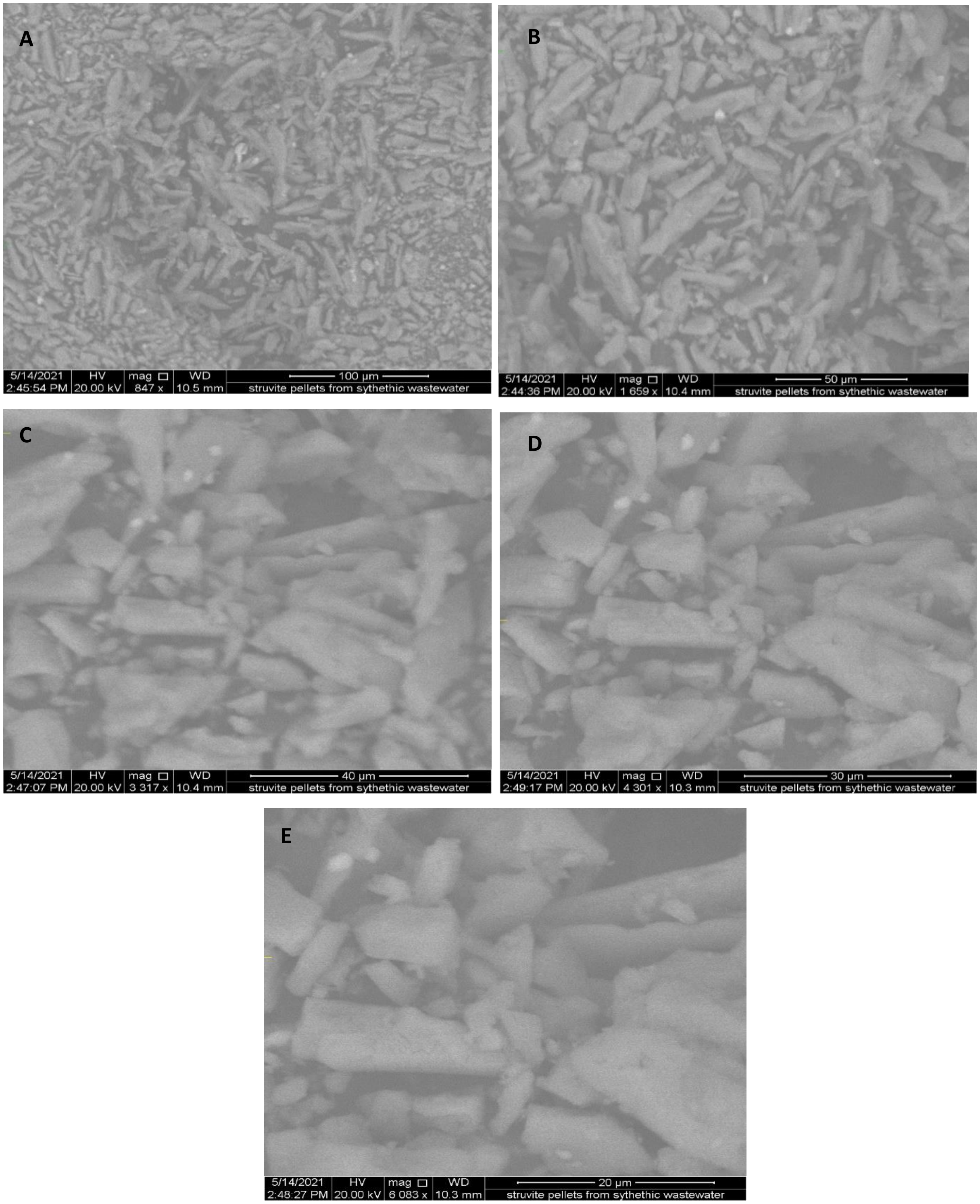
Yetilmezsoy, K., & Sapci-Zengin, Z. (2009). Recovery of ammonium nitrogen from the effluent of UASB treating poultry manure wastewater by MAP precipitation as a slow release fertilizer. *Journal of Hazardous Materials*, *166*(1), 260–269. https://doi.org/10.1016/j.jhazmat.2008.11.025

Zhang, T., Ding, L., & Ren, H. (2009). Pretreatment of ammonium removal from landfill leachate by chemical precipitation. *Journal of Hazardous Materials*, *166*(2–3), 911–915. https://doi.org/10.1016/j.jhazmat.2008.11.101

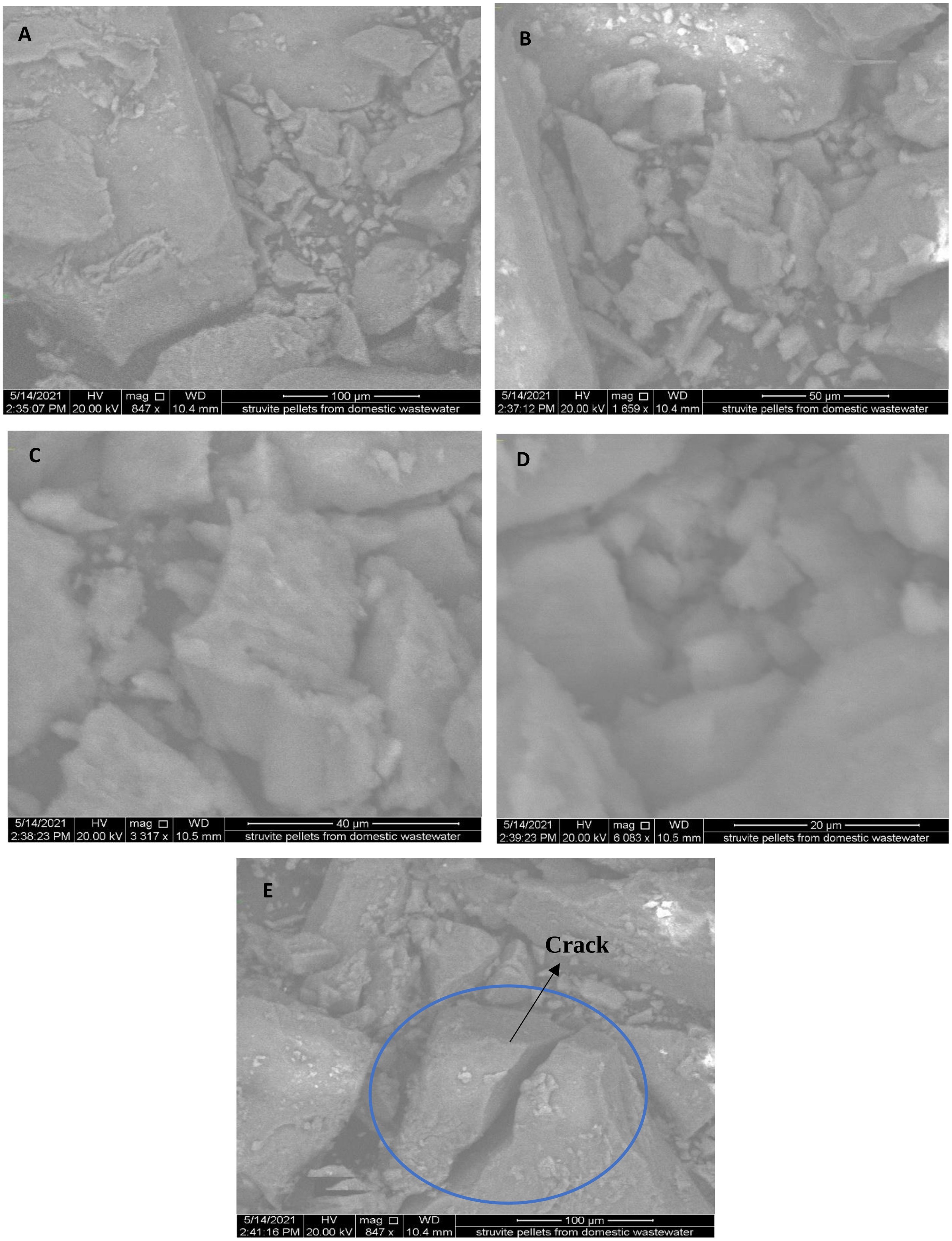
Zheng, F.-L., Huang, C.-H., & Norton, L. D. (2004). Effects of Near-Surface Hydraulic Gradients on Nitrate and Phosphorus Losses in Surface Runoff. *Journal of Environmental Quality*, *33*(6), 2174–2182. https://doi.org/10.2134/jeq2004.2174

APPENDIXES

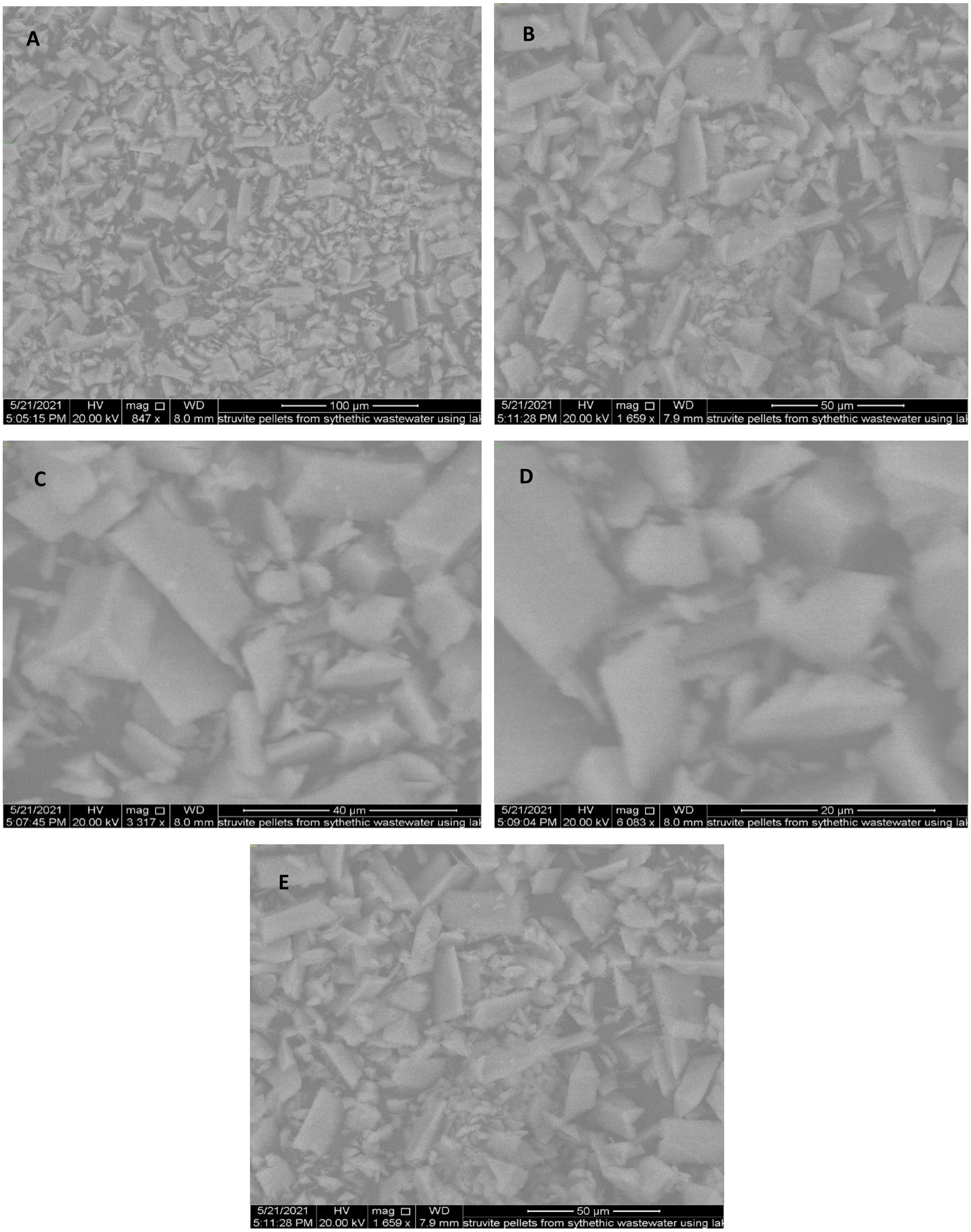
Appendix 1. SEM image of crystals harvested from synthetic wastewater under WD 10.3mm and magnification (A) 847X (B) 1659X (C) 3317X (D) 4031 (E) 6083X



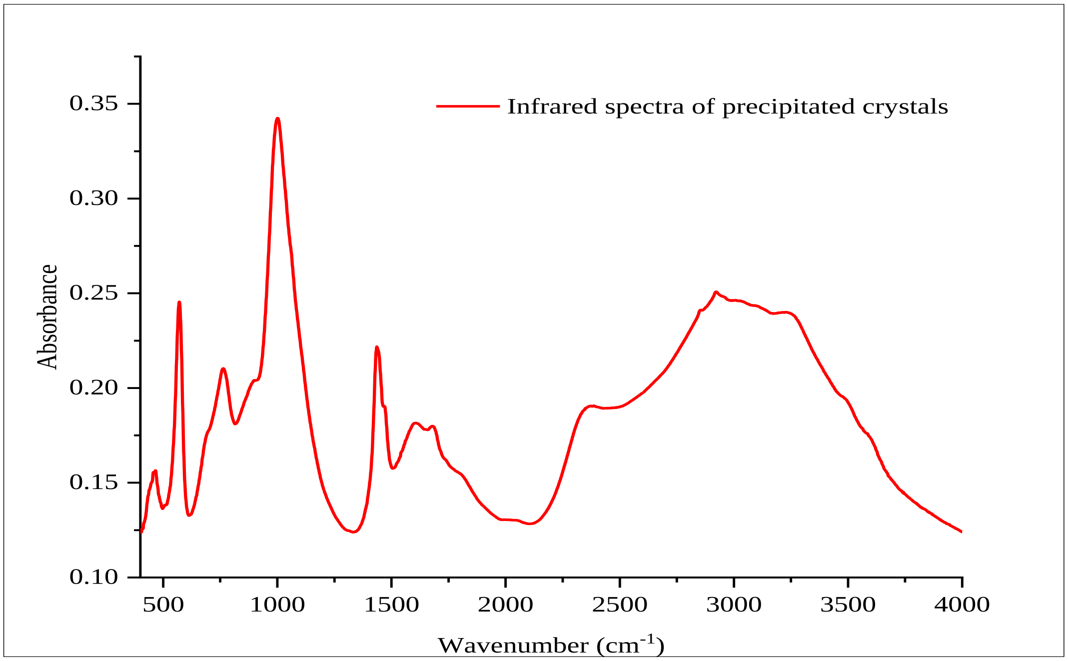
Appendix 2. SEM image of crystals harvested from synthetic wastewater under WD 10.3mm magnification (A) 847X (B) 1659X (C) 3317X (D) 6083 (E) 847X with scale 100 µm

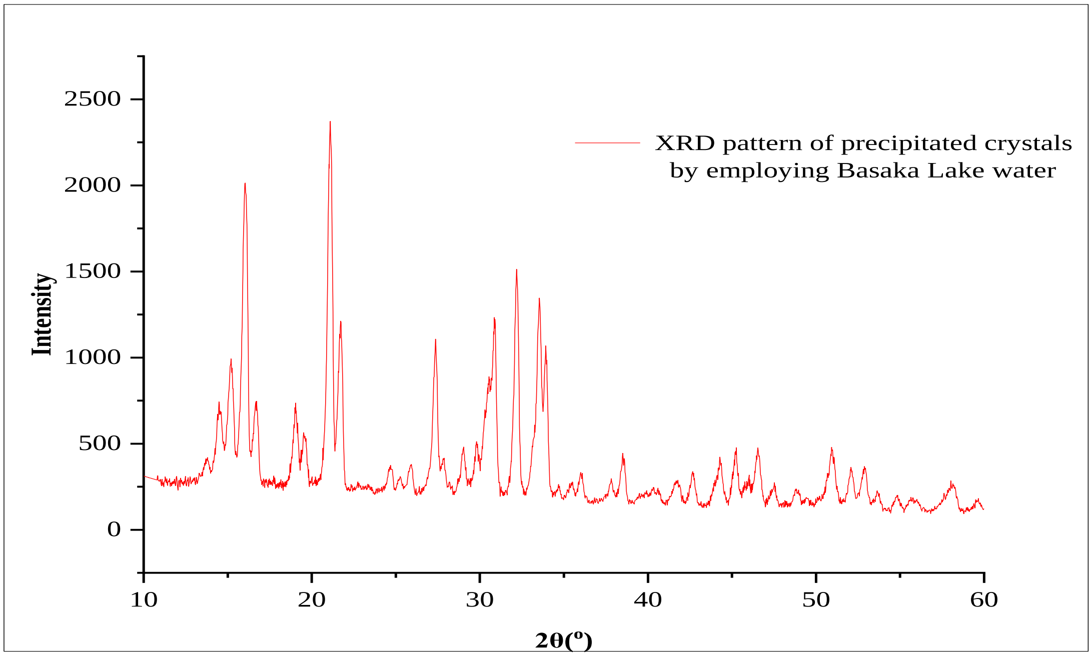


Appendix 3. Figure A.2, SEM image of crystals harvested from synthetic wastewater by employing Basaka Lake water under WD 10.3mm magnification (A) 847X (B) 1659X (C) 3317X (D) 6083 (E) 1659X with scale 50 µm



Appendix 4 FTIR (upper panel) and XRD (Lower panel) analysis of harvested crystals from synthetic wastewater by using Basaka Lake water as a source of magnesium





Appendix 5. Analysis of variance (ANOVA) of the model for phosphate removal efficiency (upper table) and response surface model for yield of struvite (lower table)

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	8522.32	14	608.74	561.13	< 0.0001	significant
A-pH	3787.59	1	3787.59	3491.41	< 0.0001	
B-NH4:PO4	35.77	1	35.77	32.97	< 0.0001	
C-Mg:PO4	643.77	1	643.77	593.43	< 0.0001	
D-HRT	918.84	1	918.84	846.99	< 0.0001	
AB	34.52	1	34.52	31.82	< 0.0001	
AC	10.40	1	10.40	9.59	0.0074	
AD	1.63	1	1.63	1.50	0.2398	
BC	7.16	1	7.16	6.60	0.0214	
BD	42.58	1	42.58	39.25	< 0.0001	
CD	35.70	1	35.70	32.91	< 0.0001	
A^2	2641.53	1	2641.53	2434.96	< 0.0001	
B^2	360.64	1	360.64	332.43	< 0.0001	
C^2	221.00	1	221.00	203.72	< 0.0001	
D^2	519.27	1	519.27	478.66	< 0.0001	
Residual	16.27	15	1.08			
Lack of Fit	13.28	10	1.33	2.22	0.1962	not significant
Pure Error	2.99	5	0.5987			
Cor Total	8538.59	29				

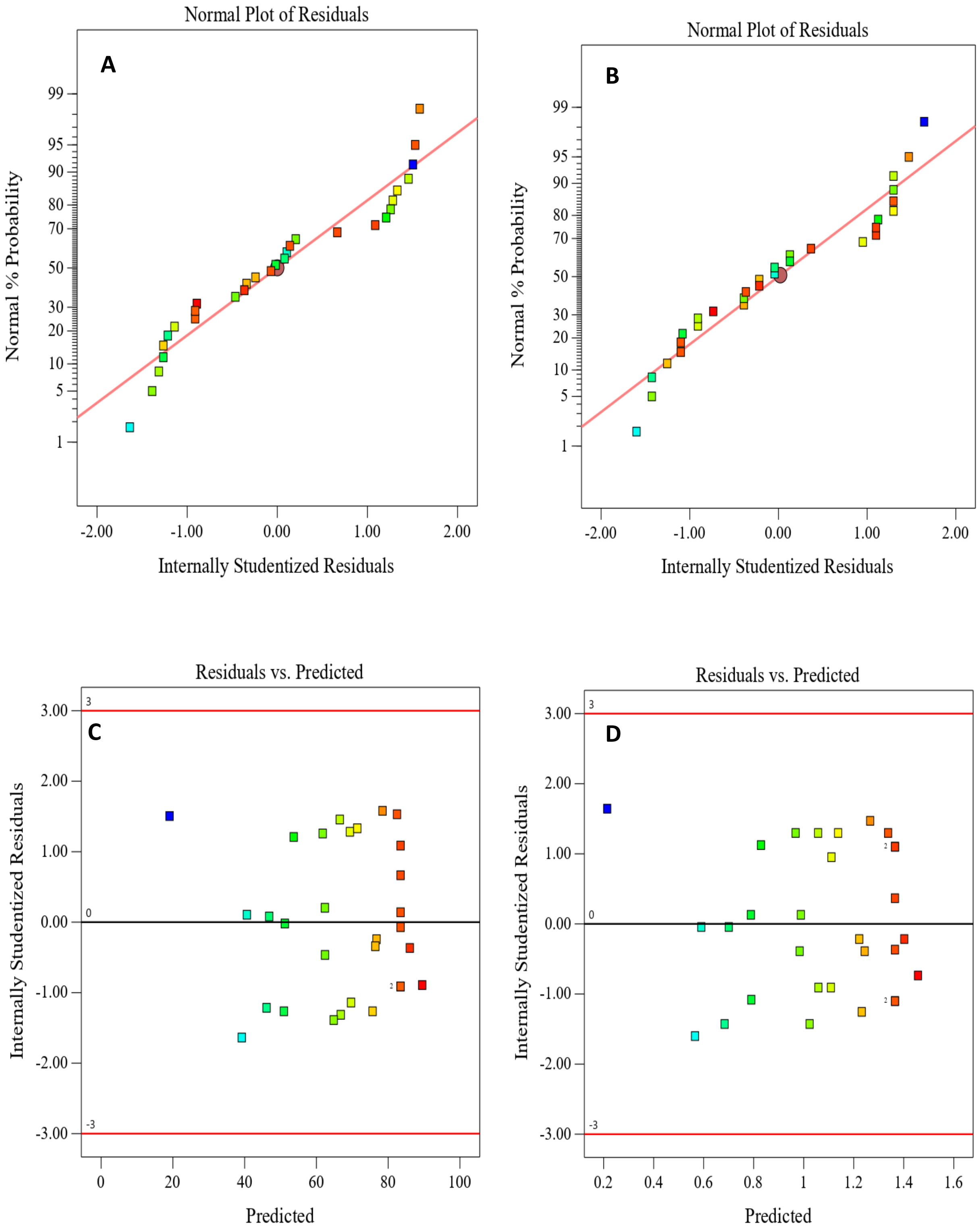
Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	2.72	14	0.1946	873.33	< 0.0001	significant
A-pH	1.21	1	1.21	5413.54	< 0.0001	
B-NH4:PO4	0.0096	1	0.0096	43.09	< 0.0001	
C-Mg:PO4	0.2053	1	0.2053	921.77	< 0.0001	
D-HRT	0.2860	1	0.2860	1283.87	< 0.0001	
AB	0.0090	1	0.0090	40.51	< 0.0001	
AC	0.0042	1	0.0042	18.97	0.0006	
AD	0.0004	1	0.0004	1.80	0.2002	
BC	0.0042	1	0.0042	18.97	0.0006	
BD	0.0169	1	0.0169	75.86	< 0.0001	
CD	0.0100	1	0.0100	44.89	< 0.0001	
A^2	0.8460	1	0.8460	3797.55	< 0.0001	
B^2	0.1227	1	0.1227	550.63	< 0.0001	
C^2	0.0774	1	0.0774	347.48	< 0.0001	
D^2	0.1728	1	0.1728	775.71	< 0.0001	
Residual	0.0033	15	0.0002			
Lack of Fit	0.0024	10	0.0002	1.26	0.4225	not significant
Pure Error	0.0009	5	0.0002			
Cor Total	2.73	29				

Appendix 6. Response surface model summary for phosphate removal efficiency (upper table) and struvite yield (lower table)

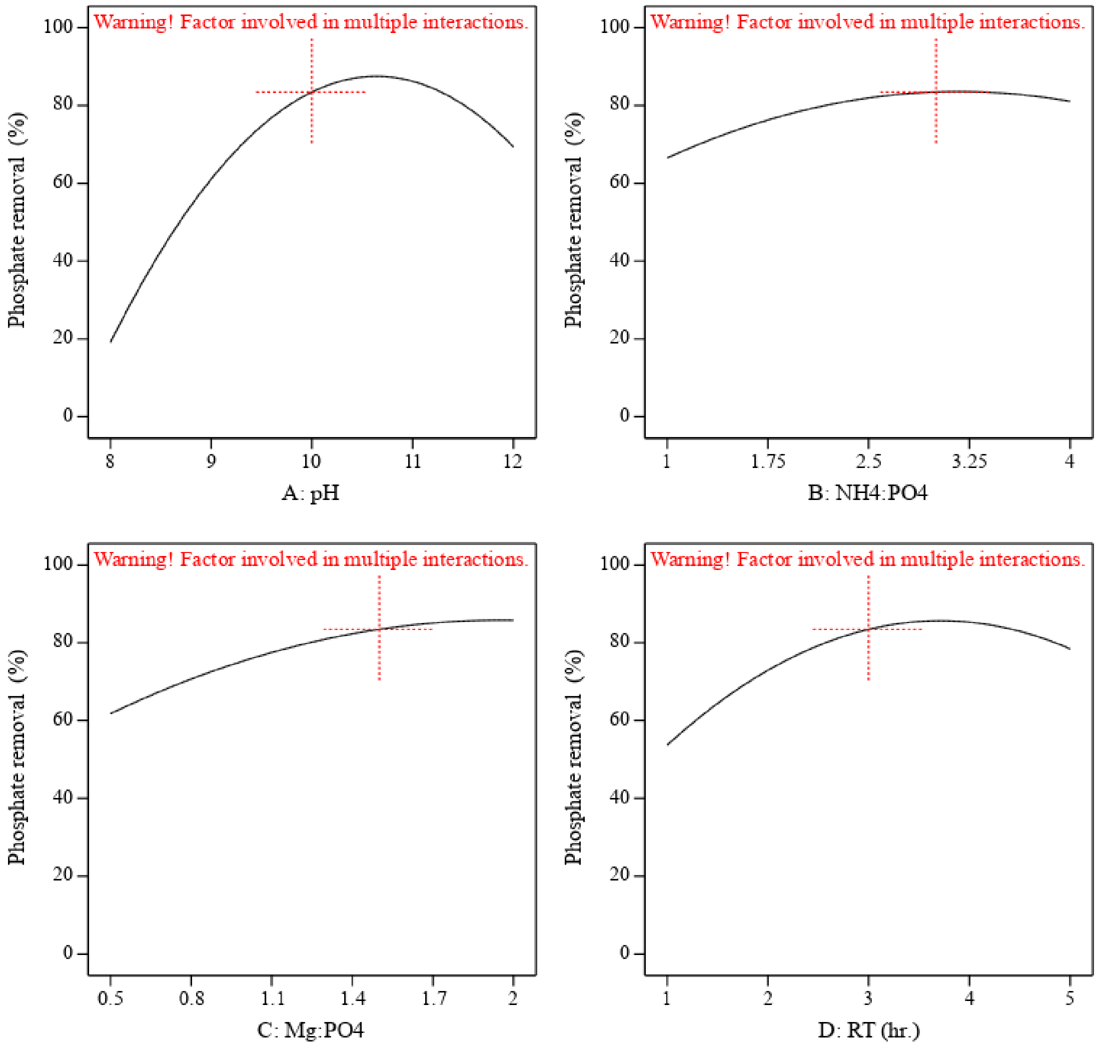
Source	**Std. Dev.**	**R^2**	**Adjusted R^2**	**Predicted R^2**	**PRESS**	
Linear	11.23	0.6308	0.5717	0.5175	4119.91	
2FI	12.61	0.6462	0.4600	0.3832	5266.52	
Quadratic	**1.04**	**0.9981**	**0.9963**	**0.9905**	**80.80**	**Suggested**
Cubic	1.51	0.9981	0.9923	0.7824	1857.95	Aliased

Source	**Std. Dev.**	**R^2**	**Adjusted R^2**	**Predicted R^2**	**PRESS**	
Linear	0.2020	0.6259	0.5661	0.5132	1.33	
2FI	0.2266	0.6423	0.4541	0.3842	1.68	
Quadratic	**0.0149**	**0.9988**	**0.9976**	**0.9944**	**0.0151**	**Suggested**
Cubic	0.0215	0.9988	0.9951	0.8794	0.3290	Aliased

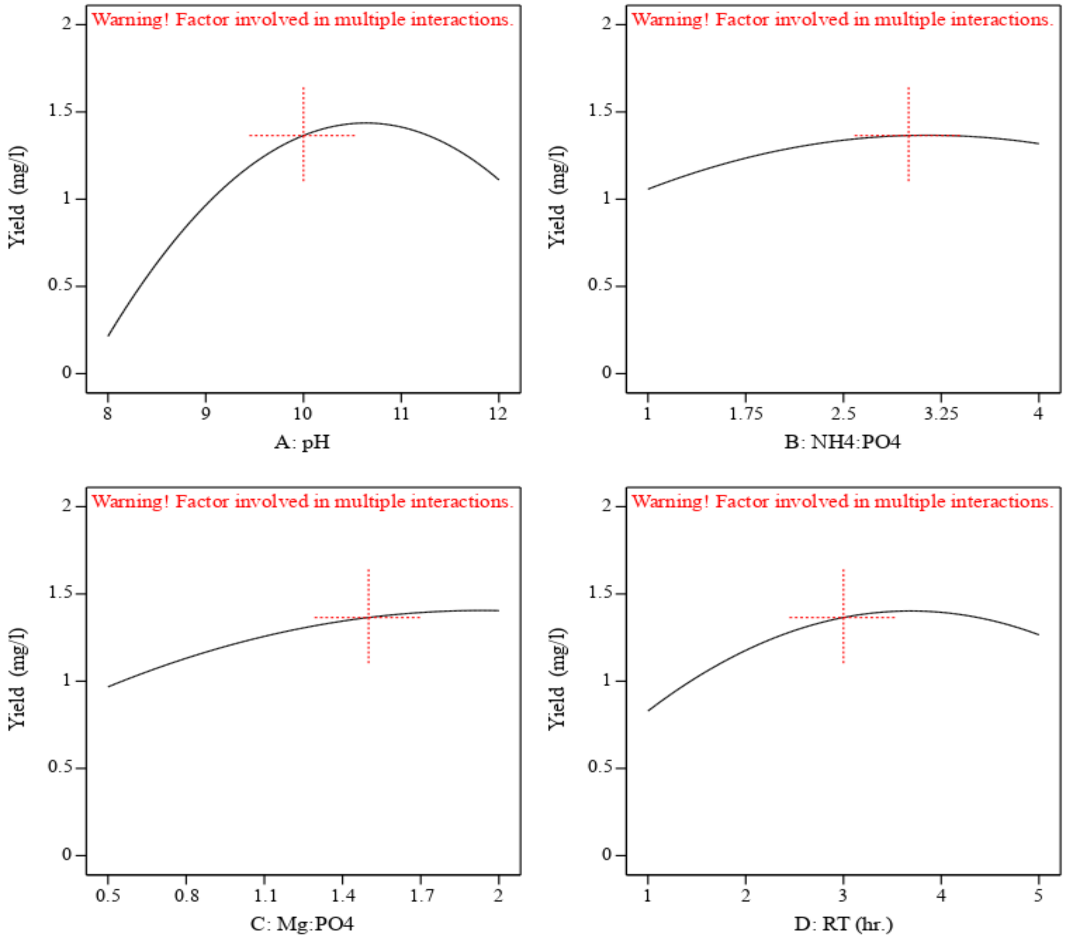
Appendix 7. Normal plot of residuals for (A) phosphate removal efficiency and (B) struvite yield and Residuals Vs Predicted plot for (C) phosphate removal efficiency and (D) struvite yield



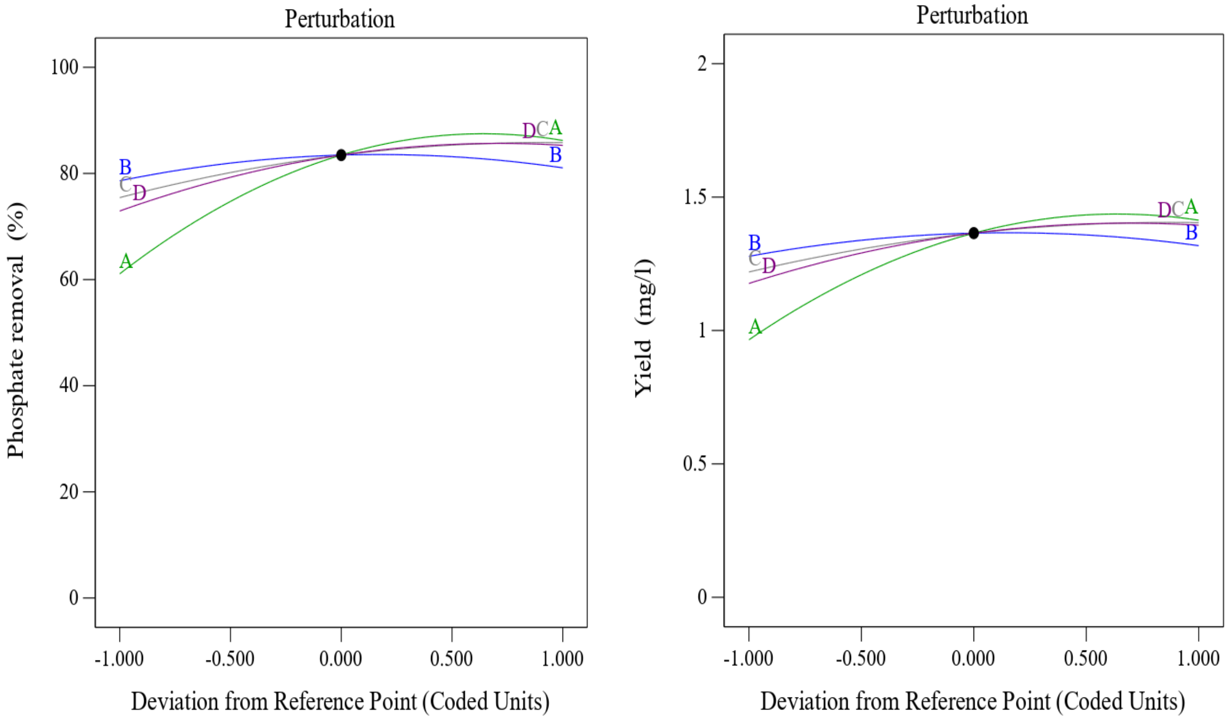
Appendix 8 Linear effect of paraments for phosphate removal efficiency (one factor plots)



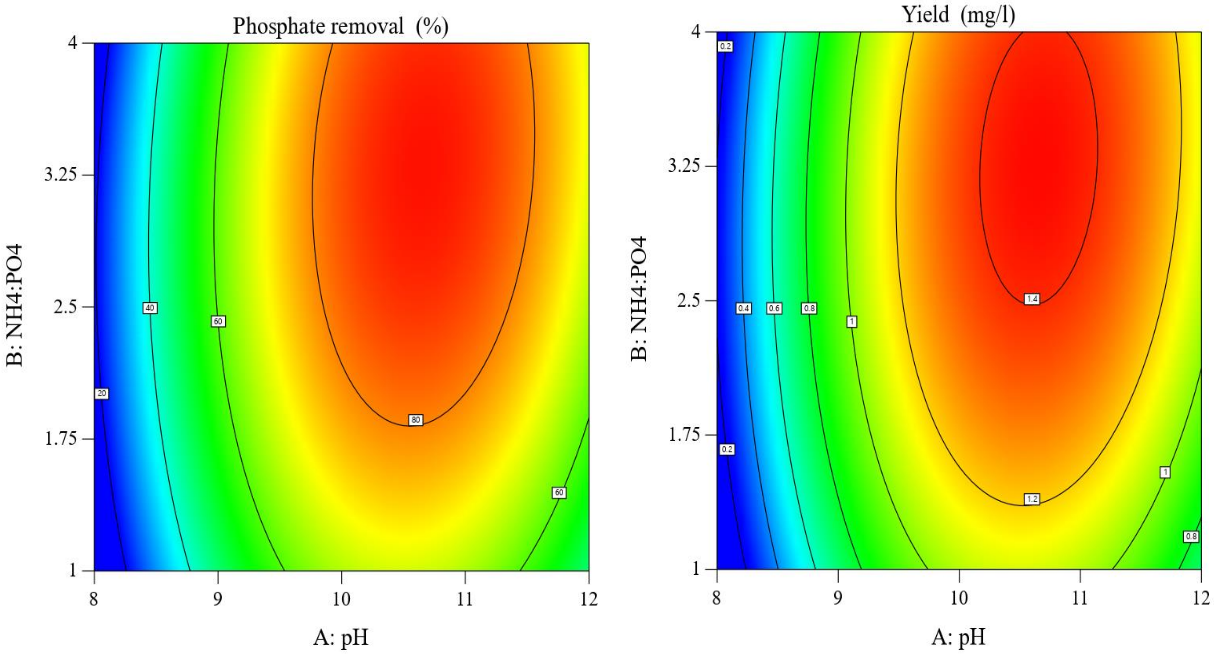
Appendix 9. Linear effect of paraments for yield of struvite (one factor plots)



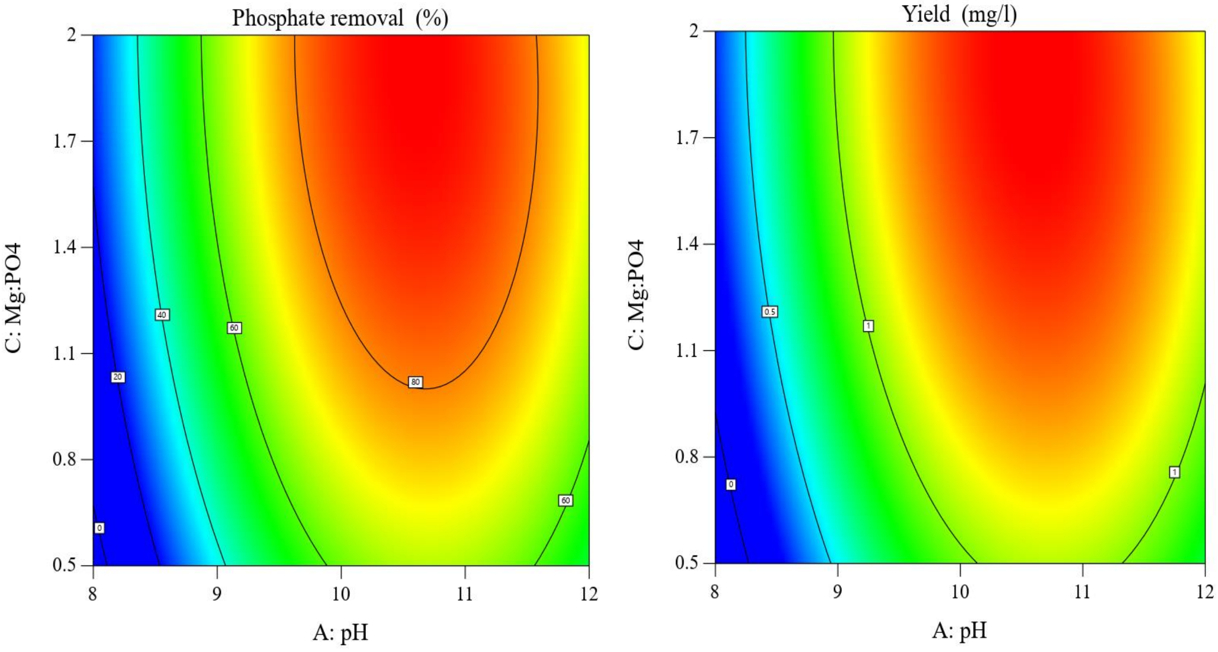
Appendix 10. Deviation from reference point for phosphate removal efficiency (left panel) and struvite yield (right panel)



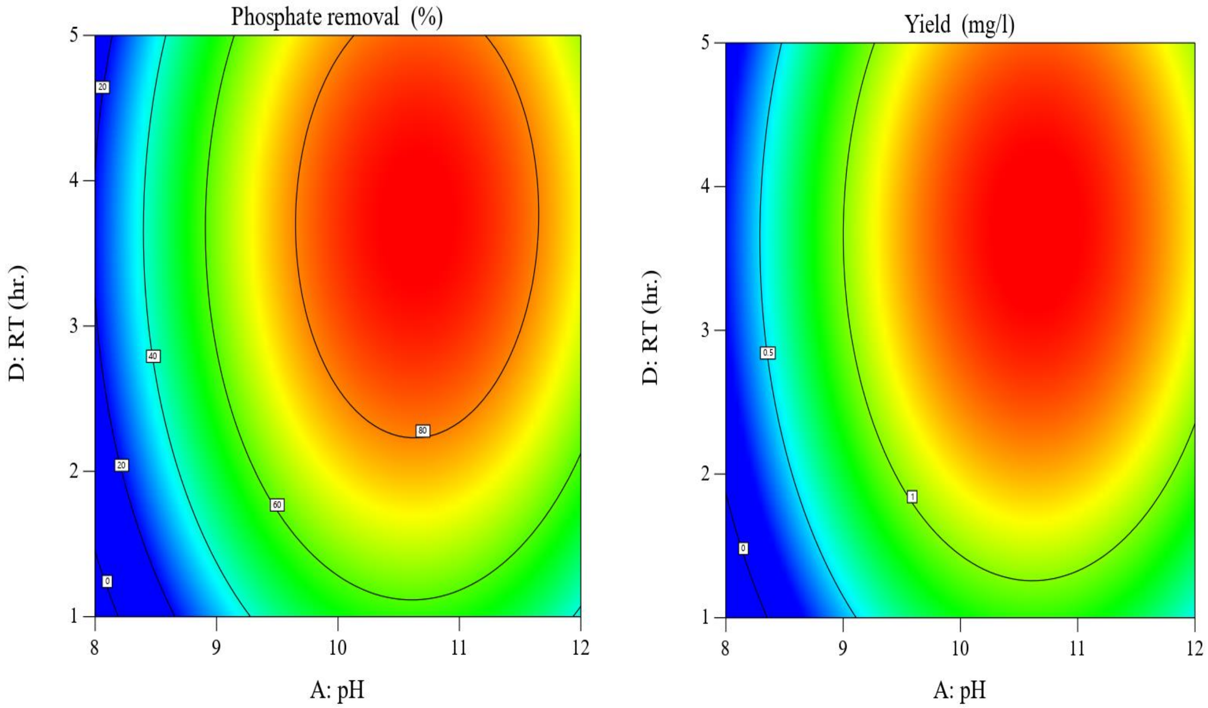
Appendix 11. Contour plot of pH and NH_4:PO_4 ratio for phosphate removal efficiency (left panel) and struvite yield (right panel)



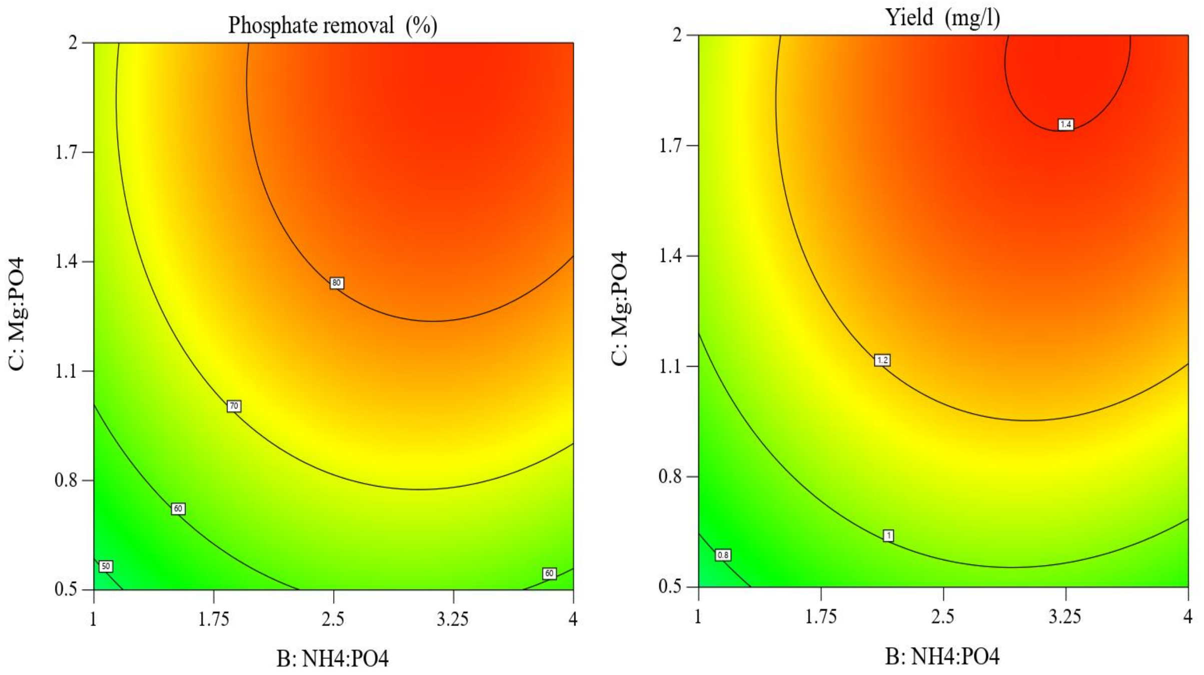
Appendix 12. Contour plot of Mg:PO_4 and pH ratio for phosphate removal efficiency (left panel) and struvite yield (right panel)



Appendix 13. Contour plot of RT and pH ratio for phosphate removal efficiency (left panel) and struvite yield (right panel)



Appendix 14. Contour plot of Mg:PO_4 and NH_4:PO_4 ratio for (A) phosphate removal efficiency and (B) struvite yield



Appendix 15. Detail methodological procedures

a. Methodology for preparation of synthetic wastewater (Run 1 in Table 3.2)

Syntactic wastewater formulation was designed as per the data given by Addis Ababa water and sewerage authority (AAWSA). Average characteristic of wastewater is given in Table Appendix C.1.

Table Appendix C.1.

Parameter	Mean Value	Standard Deviation
pH	6.8	
Phosphate (mg/l)	62	
Ammonium (mg/l)	51	

Synthetic wastewater is prepared from potassium di hydrogen orthophosphate (KH_2PO_4) as phosphate source, ammonium chloride (NH_4Cl) as ammonium source and magnesium hex hydrate ($MgCl_2. H_2O$) as magnesium source. In order to eliminate spontaneous precipitation of struvite in influent holding thermoplastic tank, magnesium ion is mixed in fluidized bed reactor from another influent holding tank while ammonia and phosphate ions put in the same influent holding tank.

- Total volume of synthetic wastewater is 12L. i.e., 10L the volume of reactor and 2L the volume of water flows in to recycling tank for recycling purpose.
- Synthetic wastewater is prepared by mixing potassium di hydrogen orthophosphate and ammonium chloride salts in 8L of liter of distilled water in one influent holding tank whereas 4L magnesium ion solution was prepared by dissolving magnesium hex hydrate salt in another influent holding tank. Similarly, 1L of sodium hydroxide solution was prepared in separate influent holding tank for pH control.
- Since small amount of sodium hydroxide solution was mixed into reactor to control the pH value, its dilution effect is negligible and not considered in chemical calculation.

Mass of (KH_2PO_4) to produce 60 mg/l of phosphate in 12 L(total volume of the solution)

Number of mole = mass of chemical / Molar mass of chemical

60 mg of phosphate exist in 1L of solution

Number of mol of phosphate = 60 mg / 94.97 g/mol ……. Molar mass of phosphate is 94.97 g/mol

Number of moles of phosphate = 0.00064 mol

Molarity of phosphate = 0.00064 mol/l

Mass of chemical = Volume of solution * Molarity * Molar mass

= 12 L * 0.00064 mol/l * 94.97 g/mol

= 0.73 g

0.73 g of phosphate is required to make phosphate concentration 60 mg/l in 12 liters of distilled water.

One mole of (KH_2PO_4) (136 g) produce 95 g of PO_4…………….. from molar mass

How many g (KH_2PO_4) is required in order to produce 1.04g of phosphate?

= (136 g * 0.73 g)/ (94.97g) = **1.06g**

- ✓ ***1.06 g of (KH_2PO_4) is dissolved in 8 l of distilled wastewater***

Note: - At the influent tank the concentration of phosphate is greater than 60 mg/l, however the concentration reduced to 60 mg/l after mixed with 4 liters of magnesian ion solution in the reactor due to dilution effect.

The molar ratio of NH_4 to PO_4 is 4 ……………. from Experimental design (Table 3.2)

*The required mole of NH_4 is 4 times mole of PO_4 = 4*0.00064mol/l*

= 0.00256 mol/l

Molarity of ammonium = 0.00256 mol/l

Mass of (NH_4Cl) to produce 0.00256mol/l of ammonium in 12 L

Mass of chemical = Volume of solution * Molarity * Molar mass

= 12 l * 0.00256 mol/l * 18 g/mol

= 0.553 g

0.553 g of ammonium is required to make the molar ratio between ammonium and phosphate 4 in 12 litters of distilled water.

One mole of (NH_4Cl) (53.5 g) produce 18 g of NH_4................ from molar mass

How many g (NH_4Cl) is required in order to produce 0.553g of ammonium?

= (53.5 g * 0.553 g)/(18g) = **1.64g**

1.64 g of (NH_4Cl) is dissolved in 12 l of distilled wastewater

The molar ratio of Mg to PO_4 is 2 ……………………. from Experimental design (Table 3.2)

*The required mole of Mg is 2 times mole of PO_4 = 2 * 0.00064mol/l*

= 0.00128 mol/l

Molarity of magnesium = 0.00128 mol/l

Mass of ($MgCl_2$ +$6H_2O$) to produce 0.00128 mol/l of magnesium in 12 L

Mass of chemical = Volume of solution * Molarity * Molar mass

= 12 l * 0.00128 mol/l * 24 g/mol

= 0.37 g

0.37 g of magnesium is required to make the molar ratio of magnesium to phosphate 1.65 in 12 litter of distilled water.

One mole of ($MgCl_2$ + $6H_2O$) (203 g) produce 24 g of Mg................ from molar mass

How many g ($MgCl_2$ + $6H_2O$) is required in order to produce 0.43g of ammonia?

= (203 g * 0.37 g)/(24g) = **3.13g**

3.13 g of ($MgCl_2$ + $6H_2O$) is dissolved in 4 l of distilled wastewater

Note: - The same procedures were applied for all experimental runs in Table 3.2.

Preparation of 0.05 mol/l sodium hydroxide (NaOH) solution

Number of mole = Mass of compound / Molar mass of compound

0.05 mol/l = Mass of sodium hydroxide / Molar mass of NaOH

Mass of sodium hydroxide = 0.05 mol/l * 39.988 g/mol

= 2 g

0.05 mol/l of sodium hydroxide was prepared by dissolving 2 g of sodium hydroxide pellet in 1 liter of distilled water.

b. Volume determination of Basaka Lake water which used for struvite crystallization.

The volume of Basaka Lake water mixed to synthetic wastewater in order to make Mg: PO_4 ratio 1. (Optimized Mg: PO_4 ratio)

Number of phosphate mols in synthetic wastewater = 60 mg / 95 $gmol^{-1}$

= 0.0006316mol

Required number of moles of magnesium = 1 * 0.0006316 = **0.0006316 mol** since Mg: PO_4 ratio is 1.

Required concentration of magnesium = Volume of wastewater * Number of moles of Mg * Molar mass of Mg

= 8 liter * 0.00006316 mol * 24 $gmol^{-1}$

= **121 mg**

Since 1 litter of Basaka Lake water has 31 mg of magnesium, 4 litter of Basaka Lake water is required in order to make 1.

Check: - $C_1V_1 = C_2V_2$ Where: -

- C_1 = PO_4 Con. in synthetic wastewater
- C_2 = PO_4 Con. in synthetic wastewater after it was mixed with Basaka Lake water
- V_1 = Volume of synthetic wastewater
- V2 = Volume of synthetic wastewater after it was mixed with Basaka Lake water

$$(60\ mg/l) * (8L) = C_2 * (12\ L)$$

$$\mathbf{C_2 = 40\ mg/l}$$

No. of mol. of PO_4 in synthetic after mixed with Basaka Lake water = C_2 / Molar mass of PO_4

= 40 mg/l / 94.97g

= 0.000421185

$C_1V_1 = C_2V_2$ Where: -

- C_1 = Mg ion Con. in Basaka Lake water
- C_2 = Mg ion Con. in synthetic wastewater after it was mixed with Basaka Lake water
- V_1 = Volume of Basaka Lake water
- V2 = Volume of synthetic wastewater after it was mixed with Basaka Lake water

$(31 \text{ mg/l}) * (4\text{L}) = C_2 * (12 \text{ L})$

$C_2 = 10.33$ mg/l

No. of mol. of PO_4 in synthetic after mixed with Basaka Lake water = C_2 / Molar mass of Mg

= 10.33 mg/l / 24.305g

= 0.000425152

Number of moles of phosphate and magnesium ions is equal (0.00042). So, the Mg/PO_4 molar ratio is 1.

The volume of Basaka Lake water mixed to domestic wastewater in order to make Mg: PO_4 ratio 1. (Optimized Mg: PO_4 ratio)

Number of phosphate mols in domestic wastewater = 93.6 mg / 95 gmol^{-1}

= 0.0009853mol

Required number of moles of magnesium = 1 * 0.0009853 = **0.0009853 mol** since Mg: PO_4 ratio is 1.

Required concentration of magnesium = Volume of wastewater * Number of moles of Mg * Molar mass of Mg

= 8 liter * 0.0009853 mol * 24 gmol^{-1}

= **189 mg**

Since 1 litter of Basaka Lake water has 31 mg of magnesium, 6 litter of Basaka Lake water was mixed in order to make Mg: PO_4 molar ratio 1.

Check: - $C_1V_1 = C_2V_2$ Where: -

- C_1 = PO_4 Con. in domestic wastewater
- C_2 = PO_4 Con. in domestic wastewater after it was mixed with Basaka Lake water
- V_1 = Volume of domestic wastewater
- V2 = Volume of domestic wastewater after it was mixed with Basaka Lake water

(93.6 mg/l) * (8L) = C_2 * (14 L)

<u>C_2 = 53.48 mg/l</u>

No. of mol. of PO_4 in synthetic after mixed with Basaka Lake water = C_2 / Molar mass of PO_4

= 53.48 mg/l / 94.97g

<u>= 0.000563185</u>

$C_1V_1 = C_2V_2$ Where: -

- C_1 = Mg ion Con. in Basaka Lake water
- C_2 = Mg ion Con. in synthetic wastewater after it was mixed with Basaka Lake water
- V_1 = Volume of Basaka Lake water
- V2 = Volume of synthetic wastewater after it was mixed with Basaka Lake water

(31 mg/l) * (6L) = C_2 * (14 L)

<u>C_2 = 13.52 mg/l</u>

No. of mol. of PO_4 in synthetic after mixed with Basaka Lake water = C_2 / Molar mass of Mg

= 13.52 mg/l / 24.305g

<u>= 0.00056</u>

Number of moles of phosphate and magnesium ions is equal (0.00056). So, the Mg/PO_4 molar ratio is 1.

c. Palintest 7100 photometer protocol for phosphate, ammonia and magnesium test.

- ✓ Calibrate the instrument.
- ✓ Prepare two standard test tubes for Palintest 7100 photometer i.e., for blank and measured water sample.

- ✓ Fill one test tube by distilled water until the cursor on the test tube (10ml). It used as blank.
- ✓ Fill another test tube by measured water sample until the cursor on the test tube.
- ✓ Add reagent or tablet in test tube with measured water sample.
  - If there is more than one reagent, all reagents added consequently into test tube with measured water sample.
- ✓ shake vigorously until the reagent is completely dissolve and wait for 10 min.
- ✓ Select measured ions on the photometer display
- ✓ Insert blank test tube into photometer
- ✓ Take away the blank test tube and insert the test tube with measured water sample.
- ✓ Read the measurement on the display of photometer.

d. Struvite purity calculation

$$P_{struvite} = \frac{nN \, * Mstruvite}{mp} * 100\%$$

where - $P_{struvite}$ is the purity of struvite

- $M_{struvite}$ is the molecular weight of struvite,
- mp is the mass of dissolved precipitates,
- nN is the mole of N in the dissolved precipitates.

Nitrogen concentration of synthetic wastewater-based struvite = 25.42 mg/l

nN = given mass / molar mass of N = 25.42 * 10^-3 g / 14.007 g mol^{-1}= 0.001815 mol

The purity of synthetic wastewater-based struvite = (0.001815 mol * 245.41 $gmol^{-1}$) / 0.5 g * 100%

= 89.1 %

Nitrogen concentration of domestic wastewater-based struvite = 19.1 mg/l

nN = given mass / molar mass of N = 19.1 * 10^-3 g / 14.007 g mol^{-1}= 0.0014 mol

The purity of synthetic wastewater-based struvite = (0.0014 mol * 245.41 $gmol^{-1}$) / 0.5 g * 100%

= 68.7 %