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# **Removal of Phosphorus from anaerobic digested blackwater by precipitation with struvite from Seawater and Magnesium Chloride**

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Health and Development

**Removal of Phosphorus from anaerobic digested blackwater by Precipitation with struvite  
from Seawater and Magnesium Chloride.**

A Thesis submitted in partial satisfaction of the requirements for the degree

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in

Environment and Natural Resources - Specialization Sustainable Water and

Sanitation, Health and Development.

By

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## Abstract

Phosphorus is a finite resource with the largest remaining resources in West Sahara and China. India and Europe have no significant mineral Phosphorus. The increase of awareness about the recovery of Phosphorus as fertilizer is an important issue for the food security and environmental protection. In this thesis the recovery of Phosphorus was carried out by precipitating anaerobic digested blackwater with Magnesium Chloride ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ) and Seawater. The main purpose was to determine the effect of mixing ratio and pH on the removal of nutrients from blackwater. Based on the main goal two hypothesis were formulated, firstly addition of Mg source is an important factor on the removal efficiency of P. The use of ratio of struvite Mg :P 1.3:1 and 1:1 led to about 90% and 80 of P removal respectively. And Secondary hypothesis was that an increase of pH from 8.5 to pH 9 increase removal efficiency.

To carry out the experiment digested blackwater was taken from Realtek laboratory and source of seawater was taken from Drøbak. The adjustment of pH was done by adding few drops of Sodium hydroxide. Analysis of nutrients was done by using LCK 350 method and the reading was taken from using Hack Lange 3900DR.

The results showed the highest total P removal of 99.7% with  $\text{MgCl}_2$  at pH 9 and Mg:P of 1.3:1 with  $\text{MgCl}_2$  and 96.3% with seawater. Also, removal of  $\text{PO}_4\text{-P}$  removal efficiency was 99% at seawater with mixing ratio of 1:1 at pH 9 and the lowest value was 95.1% with  $\text{MgCl}_2$  at pH 8.5 mixing ratio 1:1.

## Abbreviations

MgCl <sub>2</sub>	Magnesium Chloride
N	Nitrogen
P	Phosphorus
MAP	Magnesium Ammonium Phosphate
HCl	Hydrochloric Acid
Mg/l	Milligram per Liter
Mt	Million Tones
PO <sub>4</sub> <sup>3-</sup>	Phosphate
Ppb	part per million
NMBU	Norwegian University of Life Science

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## CHAPTER ONE

### 1. INTRODUCTION

Rapidly increase of global population result to the high demand of food production which can be met by investment on the agricultural sector. The use of fertilizer for agricultural is inevitable among of three essential nutrients for plants to grow NPK Phosphorous (P) is the major essential nutrient for the growth of crops(Kemacheevakul et al., 2014).Since P is very reactive when met with other elements in the soil this make P to be essential for the better growth of plants. Phosphorous element found mostly in the form of phosphate with the combination of other elements, the largest quantity of Phosphorous found conserved into terrestrial soil and sediments like oceans, lakes and freshy water.

Currently the amount of commercial P fertilizer used in the World is originated from Morocco, China, Russia and United States(Kelly et al., 2005).About 80%mined Phosphorous is used in agriculture production as a fertilizer,15% used industrial sector for production of detergents and only 5% used as additives for the manufacturing of animals foods. Development of agriculture sector depend more on the availability of enough fertilizer with affordable price, the application of fertilizer in developing countries is increasing due to severe loss natural soil fertility in most of the South Saharan countries(Cordell et al., 2011).

Demand of Phosphorous fertilizer is related with population growth and expansion of the food requirements. The global population estimated to increase by 50% in on 2050 and reach 11billion people compared to 7billion on year 2011.The peak demand of Phosphorous fertilizer is estimated to occur at 2035 the need of recovering of P in order to meet the demand of fertilizer in the future is needed(Cordell and White, 2011).

Convectional wastewater treatment system is common approach used worldwide for the treatment of wastewater but showed highly investment,construction,operations and maintenance costs(Larsen et al., 1996).Also failed to meet the rapid urbanization of many city and it fails to match with Millennium development goal number 6 which to ensure availability and sustainable management of water and sanitation for all (United Nations 2015). In 1990s source separating

system got famous as alternative method of wastewater treatment in per urban area and into the informal settlement in big towns of Africa and Asia. It has couple of benefits like energy saving, water saving, decrease greenhouse gas emission, low risk to pollute environment and easy to recovery the nutrients(Jönsson et al., 1997, Maurer et al., 2006).

Currently various biological and physio-chemical technologies have been invented for the purpose to removal of phosphorous from wastewater, the process physio chemical done by precipitation of wastewater with is insoluble salts most of aluminum and iron. During that process phosphorous particles are attached to metals particles. The challenge of this technology is the cost for chemicals and handling of sludge(Morse et al., 1998).

Recovery of Phosphorous recently has becoming a great discussion to most of decision makers and politicians in Europe. Different technologies are discovered to enhance the campaign of recovering nutrients.

The recovery process is more efficient than the removal since both the treatment and reuse are taking place simultaneously. During the process of Precipitation of Phosphorous useful form of Phosphorus is used as fertilizer and applied to the farms to increase nutrients into soil. Some of recovering and removal technologies are described table1 (Morse et al., 1998).

The recovery of Phosphorous from the wastewater showed the promise substitute for the demand of fertilizer, especially urine from domestic water contain richness values of essential elements for fertility of the soil 80% Nitrogen, 50% phosphorous P and 90% Potassium K(Zamora et al., 2017a).

In Norway NMBU is running the project of sustainable use of wastewater to improve the living and recovering of nutrient at Frederiksted old hospital in Norway. With the idea of source separation whereby nutrients from urine used as struvite to make a phosphorous fertilizer which can be used for urban agriculture at Frederiksted.

Table 1: Technologies for Recovery and removal of Phosphorous(Morse et al., 1998)

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 ( $MgNH_4PO_4$ )
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

## 2. LITERATURE REVIEW

### 2.1 Urine

(Jönsson, 2001) Define Urine as an urban waste fraction which contain high amount of nutrients.it contains about 70% of nitrogen and 50% of phosphorus in the all household waste water contents fraction. It is estimated that the adult person can produce about 1.4L of urine per day (Rose et al., 2015), the amount of urine in total household wastewater it showed to be only 1% as described in the figure1

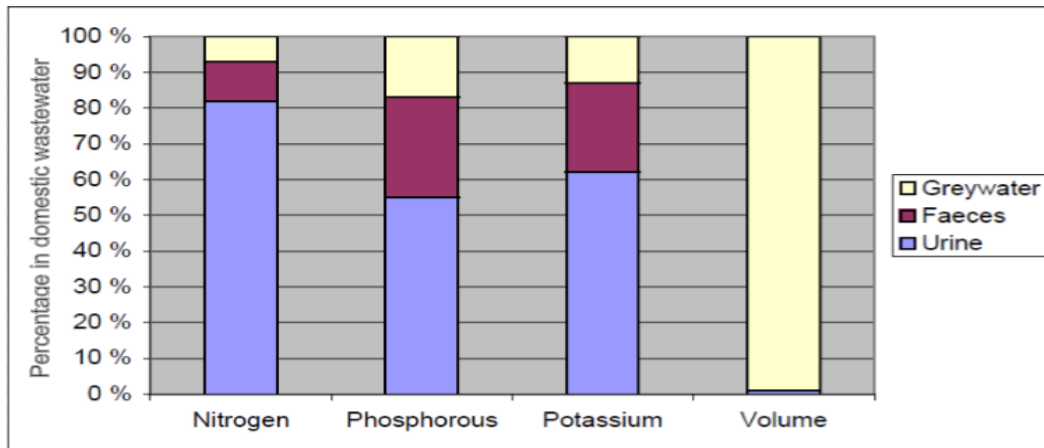


Figure 1: Nutrients components and volume of domestic water ((Jönsson, 2001)

The application of urine as fertilizer it has less health danger to human compared to the direct application of feces, but some human pathogen microorganisms like salmonella typhi and helminth eggs can be found in urine. The storage of urine with urea for six month it can reduce the possibility of urine to cause the dangerous effects to human health(Pandey and Jenssen, 2017). In the study done by (Larsen et al., 1996) showed that human urine contain about 57% of P when is separated from other domestic wastewater.

**Table 2:** Source of pollutant in domestic wastewater

Source	Total Organic Carbon	Total Kjeldahl Nitrogen	Total Phosphorus
Kitchen, Cleaning, Bathroom	15	0.2	*
Feces	17	1.5	0.6
ANS / Urine	5**	12.2	0.8
Total	37	13.9	1.4

Source: (Larsen *et al.*, 1996)

However the question about how to deal with microplastic nutrients such as plastics and pharmaceutical from urine and their effects to the quality of soil and crop products after being harvested made the direct application of urine to the industrialized societies to be difficult compared to the developing societies(Maurer et al., 2006).

## 2.2 Phosphorous

The element Phosphorus was discovered by the German scientist Henning Brandt in the 17<sup>th</sup> century where he used 50 buckets of urine and distilled it by evaporating and heating in search of the legendary ‘Philosopher’s Stone’(Emsley and Huxtable, 2000).

Phosphorus is important for the human, plants and animals life. It plays big role in the challenge of World food scarcity and soil fertility.(Scholz et al., 2013).However rapidly increase of population it threatens the capacity of currently deposit of mineral P its estimated by 2050 the population of World will be about 9billion people and the peak accumulation of P to occur in 2035.The needs of alternative source of P is inevitable since the current production capacity from minerals P rock is 20million tones(Ashley et al., 2011) figure 2.Also the overuse of P fertilizer and other P sources like from detergents has contributed to the pollution of surface water sources due to the eutrophication. Which made depletion of oxygen and growth of algal bloom which result to the disturbance of the aquatic ecosystem and scarcity of fresh water sources(Van Vuuren et al., 2010).

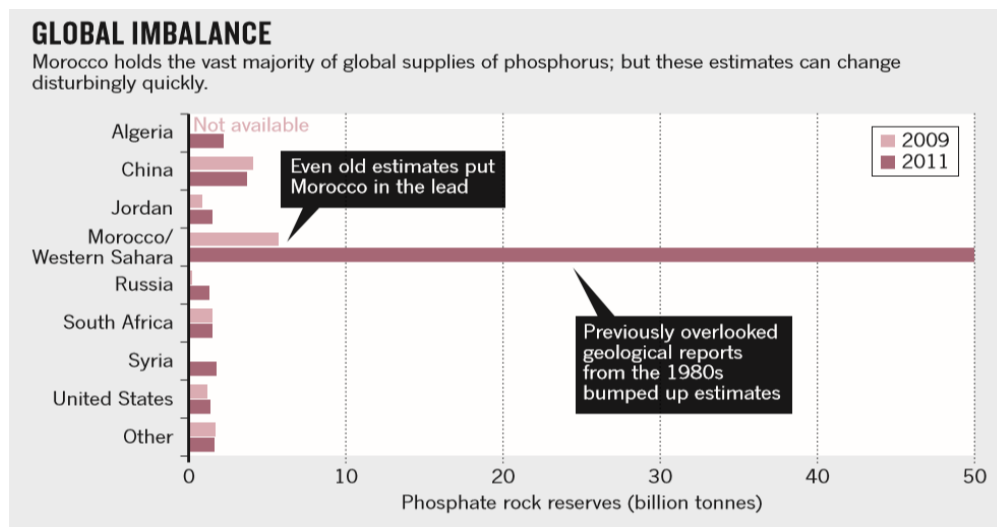


Figure 2:Global balance of Phosphorus Source (Elser and Bennett, 2011)



### 2.3 Phosphorus transport

Phosphorus transport and fate in terrestrial and aquatic ecosystem is summarized in the figure 3 whereby organic and inorganic P are dissolved and detached by means of moving across and through soil. Dissolved P can be deposited into riverbanks or carried into water reservoirs and lakes. The amount of soluble phosphorus inside lakes is taken by algae while the insoluble P is depleted.

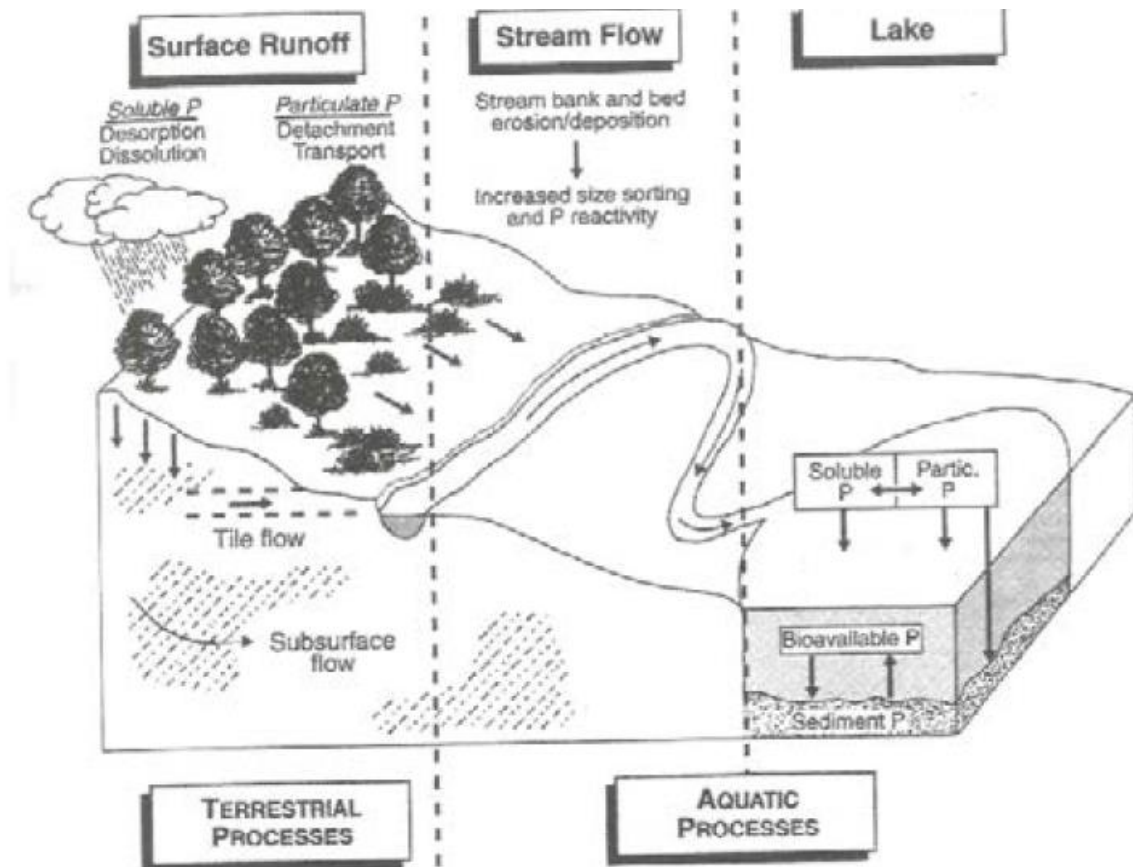


Figure 3: Phosphorus transport (Pierzynski et al., 2005)

### 2.4 Phosphorus cycle into soil

Total amount concentration of P into soil varies from 50-3000mg/kg. In mineral soils, 50-70% are in forms of inorganic. While at organic soil 20-30% are organic matter and only 60-90% of total P can be organic into soil. The amount of soil organic P such as plants and animals residuals and soil organic matter are converted into inorganic P by mineralization process since the inorganic P is the one that taken by plants. Soluble P is adsorbed to clay, Aluminum and iron oxides which make P unavailable for plants growth.

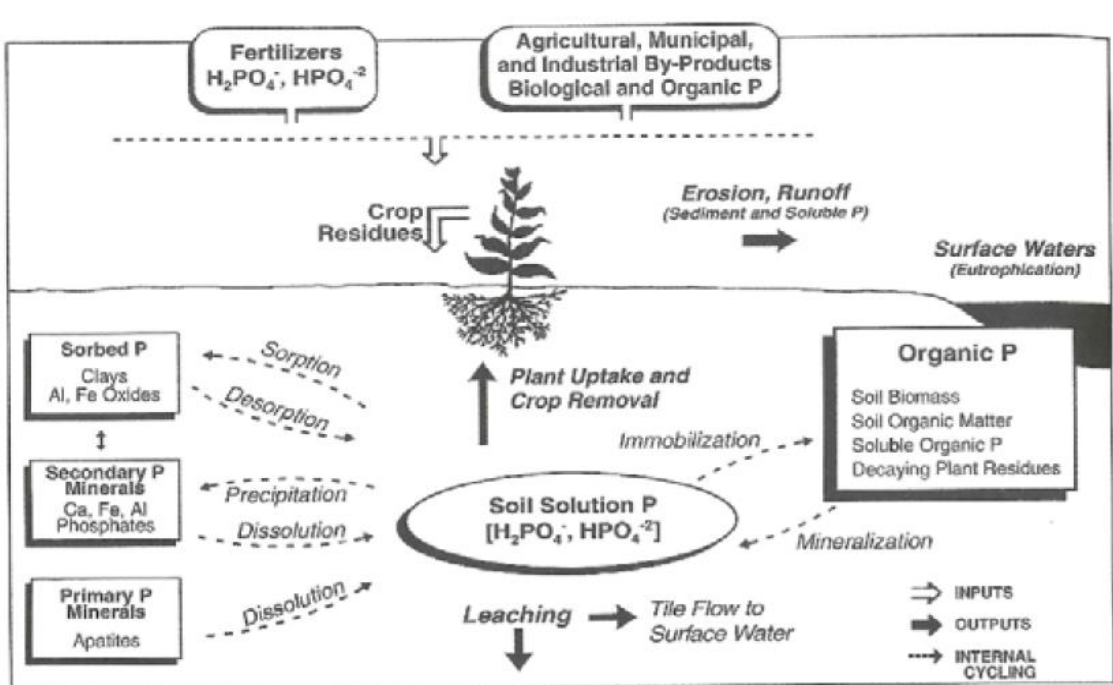


Figure 4: Phosphorus Cycle (Pierzynski et al., 2005)

Dissolved Phosphorus enter the soil in the forms of primary  $PO_4^{3-}$  and secondary in the form of ortho-Phosphate  $HPO_4^{2-}$  and  $H_2PO_4^-$ . Amount of pH is the controlling factor for the availability of primary and secondary Phosphorus into soil. Fig illustrate that at pH 4 to 6.5 Dihydrogen Phosphate is formed  $H_2PO_4^-$  while at pH above 7.5 Hydrogen Phosphate  $HPO_4^{2-}$  is dominant

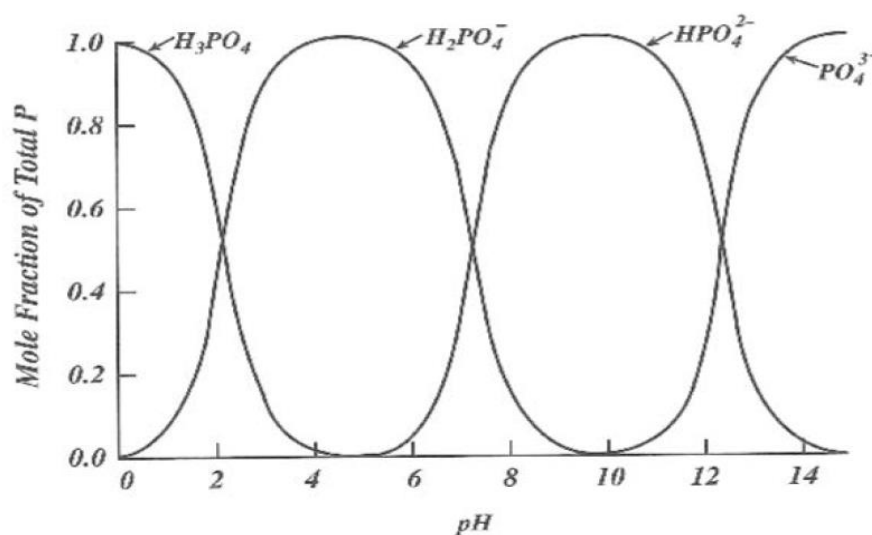


Figure 5: Effects of pH on Phosphorus (Pierzynski et al., 2005)

## 2.5 Full scale technologies for P recovery for Municipal and industrial wastewater

### 2.5.1 General P recovery in practice

Recovery technologies for Phosphorous can be applied at any points in the treatment scheme of wastewater can be recovered from liquid phase, sludge phase and from mono-incinerated and sludge ash. As showed in the figure below .High amount of P about 90% of incoming phosphorous load from wastewater is inform of sewage sludge(Cornel et al., 2009).Recovery rate of P from sewage sludge and sewage ash can have possibility to reach up to 90% while at liquid phase recovery rate ranges from 40-50%.

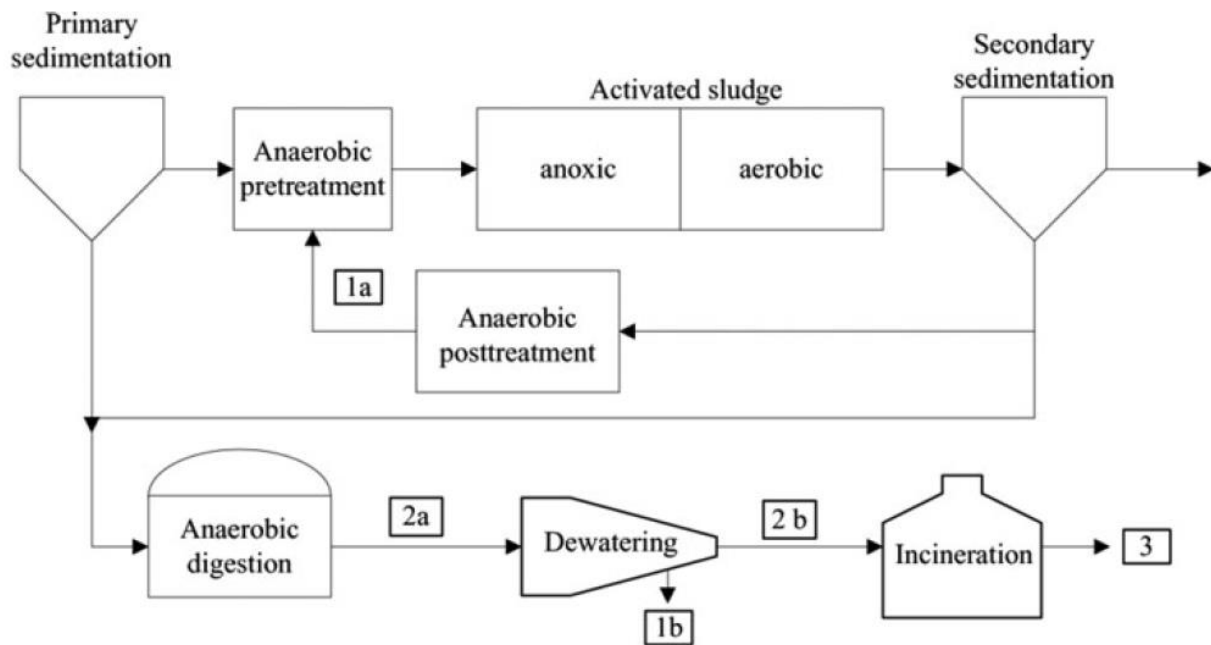


Figure 6: Possible locations for phosphorous recovery modified from (Cornel et al., 2009)

### 2.5.2 NuRESyS

Liquid phase removal of Phosphorous usually is located into WWTPs which contain biological removal process since polyphosphates are stored into cell of bacteria and are released under anaerobic conditions. Amount of P in biological removal ot ranges from 75-300mg-l(Garcia-Belinchón et al., 2013).Substantial difference between traditional P removal and modern P recovery from waste is that P recover technologies aim to have a final product which can be used as fertilizer.

### 2.5.3 Calcium phosphate

Formation of Calcium phosphate precipitation very complex and it need various parameters ionic strength, pH, temperature, supersaturation and mixing time. Forms of crystallized calcium phosphate it depends mainly o pH and kinetic of chemical reaction.

### 2.5.4 Recovery of Phosphorus from mixed tanks

This technology of P recovery was developed by Akwadok company in Belgium and it operated into two reactors a shown in Figure. NuRESyS stand for Nutrients Recycle System, operation mode of this technology is continuous compared to ANPHOS technology which operated into batch mode. Also magnesium chloride is the main source of magnesium used into this technology with addition of 29percent of NaOH. Simple bladder impeller installed for the purpose of optimizing pH between 8-8.5 also impeller help to prevent occurring of scaling(Moerman et al., 2009).

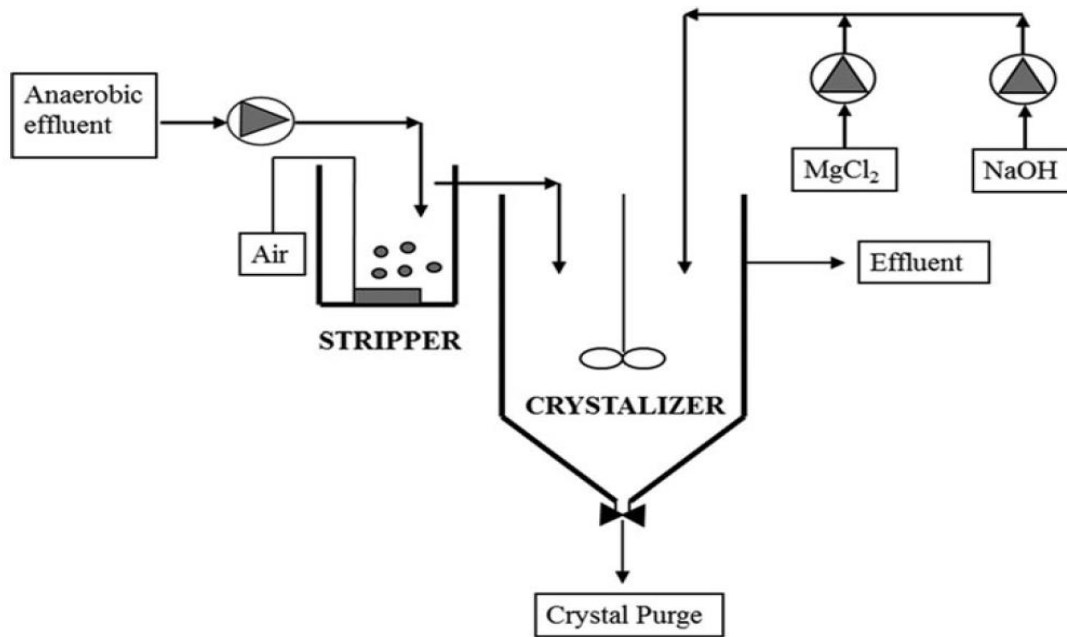


Figure 7: Schematic process overview of NuRESyS technology modified from Source: (Moerman et al., 2009).

Full scale plant was first taken into operation in 2005 in northern Germany at dairy processing company with a capacity of 1580kgstruvute-day. The removal attained was 85% of phosphate and used into agriculture.

### 2.5.5 Anphos

This process was developed by Colsen and operation is divided into two batch reactors, first reactor wastewater is aerated for purpose of raising pH due to Carbon dioxide air stripping, Second reactor MgO added for the recovery of P as struvite(Lodder et al., 2011).The removing capacity of ANPHOS is 80-90% of phosphate.

### 2.5.6 Crystalactor

This technology was invented by Dutch in 1980s for the purpose of removing hardness from drinking water, also technology was used to removal heavy metals from drinking water and wastewater.(Giensen and van der Moldeh, 1996).Calcium hydroxide is added into a reactor for the purpose of increasing pH 9,recovery rate can reach to 70-80%PO<sub>4</sub>-P by selecting good operation condition and minimizing impurities(Cornel et al., 2009)

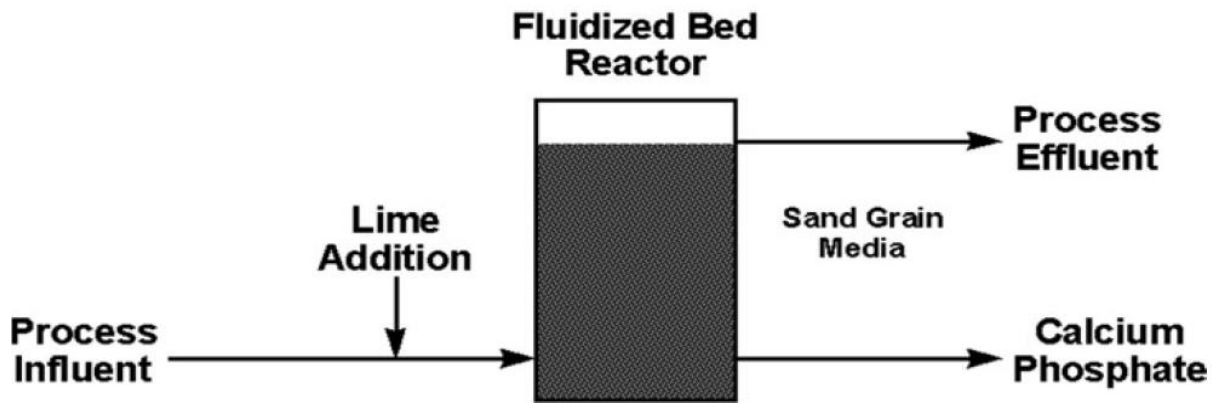


Figure 8: Crystalactor process flow diagram (Desmidt et al., 2015)

### 2.5.7 Airprex

AirPrex technology is designed to control the incrustations of wastewater pipes due to the deposition of struvite into the sides of pipe. Air Prex technology figure ...digested sludge firstly entered to cylindrical reactor with an inner cylindrical zone mixed by air up flow and sedimentation zone at bottom between inner and outer cylinder. Air bubbles help to lift sludge and to increase pH and to increase the grow of struvite crystals until they reach size to escape flow recycle flow and settle.

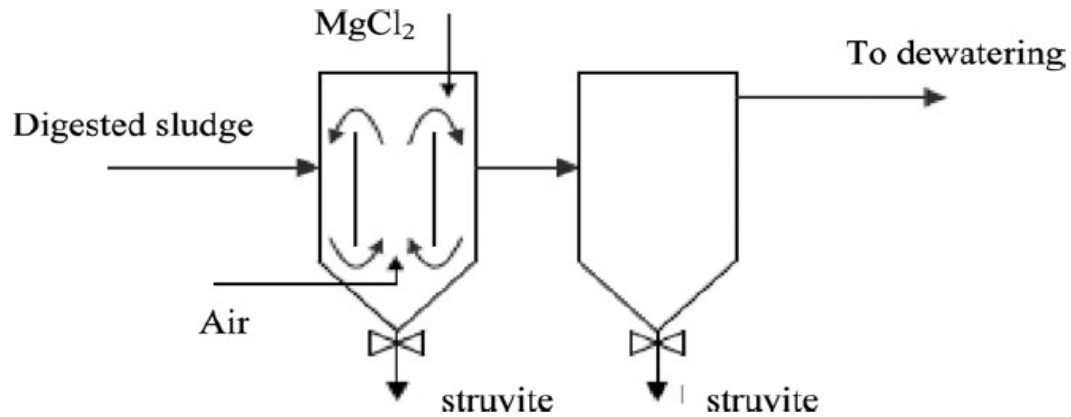


Figure 9: AirPrex schematic overview (Heinzmann, 2009)

Struvite is removed at the bottom of two tanks, an equipment for sand washing placed to ensure that recovered struvite be cleaned and purification. The GmbH, Hamburg from Germany are the owner of the AirPrex technology, and they built three treatment plant for recovery of P .Phosphate from those plant was removed at the liquid phase of digested liquid and the removal efficiency was 80-90% Phosphate.

### 2.5.8 Seaborne Technology

Seaborne technology was innovated by Seaborne Environmental Research Laboratory for the treatment of digested sewage sludge from municipal wastewater. Main purpose of this technology was to separate heavy metals, recovery of nitrogen and phosphorous and incineration of solids for the recovery of energy. Seaborne process recovered fertilizer is free from organic pollutant and heavy metals(Müller et al., 2005).

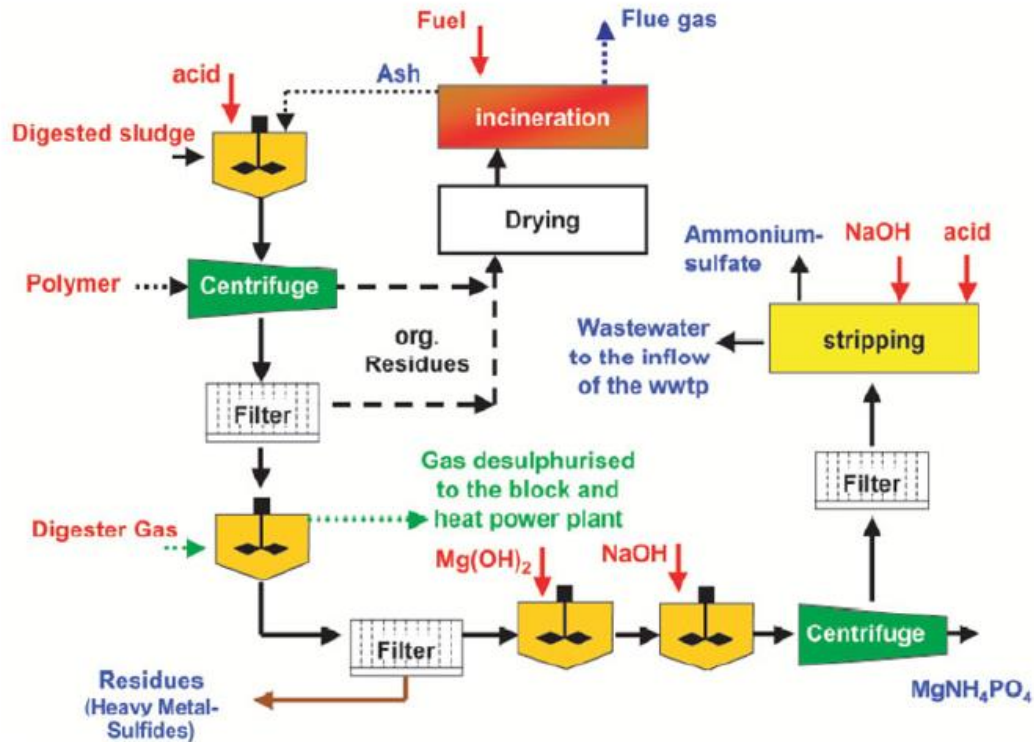


Figure 10: Process flow sheet of Seaborne Technology (Müller et al., 2005)

First Seaborne full-scale treatment plant was built in in 2006 in Germany with a capacity to serve 50000people.The recovery efficiency was 90% for phosphate and nitrogen. Addition of sulphuric acid it helps the acidification process to take place and dissolving of solids for purpose of releasing nutrients and heavy metals. Also Sodium hydroxide addition help to adjust the value of pH since struvite formation it depend on the value of pH(Müller et al., 2005).

### 2.5.9 Phospaqa technology

Phospaqa technology was developed in Netherlands by Paques. This technology is commercialized by agriculture authority in Netherlands to be used as fertilizer. The process recovers up to80% of phosphate and recovered P used in growing of potatoes. MgO is added to amend phosphate and aeration by air stripping is used to adjust pH which speed up the recovery process and reduce the amount of chemical oxygen demand(Remy et al., 2013).

### 2.5.10 Chemical precipitation methods

Chemical precipitation is the most widely methods for struvite recovery, however it requires sophisticated equipment.

### 2.5.11 Electrochemical method

This method precipitation of struvite is induced by chemical reaction. Electrochemical battery is used with anode formed by inert materials such as nickel, platinum and graphite. At cathode is the place where deposition of struvite occurs and analyte solution containing the ions of magnesium, phosphate and ammonia Figure below

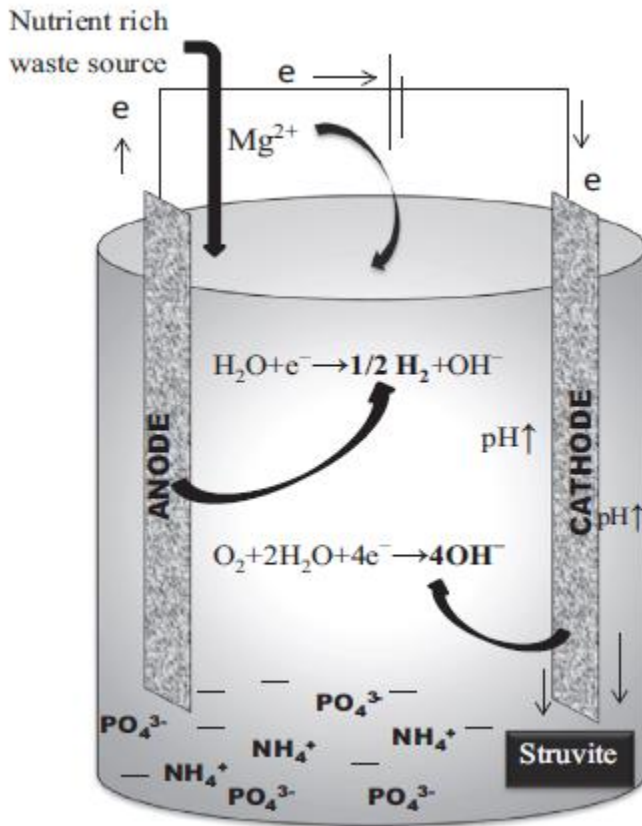


Figure 11: Electrochemical precipitation

Reduction of oxygen occur at cathode and forming hydroxide ions  $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$  while hydrogen gas is released. This reaction at cathode is very important for creating the alkaline conditions which are favorable for struvite precipitation since hydroxide help to raise the value of pH(Hao et al., 2008).



### 2.5.12 Advantages of electrochemical precipitation

There is no chemical required for the adjustment of pH, also production of hydrogen during the process can offset other cost if hydrogen gas recovery done. However drawback of electrochemical precipitation is an electric potential of 1.23V is required for the reduction of water(Wang et al., 2010, Cusick and Logan, 2012, Cusick et al., 2014).For reducing cost of energy, microbial electrochemical cell was innovated this is done by the microbes which produce electricity from organic matter released by microbes and convert into inorganic matter through oxidation at anode. Recovery capacity from microbial fuel cell is higher compared to feedstock since at a microbial inorganic phosphate is reduced and hence the amount of P available increase to 48% of the total P.Also this method retain the amount of heavy metals at the sludge matrix in the immobilized form(Fischer et al., 2011, Wang et al., 2010).

### 2.5.13 Chemical precipitation method in agitated reactor

At this method struvite is precipitate from wastewater by the addition of Mg in a mechanically agitated reactor figure. Efficiency of this method depend on pH and type of magnesium salt used. Common sources of magnesium used are  $MgCl_2$ ,  $MgO$  and  $MgSO_4$  also for the cost effective the use of seawater and wood ash are in progress as alternative source of Mg(Suzuki et al., 2007, Huang et al., 2011).The alkaline condition is important to be created for the purpose of pH adjustment which is suitable for struvite precipitation by addition of sodium hydroxide.

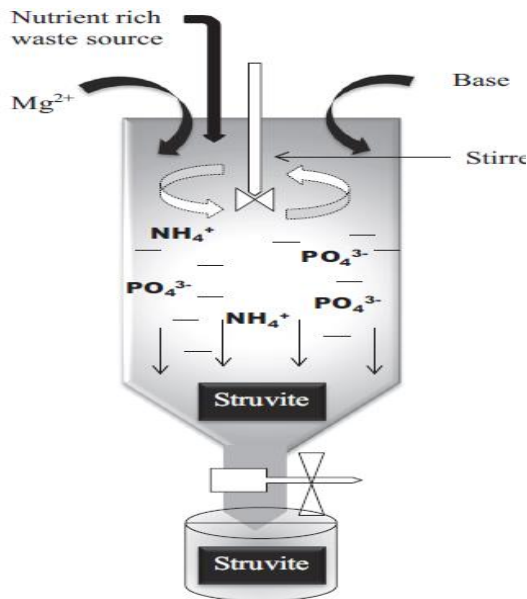


Figure 12: Chemical precipitation of struvite

#### 2.5.14 Ion Exchange method

At this method nutrients from wastewater are selectively exchanged in ion exchanger and struvite is precipitated after addition of magnesium in the controlled value of pH. In ion exchange column NaCl is added as regeneration solution where by  $\text{PO}_4^{3-}$  are exchanged for  $\text{Na}^+$  in cationic ion exchanger and  $\text{NH}_4^+$  are exchanged for  $\text{Cl}^-$  at anionic exchanger (Liberti et al., 1986).

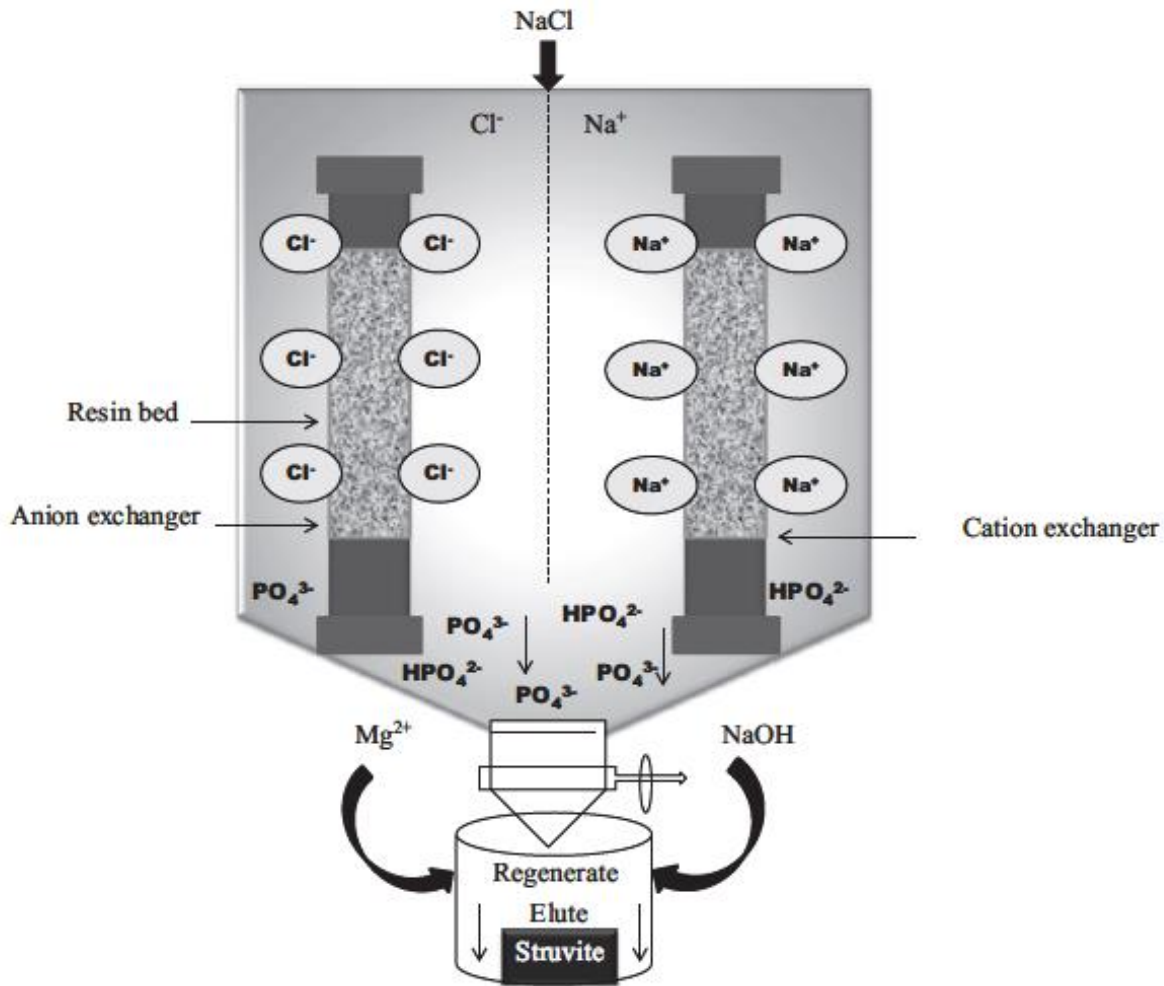


Figure 13: Ion exchange method of struvite precipitation adapted from (Kataki et al., 2016)

Externally  $\text{MgCl}_2$  added to react with regenerated  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  in stoichiometric ratio of  $\text{Mg}^{2+} : \text{NH}_4^+ : \text{PO}_4^{3-}$  equal to 1 : 1 : 1. figure above. Also, ion exchange isothermal supersaturation has been used to modify the convectional ion exchange. The main purpose is to facilitate enable spontaneous crystals of struvite formation and widening solubility of struvite precipitating solution beyond a given level of temperature (Mijangos et al., 2013, Ortueta et al., 2015).

### 2.5.15 Biomineralization method

This is the natural process of deposition of minerals by microbes for hardening their structure tissues and hence production of struvite. (Omar et al., 1998) reported that some bacteria like *Myxococcus Xanthus* and *Staphylococcus aureus* could precipitate struvite when they exposed into medium containing Mg and phosphate.

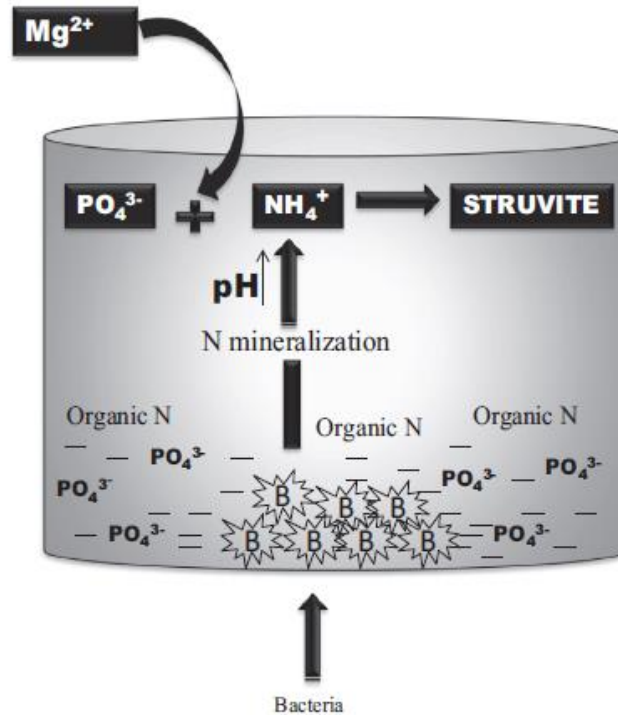


Figure 14: Schematic diagram of struvite precipitation through biomineralization (Kataki et al., 2016)

### 2.5.16 Phosphorus recovery from sludge ash

This method is used to recover P that is not recovered from liquid phase. Sewage sludge produced from different wastewater treatment plants mostly it ends up in landfills and into incinerators. Ashes from incinerators contains nutrients and organic contents, in case of nutrients from incinerator ashes phosphorus is vital resource to be recovered. Since ashes still contain concentration of heavy metal above the allowable limits used in agriculture. Dry thermal and wet thermal methods are the ones that used for the recovery of P from incinerator ashes (Kaikake et al., 2009). The remaining ashes after recovery of P can be mixed with cement or concrete to form bricks and ceramic materials.

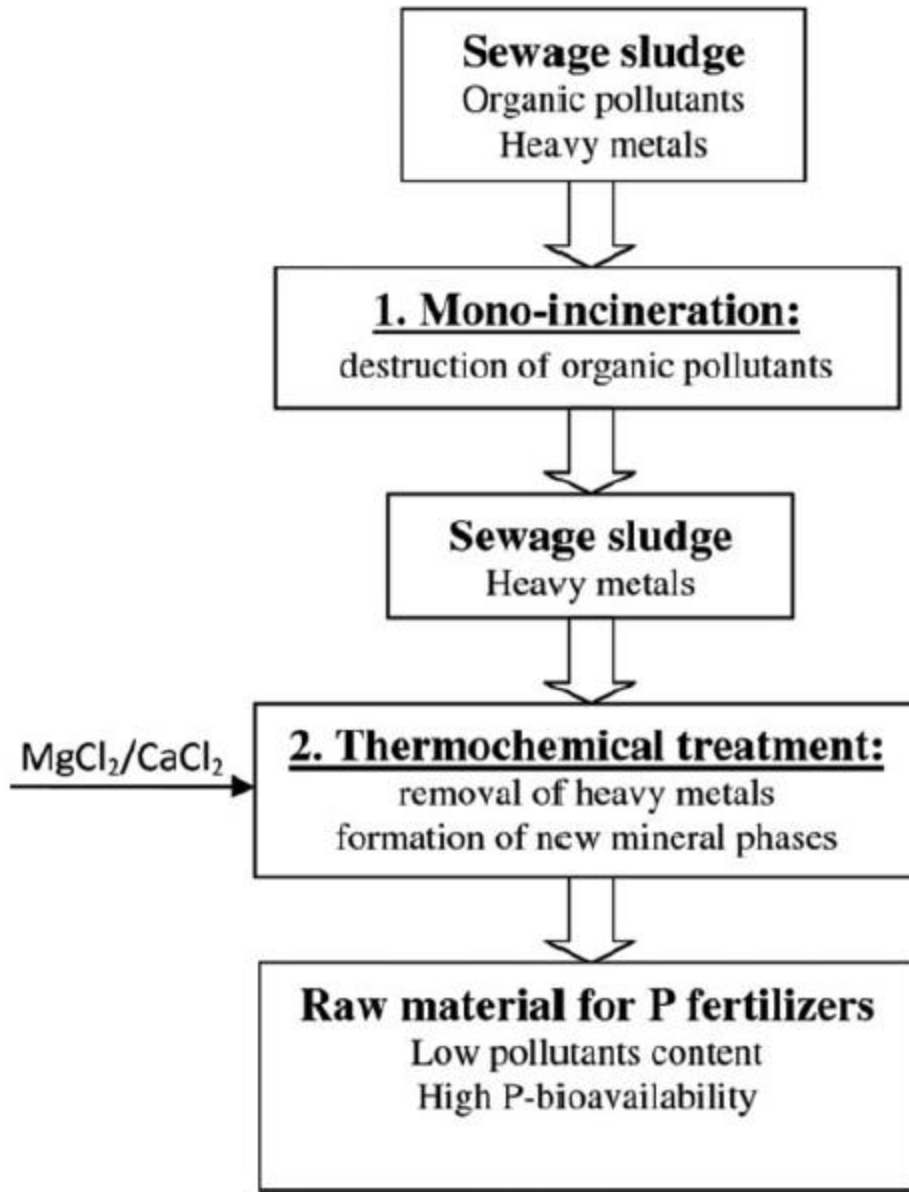


Figure 15: Schematic overview of the Ash Dec process (Adam et al., 2009)

## 2.6 Struvite

Struvite is formed by an equal molar combination of magnesium, phosphate and ammonium with six molecules of water ( $MgNH_4PO_4 \cdot 6H_2O$ ) and readily soluble in acid and neutral to alkaline also it can occur into different colors such as white, yellowish, and brownish. Presence of struvite into wastewater pipe has a tendency of reducing the durability of waste water due to the formation of scaling the precipitation of struvite lead to best option of controlling scaling of pipes.(Rahman et al., 2014).

### 2.6.1 Conditions for Struvite Precipitation

Efficiency of struvite it depends on the parameters such as Molar ratio, pH, temperature, aeration rate and presence of  $Ca^{2+}$  in the reaction media.

### 2.6.2 Crystallization

Formation of struvite crystals occur into two phases which are nucleation and crystal growth, the mechanism of these two processes is complex and controlled by different factors such as mass transfer between the liquid and solid phases and thermodynamic equilibrium between the liquid to solid phases and reaction kinetics of the compound(Ohlinger et al., 1999).Stages of both two processes it depends on supersaturation ,Nucleation stage it can be homogenous or heterogenous. Crystal growth process combined by both integration and diffusion process. Also crystal growth determine the final size of crystal according to the rate of growth(Jones, 2002).The whole procedures of nucleation are stated on the figure 16.

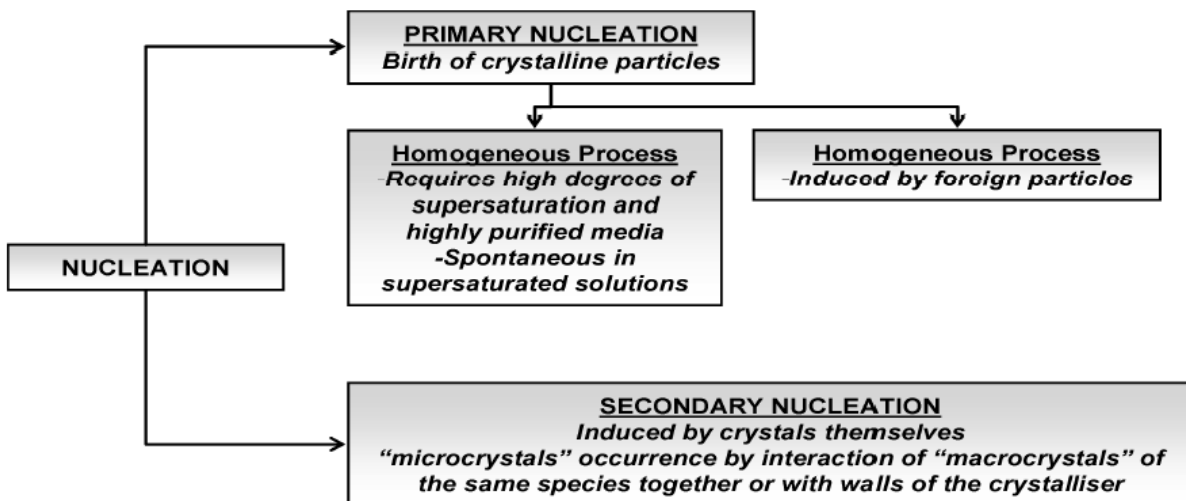


Figure 16: Mechanism of struvite Crystallization(Le Corre et al., 2009)

### 2.6.3 Molar ratio

Struvite formation depends on the mixing ratio of Magnesium Mg, Phosphate  $\text{PO}_4^{3-}$  and Ammonium  $\text{NH}_4^+$  into molar ratio of 1:1:1. Higher ratio of Mg:  $\text{PO}_4$  showed best removal efficiency of Most of researchers have been using  $\text{MgCl}_2$  as the main source of magnesium in precipitation of struvite since is available easily compared to other magnesium sources like MgO and brucite.

Table 3: Sources of magnesium

<b>Mg sources</b>	<b>References</b>
MgCl <sub>2</sub>	(Ronteltap, 2009, Liu et al., 2013a)
Brucite MgOH	(Huang et al., 2011, Münch and Barr, 2001)
MgO	(Ganrot et al., 2007)

### 2.6.4 pH

The pH play an important role during process of precipitating struvite. Struvite precipitation occurs into wide range of pH from 7-11.5 but the suitable pH is between 7.5-9 with minimum solubility (Hao et al., 2008). Increasing of pH it reduce the solubility of struvite and result to higher removal efficiency of P and N, also raising of pH to 8.3 can recover amount of P up to 90% (Adnan et al., 2003). In order to achieve the adjustment of pH done by using HCl and NaOH or by aeration.

Table 4 indicate pH range for different types of wastewater

<b>Water sources</b>	<b>pH range for struvite precipitation</b>	<b>References</b>
Farm waste	7-9	(Burns et al., 2001)
Industrial waste	9-11	(Liu et al., 2013a)
	8-11	(Moerman et al., 2009)
Municipal wastewater	8-9	(Uysal et al., 2010)

Also the amount of pH above 10 has reported by (Shin and Lee, 1998) that have a tendency to reduce the purity of struvite due to formation of amorphous precipitate.

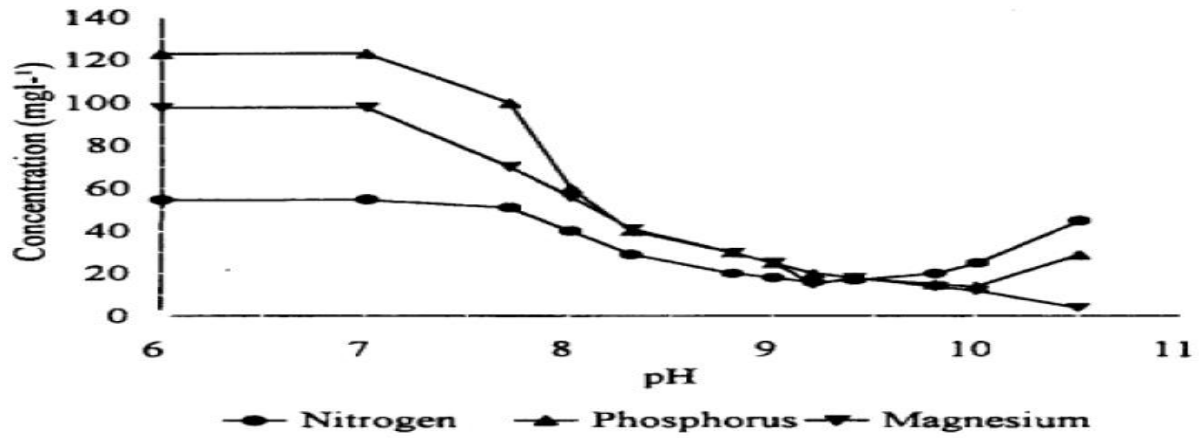


Figure 17: Concentration of nitrogen, magnesium and phosphorous versus pH at 25C (Shin and Lee, 1998)

Increase of pH it decrease the solubilty of struvite which lead to the deposition of struvite into different parts of wastewater treatment especially the distribution pipes, valves, elbow, and pumps to be affected by scaling as it showed by (Le Corre et al., 2009) on the table below

Table 3: Parts affected by struvite deposition (Le Corre et al., 2009)

Authors	Location of deposit	Effects	Type of plant
Rawn et al. (1937)	Digestion sludge process: pipes carrying supernatants liquors	Accumulation in some places to the thickness of an inch (~2.5 cm)	Wastewater treatment plant (USA)
Borgerding (1972)	Activated/digested sludge process: suction side of pump onto separating screen	310 mm-diameter of the suction side reduced to 150 mm	Hyperion waste water treatment plant (USA)
Booram et al. (1975)	Items in contact with anaerobic liquids: pump impellers, pipes, etc.	—	Livestock waste treatment and management plant (USA)
Mohajit et al. (1989)	In floating aerators, raw waste pumps, pipelines and outfall pipelines.	Accumulation: from 5.88 up to 14.44 mm in aerators; from 8 up to 28 mm in pipes carrying digester effluents	Pig waste treatment plant (Singapore)
Ohlinger et al. (1998)	Accumulation on pipe walls from sludge basins supernatant system	Accumulation along 5.6 km of pipes.	Wastewater treatment plant (USA)
Williams (1999)	Accumulation of struvite crystals in pipelines from the sludge holding tank to the centrifuges	Bore of pipes reduced from 100 to 50 mm	Wastewater treatment plant (UK)
Doyle et al. (2000)	Pipes carrying centrate liquors	Pipe diameter reduction from 150 to 60 mm in 12 weeks	Sludge destruction plant (UK)
Battistoni et al. (2004)	Pipes carrying anaerobic supernatants	Reduction of pipes diameter	Demonstrative fluidised bed reactor plant, WWTP (Italy)
Neethling and Benisch (2004)	Streaming pipes controlling polymer feed-flowmeters	Two-month build up in a 3" rubber lined 90° elbow	WWTP (USA)

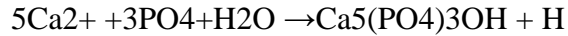
### 2.6.5 Aeration rate

Air flows has crucial role in the removal of nutrients from wastewater particularly the removal of NH<sub>4</sub>-N, airflow creates the pathway for the volatilization of NH<sub>4</sub>-N dissolved in the solutional it raises pH since it promote the process of CO<sub>2</sub> stripping (Rahman et al., 2014). Enough aeration time provide high efficiency of NH<sub>4</sub>-N as indicated by (Yetilmezsoy and Sapci-Zengin, 2009) and about 93.% of NH<sub>4</sub>-N recovered at period of 24hr with aeration rate of 0.6Lmin<sup>-1</sup>. Also increase of aeration rate promote the raise of pH as reported by (Suzuki et al., 2007) whereby pH raised from 7.5 to 8 with aeration rate of 12m<sup>3</sup>h<sup>-1</sup>.



### 2.6.6 Presence of foreign ions

Presence of impurities in solution it affects the growth rate of crystalline compounds due to the reduction of space where crystals can be formed. Especially the presence of calcium and ions in media it affects negatively the growth rate. When Calcium ion concentration is high in solution it interact with phosphate to form calcium phosphate as hydroxyapatite according to equations below as reported by (Le Corre et al., 2009).



## 2.7 Advantages of controlling and recovering of P as struvite

### 2.7.1 Sludge reduction

Sludge production and disposal is the major challenges to most of wastewater treatment plants to both of municipal and company's treatment plants. Most sludge production resulted from an increase application of coagulant to enhance settling of particles from wastewater. It was predicated that the use coagulant would increase production of sludge from 7 to 9.4 million in EU by the year of 2005.also in UK was predicted that sludge would increase from 1.1 to 1.5million tones in seasons of 2005/2006.The use of struvite was studied by(Woods et al., 1999) showed that sludge production can be reduced by 8-30% through applying phosphorus recovery as struvite.

### 2.7.2 Reduction of pollution

Increase of amount of nutrients especially Phosphorous and nitrogen into aquatic environment has led to occurrence pf eutrophication to the water bodies which result to growth of algae. Effect of eutrophication has made scarcity of good drinking water sources, also death of fish and aquatic living organism has made un imbalance of ecosystem between different species. Most experimental methods of struvite precipitation showed the promise toward to solve the problem of eutrophication if applied, since struvite has a capacity to recover both nitrogen and phosphorus as described in table 4 below

Table 4: Nitrogen removal efficiency by struvite precipitation

Sources of wastewater	Efficiency	References
Human urine	Up to 95%	(Kabdaşlı et al., 2006)
Slurry type swine	99% depending on ratio	(Kim et al., 2004)
Anaerobic digested manure	95%	(Uludag-Demirer et al., 2005)
Swine wastewater	90%	(Maekawa et al., 1995)

### 2.7.3 Uses as fertilizer

The agronomic properties of struvite as fertilizer its on going discussion nowadays, Struvite contain essential nutrients for plants growth like P,N and Mg(Li and Zhao, 2003).in Japan struvite have been commercialized as fertilizer for growing rice and vegetables, however the communication between farmers and producers of struvite fertilizer need to be increased for the purpose of widening the uses of recovered Phosphorous(Fang et al., 2015).

### 2.8 Economic value of struvite

Recovering of struvite from wastewater has numerous advantages it reduce pollution caused by excessive discharge of nutrients to water bodies, reduce scaling problems to wastewater treatment plants and also potential of fertilizer would be a benefit to the companies dealing with recovering of phosphorous (Doyle and Parsons, 2002).The sustainability of phosphorous recovering into the economy view it faced challenge on the cost effective by taking into account cost of production which include maintance,chemicals and energy. Proximately amount of Phosphorous that can be recovered as struvite from 100m<sup>3</sup> of wastewater which increase saving of cost of disposal as described into table 5 below

Table 5: Saving on recovery as struvite over disposal

Cost AUD \$/d	100 m <sup>3</sup> /d	1000 m <sup>3</sup> /d	55000 m <sup>3</sup> /d
Loss producing struvite	0.065	0.65	35.75
Gain producing struvite	0.74	7.4	407
Reduction in sludge handling <sup>a</sup>	1.10	11.0	605
Reduction in WW flow (20%)	–	–	–
Reduction in Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.27	2.7	148.5
Reduction in sludge disposal	0.033	0.33	18.34
Reduction in cleaning struvite deposit	5.5–27.4	5.5–27.4	5.5–27.4
Reduction in landfill area	0.003	0.03	1.73

Concentration of Phosphorus in wastewater typically is range from 4-14mg PO<sub>4</sub><sup>3-</sup>-P/L according to (Metcalf, 2003).The recovery of 1kg of phosphorus from 100m<sup>3</sup>-d wastewater the efficiency of p recovery rate need to be 96.78% with waste water of 4mg PO<sub>4</sub><sup>3-</sup>-P per Recovering process has reduce potential operating costs on chemical, sludge disposal and time to clean polluted water bodies by nutrients.

### 2.8.1 Recovery of P Worldwide waste stream

Mineral P available is estimated to be exhausted in 90 years, and Current world population is around 6-7 billions. Which means that issue of food security for the 90 year coming is questionable by assuming 1.5 % annual increase of demand of Supplemented of recovery of phosphorus as fertilizer will last longer since the population is increasing as it shown on figure 18 below.

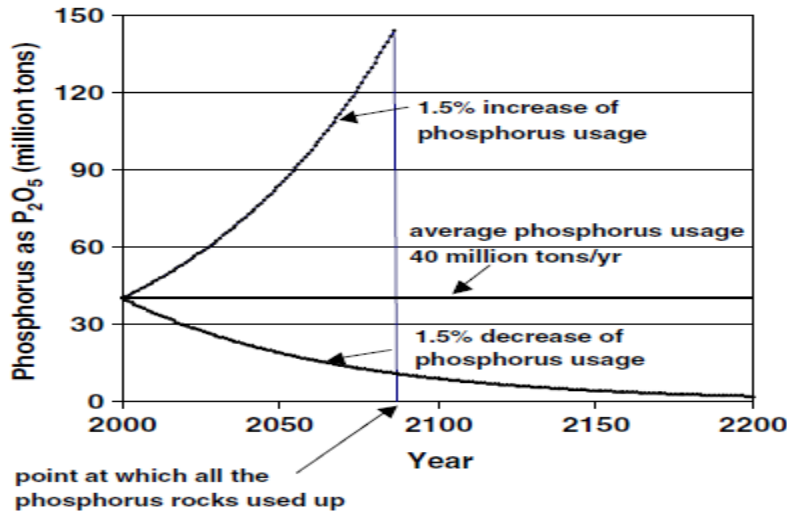


Figure 18: Phosphorous usage scenarios at 1.5% increase per annum and 1.5% decrease per annum

### 2.8.2 Population growth on P recovery

At worst case scenarios whereby all amount of mineral P assumed be exhausted, the only hope for Phosphorous will remain in recovery of P as struvite from WWTPs. Research done by indicated that an increase of population by 1 billion I earth will increase the load of phosphates into WWTPs by 0,3millions tones Table 6 below. Also demand of food will increase

Table 6: Contribution of recovered P from WWTPs worldwide to the reduction of mineral P rock

Population billions	Recovered P <sub>2</sub> O <sub>5</sub> /yr (million tons)	kg/ha/yr of P <sub>2</sub> O <sub>5</sub> from recovered phosphorus	% reduction in rock mining
6	2.31	1.25	5.76
7	2.69	1.45	6.72
8	3.07	1.66	7.68
9	3.46	1.87	8.64
10	3.84	2.08	9.60

Assume the entire world population is connected to WWTPs and phosphorus recovery is 100%. Assume at present, P<sub>2</sub>O<sub>5</sub> consumption = 40 million tons/yr and 80% of it is used as fertilizer. World arable land 1.48 billion ha.

## 2.9 Cost of struvite production

Challenge of production cost of struvite depends on the amounts of chemicals to be used in the whole process and the quantities of energy require for the mixing process during the crystallization(Jaffer et al., 2002, Münch and Barr, 2001).Most studies showed high amount of chemicals is used in the adjustment of pH of precipitation by adding NaOH and amount of MgCl<sub>2</sub> to reach an appropriate mixing ratio of Mg:N:P molar ratio(Jaffer et al., 2002) estimated that sodium hydroxide addition would took 97% of all expenses in chemicals for daily operation costs of the WWTPs ranging from 0.0014-0.51 €/m<sup>3</sup>.The use of air stripping method as alternative for pH adjustment of struvite precipitation, could be used as way of minimizing cost of NaOH(Battistoni et al., 2005).

The use of seawater or brine as source of magnesium could reach the removal of Phosphorous up 95% compared to 97% of MgCl<sub>2</sub>.But an issue of where to get brine can increase the cost of production if wastewater treatment plant located far from the sea(Shin and Lee, 1998).

## 2.10 Commercialization and application of struvite precipitation

Struvite precipitation is commercially used by different manufacturers to recover fertilizer from wastewater some of these technologies have been mentioned by (Lin et al., 2015) recently technologies are air prex from Germany,PHOSNIX from Japan, Crystalactor® from Netherlands. These technologies have made struvite precipitation to be become famous and efficiency technology compared to adsorption, incineration and hydrolysis.

## 2.11 Legal and regulation of phosphorous

The use of recovered phosphorous in European Union is increasing daily especially in Germany. In 2017 German government regulated the use and application of fertilizer and other ingredient to agriculture sector according to good professional coding. Struvite is termed as slow release fertilizer(Escher et al., 2006).The full scale technologies for recovery of Phosphorus

## 2.12 Anaerobic digestion

Anaerobic digestion is a biological process whereby organic carbon is converted into most oxidized state CO<sub>2</sub> and its most reduced state methane CH<sub>4</sub>.Also anaerobic digester is good for the treatment of sludge which contain large volume of solid particles both suspended and volatiles occurs in the limited supply of oxygen with the help of microorganism catalyze. The mixture of

different gas results to the formation of biogas. Main output of anaerobic digestion process are methane and carbodioxide,also small amount of nitrogen, ammonium and hydrogen sulphide gas(Angelidaki et al., 2003).

### 2.12.1 Sustainable cycle of anaerobic digestion

Rapidly increase of production in meat industry has made high amount of animals slurries and manures to be produced daily. Also wet organic waste from animals bleeding nowadays have increased threats to the pollution of environment. The needs of closing the loop of pollution as it have shown in the fig 19, it emphasizing the innovations of good sustainable technologies which can be affordable and gave positive results to the environment and improve the soil fertility and energy consumption through using biogas.

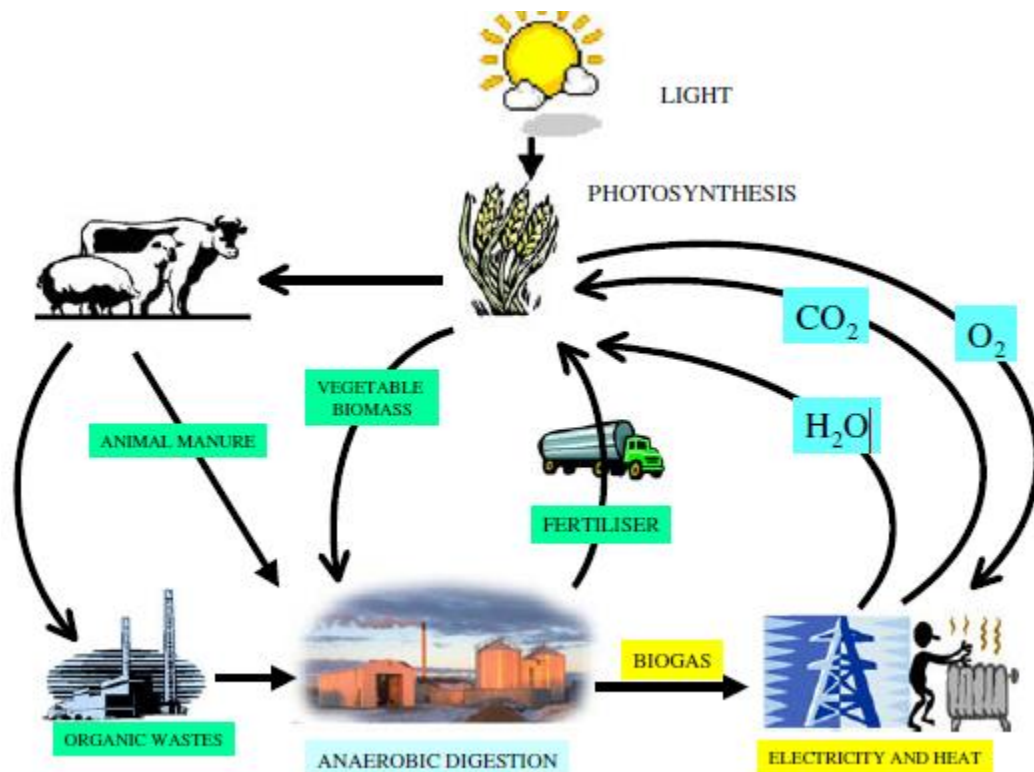


Figure 19: Sustainable use way of closing loop of animal manures by anaerobic digestion(Holm-Nielsen et al., 2009)

Poor management of animal manures or when is untreated it results to the main source of aquatic and air pollution. Hence made scarcity of surface drinking water due to concentration of nitrogen, phosphorous.ammonia and pathogen contamination. Also (Steinfeld et al., 2006)reported that the animals sector contribute to the environmental pollution especially increase of greenhouse gas

emission about 37% of anthropogenic N<sub>2</sub>O and 64% of anthropogenic NH<sub>3</sub> gas are in the World are originated from animal production sector.

Production of biogas from anaerobic process offer multiple benefits compared to other form of energy production. It reduces the greenhouse gas emission compared to fossils fuel. The digestate is an important resource which can be used as fertilizer in the agriculture and be a substitute for the mineral fertilizer(Weiland and biotechnology, 2010).

### 2.12.2 Biochemical process of Methane production

Process of methane formation is a complex process which is divided into four phases, hydrolysis, acinogenesis, dehydrogenation and methanogenesis. All four phases of digestion process depend on the degradation rates. Equal sizes of degradation rates it prevents the drops down on pH because the drop down can affect the methanogenic bacteria.

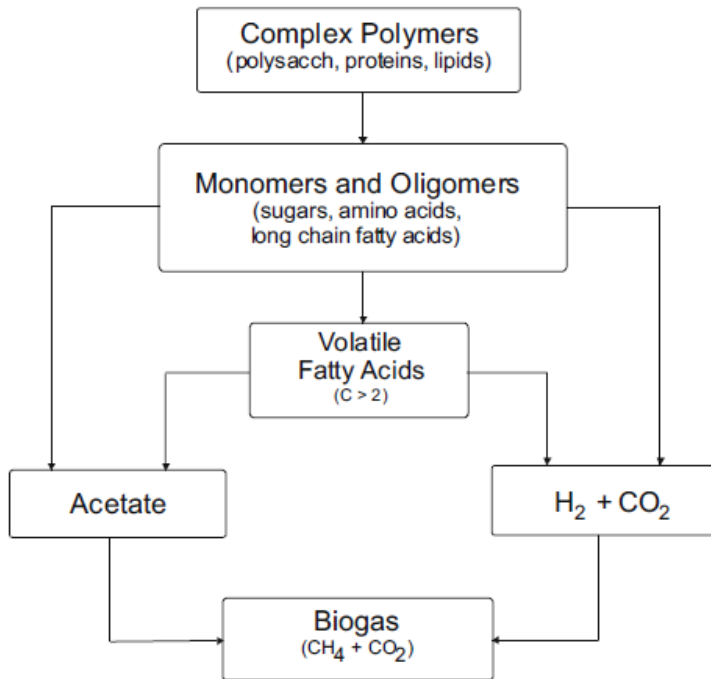
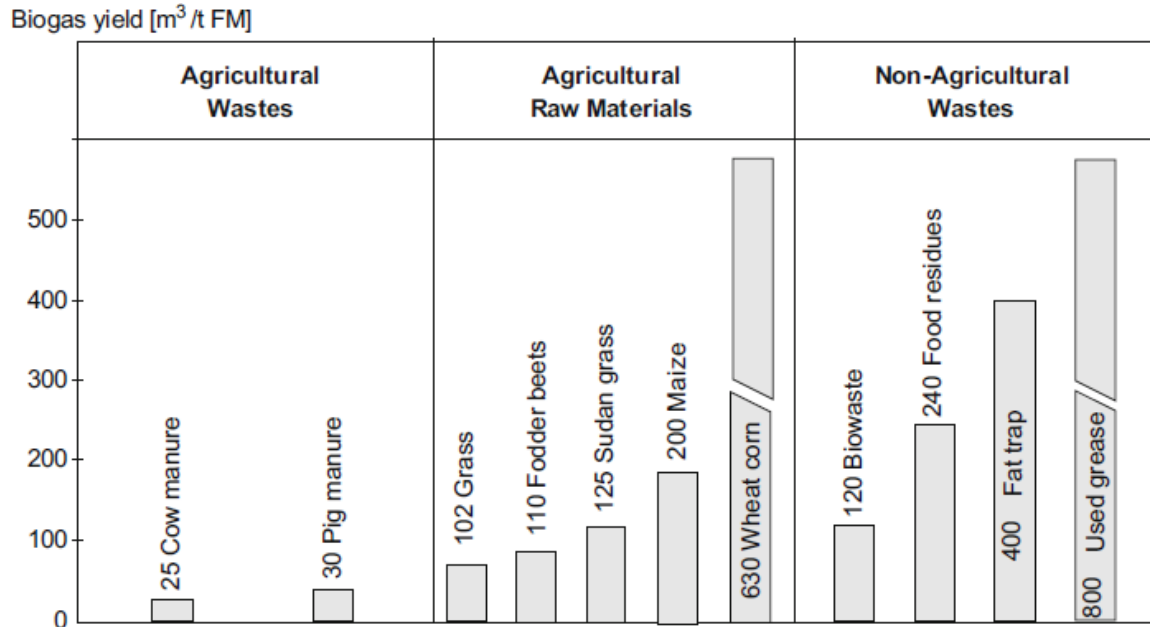


Figure 20: Methane production

Digestion process takes place at mesophilic 35-42C and thermophilic 45-60C temperature conditions it is important to keep constant temperature during digestion process, as temperature changes or fluctuations will affect the biogas production negatively. various substrate can be used

for the production of biogas as they have shown by (Weiland and biotechnology, 2010) this substrate have shown on the table below.

Table 7: Different substrate for biogas production



### 2.12.3 Biomass of biogas

There are three main types of biomass for biogas production which are (substrate from private households and municipal wastewater, substrate from farm such as liquid manure, harvest waste and feed waste, industrial byproducts from food processing of fat separators). The degradation of substrate depends on uniform pH, optimum temperature, nutrients supply and the absence of oxygen gas (Gerardi, 2003)

### 2.13 Feed stock

Feed stock is any substrate that can be converted to methane by anaerobic bacteria. The increase of environment awareness and good ways of management of waste in 1970s lead for the formation of word biogas feedstock. Various sources of feedstocks as they have been by (Steffen et al., 1998) on the table below were categorized into agriculture, community waste and industry.

## AGRICULTURE

- manure (cattle, pig, poultry)
- energy crops
- algal biomass
- harvest remains

## INDUSTRY

- food/beverage processing
- dairy
- starch industry
- sugar industry
- pharmaceutical industry
- cosmetic industry
- biochemical industry
- pulp and paper
- slaughterhouse/rendering plant
- etc...

## COMMUNITIES

- OFMSW
- MSW
- sewage sludge
- grass clippings/garden waste
- food remains
- etc...

Figure 21: Feedstocks from different sources

Feedstock from anaerobic digester contain nutrients which are essential to plant both micro and macro nutrients, also it happen containing heavy metals and organic compound which are resulted from the food of animal and from some medicine. Most of animals they do not use macro nutrient they give out as excreta and this nutrients are important for the life of animals, bacteria and plants composition of animals manure depends on the digestive system of animals, also geographical location and climatic condition of the area. Example composition of manures from different animals in UK has shown on table 8 below.

Table 8: Composition of manure from different animals in  $\text{Kgm}^{-3}$  in UK (Lukehurst et al., 2010)

Feedstock	TS %	Total N	$\text{NH}_4\text{-N}$	P	K	S	Mg
Dairy cow slurry	6	3.0	2.0	0.5	2.9	0.4	0.4
Pig slurry	4	4.0	2.5	0.9	2.1	0.4	0.2
Poultry:							
Layer manure	30	16.0	3.2	5.7	7.5	1.5	1.3
Broiler/turkey litter	60	30.0	12	10.9	15	3.3	2.5
Farmyard Manure							
Cattle	25	6.0	0.6	1.5	6.7	0.7	0.4
Pig	25	7.0	0.7	3.1	4.2	0.7	0.4

### 2.13.1 Storage of digested

For the application of digested manure as fertilizer the storage is important since manures is produced every day from animals. Storage time it varies from one country to another due to different in climatic conditions, geographical location, winter seasons, soil type, crop rotations and rules and regulation governing the application of manure. Usually the recommended time for



storage of manure is 6-9 months. Some countries have put the storage time of before applied to the farms as is shown on the table

**Table 9:** Examples national limit regulating storage time of digested amended from Nordberg 1992

	Maximum nutrient load	Required storage capacity	Compulsory season for spreading
Austria	170 kg N/ha/year	6 months	28 Feb–5 Oct
Denmark	170 kg N/ha/year (cattle) 140 kg N/ha/year (pig)	9 months	1 Feb–harvest
Italy	170–500 kg N/ha/year	90–180 days	1 Feb–1 Dec
Sweden	170 kg N/ha/year (calculated from livestock units per ha)	6–10 months	1 Feb–1 Dec
Northern Ireland	170 kg N/ha/year	4 months	1 Feb–14 Oct
Germany	170 kg N/ha/year	6 month	1 Feb–31 Oct Arable land 1 Feb–14 Nov Grassland

Source: (Holm-Nielsen et al., 2009)

For the purpose of minimizing emission of methane and ammonia gas, most storage of digestate slurries are covered by a protective layer which can be plastic a floating layer or natural crust of 10-20cm (Lukehurst et al., 2010)

### 2.13.2 Application of digestate

The machine used for the spreading of farmyard manure it can also be used for the application of raw slurry and digestate. For optimum use of fertilizer, the digestate must be applied to the farm during the growing season.



Annex 1 covered storage of digestate pig slurries farm

Annex 2 Application of digestate into farm

## 2.14 Environmental effects of using digestate as fertilizer

### 2.14.1 Odors

Manures from animals and organic waste contains volatiles organic compound like butanoic acid, iso-butanoic and valeric acid. These organic compounds are the ones that produce unpleasant smell. Proper spreading method and digestion of manures it helps to reduce the concentration of organic compound as reported by (Prapasongsa et al., 2010).

### 2.14.2 Plant pathogen reduction

Few studies have tested the effects of Anaerobic digestate on the survival of the rate of pathogen that affects the plants.(Haraldsson, 2008) Showed that the using of mesophilic digestion hydraulic retention time between 25-30days, the chance of inhibiting fungal diseases of plants is higher. Also the combination of factors for operation of digester which are temperature, time, pH level, quantities of volatiles fatty acid and hydrogen sulphide,the combination of these factors create the holistic environment for the growth of fungi spores.

## 2.15 Agricultural waste suitable for Anaerobic digestion

### 2.15.1 Pig slurry

Pig meat production global has increased in recent decades, which result to the production of large volume waste that cannot be recycled. The amount of Phosphorus and nitrogen in pig excreta is

about 70%(Perera et al., 2007).Pig farming is the major agricultural industry in the European Union now days, due to its increasement the EU has made some of regulation and rules to direct the farmers on how to use pig manure as direct fertilizer to the farms since manure from pig contained high amount of odor and organic contents which threatens the health of farmers(Karakashev et al., 2008).Also production of manure claimed to contribute the increase of greenhouse gas emission. The need of suitable and sustainable ways to control and manage pig manure for the purpose of minimizing N<sub>2</sub>O gas emission and recovering of Phosphorus and nitrogen. The best way to close the loop of N<sub>2</sub>O gas emission is to practice recycling measures from the production to utilization of different sources of wastewater as described by Anaerobic digestion of pig manure in full scale biogas plant it offers a lot of advantages such as production of renewable energy methane, recycling nutrients back to the soil, odor and pollution reducing. In order to meet the wastewater discharge effluents, treatment of pig manure it advised to be like of treating domestic wastewater. Ways of treatment that are used frequently are upflowed anaerobic sludge blanket, phosphorus removal by struvite precipitation,complet autotroph nitrogen removal over nitrite (Sliemers et al., 2002).Also in Europe production of animal manures is about 1500million tones every year( table 10)this it include manures from pigs, cattle production industry and from poultry, fish and fur all of this can be used for the production of biogas and recovering of nutrients as fertilizers.

#### 2.16 Pharmaceutics, hormones and Struvite

In convectional wastewater treatment, the removal of micro -pollutant such as hormones and Pharmaceutical is difficult since they require sophisticated technology for removing it from wastewater. (Winker et al., 2009)Showed that in source separation treatment the concentration of hormones and pharmaceutical based on urine or blackwater are present at higher concentration ( $\mu\text{g/L}$  to  $\text{mg/L}$  range) as shown on table 10 .Also for a safe use of urine as fertilizer World Health organization advises a period of more than six month of storing urine before applying as fertilizer. Hormones and pharmaceutical are considered potential danger in both aquatic and human being.Few nanograms per liter of these micro-pollutant can affect the reproductive system and imbalance I hormones for the riverine fish(Baronti et al., 2000).

Also(Clausen et al., 2001) reported that ionic and non -ionic molecules can adsorb to the surface of inorganic minerals, the need of investigating if hormones and pharmaceutical precipitate together with struvite and they can adsorb to the struvite crystals. List of Pharmaceutical and hormones at table 10

Table 10: List of Pharmaceutical and hormones

Drug	specification	study
Diclofenac	Anti-inflammatory	(de Boer et al., 2018, Ronteltap et al., 2007)
Propranolol	Betablocker	(de Boer et al., 2018)
Estradiol E2	Natural hormone	(Ronteltap et al., 2007, de Boer et al., 2018).
Ethinylestradiol EE2	Synthetic steroid oral contraceptive	(Ronteltap et al., 2007)
Estrone E1	Natural hormone	(Ronteltap et al., 2007)
Tramadol	Opioid analgesic	(Schürmann et al., 2012)
Nebivolol	Betablocker	(Schürmann et al., 2012)
Metoprolol	Betablocker	(Schürmann et al., 2012)

Drug	specification	study
Diclofenac	Anti-inflammatory	(de Boer et al., 2018, Ronteltap et al., 2007)
Propranolol	Betablocker	(de Boer et al., 2018)
Estradiol E2	Natural hormone	(Ronteltap et al., 2007, de Boer et al., 2018).
Ethinylestradiol EE2	Synthetic steroid oral contraceptive	(Ronteltap et al., 2007)
Estrone E1	Natural hormone	(Ronteltap et al., 2007)
Tramadol	Opioid analgesic	(Schürmann et al., 2012)
Nebivolol	Betablocker	(Schürmann et al., 2012)
Metoprolol	Betablocker	(Schürmann et al., 2012)

To see the if hormones and pharmaceutical they can adsorb struvite crystal (Escher et al., 2006) stimulated an average population in their study, whereby the urine collected was spiked with pharmaceutical and hormones. From table 11 it shows the results from different studies about the recovery efficiency of pharmaceutical is interpreted as the number of pharmaceuticals which are remaining in the solution after struvite precipitation. High recovery rate it indicates the clean of struvite crystals.

Table 11: Concentration and recovery efficiency of Pharmaceutical after batch Experiment with Struvite

		Unit	PO4-P	Mg	Propranolol	Ibuprofen	Diclofenac	Carbamazepine
1 <sup>a)</sup>	Initial	[mg.L-1]	255	-	19.65	37.84	54.12	63.90
	Effluent	[mg.L-1]	2	56	19.09	37.88	52.88	53.35
	Struvite	[mg.L-1]	278	241	0.15	<LOD	<LOD	0.20
	Recovery	[%]			95.3	99.2	97.1	83.0
2 <sup>a)</sup>	Initial	[mg.L-1]	255	-	19.86	36.95	54.15	53.99
	Effluent	[mg.L-1]	2	76	19.53	37.74	53.35	54.75
	Struvite	[mg.L-1]	286	214	0.15	<LOD	<LOD	0.14
	Recovery	[%]			96.6	98.7	98.0	99.8
3 <sup>b)</sup>	Initial	[mg.L-1]			0.014	2.7	0.640	0.234
	Effluent	[mg.L-1]			0.006	3.2	0.550	0.180
	Struvite							
	Recovery	[%]			58%	-7%	14%	24%
4 <sup>c)</sup>	Recovery	[%]			99.2	> 99.9	> 99.9	99.7

<sup>a)</sup>(Ronteltap et al. 2007); <sup>b)</sup>(Boer et al. 2018); <sup>c)</sup>(Escher et al. 2006)

The lowest recovery of Carbamazepine in batch 1 was likely caused by contamination (Ronteltap et al., 2007). Also difference from Escher and Ronteltap recovery rates are significant lower due different in concentration used from table 11 it is easy to recover larger quantity of higher amount than one which contain small quantity of micro- pollutant.

Also the ratio of Mg:P plays an important roles in the uptake of pharmaceutical as showed by (Kemacheevakul et al., 2014). Ronteltap used a ratio of 1.5:1 while De Boer used 1.2:1. Lower ratio have a capacity to uptake hormones and pharmaceutical due to higher potential of amorphous impurity to adsorb in the struvite (de Boer et al., 2018).

### 2.17 Heavy metals

Heavy metals are natural element and have density of at least five times than of water. Heavy metals are widely used in industries, agricultural, medical and technological application led to their distribution in the environment. Their toxicity affect environment and living organisms depending on the route, degree of exposure and chemical sources (Tchounwou et al., 2012).

Presence of trace element silver,mercury,cadmium,lead, and chromium in struvite it can increase the possibility of affecting human being, it was reported that heavy metal can substitute P,Mg and NH<sub>4</sub>.Also cadmium is important matter for the growth of plant but it has health impacts if consumed by human it results to the kidney failure, skeletal and respiratory systems to perform worse (Zamora et al., 2017b).

Pure urine from healthy person contain less concentration of heavy metals than convectional fertilizers(Ronteltap et al., 2007).Presence of heavy metals in fertilizer is undesirable in the sustainable agriculture ,since may accumulate into soil diffuse into aquatic environment and led to adverse impact on both plants and animals. (Liu et al., 2013b) did a study to investigate the concentration of heavy metals from different sources and compared with the legal limit table 12.

Table 12: Comparison of heavy metals concentration in struvite produced from various wastewater with legal limits(Liu et al., 2013b)

Heavy metal (mg kg <sup>-1</sup> )	Legal limit			Recovered struvite							
	Germany	Turkey	Queensland	Digested sludge	Digested sludge	Anaerobic digester	Anaerobic digester	Landfill leachate	Swine wastewater	Fosfomycin pharmaceutical	Potato processing
Mercury (Hg)	1	5	5	0.06	0.05	4.23	0.2	ND	ND	ND	ND
Cadmium (Cd)	1.5	ND	350	<0.4	<0.5	ND	<4	ND	0	0.12	<0.2
Nickel (Ni)	80	120	ND	<0.4	1.1	<1.29	ND	0.33	0	ND	<1.0
Copper (Cu)	70	ND	ND	1.67	1.8	ND	ND	2.11	16.06	0.30	21
Lead (Pb)	150	ND	100	<0.4	<0.5	ND	<5	ND	0	ND	<3
Chrome (Cr)	2	270	ND	0.45	8.6	<1.35	ND	ND	0	3.27	<3
Zinc (Zn)	1000	1100	ND	7.7	5.2	13	ND	20.1	81.44	0.29	<10
Arsenic (As)	ND	ND	ND	ND	ND	<0.125	ND	0.56	ND	ND	<1
References	119	40	40	120	121	28	40	24	15	122	45

### 2.18 Application of struvite in agriculture

Struvite is currently considered, recyclable, environmental friendly fertilizer because as good slow release Phosphorus-based on the small content of magnesium and ammonia, have low content of heavymetals,has less loss of N compared to urea (Doyle and Parsons, 2002).Different trials conducted based on the pot evaluation showed that MAP have good quality and efficiency on the improving growth of fruits,grasses,turf , seedling and vegetables(Münch and Barr, 2001).

MAP has been found to good effective slow release fertilizer source of N,P and Mg. The behavior of MAP on slow release made it to be advantageous when highly soluble fertilizer are undesirable to some environmental conditions like grassland,coastal agriculture and forests.Also MAP can be applied frequent into plants since it has no burning effects to the roots of plants(Nelson et al., 2000).

### 3.0 Hypothesis, Goals and objectives

Struvite removal and recovery from anaerobic digested blackwater from Kaja precipitation with struvite from seawater and magnesium chloride is important for the protection of environmental and increasing soil fertility by adding slow struvite as fertilizer into soil. The main goal of this Thesis is to compare removal efficiency of Phosphorous from wastewater by using struvite precipitation with seawater and Magnesium chloride. In order to investigate this goal, the objectives that should be considered and developed fall into following parts.

Study the effects of type of magnesium source and its mixing ratio on the removal of P from both digested blackwater digestate wastewater from anaerobic reactor.

**Hypothesis:** Addition of Mg source is an important factor on the removal efficiency of |P. The use of ratio of struvite Mg :P 1.3:1 and 1:1 led to about 90% and 80 of P removal respectively.

Study the effect of pH on the removal efficiency of P

**Hypothesis:** Maintain of pH to pH 9 increase removal efficiency and reduce the cost of sodium hydroxide for pH adjustment

Study different technology available for the removal and recovery of P

## 4.0 MATERIALS AND METHODS

Different sources of information were used but most scientific journals were used since they are currently updated compared to books. This chapter give an overview of different reagents and chemicals used for the laboratory experiment.

### 4.1 Wastewater sample collection

#### 4.1.1 Digested black water from Kaja

500ml of digested blackwater were taken from the anaerobic biogas reactor found at Realtek laboratory NMBU and stored at room of 4C temperature.

### 4.2 Magnesium sources

#### 4.2.1 Seawater

Seawater was collected into 7lites plastic bottle at 9<sup>th</sup> April,2019 in Drøbak Norway the eastern shore of Oslo Fjord. Sample were stored in REALTEK laboratory fridge since there were no any visible turbidity during the sampling. Whatman glass microfibre GF/C filter of pore size 1.2  $\mu\text{m}$  with pressure filtration were used for filtration of sample in order to remove the unwanted suspended particle since unwanted particles can alter the reaction. Sample were taken to REALTEK lab for the analysis of Total P, N and PH of sea water.

#### 4.2.2 Magnesium chloride

Magnesium chloride powdered were used as source of Magnesium because it has the good capacity to precipitate struvite, easy to handle, short reaction rate and availability.  $\text{MgCl}_2$  solution was prepared dissolving 40grams of  $\text{MgCl}_2$  into 100ml of deionized water to form 2molar of  $\text{MgCl}_2$  solution.

### 4.3 Adjustment of pH

The value of pH is an important factor for struvite precipitation, the adjustment of pH were done by adding few drops sodium hydroxide solution. Struvite precipitation occurs at pH range of 8 to 9 (Le Corre *et al.*, 2009)also wastewater pH is valid due to poor buffer capacity and low concentration of ammonium compared to urine(Zamora *et al.*, 2017a).The pH were measured by using portable pH 20 VWR electrode were pH meter calibrated by measuring the pH on a pH 7 buffer at a room temperature .Also the pH meter were rinsed in tap water and dried by a paper tissue and placed in 3M Potassium chloride solution. The initial pH value of Kaja wastewater was



pH 7.4 the adjustment of pH was done by adding few drops of 2M NaOH and reached to pH 8.5 and 9 which are favorable for struvite precipitation.

#### 4.5 Mixing

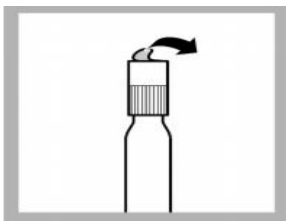
Speed of stirring need to be slow because it can limit the crystal growth and lead scaling on the walls of the reactor(Wilsenach et al., 2007).Magnetic stirrer was used to ensure that wastewater and source of magnesium they are mixed well for this experiment stirring was done at 300rpm for three minutes and lowered to 2minutes.The mixing time of sea water was limited to 10minutes before the filtration process started. Stirring is vital for struvite precipitation since it enhance the pH caused by carbon dioxide stripping and it increase the removal efficiency from 72.2% without stirring to 97.3% with mixing (Liu et al., 2013a).

#### 4.6 Chemical analysis

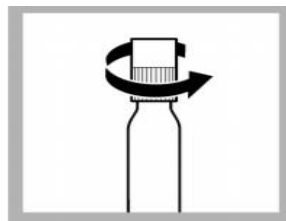
##### 4.6.1 Sample treatment

##### 4.6.2 Sample preparation for Total Phosphorous

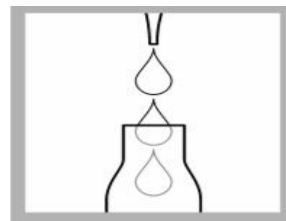
All samples for Total P was done according to LCK350 method as it shown on the figure. Whereby for total P all the procedures from 1to 14 were followed. Finally, the sample were placed into a Hach Lange 3900 DR for N and Total P and Phosphate for reading values.



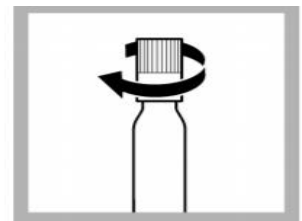
1. Carefully remove the foil from the screwed-on DosiCap Zip.



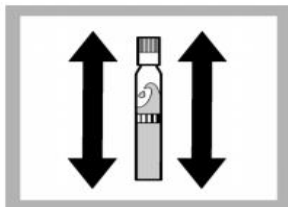
2. Unscrew the DosiCap Zip.



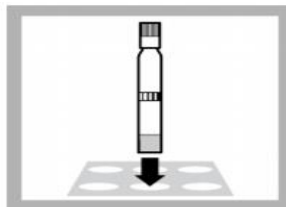
3. Carefully pipet 0.4 mL of sample.



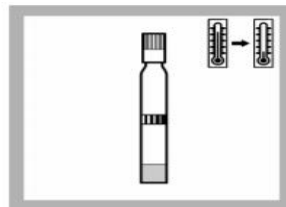
4. Immediately screw the DosiCap Zip back on tight; fluting at the top.



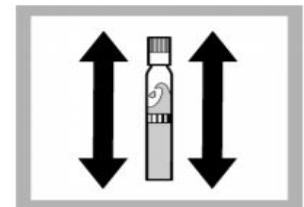
5. Shake vigorously.



6. Heat in the thermostat. **HT 200 S:** in the standard program HT for 15 minutes. **Thermostat:** for 60 minutes at 100° C (212° F) or for 30 minutes at 120° C (248° F).



7. Allow to cool to room temperature. **NOTE: Check if the cap is still tight after cooling.**



8. Shake vigorously.

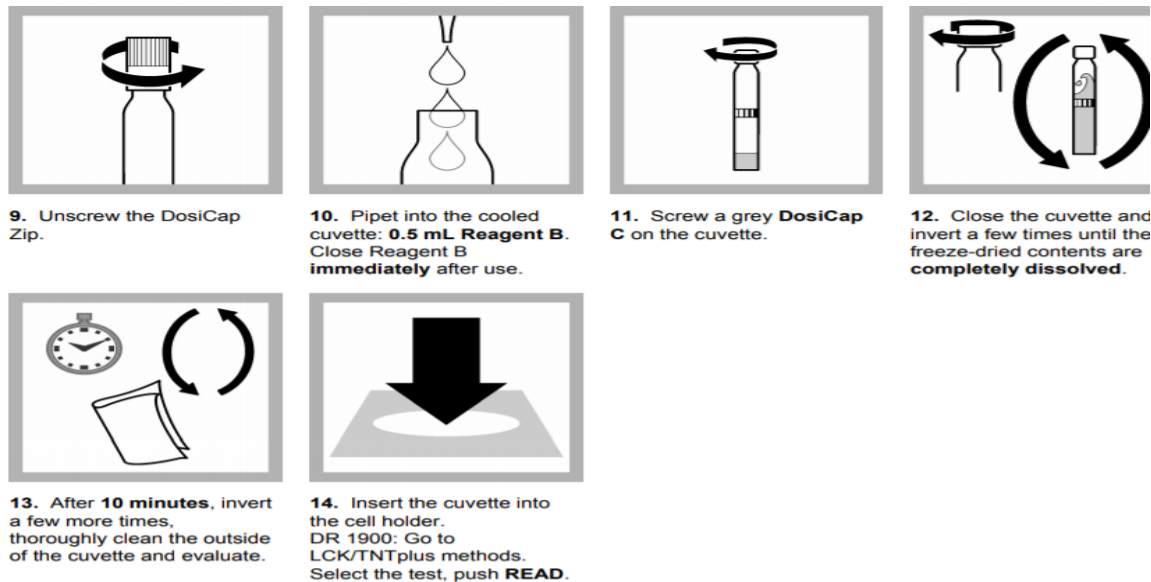


Figure 22 Total P procedures according to LCK 350 method

*Phosphate*

Sample for Phosphate were prepared by taking procedure from 1-5

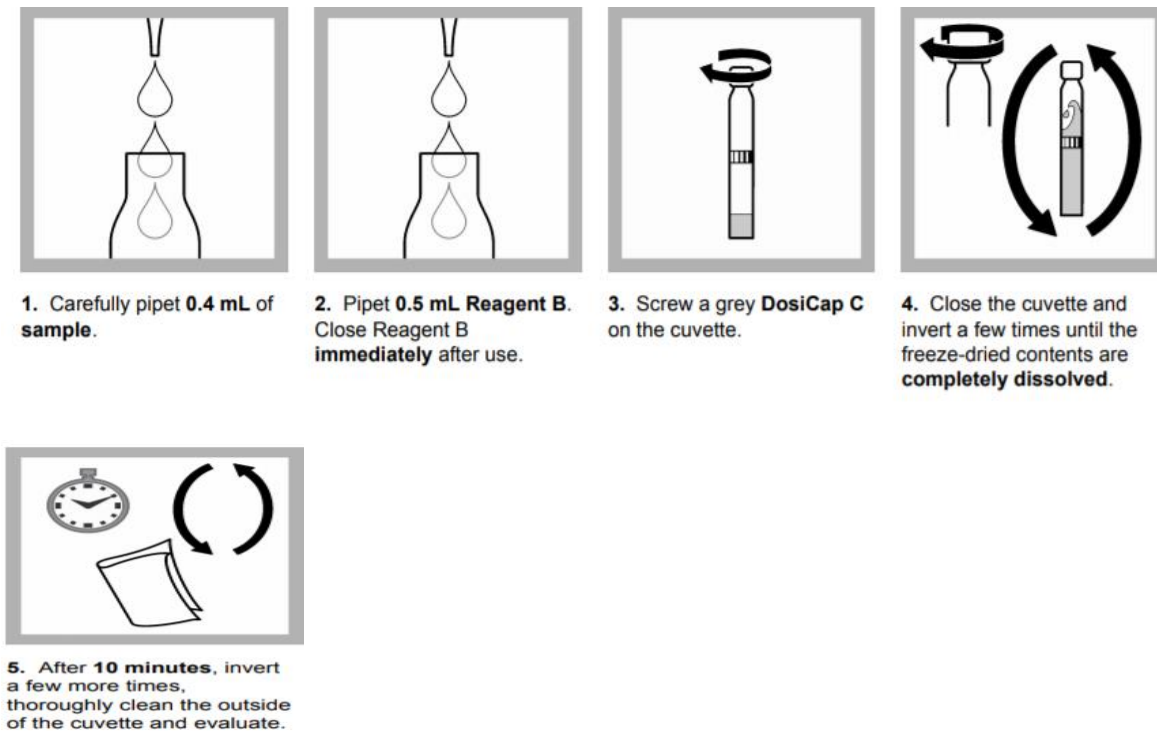


Figure 23 Phosphate Sample preparation according to LCK 350 method.

#### 4.7 Design of experiment

According to the theory and hypothesis, maximum P removal should occur under the conditions which are shown on Table 11. For the better removal efficiency the value of PO<sub>4</sub> was kept constant while value of Mg is changed as in ratio 1 : 1 and 1.3 : 1 of Mg : PO<sub>4</sub> respectively. The experiment carried out at constant pH 9 and Mixing time.

Table 13: Conditions for struvite precipitation

Mixing ratio	Digested black water from Kaja	Seawater	MgCl <sub>2</sub>	pH	Mixing time
1 : 1	25ml	25ml	25ml	9 and 8.5	10
1.3 : 1	25ml	32.5ml	32.5ml	9 and 8.5	10

Table 14: Characteristics of pretreated Digested blackwater

Parameters	Digested anaerobic blackwater
pH	7.4
Total Phosphorous mg-l	112.0
PO <sub>4</sub> -P mg-l	101.0
NH <sub>4</sub> -N mg-l	1230.0

#### 4.8 Removal efficiency

The removal efficiency for both total P and PO<sub>4</sub>-P was calculated by the following

$$\% \text{ Removal efficiency} = [C_i - C_e] / C_i * 100$$

where:

C<sub>i</sub> = initial concentration in mg/l

C<sub>e</sub> = effluent concentration after treatment with seawater or MgCl<sub>2</sub> in mg/l

## 5.0 RESULTS AND DISCUSSION

In this chapter, the key findings of the experiment on the removal of phosphorous, influence of pH, the crystallization reaction formula, influence of Mg source, total phosphorous removal and NH<sub>4</sub>-N removal are presented.

### 5.1 Removal of Phosphorous

Table 15: Results removal of Phosphorous by using seawater and MgCl<sub>2</sub> at pH

Magnesium source	pH	Total P-mg/L	Total P% removal	PO <sub>4</sub> -P mg/L	PO <sub>4</sub> -P % removal	NH <sub>4</sub> -N mg/L	NH <sub>4</sub> -N% removal
<b>Seawater</b>							
<b>1:1</b>	8.5	8.1	92	1.43	98.6	631	48.7
	9.0	4.9	95.6	1.00	99.0	559	54.6
<b>Seawater</b>							
<b>1.3:1</b>	8.5	4.7	95.8	1.60	98.4	451	63.3
	9.0	4.1	96.3	1.20	98.8	487	60.4
<b>MgCl<sub>2</sub></b>							
<b>1:1</b>	8.5	4.2	96.3	4.90	95.1	618	49.8
	9.0	0.7	99.4	2.40	97.7	546	55.6
<b>MgCl<sub>2</sub></b>							
<b>1.3:1</b>	8.5	5.0	95.6	4.20	95.9	625	49.2
	9.0	0.3	99.7	3.10	97	455	63.0

Source: Own Data 2019

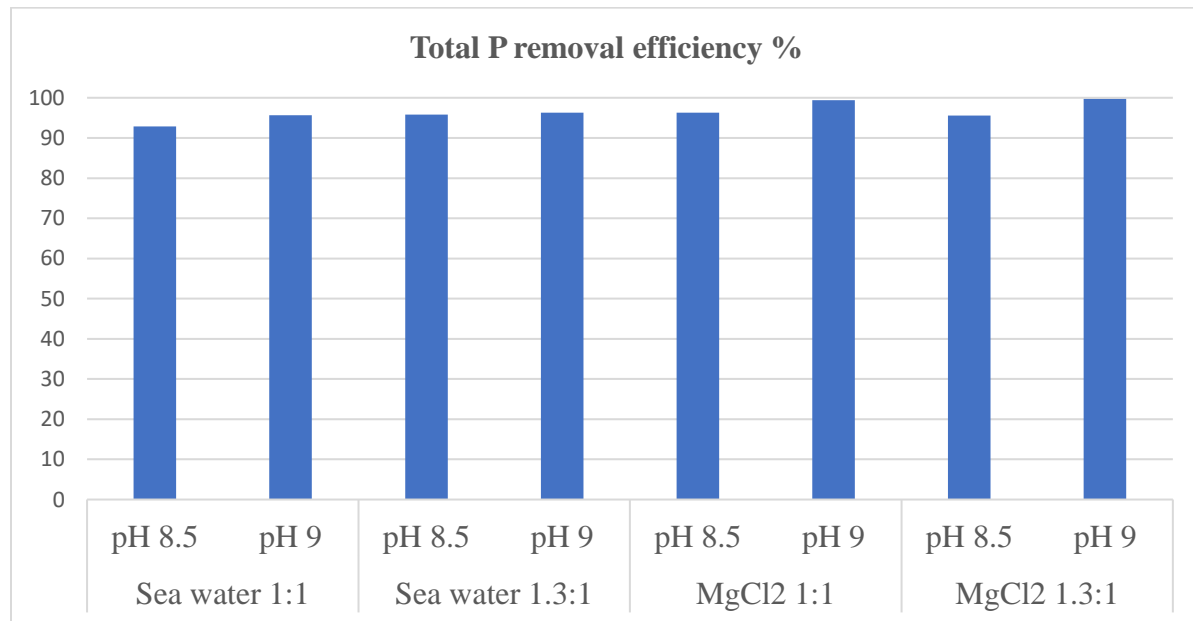


Figure 24: Removal of total Phosphorous

## 5.2 Influence of pH

The value of pH is most important factors controlling the crystallization formation of struvite. All the experiments were performed at pH 8.5 and pH 9 while the molar ratio were 1 :1 and 1.3 :1 of Mg :N : P. High removal efficiency for both total P, Phosphate and NH<sub>4</sub>-N were found at high pH of 9 .

The crystallization reaction formula

The concentration of ions participating in the reaction most of time vary with the condition of solution, especially with pH value. When the ionic activity products of MAP components it exceeds the solubility product of MAP, it enhances the reaction of precipitation to occur. The value of pH is very important for the crystallization of struvite.



In this study results obtained showed that the removal efficiency was above 90% for all total P and PO<sub>4</sub>-P except for NH<sub>4</sub>-N this due to the ammonia stripping effect whereby some amount of ammonia gas escaped this was noticed by pungent smell of ammonia during stirring of samples. Also the recommended value of pH for high removal efficiency was at range since the pH value above pH10 can result to the decrease of removal efficiency because at high pH value magnesium hydroxide has a tendency to reduce the Mg<sup>2+</sup> available for MAP crystallization, and NH<sub>4</sub><sup>+</sup> may converted to ammonia gas which is difficult to be removed by MAP crystallization. On the previous study the pH used was at range of 9 to10.5 and the removal efficiency was 93%(Song et al., 2007).

## 5.3 Influence of Mg

To understand the effect of molar ratio on the Crystallization formation of struvite the molar ratio of Mg : P of 1.3 :1 and 1 :1 were adopted digestate black water in Fig19.It shows that the P and PO<sub>4</sub> removal efficiency increase with an increase of Mg : P at both pH 8.5 and pH of 9.The increase of concentration of Mg<sup>2+</sup>,NH<sub>4</sub><sup>+</sup> it increase the crystallization efficiency of MAP.

At high mixing ratio of Mg : P of 1.3 :1 in this study the removal efficiency was above 92% in both total P and PO<sub>4</sub>-P. however seawater has shown high removal efficiency compared to MgCl<sub>2</sub>, This means that sea water can be used as alternative source struvite to the place which are located near the ocean but its challenge is on transportation cost if the wastewater treatment plant is far. Also on the study done by (Shin and Lee, 1998) showed that removal efficiency of P was 95% and 97% respectively of both MgCl<sub>2</sub> and seawater. At mixing ratio of 1:1 removal efficiency was also above 92% in this study. in the study done by (Rahman et al., 2011) found that 93% of P was removed at the ratio of 1:1 which is the same as in this study. Since hypothesis was to achieve removal efficiency higher than 90% with an increase of the molar ratio.

#### 5.4 Total Phosphate

Removal efficiency is the same almost for both ortho phosphate and total P and it was above 92% removal in this study for both ortho and total P as shown in fig 24 and fig 25. The increasing of Mg<sup>2+</sup> concentration is significant for achieving higher removal efficiency.

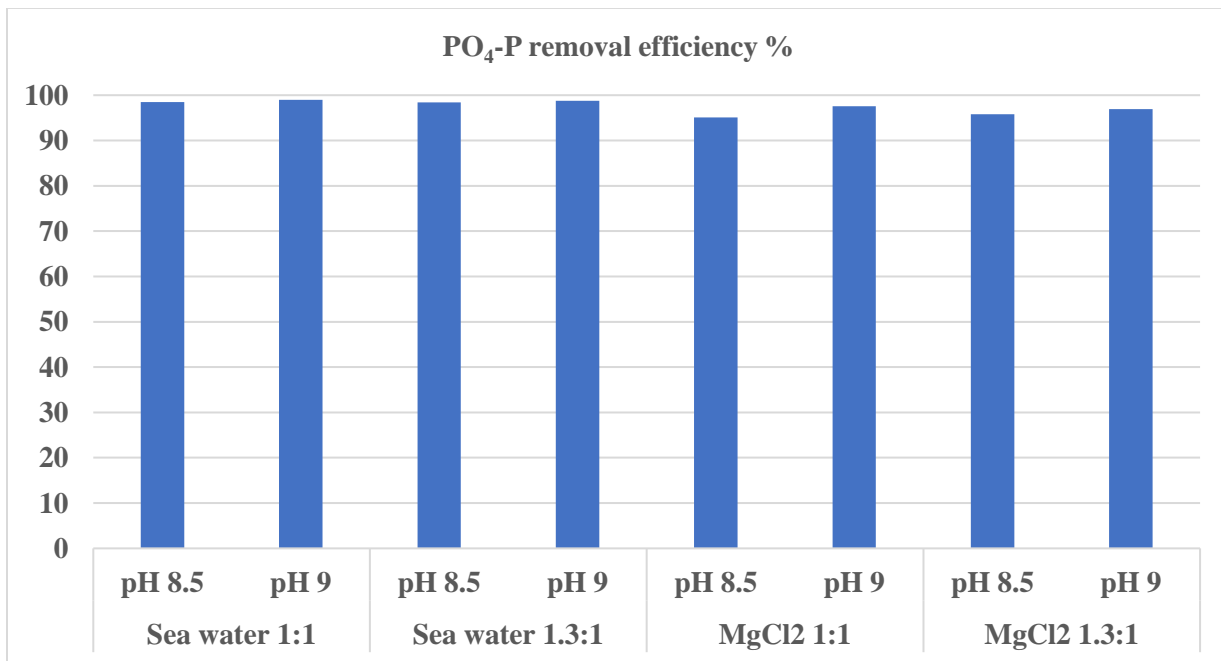


Figure 25: *Phosphate removal*

#### 5.5 NH<sub>4</sub>-N removal

Maximum removal efficiency for NH<sub>4</sub>-N in this study was 63% as shown at figure 23 at seawater with mixing ratio of 1.3:1 and the lowest was 48.69% with mixing ratio of 1:1 with seawater. While by using MgCl<sub>2</sub> the removal efficiency was 63% as highest and lowest was 48% at mixing

ratio of 1.3: 1 and 1: 1 and pH 9 and 8.5 respectively. The lowest removal efficiency is likely due to Ammonia stripping during the stirrings process. However also(Kim et al., 2007) found that removal efficiency of NH<sub>4</sub>-N from blackwater was below 50% by using both seawater and MgCl<sub>2</sub>.On the study done by Linda 2018 by using urine as source of wastewater found removal efficiency by using seawater 83% and 70% by using MgCl<sub>2</sub>.

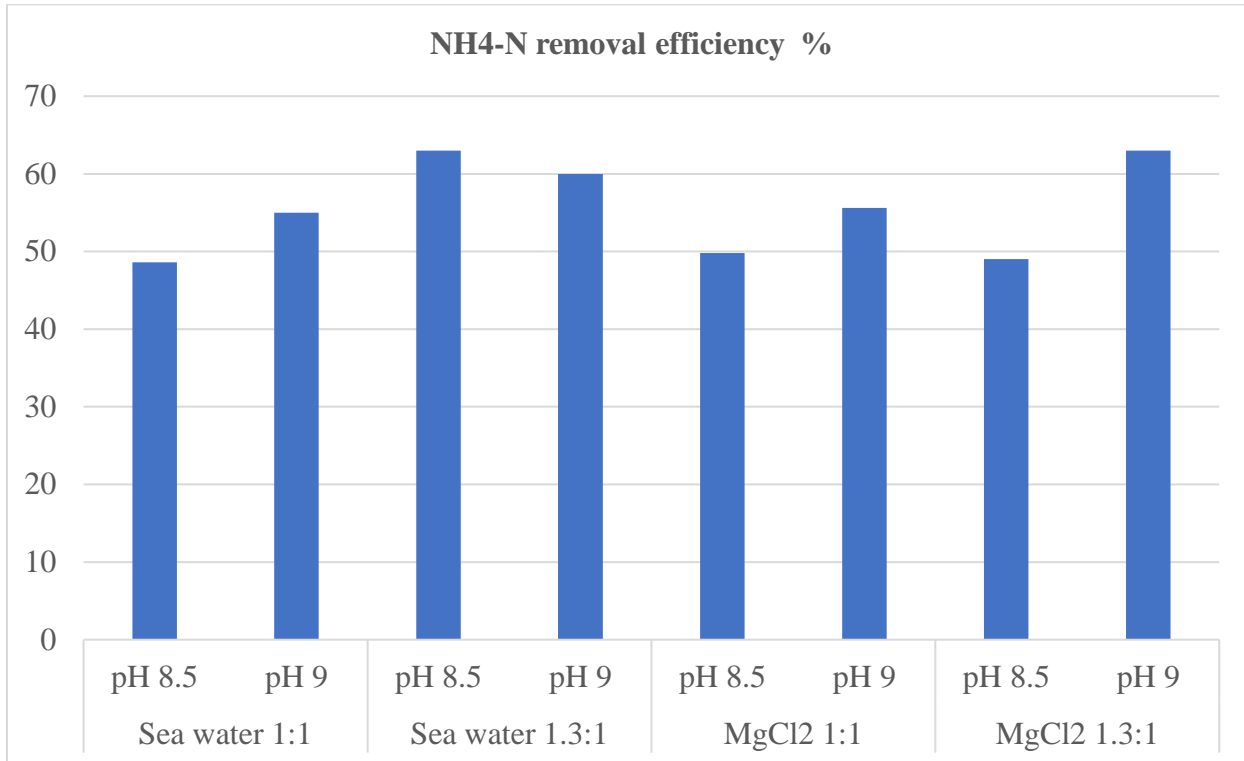


Figure 26 Removal of NH<sub>4</sub>-N

## 6.0 CONCLUSION

Increase of pH it increases the removal efficiency for all nutrients

Increase of Mixing ratio it increases the removal efficiency of total P, PO<sub>4</sub>-P and NH<sub>4</sub>-N

Further study should be done on the studying on the determination of precipitated

Struvite precipitation with both seawater and MgCl<sub>2</sub> showed better results for the removal of

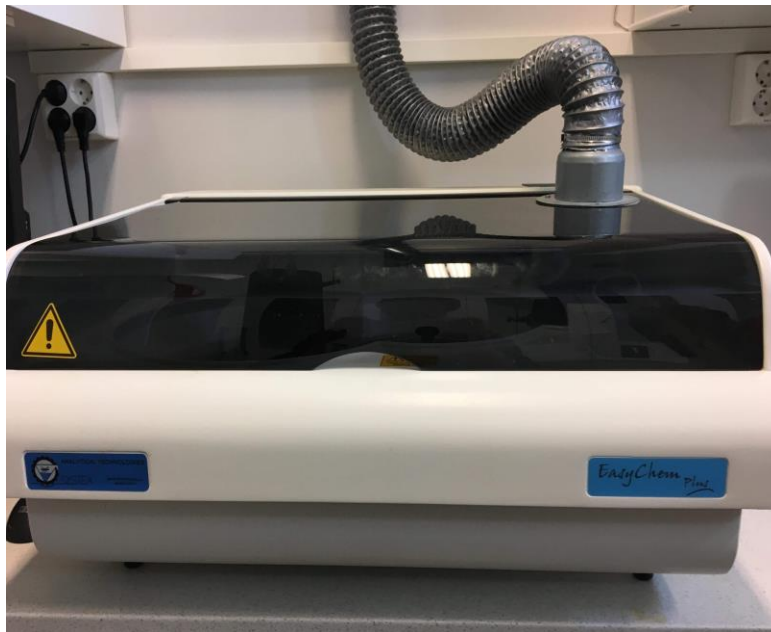
Total P and Orthophosphate this could be a better way to protect the aquatic living organism

and minimizing the pollution of water sources due eutrophication.



## 7.0 APPENDICES

### Appendix 1: Laboratory Activities



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