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Phosphorus Removal from Wastewater through Struvite Precipitation

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Development

Phosphorus was probably discovered by German alchemist H. Brandt around 1669. The word Phosphorus is derived from Greek, means light-bearing.

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Abstract

Phosphorus is an essential nutrient to sustain life. With regards to limited Phosphorus resources, recovery and reuse of Phosphorus are necessary. Wastewater usually contains large amount of Phosphorus which could cause severe environmental problems such as eutrophication in water bodies. Thus, recovery of Phosphorus from wastewater removes the excess amount and prevents environmental pollution. The recovered Phosphorus could also be considered as a rich fertilizer and helps to sustainable use of Phosphorus resources. Struvite precipitation is a new method to remove and recover Phosphorus from wastewater. In this method, Magnesium, Ammonium and Phosphate are mixed in specific molar ratios and Phosphorus precipitates as struvite. Generally, struvite consists of 13% Phosphorus, 6% Nitrogen and 10% Magnesium. The precipitated struvite could be reused as slow release fertilizer. On the other hand, addition of chemicals like Iron and Aluminum in order to remove Phosphorus in wastewater treatment plants is costly and also affects adversely the plant availability of Phosphorus. Therefore, struvite crystallization as a no chemical method would increase the efficiency in Phosphorus removal and reuse capacity.

In this study, the main goal was to achieve the highest Phosphorus removal from municipal wastewater by means of struvite precipitation. The obtained wastewater and reject water from HIAS wastewater treatment plant were enriched by 189 mg/l and 2220 mg/l $\text{PO}_4^{3-}\text{-P}$ and $\text{NH}_4\text{-N}$, respectively. MgCl_2 was used as Magnesium source in three Mg: PO_4 molar ratios of 0.6, 0.8 and 1.1. Also, two $\text{NH}_4\text{:PO}_4$ molar ratios of 5 and 10 were added into the wastewater. All the experiments were conducted during 20, 40 and 60 minute of stirring with magnet. pH of the solution was fixed at 8.3 by addition of NaOH 2 molar.

The results demonstrate that Ortho-P removal from wastewater increased from 78.3% to 92.9% by increasing Mg: PO_4 molar ratio from 0.6 to 1.1. Thus, the struvite mass has increased from 443 mg to 528 mg. The effect of different NH_4 concentrations and mixing time was not significant regarding Phosphorus removal. Also, the produced struvite through this study consists of 10.5-16.5% Phosphorus and 6-10.8% Magnesium. Furthermore, the effect of different Mg and Ammonium concentrations along with different mixing time had no significant effect on heavy metals concentration except Zink.

Keywords: Phosphorus, Struvite, Wastewater

Abbreviations

ACP – Amorphous Calcium Phosphate

Al – Aluminum

As – Arsenic

Ca – Calcium

Cd – Cadmium

CO₂ – Carbon dioxide

Cr – Chromium

Cu – Copper

Fe – Iron

HCl – Hydrochloric Acid

Hg – Mercury

ICP-MS – Inductively Coupled Plasma Mass Spectrometry

K – Potassium

M³h⁻¹ - Cubic meter per hour

MAP – Magnesium Ammonium Phosphate

Mg – Magnesium

MgCl₂ – Magnesium Chloride

MgO – Magnesium Oxide

Mg/kg – Milligram per kilogram

Mg/l – Milligram per Liter

ml – Milliliter

Mt – Million tons

Ms/cm – Millisiemens per Centimeter

NPK – Nitrogen Phosphorus Potassium

Na – Sodium

NH₄ – Ammonium

Ni – Nickel

NTU – Nephelometric Turbidity Unit

Ortho-P – Ortho Phosphate

P – Phosphorus

Pb – Lead

PO₄³⁻ - Phosphate

ppb – part per million

SI – Saturation Index

Total-P – Total Phosphorus

Ug/l – Microgram per Liter

WAS – Waste-Activated Sludge

Zn – Zink

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Introduction

Phosphorus

Phosphorus is an essential nutrient to sustain life. Phosphorus plays a key role in energy metabolism, structural strength, genetic components and photosynthesis process (Smit et al., 2009). Also together with Nitrogen and Potassium, Phosphorus is the main part of fertilizers (NPK fertilizer). In agricultural point of view, the optimum range of Phosphorus concentration is vital to sustain soil fertility and food crops production (Pierzynski et al., 2005). Therefore, lack of Phosphorus along with its low solubility causes growth limit for plants.

The element Phosphorus does not occur in nature by itself. It is always combined with other elements to form Phosphate (Johnston & Steen, 2001). The majority of the earth's Phosphorus is conserved in terrestrial soil and sediment in water bodies such as oceans and fresh waters. Most Phosphorus fertilizer production is based on acidification of apatite from Phosphate rock.

Global Phosphorus cycle

Phosphate rock is the main global source of Phosphorus. These rocks contain high concentration of Phosphate minerals, mostly apatite. The Phosphorus cycle starts with release of Phosphate minerals through weathering. Then the inorganic Phosphorus, which is the soluble part, is available for plants to be adsorbed. By the plant uptake, Phosphorus ends in the food chain and is returned to environment via animal manure and human excreta (Ronteltap, 2009, p. 3). Worldwide, domestic animals produce 12-14 million tons (Mt) of Phosphorus per year. Also, the Phosphorus amount taken up by humans does not exceed 3-4 Mt Phosphorus per year which almost the same amount is also excreted (Smit et al., 2009).

Phosphorus transport

Figure 1 summarizes the transport and fate of Phosphorus in terrestrial and aquatic ecosystems. Organic and inorganic Phosphorus is dissolved or detached by means of flowing water through or across the soil. The particulate Phosphorus can either be leached into the soil or enter streams and rivers. Then the dissolved Phosphorus can be deposited in the river bed or carried into lakes and reservoirs. The soluble Phosphorus inside the lakes is taken by aquatic organisms such as algae. While the soluble Phosphorus is depleted, the Phosphorus bound to deposited sediments may become available for organisms (Pierzynski et al., 2005; Sharpley et al., 1994).

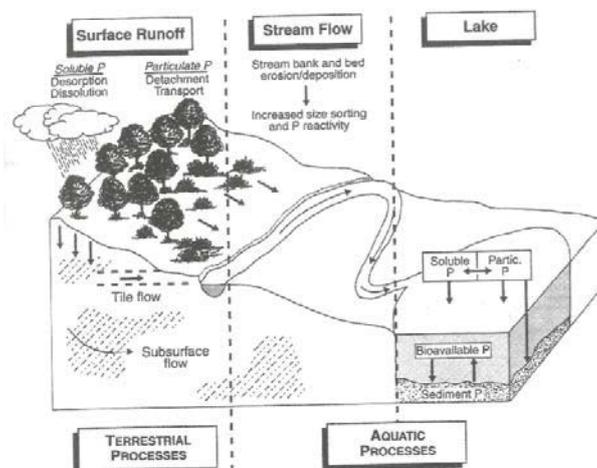


Fig 1. Transport and fate of Phosphorus in terrestrial and aquatic ecosystems

Soil Phosphorus cycle

Total Phosphorus concentration in soils varies normally from 50 to 3000 mg/kg. In mineral soils, 50 to 70% is in inorganic form. On the other hand, in organic soils with more than 20-30% organic matter, 60 to 90% of Total Phosphorus can be organic. The soil organic Phosphorus such as soil biomass, plant residues and soil organic matter can be mineralized (decomposition of organic compound) to inorganic Phosphorus. Then, inorganic Phosphorus is taken by plants. The inorganic soluble Phosphorus can be immobilized to organic Phosphorus vice versa. Also, the soluble Phosphorus can be adsorbed to Clay, Al and Fe oxides which make it unavailable for plants. Moreover, inorganic Phosphorus can also precipitate as secondary Phosphate minerals. In addition, the soluble Phosphorus can be leached into shallow ground water or tile drainage system (Figure 2) (Pierzynski et al., 2005).

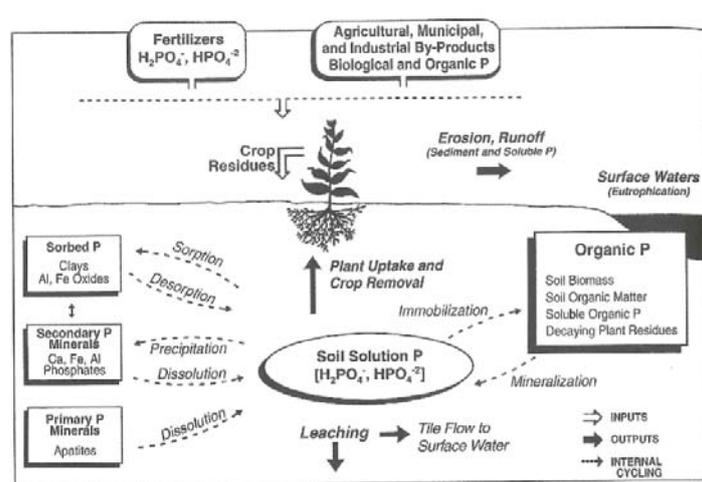


Fig 2. Soil Phosphorus cycle

As the Phosphorus dissolved or desorbed, it enters the soil solution in forms of primary (PO₄³⁻) and secondary Ortho-Phosphates (HPO₄²⁻ and H₂PO₄⁻). The concentration of primary and secondary Ortho-Phosphates depends on soil pH. As figure 3 illustrates at pH of 4 to 6.5, Dihydrogen Phosphate (H₂PO₄⁻) and at pH of more than 7.5, Hydrogen Phosphate (HPO₄²⁻) dominates (Pierzynski et al., 2005).

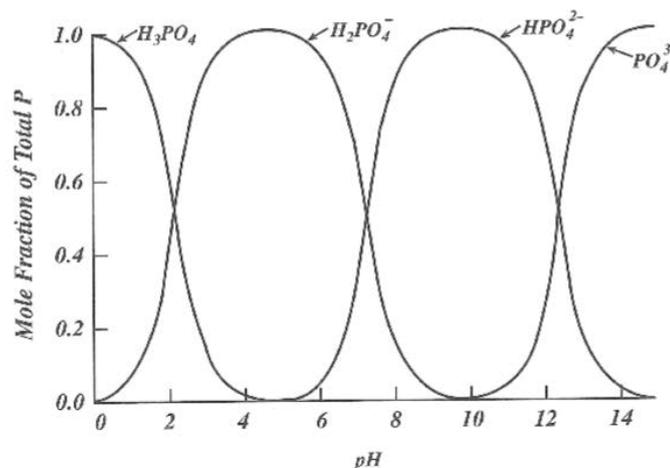


Fig 3. Changes in the form of soil Phosphorus

Eutrophication

Environmental concerns associated with Phosphorus mainly involves its impact on water bodies. In most aquatic ecosystems due to low concentration of Phosphorus and adequate levels of dissolved oxygen, the biological productivity is limited. Presence of external Phosphorus input via urban wastewater systems, surface run-off or subsurface groundwater flow can reduce the oxygen content and stimulate the growth of microorganisms in water bodies to undesirable levels. Total Phosphorus concentration of more than 100 ppb is regarded as a highly unacceptable level in most surface waters. On the other hand, even low concentrations as 10 ppb can cause environmental concerns for some waters. Eutrophication is defined as “an increase in the fertility status of natural waters that causes accelerated growth of algae or water plants.” Eutrophication limits the growth and diversity of aquatic biota and under extreme conditions causes fish kill. In this phenomenon, high turbidity inhibits the penetration of light into lower depths of water bodies which results in reduced growth of submerged aquatic vegetation and benthic organisms. Phosphorus and Nitrogen are the main triggering elements for fresh and coastal water bodies eutrophication, respectively (Pierzynski et al., 2005). In the last half century, Phosphorus concentrations in freshwater and terrestrial systems have increased by at least 75% while the estimated Phosphorus flow into the oceans from the total land areas has risen to 22 million tons per year. This amount exceeds the world’s annual Phosphorus fertilizer consumption of estimated 18 Mt in 2007 (Syers et al., 2011). Therefore, by excessive use of nutrients especially Phosphorus, eutrophication should be considered as an important environmental concern which needs to be reduced and controlled by means of severe measurements.

Phosphorus resources

Phosphate rocks and ores are the main source for Phosphorus fertilizer production. While Phosphorus is the 11th abundant element in earth’s crust, only a small percentage in desired concentration can be used by humans to produce fertilizers. Being physically inaccessible (like on the deep sea bed) and containing levels of contamination (such as Cadmium) are of the reasons for the scarcity of high concentration Phosphate rocks. Further ecological, social and physical constraining factors limit the productive utilization of Phosphate rocks. Therefore, from 4×10^{15} tons of estimated Phosphorus in earth crust, only 2×10^9 tons are estimated as Phosphate rocks reserves (Schroder et al., 2010). In addition, Phosphate rock is a non-renewable resource which becomes scarcer due to continuous exploitation of high concentration resources (Schroder et al., 2010). According to Smit et al. (2009) the Phosphate rock reserves will be depleted in 69-100 years. The peak Phosphorus production is estimated to be occurred by 2035. After the peak, the production is expected to be reduced due to lower supply despite the rising demand (Cordell et al., 2009).

Current usage

Majority of the mined Phosphorus, nearly 80%, is used for agricultural fertilizer, while 5% is utilized as additions in animal feed and 15% in industrial uses such as detergent production. The largest deposits of Phosphorus are located in Morocco, China and United States, respectively (Smit et al., 2009). Modern agriculture is dependent on Phosphorus fertilizers. Phosphorus fertilizer consumption has stabilized in most of developed countries while the consumption rate is still increasing in developing countries (Syers et al., 2011). The need for Phosphorus fertilizers is higher in areas like Africa due to severe lack of Phosphorus in soil.

China and India, as most populated countries in the world, consume 30.5% and 14.6% of total annual Phosphorus fertilizers, respectively (Schroder et al., 2010).

Future demand

The demand for Phosphorus fertilizer is strongly related to population growth, food requirements and agricultural outputs. The medium and high predictions for population in year 2050 are nearly 9 and 11 billion, respectively. This means 30 to 50% increase than the population in 2011 which was almost 7 billion (Schroder et al., 2010). So the global consumption of Phosphorus should increase in same percentage, while the estimations illustrate that the peak Phosphorus production occurs at 2035 (Cordell et al., 2009). Therefore, in order to meet the future Phosphorus fertilizer demands, the existing resources are inadequate and further solutions such as Phosphorus recovery are extremely needed.

Wastewater

The term wastewater can have different definitions. Corcoran (2010) has considered wastewater as a combination of one or more of:

- Domestic effluent consisting of Blackwater (excreta, urine and faecal sludge) or Greywater (kitchen and showers)
- Discharged water from institutions such as hospitals
- Agricultural, horticultural and aquaculture effluent, either dissolved or as suspended
- Industrial effluent, storm water and urban run-off

Wastewaters contain high amount of organic matter, Phosphorus, Nitrogen, heavy metals, Magnesium and wide range of macro and micro nutrients. These polluting agents originate from anthropogenic, livestock, natural or industrial sources. 34% of the Phosphorus in wastewaters is from sewage, both human source and detergents. Furthermore 34, 16, 7 and 9 percent of wastewaters are from livestock, fertilizers, industry and other sources, respectively. Phosphorus and Nitrogen, are the most important nutrients for animal and plant production (Md Mukhlesur Rahman et al., 2014). Thus, in order to avoid unfavorable environmental impacts, removal and recovery measurements should be implemented.

Phosphorus removal

Currently, several methods are used in order to Phosphorus removal from wastewater. These methods are mainly based on physio-chemical and biological methods. In physio-chemical processes, the Phosphorus removal leads to precipitation of insoluble salts. Addition of metal salts such as Fe and Al into the wastewater, triggers coagulation process. In this process Phosphorus particles are attached to metal salts and precipitate from wastewater by means of rapid mixing, followed by slow speed mixing (Flocculation). The precipitated Phosphorus in this removal method cannot be used easily as fertilizer. The main disadvantages of physio-chemical removal processes are the cost of chemicals and the huge sludge production (Ronteltap, 2009).

In biological Phosphorus removal processes, the Phosphorus ends as a microbial mass in activated sludge. These removal methods are considered as an alternative for chemical methods to reduce the sludge production. Biological Phosphorus removal is performed by Phosphate Accumulating micro-Organisms (PAO) in presence of oxygen. The main disadvantage of biological methods is being less stable due to its dependency to composition of wastewater (Ronteltap, 2009).

Phosphorus recovery

Physio-chemical removal technologies could cause decrease in the plant availability of removed Phosphorus. Thus, usage of removed Phosphorus as fertilizer can also increase the environmental concerns related to Phosphorus transportation towards water bodies. On the other hand, biological technologies produce smaller amount of sludge, but the removed Phosphorus can still release during sludge handling (Ronteltap, 2009). Thus, recovery of the Phosphorus from wastewater can be more efficient than removal. In recovery process, both treatment of wastewater (removal phase) and reuse of removed Phosphorus as a rich fertilizer are provided simultaneously. Precipitation of Phosphorus minerals is served as a recovery method. During precipitation process, the unfavorable concentration of Phosphorus is removed from wastewater and the useful form of Phosphorus is produced, which further can be applied as Phosphorus fertilizer in farm lands. Process summary of Phosphorus removal and recovery technologies are illustrated in table 1 (Morse et al., 1998).

Table 1. Phosphorus removal and recovery technologies

Technology	Objective	Process summary	Main input	Main output
Chemical precipitation	P removal	Addition of metal salt to precipitate P removed in sludge	Wastewater	Chemical sludge
Biological precipitation	P removal (may also include N removal)	Uptake of P by bacteria in aerobic stage following anaerobic stage	Wastewater (primary effluent)	Biological sludge
Crystallization	P removal and recovery	Crystallization of Calcium Phosphate using sand as a seed material	Wastewater (secondary effluent)	Calcium Phosphate, Sand
Advanced chemical precipitation (HYPO)	P and N removal	Crystallization of P/organic matter to produce Carbon source for N removal	Wastewater (primary effluent)	Chemical sludge
Ion exchange	Fertilizer (struvite production)	Phosphate and Ammonium are removed via precipitation	Wastewater (secondary effluent)	Struvite (MgNH ₄ PO ₄)
Magnetic	P removal	Precipitation, magnetic attachment, separation and recovery	Wastewater (secondary effluent)	Primarily Calcium Phosphate

P adsorbents	P removal	Adsorption and separation	Wastewater	No information
Tertiary filtration	Effluent polishing	Filtration	Wastewater (secondary effluent)	Tertiary sludge
Sludge treatment	Sludge disposal	E.g. sludge drying, reaction with cement dust	Sludge	Soil conditioner
Recovery from sludge ash	P recovery	Extraction from sludge ash	Sludge ash from biological removal	NA

Struvite (Magnesium Ammonium Phosphate, MAP)

Struvite (MAP) is a crystalline substance consisting of Magnesium, Ammonium and Phosphate in equal molar concentration of 1:1:1, typically surrounded by six water molecules (Eq 1).



Pure struvite is more likely fine white powder which dissolves poorly in water and alkaline environment, while more easily dissolved in acidic solutions. Also, struvite can occur in wide range of crystal sizes in yellowish or brownish white color. Struvite was first described in Hamburg, 1845, when it was found in sewer systems. The molecular weight of struvite is 245.43 gram per mol. According to the structure, struvite contains 13% of Phosphorus, 6% Nitrogen and 10% Magnesium as effective nutrient sources. Struvite is known as a problematic compound in wastewater treatment plants and sludge treatment facilities which can cause heavy scaling inside the pipes and walls of the anaerobic digestion system. Therefore, forced precipitation of struvite can prevent the scaling of the facilities (Md Mukhlesur Rahman et al., 2014; Ronteltap, 2009, p. 16).

Crystallization

The primary particle formation processes occurring during crystallization are based on nucleation or crystal birth following by crystal growth until equilibrium. Both stages of crystallization depend on the degree of supersaturation. Nucleation can be either primary or secondary. Primary nucleation occurs at higher supersaturation and can be homogeneous and heterogeneous. Homogeneous nucleation takes place in absence of foreign particles in clear solution while heterogeneous is induced by impurities in the solution. Secondary nucleation occurs at lower supersaturation and in presence of existing crystals. Crystal growth is a diffusion and integration process, modified by the effect of solid surface on which it occurs. Growth of crystals take place in two major steps (Jones, 2002):

1. Mass transport from solution to the crystal surface via diffusion, convection or combination of both mechanisms
2. Incorporation of material into the crystal structure via surface integration (surface reaction process)

Supersaturation

Supersaturation is an important parameter in crystallization process to define the state of compound in the solution. The state of crystals in the solution can be fall into three zone:

1. Undersaturated zone, in which all the added solids can dissolve in the solution. Crystal formation does not take place in this state
2. Metastable zone, the solution is oversaturated but the free energy is still too low for nucleation process
3. Oversaturated zone, where the solute concentration exceeds the equilibrium and nucleation takes place due to high free energy

Figure 4 illustrates the possible solution states regards to supersaturation. In order to overcome the supersaturation curve, the solution can be either (1) cooled at constant concentration or (2) the solvent can be concentrated by evaporation or solute addition in constant temperature. Also, combination of both methods can be happened (3) (Le Corre, 2006, pp. 22-23).

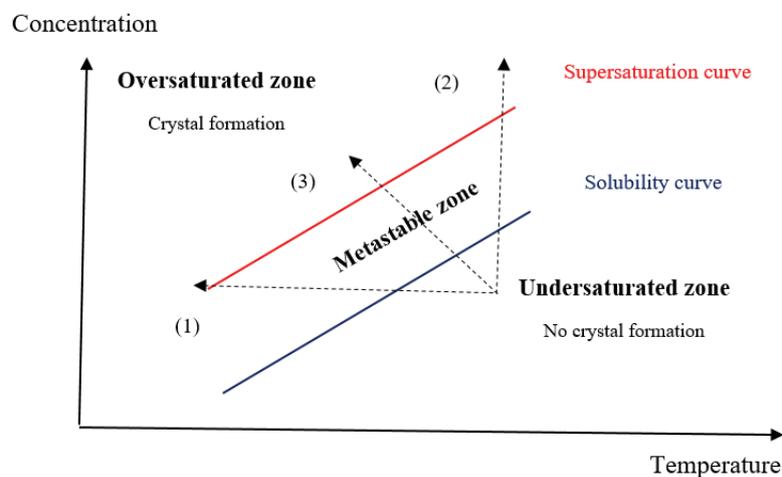


Fig 4. Solution states during crystallization process

Effective parameters on struvite formation

Efficiency of struvite (MAP) formation depends on parameters such as pH, concentration and molar ratios of Magnesium, Ammonium and Phosphate, temperature, aeration rate and presence of Calcium in the reacting media.

pH

pH plays an important role during struvite precipitation. Struvite can be precipitated in the wide pH range of 7 to 11 but the most suitable range, minimum solubility, is 7.5 to 9. The rate of pH influences the rate of crystal growth and quality of precipitated crystals. During struvite formation, protons are released into solution which decreases the pH (Saidou et al., 2009). Decreasing pH would increase the solubility of struvite which is not favorable for crystal formation process (Md Mukhlesur Rahman et al., 2014). Generally, the higher Phosphate and Ammonium removal occur at alkaline pH. On the other hand, increasing pH values can cause decrease in precipitated aggregate size (Z. Ye et al., 2014). The pH adjustment can be achieved by aeration or use of chemicals such as NaOH and HCl. Table 2 illustrates some of the reported pH values for struvite precipitation.

Table 2. pH range for struvite precipitation

Waste Source	pH	Reference
Industrial waste	9-11	(Kumar & Pal, 2013; Li et al., 2012; Yu et al., 2012; Zhang, Ding, Ren, et al., 2009)
	8-9	(Huang et al., 2012; Moerman et al., 2009; Türker & Çelen, 2007)
Farm waste	7-9	(Burns et al., 2001; Huang et al., 2011; Ryu & Lee, 2010; Suzuki et al., 2007)
Municipal waste	8-9	(Pastor et al., 2010; Uysal et al., 2010)

Aeration rate

Aeration rate has crucial impact in removal of $\text{NH}_4\text{-N}$ from the solution. Dissolved Ammonia can be volatilized by means of the removal pathways which are prepared by air flow. On the other hand, aeration increases pH in the solution by enhancing the CO_2 stripping (Md Mukhlesur Rahman et al., 2014). Liu et al. (2011) has reported that by increasing aeration rate, struvite formation and Phosphorus removal also increase. In addition, aeration would clean crystals from suspended particles which makes aeration interesting for struvite formation. Also, aeration could promote the Ammonium volatilization (Pastor et al., 2010). In order to eliminate the chemical use, aeration can be utilized to increase the pH to values 8-8.6 which is favorable for crystallization process (Battistoni et al., 1997; Suzuki et al., 2002). Suzuki et al. (2007) reported the pH value of 7.5-8 by aeration rate of $12\text{m}^3\text{h}^{-1}$ which was raised to 8-8.5 by increasing the aeration rate to $16\text{m}^3\text{h}^{-1}$. Quintana et al. (2008) have observed the pH increase from 7.31 to 8.25-8.28 by 30 minute of aerating domestic wastewater.

Molar mixing ratio

Struvite (MAP) formation is also dependent on mixing ratios of PO_4^{3-} , NH_4^+ and Mg^{2+} . The nucleation process is triggered in equal molar ratio of 1:1:1. Higher Mg: PO_4 molar ratio has positive effect on efficiency of Phosphorus removal. The important factor in utilizing chemicals and mixing ratios, which should be considered, is being economically justified. Majority of the struvite precipitation systems, either small or full scale, have utilized MgCl_2 as the most popular, cheap and easily accessible Mg source rather than other sources such as MgO or Brucite which could be considered both as Mg source and pH increasing agent (Table 3).

Table 3. Mg source for struvite precipitation

Mg Source	Reference
MgCl ₂	(Kumar & Pal, 2013; Liu et al., 2011; Ronteltap, 2009; Suzuki et al., 2007; Uysal et al., 2010; Z. Ye et al., 2014; Zhang, Ding, Ren, et al., 2009)
Brucite, Mg(OH) ₂	(Huang et al., 2011; Münch & Barr, 2001)
MgO	(Chimenos et al., 2003; Ganrot et al., 2007; Suschka & Popławski, 2003)

Also, increasing the NH₄:PO₄ molar ratio might cause better Phosphorus removal. Pastor et al. (2010) has investigated the effects of Mg: PO₄ and NH₄:PO₄ molar ratios of 0.5-1.8 and 5-23.1, respectively, on struvite formation. In another experiment, the molar ratios of Mg:NH₄:PO₄ fluctuated between 1:10:1 and 1:25:1 as high and low Ammonium and Phosphate concentrations, under the pH range of 7.57 and 8.13 (Lahav et al., 2013). Also, extreme molar ratios of Mg:NH₄:PO₄ such as 0-1.2:85:1 has been considered for struvite formation process (Liu et al., 2011). The applied Mg: PO₄ molar mixing ratios at further struvite formation experiments are demonstrated in table 4.

Table 4. Struvite precipitation experiments

Waste Source	pH Range	Mg: PO ₄ Molar ratio	Reference
Landfill leachate	8.5-11	1-1.25:0.9-1.2	(Zhang, Ding, & Ren, 2009)
Digested swine wastewater	8-11	1:0.6	(Z.-L. Ye et al., 2011) Referred to by (Md Mukhlesur Rahman et al., 2014)
MAP containing slurry	8-9	1:1	(Cho et al., 2009) Referred to by (Md Mukhlesur Rahman et al., 2014)
Human urine	6.5-10	1.71:2.21	(Lind et al., 2000)
Anaerobic effluent from potato industry	8.5-8.7	1-1.2:1	(Moerman et al., 2009)
Domestic wastewater	8.25-8.28	1.6:1	(Quintana et al., 2008)

Presence of Calcium

The Calcium ion in the wastewater might react with PO_4^{3-} to produce Dicalcium Phosphate. Also, high concentration of Calcium would cause presence of Amorphous Calcium Phosphate (ACP) in the struvite which might be the cause for impurity of the struvite crystals. Moreover, Calcium Phosphate inhibits formation of struvite (Md Mukhlesur Rahman et al., 2014). According to Le Corre et al. (2005) presence of Calcium can cause decrease in crystal size and inhibits crystal growth. Generally, higher molar ratio of Ca: Mg would affect adversely the struvite formation process (Pastor et al., 2008). Moreover, Ca:PO₄ molar ratio of more than 1 reduces the purity of struvite crystals (Huchzermeier & Tao, 2012). Although inhibitory effect of Calcium ion on struvite formation and its purity is widely accepted, further studies are still required to clarify the co-precipitation process with regards to various ionic concentration conditions (S.-H. Lee et al., 2013).

Why struvite?

Struvite precipitation prevents the scaling problem of the pipes and treatment facilities in wastewater treatment plants. This problem is common in most of treatment plants mainly due to use of chemicals such as Aluminum and Iron. On the other hand, struvite contain high concentration of Phosphorus and can be used as slow release fertilizer in agriculture. Low solubility of struvite releases the nutrients at slower rate than soluble fertilizers (Münch & Barr, 2001). Also, struvite can provide other necessary nutrients for plants such as Magnesium and Nitrogen. In addition, recovery of Phosphorus via struvite formation would decrease the use of limited Phosphate deposits to produce fertilizer. Therefore, compared to the industrial fertilizers manufactured from Phosphate rocks, the metals content of struvite might be much lower (Driver et al., 1999).

Commercial scale struvite plants

Commercial struvite recovery facilities are currently in operation in countries such as USA, Canada, England, Japan, Germany, Australia, Italy and The Netherlands (Kataki et al., 2016).

Pearl technology (North America, UK) was developed by university of British Colombia, Canada. The technology was first implemented at pilot scale in North America, 2007. 2 years later the commercial scale was installed in 2009, Oregon, USA. Pearl technology is based on side-stream treatment of the highly Phosphorus and Ammonium concentrated effluent in a fluidized-bed reactor. The process was modified by addition of an anaerobic zone (**WASSTRIP**) before digestion in which the Phosphate is stripped from activated sludge and added to the reject water (Figure 5). Final struvite fertilizer is named as Crystal Green. Currently, 14 commercial installations are performing in 5 countries worldwide (Ostara, 2016). The average Phosphate and Nitrogen recovery efficiency is 80% and 10-15%, respectively (Kataki et al., 2016). World's biggest Phosphate recovery installation was implemented in partnership with Ostara in 2016, Chicago, USA. The facility contains three Pearl reactors produce 8200-9100 tons per year struvite fertilizer (Platform, 2017).

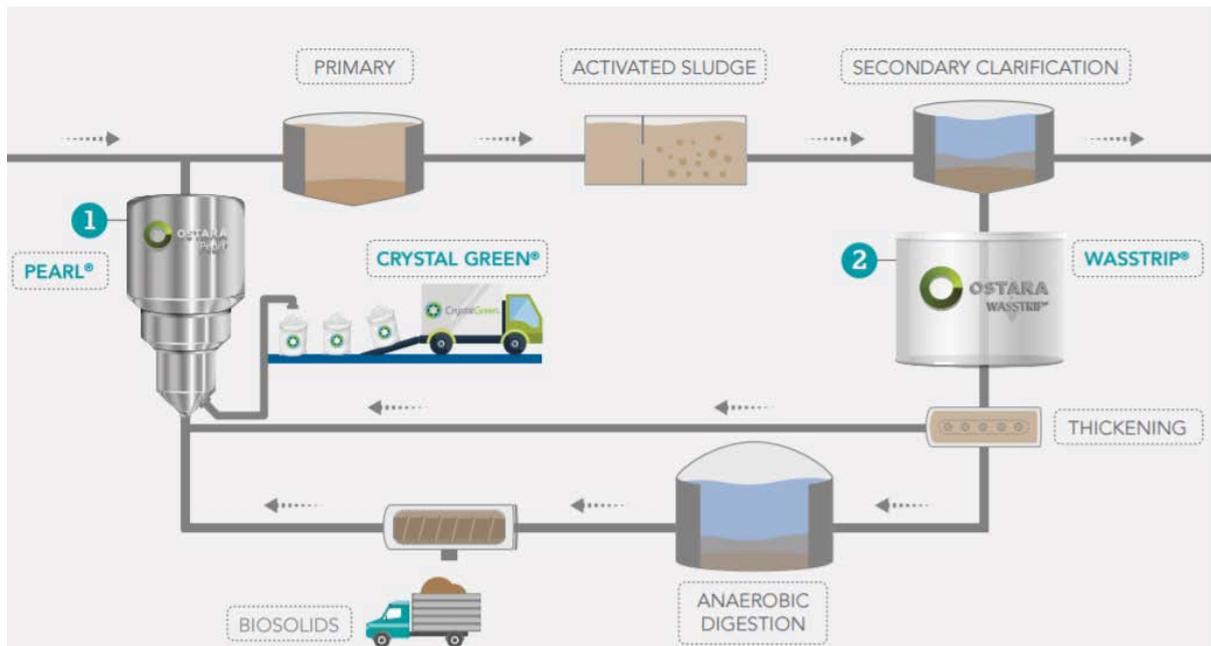


Fig 5. Pearl technology.

Phospaq (Netherlands) technology is utilized commercially to recover struvite by means of an aerated reactor. MgO is added to precipitate Phosphate. The pH is fixed at 8.2-8.3 via CO₂ stripping by aeration. Initial Phosphate concentration in wastewater is 50 mg/l which can be recovered up to 80% during Phospaq technology. The process is boosted by implementing an extra unit in which the Ammonium is converted into Nitrogen gas via nitrification and Anammox bacteria involving. The **Anammox** process recovers the ammonium up to 90% (Kataki et al., 2016).

AirPrex (Germany, Netherlands) technology precipitates and collects struvite from digested sludge before dewatering process. MgCl₂ is added to the sludge tank after digestion. The tank is aerated from the bottom to remove CO₂ and increase the pH to 8. The Phosphate recovery is up to 90-95% in this technology. The process installation after anaerobic digestion and prior to dewatering enhances the sludge dewatering and inhibits downstream struvite precipitation and clogging (Kataki et al., 2016).

Multiform (America) technology is under trial operation at two dairies in the USA. The process occurs after anaerobic digestion and dewatering processes. The Phosphate and Nitrogen removal are 80% and 20%, respectively (Kataki et al., 2016). Many wastewater treatment plants strip and release Phosphorus from waste-activated sludge (WAS). These P-release plants can utilize Multiform systems to avoid the struvite formation in the digester up to 90% (Multiformharvest, 2015) (Figure 6).

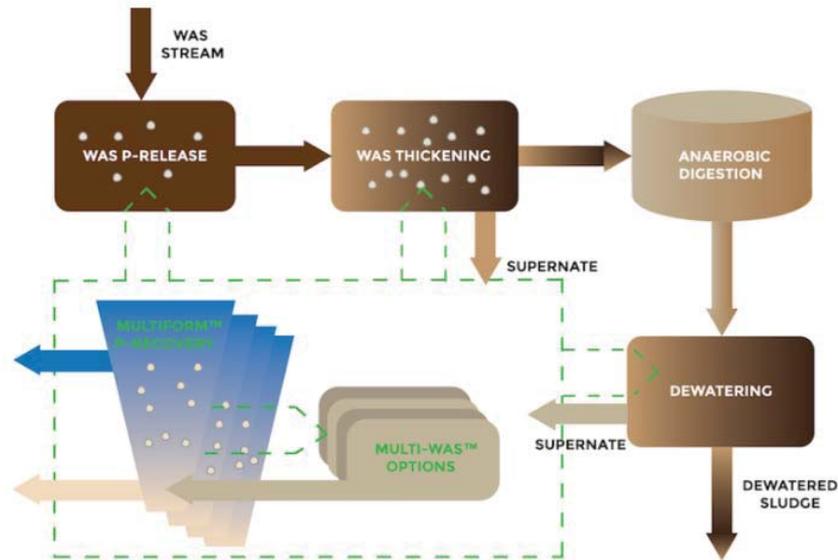


Fig 6. Multiform technology.

Naskeo environment has developed the first full-scale struvite plant in France in 2014. The crystal formation is taken place in a fluidized bed reactor which is designed by Naskeo. MgO is utilizing in order to precipitate Phosphate. The daily recovered Ammonium and Phosphate are 5 and 12 kg, respectively. Also, with regards to 85-90% Phosphorus removal via this process, the dry weight of produced struvite is 90 kg per day (Platform, 2016).

Goal and objectives

HIAS wastewater treatment plant is planning to build a new struvite unit in coming years. The main goal of this thesis is to evaluate efficiency of struvite precipitation through wastewater and suggest the optimum design parameters including pH, mixing molar ratios and mixing time to achieve the maximum Phosphorus removal (from wastewater) and recovery as struvite fertilizer. In order to investigate this goal, the objectives that should be considered and developed fall into the parts:

1. Evaluate the effects of Mg source and its mixing ratio on struvite precipitation and Phosphorus removal from wastewater.

Hypothesis: Addition of Mg source is an important step in struvite precipitation. The mixing ratio of Mg: PO₄ affects the Phosphorus removal efficiency. The preliminary ratio of 1:1 is crucial to generate the precipitation process. Increasing this ratio, could cause higher Phosphorus removal. Determining the optimal Mg: PO₄ mixing ratio by considering the economic justification of chemical use is necessary.

2. Study the impacts of mixing or reaction time on struvite precipitation.

Hypothesis: Mixing time plays an important role in struvite production process. The optimal mixing time provides favorable reaction time for chemicals and ingredients. Mixing time can cause both positive and adverse effect on struvite formation efficiency following Phosphorus removal.

3. Investigate the effect of different NH₄:PO₄ mixing ratio on Phosphorus removal with regards to production ratios in HIAS wastewater treatment plant

Hypothesis: Higher mixing ratio can cause boost in Phosphorus removal through struvite formation.

Method and materials

Sampling

Samples were taken from HIAS wastewater treatment plant located in Hamar, Norway. For this purpose, two 25 liter containers of high concentration Ammonium wastewater originating after anaerobic digestion, and high concentration Phosphorus wastewater coming from bio-P, were provided. The samples were transported to Norwegian University of Life Sciences (NMBU) in order to further analysis and studies.

HIAS wastewater treatment plant

HIAS wastewater treatment plant is located in Hamar, Norway. The plant is responsible to treat the wastewater produced from municipality (nearly 65000 people) and industry. The amount of Phosphorus in the wastewater is estimated 53 tons per year. The plant includes mechanical, biological and chemical treatment units. Currently, the sludge which is produced from each treatment unit, will be treated and used as biomass in agriculture. The main challenge regards to this agricultural amendment, due to use of chemicals in treatment process, is high concentration of Aluminum which inhibits the Phosphorus uptake by plants. Also, the reject water from sludge treatment unit contains high concentration of Ammonium.

Mechanical treatment

In mechanical treatment step, the most visible and coarse contaminants will be removed. Therefore, the influent flows through screens to remove large particles. Furthermore, the wastewater flows through the grit chamber. In this step, the sand and grease will be trapped. The air is blown inside the tank and sand particles will be settled down and grease, oil and fat will flow to the surface. Finally, the water flows through primary sedimentation tank. The produced sludge in this unit, will be pumped to the sludge treatment unit. Figure 11 demonstrates the mechanical treatment unit at HIAS wastewater treatment plant.

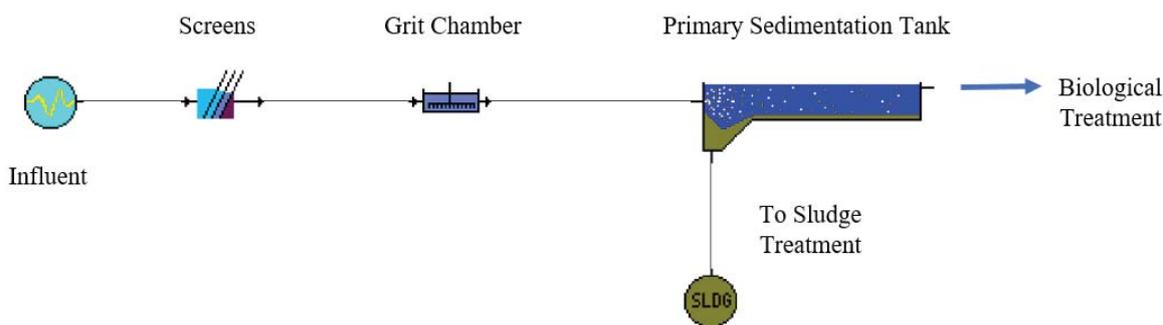


Fig 11. Mechanical treatment unit at HIAS

Biological treatment

In biological treatment step (figure 12), the microorganisms need oxygen and food to survive. Thus, the air is blown into the activated sludge (aeration basin). So, the organic matter in the wastewater is removed via microorganisms. After activated sludge unit, the secondary sedimentation tank is located. In this step, the microorganisms are trapped and fall to the bottom of the basin. Part of the sludge produced in this unit, will be pumped back into aeration basin to maintain the microorganisms life chain. The residual sludge is pumped to sludge treatment unit.

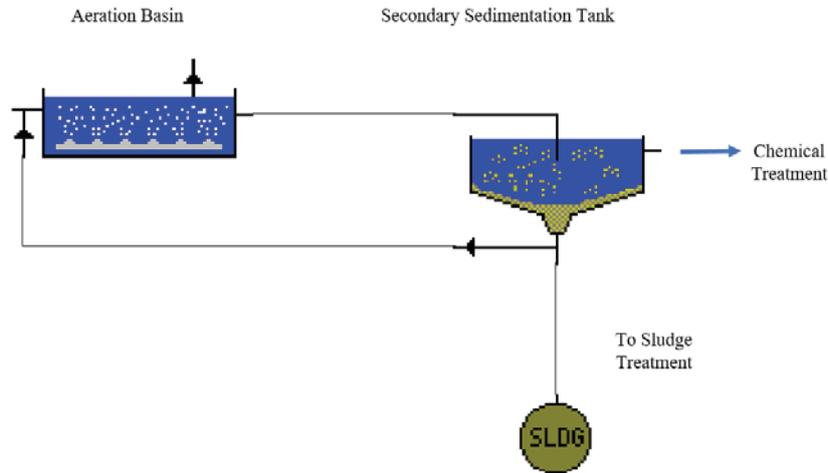


Fig 12. Biological treatment unit at HIAS

Chemical treatment

In order to remove Phosphorus from wastewater, chemical treatment is utilized (Figure 13). Alum is added to the water after biological treatment. The wastewater, after chemical addition, flows into flocculation step. During flocculation, Phosphorus binds to Aluminum, to form larger particles. Then, the Phosphorus containing particles are settled down in sedimentation basin. The sludge is pumped to sludge treatment unit and the purified water returns into Mjøsa Lake.

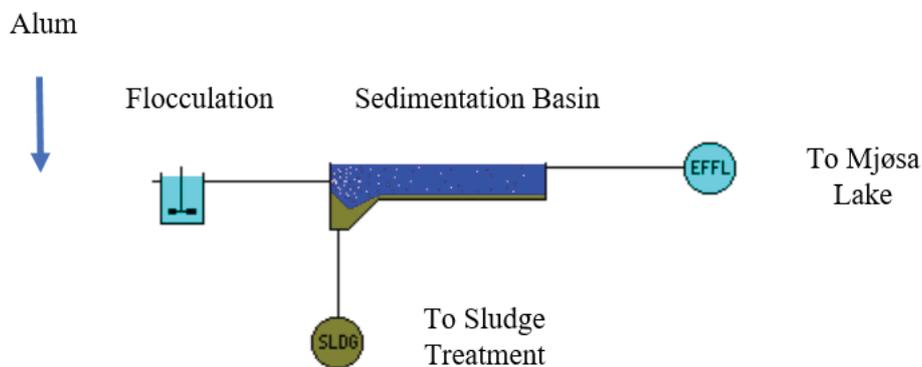


Fig 13. Chemical treatment unit at HIAS

Sludge treatment

Sludge from three treatment units is pumped into sludge treatment step. In this unit, the sludge is thickened. After sludge thickening, the sludge contains 1-2.5% dry solids. Then the sludge loses more water in dewatering unit. The dry matter content is increased to at least 15% after dewatering. The slurry is stored temporarily in silos before thermal hydrolysis. In thermal hydrolysis, the slurry are heated in a three-step process up to 160 degrees by utilizing steam injection. The thermal hydrolysis, makes the organic matter more easily degradable for microorganisms. In this step the sludge is sterile. After pressure reduction and heat exchange to nearly 38 degrees, the sludge is pumped into digestion units in which microorganisms convert organic matter to biogas. Eventually, the reject water returns into wastewater treatment

process and the dewatered sludge is packed and ready to use. Schematic design of sludge treatment unit is illustrated at figure 14.

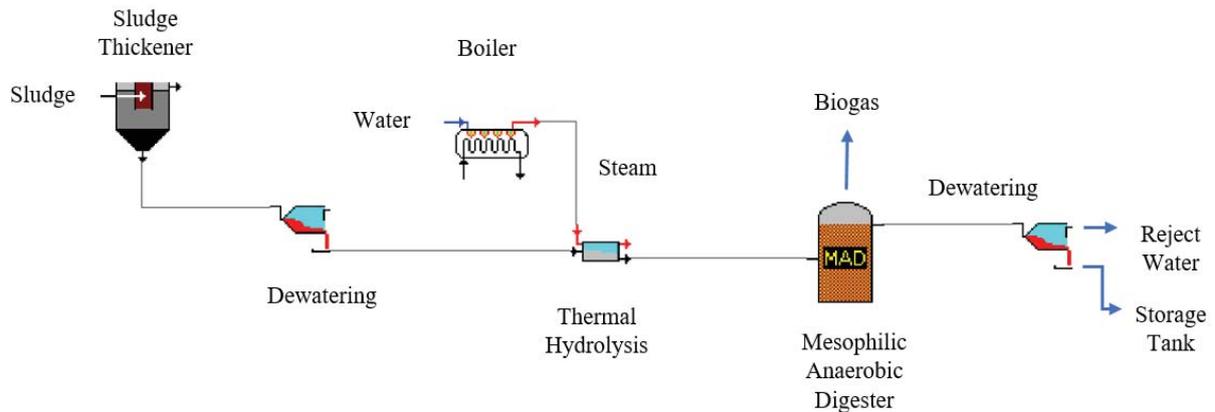


Fig 14. Sludge treatment unit at HIAS

Future design

The HIAS wastewater treatment plant is planning to eliminate the chemical treatment unit and design a new struvite precipitation unit. Thus, by avoiding use of chemicals to remove Phosphorus from wastewater, the biomass which is produced after sludge treatment unit can be utilized in agricultural farms without any concern related to limited availability of Phosphorus for plants. On the other hand, by addition of new struvite precipitation unit, Ammonium (from reject water after sludge treatment) and Phosphorus can be recovered. Moreover, the precipitated struvite can be used as nutrient enriched slow release fertilizer.

Experiments

The experiments were conducted in the laboratory of IMV department. Ammonium production rate at HIAS is 100 m³ per day with concentration of nearly 3000 mg/l. Also, Phosphate production rate is around 260 m³ and the concentration is estimated to fluctuate between 150 and 350 mg/l depending on operating factors and seasonal variations. After initial sample analysis, the molar ratio of NH₄:PO₄ production at HIAS facilities were determined 10:1 (350 mg/l Phosphate) and 5:1 (150 mg/l Phosphate). Therefore, two molar ratio of 10:1 and 5:1 for NH₄:PO₄ were considered in this study. The pH was constant and fixed by chemicals (NaOH) at 8.3, which could be the highest achievable pH at HIAS plant. The struvite formation process were investigated at 20, 40 and 60 minute of mixing time. Also, MgCl₂.6H₂O was used as additional Mg source and was added in Mg: PO₄ molar ratios of 0.6, 0.8 and 1.1. Experimental design is demonstrated in figure 7. All experiments were replicated 3 times. Overall, 18 experiments were conducted for each replication.

Mg: PO ₄ (molar)	NH ₄ :PO ₄ (molar)	pH	Mixing Time (min)
0.6	5	8.3	20
0.8			40
1.1	10		60

Fig 7. Experimental design

For each experiment 400 ml of Phosphate sample was mixed with 81 ml (5:1 molar ratio) or 151 ml (10:1 molar ratio) of reject water. The initial Mg concentration in Phosphate wastewater was deducted from required Mg source and the remaining amount was added, as $MgCl_2 \cdot 6H_2O$ in order to supply molar ratios of 0.6-1.1. Thus, with regards to the experimental design, 140, 250 and 400 mg Magnesium Chloride was added as ratios of 0.6, 0.8 and 1.1, respectively. The mixing process was taken place in 1000 ml beakers by means of magnetic stirring. At the beginning of experiments, 30 seconds mixing process was taken place with speed of 300 RPM, as fast mixing, and then the main experiment continued under the speed of 100 RPM, as slow mixing stage. All the experiments were done at room temperature (25 Celsius degree).

pH adjustment

pH was measured during 30 seconds fast mixing as the initial pH and then it was being measured continuously using the portable Orion SA 720 pH-meter. In order to fix the pH at 8.3 (+/- 0.02), NaOH 2 molar was added into the solution whenever the pH was dropped to around 8.28. Figure 8 illustrates the struvite crystallization process at mixing speed of 100 RPM and continuous pH adjustment.

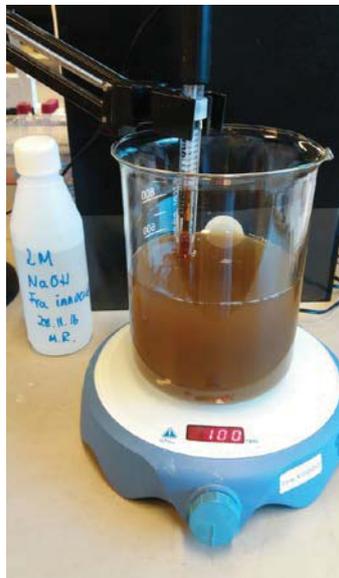


Fig 8. Struvite formation process

Saturation index

In order to calculate the saturation index, with regards to the experimental design and the concentration of ions, Visual MINTEQ software was utilized. The saturation index is essential for struvite formation as the process can be triggered only in supersaturation ($SI > 1$) situation.

Struvite separation

After the mixing stage, the separation of produced struvite from the solution was taken place by use of centrifuge Avanti JXN-26 developed by BECKMAN COULTER. The separation process was done by rotating speed of 3000 RPM for 10 minutes at 25 Celsius degrees (Figure 9).



Fig 9. Centrifuge for struvite separation

Sample analysis

Turbidity and Conductivity

In order to measure turbidity and conductivity, after the centrifuge step, the portable Thermo Orion Star A329 was utilized (Figure 10). Turbidity and conductivity of the initial wastewater also were measured after centrifuging the samples.



Fig 10. Turbidity and conductivity measurement

Spectrophotometry

Concentration of Ortho-Phosphate was determined by means of colorimetric method, Gilford Spectrophotometer at wave-length of 700 nm. The samples were diluted 100 times, then 10 ml of samples were mixed with 0.4 ml Ascorbic acid and 0.4 ml Molybdate Ammonium.

Flow Injection Analysis (FIA)

As the initial concentration of Ammonium in wastewater was expected to be very high and to avoid the interference of other elements such as Calcium, the Flow Injection method was used

to detect accurately the Ammonium concentration of initial wastewater and the samples after struvite precipitation.

ICP-MS

In order to analyze the concentration of metals and non-metals exist in the water samples, Inductively Coupled Plasma Mass Spectrometry (ICP-MS) technology was utilized, in which the concentration of metals and non-metals, even in very low quantities, can be detected very accurate along with the efficient removal of interferences. The concentrations of Aluminum, Iron, Zink, Total Phosphorus, Arsenic, Nickel, Copper, Calcium, Chromium, Magnesium, Potassium, Cadmium and Mercury, for both initial wastewater and samples after crystallization, were measured by means of the Agilent 8800 Triple Quadrupole ICP-MS.

Statistical analysis

In order to statistically analyze the results and data achieved from experiments, the R 3.3.3 language software was utilized. P-value < 0.05 and confidence interval of 95% were used to distinguish the significant difference between tested nutrient removals and further analysis. With regards to the experimental design, number of variables and the response characteristics, multiple linear regression was considered the most suitable analysis for this study. In addition, Minitab 17 statistical package was used to predict the highest Phosphorus and other elements removal due to the experimental design, and compare with the results concluded through this study. Also, Microsoft Excel was used to make required tables in all chapters and scatter plots in results section.

Results

Initial sample analysis

The samples were divided into reject water (high concentration of Ammonium) and Phosphorus-rich wastewater which were taken after sludge treatment unit and bio-P, respectively. Table 5 demonstrates the characteristics of the initial wastewater and reject water samples from HIAS treatment plant. Turbidity measurements were done without centrifuging. Also, the Ammonium concentration were analyzed both with and without filtration. The Ammonium concentration with filtration was detected 2168 mg/l. The small difference between the Ammonium concentration with and without filtration (Table 5), showed that the collected reject water had not considerable number of particles. Therefore, all the Ammonium measurements were done without filtration. On the other hand, according to turbidity data, the accumulation of invisible particles in wastewater was much higher (nearly 3 times) than reject water.

Table 5. Characteristics of initial samples

Sample	NH ₄ ⁺ -N mg/l	PO ₄ ³⁻ -P mg/l	pH	Turbidity NTU	Conductivity ms/cm
Wastewater		189	5.14	453	2.01
Reject water	2220		8.32	144	14.3

Furthermore, concentration of metals and Total Phosphorus were also analyzed for both initial wastewater and reject water samples (Table 6).

Table 6. Wastewater analysis

Sample/Element	Na mg/L	Mg mg/L	Al mg/L	Total P mg/L	K mg/L	Ca mg/L	Cr ug/L	Fe mg/L
Wastewater	96	47.5	0.53	200	150	110	3.6	14
Reject Water	57	24	1.5	8.8	210	23	11	5.1

Table 6. Wastewater analysis (continue)

Sample/Element	Ni ug/L	Zn ug/L	Cu ug/L	As ug/L	Cd ug/L	Hg ug/L	Pb ug/L
Wastewater	12	81.5	12.5	2.9	0.022	0.16	0.4
Reject Water	48	66	56	28	0.025	0.15	0.82

The experiments through the current study were implemented by means of mixing the initial wastewater and reject water in various NH₄: PO₄ molar ratios of 5:1 and 10:1. Table 7 illustrates the sample analysis with regards to the mixture ratios.

Table 7. Experiment's samples analysis

NH ₄ : PO ₄	Na mg/L	Mg mg/L	Al mg/L	P mg/L	K mg/L	Ca mg/L	Cr ug/L	Fe mg/L
5:1	90	42.5	0.93	170	160	94	5.7	12
10:1	83	42.5	1.6	150	160	92	5.9	12

Table 7. Experiment's samples analysis (continue)

NH ₄ : PO ₄	Ni ug/L	Zn ug/L	Cu ug/L	As ug/L	Cd ug/L	Hg ug/L	Pb ug/L
5:1	24	92	45	6.8	0.03	0.05	1.2
10:1	25	86	40	9.4	0.02	<0.05	1.3

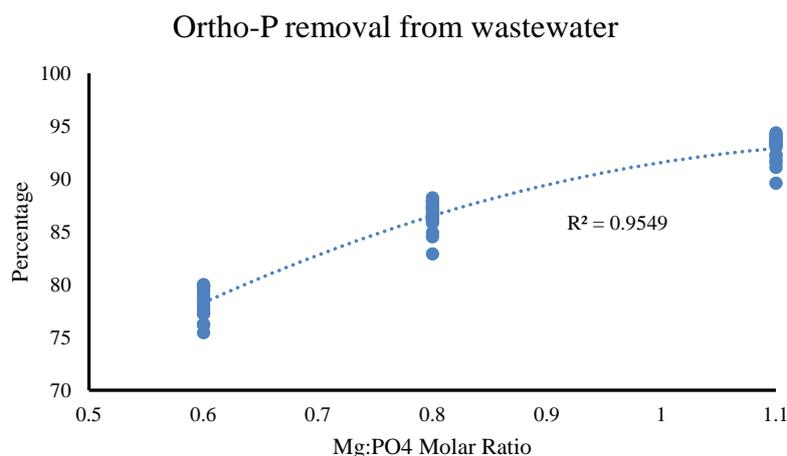
Ortho-Phosphate

Table 8 illustrates the results of Ortho-P removal from wastewater through struvite precipitation at different applied Mg amounts. According to statistical analysis, Ortho-P removal was increased significantly by increasing the Mg: PO₄ molar ratio from 0.6 to 1.1 (P-value = 0.001).

Table 8. Phosphorus removal vs molar ratio

Mg: PO ₄ Molar Ratio	PO ₄ ³⁻ -P (mg/l) Initial	PO ₄ ³⁻ -P (mg/l) After Precipitation	Removal %
0.6		41.1	78.3
0.8	189	25.5	86.5
1.1		13.5	92.9

According to figure 11, and with regards to the results, Ortho-P removal from solution would be the highest at Mg: PO₄ molar ratio of 1.1 and is expected to be almost constant at further molar ratios ($R^2 = 0.95$).

Fig 11. Ortho-P removal from wastewater vs Mg: PO₄ molar ratio

The results showed that Ortho-P removal from wastewater at NH₄: PO₄ molar ratios of 5 and 10 were 85.5% (from 189 to 27.4 mg/l) and 86.3% (189 to 25.9 mg/l), respectively. This slight increase was not significantly different (P-value > 0.05). Also, the scatter plot illustrates that the Ortho-P removal from solution was mainly in same range at most of various NH₄: PO₄ molar ratio treatments (Figure 12).

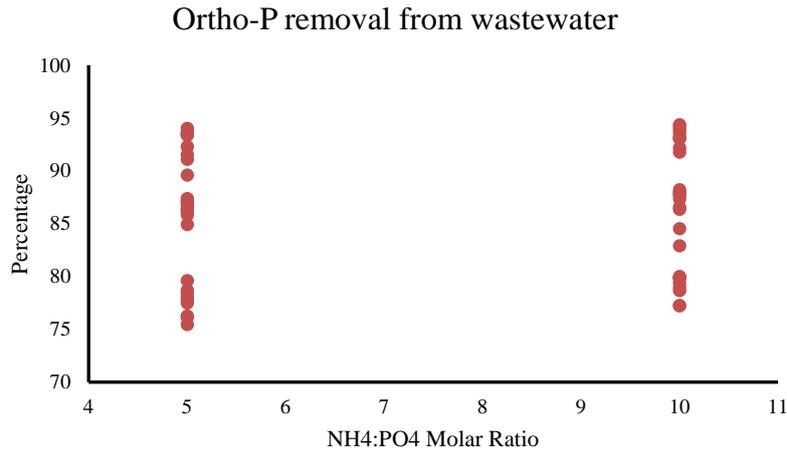


Fig 12. Ortho-P removal from solution vs NH₄: PO₄ molar ratio

The results demonstrated that increasing mixing time from 20 minute to one hour had not significant effect on Ortho-P removal from wastewater (P-value > 0.1). The results of Ortho-P removal from wastewater through crystal formation was around 86% in all mixing time intervals (Table 9).

Table 9. Ortho-P removal from wastewater vs mixing time

Mixing Time Minute	PO ₄ ³⁻ -P (mg/l)		Removal %
	Initial	After Precipitation	
20		27.8	85.3
40	189	26.1	86.2
60		26.1	86.2

Furthermore, statistical analysis did not illustrate any significant effect of interconnection between the treatments (Mg*NH₄, Mg*Time, NH₄*Time and Mg*NH₄*Time) on Ortho-P removal from solution (P-value > 0.1). For instance, considering the results from Minitab 17, the interaction between Mg amount and mixing time would affected the Ortho-P removal from wastewater as shown in figure 13 but this reduction was not significant. In this case, Ortho-P removal was nearly 78% at Mg molar ratio of 0.6 along 20 and 60 minute mixing time. But at Mg molar ratio of 1.1, the removal increased from 91.5% to 93.5% by increasing mixing time from 20 to 60 minute.

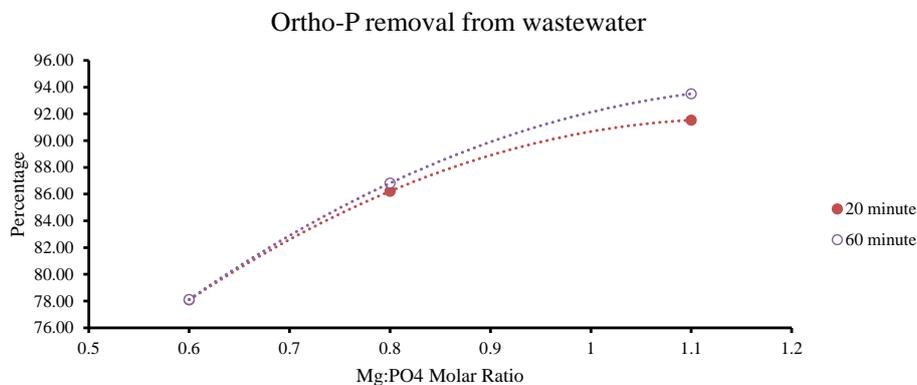


Fig 13. Ortho-P removal from wastewater vs Mg*Time interaction

Moreover, Ortho-P removal from solution through the experiments are demonstrated in table 10.

Table 10. Ortho-P removal from solution through struvite precipitation

Mg: PO ₄ Molar Ratio	NH ₄ : PO ₄ Molar Ratio	pH	Mixing Time	PO ₄ ³⁻ -P Concentration		Removal %
			Minute	Initial (mg/l)	After (mg/l)	
0.6	5	8.3	20	189	44.1	76.7
			40	40.3	78.7	
			60	43.1	77.2	
	10		20	38.8	79.5	
			40	40.6	78.5	
			60	39.7	79	
0.8	5	20	26.2	86.2		
		40	25.4	86.6		
		60	25.4	86.6		
	10	20	26	86.3		
		40	26	86.3		
		60	24.1	87.3		
1.1	5	20	17.5	90.7		
		40	12.2	93.5		
		60	12.8	93.2		
	10	20	14.5	92.3		
		40	11.9	93.7		
		60	11.7	93.8		

In addition, the results of regression fit model and optimizing response (at 95% confidence level) from Minitab 17, showed that the highest Ortho-P removal from wastewater could be expected to achieve 94.27% at Mg:NH₄:PO₄ molar ratio of 1.1:10:1 and 60 minute of mixing. The obtained Ortho-P removal during the same experiment was found very similar as 93.8%. The predicted alternative solutions for the highest Ortho-P removal from wastewater are shown in table 11.

Table 11. Predicted alternatives for highest Ortho-P removal from wastewater

Mg: PO ₄ Molar Ratio	NH ₄ : PO ₄ Molar Ratio	pH	Mixing Time	Predicted PO ₄ ³⁻ -P Removal %
			Minute	
1.1	5	8.3	60	93.5
1.1	10		40	93.3
1.1	5		40	92.5
1.1	10		20	92.3
1.1	5		20	91.5

Ammonium

Table 12 illustrates the Ammonium removal from wastewater based on mixing time and Mg source. Ammonium reduction was nearly 74-75% regards to these treatments while according to statistical analysis, removal was not significantly different between the mentioned treatments (P-value > 0.1).

Table 12. Ammonium removal from wastewater vs Mg source and mixing time

Mg: PO ₄ Molar Ratio	Ammonium Concentration Initial (mg/l)	Ammonium Concentration After (mg/l)	Removal %	Mixing Time Minute	Ammonium Concentration mg/l	Removal %
0.6		569	74.4	20	543	75.5
0.8	2220	552	75.1	40	576	74.1
1.1		559	74.8	60	555	75

On the other hand, as demonstrated at figure 14, by increasing the NH₄: PO₄ molar ratio from 5 to 10, the Ammonium removal from solution was decreased significantly (P-value = 0.001).

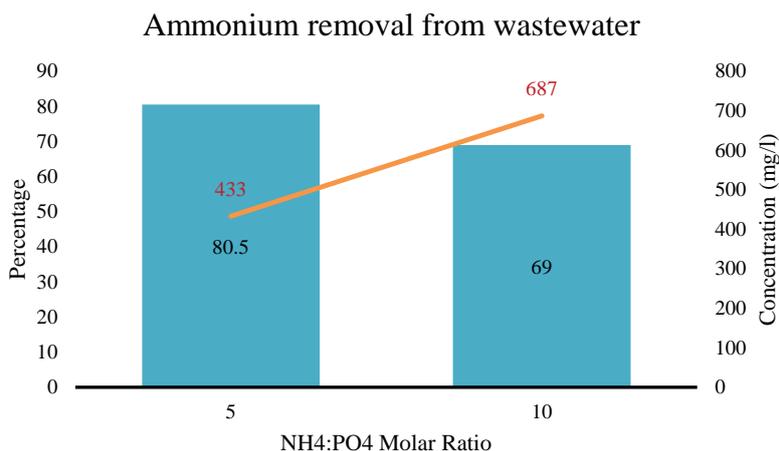


Fig 14. Ammonium removal from wastewater vs NH₄: PO₄ molar ratio

The results also showed that the Ammonium removal from solution was decreased from around 80% to 69% by considering the interaction between Mg and Ammonium molar ratio (Mg*NH₄), in which the reduction was significantly different (P-value = 0.01) (Figure 15).

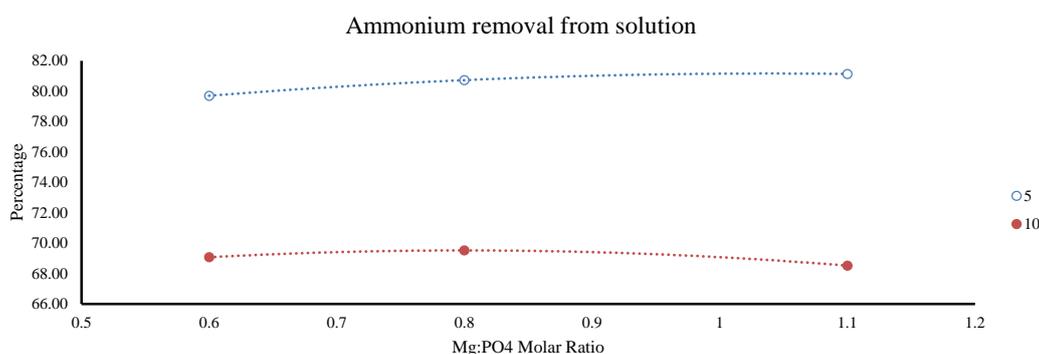


Fig 15. Ammonium removal from solution vs Mg*NH₄

The results of Ammonium removal from wastewater through struvite formation process are presented at table 13.

Table 13. Ammonium removal through struvite formation process

Mg: PO ₄ Molar Ratio	NH ₄ : PO ₄ Molar Ratio	pH	Mixing Time Minute	NH ₄ -N Concentration		Removal %
				Initial (mg/l)	After (mg/l)	
0.6	5	8.3	20		449	79.8
			40		460	79.3
			60		443	80
	10		20		673	69.7
			40		707	68.2
			60		680	69.4
0.8	5	20		417	81.2	
		40		451	79.7	
		60	2220	417	81.2	
	10	20		677	69.5	
		40		710	68	
		60		643	71	
1.1	5	20		380	82.9	
		40		437	80.3	
		60		441	80.2	
	10	20		700	68.5	
		40		690	68.9	
		60		707	68.2	

The prediction results to achieve the highest Ammonium removal from solution through the process, via Minitab 17 optimization analysis, and the results from experiments are shown and compared in table 14.

Table 14. Ammonium removal from solution through experiments vs prediction

Mg: PO ₄ Molar Ratio	NH ₄ : PO ₄ Molar Ratio	pH	Mixing Time Minute	NH ₄ -N Removal %	
				Prediction	Experiments
1.1			20	82.3	82.9
0.8			20	81.5	81.2
0.8	5	8.3	60	80.8	81.2
1.1			60	80.6	80.2
1.1			40	80.4	80.3

The Pearson two-sided correlation test, showed that there was no significant relationship among Ortho-P and Ammonium removal from wastewater in all replications (Figure 16) (P-value > 0.1).

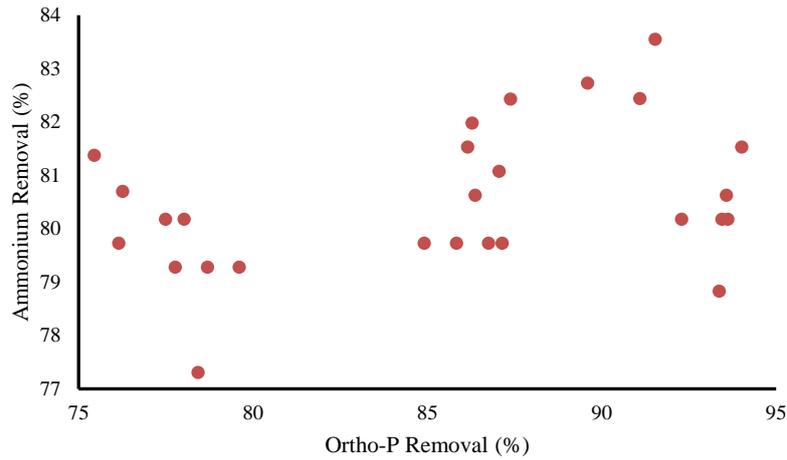


Fig 16. Ammonium removal vs Orho-P removal from wastewater in all replications

Calcium

The results of Calcium reduction from wastewater are shown in figure 17. The statistical analysis demonstrated that the reduction was significantly decreasing among Mg molar ratios of 0.6, 0.8 and 1.1 (P-value = 0.001).

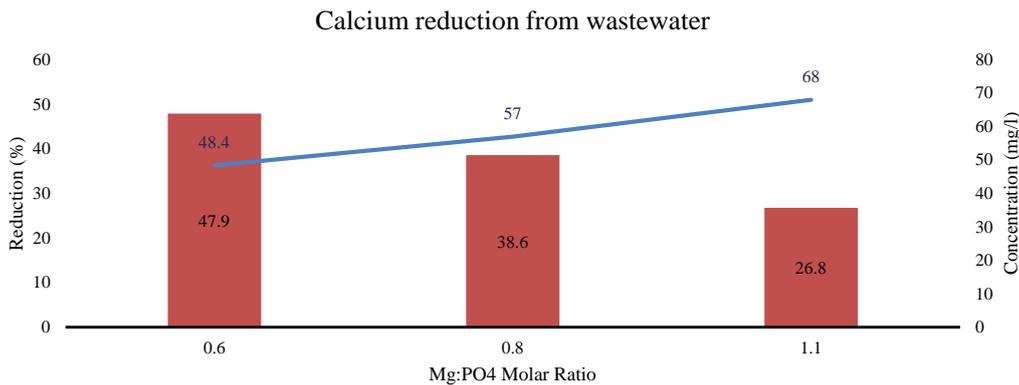


Fig 17. Calcium reduction from wastewater vs Mg: PO₄ molar ratio

Table 15 illustrates the results of Calcium reduction from solution with regards to different NH₄: PO₄ molar ratios. The observed nearly 5% less Calcium removal by increasing NH₄: PO₄ molar ratio was significant due to statistical analysis (P-value = 0.001).

Table 15. Calcium reduction from solution vs NH₄:PO₄ ratio

NH ₄ : PO ₄ Molar Ratio	Calcium Concentration		Removal %
	Initial (mg/l)	After (mg/l)	
5	94	56.7	40.2
10	92	58.9	36

The scatter plot of Calcium reduction from solution vs NH₄:PO₄ molar ratio is shown at figure 18.

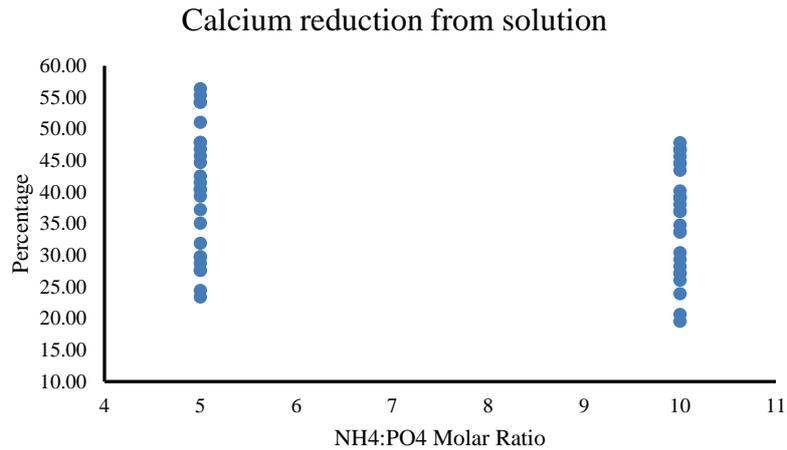


Figure 18. Calcium reduction from solution vs NH₄:PO₄ molar ratio

On the other hand, as illustrated in table 16, Calcium reduction from wastewater was statistically significant by increasing the mixing time (P-value = 0.01).

Table 16. Calcium removal vs mixing time

Mixing Time	Calcium Concentration	Removal
Minutes	mg/l	%
20	58.9	37.1
40	58.8	36.8
60	55.8	40

Prediction and optimization of Calcium reduction from wastewater via Minitab 17, demonstrated that the treatment of 0.6:5:1 as Mg: NH₄: PO₄ ratios at 60 minute mixing time could achieve the highest Calcium removal of 52.6%. During the experiments, Calcium reduction of 55% was achieved for the same treatment (Figure 19).

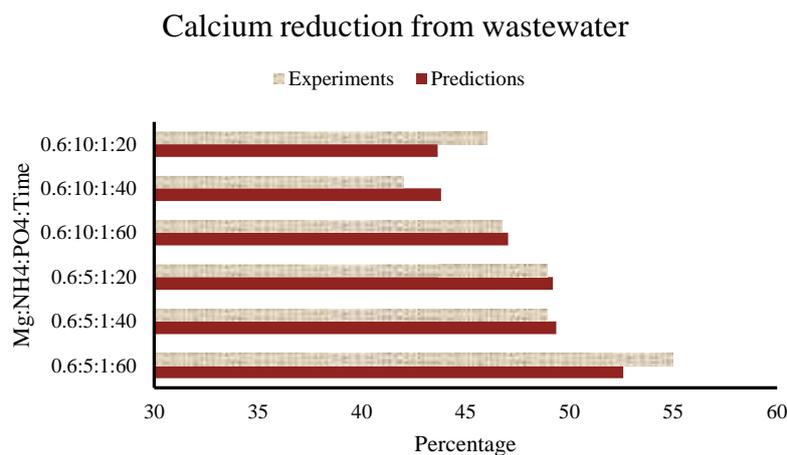


Fig 19. Calcium reduction from wastewater through experiments vs prediction

The Pearson two-sided correlation test, showed high dependency between Calcium reduction and Ortho-P removal from wastewater in all replications (cor = -0.89, P-value = 0.000). The mentioned relationship between Calcium and Ortho-P removal is demonstrated at figure 20.

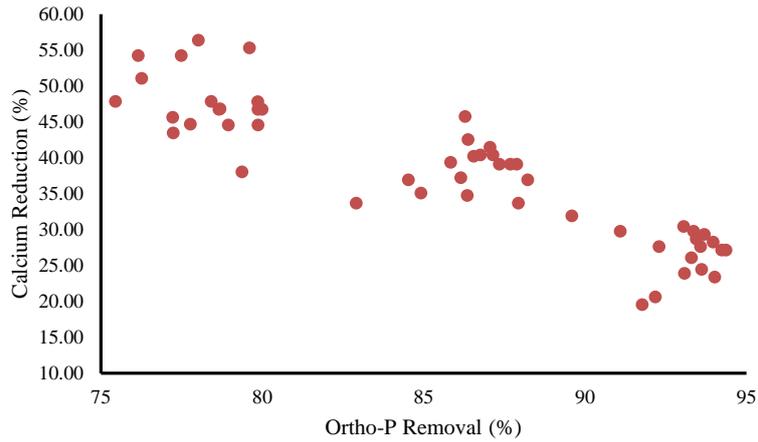


Fig 20. Calcium reduction vs Ortho-P removal from wastewater in all replications

The results of Calcium reduction from wastewater through struvite crystallization process are shown in table 17.

Table 17. Calcium reduction from wastewater through struvite precipitation

Mg: PO ₄ Molar Ratio	NH ₄ : PO ₄ Molar Ratio	pH	Mixing Time Minute	Calcium Concentration Initial (mg/l)	After (mg/l)	Reduction %
0.6	5	8.3	20		48	21.4
			40	94	48	48.9
			60		42.3	55
	10		20		49.7	46
			40	92	53.3	42
			60		49	46.7
0.8	5	20		60	36.2	
		40	94	56.3	40.1	
		60		53.3	43.3	
	10	20		58.3	36.6	
		40	92	59.7	35.1	
		60		55.7	39.5	
1.1	5	20		65	30.9	
		40	94	68.7	27	
		60		68.7	27	
	10	20		72.3	21.4	
		40	92	66.7	27.5	
		60		65.7	28.6	

Magnesium

According to statistical analysis, Magnesium removal from wastewater was significantly different among various Mg: PO₄ molar ratios of 0.6 – 1.1 (Figure 21) (P-value = 0.001). The results of Mg reduction from solution through the precipitation process are shown in table 18.

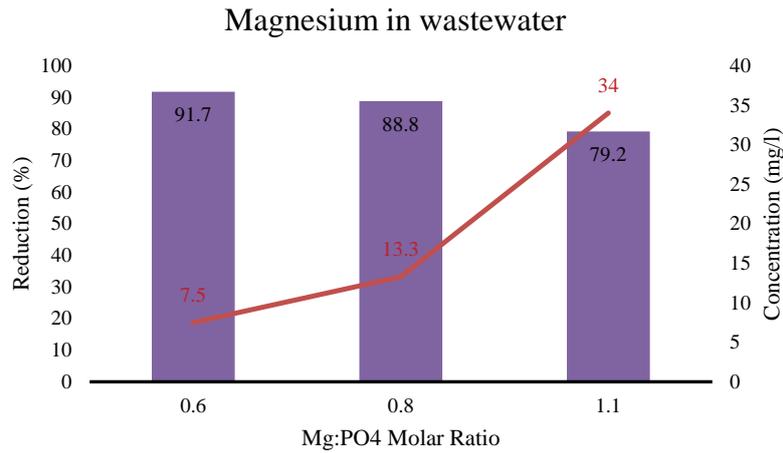


Fig 21. Magnesium changes in wastewater vs Mg: PO₄ molar ratio

Table 18. Mg reduction from solution through precipitation process

Mg: PO ₄ Molar Ratio	NH ₄ : PO ₄ Molar Ratio	pH	Mixing Time Minute	Mg Concentration Initial (mg/l)	Mg Concentration After (mg/l)	Reduction %
0.6	5	8.3	20	89.2	7.26	91.9
			40		7.83	91.2
			60		7.5	91.6
			20		6.83	92.3
			40		8.37	90.6
			60		6.9	92.3
0.8	5	8.3	20	119	13.3	88.8
			40		15.3	87.1
			60		12.7	89.4
			20		12	89.9
			40		14.3	88
			60		12	89.9
1.1	5	8.3	20	164	31	81.1
			40		34.7	78.8
			60		34.7	78.8
			20		35.7	78.2
			40		32	80.4
			60		36	78

On the other hand, Mg reduction from solution was not significantly different through both mixing time and Ammonium mixing ratio treatments (P -value > 0.1). Magnesium reduction from solution was nearly 86% for both treatments, independent of various treatments (Table 19).

Table 19. Mg reduction vs NH₄ molar ratio and mixing time

NH ₄ : PO ₄ Molar Ratio	Mg Concentration mg/l	Reduction %	Mixing Time Minute	Mg Concentration mg/l	Reduction %
5	18.3	86.5	20	17.7	87
10	18.2	86.6	40	18.8	86
			60	18.3	85.4

The Pearson two-sided correlation test, demonstrated the significant relationship between Mg reduction and Ortho-P removal from wastewater in all replications (cor = -0.86, P-value = 0.000). Also, the correlation test showed the same result for Mg and Calcium reduction from solution in all replications (cor = 0.88, P-value = 0.000). Figures 22 and 23 illustrate the scatterplot of Mg reduction vs Ortho-P and Calcium removal, respectively.

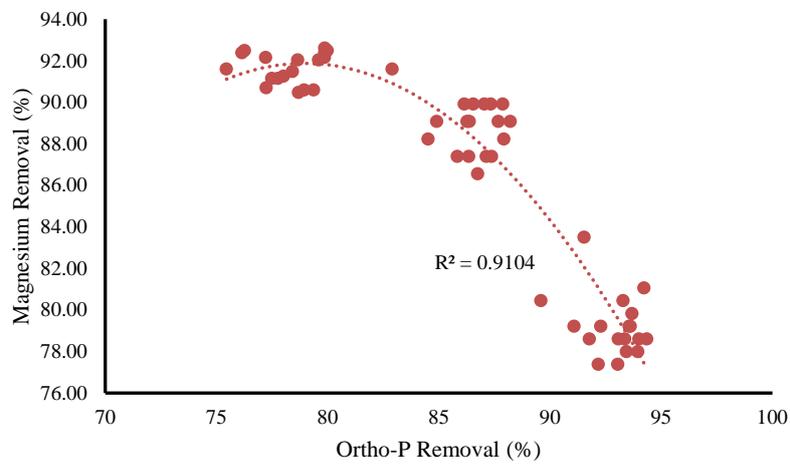


Fig 22. Mg removal vs Ortho-P removal from wastewater in all replications

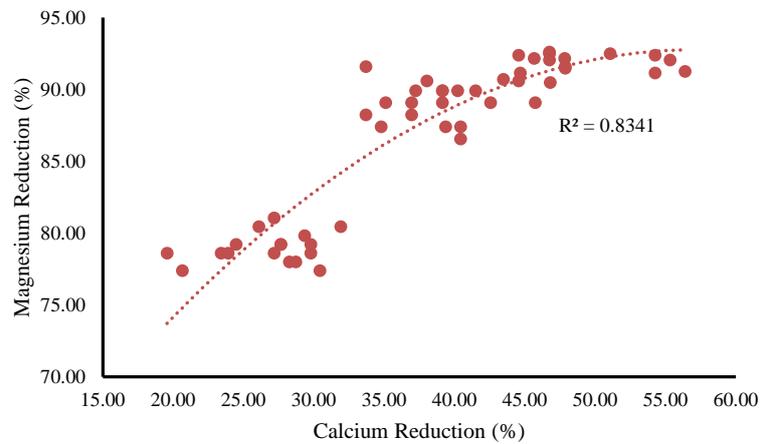


Fig 23. Mg reduction vs Ca reduction from solution in all replications

Furthermore, the prediction and optimization results of Mg reduction from wastewater based on highest removal, by means of Minitab 17, demonstrated that the highest Mg reduction could be achieved by neglecting the various $\text{NH}_4:\text{PO}_4$ molar ratios (Table 20).

Table 20. Predicted highest Mg removal treatments

Mg: PO ₄ Molar Ratio	Mixing Time Minute	Predicted Mg Removal %
0.6	20	92.1
0.6	60	91.7
0.6	40	91.1
0.8	20	89.3
0.8	60	88.9
0.8	40	88.3

Iron

The results showed that concentration of Iron in the solution has increased by increasing the Mg molar ratio (Figure 24). According to statistical analysis, the Fe reduction was significant through various Mg molar ratios (P-value = 0.001).

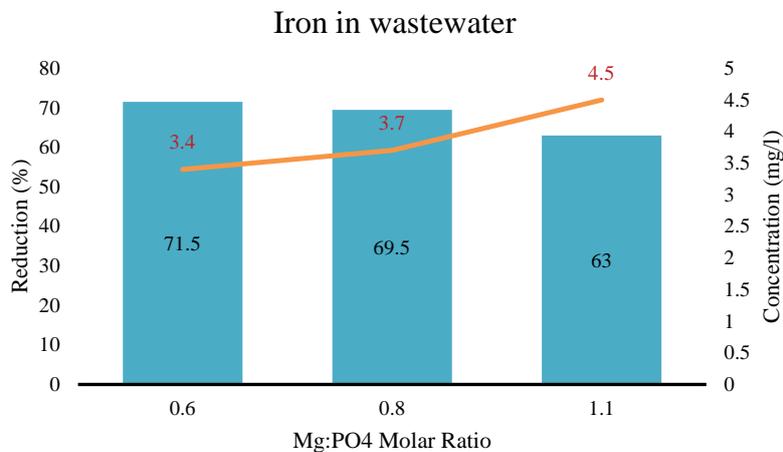


Fig 24. Fe reduction from wastewater vs Mg: PO₄ molar ratio

Table 21 illustrates the Fe reduction from solution through struvite precipitation process with regards to Ammonium treatments. The decrease in Iron removal by increasing NH₄:PO₄ molar ratio was found significant due to statistical analysis (P-value = 0.001).

Table 21. Fe reduction from solution vs NH₄:PO₄ molar ratio

NH ₄ : PO ₄ Molar Ratio	Iron Concentration		Reduction %
	Initial (mg/l)	After (mg/l)	
5	12	3.4	76.2
10		4.3	68.6

On the other hand, as shown at figure 25, Iron reduction from wastewater has increased in significant by increasing mixing time (P-value = 0.01).

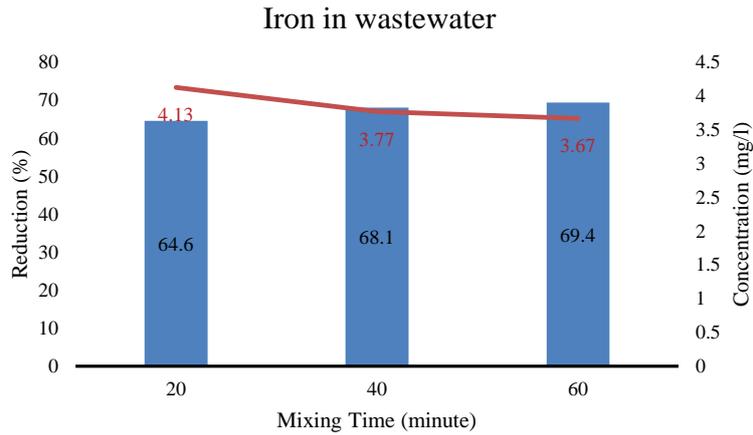


Fig 25. Fe reduction from wastewater vs mixing time

The plots of Fe reduction from solution with regards to interaction of Mg and Ammonium molar ratios ($Mg \cdot NH_4$) and Mg molar ratios and mixing time ($Mg \cdot Time$) are demonstrated at figures 26 and 27, respectively.

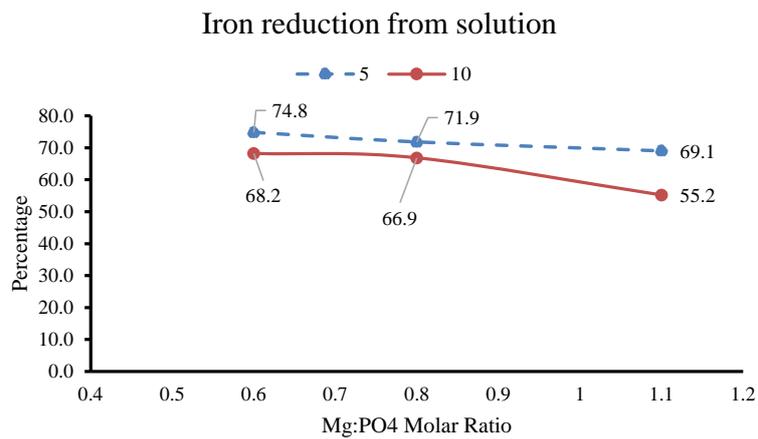


Fig 26. Interaction plot ($Mg \cdot NH_4$) for Fe reduction from solution

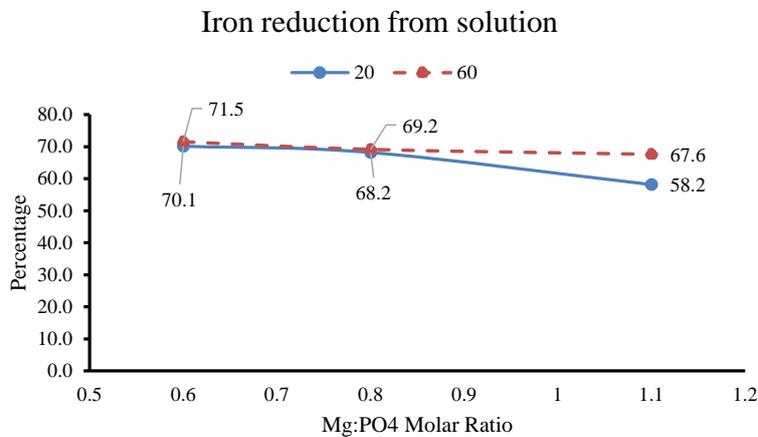


Fig 27. Interaction plot ($Mg \cdot Time$) for Fe reduction from solution

Prediction and optimization analysis has shown that the highest Iron removal from solution could be expected through the Mg: PO₄ and NH₄:PO₄ molar ratios of 0.6 and 5 along with 60 minute of mixing time (Table 22). The Fe reduction of 80% was achieved through the same treatment during the experiments.

Table 22. Predicted Fe reduction from solution via statistical analysis

Mg: PO ₄ Molar Ratio	NH ₄ : PO ₄ Molar Ratio	Mixing Time Minute	Predicted Fe Removal %
0.6		60	74.6
0.6		40	74.6
0.6	5	20	74.5
0.8		60	74.3
1.1		60	73.8
0.8		40	72.3

Iron removal from wastewater through struvite precipitation experiments are illustrated in table 23.

Table 23. Fe reduction through experiments

Mg: PO ₄ Molar Ratio	NH ₄ : PO ₄ Molar Ratio	pH	Mixing Time Minute	Iron Concentration Initial (mg/l)	After (mg/l)	Removal %
			20		3.4	71.9
	5		40		2.9	76.1
0.6			60		2.8	76.4
			20		3.8	68.3
	10		40		3.6	69.7
			60		4	66.7
			20		3.6	70
	5		40		3	74.7
0.8		8.3	60	12	3.5	70.8
			20		4.2	65.4
	10		40		3.9	67.2
			60		3.9	67.5
			20		4	66.9
	5		40		3.6	70
1.1			60		3.6	70.3
			20		3.9	45
	10		40		3.5	50.8
			60		4.2	65

The Pearson two-sided correlation test, showed that Fe reduction from solution had positive relationship with Calcium reduction in all replications (Figure 28) (cor = 0.67, P-value = 0.000).

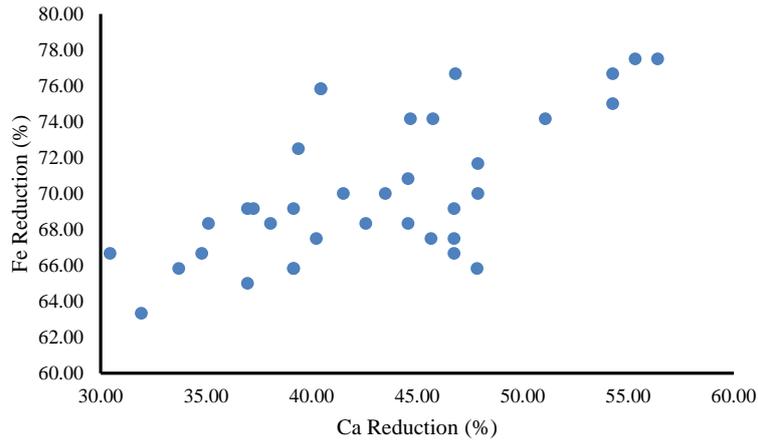


Fig 28. Fe reduction vs Ca reduction from solution in all replications

Aluminum

The results showed that Al removal from wastewater has decreased by increase in Mg: PO₄ molar ratio. Also, Aluminum removal from wastewater had increased at higher NH₄:PO₄ molar ratio of 10 (Table 24). According to statistical analysis, the observed Aluminum reduction from solution through various Mg and Ammonium molar ratio treatments was significant.

Table 24. Al removal from solution vs Mg: PO₄ and NH₄:PO₄ molar ratio

Mg: PO ₄ Molar Ratio	Al Concentration mg/l	Removal* %	NH ₄ : PO ₄ Molar Ratio	Al Concentration Initial (mg/l)	Al Concentration After (mg/l)	Removal** %
0.6	0.22	82.3	5	0.93	0.2	78.6
0.8	0.25	79.5	10	1.6	0.32	80.2
1.1	0.3	76.3				

* P-value = 0.001, ** P-value = 0.05

On the other hand, as demonstrated at figure 29, Aluminum removal from wastewater was not significantly changed by increasing the mixing time (P-value > 0.1).

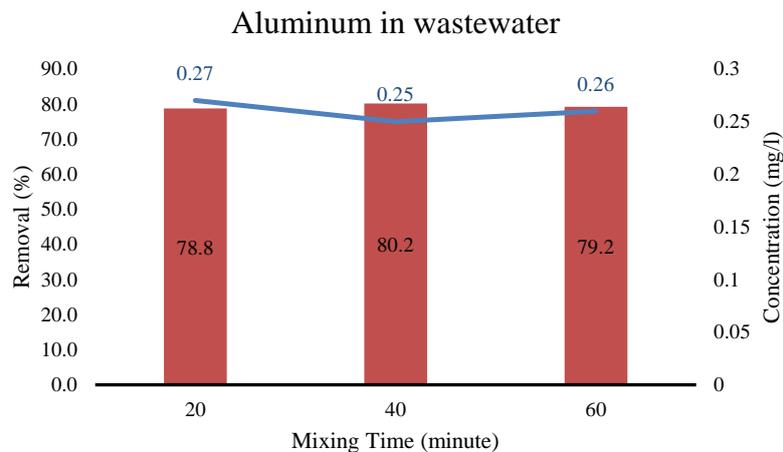


Fig 29. Al removal from wastewater vs mixing time

The results of Aluminum reduction from solution through the experiments are shown in table 25.

Table 25. Al removal from solution through struvite precipitation

Mg: PO ₄ Molar Ratio	NH ₄ : PO ₄ Molar Ratio	pH	Mixing Time		Al Concentration		Removal %
			Minute	Initial (mg/l)	After (mg/l)		
0.6	5	8.3	20		0.19	79.9	
			40	0.93	0.16	82.4	
			60		0.17	82.1	
			20		0.25	84.6	
			40	1.6	0.28	82.7	
			60		0.29	82.1	
0.8	10	8.3	20		0.2	78.1	
			40	0.93	0.19	79.6	
			60		0.22	76	
			20		0.3	81.3	
			40	1.6	0.3	81	
			60		0.3	81.3	
1.1	5	8.3	20		0.21	77.1	
			40	0.93	0.22	76.7	
			60		0.23	75.3	
			20		0.45	71.7	
			40	1.6	0.34	78.5	
			60		0.34	78.5	

According to the prediction analysis via Minitab 17, the highest Al removal from solution could be expected to be achieved as 83% through Mg: PO₄ and NH₄:PO₄ molar ratios of 0.6 and 10.

Also, the Pearson two-sided correlation test, showed that the Al reduction from solution had positive relationship with Mg reduction (cor = 0.65, P-value = 0.000) and Ca reduction from solution in all replications (cor = 0.69, P-value = 0.000) (Figure 30).

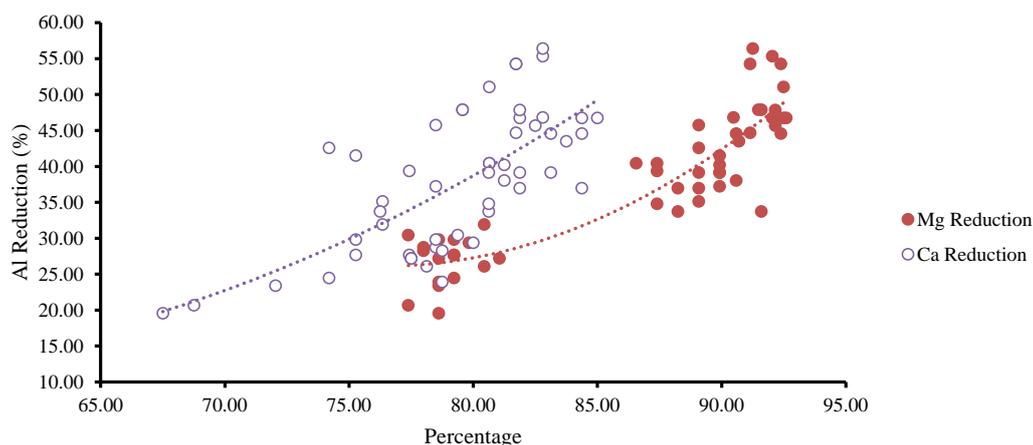


Fig 30. Al reduction vs Mg and Ca reduction from solution

Total Phosphorus

The results demonstrated that the Total Phosphorus reduction from wastewater through crystallization process has increased significantly by increasing the Mg: PO₄ molar ratio in the solution (Table 26) (P-value = 0.001).

Table 26. Total-P removal from wastewater vs Mg: PO₄ molar ratio

Mg: PO ₄ Molar Ratio	Total-P Concentration mg/l	Removal %
0.6	45.4	71.6
0.8	29.5	81.6
1.1	15.8	90

On the other hand, the various NH₄:PO₄ molar ratio has influenced Total-P removal from solution. Increasing the NH₄:PO₄ molar ratio from 5 to 10 has decreased the removal from 81.7% (170 mg/l to 31.2 mg/l) to 80.5% (150 mg/l to 29.3 mg/l) in significant (P-value = 0.05) (Figure 31).

But the Total-P reduction from wastewater (nearly 81%) was not significantly changed with regards to mixing time (P-value > 0.1) (Figure 32).

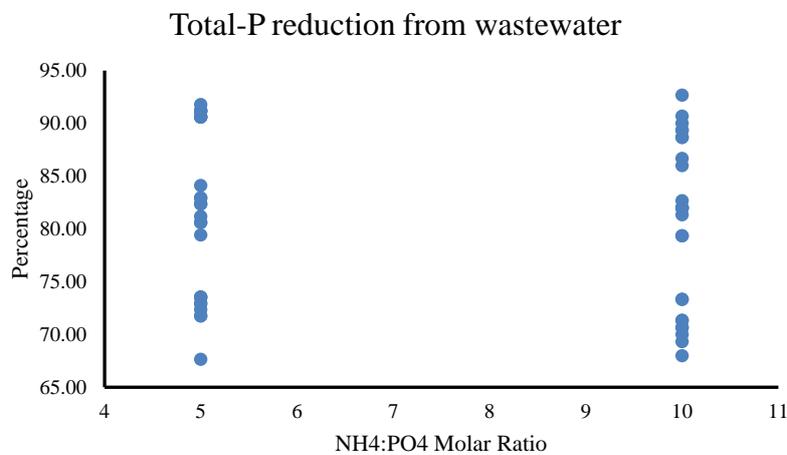


Fig 31. Total-P reduction from wastewater vs NH₄:PO₄ molar ratio

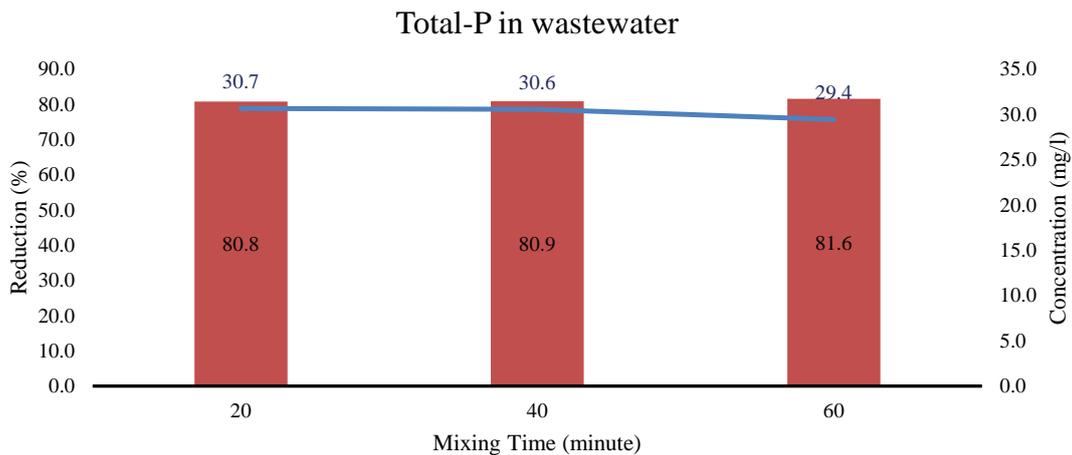


Fig 32. Total-P reduction from wastewater vs mixing time

The Pearson two-sided correlation test, illustrated that positive relationship was between Total-P reduction and Ortho-P removal from solution in all replications (cor = 0.97, P-value = 0.000). Also, Total-P reduction from wastewater was found highly correlated with Mg removal (cor =

-0.89, P-value = 0.000), Ca reduction (cor = -0.85, P-value = 0.000) and Al reduction from wastewater in all replications (cor = -0.63, P-value = 0.000), respectively (Figures 33-36).

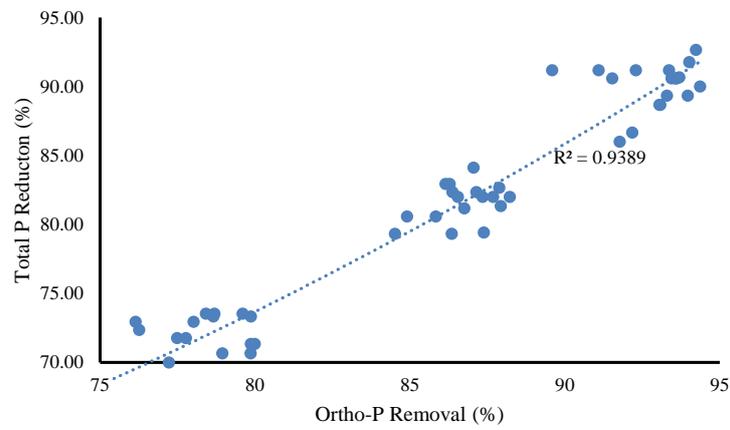


Fig 33. Total-P reduction vs Ortho-P removal from wastewater in all replications

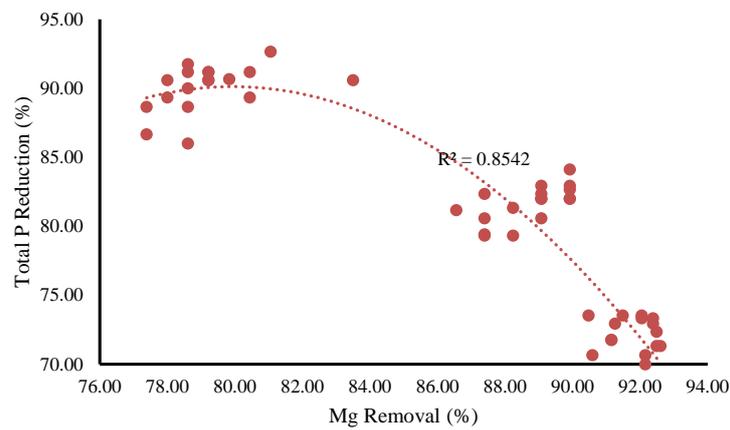


Fig 34. Total-P reduction vs Mg removal from wastewater in all replications

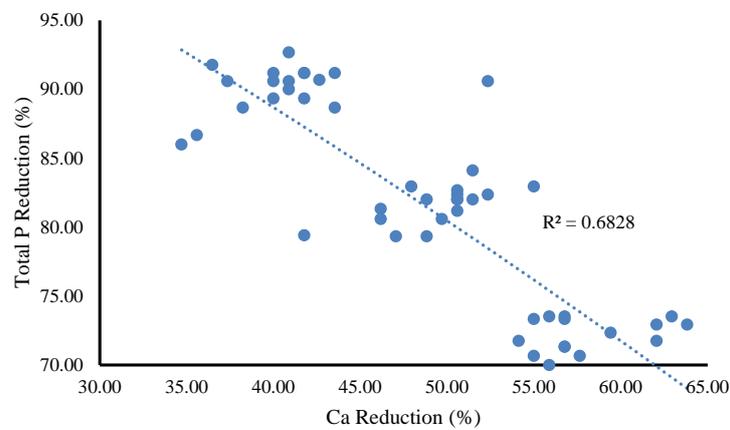


Fig 35. Total-P reduction vs Ca reduction from wastewater in all replications

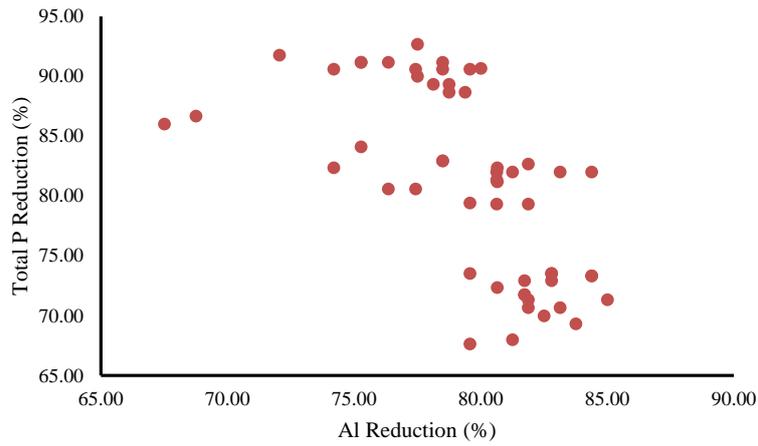


Fig 36. Total-P reduction vs Al reduction from wastewater in all replications

Table 27 demonstrates the results of prediction and optimization of highest Total-P removal from solution and the alternatives through the process.

Table 27. Predicted Total-P removal from solution through struvite formation process

Mg: PO ₄	NH ₄ : PO ₄	Total P Removal %
Molar Ratio	Molar Ratio	Prediction
1.1	5	90.7
1.1	10	89.4
0.8	5	82.2
0.8	10	80.9
0.6	5	72.2
0.6	10	70.9

The results of Total-P removal from wastewater through the struvite precipitation experiments are shown in table 28.

Table 28. Total P removal through the experiments

Mg: PO ₄ Molar Ratio	NH ₄ : PO ₄ Molar Ratio	pH	Mixing Time Minute	Total-P Concentration		Removal %
				Initial (mg/l)	After (mg/l)	
0.6	5	8.3	20		49	71.2
			40	170	46	72.9
			60		46.7	72.6
	10		20		41	72.7
			40	150	46	69.3
			60		44	70.7
0.8	5	20		32.3	81	
		40	170	31.7	81.4	
		60		28.7	83.1	
	10	20		27	82	
		40	150	30	80	
		60		26.7	82.2	
1.1	5	20		15.3	91	
		40	170	16	90.6	
		60		14.7	91.4	
	10	20		19.3	87.1	
		40	150	13.7	91	
		60		16	89.3	

Potassium

The results showed that the average Potassium concentration in the solution was increased from 153 mg/l to 161 mg/l significantly by increasing the Ammonium molar ratio (P-value = 0.001) (Figure 37).

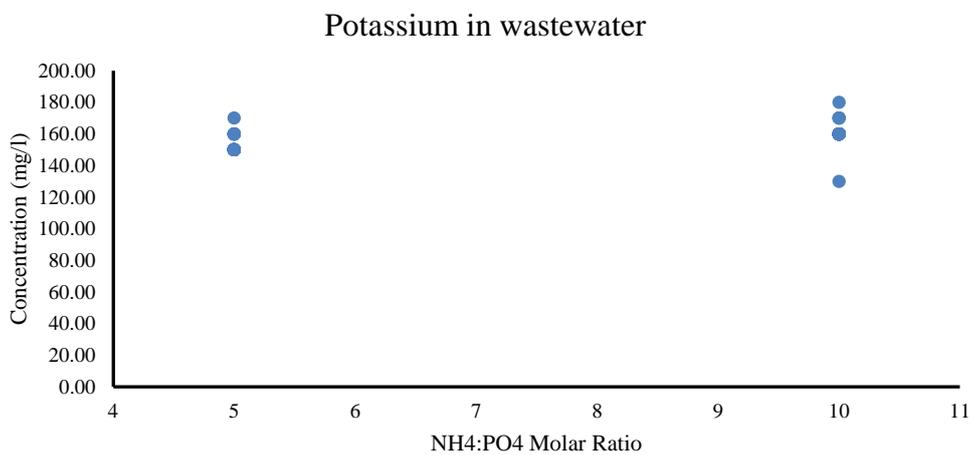


Fig 37. Potassium concentration in solution vs NH₄:PO₄ molar ratio

The Potassium concentration in wastewater changes was not significant with regards to Mg: PO₄ molar ratio and mixing time treatments (P-value > 0.1) (Table 29).

Table 29. Potassium concentration in wastewater vs Mg: PO₄ molar ratio and mixing time

Mg: PO ₄ Molar Ratio	Potassium Concentration mg/l	Mixing Time Minute	Potassium Concentration mg/l
0.6	158	20	157
0.8	154	40	157
1.1	158	60	156

Table 30 demonstrates Potassium concentration changes in wastewater through the struvite formation experiments.

Table 30. Potassium concentration through struvite precipitation experiments

Mg: PO ₄ Molar Ratio	NH ₄ : PO ₄ Molar Ratio	pH	Mixing Time Minute	Potassium Concentration mg/l
0.6	5	8.3	20	160
			40	150
			60	153
	10		20	160
			40	167
			60	160
0.8	5	20	150	
		40	157	
		60	150	
	10	20	150	
		40	160	
		60	160	
1.1	5	20	153	
		40	150	
		60	153	
	10	20	170	
		40	160	
		60	160	

Turbidity

Figure 38 illustrates the results of turbidity reduction with regards to various NH₄:PO₄ molar ratios. Increasing Ammonium molar ratio from 5 to 10 has caused significant increase in turbidity of the solution (P-value = 0.001).

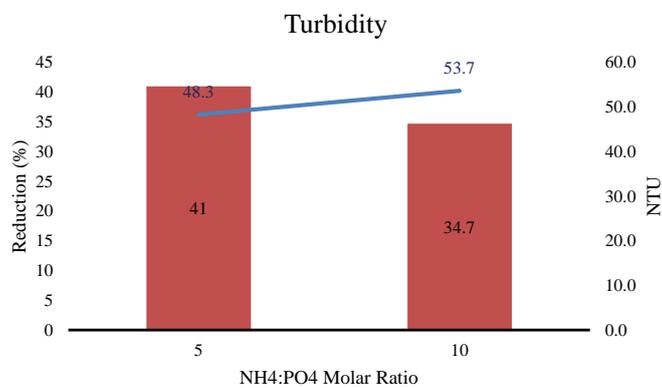


Fig 38. Turbidity reduction vs NH₄:PO₄ molar ratio

Also, according to statistical analysis, turbidity has decreased by increasing the Mg: PO₄ molar ratio in significant (Table 31) (P-value = 0.05), while increasing mixing time had not any significant impact on turbidity level (P-value > 0.1).

Table 31. Turbidity reduction vs Mg molar ratio

Mg: PO ₄ Molar Ratio	Turbidity Reduction %
0.6	36.2
0.8	37.7
1.1	39.7

The results of turbidity reduction through the crystallization process are shown in table 32. In order to compare turbidity after struvite precipitation, the initial turbidity was considered after centrifuging. Thus, the initial turbidity were detected 82.2 and 81.9 NTU for mixed ratios of 10:1 and 5:1 of NH₄: PO₄.

Table 32. Turbidity reduction through the experiments

Mg: PO ₄ Molar Ratio	NH ₄ : PO ₄ Molar Ratio	pH	Mixing Time Minute	Turbidity Initial (NTU)	Turbidity After (NTU)	Reduction %
0.6	5	8.3	20	81.9	54.3	33.7
			40	81.9	45.1	44.9
			60	81.9	49	40.2
	10		20	82.2	54.9	33.2
			40	82.2	51	38
			60	82.2	59.8	27.3
0.8	5	20	81.9	51.3	37.3	
		40	81.9	42.7	47.8	
		60	81.9	52.9	35.4	
	10	20	82.2	52.2	36.5	
		40	82.2	52.3	36.3	
		60	82.2	55.3	32.7	
1.1	5	20	81.9	47.1	42.5	
		40	81.9	45.7	44.2	
		60	81.9	46.6	43.1	
	10	20	82.2	53.8	34.5	
		40	82.2	49.6	39.6	
		60	82.2	54.1	34.2	

Conductivity

According to the results, conductivity of the solution have increased significantly from 5.13 us/cm to 6.34 us/cm by increasing the NH₄:PO₄ molar ratio from 5 to 10 (P-value = 0.001). In addition, the conductivity has also increased significantly by increasing the Mg: PO₄ molar ratio (P-value = 0.05) while the mixing time had not any considerable effect on conductivity of solution (P-value > 0.1) (Table 33). The initial conductivity level of the solution was detected 4.25 us/cm and 5.76 us/cm at molar ratio of 5:1 and 10:1, respectively.

Table 33. Conductivity vs Mg: PO₄ molar ratio and mixing time

Mg: PO ₄ Molar Ratio	Conductivity us/cm	Mixing Time Minute	Conductivity us/cm
0.6	5.67	20	5.78
0.8	5.71	40	5.66
1.1	5.83	60	5.78

The Pearson two-sided correlation test, showed that conductivity of the solution had negative relationship with Ammonium removal from wastewater in all replications (cor = -0.94, P-value = 0.000) (Figure 39).

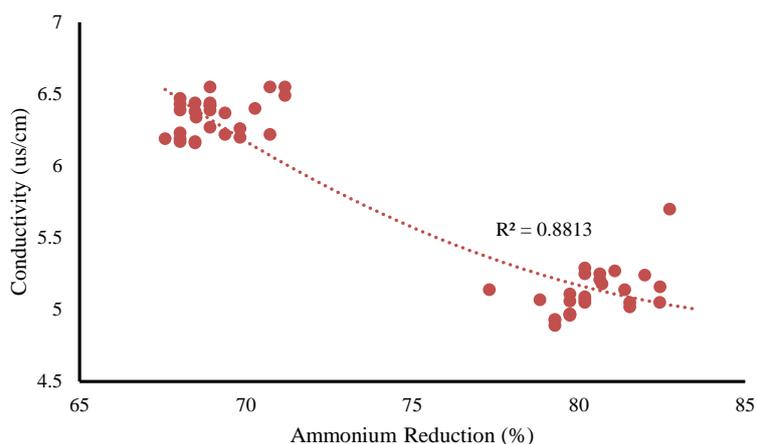


Fig 39. Conductivity vs Ammonium reduction from wastewater in all replications

Table 34 shows the measured conductivity of solution after struvite precipitation experiments.

Table 34. Conductivity through struvite precipitation experiments

Mg: PO ₄ Molar Ratio	NH ₄ : PO ₄ Molar Ratio	pH	Mixing Time Minute	Conductivity us/cm
0.6	5	8.3	20	5.15
			40	4.92
			60	5.08
	10		20	6.33
			40	6.17
			60	6.37
0.8	5	8.3	20	5.05
			40	4.97
			60	5.24
	10		20	6.24
			40	6.20
			60	6.53
1.1	5	8.3	20	5.43
			40	5.26
			60	5.05
	10		20	6.44
			40	6.42
			60	6.40

Heavy metals

Nickel

The results demonstrated that the Nickel concentration in wastewater has increased significantly by increasing the NH₄:PO₄ molar ratio (P-value = 0.001). On the other hand, various Mg: PO₄ molar ratio and mixing time did not affect the Ni concentration in wastewater in significant (P-value > 0.1) (Table 35).

Table 35. Nickel concentration in wastewater

NH ₄ : PO ₄ Molar Ratio	Nickel Concentration* ug/l	Mixing Time Minute	Nickel Concentration ug/l	Mg: PO ₄ Molar Ratio	Nickel Concentration ug/l
5	16.9	20	18.6	0.6	19
10	21.3	40	19.6	0.8	18.9
		60	19	1.1	19.2

* P-value = 0.001

According to the Pearson two-sided correlation test, Ni concentration in the solution had close relationship with Ammonium reduction from wastewater in all replications (cor = -0.93). Also, the Ni concentration was highly correlated with conductivity in all replications (cor = 0.86) (Figure 40 and 41).

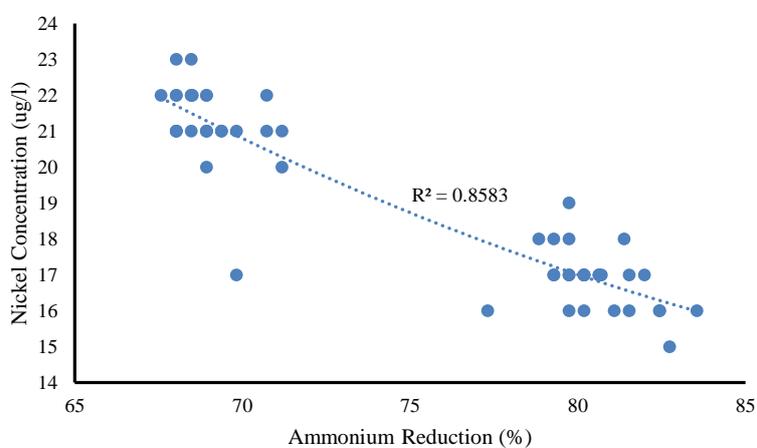


Fig 40. Nickel concentration in the solution vs Ammonium reduction from wastewater in all replications

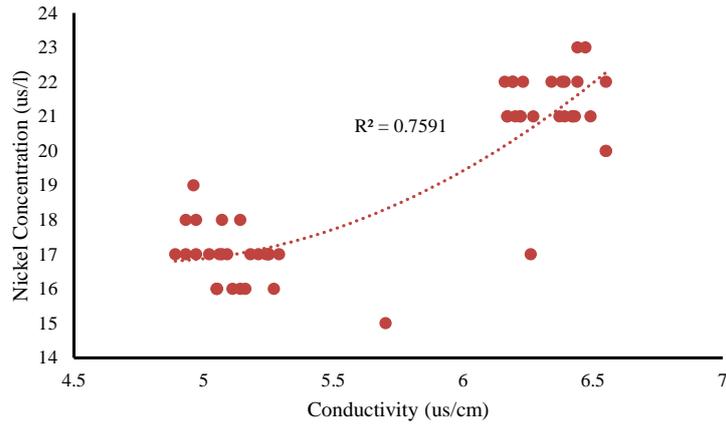


Fig 41. Nickel concentration in the solution vs Conductivity in all replications

The results of Nickel concentration in wastewater through the struvite precipitation are shown in appendix A.

Chromium

The results illustrated that the chromium concentration in the solution has increased from 2.93 ug/l to 4.22 ug/l by increasing the $\text{NH}_4:\text{PO}_4$ molar ratio in significant (P-value = 0.001). The Mg: PO_4 molar ratio and mixing time had not significant effect on Cr concentration changes (P-value > 0.05).

The Pearson two-sided correlation test, showed that Cr concentration in the solution had relationship with Ammonium reduction from solution (cor = -0.85), Ni concentration in the solution (cor = 0.88) and conductivity of the solution in all replications (cor = 0.86) (Figure 42).

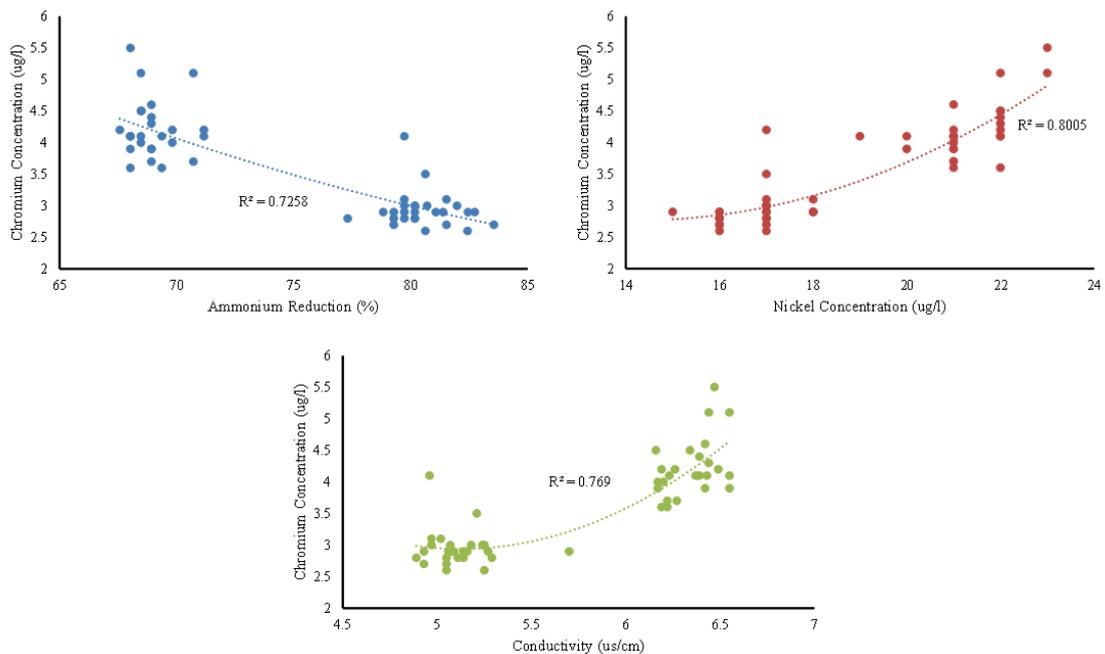


Fig 42. Cr concentration in the solution vs Ammonium reduction from solution, Ni concentration and Conductivity

The Cr concentration changes in wastewater through the experiments are demonstrated in the appendix A.

Copper

The statistical analysis showed that the Cu concentration in the solution has increased significantly by increasing the NH₄:PO₄ molar ratio, while the concentration has decreased significantly by increasing mixing time (P-value = 0.001) (Table 36). Mg: PO₄ molar ratio differences made not any significant change in Cu concentration of solution (P-value > 0.1).

Table 36. Cu concentration in the solution vs NH₄:PO₄ molar ratio and mixing time

NH ₄ : PO ₄ Molar Ratio	Copper Concentration ug/l	Mixing Time Minute	Copper Concentration ug/l
5	11.6	20	15.9
10	16.3	40	13.9
		60	12.1

With regards to the Pearson two-sided correlation test, as shown in figure 43, Cu concentration in the solution was related to Ammonium reduction from solution (cor = -0.71), conductivity levels (cor = 0.71) and Fe reduction from solution in all replications (cor = -0.66).

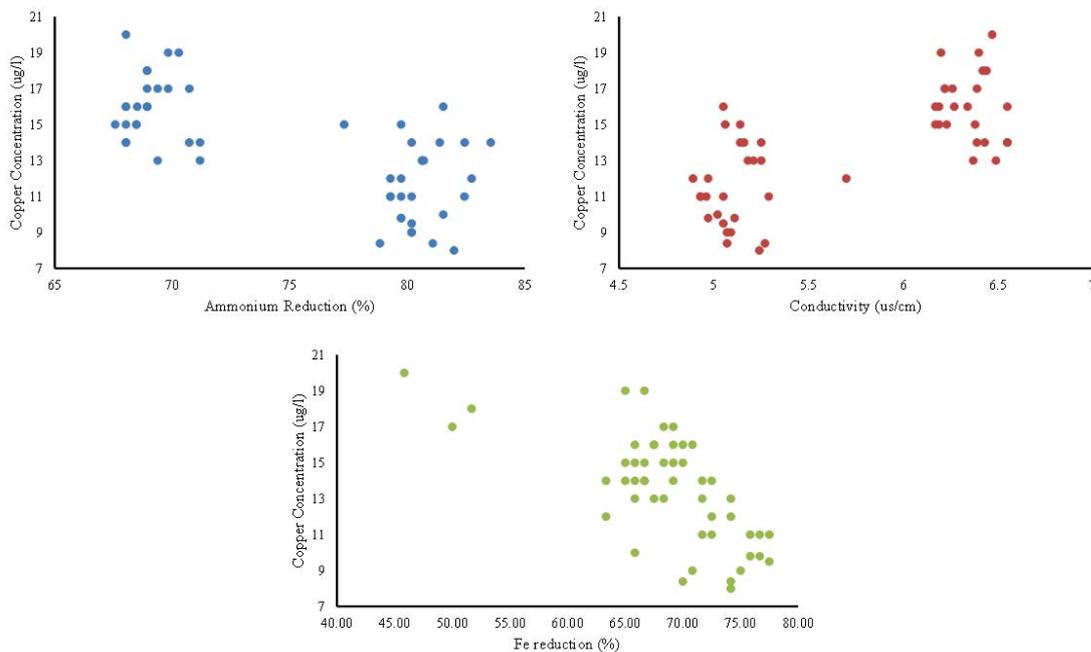


Fig 43. Cu concentration in the solution vs Ammonium reduction from solution, Conductivity and Fe reduction from solution in all replications

Copper concentration changes in the solution through the crystallization process experiments are enclosed in appendix A.

Zink

According to the results, Zink concentration in wastewater through the experiments were affected significantly by various Mg: PO₄ and NH₄:PO₄ molar ratio and mixing time treatments (P-value = 0.001). By increasing Mg: PO₄ and NH₄:PO₄ molar ratios (Table 37), Zn

concentration in wastewater was increased while the concentration decreased by increasing the mixing time (Figure 44).

Table 37. Zink concentration in wastewater vs Mg: PO₄ and NH₄:PO₄molar ratio

NH ₄ : PO ₄ Molar Ratio	Zink Concentration Initial (ug/l)	Zink Concentration After (ug/l)	Mg: PO ₄ Molar Ratio	Zink Concentration ug/l
5	92	39.1	0.6	35.9
10	86	45.3	0.8	39.9
			1.1	46.3

With regards to the Pearson two-sided correlation test, the considerable relationship between Zn concentration in the solution with Ca (cor = -0.7) and Fe (cor = -0.86) reduction from solution and Cu concentration changes in the solution (cor = 0.71) was observed in all replications (Figure 45).

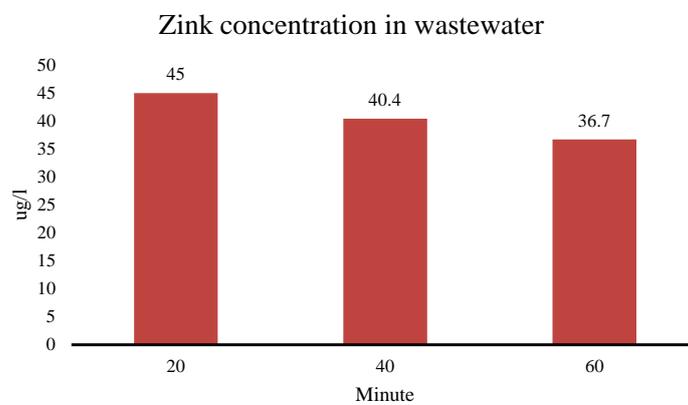


Figure 44. Zink concentration in wastewater vs mixing time

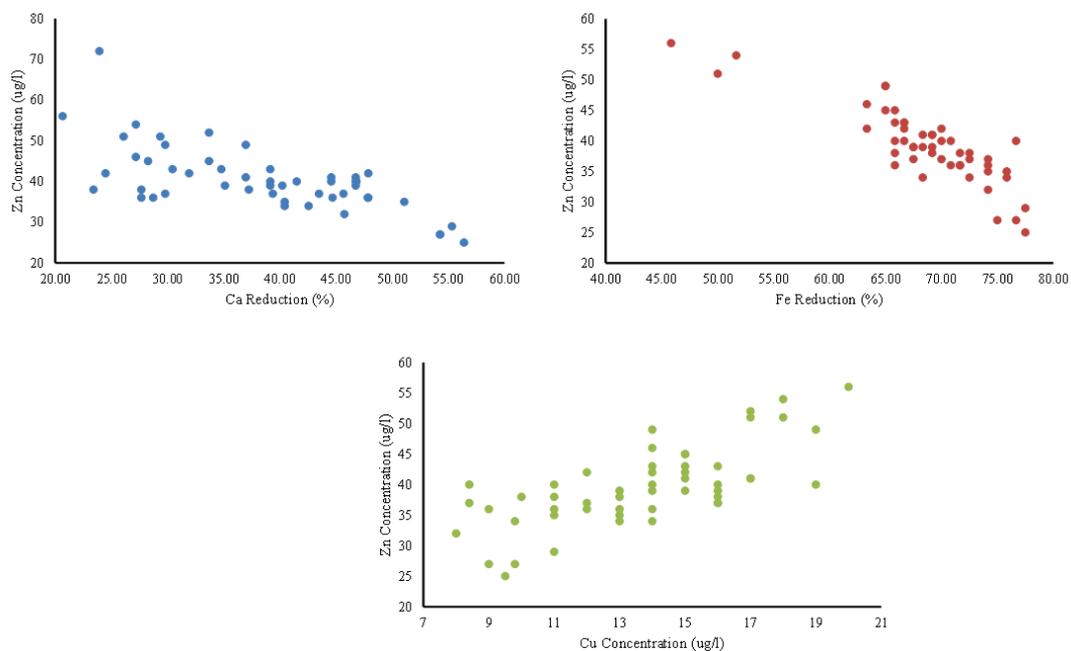


Fig 45. Zn concentration in the solution vs Ca and Fe reduction from solution and Cu concentration changes in the solution in all replications

The results of Zn analysis in wastewater through the experiments are attached in appendix A.

Arsenic

The results demonstrated that the Arsenic concentration in the solution has increased significantly, due to statistical analysis, by increasing the $\text{NH}_4:\text{PO}_4$ molar ratio (P-value = 0.001) (Table 38). On the other hand, Arsenic concentration was not affected in significant by different Mg: PO_4 molar ratio and mixing time treatments (P-value > 0.1).

Table 38. As concentration in the solution vs $\text{NH}_4:\text{PO}_4$ molar ratio

$\text{NH}_4:\text{PO}_4$ Molar Ratio	Arsenic Concentration	
	Initial (ug/l)	After (ug/l)
5	6.8	6.57
10	9.4	9.1

The results of the Pearson two-sided correlation test are shown in figure 46. Furthermore, Arsenic concentration changes in the solution are illustrated in appendix A.

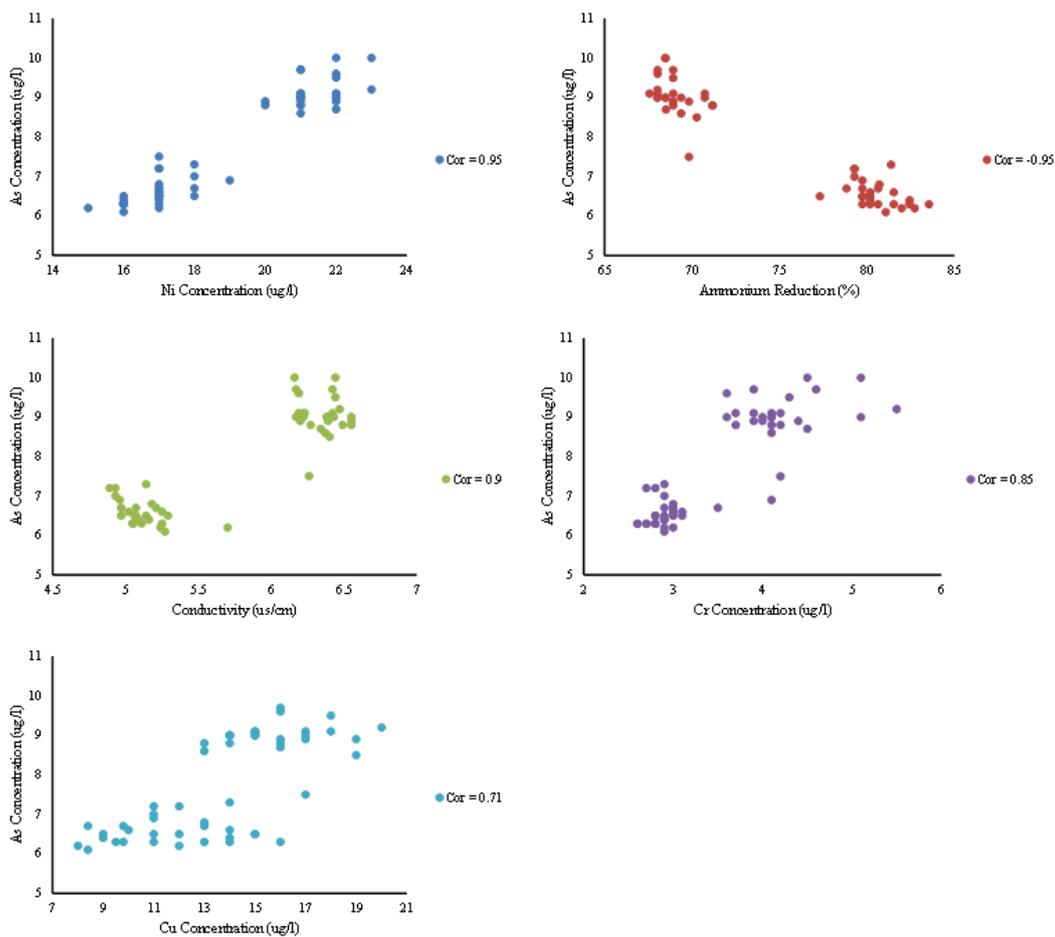


Fig 46. Arsenic correlation tests in all replications

Cadmium & Lead

Statistical analysis showed that concentration of Cd and Pb in the solution were not significantly affected by various Mg: PO_4 and $\text{NH}_4:\text{PO}_4$ molar ratios or mixing time treatments

(Ca: P-value > 0.1 and Pb: P-value > 0.05). The changes of Cd and Pb concentration in the solution are illustrated in appendix A.

Precipitated struvite mass

The results showed that increasing Mg: PO₄ molar ratio affected the struvite powder mass in significant (P-value = 0.001). Figure 47 illustrates the struvite mass increased by increasing Mg: PO₄ molar ratio.

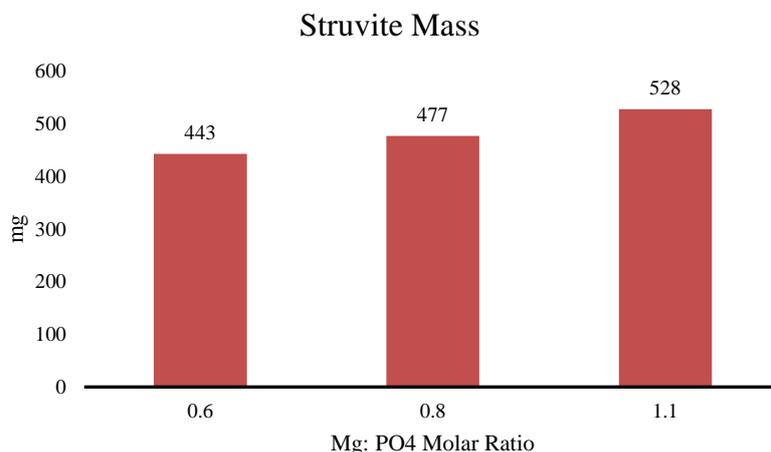


Fig 47. Struvite mass vs Mg: PO₄ molar ratio

Also, statistical analysis demonstrated that the struvite mass has decreased significantly by increasing mixing time (P-value = 0.05) (Table 39). On the other hand, the relationship between struvite mass and NH₄:PO₄ molar ratio was not significant (P-value > 0.1).

Table 39. Struvite mass vs mixing time

Mixing Time	Struvite Mass
Minute	mg
20	502
40	498
60	448

Table 40 illustrates mass of precipitated struvite through the experiments.

Table 40. Struvite mass through the experiments

Mg: PO ₄ Molar Ratio	NH ₄ : PO ₄ Molar Ratio	pH	Mixing Time Minute	Struvite Mass mg
0.6	5	8.3	20	550
			40	523
			60	373
	10		20	423
			40	423
			60	363
0.8	5	8.3	20	453
			40	457
			60	453
	10		20	557
			40	497
			60	447
1.1	5	8.3	20	553
			40	500
			60	540
	10		20	473
			40	587
			60	513

Discussion

Ortho-Phosphate

Higher Magnesium concentration in the solution leads to more Phosphorus removal from wastewater through the struvite precipitation process. By increasing the Mg: PO₄ molar ratio from 0.6 to 1.1 in this study, the Ortho-P removal increased nearly 15% (from 78.3% to 92.3%). Liu et al. (2011) reported the same pattern for Ortho-P (OP) removal. They have observed 32% more OP removal (64% to 96%) by increasing Mg: PO₄ molar ratio from 0.5 to 1.2. Also, according to Uysal et al. (2010) high Magnesium concentration leads to lower Phosphorus concentration in the effluent. They have concluded 95% OP removal at Mg: PO₄ molar ratio of 1.5. Furthermore, it is found that most effective ratio of Mg: PO₄ molar ratio was 1:1 or 1.2:1 (Md M Rahman et al., 2011). They have reported 93% of OP removal at molar ratio of 1:1 which admits the results observed through the current study. Also, Huang et al. (2012) demonstrated that increasing Mg: PO₄ molar ratio from 0.9 to 1.3, at pH of 8.5, has decreased the residual OP concentration from 175 mg/l to less than 25 mg/l. Therefore, the results support the initial hypothesis of increasing OP removal by increasing the Magnesium concentration.

The impact of different NH₄: PO₄ molar ratio was not found significant on OP removal. By increasing the Ammonium molar ratio from 5 to 10, the OP removal increased from 85.5 to 86.3%. Pastor et al. (2010) has reported the similar results. They found that the OP removal at NH₄: PO₄ molar ratios of 5.4 and 8 were 90%. On the other hand, they also concluded that the Ammonium molar ratio of 10.5 caused 95% OP reduction. The main reason for this significant increase was increase in Mg molar ratio from 0.8 to 1.1. Thus, the results demonstrated that the increase in Ammonium concentration could not boost the OP removal alone. But increase in NH₄: PO₄ molar ratio can increase the OP removal under certain conditions such as higher Mg concentration. On the other hand, Capdevielle et al. (2014) concluded that increasing NH₄: PO₄ molar ratio (from 0.71 to 3.11) and stirring rate (from 10 to 90 RPM) have increased the struvite precipitation rate. While, in the current study, total mass of precipitated struvite was decreased from 4403 mg to 4283 mg. This reduction in struvite mass was not significantly different with regards to NH₄: PO₄ molar ratios of 5 and 10.

The results illustrate that the different reaction times had no significant effect on OP removal. After 20 minute of mixing the OP reduction was found 85% which was increased very slight by increasing the reaction time to 40 and 60 minute (nearly 86%). Huang et al. (2011) concluded that increasing the mixing time from 0.5 to 8 hours, along with increasing Mg: NH₄ ratio could boost OP removal (96% at 6 hours). On the other hand, Capdevielle et al. (2014) reported that OP removal was completed in less than 1 hour, positively influenced by added MgO. They found that at first 30 minute, OP was precipitated with the co-precipitation of Amorphous Calcium Phosphate (ACP). After 30 minute, dissolution of ACP limited the crystal growth. In current study the initial Ca concentration of wastewater was detected 110 mg/l. Therefore, according to Capdevielle et al. (2014), it could be concluded that by 20 minute of mixing time, 85% OP removal was achieved but by increasing the reaction time to 40 and 60 minute, due to high Ca concentration, the OP reduction was not increased in significant. In addition, with regards to S. Lee et al. (2003), most of potential P would remove from solution in the first minute after adding Mg source (bittern). They also reported that beyond 10 minute, changes in P concentration in the solution are negligible. In another study, Li et al. (2012) found that at 20 minute mixing time, the Ortho-P concentration was decreased to the lowest

level in the solution but by increasing mixing time from 20 to 60 minute, the residual Ortho-P concentration in wastewater was increased.

Ammonium

High pH favors the Ammonia volatilization by driving the equilibrium between NH_3 and NH_4^+ to NH_3 , and NH_3 can react with Nitrate and Sulphate in the atmosphere (Escudero et al., 2015). They reported that 95% of NH_4^+ was removed from anaerobically treated effluent in only 30 seconds (5 minute experiment and Mg: NH_4 : PO_4 molar ratio of 1:1:1). Also they concluded that by increasing Mg and P concentration, residual Ammonium concentration in the effluent decreased. Zhang, Ding, Ren, et al. (2009) reported 45% and 70% Ammonium removal from landfill leachate at pH of 8.5 and 9, respectively (Mg: NH_4 : PO_4 molar ratio of 1:1:1). They have concluded that pH value of 9.5 was optimum for highest Ammonium removal. They also observed that by increasing Mg concentration in the solution, Ammonium removal from landfill leachate was increased. While through the current study, the change in Ammonium reduction from wastewater by increasing Mg concentration was found insignificant. Nearly 75% NH_4^+ reduction from wastewater was observed through various Mg: PO_4 molar ratios at pH of 8.3. High pH and contact with the atmosphere during the experiments, could cause high Ammonium removal from the solution.

On the other hand, increasing mixing time from 20 to 60 minute did not affect Ammonium reduction from the solution in significant. During all mixing time experiments, approximately 75% of NH_4^+ was removed from the solution. This could because most of the Ammonium removal takes place in the first minute of struvite precipitation process (S. Lee et al., 2003). In another conclusion, Huang et al. (2011) reported that by increasing Mg: NH_4 ratio and mixing time, Ammonium removal from solution was increased. In another study, Li et al. (2012) reported that at Mg: NH_4 : PO_4 molar ratio of 1:1:1 and pH value of 9, Ammonium removal was observed to be similar by increasing mixing time from 5 to 60 minute. But through the current study, Ammonium concentration was much higher than highest added Mg concentration. Thus the same results of increasing NH_4 removal was not observed.

The Ammonium reduction from wastewater decreased significantly from 80% to 69% by increasing NH_4 : PO_4 molar ratio from 5 to 10. Pastor et al. (2010) reported the same pattern for Ammonium removal from digested sludge. They observed that Ammonium concentration in solution was increased (less removal from sludge) by increasing the NH_4 : PO_4 molar ratio from 5.4 to 8.

In addition, according to Huang et al. (2011), presence of Ca and K ions can cause less Ammonium and Phosphorus removal from solution. Thus, high Ca (110 mg/l) and K (150 mg/l) contents in wastewater and high concentration of K in reject water (210 mg/l), might affect the Ammonium and Phosphorus reduction from wastewater through the current study.

It also should be considered that the experiments through the current study were done in direct contact with the atmosphere. Thus, more Ammonium could be volatilized into the atmosphere than the experiments which were conducted in close systems.

Calcium

Presence of Calcium in wastewater can limits the struvite crystallization process and its purity. According to X. Wang et al. (2013) adapted from Kataki et al. (2016), Ca concentration range of 40-160 mgL^{-1} in the municipal wastewater along with Ca: Mg molar ratio of >1 could

decrease the struvite purity. Also, at $\text{pH} > 10$, precipitation of Calcium Phosphate takes place. Thus, with regards to Ca and Mg concentration of 110 and 47.5 mgL^{-1} in wastewater sample, initial Ca: Mg molar ratio of 1.39, impurity of struvite crystals with regards to the color (grayish white) were observed. Capdevielle et al. (2014) reported that Mg ion stabilizes the ACP structure. Also, Escudero et al. (2015) reported similarly that by increasing Mg and PO_4^{3-} concentration in solution, Ca concentration decreased in wastewater. This means that the Ortho-P precipitation takes place as ACP rather than struvite. But in this study, by increasing MgCl_2 concentration through the experiments, Ca concentration in the wastewater was increased. This might be because of replacement of Ca and Mg cations. Therefore, Mg ion was attached to Ortho-P and precipitated while Ca reacted with Cl ion and formed CaCl_2 which is highly soluble in water. Also, high negative correlation between Ortho-P and Ca reduction from wastewater emphasize that by increasing the Ortho-P concentration is struvite, less calcium precipitated. This means that Ortho-P precipitated mainly as struvite rather than ACP.

The results demonstrated that by increasing $\text{NH}_4:\text{PO}_4$ molar ratio, Ca concentration was increased in the solution. According to Pastor et al. (2010), by increasing $\text{NH}_4:\text{PO}_4$ molar ratio from 5.4 to 8 and to 10.5, Ca concentration was first decreased and then increased in the wastewater.

On the other hand, according to the results, Ca removal from wastewater through the experiments at 20 and 40 minute mixing time were observed very similar while by increasing the mixing time to 60 minute, Ca reduction from wastewater was also increased. It might demonstrates that Ortho-P removal from 40 to 60 minute, was along with Ca precipitation which means more ACP precipitation than struvite. In addition, it was also observed that by decreasing the Ortho-P concentration in wastewater, the Ca concentration was increased in wastewater through the experiments. It emphasizes that by increasing Mg concentration in the solution, more Ortho-P was precipitated as struvite than ACP. Thus, further studies should be implemented to realize the effect of mixing time on Ca reduction from the solution and its relation with Ortho-P precipitation.

Magnesium

With regards to the results, residual Mg concentration has increased in wastewater by increasing Mg: PO_4 molar ratio. This means that by increasing Mg concentration in solution, although more Ortho-P was precipitated as struvite but the amount of Mg was still excess. Thus, by increasing Mg: PO_4 molar ratio, Ortho-P concentration in solution decreased but residual Mg concentration also increased. Furthermore, by increasing Ammonium concentration from 5 to 10 and also mixing time, the change in Mg concentration in wastewater was not significant.

Iron

According to Yan and Shih (2016), presence of Ferric ions in wastewater inhibits struvite formation. Surface adsorption is suggested to be considered as the main mechanism in which Fe^{3+} affects crystallization process. In this study, by increasing Mg concentration in the solution, less Iron concentration was detected in struvite. The main reason could be more Phosphorus attachment to Mg ions than Fe ions and further struvite formation process.

On the other hand, increasing Ammonium concentration in wastewater, has also increased Iron concentration in the solution. This means that increasing Ammonium concentration, could affect positively increasing Ortho-P precipitation in struvite formation process, therefore, less

Iron ions precipitate in struvite. While in the current study the same influence was not observed in Ortho-P reduction from wastewater. In addition, with regards to the results, by increasing mixing time, more Iron ions were precipitated into struvite crystals.

Aluminum

With regards to the results, by increasing Mg: PO₄ molar ratio, Al concentration in wastewater also has increased. This might be related to more Ortho-P precipitation along with higher Mg ion concentration rather than Al or Fe ions. In addition, correlation test illustrated that by increasing Mg concentration in the solution, as more Ortho-P has precipitated, more Al concentration has detected in wastewater.

Total Phosphorus

According to initial concentration of Total Phosphorus and Ortho-P in wastewater, more than 90% of Total-P was Ortho-P. Thus, the same results were observed for Total-P and Ortho-P concentration in wastewater during the experiments. Therefore, by increasing Mg ion concentration in the solution, more precipitation was observed. Also, based on correlation tests, by increasing Total-P precipitation, more Ca ion concentration was observed in wastewater. Moreover, by increasing Total-P removal from wastewater, less Al ion has removed from the solution.

On the other hand, Total-P concentration in wastewater was increased significantly by increasing Ammonium concentration while the same pattern was not observed in Ortho-P removal from wastewater.

Potassium

The results showed that by increasing NH₄:PO₄ molar ratio, Potassium concentration was increased in wastewater. While, Pastor et al. (2010) reported that by increasing NH₄:PO₄ molar ratio, Potassium concentration was not changed during the precipitation process.

Turbidity

With regards to the initial analysis, turbidity of wastewater was high, 453 and 144 NTU for wastewater and reject water before centrifuge. According to Meozzi (2011), by increasing Particulate Phosphorus (PP) concentration in the solution, turbidity has increased. Thus, decreasing the Phosphorus term which is bond to suspended solids could affect reduction in turbidity level of solution. Results demonstrated that by increasing Mg concentration, turbidity of solution has decreased significantly. The main reason for turbidity reduction, similar to Meozzi (2011), might be less Phosphorus concentration in wastewater based on more precipitation. Figure 48 illustrates the comparison between wastewater turbidity level before and after struvite formation process.



Fig 48. Turbidity before (left) and after (right) struvite precipitation

On the other hand, turbidity level has increased during the experiments by increasing Ammonium concentration. This might only because of the initial turbidity level of reject water. Therefore, addition of more reject water could simply increase turbidity. Also, various mixing time intervals had not significant effect on turbidity level.

Conductivity

The results demonstrated that by increasing Ammonium concentration in solution, conductivity also has increased significantly. The same pattern was observed by increasing Mg: PO₄ molar ratio. This might be because of increase in content of dissolved ionic salts in wastewater. Conductivity also could be considered as alternative measure of dissolved solids in water. Therefore, higher conductivity level illustrates more dissolved Mg and N in the solution, which was mainly due to more addition of these ions into wastewater.

Heavy metals

According to the results, by increasing Ammonium concentration in the solution, concentration of Ni, Cr, Cu and As increased significantly. This change might be because of higher concentration of mentioned metals in reject water than wastewater. While the various Mg concentrations and mixing times had not any significant effect on these metals. Ronteltap et al. (2007) reported that during struvite precipitation in urine, between 20% and 63% of added heavy metals were found in struvite. While the average Ni reduction from wastewater were approximately 22% in both different Mg and mixing time treatments. This reduction from solution for Cr and As were found 39% and 4%, respectively, for both Mg and mixing time treatments.

On the other hand, the change in Cd and Pb concentration were not significant in all treatments. While H. Wang et al. (2017) found that by increasing reaction time from 0 to 60 minute, adsorption of Cd to MAP was increased.

Zink concentration in the solution was increased significantly by increasing both Ammonium and Mg concentrations. Also, the results demonstrated that increasing mixing time caused less concentration of Zn in wastewater. According to Ronteltap et al. (2007) adapted from Chand and Agarwal (1991) Magnesium could be replaced by Zn. Thus, by increasing Mg concentration and reaction between Mg and Ortho-P in order to produce struvite crystals, Zink ions might replace excess Mg ions in the solution, which could cause higher Zn concentration in solution. During the current study by increasing Mg: PO₄ molar ratio from 0.6 to 1.1, Zn removal from wastewater was reduced from approximately 60% to 48%.

Precipitated struvite mass

With regards to the results by increasing the Mg: PO₄ molar ratio, the mass of precipitated struvite was increased significantly. It was obviously because of more Ortho-P precipitation from the solution by increasing Mg concentration. Based on molecular mass of struvite and ions, struvite consists of nearly 13% P, 6% N and 10% Mg ions (Md Mukhlesur Rahman et al., 2014). During the current study, precipitated Phosphorus was determined approximately 10.5%-16.5% of total struvite mass. Also, for Mg ion, the amount in struvite was detected about 6%-10.8%. While, the amount of N in struvite was not detected as part of Ammonium was volatilized into the atmosphere.

Also, by increasing mixing time, the amount of precipitated struvite has decreased. This might illustrate that by increasing reaction time more than optimum, the crystallization process takes place slower and the production rate decreases, but the Ortho-P precipitation results did not demonstrate change during 40 and 60 minute. Thus, in order to conclude better, more investigation should be considered.

In addition, increasing Ammonium concentration in the solution, had not significant influence on precipitated struvite mass.

Conclusion

Ortho-P concentration of wastewater decreased significantly by adding of Magnesium into the solution with high concentration of $\text{PO}_4^{3-}\text{-P}$ and $\text{NH}_4\text{-N}$. Moreover, by increasing the Mg: PO_4 molar ratio, Ortho-P removal from the solution has also increased. Thus, the highest Ortho-P removal was achieved at Mg: PO_4 molar ratio of 1.1. With regards to the results, by increasing Mg: PO_4 molar ratio more than 1.1, the Ortho-P removal might become constant. Various $\text{NH}_4\text{:PO}_4$ molar ratios and mixing times had no significant effect on Ortho-P removal.

On the other hand, Ammonium reduction from the solution was not affected significantly by various Mg: PO_4 molar ratios and mixing time. As the experiments were conducted in direct contact of the solution with atmosphere, high amount of Ammonium might be removed by volatilization.

Calcium concentration in the solution increased by increasing the Mg: PO_4 molar ratio. This might be because of cation exchange in the solution. Higher Ca concentration in the solution, could illustrate more precipitation in form of struvite than Amorphous Calcium Phosphate (ACP). The results also showed that by increasing mixing time, Ca precipitation also increased. This could mean that more ACP precipitated after 40 minute of mixing.

With regards to the results, Fe and Al concentrations in the solution have increased by increasing Mg: PO_4 molar ratio. It illustrates that by presence of more Mg ions in the solution, more Phosphorus ions prefer to react with Mg and produce struvite instead of Fe and Al. The elimination of Al and Fe from reaction with Phosphorus ions, is of importance for the struvite precipitation method.

By increasing the Mg concentration in the solution more Ortho-P precipitated, but the concentration of remained Mg ions in the solution also increased. This might demonstrate that by addition of optimum Mg: PO_4 molar ratio, both desirable (not maximum) amount of Phosphorus could precipitate and less (or no) amount of excess Mg ions remain in the wastewater.

Furthermore, increasing Mg: PO_4 molar ratio, decreased the turbidity of the solution. This could be due to higher Ortho-P removal from wastewater. Also, by increase in $\text{NH}_4\text{:PO}_4$ and Mg: PO_4 molar ratios, the conductivity level of the solution increased. The main reason could be higher dissolution of the above mentioned salts in the solution.

The analysis of precipitated struvite mass illustrated that by increasing the Mg: PO_4 molar ratio, more struvite was produced. The main reason was higher Ortho-P precipitation during the experiments.

The effect of different Mg and Ammonium concentrations and also mixing time, had no significant effect on heavy metals concentration, except Zinc, in the solution. In the current study, Zn concentration increased by increasing Mg: PO_4 molar ratio. This might be due to cation exchange (mainly with Mg ion) in the solution.

Suggestions

During the current study the effects of various Mg: PO₄ and NH₄:PO₄ molar ratios along with different mixing time, at constant pH, on Phosphorus removal from wastewater were investigated. But in order to fully understand the struvite crystallization method in all aspects, further investigations should be implemented such as:

- The effect of different mixing speed on crystal characteristics
- Struvite analysis
- Deep investigation on the influence of this method on heavy metals
- The effect of higher pH on the crystals precipitation and purity
- Repeat the current study in close batch reactor
- The effect of the method on cations concentration like Potassium and Calcium
- Plant availability of the precipitated Ortho-P (fertilization)
- Finding more affordable reagent instead of Mg ion (if the aim is only P removal and fertilization is not goal, as currently struvite is not used as fertilizer in many plants because of heavy metals, Ca source could be more affordable)

Appendix A - Heavy metal concentrations in wastewater

Table 42. Heavy metals concentration in wastewater after the experiments

Mg: PO ₄ Molar Ratio	NH ₄ : PO ₄ Molar Ratio	pH	Mixing Time Minute	Ni ug/l	Cr ug/l	Cu ug/l	Zn ug/l	As ug/l	Cd ug/l	Pb ug/l
0.6	5	8.3	20	17	2.90	14	37.7	6.87	0.014	0.64
			40	17.3	2.80	11.3	35	7.13	0.023	1.02
			60	16.3	2.83	9.4	26.3	6.33	0.012	0.70
	10		20	20.7	3.73	16.7	40.3	9	0.019	0.71
			40	21.7	4.00	16	38.5	9.77	0.031	1.20
			60	21.5	4.30	16	37.7	8.60	0.019	1.10
0.8	5	20	16.3	2.73	14	38.3	6.37	0.026	0.85	
		40	18	3.40	10.9	35.3	6.70	0.024	1.03	
		60	16.7	3.13	9.8	35.3	6.33	0.02	0.54	
	10	20	19.7	3.97	17.3	48	8.40	0.017	0.97	
		40	21.7	4.10	15	43	9.07	0.018	0.57	
		60	21	4.47	13.7	39.3	8.87	0.022	0.69	
1.1	5	20	15.7	2.83	13.3	41.7	6.30	0.017	0.81	
		40	17	2.80	12.7	38.7	6.47	0.024	2.57	
		60	17.3	3.00	9.1	37	6.60	0.020	0.40	
	10	20	22.3	5.07	20	64	9.63	0.035	2.57	
		40	21.7	4.20	17.7	52	9.17	0.02	0.73	
		60	21.3	4.10	14.3	44.7	9	0.021	0.55	

Appendix B – Statistical analysis results

Signif. code: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Ortho-Phosphate

	Estimate	Std. Error	t value	Pr(> t)	
(Intercept)	60.0374	1.44127	41.656	<2e-16	***
Mg	28.61579	1.1312	25.297	<2e-16	***
N	0.16156	0.09298	1.738	0.0886	.
Replication	-0.05194	0.28468	-0.182	0.856	
Time	0.02253	0.01423	1.583	0.1199	

Ammonium

	Estimate	Std. Error	t value	Pr(> t)	
(Intercept)	91.60867	1.037039	88.337	<2e-16	***
Mg	0.735819	0.813938	0.904	0.37	
N	-2.29719	0.066899	-34.338	<2e-16	***
Replication	0.025833	0.204836	0.126	0.9	
Time	-0.0066	0.010242	-0.644	0.522	

Calcium

	Estimate	Std. Error	t value	Pr(> t)	
(Intercept)	74.33046	2.69123	27.62	< 2e-16	***
Mg	-41.9718	2.08733	-20.108	< 2e-16	***
N	-0.73831	0.17217	-4.288	8.88E-05	***
Replication	0.29025	0.53141	0.546	0.58752	
Time	0.08498	0.02663	3.191	0.00252	**

Magnesium

	Estimate	Std. Error	t value	Pr(> t)	
(Intercept)	107.8881	1.362332	79.194	<2e-16	***
Mg	-25.4292	1.069249	-23.782	<2e-16	***
N	0.023037	0.087884	0.262	7.94E-01	
Time	-0.00924	0.013454	-0.686	0.496	
Replication	0.034167	0.269089	0.127	0.899	

Iron

	Estimate	Std. Error	t value	Pr(> t)	
(Intercept)	90.01541	3.75064	24	< 2e-16	***
Mg	-18.492	2.95069	-6.267	1.15E-07	***
N	-1.69803	0.24178	-7.023	8.42E-09	***
Replication	0.69448	0.7375	0.942	0.35128	
Time	0.11025	0.03696	2.983	0.00456	**

Aluminum

	Estimate	Std. Error	t value	Pr(> t)	
(Intercept)	85.45814	2.24921	37.995	< 2e-16	***
Mg	-11.9227	1.76533	-6.754	1.60E-08	***
N	0.32274	0.1451	2.224	3.08E-02	*
Time	0.01076	0.02221	0.485	0.6301	
Replication	0.50361	0.44426	1.134	0.2625	

Total Phosphorus

	Estimate	Std. Error	t value	Pr(> t)	
(Intercept)	52.00252	1.68013	30.951	<2e-16	***
Mg	36.33093	1.3115	27.702	<2e-16	***
N	-0.26567	0.10886	-2.44	1.84E-02	*
Time	0.02266	0.01675	1.353	0.1824	
Replication	-0.08929	0.33498	-0.267	0.791	

Potassium

	Estimate	Std. Error	t value	Pr(> t)	
(Intercept)	143.6404	5.74006	25.024	< 2e-16	***
Mg	-0.1462	4.50518	-0.032	9.74E-01	
N	1.55556	0.37029	4.201	1.12E-04	***
Replication	1.38889	1.13378	1.225	0.226428	
Time	-0.02778	0.05669	-0.49	0.626318	

Turbidity

	Estimate	Std. Error	t value	Pr(> t)	
(Intercept)	41.45902	4.41487	9.391	1.55E-12	***
Mg	6.98962	3.46508	2.017	4.92E-02	*
N	-1.25904	0.2848	-4.421	5.45E-05	***
Time	-0.02007	0.0436	-0.46	0.6473	
Replication	0.40917	0.87203	0.469	0.641	

Conductivity

	Estimate	Std. Error	t value	Pr(> t)	
(Intercept)	3.655366	0.114808	31.839	< 2e-16	***
Mg	0.305114	0.091658	3.329	1.68E-03	**
N	0.245074	0.007481	32.76	< 2e-16	***
Replication	-0.01681	0.023023	-0.73	0.46896	
Time	0.000451	0.001151	0.392	0.69669	

Nickel

	Estimate	Std. Error	t value	Pr(> t)	
(Intercept)	11.17563	0.84615	13.208	<2e-16	***
Mg	0.385028	0.671788	0.573	5.69E-01	
N	0.882184	0.055052	16.024	<2e-16	***
Time	0.009854	0.008471	1.163	0.25	
Replication	0.275142	0.169426	1.624	0.111	

Chromium

	Estimate	Std. Error	t value	Pr(> t)	
(Intercept)	1.097693	0.321371	3.416	1.30E-03	**
Mg	0.469541	0.255148	1.84	7.19E-02	.
N	0.254057	0.020909	12.151	2.97E-16	***
Replication	0.04451	0.064349	0.692	0.4925	
Time	0.002219	0.003217	0.69	0.4937	

Copper

	Estimate	Std. Error	t value	Pr(> t)	
(Intercept)	9.870567	1.310173	7.534	1.45E-09	***
Mg	1.015204	1.056622	0.961	3.42E-01	
N	0.907672	0.085582	10.606	6.06E-14	***
Replication	0.002331	0.261535	0.009	0.993	
Time	-0.09084	0.013105	-6.932	1.15E-08	***

Zink

	Estimate	Std. Error	t value	Pr(> t)	
(Intercept)	20.70043	3.67073	5.639	9.42E-07	***
Mg	19.63022	2.95189	6.65	2.78E-08	***
N	1.75858	0.24046	7.313	2.74E-09	***
Replication	-0.98969	0.73244	-1.351	0.183	
Time	-0.19311	0.03663	-5.272	3.33E-06	***

Arsenic

	Estimate	Std. Error	t value	Pr(> t)	
(Intercept)	4.117398	0.356106	11.562	1.31E-15	***
Mg	-0.10088	0.279496	-0.361	7.20E-01	
N	0.497778	0.022972	21.669	< 2e-16	***
Replication	0.091667	0.070338	1.303	0.199	
Time	-0.00347	0.003517	-0.987	3.28E-01	

Cadmium

	Estimate	Std. Error	t value	Pr(> t)
(Intercept)	1.19E-02	7.65E-03	1.559	1.25E-01
Mg	6.31E-03	6.00E-03	1.051	2.99E-01
N	4.39E-04	4.93E-04	0.889	3.78E-01
Replication	1.57E-03	1.51E-03	1.041	0.303
Time	-5.69E-05	7.55E-05	-0.754	4.54E-01

Lead

	Estimate	Std. Error	t value	Pr(> t)
(Intercept)	3.88E-01	6.33E-01	0.613	5.43E-01
Mg	8.20E-01	4.97E-01	1.649	1.06E-01
N	1.19E-02	4.09E-02	0.292	7.72E-01
Replication	1.24E-01	1.25E-01	0.995	0.3248
Time	-1.07E-02	6.26E-03	-1.714	9.29E-02

Struvite mass

	Estimate	Std. Error	t value	Pr(> t)	
(Intercept)	438.8012	53.9158	8.139	1.17E-10	***
Mg	169.883	42.3168	4.015	0.000204	***
N	-2.6667	3.4781	-0.767	0.446938	
Replication	-12.2222	10.6495	-1.148	0.256672	
Time	-1.3333	0.5325	-2.504	0.015657	*

Signif. code: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

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