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**Recovery of Phosphorus and Nitrogen from
Domestic Wastewater through Struvite Precipitation
using Conical Fluidized Bed Reactor**

By:

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**Addis Ababa,
Ethiopia**

October, 2019



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A thesis submitted to the School of Graduate Studies of Addis Ababa University in
Partial fulfillment of the Degree of Master of Science in Water Supply and
Environmental Engineering.

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Abstract

Recovery of nutrients as struvite before it forms and accumulates is in line with sustainable wastewater management. It prevents water pollution and enables use of the nutrients as fertilizer to increase agricultural productivity. A bench-scale fluidized bed reactor (FBR) was used to recover phosphate (PO_4) and ammonium (NH_4) through struvite crystallization, from synthetic wastewater and aerobic digester domestic wastewater supernatant collected from, Haile Garment Addis Ababa and Oromia Condominium Wastewater Treatment Plant.

Struvite crystallization is a promising nutrient recovery method. Its recovered precipitate can be used as a slow release fertilizer and raw material for chemical industry. The objective of this research was to examine the influence of different parameters affecting the performance of FBR for phosphorus (P) and nitrogen (N) removal and recovery efficiencies.

In this study, the impacts of important factors on nutrient recovery in a laboratory scale (FBR) were examined using synthetic wastewater to get optimal values. The nutrient recovery of the FBR from real wastewater was also evaluated by using the optimum parameter values. The recoveries of PO_4 and NH_4 were evaluated by changing the values of the following parameters: pH (7.5-10), molar ratio of Mg/P (0.75-1.75), Hydraulic retention time ($HRT = 1-5hr$), and settling time (15-90min). The optimum values of pH, Mg/P, HRT, and settling time were found to be 9, 1.5:1, 2hr, and 30min respectively. Under these optimum values, the P and N removal efficiencies of conical FBR from synthetic and real wastewater were 97% and 95% and 67.2% and 64.7%, respectively. Moreover, different techniques were used to enhance nutrient recovery efficiency including use of a reactor that has three parts and insertion of cones in each part.

The findings of the study show pH, Mg/P molar ratio, HRT, and settling time to be important factors that influence Phosphorus and nitrogen removal efficiency in FBR. A conical FBR with three distinct parts gives a good nutrient recovery through struvite precipitation.

Keywords: *Efficiency, fluidized bed reactor, Recovery, Removal, Struvite, nutrient, wastewater*

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Acronyms and Abbreviations

AAWSA.....	Addis Ababa water and sewerage authority
APHA.....	American Public Health Association
AOPs.....	Advanced oxidation processes
Ca.....	Calcium
DAP	Di ammonium phosphate
EBPR.....	Enhanced biological phosphorus removal
FBR.....	Fluidized bed reactor
HRT.....	Hydraulic retention time
MAP.....	Magnesium ammonium phosphate
Mg.....	Magnesium
MUDHCo.....	Ministry of Urban Development, Housing and Construction
N.....	Nitrogen
NH ₄ ⁺	Ammonium
NaOH.....	Sodium hydroxide
P.....	Phosphorus
PAOs.....	Polyphosphate accumulating organisms
PHA	Poly hydroxyl alkanooates
PO ₄ ³⁻	Phosphate
RAS.....	Returned activated sludge
RPM	Revolution per minute

RWW.....Real wastewater

SWW.....Synthetic wastewater

WWTP.....Wastewater treatment plant

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1. Introduction

1.1 Background

A supply of clean water is an essential requirement for the establishment and maintenance of diverse human activities. Water resources provide valuable food through aquatic life and irrigation for agriculture production (Chowdhury and Mete, 2018) . However, rapid urbanization, population growth, and industrialization affect its quality and release enormous volumes of wastewater (Rajasulochana and Preethy, 2016, Halder and Islam, 2015).

Wastewater is any water that has been adversely affected in quality by any anthropogenic influence and comprises liquid waste discharged from domestic houses, industrial, agricultural or commercial processes. Domestic wastewater is the water that has been used by a community and which generally consists of black water composed of fecal matter (human and animal wastes) together with grey water sources collected from various wastewater constituents. These components originate from a range of household activities (washing and bathing) with each forming approximately 32.5% and 67.5% of domestic sewage respectively (Naidoo and Olaniran, 2013a). Initially, this water is used for home every day activities, such as drinking, food preparation, bathing, washing clothes and dishes, flushing toilets, and watering lawns and gardens (Asiwal *et al.*, 2016) .

According to study by (Narmadha and Kavitha, 2012) , wastewater generated from domestic source contains a high amount of organic matter, considerable amounts of odors, non-pathogenic bacteria, nitrogen and phosphorus, significant amount of magnesium, different macro and micro elements, food wastes , heavy metals , other inorganic materials (sand, grit), and Emulsions (paints, adhesives, mayonnaise, hair colorants, emulsified oils). These untreated wastewater usually have a vast range of effect on the environment conditions in streams, rivers, lakes and any other liquid wastes receiving water bodies, nutrients mainly nitrogen and phosphorus that can stimulate the growth of aquatic plants, which in turn results in eutrophication problem posing a risk to the humans and the aquatic life (Mehta *et al.*, 2015).

Phosphorus is also a key element in fertilizer in the current food production and consumption system. The main source of phosphorus is phosphate rock, a nonrenewable resource rapidly being depleted as a result of the increasing exploitation of rock and sedimentation through the natural phosphorus cycle (Cordell *et al.*, 2011). Therefore, the above mentioned pressures from environmental pollution, and the non-renewable nature of phosphate rock have been driving focus on nutrient recovery.

Wastewater treatment technics that comprise nutrient recovery are supposed to be an alternative approach leading to sustainable development (Le Corre *et al.*, 2009b). Different scholars about struvite crystal formation from different liquors can be found in the literatures which show the importance of recovering nutrients and the value of the struvite product. Between these liquors municipal wastewater streams (Woods *et al.*, 1999), swine wastewater (Suzuki *et al.*, 2007), dairy manure (Harris *et al.*, 2008), urine (Etter *et al.*, 2011), landfill leachate, bone disposal, abattoir, and industrial wastes (Doyle and Parsons, 2002, Schneider *et al.*, 2006) have been studied.

Phosphorus removal from wastewater can be accomplished by chemical precipitation, crystallization, biological degradation, adsorption, tertiary filtration and ion exchange processes, membrane processes, and electrochemical processes (Peng *et al.*, 2018b, de-Bashan and Bashan, 2004). Most of these methods are challenging because they produce low purity products, have high investment, and/or are operationally complex. On the other hand, crystallization is a broadly researched approach with a relatively high recovery rate and considerable economic efficiency; it produces valuable products (Mavinic *et al.*, 2007). Earlier scholar showed that the best phosphorus crystallization product in wastewater treatment plants is struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) (Pastor *et al.*, 2010) occurs when ammonium, magnesium and phosphate combine in water in equal molar ratio.

Struvite crystallization can happen either spontaneously or controlled. Spontaneously struvite formation most likely occurs in pipeline locations (such as junctions, elbows) which in turn consequences clogging of pipelines, breakdowns of centrifuges pumps, heat exchangers and other pieces of equipment that eventually lead to an increase in pumping costs, as the diameter of the pipe is reduced, more energy is required to pump the sludge through the pipe work also the

time taken for the sludge to be moved from one place to another increases, reducing plant capacity and increase maintenance costs (Doyle and Parsons, 2002, Britton et al., 2005a).

In contrast, controlled struvite formation is now getting more attention as it has numerous advantages, including serving as slow released fertilizer, reducing sludge volume, removing phosphorus and nitrogen simultaneously, replacing natural phosphate used in industries, avoiding pipe clogging/treatment failures, and making a marketable product (Guadie *et al.*, 2014).

In order to produce struvite precipitation many scholars have been done nutrient recovery from different types of wastewater like anaerobic digester liquor, landfill leachate, synthetic, industrial, swine, slaughter house and calf manure wastewater by using several type of reactors. Therefore, this study was proposed to evaluate nutrient recovery efficiency of fluidized bed reactor using domestic wastewater from aerobic digester liquor part.

1.2 Statement of the problem

Phosphorus (P) and nitrogen (N) are essential elements needed by all living organisms for growth and development. The major source of P is in the form of mined phosphate rock and used as mineral fertilizer for crop production, human food, animal feed, and industrial products. Since the last century, processed mineral P from mined phosphate rock has been used regularly in European agriculture as a source of phosphate fertilizer. Its use developed significantly in the century and today much of the crop production on a worldwide scale is dependent on inputs of mineral phosphate fertilizer. An input of P is critical for food production since all plants need an adequate supply of it for successful growth.

The demand for food increases with world population growth, which is particularly evident in the third world countries. This required the production and use of large amounts of nitrogen and phosphorus-based fertilizers to increase agricultural productivity. According to the International Water Management Institute, by 2050 the production of P will grow by 70% overall and even by up to 100% in developing countries, in order to satisfy the rapidly growing demand for P (Zhou *et al.*, 2016, Guedes *et al.*, 2014). However, the actual amount of commercially viable global phosphate reserve remains a subject of considerable doubt in the recent years (Schröder *et al.*, 2010b). It has been estimated that the increasing demand for P fertilizer will result in exhaustion of global reserves of non-renewable natural rock phosphate within the next 50–100 years (Cordell *et al.*, 2011).

It is also estimated that in the middle of this century the world's population will exceed 9 billion, which means that food production will have to be increased by almost 30%. Currently, about 82% of the mined P is used in agriculture, while 7% is used for the production of animal feed. The remaining 11% of the mined P is used in industry and medicine for the production of pharmaceuticals, oils, detergents, or even textiles (Konieczka, 2017, Sorensen *et al.*, 2015). Based on the consumer behavior and the availability of P, the global P production is projected to reach the peak point in the next 20-30 years (Cordell *et al.*, 2009).

On the other hand, wastewater releases excessive levels of N and P to the environment causing accelerated eutrophication, which has adverse impacts on the socio-economic and ecological values of surface water bodies and water treatment plants. Wastewater treatment plants,

particularly those that employ secondary treatment and anaerobic sludge digestion, have historically encountered struvite precipitation, which foul and encrust the sludge return lines, and the associated pumps and valves. This growth of ‘uncontrolled’ struvite can be a nuisance, increases pumping and maintenance cost, and reduces the overall hydraulic and biological treatment performance of the plant.

Nutrients are limited non-renewable resources that are vital for high agricultural productivity. Recent researches indicate that future supply of phosphate rock will become scarcer and more expensive to excavate. However, Phosphorus reach domestic wastewater is directly discharged into the environment causing unnecessary abundant plant growth. It is, therefore, important to innovate and promote appropriate resource-oriented wastewater management technologies that contribute to environmental pollution control and recovery of valuable nutrients. This research tried to investigate the potential to recover phosphorus from domestic wastewater in the form of magnesium ammonium phosphate (struvite). It is important to know the various factors that influence the process and their optimum values which result in high level of phosphorus recovery.

1.3 Objective of the study

1.3.1 General objective

The general objective of this study is to recover nutrients from domestic wastewater in the form of magnesium ammonium phosphate crystal precipitation (struvite).

1.3.2 Specific objectives

- To design and produce a lab-scale conical fluidized bed reactor (FBR) for struvite precipitation
- To examine the influence of various factors on the efficiency of phosphorus and nitrogen recovery.
- To evaluate the removal efficiency of FBR using actual wastewater.

1.4 Research Questions

- Is a fluidized bed reactor with cones and different parts efficient in recovering nutrients from domestic wastewater?
- How do different operational parameters, i.e., feed type, pH, molar ratio of magnesium- phosphorus (Mg/p), HRT and settling time affect struvite crystal formation?
- What are the optimum values of these operational parameters in terms of nutrient recovery?
- What is the phosphorus removal efficiency of conical FBR from domestic wastewater?
- What is the nitrogen removal efficiency of conical FBR from domestic wastewater?

1.5 Significance of the study

This research demonstrated the potential for sustainable wastewater management where phosphorus and nitrogen can be recovered and used as a resource instead of becoming cause of water pollution. It provides important information about the various factors that influence the nutrient recovery process. This can contribute to the development of nutrient recovery technologies and processes at industry scale. Struvite that is produced in large quantity has the potential to minimize eutrophication problem and the demand for chemical fertilizers.

1.6 Scope and limitation of the study

This research was done at laboratory scale using synthetic wastewater and real domestic wastewater supernatant. The real domestic wastewater samples were collected from Membrane Bioreactor Wastewater Treatment Plant giving service to a condominium site in Addis Ababa.

Due to limited financial support and time, it was not possible to conduct comprehensive laboratory tests for adequate characterization of the struvite in terms of different parameters such as particle density, size, level of purity and morphology.

1.7 Thesis outline

The thesis is divided into five chapters as outlined below.

Chapter 1 Introduction: this chapter deals with an introduction about supply of clean water; wastewater and part of it, source of pollution and its consequence on living things and surrounding environment, and the prefer way of treatment mechanism. The determination for this study was described in the statement of problem part and the general as well as specific objectives of the study were also covered.

Chapter 2 Literature Review: this chapter devoted to describe the relevant research works that have been done by previous researchers. The effects of different factors on the process have been discussed in conjunction with the data acquisition and processing which were employed. Overall, this chapter is dedicated in appraising and highlighting previous study and providing theoretical framework for this study.

Chapter 3 Materials and Methods: presents the data acquisition and processing used in this project to achieve the objectives compared to the previous researches. All experiments in this study were designed explicitly. Details of each experiment work, including sample collection and preparation, qualitative analysis.

Chapter 4 Results and Discussion: This chapter details the laboratory studies for the optimization of pH and the performance of different Mg^{2+} : PO_4^{3-} molar ratio for production of MAP and removal of NH_4^+ and PO_4^{3-} .

Chapter 5 Conclusion and Recommendations: draws conclusion and provides recommendation for future research investigations in this filed.

2 Literature review

2.1 Wastewater

Safe drinking water and proper sanitation have constantly been recognized as essential factors to sustain life. Nevertheless, despite remarkable global progress to improve access to drinking water facilities, currently there are millions and an additional billions people lacking improved water sources and sanitation respectively (Schwarzenbach *et al.*, 2010). This crisis is further compounded by factors such as increasing poverty, accelerated population growth and rapid urbanization coupled with hydrological variability and climate change. These socio-economic and environmental factors place even further stress on the deteriorating water and sanitation infrastructure, more so in developing regions, where billions are still at risk of Water, Sanitation and Hygiene (WaSH) related diseases. Despite meeting the Millennium Development Goals regarding access to potable water, the depletion of existing finite water resources still continues to be a major problem. This together with the above named factors serve as the major driving force behind the increased use of wastewater, surrounding surface water and grey water for various recreational, agricultural and aquaculture activities (Naidoo and Olaniran, 2014).

2.1.1 Wastewater characteristics

Wastewater generally contains high levels of organic material, numerous pathogenic microorganisms, as well as nutrients and toxic compounds. It thus entails environmental and health hazards and, consequently, must immediately be conveyed away from its generation sources and treated appropriately before final disposal (Cabral, 2010). The ultimate goal of wastewater management is the protection of the environment in a manner commensurate with public health and socio-economic concerns. Fundamental studies in the fields of chemistry and microbiology and findings from research into process techniques provide the foundations on which new methodologies for planning and laying out wastewater treatment systems are currently built (Turkar *et al.*, 2011).

2.1.2 Wastewater treatment technologies

There is agreement that more effective wastewater treatment technologies are needed for the removal of recalcitrant pollutants that are increasingly encountered in both domestic and industrial effluents. This is mainly due to the need for environmental protection on one hand, and the need to have cost-effective wastewater treatment technologies on the other (Bello et al., 2017b). Driven by these reasons, industries have intensified efforts to adopt cleaner production using strategies such as zero-discharge (Tabassum *et al.*, 2015), process modifications (Zhang and Wang, 2015) and other appropriate methods. Adopting zero-discharge through wastewater reuse is attractive (Othman *et al.*, 2014) as it can lower production cost and ensure environmental sustainability. Unfortunately, conventional wastewater treatment technologies are not effective in degrading recalcitrant pollutants which are hydrophobic and generally of high molecular weight (Pouran *et al.*, 2014). Thus, the last few years have seen increased research towards developing treatment technologies that can degrade recalcitrant pollutants while meeting the cost-effectiveness needed by industries. Among the possible technologies for treating recalcitrant wastewater, Advanced oxidation processes (AOPs) have received wide attention. Another attractive technology is biological treatment which is widely used to treat both domestic and industrial wastewaters. While interest on AOPs is due to their effectiveness in degrading recalcitrant pollutants, biological processes are considered inexpensive and eco-friendly. In either case, an effective contacting device is essential for proper application of the technology (Oturán and Aaron, 2014).

2.1.3 Wastewater treatment processes

Most wastewater treatment plants worldwide could be operated as a three- step process in order to make the effluent suitable for discharge or reuse. The three-step process includes Physico-chemical treatment, biological treatment, and tertiary treatment.

2.1.3.1 Physico-chemical treatment

The main purpose of the physico-chemical treatment is to reduce any settleable solids, as well as oils, grease, fats, sand and grit within the wastewater via settling and sedimentation processes. The steps involved in physico-chemical treatment are entirely mechanical and by means of

filtration and sedimentation (Slavov, 2017). After initial screening to remove larger debris, wastewater still contains dissolved organic and inorganic constituents as well as suspended solids which are removed via the process of primary settling, sedimentation, chemical coagulation or filtration. This allows for separation of the solid and liquid phases in the wastewater by removing those settled organic solids as well as any floating materials such as fats, oil and grease (Naidoo and Olaniran, 2013a). Wastewater enters a sedimentation tank, where the flow rate gradually slows down, enabling the wastewater to settle in these settling tanks which have been designed to hold the wastewater for several hours. During this time, most of the heavy solids fall to the bottom of the tank forming primary sludge thereby reducing the suspended solid content of the wastewater. In addition, any surface floating materials is usually siphoned off (Sandra *et al.*, 2017).

2.1.3.2 Biological treatment

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

Aerobic versus Anaerobic treatment

Aerobic biodegradation involves in the presence of air (oxygen); while anaerobic means in the absence of air (oxygen). These two terms are directly related to the type of bacteria or microorganisms that are involved in the degradation of organic impurities in a given wastewater and the operating conditions of the bioreactor (Yoshikawa *et al.*, 2017). Therefore, aerobic treatment processes take place in the presence of air and utilize those microorganisms (also called aerobes), which use molecular/free oxygen to assimilate organic impurities i.e. convert them in to carbon dioxide, water and biomass (Han *et al.*, 2011). Anaerobic treatment on the other hand, is used to treat high concentration of biodegradable contaminants in wastewater such as domestic sewage, animal manure slurry, and wastes from bio-solids and food processing. This process is known as the primary method for protecting the environment and preservation of resources because it provides a sustainable wastewater treatment when combined with another appropriate system. The process stabilizes water with little production of biomass.

Anaerobic process can be divided into hydrolysis (an enzyme-mediated conversion of complex organic compounds into simple product such as amino acids and sugars), acidogenesis (conversion of the simple products into simple organic acids such as acetic acid and propionic acid) and methanogenesis (conversion of the organic acids into biogas (methane and carbon dioxide). Hydrolytic microorganisms use a hydrolytic enzyme to create a suitable environment for acid forming bacteria. The acid formers are microorganisms that involved in acidogenesis and produce various acids while microorganisms involved in methanogenesis are known as methane formers as they convert acids into methane (Jia and Yuan, 2016).

2.1.3.3 Tertiary treatment

Tertiary wastewater treatment includes odor management, disinfection, filtration, lagooning, nitrogen and phosphorus removal and recovery. The removal and recovery of nitrogen and phosphorus has been a critical issue. It is well known that excessive amount of nutrients like ammonium (NH_4^+) and phosphate (PO_4^{3-}) will result in severe environmental problems, such as, eutrophication, contamination of land and underground water (Andrea *et al.*, 2015, Battistoni *et al.*, 2005).

Nitrogen removal

Biological (activated sludge) treatment is the most commonly used process for nitrogen removal in wastewater treatment plants (WWTPs). There are two steps for removing nitrogen in biological treatment, nitrification and denitrification. In this process, nitrifiers, including ammonia-oxidizing bacteria (AOB) and nitrite-oxidizing bacteria (NOB), convert total ammonia (free ammonia and un-ionized ammonia) to nitrate. Denitrification happens in an anoxic environment in which denitrifiers reduce nitrate and nitrite to nitrogen gas. It takes 4.57 grams of O_2 to oxidize per gram of total ammonia to nitrate (Qian *et al.*, 2016). Physicochemical, ammonia removal from highly concentrated wastewaters can be accomplished by air or steam stripping.

Ammonia stripping is the best known with the most extensive applications in concentrated wastewater treatment, while very few applications in sewage treatment are known. In ammonia stripping, lime or some other caustic substance is generally added to the wastewater until pH

reaches 10.8-11.5 standard units, converting ammonium hydroxide ions to ammonia gas according to equilibrium reaction (Lee *et al.*, 2003).

2.2 Scheme of wastewater management in Addis Ababa

The major categories of the Addis Ababa city dwellers contributing to liquid wastewater production and pollution of the environment are: domestic households, industries, public toilets, hotels, hospitals and institutions. From domestic sources, quite a significant quantity is generated each day (MoWIE, 2017). Domestic liquid waste from overflowing and seeping pit latrines, septic tanks, public and communal toilets, open ground excreta defecation, etc. comprise the municipal liquid waste. It is estimated that approximately 57,400 cubic meter waste water is produced in Addis Ababa per day from domestic activities such as bathrooms and kitchens alone as 80% of the consumed water is disposed in the form of waste. In addition to this 30% of the city dwellers have no facility at all to dispose of their liquid waste (Mohamed and Elsa, 2003). The city administration is only capable of treating 10% of the liquid waste produced in the municipality. So, sanitation and sewerage management and disposal is a serious socioeconomic problem of the city as the system is not well developed (Mohammed and Elias, 2017).

2.3 Domestic wastewater management in Addis Ababa

The absence of proper sewage networks line and treatment plants complicates the collection and treatment of wastewater in Addis Ababa. It has a very limited sewer network coverage accounting for 7.5% of the built-up areas (MUDHCo, 2012). Since parts of the older sections of the city are only connected to the central sewer system, both residential and business premises use septic tanks although their availability is severely limited in many of the old neighborhoods (MUDHCo, 2015). Even though the city has a centralized sewerage system (sewer line) and two wastewater treatment plants (at Kotebe and Kality) they are currently operating below their capacities of 350 and 40,000 cubic meters per day respectively due to inefficient waste collection. Nowadays it can be said Kality site is the only functional wastewater treatment plant. The majority of the transportation service is covered by private vehicle owners and investors.

2.4 Introduction to phosphorus in the environment

Undesirable changes in the freshwater environment in some countries led to a growing concern for the aquatic environment in general. These changes were considered to be related to the increasing concentration of nutrients in the water. Nutrients are essential for plant growth in all ecosystems, as much in water as on land. The natural nutrient status of a water body such as a lake depends on its size, depth, geology, retention time and the use of land in its catchment area. Some soils release more salts and nutrients than others and therefore different water bodies in their natural state can be at different trophic, i.e. nutrient concentration, levels (Betts *et al.*, 2018). However, this term has become associated with adverse water quality and is now frequently used to describe the negative consequences of nutrient enrichment. Nitrogen, phosphorus, carbon and, in some cases, silicon are the nutrients of most concern in relation to eutrophication. However, because phosphorus is the most limiting nutrient in the fresh water environment, it attracts the most attention when the problem of eutrophication is considered in relation to fresh water (Walter *et al.*, 2017).

2.4.1 Phosphorus: waste or resource? A historical perspective

As long as people lived together in relatively small groups, nature could break down their waste products without any problems. When people started to live close together in bigger settlements, their liquid and human waste became a burden. During the process of urbanization in the second half of the 19th century the amount of human waste within the city limits became problematically large and led to problems with public health.

Human waste was collected with buckets and, analogue to animal wastes which have been known for centuries to be beneficial for the land, transported to agricultural fields. In several cities this was replaced by a system of vacuum sewers, sucked empty by the Liernur vacuum pump truck. With the construction of the first wastewater treatment plants in the first decade of the 20th century, the wastewater no longer found its way back to the agricultural fields, but was channeled to the wastewater treatment plants (Henze *et al.*, 2008). Although the upcoming of the municipal wastewater treatment plants offered much improvement in terms of removal of organic pollutions with respect to nutrients a new problem was created. The early versions of wastewater treatment did not comprise of nutrient removal schemes, and phosphorus and

nitrogen derived from human waste ended up in local high concentrations in receiving water bodies (Demirbas *et al.*, 2017). This process of discharging the nutrient-rich effluent into sensitive water bodies led to eutrophication.

Phosphorus removal from wastewater implies the transformation of dissolved phosphorus to a solid phase, typically sludge. For a long time, the phosphorus-rich sludge was transported from the wastewater treatment plant to the agricultural plots, and the nutrient cycle- is more extended remained more or less intact. However, for a number of reasons independent from phosphorus contents, agricultural re-use of sewage biosolids is diminishing throughout Europe (Omoike and Vanloon, 1999) This break in the nutrient cycle is twofold problematic. First, it means that phosphorus needs to be mined more intensively. With phosphate rock being a finite resource, this is an unsustainable practice. Second, another pathway to dispose of the biosolids has to be found. Typically this is done by incineration, where phosphorus ends up as sludge incineration ash in a landfill. To reach a more sustainable situation, phosphate from waste streams should be recovered rather than being disposed. Making use of recycling or reuse processes is not only good practice from an environmental and sustainability point of view. But also the current price developments for raw phosphate rock, recycling also becomes essential from an economical viewpoint. The recovery of phosphate for recycling can be done at several locations within the wastewater treatment process. The recovered phosphorus can become a recycling product within the phosphate industry.

2.4.2 Applications of phosphorus in agriculture

Phosphorus is a critical nutrient for the agricultural production and living organism survival (Ryan *et al.*, 2012). Agriculture has seen many revolutions, whether the domestication of animals and plants a few thousand years ago, the systematic use of crop rotations and other improvements in farming practice a few hundred years ago, or the “green revolution” with systematic breeding and the widespread use of man-made fertilizers and pesticides a few decades ago (Schröder *et al.*, 2010a).

Fertilizers have been largely responsible for the massive increases in world food production in the past half century that permitted accelerated global population growth to current unprecedented levels (Kebreab *et al.*, 2013). Attention to sustainable phosphorus use is no longer

solely focused on reducing detrimental environmental impacts, but also explicitly linked to food security. That is sustainable phosphorus use must ensure that all the world's farmers have sufficient accesses to phosphorus in the long to produce enough food to feed humanity's (Dhakal, 2008).

2.4.3 Applications of phosphorus in animal feeding

Phosphorus (P) is an essential macro-mineral necessary for many body functions and needs to be supplied in sufficient quantities to optimize animal performance. Phosphorus and calcium are the two most plentiful minerals in ruminants (Finkler *et al.*, 2018); as well as, Phosphorus is one of the vital elements needed for animal growth and milk production including in metabolic activities in soft tissues, the maintenance of appetite, optimal growth, fertility, bone development and the prevention of bone diseases. In many cases excess phosphorus is used in order to maximize the production of livestock. However, feeding excess phosphorus increases phosphorus levels in animal waste streams. Only 14 percent of phosphorus in corn and 31 percent of soybean meal phosphorus can be digested by swine. Because a large percentage of phosphorus is unavailable, much of it is excreted. To overcome the limited availability excess phosphorus is fed to animals. The waste stream is therefore very rich in phosphorus (Amann *et al.*, 2018).

2.4.4 Sources of Phosphorus in streams

Streams are biogeochemical active systems that alter the amount and chemical form of nutrients and organic matter transported from their catchments to downstream systems (FN and MF, 2017). Under natural conditions phosphorus (P) is typically scarce in water. Human activities, however, have resulted in excessive loading of phosphorus into many freshwater systems. Water quality can be further reduced when bacteria consume dead algae and use up dissolved oxygen, suffocating fish and other aquatic life. Under normal water flows, roughly two-thirds ($2/3$) of the total phosphorus load to lakes and rivers comes from nonpoint sources such as runoff from pasture and croplands, atmospheric deposition, stream bank erosion, urban runoff, non-agricultural rural runoff and seepage from individual sewage treatment systems (Sarvajayakesavalu *et al.*, 2018).

On the other hand, the remaining load of phosphorus to stream come from identifiable source (point source) like ditch, pipe industry, storm drain and sewage treatment plants.

Phosphorus deposited in the oceans via natural runoff will eventually be transformed into sediments and rock formations over millions of years, to be eventually, released again through weathering, and the cycle starts over. Societal need to produce food for a continually growing population has interrupted this natural Phosphorus cycle by converting mined and relatively inactive phosphorus rock (PR) into a range of more soluble and reactive Phosphorus compounds that have increased the bioavailability of Phosphorus to crops, animals, and humans, and for use in industry (FN and MF, 2017).

2.4.5 Impacts of excessive phosphorus in water streams

Wastewaters contain a high amount of organic matter, nitrogen and phosphorus, a considerable amount of Magnesium, different macro and microelements, and heavy metals due to which it is considered as one of the major polluting agents discharged into the environment; these pollutants come from anthropogenic, livestock, natural or industrial sources (Rahman *et al.*, 2014). The input of high-concentration phosphorus wastewater leads to serious deterioration of surface water bodies, which can lead to the death of aquatic organisms and have negative effects on natural, economic, and social systems (Ghayebzadeh *et al.*, 2015).

2.4.6 Phosphorus removal

Removal of phosphorus from wastewater can not only prevent nutrient enrichment of streams, but recovery from the wastewater streams can also lengthen the availability of a finite resource. There are two processes applied to remove phosphorus, namely chemical process and biological process. Biological phosphorus removal is accomplished through a process commonly known as Enhanced Biological Phosphorus Removal (EBPR). In an EBPR-activated sludge plant, the influent wastewater sequentially flows through an anaerobic zone and aerobic zone, after being mixed with the returned activated sludge (RAS) from the clarifier to form the mixed liquor (Sartorius *et al.*, 2011).

The cycling of the microbial biomass along with the influent wastewater through anaerobic and aerobic zones brings about a selection of microorganisms having a high capacity to accumulate polyphosphate intracellular in the aerobic period (Goel and Motlagh, 2013). This group of bacteria is known as polyphosphate accumulating organisms (PAOs). They are inoculated into sludge and are then subjected to cycles of carbon-rich anaerobic and carbon-poor aerobic zones. In the anaerobic zone, PAOs store readily biodegradable organic compounds from the wastewater intracellular in the form of glycogen and poly hydroxyl alkanoates (PHA), the energy for which is derived from converting polyphosphate (ATP) into orthophosphate.

In the subsequent aerobic zone, the PAOs metabolize the stored glycogen and PHA, and the energy released from this process is used to take up orthophosphate back into the cell and convert it to polyphosphate (Tarayre *et al.*, 2016). The amount of orthophosphate taken up in the aerobic zone ends up being more than what was released in the anaerobic zone, thus reducing the overall phosphorus concentration of the wastewater. A settling period allows the microbial population to sediment. The sludge, now high in organic matter and microbial content, is wasted, recycled or used for biogas production.

As with chemical phosphorus removal, the sludge is removed using a solid/liquid separation step (Bunce *et al.*, 2018). The chemical process is based on the precipitation of phosphorus using salts. The most common chemical Phosphorus removal options involve dosing metal salts to either pre-treated influent, conventional activated sludge (CAS) reactors, or to the outlet from the secondary clarifier. Mechanism of Phosphorus Precipitation is done by the added salt (e.g., trivalent metal salts, ferric chloride) to precipitates Phosphorus in the wastewater and resulting solids residuals are removed either by settling under gravity or by filtration (Ateeq, 2016).

2.4.7 Comparison of phosphorus removal techniques

Starting 1950s, technologies started too developed for removal of phosphorus in response to the issue of eutrophication (Morse *et al.*, 1998). Technologies include chemical precipitation, biological phosphorus removal, and crystallization which are most common for phosphorus removal and recovery from wastewater. Studies show that an average 0.6 mg/l of total phosphorus in the effluent can be attained by chemical precipitation that is alum at an average

dose of 45 mg/l (Patoczka, 2005). In real wastewater, crystallization can remove 45 mg/l of phosphorus to 6 mg/l of phosphorus within a pH value of 8.7 (Wang *et al.*, 2003).

Biological phosphorus removal technology can remove 6 mg/l of average influent total phosphorus concentration to 1.5 mg/l of total (Park *et al.*, 1997). Waste stabilization and phosphorus removal may potentially be addressed with low-rate aeration and struvite precipitation. Struvite has numerous benefits; it's highly stable crystal structure, providing three essential nutrients at sustained low release rates. A viable market value has not developed for struvite so far due to the limited amount produced, and the low cost of fertilizers produced from phosphorus rich mineral rock, which are finite. As resources decrease and if a struvite generation stream exists value will increase as struvite is a desired fertilizer. The “waste to product” potential is particularly attractive for struvite overall.

2.5 Ammonium and phosphate recovery by the precipitation of struvite

The most intensively studied technology for recovery of ammonium and phosphate is a crystallization process through chemical precipitate reaction among ammonium, phosphate, and magnesium in wastewater. Due to this crystallization reaction, the precipitates addicted to the inner surface of pipes and resulted in blockage (Ohlinger *et al.*, 1998).

The chemical species that may be formed in solution are probably $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ (newberyite), $\text{MgNH}_4\text{PO}_3 \cdot 6\text{H}_2\text{O}$ (MAP), $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ (bobierrite) and $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$. Ca^{2+} is another most common cation reacting with PO_4^{3-} to form following compounds: $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ (hydroxyapatite), $\text{Ca}_3(\text{PO}_4)_2$ (Whitelockite), $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ (Brushite), CaHPO_4 (Monenite), $\text{Ca}(\text{OH})_2$, $\text{Ca}_8(\text{HPO}_4)_2(\text{PO}_4)_4 \cdot 5\text{H}_2\text{O}$ (Octacalcium phosphate). Furthermore, MgCO_3 (Magnesite), $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ (nesquehonite), $\text{CaMg}(\text{CO}_3)_2$ (dolomite), $\text{CaMg}_3(\text{CO}_3)_4$ (hunite), and $\text{Mg}(\text{OH})_2$ (brucite) may also be precipitated in the solution under certain conditions (Demirer and Maazuza 2009). Some of the chemical which contains NH_4^+ and PO_4^{3-} used as fertilizers such as $\text{MgNH}_4\text{PO}_3 \cdot 6\text{H}_2\text{O}$, $\text{Ca}_3(\text{PO}_4)_2$. Not this method can only remove NH_4^+ -N and PO_4^{3-} -P at the same time, but also recover these two nutrients in a sustainable manner (Jia, 2016).

2.6 Formation of struvite

$MgNH_4PO_4 \cdot 6H_2O$ (crystal form), which tells as that struvite crystals are created when Ammonium, magnesium and phosphate combine in water in a mole to mole ratio of 1:1:1. Wastewater treatment plants, wastewater temperature and its pH are also contributing factors to struvite precipitation. The higher the wastewater pH the more likely the mole to mole to mole balance will be affected and the formation of struvite crystal will occur (Rahaman, 2009). Though, this does not mean continued increases in pH are associated with struvite crystal, because at higher pH ammonia is changed in to gas due to detachment of ammonium ions in the reaction solution. This phenomenon has a negative effect on struvite precipitation. Struvite crystallization can be formed either spontaneous or intentionally. Spontaneous struvite formation most likely occurs in pipeline locations (such as junctions, elbows, etc.) where carbon dioxide stripping and causing pH raise, which in turn causes clogging of pipelines and pumps that eventually leads to process failure and economic loss . In contrast, intentional struvite formation is now getting more attention as it has numerous advantages, including serving as slow released fertilizer, reducing sludge volume, removing phosphorus and nitrogen simultaneously, replacing natural phosphate used in industries, and avoiding pipe clogging/treatment failures (Fang *et al.*, 2016).

In the precipitation crystallization reactions, the primary processes involved are firstly, the nucleation, which determines the initial formation of the particles and secondly, their subsequent growth. The growth determines the size of the crystals. Other secondary processes such as agglomeration and breakage of the particles are also likely to take place in the crystallization processes. Moreover, many factors affect the process of struvite crystallization, like the initial concentration of phosphorus, the molar ratio of Magnesium and Phosphorus , the solution PH value, coexisting ions (such as calcium ion, carbonate ion, suspended solids and heavy metal ions). The initial concentration of phosphorus could determine if struvite could be formed because of the limited struvite solubility product (K_{sp}) constant 10-13.26 (at 298 k and standard atmospheric pressure). Solubility products are generally reported as the negative log of the solubility product or pK_{sp} .

$$K_{sp} = [Mg^{2+}][NH_4^+][PO_4^{3-}]$$

The molar ratio of Magnesium and Phosphorus is 1.0 in theory, but this ratio is always over 1 for the extra consumption of other coexisting ions (like OH^- and CO_3^{2-}). The solution pH value influences the Phosphorus forms and dominant crystal type. The crystal can be struvite only under the pH value between 7.0 and 10.0. Otherwise, $\text{Mg}_3(\text{PO}_4)_2$ or $\text{Mg}(\text{OH})_2$ could be formed at a higher pH value. The coexisting ions could reduce the size of struvite, change crystal growth direction, or delay the nucleation rate and the growth rate of struvite (Lee *et al.*, 2009).

2.6.1 Physical and chemical nature of struvite

A crystal form of an equal molar concentration of magnesium, ammonium, and phosphate combined with six water molecules of struvite has a molecular weight of 245.43 g/mol , and it is carefully soluble under natural and alkaline conditions but readily soluble in acid (Munch and Barr, 2001). Struvite is also defined by way of a soft mineral with a low specific gravity 1.7, which is not flown away by rainfall, and can be successfully used as fertilizer in flooded areas (Adnan *et al.*, 2003a). Pure struvite occurs by means of white crystalline powder; on the other hand also can occur either as large single crystals, very small crystals, curds or a gelatinous mass. Sometimes it appears as tight aggregates of fine crystals. The average sizes of the crystals ($2 \pm 3.8\text{mm}$) were found by (Rahmana *et al.*, 2011). He stated that, the crystal growth size was influenced by the influent phosphorus concentration and particle retention time in the reactor. He also report that the crystal growth rate was 0.173 mm/d with influent Phosphorus concentration ($> 200\text{mg/l}$) and 0.061mm/d for a low influent Phosphorus concentration ($34 \pm 100 \text{ mg/l}$). Chemically, struvite is carefully soluble under neutral conditions, but highly insoluble in alkaline media (Ali and Schneider, 2008).

2.6.2 Background theory of struvite nucleation

Struvite or magnesium ammonium phosphate hexahydrate (MAP) was first found in wastewater in 1939 and since then its consequence is well known for clogging of pipe, fouling pumps, aerators, screens, and other equipment (Ohlinger *et al.*, 1999). The nucleation and crystal growth stages are the two chemical phases responsible for occurrence and enlargement of struvite crystal. Forecasting these stages are complex phenomenon, as it is controlled by a combination of factors such as thermodynamic of liquid-solid equilibrium, phenomena of mass transfer between solid and liquid phases (Rahman *et al.*, 2014) and kinetics of reaction (Topare *et al.*,

2011). The nucleation relates to the specter of new particles. Numerous mechanisms are possible for struvite crystallization depend on the supersaturating level in the crystallizer. Homogeneous primary nucleation relates to nuclei specter (apparition) directly in the supersaturated solution.

Heterogeneous primary nucleation takes place on foreign surfaces, which can be dust in suspension. Surface secondary nucleation (called true secondary nucleation), needs to have already suspension particles of the same specie as the solid which is crystallized.

Certainly, surface secondary nucleation corresponds to the nuclei formation on the surface of these particles. The new born surface nuclei are then detached by the shear exerted by the fluid. Among the different nucleation mechanisms, homogeneous primary nucleation requires the highest super saturation level to spontaneous development. It is followed by heterogeneous primary and secondary nucleation respectively. Several physic-chemical parameters also influence these mechanisms such as pH, of the solution, super saturation, mixing energy, temperature, and presence of foreign ions. Free Mg^{2+} , NH_4^+ and PO_4^{3-} ions react to form struvite are subjected to a range of speciation in a standard pH. It is therefore, important to understand the equilibrium to calculate the free ion concentrations and other thermodynamic properties during crystallization. Mixing effect occurs if the reaction and crystallization kinetic rates are faster, resulting in competition among mixing, reaction, and nucleation. In this case mixing kinetics show a strong effect on the number crystals formed and consequently, on their size (Naidoo and Olaniran, 2013b).

2.7 Key factors influencing MAP crystallization process

MAP crystallization is a complex process that includes nucleation and crystal growth and is affected by a combination of physicochemical factors such as supersaturation, pH, Effect of Mg^{2+} : (NH_4^+ -N): (PO_4^{3-} -P) on struvite crystallization, temperature, coexisting foreign ions.

2.7.1 Supersaturation

Supersaturation is measured to be one of the driving forces for all crystallization processes (Pastor *et al.*, 2008). It mainly affects the induction time of crystallization and the crystal growth rate (Le Corre *et al.*, 2009b). (Kofina and Koutsoukos, 2005) discovered the role of supersaturation in crystallization in a study of spontaneous precipitation of struvite from

synthetic wastewater systems. Their results suggested that the induction time of struvite formation is inversely proportional to the solution supersaturation and corresponded well with the dependence calculated by the classical nucleation theory. Moreover, the high order (>1) of dependence of crystallization over the solution supersaturation indicated a surface diffusion controlled mechanism for struvite formation.

2.7.2 Effect of pH

Both industry practices and laboratory experiments have demonstrated that pH is one of the most important factors in the struvite crystallization process also it is one of a predominant operating factor which has significant impact on driving the precipitation reaction, and importantly precipitate formation and crystallization. In order to maximize the struvite formation efficiency and purity, pH must be maintained at certain range. The precipitate formation of struvite normally occurs at increasing pH medium, and the optimal pH value for struvite crystallization is reported in the range 8.0-11 (Folettoa *et al.*, 2013). The solubility of struvite decreases with increasing of pH, thus facilitating higher P & N removal and recovery for a given feed strength.

In another study (Zhang and Chen, 2009) conducted experiments with landfill leachates with molar ratio of $Mg^{2+}: NH_4^+: PO_4^{3-} = 1:1:1$. They found that the optimal pH was 9.5. NH_4^+ removal efficiency was lower at pH less than 9.5. However, $Mg_3(PO_4)_2 \cdot 22H_2O$ and $Mg(OH)_2$ rather than struvite were crystallized when pH was higher than 9.5. (Nelson *et al.*, 2003) compared results of experiments from two treatment plants and found that the best pH value for struvite precipitation was 8.9 and 9.25 respectively. They also reported that the best pH was not affected by the molar ratio of $Mg^{2+}; PO_4^{3-}$ removal was significantly affected by pH. pH is a critical factor for MAP crystallization, which determines the equilibrium concentration and type of the MAP formation ion. As shown in many scholars, the recovery rates of N and P rapidly increased with the increase in the pH ranging from 8 to 9.

When the pH value further increased to 10, the recovery rate of P become decrease; whereas the recovery rate of N slowly increased when the pH value was higher than 9.0 (Gong *et al.*, 2018a). This difference can be explained by the following reason: when pH is above 9, NH_4^+ can deprotonate into NH_3 and this result in NH_3 vaporization that inhibits the MAP crystallization process, thus increasing the recovery rate of N. In previous studies, (Booker *et al.*, 1999) found

the optimum pH for struvite formation in wastewater treatment plants was 9.2, and (Liao *et al.*, 1995) indicated that the optimum pH for struvite formation in synthetic wastewater treatment was 10.5. pH has also a significant effect on struvite crystal size and purity. (Hutnik *et al.*, 2016) demonstrated that an increase of pH from 8 to 11 could decrease five times the mean crystal size of struvite formed in synthetic solutions ($\text{NH}_4\text{H}_2\text{PO}_4/\text{MgCl}_2/\text{NaOH}$). They also stated that an increase of pH from 9 to 11 decreased the crystal size by more than 2 times in a continuous flow struvite crystallizer. It is recognized through several researches that a comparative higher pH reduces the struvite crystal size within the same reaction time.

2.7.3 Effect of Mg^{2+} : (NH_4^+ -N): (PO_4^{3-} -P) on struvite crystallization

The stoichiometric ratio of ($\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$) also influenced the purity and quality of the obtained products. For the MAP crystallization, NH_4^+ , Mg^{2+} and PO_4^{3-} are removed according to the stoichiometric relationship 1:1:1 theoretically. However, in order to improve phosphorus removal rate, NH_4^+ and Mg^{2+} need to be excessive. It is found that the phosphorus removal rate increased with the increase of NH_4^+ concentration. The concentration of ammonia nitrogen in wastewater is generally high, so it is necessary to add Mg^{2+} . When dosage is insufficient, the removal of nitrogen and phosphorus in wastewater is not complete. While dosage is excessive, it will not only increase the processing cost, but also cause secondary pollution.

Most of the studies found a wide range of PO_4 and Mg ratio applied for struvite precipitation, but (Xuan My *et al.*, 2017) demonstrated their experiment from Piggery wastewater, the optimum struvite crystallization was occurred when the $\text{Mg}:\text{PO}_4$ molar ratio as (1.2:1) at pH value of 9. (Dogan *et al.*, 2018) Showed result from landfill leachate by using series of experiments to see the effect of Mg, NH_4 and PO_4 ratio on struvite precipitation, they found maximum ammonium removal efficiency (99.8) at molar rate of 1.2 for Mg/N and 1.27 for N/P for a constant 9.2 pH value. (Zhang *et al.*, 2009) compared different chemical combinations of Mg^{2+} and PO_4^{3-} , and concluded that the combination of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ could lead to the highest ammonium removal. (Pastor *et al.*, 2008) reported that the removal efficiency could be higher than 80% and would be increased further by increasing magnesium to phosphorus molar ratio.

(Lee *et al.*, 2009) also concluded that continuous formation of struvite can be obtained when the molar ratio of magnesium and phosphate is either more than 0.07M (Mg/P) or less than 0.05M (Mg/P). The amount of struvite increased with an increase in magnesium concentration under magnetic stirring and aeration (Quintana *et al.*, 2005).

2.7.4 Effect of temperature

In addition to pH and other operation parameter, temperature is one of the operating parameter which directly affects the solubility of crystal solid (the struvite precipitation chemistry) and thus affects struvite production and crystal morphology. Previous author studied that in the MAP formation processes the majority of crystallization was newberyite rather than struvite when the temperature was risen from 25°C to 37°C (Abbona *et al.*, 1982). Temperature affects the solubility of chemicals and reaction activities in the solution. Controlling temperature in MAP crystallizers ensures the purity of the recovered struvite. Theoretically, at low temperatures (5–20°C) the solubility of struvite decreases. Consequently, this results leads in the precipitate struvite smaller particles size (Darwish *et al.*, 2016). On the other side, struvite is significantly affected by high temperatures. As found by (Chen *et al.*, 2015), the structure of struvite crystals is stable under temperatures less than 55°C, at which mass loss begins. This is because solubility of struvite increases with increasing temperature. Accordingly, struvite should be dried at a temperature between 30–50°C to avoid mass loss and phase transformation (Darwish *et al.*, 2016).

It shows a gradual decrease of some ammonia and was partially transformed into bobierite when it was boiled with a temperature less than or equal to 100 °C for 24 hr. (Hanhoun *et al.*, 2011) similarly developed a thermodynamic model for struvite precipitation to investigate the phosphate conversion rate and assess struvite solubility between 15°C and 35°C, he reported that struvite reaches its minimum solubility at 30°C. Boiling struvite in excess water resulted in the loss of five water molecules from its structure and transformed into the monohydrate (dittmarite). As a result, dittmarite contains a higher P₂O₅ (45.7%) or P (19.9%) whereas, struvite contains only 28.9% P₂O₅ or 9.8% P (Bhuiyan *et al.*, 2008). The conditions for the transformation of struvite to dittmarite could be exploited for intentional dittmarite formation that would extend the field of P recovery from wastewater.

2.7.5 Coexisting foreign ions

Compared with other well-known factors, few studies have been showed to examine the influences of foreign ions on MAP crystallization. (Kabdazsli et al., 2006b) evaluated the effects of Na^+ , SO_4^{2-} , CO_3^{2-} , and Ca^{2+} ions on the induction time of struvite formation by means of absorbance measurements, and monitored the pH and conductivity of solutions. Their results demonstrated that all of the tested ions retarded the induction time of struvite crystallization, but only a minor effect was observed from the carbonate ions. (Le Corre et al., 2005a) conducted a series of struvite precipitation experiments to estimate the mechanism by which calcium ions affect struvite's shape, crystal size, and purity. The pH was measured in the entire reaction process and used as an indicator of struvite's crystallization rate. Struvite's purity was determined with the energy-dispersive X-ray method, based on the comparison of elemental distribution. (Muryanto and Bayuseno, 2014) studied the kinetics of MAP crystallization and found that both Zn^{2+} and Cu^{2+} inhibited the MAP crystallization rate in trace amounts (0–5 ppm). Due to coexisting ions in wastewater, the effects of calcium ions (Ca) on struvite crystallization are particularly concerning owing to its high concentration in most types of wastewater. The molar ratio of Ca/Mg ranges from 1.4 to 3.7 in settled sludge liquors (Parsons *et al.*, 2001b). Moreover, calcium phosphates are precipitated in an overlapped pH range of struvite formation, and hence show significant effects on struvite production.

2.8 Up flow Fluidized Bed Reactor Technologies

Fluidized bed reactor is widely applied in many industries for various applications recently. It has been found promising to use fluidized bed reactor for water treatment procedures. When the conventional treatment procedures failed to remove recalcitrant compounds in waste water, advanced oxidation processes came as a foremost choice by the researchers. However, AOPs are yet not without limitations (Tisa *et al.*, 2014). Some authors have used fluidized bed reactor with conventional treatments procedures, such as, the milk industry (Souza *et al.*, 2004) anaerobic treatment (Battistoni *et al.*, 2006). Current methods for phosphorus removal from wastewater treatment plants (biological or chemical) lead to a higher amount of phosphorus and nitrogen in sludge and spontaneous buildup of struvite in WWTP pipes. Crystallization of struvite and calcium phosphate has become a more popular and feasible option for lowering phosphorus

concentrations within the plant while simultaneously selling the products as a fertilizer to offset cost of treatment costs. Fluidized bed reactors are the most commonly used method for removal of phosphorus as a usable by-product and has been implemented worldwide (Bhuiyan *et al.*, 2008). Struvite precipitation utilizing the fluidized bed reactor can create a dense product up to 3.5 millimeters in size that solubilizes slowly when applied on agricultural land. This maximizes a crop's fertilizer utilization while decreasing waste and runoff associated with fertilizer application.

3 Materials and methods

3.1 Sample collection

The study was carried out at lab-scale. In this study, the domestic waste sample was collected from commonly called Haile Garment area in Addis Ababa from Membrane Bio-Reactor system. This waste was originated from two nearby condominiums, collected for treatment deployed by Addis Ababa Water and Sewerage Authority (AAWSA). The membrane reactor was installed in November 2015 and treats 1700m³/day of wastewater and produces an average sludge volume of 600m³/day. The effluent sludge was collected from the site using 10 liter containers then transported to laboratory. The collected waste sludge was kept undisturbed till settled at room temperature (20-25°C) about 24hrs at laboratory of wastewater (AAiT). Then the supernatants were collected for analysis.

3.2 Preparation of synthetic wastewater sample for optimal struvite recovery

In this study, synthetic wastewater was used as influent for optimizing the parameters. The reason behind using synthetic supernatant is, to avoid the fluctuations of various characteristics in real domestic wastewater and/or to optimize parameters which affect the process. The reagent salts used to prepare this synthetic wastewater were commercial grade magnesium chloride anhydrous (MgCl₂) for Mg feed, tri-Potassium phosphate 3-hydrate (K₃PO₄·3H₂O) for P feed, and ammonium chloride (NH₄Cl) for N feed.

Depending on wanted experimental conditions, different concentration of tri-potassium phosphate (2.1345mmol/L), ammonium chloride (18.788mmol/L) and magnesium chloride (3.738mmol/L) were prepared by using distilled water and fed to the reactor from a 30 L influent holding tank as used by (Guadie *et al.*, 2014).

Sodium hydroxide with low concentration (NaOH feed, 0.0125mol/L) was used to easily achieved the reaction pH to the desired value or required range as practiced by other scholars (Pastor *et al.*, 2008, Adnan *et al.*, 2004), however different pH increasing methods were stated. The aim of selected NaOH in this study was due to its more effectiveness recommended by different scholars (Adnan *et al.*, 2003b, Fattah *et al.*, 2008b).

The level of pH was monitored continuously in middle and top part of the reactor using Hanna instrument pH meter. Whenever, pH deviation was observed, the pump head rpm was adjusted to raise or lower the value.

3.3 Reactor design and operation

To study struvite nucleation and growth, continuous feed struvite precipitation experiments were conducted using a fluidized bed reactor (FBR) system. The reactor was made of easily available transparent plastic materials in order to see the entire process clearly. It had three different parts, bottom (volume 734ml, diameter 60mm), middle (volume 2647ml, diameter 85mm), and top (volume 2878ml, diameter 140mm), in which the size increased from bottom to top and the up flow velocity is highest in bottom section, and decreases for middle and top parts as cross-sectional areas increase. The total volume and height of the reactor is about 6.2 liter and 0.84 meter.



Figure 1 Fluidized bed reactor with cone and whole FBR systems

The up flow transitions served a dual purpose, to sort and classify the larger, growing struvite particles into the faster velocity fields and to bring as much as possible turbulence into the FBR. These three sections were harvest or/and reaction zones, settling zone, and top clarifier zone. The clarifier zone was placed at the top of the reactor and was designed to achieve to delay fine material and provide continuous reseeded of the reactor. The reactor design follows the concept of efficient FBR system where the cross-sectional area and up flow velocity differ in the three parts as shown in table 1.

Table 1 The dimension and operating condition of FBR

Reactor part	Length (mm)	Diameter (mm)	Area (mm ²)	Volume (ml)
Top	150	140	15386	2878
Middle	430	85	5671.625	2647
Bottom	260	60	2826	734

The rationale behind inserting conical shape structures at an angle of 45° between the parts, the varying cross-sections area, and hence, the different up flow velocities in the bench-scale MAP crystallizer were to prevent the accumulation of solid particles or/and to reducing the washout (loss) of the tiny crystals in the effluent. At the top part of the FBR, a lid was also located to decrease ammonia Stripping.

The whole layout contains eight harbors on the FBR five harbors at the bottom for feed supply and product recovery, one harbor at the middle for sample removal or/and pH control, and two harbors at the top for effluent drainage and pH control. The FBR system also contain, an external recycler with volume of 20000ml, peristaltic pump, influent (30000ml) and effluent tanks, and two chemical holding tanks having capacity of 10000ml. Whereas the entire system was continuously functioned, wastewater influent, salt and alkaline solutions were supplied to the FBR at the bottom harbors (to facilitates complete mixing) using peristaltic pumps which could be adjustable up to 99 revolutions per minute (rpm).

Before, a continuous mode of operation was functional, the flow rate capacity of each pump was checked ($1\text{rpm}=3\text{ml. min}^{-1}$) by allowing the liquid drop to measuring cylinder for one minute. As the waste containing liquid moves-up (fluidized) on different cross-sectional areas, its velocity decrease for middle and top sections leading crystals gradually getting larger and larger and separation of formed crystal. As time gone, larger particles tend to settle in the bottom portion of the reactor, while the liquid plus very fine particles were flow out from the reactor to external recycler and are recycled back with effluent through the external recycler. In addition to recycle the effluent back in to the reactor, the external reactor was also used to trap the washed out fine crystals from the reactor. Finally, the remaining liquid volume to the supernatant (effluent) tank connected by tube at the top part of the external recycler.

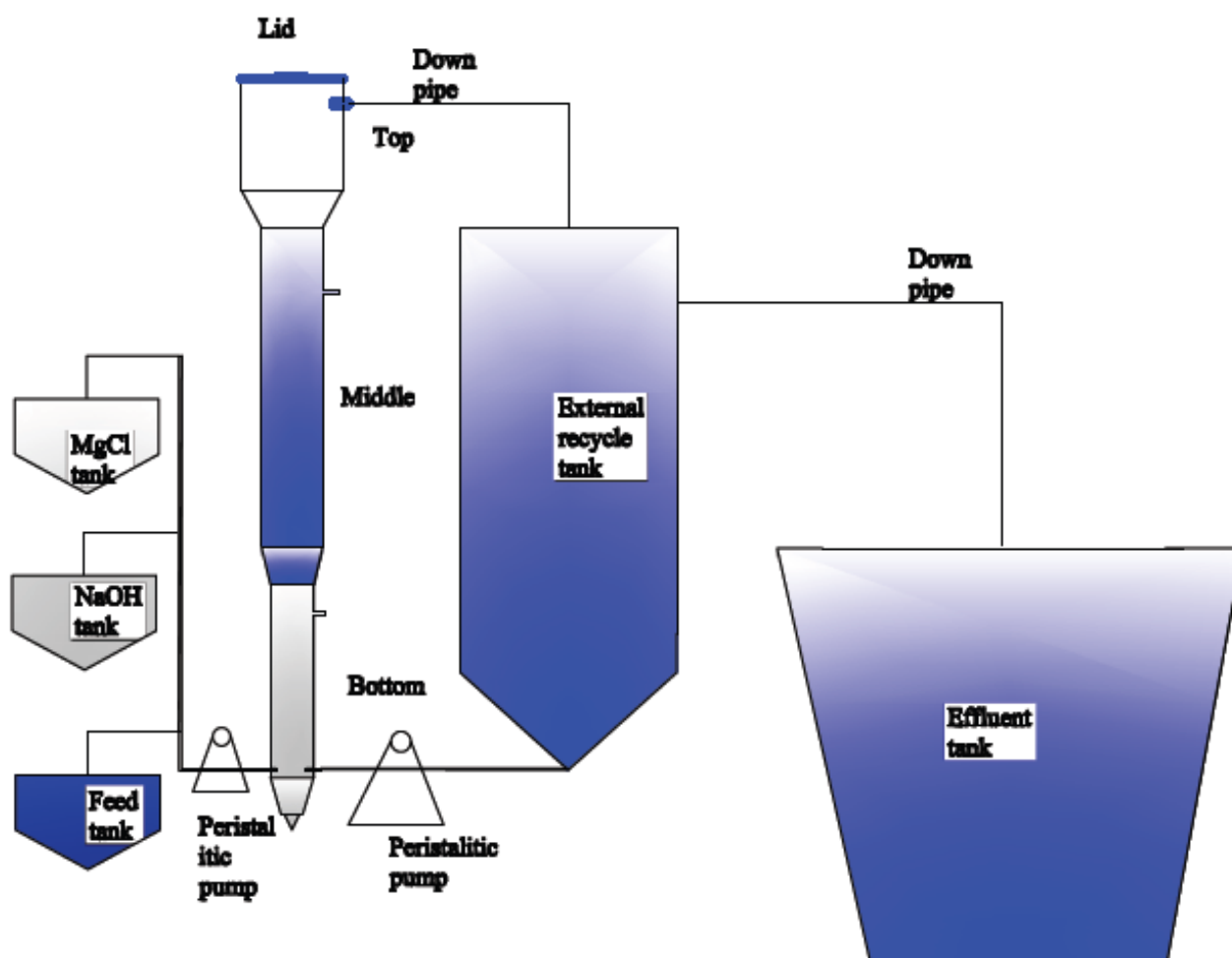


Figure 2 Schematic diagram of FBR

When an adequate amount of large crystals stored in the FBR, they were removed by opening the bottom valve. The bottom section would enhance crystal growth because of the high turbulence. The larger crystals are then harvested from the bottom section after they are big enough. This then gives the smaller crystals an opportunity to move towards the lower sections.

3.4 Experimental procedures

Experimental run was conducted from mid-January to October 2019. To have a better regulation and understanding of the MAP crystallization process, several parameters were monitored and recorded each day. For each run, different experimental settings were studied including pH (7.5, 8, 8.5, 9, 9.5 and 10), Mg/P (0.75, 1, 1.25, 1.5, and 1.75), HRT (1, 2, 3, 4, and 5hr) and settling time (15, 30, 45, 60, 75, and 90min). In each trial, the parameters were varied at 5 to 6 stages by monitoring the concentration of synthetic wastewater constituents. When one parameter was varied, the remaining parameters were kept constant. All experiments were carried out at ambient temperature.

3.5 Sampling and analyses

Influent and effluent samples were collected daily and subsequently filtered (to trap fine from the solution) for chemical analysis. Influent synthetic wastewater samples for N, and P were collected from their dosing tanks, whereas the effluent samples were collected from the external clarifiers. The components that were analyzed in this study included total ammonia-nitrogen ($\text{NH}_4^+\text{-N}$), and total orthophosphate ($\text{PO}_4^{3-}\text{-P}$). Both samples were filtered using whatman filter papers with a pore size of 125mm to remove fines from the sample. The constituents of orthophosphate-phosphorus ($\text{PO}_4^{3-}\text{-P}$) and ammonium- nitrogen ($\text{NH}_4^+\text{-N}$) were analyzed following standard methods by using UV-Visible spectrophotometer. All the analyses were done in triplicate and the results are presented as an average.

Phosphorus/nitrogen removal calculation

The percentages of P and N removals were calculated by using Equation [1]:

$$\text{P/N- removal (\%)} = (\text{P/N influent} - \text{P/N effluent})/\text{P/N influent} \times 100 \dots \dots \dots \text{Equation [1]}$$

Where P/N influent is the concentration of $\text{PO}_4\text{-P}/\text{NH}_4\text{-N}$ at the inlet and P/N effluent is the concentration of $\text{PO}_4\text{-P}/\text{NH}_4\text{-N}$ in the effluent collected from the external clarifier (in mg/l).

3.6 Crystal harvesting procedure

Crystal products were harvested from the reactor after the wastewater feed, recycle, and alkaline and salt chemicals feed flow were stopped and then crystals were allowed to settle on the bottom (reaction) part. To remove the harvesting crystals, the valve was opened and the crystals were allowed to fall into a beaker. Supernatant water was used to flush out some of the crystals which were settled in the junction part. The crystals were then air dried at room temperature for minimum two days.

3.7 Quality Control

All reagents used in the laboratory test procedures were of analytical grade and standard approved make. The glassware, containers, reactor, bottles, and other materials which are beneficial used for the sampling and analysis were initially cleaned with tap water using detergent and rinsing with distilled water. For calibration of measuring instrument, standard solutions and necessary reagents were prepared on a regular basis to achieve the best possible results. “Blank control” tests were prepared conducted whenever necessary in order to determine the background concentrations during the sample analysis. Samples were properly prepared following sampling procedures with accurate measurement, vigorously shaken to obtain homogenous quality and the cuvettes were cleaned formally in order to prevent contamination and safety of final result before they were put in for any test analysis. Approximately 40 liter of domestic wastewater samples were collected in well closed lid plastic sampling Jerrican from Membrane Bio-Reactor treatment type at a WWTP in condominium area. The wastewater samples were put for a period of 24hr to give suspended particles to settle then after the supernatant wastewater sample was sort for further analysis. The harvested struvite crystals were air dried at room temperature for 2 days and solids were collected in beakers and be labeled also closed using aluminum foil. All experimental development, instrumental calibrations, standard preparations, experimental methods, data generation, and documentation of activities were conducted on the guidelines of APHA.

4 Results and Discussion

4.1 Performance of FBR for nutrient recovery

The key result of this study was that the FBR achieved high Phosphate and ammonium recoveries from both synthetic and domestic wastewaters. To evaluate the recovery performance of the reactor, efficiencies were calculated on the basis of phosphorus and nitrogen removal from the solution. It was calculated as the ratio between the difference of the influent and effluent nutrient (N and P) concentration and the influent concentration.

Table 2 Range of the operational conditions and summary of results of the lab-scale MAP experiments.

	Synthetic wastewater	Real wastewater
Influent PO ₄ -P concentration at the inlet (mg/l)	65-67	67.8-68.2
Effluent PO ₄ -P concentration (mg/l)	1.85-16.2	2.8-17.7
Influent NH ₄ -N concentration at the inlet (mg/l)	69-72.2	72.3-73.1
Effluent NH ₄ -N concentration (mg/l)	17.6-51.26	19.8-56.5
PH	7.5-10	7.5-10
Mg:P molar ratio	0.75-1.75	0.75-2
P-removal efficiency (%)	75.8-97.2	74-95
N-removal efficiency (%)	26.8-74.8	22.3-72.8
P-removal efficiency (%) with Mg:P molar ratio	77.4-94.3	74.6-91.4
N-removal efficiency (%) with Mg:P molar ratio	36.3-70.5	33.4-69.9

Insertion of cones in the reactor and having different reactor parts are two important factors for better nutrient removal efficiencies as mentioned by researchers. In this study the phosphorus removal efficiencies of about 97% and 95% were observed for synthetic and real wastewaters, respectively. This is almost due to the insertion of conical shape in the FBR and the increased number of reactor parts, which reduced undesirable crystal loss at each junction. In the concept of FBR design having a large number of cones attained higher removal efficiency of phosphorus rather than reactors built with small number of or without cones. A study done by (Le Corre *et al.*, 2009a) to recover struvite from wastewater used two cones at the bottom and middle part of the reactor and achieved more removal performance than (Pastor *et al.*, 2008), who inserted only one cone. Furthermore, struvite crystallization process has been widely examined by (Guadie *et al.*, 2014) with and without cones and the results showed that the reactor with cone-inserted had better removal efficiencies than reactors without cones.

The removal efficiency of nutrients also depends on the number of reactor parts. (Ye *et al.*, 2016) and (Britton *et al.*, 2005b) used four reactor parts without cones and had got higher removal performance compared with others who used a smaller number of reactor parts (Ohlinger *et al.*, 2000). This study used three reactor parts and has got higher removal efficiency and this result showed that using a number of cones and parts plays important role in nutrient removal efficiencies.

4.2 Factors influencing the process

Struvite precipitation is mainly affected by a combination of key parameters such as supersaturation, pH, Mg^{2+} : $(NH_4^+ -N)$: $(PO_4^{3-} -P)$ molar ratio, temperature, HRT, coexisting foreign ions concentration, mixing speed and precipitation time. In this paper effect of pH, Mg/P ratio, HRT, and settling time (precipitation time) were investigated.

4.2.1 The effect of pH on nutrient removal from synthetic and real wastewater

The solution pH is one of the most important parameters for Struvite precipitation process because it is related with the supersaturation and the solubility products of the solution. In this study, the pH values were made to vary from 7.5 to 10 by regulating the flow rate of NaOH. Over 95% P-removal in both synthetic and real wastewaters was obtained at pH 9.

As shown in Figure 3; when the reactor pH was raised from 7.5 to 10, the phosphorus removal efficiencies of both synthetic and actual wastewaters increased from 75.8% to 97% and 74% to 94.9%, respectively. Lower phosphorus removal efficiencies were achieved at pH 7.5. This is in agreement with studies by (Rahman *et al.*, 2014, Parsons *et al.*, 2001a) on struvite precipitation chemistry, who reported relatively poor nutrient removal efficiencies at low pH values because of struvite solubility under acidic conditions.

Conversely, N removal efficiencies in the FBR were lower and showed more variability (26.7% - 74.8% and 22.35% - 72.38%) for SWW and RWW. When the pH value progressively increased from 8.5 to 10, N removal sharply rose; this could be due to ammonia loss by stripping at these pH ranges rather than struvite formation. Ammonium ion (NH_4^+) is converted to ammonia (NH_3) at high pH values. This result is supported by findings of similar studies e.g. (Wang *et al.*, 2005, Crutchik and Garrido, 2016). In this study the removal efficiency of P and N increased in the case of SWW when compared with that of RWW. This may be due to high organic and inorganic matter content in the real domestic wastewater which influences the struvite precipitation chemistry.

This is because domestic wastewater contains a lot of organic and inorganic matter (high amount of impurity matter), or coexisting ions, mainly calcium ions, which influence struvite precipitation chemistry. To support this idea (Le Corre *et al.*, 2005b) conducted a series of struvite precipitation experiments to estimate the mechanism by which calcium ions affect struvite's shape, crystal size, and purity. And also (Kabdazli *et al.*, 2006a) evaluated the effects of Na^+ , SO_4^{2-} , CO_3^{2-} , and Ca^{2+} ions on the induction time of struvite formation by means of absorbance measurements, and monitored the pH and conductivity of solutions. Their results demonstrated that all of the tested ions retarded the induction time of struvite crystallization, but only a minor effect was observed from the carbonate ions.

Struvite can be precipitated in a wide range of pH 7.0–11.5, but the appropriate pH ranges that could result in more than 90% removal performance is between 8 to 10 (Tao *et al.*, 2016, Peng *et al.*, 2018a, Rahman *et al.*, 2011, Matynia *et al.*, 2013, Shih *et al.*, 2017, Tian *et al.*, 2016). All these investigations have found higher P and N removal efficiencies with increase in pH. According to (Battistoni *et al.*, 2006) who conducted similar study on anaerobic supernatant

waste, concluded that the operating pH should be elevated up to 8.2 to get more than 90% P-removal. They increased the operational pH gradually to a higher value and found a smoother operation of the reactor. However, when the pH value further increased to 10, the recovery rate of P decreased; whereas the recovery rate of N slowly increased when the pH value was higher than 9.0. This difference can be explained by the following reason: when pH is above 9, NH_4^+ can deprotonate into NH_3 and this results in NH_3 vaporization that inhibits the MAP crystallization process, thus increasing the recovery rate of N (Gong *et al.*, 2018b). These findings of high phosphorus removal efficiency at high pH values are consistent with this study. But, (Fattah *et al.*, 2008a) demonstrated that high removal rates (above 80%) were obtained at a relatively low pH of 7.5 from filter press concentrate in a secondary wastewater treatment plant.

Using synthetic wastewater supernatant, (Adnan, 2002) also found that it was possible to achieve 79%, or higher, phosphorus removal rates with a pH of 7.1. The findings of these researches are contradictory to this study. This may be due to differences in the wastewater characteristics and experimental setups.

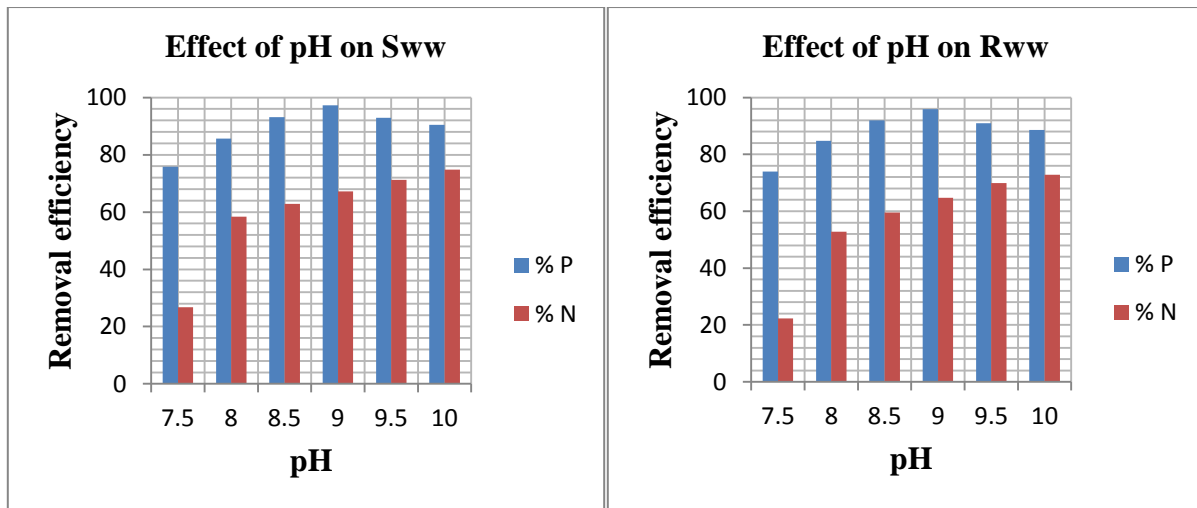


Figure 3 Effects of pH on nutrient removal efficiencies

4.2.2 The effect of Mg: P ratio on nutrient removal efficiencies

The ratio of ($\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$) influenced the purity and quality of the struvite products. Theoretically, MAP precipitation can form when the Mg:N:P molar ratio is 1:1:1 (Barnes and Bowers, 2017). However, this does not indicate that the method of struvite crystallization can continue only if Mg:N:P molar ratio has 1:1:1. Uncontrolled struvite crystallization at different treatment plants occurs at different Mg:N:P molar ratios. In the case of controlled MAP crystallization, when the Mg:P ratio falls below unity the system becomes under optimized in terms of nutrient removal efficiencies, since Mg ions become limiting.

In this study, a range of Mg/P molar ratios (0.75-1.75) was assessed to optimize the process using SWW. The optimum Mg/P molar ratio value was used to evaluate the nutrient recovery level from real domestic wastewater. At lower value of Mg: P molar ratio (0.75), removal efficiencies of phosphorus and nitrogen were low 77.38% and 36.3% and 74.6% and 33.4% for SWW and RWW, respectively. When the Mg/P molar ratios increased from 0.75 to 1.75, the FBR P and N removal efficiencies varied from 77.38 to 93.49 and 36.3 to 65.46% and 74.6 to 90.6% and 33.4 to 64.2% respectively as shown in Figure 4.

The reactor also attained 81% and 78.8% and 47% and 46.5% removal efficiencies of phosphorus and nitrogen respectively when adjusted to the theoretical struvite formation (Mg: P ratio of 1) for both wastewaters. When Mg/P molar ratios increased from 1.25 to 1.75, the removal efficiencies of phosphorus for RWW and SWW were found in the range of 89.9 to 93.49%. (Yetilmezsoy and Sapci-Zengin, 2009) conducted similar studies on poultry manure wastewater at lab-scale by applying various molar ratios of Mg:N:P, including both overdose (1.2:1:1, 1.5:1:1, 1:1:1.2, and 1:1:1.5) and under dose (0.5:1:1, 0.8:1:1, 1:1:0.5, and 1:1:0.8). They also used N dosage at constant value of 1, to examine the effect of molar ratio on NH_4^+ -N removal, as well as on COD and color reductions. Their results showed that overdose of Mg increased the removal efficiency of ammonium.

Another study by (Bouropoulos and Koutsoukos, 2000) also confirmed that Mg ions influence the micro electrophoretic mobility of struvite distributions with an isoelectric point at Mg:P = 1.75, which suggests that greater Mg supersaturation is beneficial to struvite crystallization.

Similarly (Huang *et al.*, 2006) observed that high magnesium dosage has a beneficial effect on the crystal growth and aggregation, leading to the larger final size. However, considering the costs of magnesium supply, this research used Mg:P molar ratio of 1.5 for MAP crystallization design.

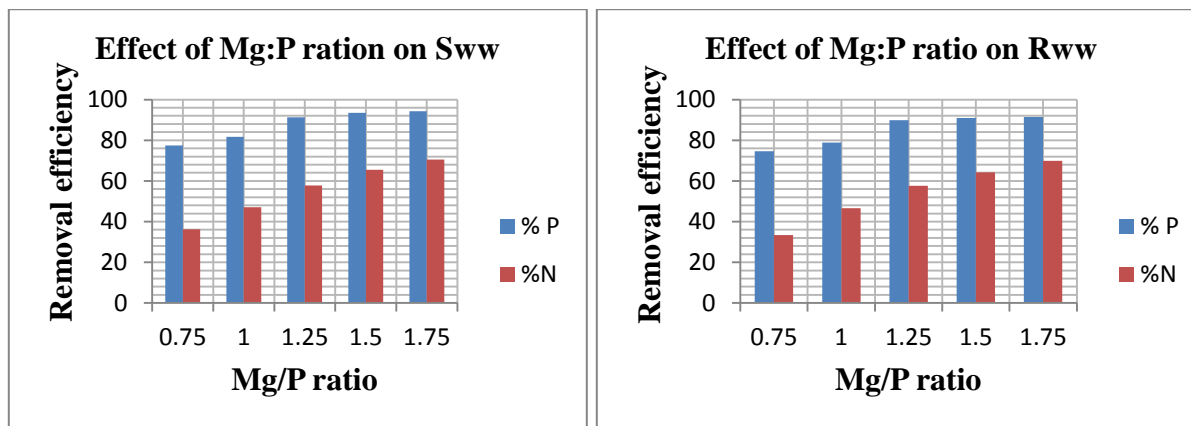


Figure 4 Effect of Mg: P ratio on nutrient removal efficiencies

4.2.3 The effect of Hydraulic retention time (HRT) on nutrient removal efficiencies

HRT is the average length of time the wastewater stays in the reactor. It is one of the most significant parameters affecting the reactor performance and directly related to the up flow velocity. In this study HRTs of 1, 2, 3, 4, and 5 hrs were evaluated for the optimization using SWW. Nutrient recovery from RWW was evaluated using the optimal RWW value. Results of the analysis showed 82% phosphorus and 21.9% nitrogen removal efficiencies for 1 hr HRT. When the HRT increased from 2 to 3 hrs the phosphorus removal efficiencies correspondingly increased from 91.3% and 92.8%. But, when the HRT time increased from 3 to 5 hrs, the removal efficiencies of P and N sharply decreased, leading to dispersal of formed crystals. As reported by (Bello *et al.*, 2017a), long HRT leads to a better performance of FBR until the optimum time is reached. Above the optimum HRT, there is usually little or no further removal of the pollutant. In continuous mode of FBR operations, (Song *et al.*, 2011) revealed that high removal efficiencies of phosphorus and nitrogen were found 6 hrs HRT.

According to Liu *et al.* (2008), enhanced phosphorus removal was observed before HRT of 1.14 hr and beyond this time no further improvement was achieved. Le Corre *et al.* (2007), found similar (79%) removal efficiency of phosphorus from synthetic wastewater after 1 and 24 hrs. The findings of this study agree with the performances reported by these researchers.

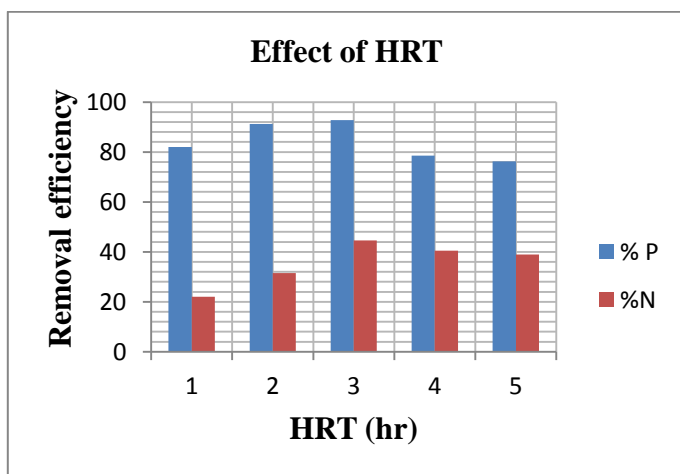


Figure 5 Effect of HRT on nutrient removal efficiencies

4.2.4 Effect of settling time on nutrient removal efficiencies

Settling is the last treatment stage before the effluent is discharged to the receiving environment. In this process suspended particles have a chance to separate from water which is denser by means of gravity settling. Nutrient removal levels at different settling times of 15min, 30min, 45min, 1hr, 1hr.15min, and 1hr.30min were determined. The analysis showed 78.0% phosphorus and 59.3% nitrogen removal efficiencies in the first 15min. When the precipitation time increased from 15min to 30min, the removal efficiencies of both phosphorus and nitrogen increased by 90.8% and 76.5%, respectively. Settling time increase from 45min to 1hr.30min showed a decrease in Phosphorus and nitrogen removal efficiencies. These results agree with the findings of (Teferra, 2018, Liu *et al.*, 2013, Le Corre *et al.*, 2007).

According to the findings of Teferra (2018), better P and N removals were observed when the precipitation time was 30 min. He concluded that, giving too long time for precipitation would result in resuspension of precipitated struvite crystals and, therefore, reduction of nutrient recovery. Liu *et al.*, (2013) confirmed that in struvite crystallization practices the P removal

efficiency showed a slight increasing trend with a longer reaction time, but did not change significantly beyond 30 min precipitation time. Le Corre *et al.*, (2007) also revealed that the settling time had no major effect on the P concentration. This finding may be due to the fact that the reaction of struvite crystals in solution is completed within several minutes, which indicates the rapid formation of crystals. Therefore, 30min precipitation time was considered to be optimal for MAP formation in this study.

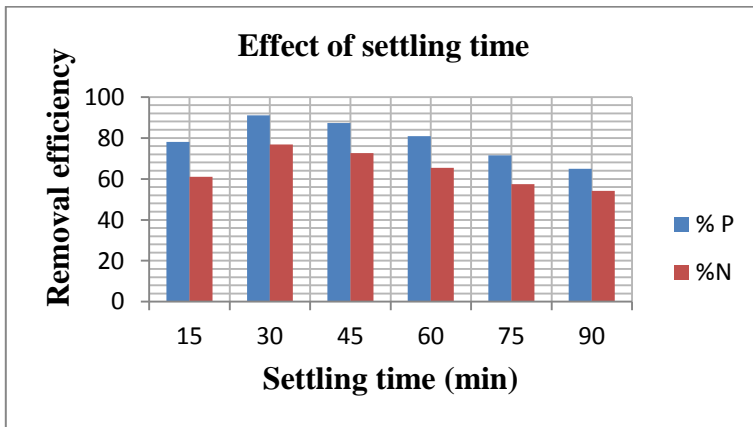


Figure 6 Effect of settling time on nutrient removal efficiencies

5 Conclusions and Recommendation

5.1 Conclusions

Excessive nutrients in surface water bodies can lead to eutrophication problems and abundant plant growth which in turn has adverse socio-economic and ecological impacts. It also results in loss of valuable nutrients which could otherwise be used as fertilizer to increase agricultural productivity. Nutrient recovery from domestic wastewater and its use as fertilizer is in line with the new resource-oriented urban waste management approach.

This investigation has demonstrated that fluidized bed reactor is an effective method to remove and recover phosphorus and nitrogen from synthetic and domestic wastewater. The effects of various operational parameters were evaluated and optimized using synthetic wastewater. The optimum parameter values were further used to evaluate nutrient recovery potential from actual wastewater streams.

Fluidized bed reactor with inserted cones and different parts is more effective in recovering phosphorus and nitrogen. Three reactor parts with inserted cones in the bottom, middle, and top parts showed high nutrient removal efficiencies and reduced undesirable crystal losses. The results showed that under the optimal operating conditions of (pH = 9, HRT = 2 hrs. Settling time = 30 min, and Mg/P ratio of = 1.5), the removal efficiencies of phosphorus were more than 90% using both synthetic and real wastewaters.

Overall, the use of properly designed fluidized bed reactor under optimal operating conditions has a good potential to recover phosphorus and nitrogen from domestic wastewater.

5.2 Recommendation

Nutrient recovery from wastewater through struvite precipitation is found to be promising. It is recommended to continue scientific investigations to refine and advance the knowledge base in the area. Specifically, further studies are recommended in the following area:

- ❖ To evaluate more reactor models and identify the one that is more efficient.
- ❖ To design and conduct similar experimental investigations at pilot and field scales
- ❖ To characterize the struvite crystals in terms of quality, size, density and morphology using advanced techniques
- ❖ To assess the influence of other operational parameters, total solids and organic matter content on the quality and size of struvite crystals formed
- ❖ To evaluate the nutrient recovery potential from other wastewater sources that have high nutrient levels
- ❖ To assess the bioavailability of struvite in a greenhouse experiment

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Appendix

Spectrophotometer protocol for phosphate test (for the determination of orthophosphate)

Reagents and auxiliaries

- 1 bottle of reagent PO₄-1
- 1 bottle of reagent PO₄-2
- 1 blue dose-metering caps (each can be used for 50 dosages)
- 1 Autoselector
- Pipettes, for pipetting volumes of 0.50 and 8.0ml.
- Rectangular cells 10mm
- Water for analysis
- Phosphate standard solution

At the first use replace the screw cap of the reagent bottle PO₄⁻² by the blue dose-metering cap.

Hold the reagent bottle vertically and, at each dosage, press the slide all the way into the dose-metering cap. Before each dosage ensure that the slide is completely retracted.

Preparation

- Use only phosphate –free detergent to rinse glassware. Otherwise fill with hydrochloric acid (approx.10%) and leave to stand for several hours.
- Analyze immediately after sampling.
- pH must be within the range 0-10.
Adjust, if necessary, with sulfuric acid.
- Filter turbid samples.

Procedure

Distilled water (10-35°C)	8.0ml	pipette in to a test tube.
Pretreated sample (10-35°C)	0.50ml	Add with pipette and mix.
Reagent PO ₄ ⁻¹	0.50ml	Add with pipette and mix
Reagent PO ₄ ⁻²	1 dose	Add and shake vigorously until the reagent is completely dissolve

Leave to stand for 5min (reaction time), then fill the sample into a 10-mm cell, and measure in the photometer.

Note on the measurement:

- Certain photometers may require a blank (preparation as per measurement sample, but with distilled water instead of sample).
- For photometric measurement the cells must be clean, wipe, if necessary, with a clean dry cloth.
- Measurement of turbid solutions yields false –high readings.
- The pH of the measurement solution must be within the range 0.80-0.95.
- The color of the measurement solution remains stable for at least 60 min after the end of the reaction time stated above.

Analytical quality assurance

- To check the photometric measurement system (test reagents, measurement device, and handling) and the mode of working, a dilute phosphate standard solution can be used.
- Sample-dependent interferences can be determined by means of standard addition.

Ammonium Test

Reagent and auxiliaries

1 bottle of reagent NH_4^- 1

1 bottle of reagent NH_4^- 2 (contains granulate + desiccant capsule)

2 Auto selectors

Measuring range 10-400mg/l NH_4^+

Pipettes, for pipetting volumes of 0.10, 0.20, and 5.0ml.

Rectangular cells 10mm (2pcs).

Preparation

- Rinse glassware ammonium-free with distilled water. Do not use detergent;
- Analyze immediately after sampling.
- Check the ammonium content with “Ammonium Test”. Samples containing more than 150mg/l $\text{NH}_4\text{-N}$ must be diluted with distilled water.
- The pH must be within the range 4-13.

Adjust, if necessary, with sodium hydroxide solution or sulfuric acid.

- Filter turbid samples.

Procedure

Measuring range 2.0-75.0 mg/l NH₄-N (2.6-96.6 mg/l NH₄⁺)

Reagent NH ₄ -1 (20-30°C)	5, 0 ml	pipette in a test tube.
Pretreated sample (20-30°C)	0.20 ml	add with pipette and mix
Reagent NH ₄ -2	1 level blue the	add and shake vigorously until
	micro spoon (in the cap of the NH ₄ -2 bottle)	reagent is completely dissolved.

Leave to stand for 15min (reaction time), then fill the sample in to a 10-mm cell, and measure in the photometer.

Measuring ranges 5-150mg/l NH₄-N (6-193mg/l NH₄⁺):

Reagent NH ₄ -1 (20-30°C)	5,0 ml	pipette into a test tube.
Pretreated sample (20-30°C)	0.1 ml	Add with pipette and mix.
Reagent NH ₄ -2	1 level blue microspoon (in the cap of the NH ₄ -2 bottle)	Add and shake vigorously until the reagent is completely dissolved.

Leave to stand for 15min (reaction time), then fill the sample into a 10-mm cell, and measure in the photometer.

Notes on the measurement:

- Due to the strong temperature dependence of the color reaction, the temperature of the reagents should be between 20 and 30°C.

- Certain photometers may require a blank (preparation as per measurement sample, but with distilled water instead of sample).
- For photometric measurement the cells must be clean, wipe, if necessary, with a clean dry cloth.
- Ammonium-free samples turn yellow on addition of reagent $\text{NH}_4\text{-2}$
- The pH of the measurement solution must be within the range 11.5-11.8.
- The color of the measurement solution remains stable for at least 60 min after the end of the reaction time stated above.

Table 3 Comparison of phosphorus removal efficiencies of the fluidized bed reactor used in current and previous studied

Volumes (L)	Number of cones	Number of parts	Wastewater types	pH control & value	P-removal (%)	Reference
6.2	3	3	Synthetic & actual ww	NaOH (7.5-10)	62-97	This study
9.5	3	3	Synthetic ww	NaOH (7.5-10)	60-98	Guadie et al., (2014)
21	1	2	Synthetic ww	NaOH (8.2-9.5)	40–80	Pastor et al., (2008)
12.8	1	2	Belt press liquors	Aeration (8.0-8.8)	60-91	Battistoni et al., (2001)
Not described	1	2	Anaerobic liquor	Aeration (7.6-8.2)	68.5-86.6	Battistoni et al., (2005)
24.4	No	4	Digester liquor	NaOH (>8.3)	>90	Huang et al., (2006)
24.4	No	4	Digester liquor	NaOH (>8.3)	>90	
650 (m ³ /day)	2	2	Digester liquor	NaOH (8.2-8.8)	>90	Ueno and Fujii.,(2001)
3.2	No	1	Digester liquor	NaOH (8.3)	>80	Ohlinger et al., (2000)
Not described	No	4	Belt press liquors	NaOH (7.5)	>80	Fattah et al.,(2008)
19.0	No	4	Digester liquor	NaOH (7.6-8.8)	30-90	Britton et al., (2005)
Not described	1	2	Anaerobic digester liquor	NaOH/Air (8.7)	75-98	Pastor et al., (2010)

Preparation of standard solutions

For NH₄Cl preparation

- Concentration 2.5M, 2M, 1.5M, 1M, 0.5M.
- Atomic weight of NH₄Cl
- N = 14g
- H = 1*4 = 4g
- Cl = 35.5g
- At. Weight = 53.5g

For Mole calculation

- $n = M \cdot V$
- M= Molarity
- V= volume of distilled water used 250ml
- No. of mole = $2.5M \cdot 0.25L = 0.625\text{mol}$
- $M = 0.625 \cdot 53.5g = 33.4375g/l$

For 2.5M concentration add 33.4375g in to 0.25L distilled water.

- $M_2 = 2M$
- By rule of dilution, $V_1M_1 = V_2M_2$
- $V_1 = V_2M_2/M_1$
- $V_1 = (250 \cdot 2)/2.5 = 200\text{ml}$
- $V_2 - V_1 = 250\text{ml} - 200\text{ml} = 50\text{ml}$

For 2M concentration = 200ml solutions add 50ml distilled water.

For 1.5M concentration

- By rule of dilution, $V_1M_1 = V_2M_2$
- $V_1 = V_2M_2/M_1$

- $V_1 = (250\text{ml} * 1.5\text{M}) / 2\text{M} = 187.5\text{ml}$
- $V_2 - V_1 = 250\text{ml} - 187.5\text{ml} = 62.5\text{ml}$

For 1.5M concentration = 187.5ml solutions add 62.5ml distilled water.

For 1M concentration

- By rule of dilution, $V_1M_1 = V_2M_2$
- $V_1 = (250\text{ml} * 1) / 1.5\text{M}$
- $V_2 - V_1 = 250 - 166.7\text{ml} = 83.3\text{ml}$
- 1M = 166.7ml solutions add 83.3ml distilled water.

For 0.5M concentration

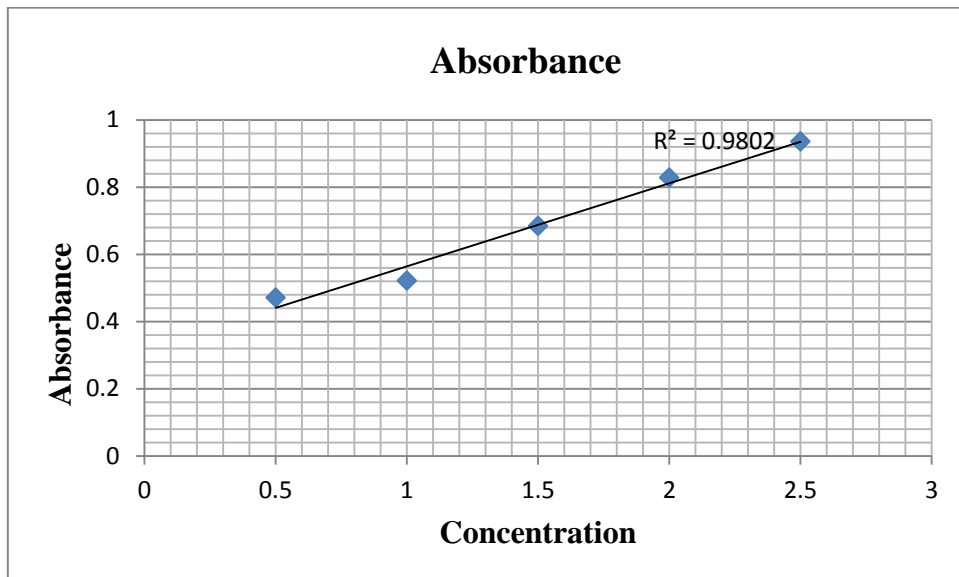
- By rule of dilution, $V_1M_1 = V_2M_2$
- $V_1 = V_2M_2 / M_1$
- $V_1 = 250\text{ml} * 0.5\text{M} / 1\text{M} = 125\text{ml}$
- $V_2 - V_1 = 250 - 125 = 125\text{ml}$

For 0.5M concentration = 125ml solutions add 125ml distilled water.

Note: The same procedures follow for phosphate solution

Table 4 Concentration against absorbance for calibration of spectrophotometer

Concentration (M)	Absorbance
0.5	0.471
1	0.521
1.5	0.684
2	0.828
2.5	0.935



Preparation of NaOH solution from NaOH pellet

For pH adjustment 0.0125mol/l of NaOH was used. How to prepare 0.0125mol/l NaOH from NaOH pellet.

- $M = 0.0125\text{mol/L}$
- Let $V = 6$ liter
- Molecular Weight of NaOH = 40g/m
- $M = n/v$
- $n = MV$
- $n = MV$ weight
- $m = M \cdot V \cdot M_o$
- $m = 0.0125 * 6 * 40$
- $m = 3\text{g}$
- 30g of NaOH pellet was dissolved in 6 liter of distilled water



Hanna educational pH meter- HI 8010



Centrifuge tube 50ml



Chemicals used to prepare synthetic wastewater

Annex

Volume calculation for a novel-cone fluidized bed reactor

1. Top volume

$$v_1 = \left(\frac{\pi d^2}{4} \right) h$$

Since diameter of cylinder = 140mm

Height of cylinder = 150mm and

The angle of cylinder = 45°

$$v_1 = \left(\frac{3.14 * 0.14^2}{4} \right) * 0.15$$

$$v_1 = 0.0023079 m^3$$

Frustum of cone

$$v_2 = \frac{\pi h}{3} (R^2 + r^2 + Rr)$$

$$v_2 = \frac{3.14 * 0.05}{3} (0.07^2 + 0.05^2 + (0.05 * 0.07))$$

$$v_2 = 0.0005704333 m^3$$

Then total volume that means volume of cylinder and volume of frustum of cone

$$v_T = v_1 + v_2$$

$$v_T = 0.0023079 + 0.0005704333$$

$$V_T = 0.0028783333 m^3$$

$$V_T = 2.8783333 L$$

2. Middle Volume

Cylinder volume

$$v_1 = \left(\frac{\pi d^2}{4} \right) h$$

$$v_1 = \left(\frac{3.14 * 0.085^2}{4} \right) 0.43$$

$$v_1 = 0.0024388 m^3$$

Frustum of cone Volume

$$v_2 = \frac{\pi h}{3} (R^2 + r^2 + Rr)$$

$$v_2 = \frac{3.14 * 0.05}{3} (0.0425^2 + 0.03^2 + (0.0425 * 0.03))$$

$$v_2 = 0.0002083520 m^3$$

$$v_M = v_1 + v_2 \text{ then } v_M = 0.002647152 m^3$$

$$v_M = 2.647152 L$$

3. Bottom volume

Cylinder volume

$$v_1 = \left(\frac{\pi d^2}{4} \right) h$$

$$v_1 = \left(\frac{3.14 * 0.06^2}{4} \right) 0.26$$

$$v_1 = 0.00073476 m^3$$

$$v_1 = 0.73476 L$$

Finally volume of a novel-cone fluidized bed reactor

V =6260 ml

V= **6.26L**

Table 5 Optimization of pH with different value on SWW

pH	Initial P (mg/l)	Final P (mg/l)	Initial N (mg/l)	Final N (mg/l)	% P	% N
7.5	40	9.65	65	47.6	75.88%	26.77%
8	42	6	60	25	85.71%	58.33%
8.5	43.5	3	62	23	93.10%	62.90%
9	43.5	1.2	64	21	97.24%	67.19%
9.5	42.5	3	62.5	18	92.94%	71.20%
10	42	4	64.9	16.3	90.48%	74.88%

Table 6 Optimization of pH with different value on SWW

pH	Initial P (mg/l)	Final P (mg/l)	Initial N (mg/l)	Final N (mg/l)	% P	% N
7.5	68.03	17.7	72.77	56.5	74.0	22.35
8	68.03	10.37	72.77	34.37	84.8	52.77
8.5	68.03	5.5	72.77	29.4	91.9	59.60
9	68.03	3.5	72.77	25.6	94.9	64.77
9.5	68.03	6.17	72.77	21.9	90.9	69.90
10	68.03	7.8	72.77	20.10	88.5	72.38

Table 7 Optimization of Mg/P ratio keeping pH constant on SWW

pH	Mg:P	Initial P (mg/l)	Final P (mg/l)	Initial N (mg/l)	Final N (mg/l)	% P	%N
9	0.75	22	5	41	26.2	77%	36.1%
"	1	24	4.5	43.5	23	81%	47.1%
"	1.25	35	3	45	19	91.4%	57.8%
"	1.5	54	3.5	46.3	16	93.5%	65.4%
"	1.75	54.9	3	44.8	13	94.5%	71.0%

Table 7 Optimization of Mg/P ratio keeping pH constant on SWW

pH	Mg:P	Initial P (mg/l)	Final P (mg/l)	Initial N (mg/l)	Final N (mg/l)	% P	%N
9	0.75	68.03	17.3	72.77	48.47	74.6	33.4
"	1	68.03	14.40	72.77	38.90	78.83	46.5
"	1.25	68.03	6.87	72.77	30.83	89.91	57.6
"	1.5	68.03	5.83	72.77	21.9	91.4	69.9
"	1.75	68.03	6.40	72.77	26.0	90.6	64.2

Table 9 Optimization of HRT with keeping pH and Mg/P ratio constant

pH	Mg:P	HRT (hr)	Initial P (mg/l)	Final P (mg/l)	Initial N (mg/l)	Final N (mg/l)	% P	%N
9	1.25	1	38.9	7	41	32	82.0%	22.0%
"	"	2	40	3.5	42.3	29	91.3%	31.4%
"	"	3	41.5	3	41.9	23.2	92.8%	44.6%
"	"	4	35	7.5	43	25.4	78.6%	40.9%
"	"	5	37.9	9	42.6	26	76.3%	39.0%

Table 10 Optimization of settling time with keeping pH, Mg/P ratio, and HRT constant

pH	Mg/P	HRT(hr)	Settling time (min)	Initial P (mg/l)	Final P (mg/l)	Initial N (mg/l)	Final N (mg/l)	% P	% N
9	1.25	2	15	32.47	7.133	42.93	17.483	78.0%	59.3%
"	"	"	30	"	2.997	42.93	10.103	90.8%	76.5%
"	"	"	45	"	4.18	42.93	11.743	87.1%	72.6%
"	"	"	60	"	6.247	42.93	15.13	80.8%	64.8%
"	"	"	75	"	9.16	42.93	18.75	71.8%	56.3%
"	"	"	90	"	11.47	42.93	20.82	64.7%	51.5%



Figure 7 Recovered struvite crystals



Figure 8 Whole lay out of FBR

