RECOVERY OF PHOSPHATE FROM LIVESTOCK/AQUEOUS WASTEWATER USING STRUVITE CRYSTALLIZATION

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A project report submitted in partial fulfilment of the
requirements for the award of Bachelor of Engineering
(Hons.) Chemical Engineering

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DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

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APPROVAL FOR SUBMISSION

I certify that this project report entitled **"RECOVERY OF PHOSPHATE FROM LIVESTOCK / AQUEOUS WASTEWATER USING STRUVITE CRYSTALLIZATION"** was prepared by **FOO JIA QI** has met the required standard for submission in partial fulfilment of the requirements for the award of Bachelor of Engineering (Hons.) Chemical Engineering at Universiti Tunku Abdul Rahman.

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ABSTRACT

Phosphate (PO_4^{3-}) from intensively discharge of livestock wastewater to water bodies leads to various environmental problems especially eutrophication. Besides, phosphate rock which is mainly used for plant fertilizer is a non-renewable resource which is depleting in the next century. It is thus important to seek for a technology that is not only able to effectively remove phosphate but also recover it from the wastewater discharged. Struvite crystallization is one of the methods to recycle phosphate from wastewater into a crystallize product, namely magnesium ammonium phosphate (known as struvite). It is a slow release fertilizer that can be effectively taken up by plant, thereby reducing the phosphate from mining. In order to achieve optimum phosphate recovery via struvite crystallization, it is important to study the effects of the major parameters that give significant impacts on the process, including pH, Mg: P molar ratio and precipitation time. Synthetic livestock wastewater as pure system was applied to investigate the effects of these parameters. Eventually, the optimum parameter conditions would be applied to the actual livestock wastewater to evaluate the feasibility of struvite crystallization in practical condition. Furthermore, kinetics study and solids analysis were carried out to determine the crystal growth rate and impact of parameters on solid crystals. The results showed that the phosphate recovery efficiency of struvite crystallization was excellence at alkaline condition of pH 10. With higher molar concentration of Mg^{2+} provided, the solution reached supersaturation state and achieved higher phosphate recovery efficiency. It was found that the precipitation time of 60 minutes was required to reach equilibrium. In terms of maximum phosphate recovery, the efficiency in synthetic wastewater was 84.18 %, as opposed to actual livestock wastewater which was only 47.62 %. Solids analysis showed that co-precipitation might occur, which influenced the struvite formation. However, the feasibility study confirmed that struvite crystallization was considered as promising technologies for phosphate recovery for livestock wastewater from the perspective of economics and green chemistry.

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GDP	Gross Domestic Profit
COD	Chemical Oxygen Demand
EBPR	Enhanced Biological Phosphates Removal
PAO	Phosphorus Accumulating Organisms
K_{sp}	Constant Solubility of Product
K_{so}	Activity Solubility of Product
a_i	Activity of the i^{th} Ion
I	Ionic Strength
γ_i	Activity Coefficient of Ionic Specie i
C_i	Total Concentration of respective i
Ω	Supersaturation Ratio
ΔC	Concentration Driving Force
SI	Saturation State of Struvite Crystallization
IAP	Ionic Activity Product of Struvite
t	Crystallisation Time, min
C	PO_4^{3-} at any time, t
C_{eq}	PO_4^{3-} at Equilibrium
C_0	Initial $[PO_4^{3-}]$ at Time zero, (t = 0)
k	Reaction Rate Constant
XRD	X-ray diffractometer
SEM	Scanning Electron Microscope
EDX	Energy-dispersive X-ray Spectroscopy
$C_{initial}$	Initial Ion Concentration
C_{final}	Final Ion Concentration
$M_{initial}$	Initial Ion Concentration, mol/L
M_{final}	Final Ion Concentration, mol/L
$MW_{struvite}$	Molar Weight of Struvite, 245.41 g/mol
P	Phosphorus
PO_4^{3-}	Phosphate
Mg^{2+}	Magnesium
N	Nitrogen

NH_4^+	Ammonium
Ca^{2+}	Calcium
Zn^{2+}	Zinc
Cu^{2+}	Copper
Cl^-	Chloride
CBA	Cost-Benefit Analysis

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Livestock industry is one of the pillar industries in the Malaysia’s agricultural development. In 2017, Malaysia livestock industry contributed 11.4 % of 8.2 % of Malaysia gross domestic profit (GDP), which was about 10.94 Billion Malaysia Ringgit (Department of Statistics, 2015), thence it becomes an indispensable sector in country economic. Besides , it supports the country food demand and reduces the meat import quantity from other countries (Mohammad Nor and Rosali, 2015). Therefore, livestock industry in Malaysia has been progressively developing in the recent years.

The development of livestock industry leads to annual demand increase in terms of livestock population. As a result, heavily contaminated wastewater produced from livestock farming is also intensivelly increased. This type of contaminated wastewater is mostly characterized by high suspended solids, high COD and BOD, nitrogen, and also phosphate (Ghani and Mahmood, 2011). If the livestock wastewater is not treated properly, excessive input of phosphate into the surface water will lead to eutrophication. Eutrophication is a process where the water source body becomes exteremely nutrient rich, eventually algae bloom occurs. This will induce undesirable and harmful disturbances toward the organisms that are existing in the water bodies. According to the study on the Status of Eutrophication of Lakes in Malaysia by National Hydraulic Research Institute of Malaysia (NAHRIM), there were about 56 over 96 of lakes and reservoirs evaluated were eutrophic in Malaysia (Sharip and Zulkifli, 2007). Also, numerous amount of phosphates that could be reused had lost and wasted during wastewater discharge. Thence, it is extremely important to determine a sustainable way to control the phosphate level in the discharged livestock wastewater.

In organic chemistry, phosphate is a type of ester of phosphoric acid, while it is a type of salt of phosphoric acid with chemical formula $[\mathrm{PO_4^{3-}}]$ in inorganic chemistry. Phosphate can be widely found in phosphate minerals. It represents the main source of phosphorus (P). In fact, phosphorus is a non-renewable, non-recyclable and considerably valuable resource (Zhang, Jiang and Deng, 2017). It is energy currency for the organisms at cell level, while it has the ability to control the biological productivity (Le Corre et al., 2009). For these reasons, phosphorus becomes one of the most important nutrient for sustainable crop grow. This is the reason why phosphate is always served as high nutritional fertilizer. As the demand of fertilizer increases gradually, it is predicted that the phosphorus can only last for about 125 years, and consequently global scarce of phosphorus is one of the most difficult challenges in the 21st century (Zhang et al., 2014). These are the reasons why the phosphate pollution control with recovery system in livestock wastewater treatment is essientally important.

In fact, numerous phosphate recovery technologies have been studied and developed. For instances, enhanced biological phosphates removal (EBPR), chemical precipitation, electrochemical and struvite crystallization. EBPR method removes phosphorus by utilizing the polyphosphate organisms to grip the phosphorus in their own cell but this method has difficulty on incubating the pure organisms (Zhang, Jiang and Deng, 2017). Chemical precipitation method always requires high cost chemicals and produces huge amount of chemical sludge (Zhang, Jiang and Deng, 2017). Electrochemical method can only be applied in handling small wastewater treatments and requires long-term electrode maintenance cost (Bektaş et al., 2004).

Struvite crystallization, in turn, is a more efficient and more economical way to remove and recover phosphate simultaneously from livestock wastewater. Struvite is a crystalline substance which consists of phosphate ($\mathrm{PO_4^{-3}}$), ammonium ($\mathrm{NH_4^+}$) and magnesium ($\mathrm{Mg^{2+}}$). As long as molar ratio of each component is in an equal molar ratio of 1: 1: 1 ($\mathrm{P{:}\,N{:}\,Mg}$), the struvite crystal begins to form (Zhang et al., 2014). In short, struvite crystallization process removes the phosphate in the livestock wastewater by combining phosphate along with ammonium and magnesium to form the struvite crystal. Usually, magnesium will be added into the livestock wastewater during the process in order to acheive equal molar ratio. This is because common livestock wastewater is rich in ammonium and phosphate but absence of magnesium. Eventually, collected struvite which consist of high nutrient level becomes a valuable ingredient for the fertiliser.

Due to the nutrient value of struvite, struvite crystallization has gained big interest as a choice for phosphate recovery over the past few decades. Several studies regarding the struvite crystallization efficiency on phosphate recovery have been conducted. Prior to the determination of the optimum conditions for the operating parameters, understanding of the mechanism of struvite crystallization is necessary.

The process of struvite crystallization is basically governed by supersaturation, while the level of supersaturation can be affected by various parameters (Ali and Rajshahi, 2005). One of the reviews conducted by Le Corre et al. (2009) has demonstrated that few parameters including pH, Mg: P ratio, supersaturation ratio, presence of foreign ions, temperatures as well as turbulence and mixing energy were related to the efficiency of struvite crystallization, and this finding was further confirmed by Fang et al. (2016).

1.2 Importance of the Study

This study will be very useful for the further assessment of struvite crystallization in recovering phosphate from the livestock wastewater. Based on this study, modifications and improvements can be made in order to enhance the efficiency of struvite crystallization. This study might also inspire the interest in different wastewater industries to further examine and start using this phosphate recovery technology.

1.3 Problem Statement

Contaminated wastewater along with excessive phosphate produced from livestock industry has become a major issue for the Malaysia farmers due to intensive livestock farming. Excessive phosphate causes eutrophication in surface water bodies. Toxicity caused by eutrophication devastates the aquatic life present in the contaminated surface water. In addition, excessive nutrients with phosphates also cause soil acidification, further results in burning of roots and eventually death of plants. Moreover, the water taken in Malaysia is mostly from surface water, and therefore improper treatment of livestock wastewater gives unpredicatable impact on human health. Last but not least, non-renewable phosphate is running out gradually.

Recovery of phophate from livestock wastwater using struvite crystallization is a promising technique. The key valuable feature of this technique is the combination of removal and recovery of phosphate. In short, this technique not only removes the phosphate as what others can do, meanwhile it can also recover the phosphate in the form of struvite as a useful fertilizer.

In order to duel with intensive amounts of livestock wastewater, the efficiency in recovering the phosphate by struvite crystallization is crucial. Recovery efficiency depends on operating conditions as well as process parameters. Also, it is much important to evaluate the feasibility of using the struvite crystallization in the livestock wastewater treatment.

1.4 Aim and Objectives

The main aim of this project study was to apply the struvite crystallization technique in recovering the phosphate from the livestock wastewater.

The main objectives of this study are listed as follows:

1. To determine the best conditions to maximize phosphate recovery efficiency.
2. To examine the kinetics of struvite crystallization.
3. To analyse the effects of parameters on the final product characteristics.
4. To evaluate the feasibility of the struvite crystallization on recovering the phosphate from nutrient rich wastewater in livestock industry.

1.5 Scope and Limitations of the Study

Based on the aim and objectives, the scope of this study was to assess the effects of different important parameters on the struvite crystallization to recover phosphate. This is of interest because the studies of each important parameter are crucial for maximizing the struvite crystallization efficiency. The further study regarding the crystal growth kinetics was also carried out. Both synthetic and actual livestock wastewater were used for simulating the ideal and real condition in order to determine the feasibility of this technique in practical condition.

Several limitations in this study are listed in below:

1. Only measurement of phosphate concentration was conducted in this study, while the concentration of ammonium and magnesium were assumed based on specified molar ratio (P: N: Mg) due to resource limitation..
2. The results of this study might not able be transmissible to the other types of wastewater.
3. The time duration given for this study was limited. Therefore, it was not enough time to perform additional studies and only limited number of experiments were performed.

1.6 Contribution of the Study

This study focused on the best conditions to achieve maximum phosphate recovery in the wastewater treatment process. It also aimed to promote the application of struvite crystallization in wastewater treatment sector, apart from other phosphate removal technologies for instance Enhanced Biological Phosphate Removal (EBPR), Electrochemical and Chemical Precipitation etc.

1.7 Outline of the Report

Chapter 1 involves the general introduction and information that relevant to the study. The body of the report consists by Chapter 2, 3 and 4. The important literature studies such as the general background of livestock industries, current existing phosphate removal technologies, mechanism of struvite crystallization and the significant parameters for crystallization process are included in Chapter 2. Chapter 3 demonstrates the detailed methodology for carrying out the experiments. Then, the results obtained from experiments are displayed in Chapter 4, as well as discussions are made for result analyzation. Eventually, conclusion and recommendation of the study are completed in Chapter 5.

CHAPTER 2

LITERATURE REVIEW

2.1 Livestock Industry Overview in Malaysia

Livestock industry in Malaysia plays an important role in the country’s agriculture development. It provides huge amount of employments, supplies different domestic products such as meat, milk and dairy basic products to the society, that is the reason why livestock industry is known as ‘fundamental industry’. Also, it contributes adequate earning to households through sales of livestock products and provides raw material for agro industries. Development of this industry ensures the food requirement in the country and also lower the dependency on import products. Basically, livestock industry in Malaysia consists of ruminants as well as non-ruminants. Ruminant sector mainly involves dairy buffaloes, cattle, goats and sheep. In turn, non-ruminant sector consists majorly of poultry (broilers and eggs) as well as swine (Mohammad Nor and Rosali, 2015). Table 2.1 shows the populations of each livestock type in Malaysia from 2014 to 2018. As shown in Table 2.1, ruminant sector tended to slightly decrease in terms of livestock population since 2014.

Table 2.1: Livestock Population for Various Sectors in Malaysia from 2014 to 2018 (Department of Veterinary Services Malaysia, 2016)

Livestock Types	**2014**	**2015**	**2016**	**2017**	**2018**
Buffalo	121,259	118,569	119,133	114,013	114,321
Cattle	746,783	742,338	737,827	703,832	710,481
Goat	429,398	431,651	416,529	385,304	399,045
Sheep	142,435	147,033	138,479	130,658	129,994
Swine	1,844,103	2,286,823	1,654,381	1,849,351	1842,428
Poultry	288,304,256	286,620,834	289,666,002	293,301,558	311,978,594

Few factors may affect the trend such as lack of land resources, cheaper import substitutes, high feed pricing, lack of quality breeds, and etc (Mohamed, 2007). In contrast, swine and poultry as non-ruminant show potential rising trend in recent years, especially the poultry gained 3.6 million of population from 2016 to 2017, due to the well development of production capacity like farm, and also technologies. This enables Malaysia to continue to be self-sufficient in terms of poultry meat and eggs since 1990s (Mohamed, 2007). Overall, the entire population statistics show growing trend over the five years.

Figure 2.1 indicates the total consumption of various livestock products in Malaysia from 2012 to 2018. Nevertheless, yearly consumption for every livestock over the past seven years experienced some fluctuates; but in overall, consumption trend for every livestock product was gradually rising within the seven years. These might be due to the fact that Malaysia is experiencing human population growth and rapid economy development, leading to a rise in the demand-driven consumption of livestock products since these are the most important animal protein sources (Mohammad Nor and Rosali, 2015).

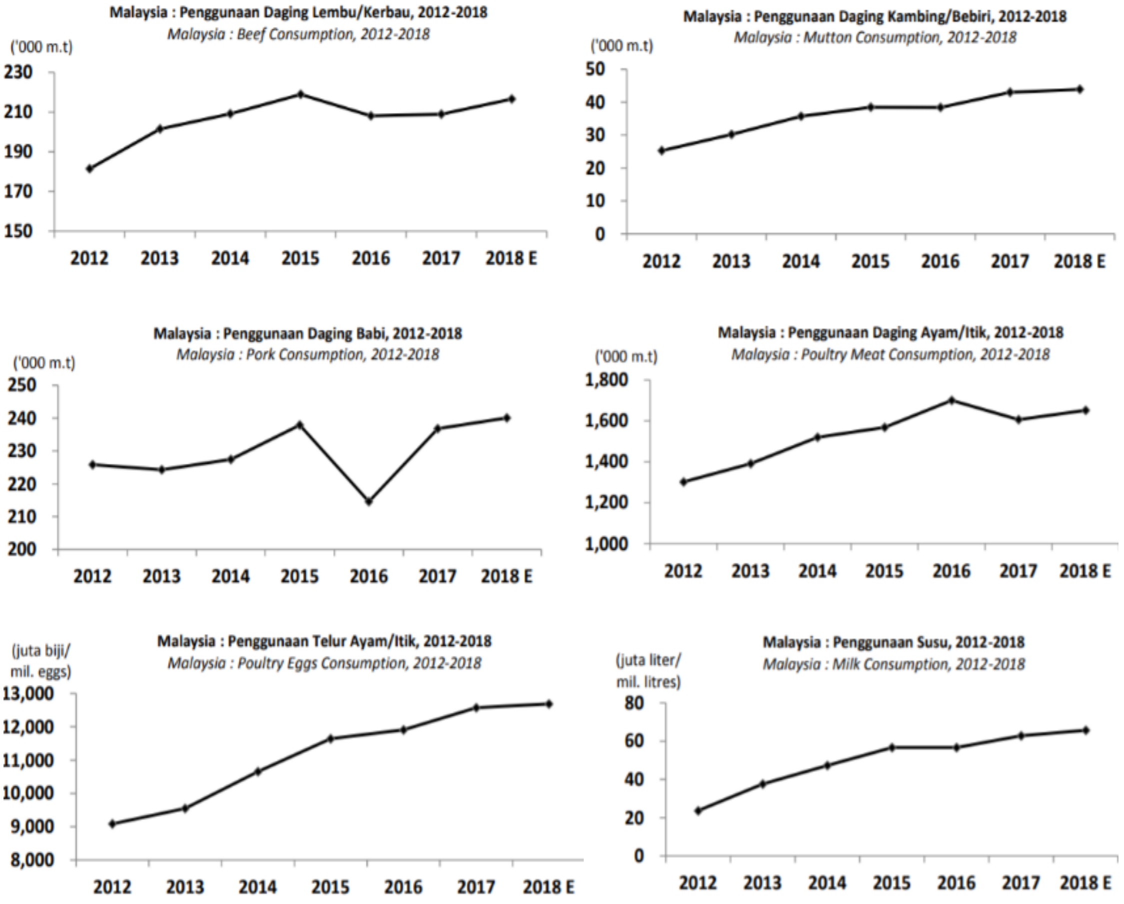


Figure 2.1: Consumption Trend for Different Livestock Products in Malaysia from 2012-2018 year (Department of Veterinary Services Malaysia, 2016)

According to the analysis of Malaysia National Agro-food Policy 2011-2020 (NAP), they predicted that the demand for livestock products would continue to rise until 2020 i.e., 1.4 million tonnes in 2010 to 1.8 million tonnes in year of 2020 with an annum growth of 2.4 % (NAP, 2011). Referring to all the analysis above, livestock industry is believed to have good prospect in the future and to receive more development. Substantially, the livestock population will continue to grow to meet the demands.

2.1.1 Environmental Problem Caused by Livestock Wastewater

The increase amount of livestock consumption and breeding activities bring positive development to Malaysia livestock industry in the recent years. However, growing concerns on environmental issues which are associated with the disposal of untreated nutrient rich livestock wastewater into natural water system. Normally, livestock wastewater consists of urine, faeces and water that used for animal washing. Contents of the wastewater highly concentrated with large amount of phosphate and ammonium, suspended solids, and organic matter (Norsyahariati and Anijiofor, 2017).

In Malaysia, swine is one of the major livestock type in Malaysia. Therefore, for the following example, livestock wastewater from pig farm was used for analysis. Commonly, one pig farm consists of at least few hundreds to thousands of pigs, huge volume of wastewater thus is produced and accumulated everyday. A proper wastewater treatment must be carried out before disposing into the river. According to the livestock (pig farm) wastewater analysis by Environment Conservation Department (ECD) Sabah, the livestock wastes normally contain valuable quantities of Nitrogen (N), Phosphorus (P), Potassium (K) as excreted by mature pig are as shown in Table 2.2.

Table 2.2: Nutrients as Excrete by Mature Pig (Kinson et al., 2001)

Element	**kg/ animal/ day**
Total Nitrogen	0.033
Phosphorus (P_2O_5)	0.026
Potassium (K_2O)	0.026

The weight of each mature pig is in an average of 150 kg, and manure production is excreted in kg/ animal/ day. Everyday, there was approximately 21.1

kg/animal of solid waste and 15.9 L/animal of liquid waste been produced (Kinson et al., 2001). Wastewater management becomes difficult when duelling with all the wastes produced by whole pigs at the farm. Therefore, treatment of livestock wastewater in Malaysia needs to be values since such big amount of animal wastewater has to be strictly treated everyday.

Among all the nutrients in the wastewater, phosphate and ammonium are the most serious components to environment. One of the major consequences caused by excessive nutrients in the water resources is eutrophication. According to the definition given by Organization for Economic Cooperation and Development, the definition of water eutrophication is ‘*an enrichment of water by nutrient salts that causes structural changes to the ecosystem’* (Eniscuola, 2016). Several most conspicuous effects of eutrophication include harmful algal blooms, depletion of various fish species, occurrence of dead zone, general deterioration of water quality and etc. When nutrients are excessively supplied into the water system, algal starts to bloom. Nutrient shortage and light reduction resulted by algal blooms in the water lead to limitation of plant growth and killing of worms. Meanwhile, lack of light penetration impacts those predators in the water that need light to catch their prey, also damages their habitats. Besides, extreme photosynthesis that associated with eutrophication will massively consume dissolved inorganic carbon and increase the pH content to the utmost levels during day time. Rising of pH weaken the chemical sensing capabilities of the organisms and leads them relying on the perception of dissolved chemical signals to survive. Eventually these algal dead, and decomposition process by microbial starts. Decomposition process will severely consume dissolved oxygen, creating a water area which is oxygen lacking, called ‘dead zone’. These consequences give serious threats to the public health, fisheries, various industry as well as recreation sector (Chislock et al., 2013).

2.2 Phosphate Chemistry

Phosphate is the natural form of the phosphorus, it is a non-renewable mineral which can be found in phosphate rock. In organic chemistry, it is an ester of phosphoric acid. In inorganic chemistry, it is a salt of phosphoric acid (New World Encyclopedia, 2008). There are different primary sources for phosphate such as livestock industry, wastewater treatment, fertilizers, soaps, detergents and industrial processes etc.

Eventually, phosphate that is released from these sources can be detected in rivers, lakes, ponds, and ocean (Oram, 2014).

2.2.1 Chemical Properties of Phosphate

The empirical formula of phosphate ion is PO_4^{3-}. Its total molar mass is 94.9741 g/mol. It is a polyatomic ion and its tetrahedral structural. As shown in Figure 2.2, there is one phosphorus atom in the central surrounded by four identical oxygen atoms. The phosphate ion possesses a negative three (-3) form change. Base on the acids and bases theory of Bronsted-Lowry, if there is single proton donated by an acid molecule to a water molecule, then it will be creating a negative ion known as 'conjugate base' and an H_3O^+ ion (Rundle, Ophardt and Emeritus, 2019). Since there are three formal change for a phosphate ion, it becomes conjugate base of phosphoric acid (H_3PO_4), dihydrogen phosphate ion ($H_2PO_4^-$) as well as hydrogen phosphate ion (HPO_4^{-2}) (Pubchem, 2020).

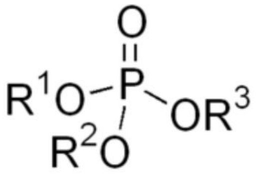


Figure 2.2: Chemical Structural of Phosphate Ion

Various kinds of phosphate salts can be formed if a positive charged ion such as sodium, aluminium, potassium or calcium attaches to the negative charged oxygen atoms of the phosphate ion. Except for the alkali metal salts, most of the phosphate ions are insoluble in the water under atmospheric temperature and pressure. There are total four forms of phosphate exist while in the diluted aqueous solution. Generally, aqueous phosphoric acid (H_3PO_4) is the main form under strongly acid conditions, dihydrogen phosphate ion ($H_2PO_4^-$) always occurs under conditions of weakly acid, hydrogen phosphate ion (HPO_4^{-2}) most common under weak basic conditions and phosphate ion (PO_4^{3-}) is prevalent under strongly basic conditions (New World Encyclopedia, 2008).

Based on the total number of phosphorus molecules, phosphate is classified into different primary groups. Different of these categories are illustrated in Table 2.3, each group will have different properties and also applications. If only single P atom, namely Orthophosphates consists of high buffering strength and can be used in detergents. While there are double P atoms, usually called Pyrophosphates and has good sequestering properties which is highly recommended for the use in metal cleaning apart from water treatment. Three P atoms is known as Tripolyphosphates, it has good dispersant ability and can perform well in meat processing. Lastly, while P atom exceeds three, all of them are called Polyphosphates. It is usually applied in kaolin production since it also has great dispersant ability (Anon, 2019).

Table 2.3: Different Primary Groups of Phosphate Ion (Anon, 2019)

Number of P Atoms	Ion Formula	Common Name
1	PO_4^{3-}	Orthophosphates
2	$P_2O_7^{-4}$	Pyrophosphates
3	$P_3O_{10}^{-5}$	Tripolyphosphates
>3	$P_nO_{(3n+1)}{}^{-(n+2)}$	Polyphosphates

2.2.2 Uses of Phosphate

Among the three primary plant nutrients, phosphate is one of them. In agriculture sector, it is an extremely important component for fertilizers. Commonly, raw phosphate will be firstly treated to make superphosphate, ammonium phosphates or triple phosphates in order to obtain higher phosphate concentration, so the plant can effectively absorb and consume since phosphate solubility is higher with greater concentration (New World Encyclopedia, 2008).

In ceramic products sector, many phosphates are applied for the processing of numerous ceramic products such as enamels, white ware, refractory products etc. Mainly, phosphates are used to provide key functional properties which can greatly improving the final product quality and characteristics of the ceramic. For instances, phosphates contribute for the bonding phase in the ceramics processing (Anon, 2019).

Besides that, phosphates are also widely used in cleaning products sector, such as laundry and dish detergents. They help to soften the water and remove grease and oil, as well as prevent film and spotting build-up in the dish detergents. Also, they are widely used in tile and porcelain cleaning products due to their mineral build-up and soap scum eliminating abilities. Lastly, specialty cleaner such as concrete cleaner is also one of the applications of phosphates (Peltier, 2019).

Occasionally, phosphate compounds are added into potable water treatment. With phosphates in the portable water, it can prevent the presences of iron and manganese. In addition, phosphate used in water distribution system able to avoid corrosion and retard scale formation, meanwhile reducing soluble copper and lead in the potable water. In addition to potable water treatment, phosphates may be found in metal polishes, flame retardants, personal care products, water-based paints and coatings and many more (Peltier, 2019).

2.2.3 Negative Effects of Excessive Phosphates

Fertilizers always contain phosphate compounds that polluting surface water. Sometimes, overuses of chemical fertilizers to grow crops that are used to feed the livestock animals, animals are then excrete manure that rich in phosphate. Spreading those phosphate-rich manures on the land that already consisting large amount of phosphate, results in phosphates run off during heavily raining, and eventually contaminate the nearby water sources. Excess phosphate in stream or lake makes water cloudy and low in oxygen. When the concentration of phosphate reaches the certain level in the water body, where 50 parts per billion in lake or 100 parts per billion in stream, it is considered as eutrophication (Beach, 2017). As mentioned in Section 2.1.1, algal bloom caused by eutrophication reduces light penetration that required by plant, and finally it is dead. Bacteria then start to break it down and massively consume the oxygen in water, where influecing the others aquatic life.

Based on the report by Deutsches Arzteblatt International, excessive phosphate is harmful to human health. Foods that containing phosphate should be properly labelled. Certain concentration of free phosphate that can be found in food additives will be resulting in high mortality in patents with renal disease, since those phosphates are wholly absorbed in the gastrointestinal tract. Furthermore, phosphate is found to damage blood vessels and induce aging processes, especially phosphate can be easily found in most of the fast food (Rattue, 2012).

2.2.4 Phosphate Control in Malaysia Livestock Wastewater

A proper manage and policy in terms of livestock wastewater control to make those wastes able to contribute positively to the environment. In fact, manure and waste produced from livestock are excellent fertilizers that consisting good nutrients to plants. In Malaysia, Department of Environment has regulated a set of parameters regarding the discharge of industrial and mixed effluents, while phosphate is one of the parameters as shown in Table 2.4, that is necessary to be complied by the industrial management. However, specific guidelines are lacked on the measurement of phosphate concentration originated from the livestock farms.

Table 2.4: List of Parameters for Discharge of Industrial or Mixed Effluent by Department of Environment Malaysia (Department of Environment, 2010)

	Parameters
i	Nitrate Nitrogen
ii	Sulphate
iii	Chloride
iv	Cobalt
v	Detergent, Anionic
vi	Molybdenum
vii	Phosphate (as P)
viii	Polychlorinated Biphenyls
ix	Beryllium
x	Vanadium
xi	Pesticides, fungicides, herbicides, rodenticides, fumigants or any other biocides or any other chlorinated hydrocarbons
xii	Any substance that either by itself or in combination or by reaction with other waste may give rise to any gas, fume or odour or substance which causes or is likely to cause pollution
xiii	Total Organic Carbon
xiv	Whole Effluent Toxicity (WET)
xv	Dioxin
xvi	Endocrine disruptors

Since 40 years ago in Malaysia, phosphorus problem has already existing especially the eutrophication concern (Radojevik and Bashkin, 1999). Many studies had been conducted and indicated that the phosphorus level in river, sea and lake in Malaysia exceeded the receiving water capacity. In order to reduce the negative impact brought by excessive phosphorus, a lot of approaches were carried out such as simple budget model, empirical models, nutrients good-web models and few more (Ghani and Mahmood, 2011).

2.3 Current Existing Phosphate Recovery Technologies

To date, there are several phosphorus recovery technologies have been developed. In this study, although struvite crystallization is the major technology, the properties and efficiency in terms of other phosphate removal technologies including enhanced biological phosphates removal, chemical precipitation and electrolysis are also briefly introduced before proceeding to the struvite crystallization.

2.3.1 Enhanced Biological Phosphates Removal (EBPR)

This technology is known as EBPR. It is one of the key methods to remove phosphate from industrial wastewater nowadays with phosphorus removal rate up to 85 to 95% (Water Environment Federation, 1998). EBPR is a process that provides an environment that suitable for Phosphorus Accumulating Organisms (PAO) to survive, as shown by Figure 2.3. Those PAOs possess the ability to convert phosphate into polyphosphate and store it in the cell mass, and finally phosphate is removed along with the waste sludge (Wisconsin Department of Natural Resources, 2009).

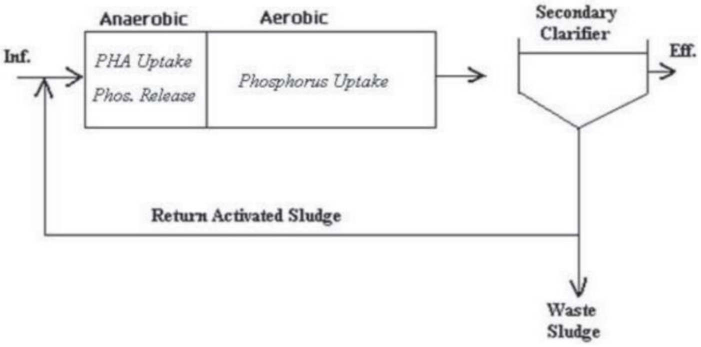


Figure 2.3: General EBPR Configuration (Wisconsin Department of Natural Resources, 2009)

There is a major concern for the nature of biological phosphate storage which is its reversible characteristic. These organisms able to release back the phosphorus into the environment after broke down the internal structure of phosphorus (Baetens, 2001). Therefore, wasting sludge must be carefully handle. Also, this technology always restricted by the difficulty of providing suitable environment for the pure bacteria culturing, as well as the lack of carbon sources (Zhang, Jiang and Deng, 2017). However, there is still important advantages for EBPR such as low sludge production and worthy product as fertiliser (Baetens, 2001).

2.3.2 Chemical Precipitation

Chemical precipitation is another key method that used for phosphate removal nowadays since its phosphorus removal rate can up to 70 to 95% (Morse et al., 1998). This technology requires additional coagulant and mixing of wastewater with coagulant. Soluble phosphorus can be formed into solid by coagulant then precipitate in the solution, in the end phosphate is removed together with the sludge. Several multivalent metal ions are necessary for this process in order to initiate the precipitation, for example aluminium, calcium or iron (Lenntech, 2012). It is important to select the optimum metal ion since the recovered phosphorus that is extremely tightly metal-bound would not able to readily reused in other applications (Morse et al., 1998).

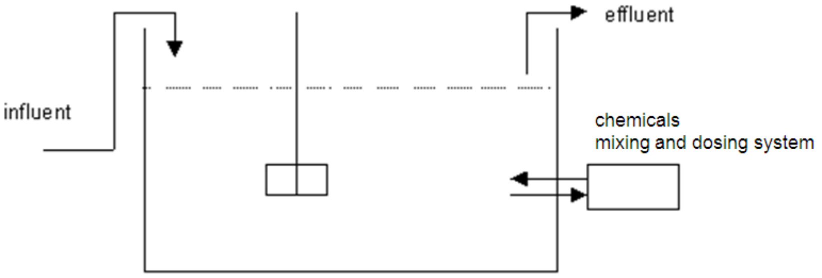


Figure 2.4: General Chemical Precipitation Process

The major disadvantages of chemical precipitation are that huge amount of sludge will be generated, also the cost of the precipitants are quite high. In addition, some negative ecological effects exist due to the aluminium concentration and iron salts in the effluent. However, this technology can remove components very specifically, which means it provides high degree of selectivity (Baetens, 2001).

2.3.3 Electrochemical

Electrochemical is a very useful method in phosphate recovery, which can up to around 80% phosphate removal (Cid, Jasper and Hoffmann, 2018). It has been used extensively to remove carbonate hardness from water bodies to avoid any scaling, called as water softening. For removal of phosphates, normally there are total two electrodes are applied in the treated solution at the same time. By using the aluminium of the electrodes to precipitate the solid aluminium phosphate through concept of coagulation from membrane bioreactor feed, while pH is an important factor. After crystallization, using centrifugal forces to proceed final separation, then settling and filtration are enhanced by adding seed crystals to allow the final recovery of phosphate components (Kappel et al., 2013).

Compared to other technologies, it has the advantage that does not any extra cost for chemicals transportation and electrode material replacement cost, as well as salts and base are not necessary for this process. However, some disadvantages still exist. With desired reactions, sometimes it requires expensive replacement costs for the electrode material. During process, if there is deposition or accumulation of precipitates on the surface of electrode, this might reduce its removal efficiency (Kappel et al., 2013). Therefore, electrodes have to be frequently replaced with new rods. Also, this technology is limited by small handling wastewater capacity (Zhang, Jiang and Deng, 2017).

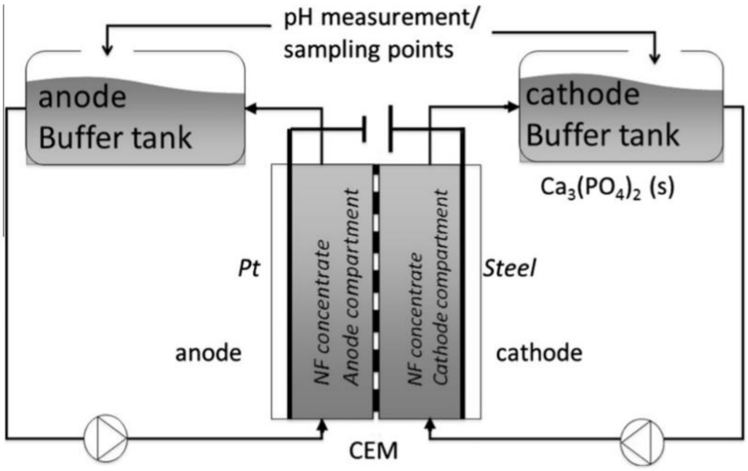


Figure 2.5: General Electrolysis Process

2.4 Struvite Chemistry

In 1845, there was one German chemist named George Ludwig Ulex (1811-1883) who first found struvite crystalline mineral inside the sewerage system in Hamburg, Germany. Struvite is a crystal that consists of three important ions include phosphate, ammonium and magnesium, and the name ‘Struvite’ was named by Ulex (1845).

2.4.1 Characteristics of Struvite

Struvite can be generated in mild alkali or neural condition while its chemical name is known as magnesium ammonium phosphate hexahydrate, with chemical formula $MgNH_4PO_4 \cdot 6H_2O$. Struvite is a while colour crystal. The molar mass of struvite is

245.43 g/mol (Le Corre et al., 2009). Its total mass is basically contributed by one mole of phosphate (PO_4^{3-}), one mole of magnesium (Mg^{2+}), one mole of ammonium (NH_4^+), as well as six water molecules (H_2O). It is very light with only low density of 1.65 to 1.7 (Zhang, Jiang and Deng, 2017). Table 2.5 concludes the properties of struvite.

Table 2.5: General Properties of Struvite (Le Corre et al., 2009)

Nature	Mineral salt
Chemical Name	Magnesium ammonium phosphate hexahydrate
Formula	$MgNH_4PO_4 \cdot 6H_2O$
Aspect	White glowing crystal
Structure	Orthorhombic (space group $Pmn2_1$): regular PO_4^{3-} octahedral, distorted $Mg(H_2O)_6^{2+}$ octahedral, NH_4 and groups all held together by hydrogen bonding
Molecular Weight	$245.43\ g.mol^{-1}$
Specific Gravity	1.711 (ρ = 1.711 $g.cm^{-3}$)
Solubility	Low in water: 0.018g.100 ml^{-1} at 25℃ in water High in acids: 0.033g.100 ml^{-1} at 25℃ in 0.001 N HCl; 0.033g.100 ml^{-1} at 25℃ in 0.001 N HCl
Solubility Constant	$10^{-13.26}$

Orthorhombic crystal is the main form of pure struvite. It consists of groups of hydrogen bonding NH_4^+, regular octahedron of PO_4^{3-} and distorted octahedron of $Mg(H_2O)_6^{2+}$. There are also alternative crystal forms such as rod like structure and irregular structure (Zhang, Jiang and Deng, 2017).

Struvite occurs spontaneously in various biological media such like animal manure, kidney stones or urinary tract calculi. In animal manure, struvite is formed through the process called microbiological combination of NH_4^+ ions with PO_4^{3-} and Mg^{2+} that could be found in the media during bacterial metabolisms (Le Corre et al., 2009). In turn medical field, formation of the struvite stones are commonly due to infection in the urinary tract which induced by urease produced by microorganisms (Prywer, Torzewska and Płociński, 2012).

In the others hand, struvite is a threat for the eutrophication water problem due to its low solubility properties in water, only $0.018\,\mathrm{g}.100\mathrm{ml}^{-1}$ in $25℃$ water (Le Corre et al., 2009). Therefore, struvite can promote encrustation to exposed surface of wastewater distribution system. Also, this nature allows struvite to help in restricting the leaching happens in groundwater and improving the efficiency of the fertilizer. Meanwhile, it can avoid burning of plant roots due to its genuine slow release property. Therefore, struvite is a potential fertilizer in nurseries, horticulture and golf courses (Schuiling and Andrade, 1999).

However, it can bring negative impact to the water treatment facilities. Along in the pipelines of sewage and wastewater treatment plants, there are always some hard solid phase or scale deposited occur especially in high turbulence zone, all these actually are crystalline deposits of struvite. Struvite scale formation is a common concern, where improper manage will cause in pipes blockage, breakdowns of pumps, heat exchangers, centrifuges and etc (Doyle and Parsons, 2002).

2.4.2 Solubility of Struvite

Solubility is very important to determine the presence of struvite. Definition of solubility is that total amount of the substance that able to dissolves in a unit volume of a specific liquid substance under certain pressure and temperature, in order to achieve saturation condition. Every salt has its own solubility curve which indicates its solubility under different temperature. Figure 2.6 shows the solubility variation of struvite at different temperatures (Borgerding, 1972). Obviously, struvite has the highest solubility at 20℃.

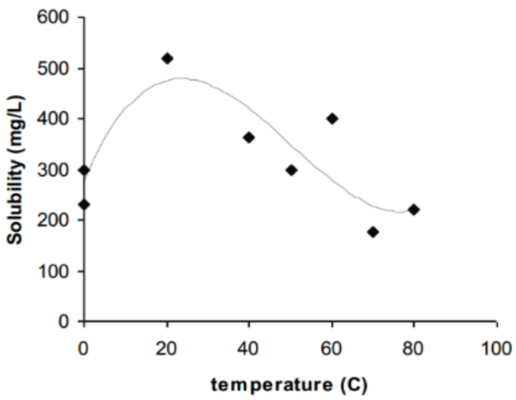


Figure 2.6: Struvite Solubility Curve at Different Temperature (Borgerding, 1972)

K_{sp} represents the constant solubility of product. In terms of struvite constant solubility, the calculation equation can be expressed as:

$$K_{sp} = [Mg^{2+}] \cdot [NH_4^+] \cdot [PO_4^{3-}] \tag{2.1}$$

where $[Mg^{2+}], [NH_4^+]$ and $[PO_4^{3-}]$ represent the respective concentration of magnesium, ammonium and phosphate in the solution. Generally, the molar ratio of three ions within struvite is 1: 1: 1 (Zhang, Jiang and Deng, 2017). When concentrations of Mg^{2+}, NH_4^+ and $H_nPO_4^{n-3}$ $(n = 0, 1 \text{ or } 2)$ are higher than the solubility product constant K_{sp}, then the solution is supersaturated, which means crystal of struvite can be generated spontaneously. The general equation for struvite precipitates:

$$Mg^{2+} + NH_4^+ + PO_4^{3-} \rightarrow MgNH_4PO_4 \cdot 6H_2O + nH^+ \tag{2.2}$$

Due to the influences of many other dissolved species, such as Ca^{2+} which can react with struvite causes efficiency reduction in terms of precipitation, and thus thermodynamic constant K_{sp} is difficult to translate to real liquor or sludge (Le Corre et al., 2009). Another more better method to determine the saturation is using activity solubility product K_{so}. It considers the activity (Ai) and the ionic strength (I) as well as pH. As a result, the value calculated by K_{sp} is lower than K_{so} since K_{sp} without consideration of I, Ai and pH in calculation. K_{so} is calculated by using the following equation (Breck, 1981):

$$K_{so} = a_{Mg^{2+}} \times a_{NH_4^+} \times a_{PO_4^{3-}} \tag{2.3}$$

where $a_i = \gamma_i \cdot [C_i]$, a_i indicates the activity of the i^{th} ion, γ_i represents the activity coefficient of ionic specie i, and C_i is the respective total concentration. In addition, γ_i = 1 happens when the solution is infinite diluted, , $K_{sp} = K_{so}$ thus can be fulfilled (Le Corre et al., 2009)

In fact, there are many ionic species such as Ca^{2+} and K^+ involve in the wastewater and this make concern in predicting the struvite formation in media, since these ionic species will react with struvite components such as Mg^{2+}, NH_4^+ and PO_4^{3-}

(Le Corre et al., 2009). Thus, the understanding of ionic activity which indicates the availability of free ions for a given pH is important. According to the study by Breck, (1981), the respective equations that make estimation on the ions concentrations in the solution are shown in Equations 2.4 to 2.8:

<u>Ammonium</u>: $$NH_4^+ \rightarrow NH_3 + H^+ \quad Log(Ka) = 9.3 \tag{2.4}$$

<u>Phosphate</u>: $$PO_4^{3-} + H^+ \rightarrow HPO_4^{2-} \quad Log\left(\frac{1}{Ka_{,3}}\right) = 12.3 \tag{2.5}$$

$$HPO_4^{2-} + H^+ \rightarrow H_2PO_4^{2-} \quad Log\left(\frac{1}{Ka_{,2}}\right) = 7.2 \tag{2.6}$$

$$HPO_4^{2-} + H^+ \rightarrow H_3PO_4 \quad Log\left(\frac{1}{Ka_{,1}}\right) = 2.1 \tag{2.7}$$

<u>Magnesium</u>: $$Mg^{2+} + OH^- \rightarrow Mg(OH)^- \quad Log\left(\frac{1}{Kd_{,Mg}}\right) = 2.7 \tag{2.8}$$

Then, according to the Equations 2.4 to 2.8, Breck, (1981) deduced:

$$\mathrm{K_{so}} = \mathrm{a_{Mg^{2+}}} \times \mathrm{a_{NH_4^+}} \times \mathrm{a_{PO_4^{3-}}} \tag{2.9}$$

$$\mathrm{K_{so}} = (\gamma_{\mathrm{Mg^{2+}}} \cdot [\mathrm{Mg^{2+}}])\ (\gamma_{\mathrm{NH_4^+}} \cdot [\mathrm{NH_4^+}])(\gamma_{\mathrm{PO_4^{3-}}} \cdot [\mathrm{PO_4^{3-}}]) \tag{2.10}$$

Also, they introduced the notion of conditional solubility product:

$$\mathrm{C_{sp}} = \mathrm{C_{T,Mg^{2+}}} \times \mathrm{C_{T,PO_4^{3-}}} \times \mathrm{C_{T,NH_4^+}} \tag{2.11}$$

where $\mathrm{C_{T,Mg^{2+}}} = (\frac{[\mathrm{Mg^{2+}}]}{\mathrm{a_{Mg^{2+}}}})$ is the magnesium's total analytical concentration, while a indicates the ionisation fraction that allow the continue of struvite forming. Lastly, based on Equations 2.9 to 2.11:

$$\mathrm{C_{sp}} = \frac{\mathrm{K_{so}}}{\mathrm{a_{Mg^{2+}} a_{NH_4^+} a_{PO_4^{3-}}} \times \gamma_{\mathrm{Mg^{2+}}} \gamma_{\mathrm{NH_4^+}} \gamma_{\mathrm{PO_4^{3-}}}} = \frac{\mathrm{K_{sp}}}{\mathrm{a_{Mg^{2+}} a_{NH_4^+} a_{PO_4^{3-}}}} \tag{2.12}$$

Conditional solubility is a function of pH. This function is useful in performing a fast assessment of the solution crystallization state. If $\mathrm{C_{sp}} \leq \mathrm{C_{T,Mg^{2+}}} \times \mathrm{C_{T,PO_4^{3-}}} \times$

C_{T,NH_4^+} means it is oversaturated state in solution, struvite begins to precipitate until reaching equilibrium. In contrast, it is undersaturated state which no precipitation of struvite happens. The value of condition solubility product will at minimum when the ionisation fractions' product is at largest value. The minimum value associated with pH minimum is known as pH of minimum solubility (Breck, 1981).

2.4.3 Saturation of Struvite

Saturation is the parameter that indicates the crystal formation potential. Generally speaking, there are three states that must be undergone for any crystallization to happen.

The first state is undersaturated state. It is impossible to form any struvite crystal within this state; crystals are only will dissolved when added into the solution. Comes to metastable state which is in between undersaturated and oversaturated state, the solution should be saturated and struvite crystal starts to form heterogeneously. Crystal formation can be induced by seed addition. Spontaneous crystallization will only occur in the oversaturated state since the solute concentration has already exceeded the equilibrium level. Struvite crystals form rapidly and abundantly without the necessary of seeding anymore (Ye et al., 2014)

Figure 2.7 illustrates the three states of solution at different temperatures and concentrations. In fact, supersaturation can be manually achieved either by using constant temperature to evaporate the solvent from A to C_3, or by cooling down the solution from A to C_1, or just combining these two methods which from A to C_2 (Le Corre et al., 2009).

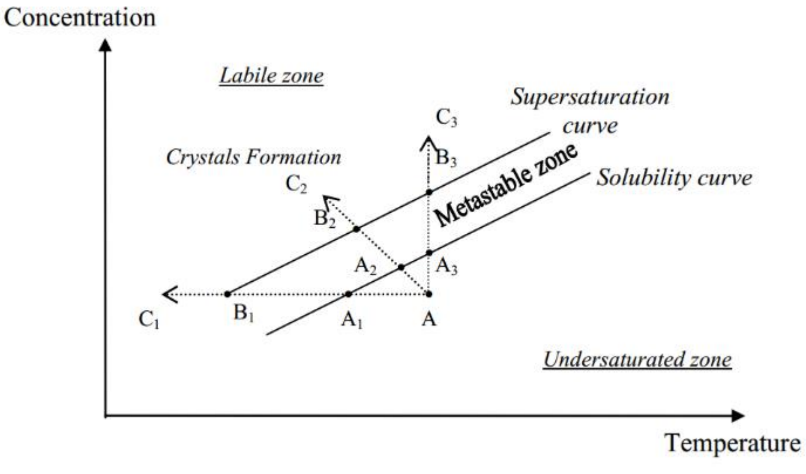


Figure 2.7: Three States of Solution in Crystallization Process (Le Corre et al., 2009)

The properties of the metabolite zone can identify the optimum pattern of crystallization process. These properties are highly related to Ω which known as supersaturation ratio. Supersaturation ratio is associated with the concentration driving force ΔC. It is the different between concentration of solution as well as the equilibrium saturation at a given temperature (Mullin, 2001). According to the studies of Bouropoulos and Koutsoukos (2000), supersaturation Ω is defined as a driving force for the crystallization. To determine the supersaturation, the equation below is applied:

$$\Omega = \left(\frac{a_{Mg^{2+}} a_{NH_4^+} a_{PO_4^{3-}}}{K_{so}}\right) \tag{2.13}$$

where K_{so} represents the struvite solubility product and a represents the ionic species' activity relevant to struvite components in solution. The supersaturation and activity of ionic species are normally determine based on series of chemical reactions related to the process studied (Doyle and Parsons, 2002)

2.5 Concept of Struvite Crystallization for Phosphate Recovery

Phosphate recovery by struvite crystallization is an efficient and economical process. It is a promising method to ease both water eutrophication and scarcity of phosphorus rock in worldwide. Livestock wastewater normally contain abundant nutrient while struvite crystallization can remove phosphate from it. Eventually in the process, struvite can be treated as valuable slow release fertilizer or raw material for chemical industries. Instead of disposing the phosphate together with wastewater, phosphate can be recovered and reuse for applications.

2.5.1 Mechanism of Struvite Crystallization

Crystal formation is critical in struvite crystallization. It is a complicated process that lead to occurrence of solid phase. This solid phase normally is in regular structure called crystal. Two classical steps involve in struvite crystal formation, which are nucleation and crystal growth.

Nucleation is the first step ever in the crystallization. At the moment when Mg^{2+}, NH_4^+ and PO_4^{3-} present under the suitable pH condition, crystal starts to birth in a liquid media. Ions are combined together to form crystal embryos. Kinetics of reaction always govern the first step. Basically, there are two stage of nucleation as shown in Figure 2.8, which is primary and secondary nucleation. The second step is crystal growth. Based on Figure 2.8, this step can be furthered categorized into orientation growth and non-orientation growth. Crystal growth associates with the development of crystal until the formation reaches the equilibrium. According to the crystallization kinetics, the crystal growth can be used to determine the final size of crystal (Le Corre et al., 2009). In order to trigger the first crystal formation, the calcium phosphate as the driving force must be reached.

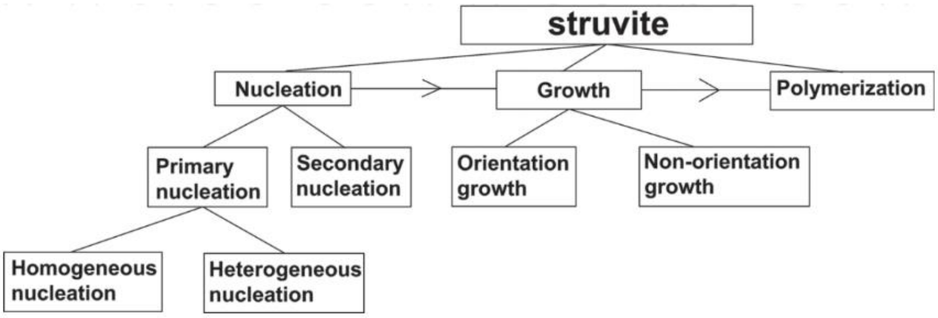


Figure 2.8: Main Stages of Struvite Crystal Formation (Zhang, Jiang and Deng, 2017)

2.5.1.1 Nucleation

Nucleation happens when Mg^{2+}, NH_4^+ and PO_4^{3-} combine to form crystal embryos under proper condition (Zhang, Jiang and Deng, 2017). Primary nucleation is further divided into two typical types; one is homogeneous while another is heterogeneous. Homogeneous primary process occurs when the crystals form spontaneously in highly supersaturated or purified solution. In contrast, when the crystal formation is induced by the presence of other particles or impurities as substrates, it is called heterogeneous primary process (Le Corre et al., 2009). Normally, struvite crystallization process in wastewater treatment is likely to be heterogeneous primary process since there are different impurities involve. However, homogeneous primary process is unlikely to be happen since it is almost impossible to achieve free foreign ions bodies (Davey and Garside, 2000).

Saturation Index (SI) normally is applied to predict and decide the development of primary nucleation is whether to homogeneous or heterogeneous. SI describes the saturation degree of the struvite crystallization, equation is as shown as below:

$$\mathrm{SI} = \log \frac{\mathrm{IAP}}{\mathrm{K_{sp}}} \tag{2.14}$$

where K_{sp} and IAP indicate the solubility product constant and ionic activity of struvite product respectively (Wang et al., 2006). Generally, the desired condition homogeneous crystallization is always happened in metastable region while this region is difficult to control. Nucleation in the region is not spontaneous, but it can avoid the occurrence of undesirable spontaneous nucleation (Adnan, Koch and Mavinic, 2003). The SI is an indication for metastable state is quite important. (Bouropoulos and Koutsoukos, 2000) reported that when SI $\approx$ 2.0 and the nucleation rate is 1 nucleus/cm^3s, the threshold value that between the homogenous and heterogeneous nucleation was found.

Secondary nucleation is considered if the presence of parent crystals. Crystal formation starts by inducing crystal themselves. Parent crystals play role in catalysing nucleation, but this will cause local fluctuations in supersaturation stage, therefore nucleation will occur always at unpredictably lower supersaturation stage (Ali and Rajshahi, 2005). Few factors govern the secondary nucleation such as dust breeding, collision breeding, impurity concentration gradient nucleation, fluid shear and etc (Myerson, 2002). In fact, secondary nucleation is a common issue in crystallization industry as it will lead to reduction of product quality.

The period between the mixing of solutions that containing precipitant constituents and the first detection of measurable precipitant, this is called induction time (Le Corre et al., 2009). Shorter induction time will have used on a highly supersaturated solution while longer or infinite induction time for lower supersaturation solution. Infinite induction time will be resulting in re-dissolving of induced crystals in solution, and this may due to high power consumption from a lower driving force. In order to eliminate these, addition of seed materials as preliminary action is necessary to induce surface diffusion of new born clusters and control crystal growth (Ali and Rajshahi, 2005).

2.5.1.2 Crystal Growth

Nucleation is followed by crystal growth stage. In this stage, the size of crystal embryos is increased until became a detectable crystal. Nucleation begins with the ions used to form struvite crystal accumulate on the crystal embryos and embryos start to grow. At this moment, two possible trends in particle development. Orientation growth is one of it while another is non-orientation growth. Orientation growth implies the arrangement of the ions in the crystal that is according to a specific lattice, whereas the ions in non-orientation growth is disorder due to fast growth rate (Zhang, Jiang and Deng, 2017).

Two different crystal growth mechanism are used to describe crystal growth state and lead to different trends. First, it is called mass transfer mechanisms which considers the solute transport onto the crystal surface from the solution, by either convection or diffusion or both. Another is the surface reaction which is the applying the surface integration mechanism to incorporate the substances into the surface lattice (Le Corre et al., 2009). Diffusion will normally become domain in terms of crystal growth and orientable growth is favoured, when the mass transfer effect is greater than integration. However, if integration effect is dominant, the result of crystal growth will be depended on the integration on the surface of solute (Zhang, Jiang and Deng, 2017).

2.5.1.3 Struvite Growth Kinetics

Kinetics study is important to provide information on how to manipulate the reaction rate in different reaction conditions. According to Equation 2.2 in previous Section 2.4.2, basically the rate of struvite crystallization can be expressed as either rate of disappearance of $\mathrm{Mg^{2+}}$, or rate of $\mathrm{H^+}$ evolution:

$$-\frac{\mathrm{d[Mg^{2+}]}}{\mathrm{dt}}=\frac{1}{2}\frac{\mathrm{d[H^+]}}{\mathrm{dt}} \tag{2.15}$$

Therefore, it is possible to calculate the concentration of $\mathrm{Mg^{2+}}$ in the solution by just observing the varying pH values. From the Equation 2.15, we can get:

$$-\frac{\mathrm{d[Mg^{2+}]}}{\mathrm{dt}}=\mathrm{k_{Mg}[Mg^{2+}]} \tag{2.16}$$

$$\frac{1}{2}\frac{\mathrm{d[H^+]}}{\mathrm{dt}}=\frac{1}{2}\mathrm{k_H[H^+]} \tag{2.17}$$

By combining the Equations 2.16 and 2.17, the following expression is derived and since pH = -log $\mathrm{[H^+]}$ then it can be integrated:

$$-\frac{\mathrm{d[Mg^{2+}]}}{\mathrm{dt}}=\frac{1}{2}\frac{\mathrm{d[H^+]}}{\mathrm{dt}}$$

$$-\int_0^t \frac{d[Mg^{2+}]}{dt} = \frac{1}{2}\int_0^t \frac{d[H^+]}{dt}$$

$$\ln[Mg^{2+}]^t = \ln[Mg^{2+}]^0 - \frac{1}{2}\ln[\frac{(H^+)^t}{(H^+)^0}] \quad (2.18)$$

Equation 2.18 is used to calculated the concentration of Mg^{2+} in the solution over the struvite precipitating time. Subsequently, the concentration of Mg^{2+} obtained from the Equation 2.18 can be applied to calculate the kinetics rate constant using the first order and second order (Equations 2.19 and 2.20) kinetics model equations. Both kinetics models in terms of linear form are expressed (Nelson, Mikkelsen and Hesterberg, 2003):

$$\ln\left(C - C_{eq}\right) = -kt + \ln(C_0 - C_{eq}) \quad (2.19)$$

$$\frac{1}{C} = \frac{1}{C_0} + kt \quad (2.20)$$

where in this study:

C = Mg^{2+} at any time, t

C_{eq} = Mg^{2+} at equilibrium

C_0 = Initial $[Mg^{2+}]$ at time zero, (t = 0)

k = Reaction rate constant

t = Crystallisation time, minutes

2.5.2 Operation Modes of Struvite Crystallization Reactor

There are numerous kinds of struvite crystallization techniques. For instances, fluidized bed, packed bed and mixed suspension mixed product removal (MSMPR). Fluidized bed provides continuous flow in terms of mother liquor and keeps the crystals in suspension to let them expose uniformly within the mother liquor (McCabe, Smith and Harriott, 1956). Packed bed able to effectively reduce nutrient concentration, but it has to be regenerated periodically as it is sensitive to concentration of liquid media (Ohlinger, Young and Schroeder, 2000). Come to the MSMPR crystallizer, by using external source of mixing energy such as impeller, solid particles being force circulated in a continuously mixing state. However, particle size distribution cannot be controlled in MSMPR. The schematic diagrams of these three reactor types are demonstrated in Figure 2.9 (Ali and Rajshahi, 2005).

Another type of struvite crystallizer is Draft Tube-baffled reactor. In this crystallizer, a baffle controls the magma circulation, as well as a downward-directed propeller agitator controls the circulation. The mother liquor basically is regulated by an addition circulation system controlled by a circulating pump at the external of crystallizer (McCabe, Smith and Harriott, 1956).

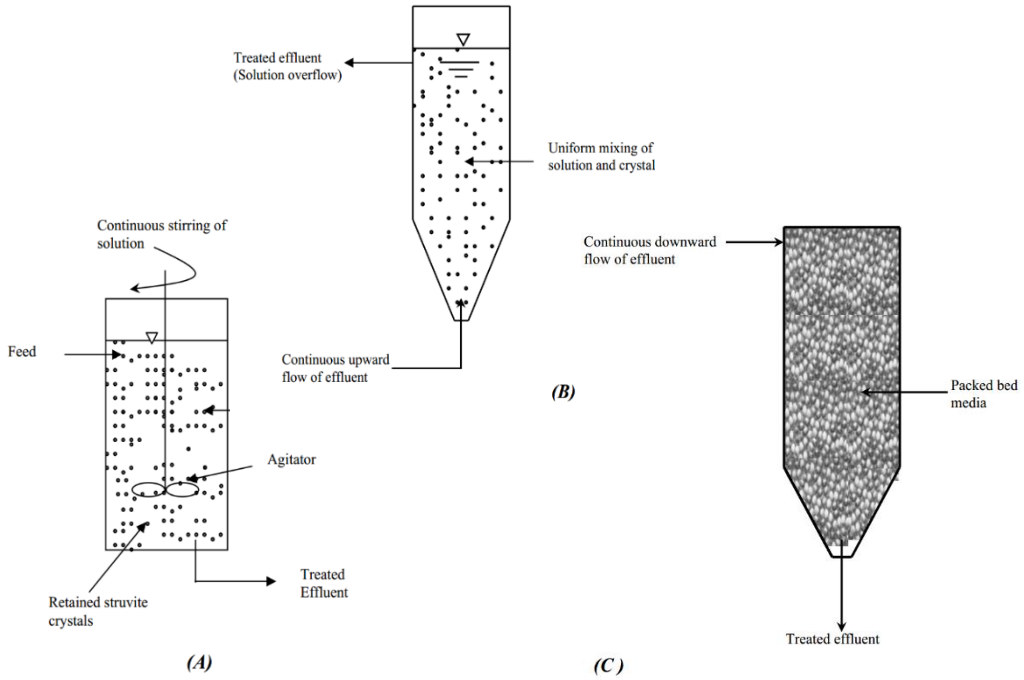


Figure 2.9: Schematic Diagram of (A) MSMPR, (B) Fluidized Bed, (C) Packed Bed

2.5.3 Parameters Affecting Struvite Crystallization

In order to obtain accurate prediction and controlling on the nucleation and growth of struvite crystallization process, there are various parameters that could affect the process necessary to be studied.

2.5.3.1 pH

pH is strongly related to the concept of solubility and supersaturation, and hence it becomes one of the major factors that controlling the performance of struvite crystallization.

Several authors that studied the effects of pH concluded the following observation. Nelson, Mikkelsen and Hesterberg (2003) reported that the pH range from

9.0 to 11.0 was the minimum struvite solubility. However, struvite still able to commence at 7.5 pH (Doyle et al., 2000). At pH of 10, Wrigley (1992) achieved up to 75% recovery of nutrients including nitrogen and phosphate. Moreover, at pH of 8.5, Munch and Barr (2001) obtained more than 80% of phosphate recovery by using struvite precipitation.

According to Equation 2.2 in Section 2.4.2, during precipitation of struvite, it releases proton into solution leads to decrease in pH. The speed of pH decrease implies that the rate at which struvite particles are crystallizing, also related to the quality of the crystals formed. Thus, it is an important indicator for struvite nucleation (Bouropoulos and Koutsoukos, 2000)

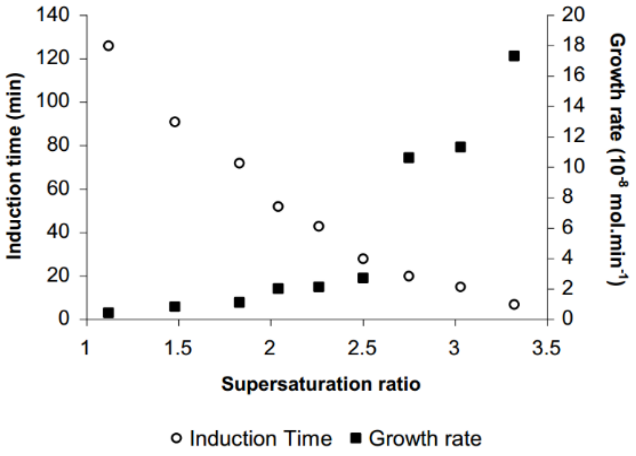
Too high of solution pH will cause the transformation of the NH_4^+ ions into ammonia in gaseous form, which decreases the efficiency of the struvite crystallization since the molar ratio of P: N :Mg of 1: 1: 1 must be sustained. In addition, inadequate pH of solution may cause to accumulation of struvite which happen on the stainless coupons when contacting with the anaerobically digested sludge supernatants. Increase in pH resulting in supersaturation state thus growth rate increase. This was shown that 30 % of different in terms of crystal growth rate between static and moderate area, and about 9 % of different between high and moderate mixing area (Le Corre et al., 2009). Anyway, as long as the phosphorus products are nontoxicity, the target of the process is reached. Usually, the initial pH value of livestock wastewater is normally fall on the range of 7.5 to 8.5 (Zhang, Jiang and Deng, 2017).

Last but not least, pH can affect struvite characteristics. According to the studies by Matynia et al. (2006), rise the pH from 8 to 11 reduced 5 times in terms of struvite crystal size in synthetic solutions. Also, Le Corre et al. (2007b) confirmed that pH of solution was related to the struvite zeta-potential which could affect struvite agglomerative properties (Le Corre et al., 2009).

2.5.3.2 Supersaturation Ratio

The level of supersaturation is crucial in crystallization process at a constant pH. It can seriously affect the induction time and the size as well as number of crystal produced. In the relevant studied by Bouropoulos and Koutsoukos (2000), it has been concluded that the struvite spontaneous precipitation depended on the struvite growth rate as well as solution precipitation, and power law is applied. In Figure 2.10, the result at an increment of supersaturation level value (Ω) from range of 1.13 to 3.33, there was 55 times increase in terms of crystal growth rate, and induction time was shorten about 20 folds (Bouropoulos and Koutsoukos, 2000). On the others hand, Kofina and Koutsoukos (2005) also completed relevant studies which applied the same method with different solvents. Result obtained is shown in Figure 2.10 as well. The struvite crystallization process in their experiment was highly dependent on the supersaturation range from 2.07 to 4.29, this implied the surface diffusion mechanism. As compare with the result obtained by Bouropoulos and Koutsoukos (2000), their growth rates over this specific supersaturation range was higher while shorter induction time.

Adapted from Bouropoulos and Koutsoukos (2000)



Adapted from Kofina and Kousoukos (2005)

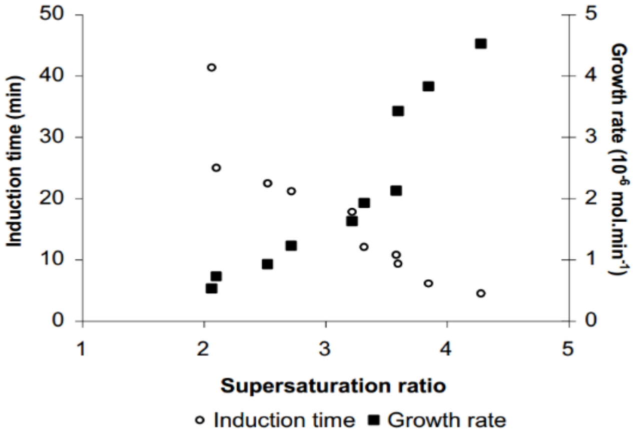


Figure 2.10: Supersaturation Ratio Effect on Induction Time and Growth Rate, at pH=8.5, 25℃

These results indicated that the different nature of solutions gave different effects in terms of nucleation rate and crystal growth. In short, different solutions would have different supersaturation ratio range, thus will provide distinct optimum effects for the induction time as well as growth rate. As shown also in Figure 2.11, at low supersaturation ratio, crystal growth rate is higher than nucleation rate therefore larger in terms of crystal size can normally be obtained, meanwhile induction time is longer. In turn, where at higher supersaturation ratio, crystal size would be smaller with poor settle ability, since nucleation rate is higher than growth rate, of course induction time is faster. Basically, level of the supersaturation can be changed by using the modified substances concentrations and also temperature change (Edahwati et al., 2018).

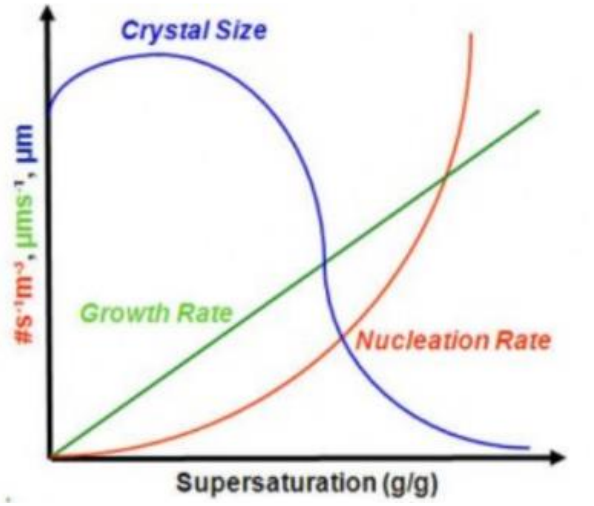


Figure 2.11: Crystallization Growth Rate and Nucleation Rate at Different Supersaturation Level (O’Grady, 2016)

2.5.3.3 Temperature

Temperature has lesser effect on crystallization compared to pH and supersaturation ratio, however it is important also to understand its impacts on struvite solubility and crystal morphology. Commonly, solubility of a solution will increase along with rising of the temperature (Durrant et al., 1999). Burns and Finlayson (1982) and Aage et al. (1997) demonstrated the effects of temperature on the struvite product’s solubility, and are concluded in Figure 2.12. Both of their results obtained show the same trends. For Aage et al. (1997), by applying radiochemical method to determine struvite product solubility, solubility increased from 0.3×10^{-14} to 3.73×10^{-14} at 10℃ to 50℃. In the others hand, Burns and Finlayson (1982) used pH and concentrations measurements and get solubility increased from 0.7×10^{-14} to 1.45×10^{-14} at 25℃

to 45℃. Solubility is closely related to the supersaturation state of the solution, while higher solubility implies that the solution requires more solute to be dissolved in order to reach the supersaturation state. In short, lower temperature range especially between 25℃ to 30℃ favours the crystallization of struvite(Le Corre et al., 2009).

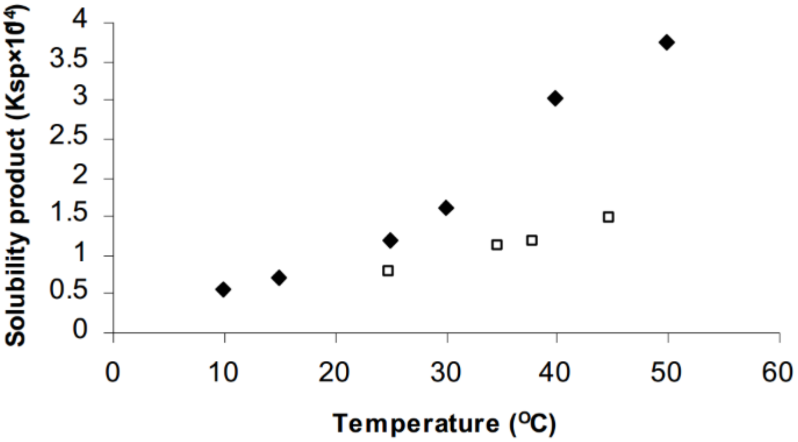


Figure 2.12: Temperature Effect on Solubility of Crystallization Product (Le Corre et al., 2009)

Another effect of the temperature is the crystal growth. Crystal growth is related to the diffusion rate and surface integration. Low crystallization temperature usually leads to surface integration growth, while high temperature leads to diffusion growth (Jones, 2002). Also, high temperature increases the crystal growth rate, as well as the size and shape of crystal. This has been proved in research of Boistelle, Abbona and Lundager Madsen (1983). In that study, struvite crystallization were conducted at two different temperatures which was 25℃ and 37℃, and two different crystal properties were obtained. At 25℃, struvite crystals presented like ‘prismatic and rectangular”; but at 37℃, they looked like ‘thick and square’ (Boistelle, Abbona and Lundager Madsen, 1983). Babić-Ivančić et al. (2002) further demonstrated by applying the same concentration range, and dendritic form of struvite crystals were obtained, where it possessed wider zone compared to 25℃. Last but not least, they also concluded that, if higher concentration of magnesium were introduced, struvite could transform faster became newberyite ($\mathrm{MgHPO_4 \cdot 3H_2O}$) in higher temperature than in lower temperature, which implied that temperature variation relates to the nature of crystal formed (Boistelle, Abbona and Lundager Madsen, 1983).

2.5.3.4 Molar Ratio of P and Mg

Phosphate and ammonium is commonly rich in livestock wastewater. Theoretically, struvite crystal forms when Mg^{2+}, NH_4^+ and PO_4^{3-} are in equimolar ratio 1:1:1. Additional of magnesium is necessary for the struvite crystallization, as it will directly affect the solubility product constant K_{sp}, which relates to the number of struvite crystal produced and the rate of phosphate recovery in livestock wastewater. However, in the actual case, ratio of magnesium to phosphate that applying for the process is larger than 1. Based on the Table 2.6, in order to obtain higher phosphate removal efficiency, the molar ratio of total phosphate to magnesium can up to 1:2 in livestock wastewater, or 1:1.4 in synthetic livestock wastewater. Mainly, it depends on the types of coexisting ions in the livestock wastewater. This is because of the presence of CO_3^{2-} and OH^- that will react with Mg^{2+} and inhibit it from participate the reaction with ammonium and phosphate, thus restrict the phosphate removal efficiency, subsequently more magnesium is needed (Zhang, Jiang and Deng, 2017). However, excessive Mg^{2+} will be resulting in too alkaline condition and high saturation degree of Mg^{2+}, which cause undesirable formation of other magnesium phosphate precipitates such as $MgHPO_4$, $Mg_3(PO_4)_2$ and $Mg(H_2PO_4)_2$ (Marti et al., 2008).

Table 2.6: Molar Ratio of Magnesium Ammonium Phosphate in Crystallization for Various Wastewater Condition (Zhang, Jiang and Deng, 2017)

Sample	**Initial Concentration of Phosphate (mg/L)**	**Molar Ratio of N, P and Mg**
Animal manure wastewater	145	16.4 : 1 : 1.05
Animal manure wastewater	189.9	1 : 1 : 0.8~1
Animal manure wastewater	60.01	63.5 : 1 : 1
Animal manure wastewater	128 ± 13	1 : 1 : 1.2
Synthetic animal manure wastewater	80	8 : 1 : 1.4
Synthetic animal manure wastewater	130.2	1 : 1 :5

2.5.3.5 Presence of Foreign Ions

In the livestock wastewater, there are numerous types of foreign ions existing and interfering with the struvite crystallization. Mainly, there are calcium ion (Ca^{2+}), suspended solids (SS), carbonate ion (CO_3^{2-}) and heavy metal ions (HMI) (Zhang, Jiang and Deng, 2017). Several studies confirmed that the Ca^{2+} and CO_3^{2-} are the most serious ions that lengthen the induction time and reduce the crystal growth rate (Le Corre et al., 2009). In high Ca^{2+} concentration sludge liquors, especially at pH value of 9, Ca^{2+} tends to interact with CO_3^{2-} and PO_4^{3-} to form calcium phosphate and calcium carbonates which are undesirable by-products for the struvite crystallization process (Le Corre et al., 2005). Zhang et al. (2009) found that the increase of calcium ions concentration would lower down the degree of supersaturation of struvite (Zhang et al., 2009). Then, Suzuki et al. (2007) demonstrated that the suspended solids with negatively charged could adsorb on the NH_4^+ and Mg^{2+} especially in alkaline condition, which brought negative impact to the crystallization rate (Suzuki et al., 2007). Also, the presence of Cu^{2+} and Zn^{2+} will temporize the rate of nucleation and reduce the struvite crystal growth rate (Zhang, Jiang and Deng, 2017).

2.5.3.6 Turbulence and Mixing Energy

Turbulence or mixing energy is one of the relevant factor. If CO_2 is used as pH adjustor in aeration system, it can effectively increase the solution pH in the high turbulence area to improve the crystallization efficiency (Le Corre et al., 2009).

However, for constant thermodynamics conditions, the crystal size and shape may be different, since in low turbulence areas where struvite precipitate are more elongated than high turbulence areas where higher mixing speed exists, thus leads to transport restriction in terms of crystal growth. In the study of Ohlinger, Young and Schroeder (1999), they found that the highest growth rates which were 22.4 $g.g.m^{-2}.d^{-1}$ often happened in highly mixing areas, while the lowest rate of 1.8 $g.g.m^{-2}.d^{-1}$ were always obtained in low mixing areas. Generally, high mixing speed allows the acceleration for the nucleation, but it will restrict the crystal growth as crystal breakage increase (Durrant et al., 1999).

2.5.4 Benefits of Struvite Crystallization as Phosphate Removal Method

Eutrophication is the major impact that caused by discharge of nutrient rich livestock wastewater. Every year, it is estimated that around $77 million is spent to remove phosphate from wastewater effluent in the UK water industry. Struvite crystallization gives promising efficiency and consistency in terms of phosphate removal in most of the study conducted, averagely not less than 60%, and its believed that this technique can effectively reduce the environment problems brought by livestock industry (Le Corre et al., 2009).

Special agronomic properties of struvite enable it to be converted into fertiliser. Struvite consists of highly valuable nutrients such as P, N and Mg for plants (Li & Zha, 2003). Its low soluble characteristic leads to slow release of nutrients in soil during plant growth, and avoid the risk burning roots (Le Corre et al., 2009).

In terms of economic, operating of struvite crystallization is quite simple. thus no scaling problem for wastewater treatment plants. Apart from phosphate recovering, it able to remove nitrogen simultaneously. Eventually, collected struvite that is converted into fertilizer brings considerable amounts of profit to the wastewater companies (Doyle and Parsons, 2002). Therefore, to date, struvite crystallization technique has been widely applied in different wastewater treatments, other than livestock wastewater, there are also biogas slurry, effluent of sewage sludge, municipal landfill leachate, multiple wastewater and etc (Zhang, Jiang and Deng, 2017).

CHAPTER 3

METHODOLOGY AND WORK PLAN

3.1 Overall Project Flow

The overall project flow is illustrated in Figure 3.1. Project began with the literature review including the background studies of livestock industry, the negative impacts brought by nutrient-rich livestock wastewater and mechanism of struvite crystallization. With the knowledge supported by literature, the optimal conditions for struvite crystallization and relevant kinetics study were identified. According to the objectives of this project, the experiments were designed to:

a. Manipulate the studied parameters that will be affecting the performance of struvite crystallization (pH, Mg: P molar ratio and precipitation time).
b. Perform kinetics study to study the rate of crystallization over the time.
c. Perform solids analysis to identify the effect of parameters on final product characteristics.
d. Study the feasibility of struvite crystallization in recovery the phosphate from livestock wastewater.

The sample wastewater used for these experiments was a typical livestock wastewater collected from Ayamas Food Cooperation and was provided by i-Chem Solution Sdn. Bhd. Due to the uncertain impurities and presence of ions that would greatly impact the experiment result, synthetic livestock wastewater was prepared to be applied for certain sets of experiment prior to the use of actual livestock wastewater.

Three important parameters including pH, Mg: P molar ratios and precipitation times were involved in the designed experiments to determine their respective effects on the struvite crystallization. After struvite crystallization, the contents in the reactor were filtered through vacuum filtration to retrieve the solids for analysis. On the others hand, filtrate was measured for ion concentration by spectrophotometer, while solid precipitates were dried at room temperature before weighing. The X-ray diffractometer (XRD) was used to characterize the crystal solid phase, while the Scanning Electron Microscope and Energy Dispersive X-Ray Analysis (SEM-EDX) analysis was performed to analyse the particle size and also surface morphology. With the result information, the recovery of phosphate was determined. Kinetics study was carried out to study the crystal growth rate over the specific durations. All of the experimental results obtained were analysed and discussed in the final report.

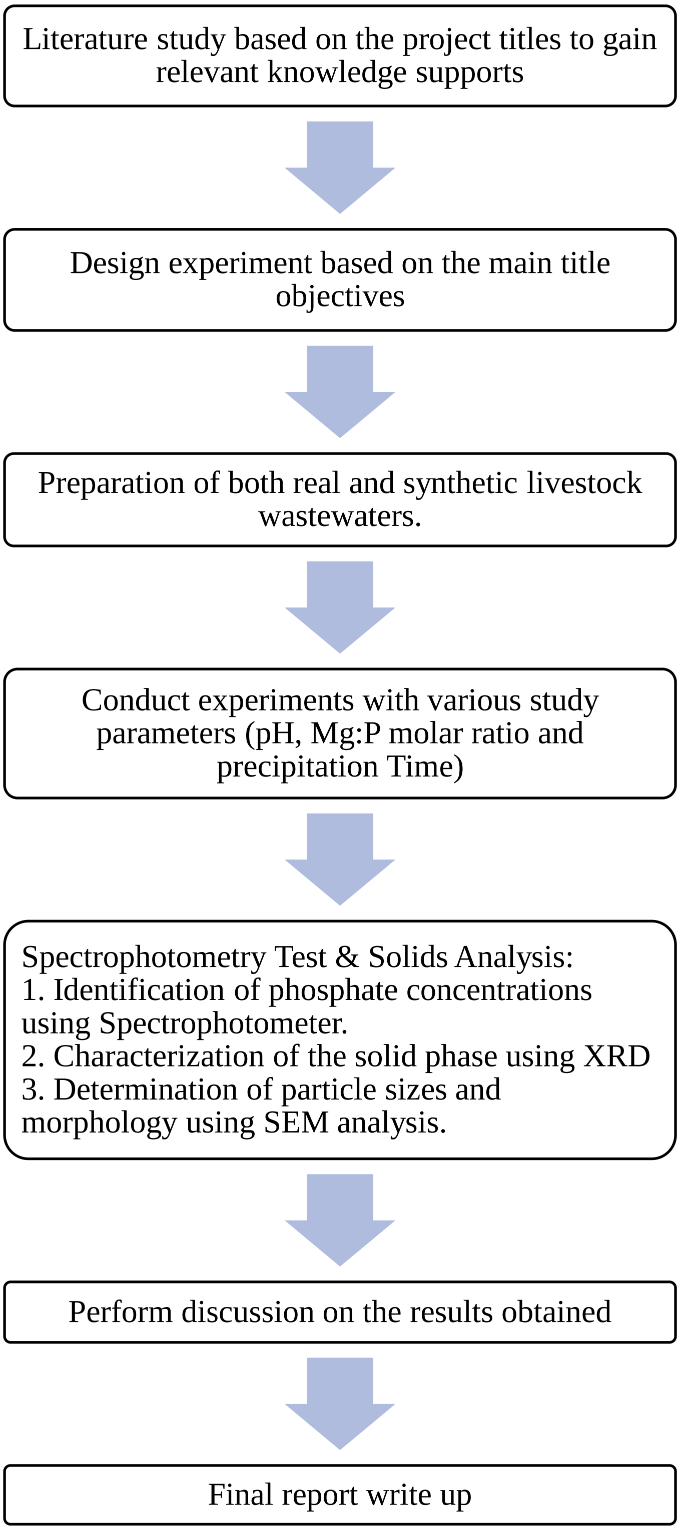


Figure 3.1: Overall Project Flow Chart

3.2 Experimental Materials

3.2.1 Synthetic Livestock Wastewater

0.5 M stock solution of potassium dihydrogen phosphate ($\mathrm{KH_2PO_4}$) and 3.0 M stock solution of ammonium chloride ($\mathrm{NH_4Cl}$) were prepared with their corresponding crystalline powders. Synthetic livestock wastewater was then prepared according to the P: N molar ratio of 1:12 which is the common ratio that exists in the livestock wastewater. The properties of synthetic wastewater are shown in Table 3.1.

Table 3.1: Composition of Synthetic Livestock Wastewater after Preparation

Synthetic Livestock Wastewater		
pH	5.7	
	mmol/L	**mg/L**
$\mathbf{PO_4^{3-} - P}$	0.95	90.00
$\mathbf{NH_4^{+} - N}$	11.40	205.54

3.2.2 Actual Livestock Wastewater

Actual livestock wastewater was provided by i-Chem Solution Sdn. Bhd. and was collected from Ayamas Food Corporation. The properties of the real livestock wastewater are shown in Table 3.2. Pre-filtration was required to reduce the content of impurities using vacuum filtration with 102 qualitative filter paper.

Table 3.2: Composition of Actual Livestock Wastewater after Filtration

Actual Livestock Wastewater		
pH	5.98	
	mmol/L	**mg/L**
$\mathbf{PO_4 - P}$	0.92	87.00
$\mathbf{NH_4 - N}$	11.00*	198.43*

***** *calculated by referring to the ideal P: N molar ratio of 1:12 without ammonium ion measurement*

3.2.3 Others Chemical Materials

0.5 M of $\mathrm{MgSO_4 \cdot 7H_2O}$ stock solution was prepared as a representative of $\mathrm{Mg^{2+}}$ ion for the purpose of assuring supersaturation level of struvite that gives continuous crystal growth in livestock wastewater solution. 0.5 M of NaOH and 0.5 M of HCl were prepared with the use of pH adjustment for the livestock wastewater throughout the experiment.

3.3 Design of Experiments

The effects of three parameters (pH, Mg: P molar ratios and precipitation time) on struvite crystallization were studied. Each parameter was set to have four different values from low to high. Every experiment was duplicated in order to obtain a more accurate result. The optimum value among the four would then be carried forward into another parameter study experiment. These studies would only be conducted with synthetic livestock wastewater in order to ensure the absence of impurities that would affect the results. Then, the optimum value from three respective studies would be applied in actual livestock wastewater. The operating conditions for the all experiments are shown in Table 3.3. Atmospheric temperature was applied without any necessary of heating or cooling. Figure 3.2 shows the set-up of the lab-scale struvite crystallization process.

Table 3.3: Sets of Condition for Struvite Crystallization Experiments

Livestock Wastewater Type	**pH**	**Mg: P ratio**	**Time (min)**
Effect of pH on the Struvite Crystallization (S1 to S4)			
Synthetic	4 7 10 12	1:1	60
Effect of Mg: P ratio on the Struvite Crystallization (S5 to S8)			
Synthetic	Optimum pH from pH study (S1-S4)	0.5:1 1:1 2:1 4:1	60
Effect of Contact Time on the Struvite Crystallization (S9 to S12)			
Synthetic	Optimum pH from pH study (S1-S4)	Optimum ratio from ratio study (S5-S8)	15 40 60 90
Optimum Parameters (S13)			
Actual	Optimum pH from pH study (S1-S4)	Optimum ratio from ratio study (S5-S8)	Optimum time from time study (S9-S12)

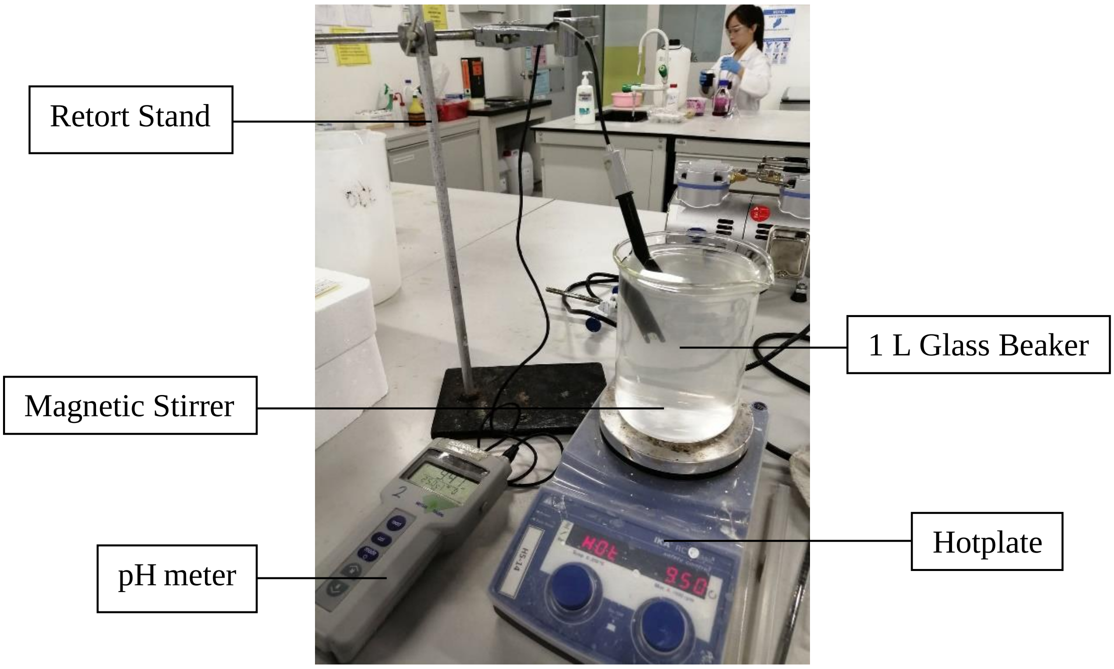


Figure 3.2: Experimental Setup for Lab-Scale Struvite Crystallization

3.3.1 Effects of Different pH (S1 to S4)

In these experiments, the recovery of P at different pH at 5, 7, 10 and 12 were studied. Beaker with 0.5 L was used as reactor to contain the synthetic livestock wastewater. Then, first spectrophotometry test was carried out to measure the initial phosphate concentration in the synthetic solution. Next, performed pH adjustment by using 0.5 M of NaOH and HCl according to the specified pH. Only synthetic livestock wastewater would be applied for these experiments. In order to achieve supersaturation condition, the prepared amount of 0.5 M $MgSO_4 \cdot 7H_2O$ stock solution was added with 1000 μL micropipette. The total volume of synthetic livestock wastewater and magnesium solution was maintained at 0.5 L. Molar ratio of magnesium to phosphate (Mg: P) was set to 1 in this case. pH was kept constant throughout the experiment and pH meter was applied to monitor the pH variation in the solution. Meanwhile, 0.5 M of NaOH and HCl were used to stabilize the solution pH with droplet. Hot plate and magnetic stirrer with 3 cm in diameter were used for uniform mixing at the speed of 300 revolutions per minute (rpm). The mixing was conducted for 60 minutes from the time when magnesium solution was added into synthetic livestock wastewater. After 60 minutes, 20 mL of sample was taken out and filtered through a 0.2 μm syringe filter. The filtrate would be proceeding to second spectrophotometer test to analyse the final phosphate concentration. In the others hand, the remaining solution was filtered through vacuum filtration to retrieve the precipitated solids for solids analysis using XRD and SEM-EDX. The filter paper used for filtration was 102 qualitative filter paper. Weighing of filter paper before and after filtration was necessary to obtain accurate net weight of precipitated solids.

3.3.2 Effects of Different Mg: P molar ratios (S5 to S8)

In these experiments, the recovery of P at different Mg: P molar ratios of 1:1, 2:1, 1:2 and 4:1 were studied. The procedures in these experiments were similar with the steps as described in Section 3.3.1. At the beginning, concentration of magnesium in the synthetic livestock wastewater was adjusted by adding 0.5 M of $MgSO_4 \cdot 7H_2O$ based on the Mg: P molar ratio that are formulated. Meanwhile, the optimum pH value from last experiments was applied and stabilized throughout the 60 minutes of experiment.

3.3.3 Effects of Different Induction Time (S9 to S12)

In these experiments, the recovery of P for different precipitation time of 15, 40, 60 and 90 min were studied. The procedures in these experiments were similar with the steps as described in Section 3.3.1. The optimum pH value and Mg: P molar ratio from previous experiments were applied throughout the four experiments.

3.3.4 Actual Livestock Wastewater (S13)

This experiment was conducted and duplicated with the actual livestock wastewater provided by i-Chem Solution Sdn.bhd. Three optimum parameters that were obtained from previous studies were used. Same, spectrophotometry test was carried out to determine the initial concentration of phosphate in actual livestock wastewater. Then, the initial ammonium concentration was assumed based on the ideal molar ratio of P: N (1:12), while initial magnesium concentration could be adjusted based on the optimum Mg: P ratio. The method of pH adjustment and mixing were the same as mentioned in Section 3.4.1. At the end of the experiment, both syringe and vacuum filtration were carried out to obtain the filtrate and solid produced. Measurement of final phosphate concentration and solids analysis were then performed for results discussion.

3.4 Analytical Equipments

3.4.1 Spectrophotometer

The model of the spectrophotometer used was HACH DR 3900. The basic principle of this instrument is that each different compound will transmit the light over a specific wavelength range, therefore by detecting the intensity of light beam that passing through the sample solution, concentration of known chemical substance are identified (Kevin Vo (UCD), 2105). Before the experiments, the first testing was applied for the purpose of measuring the initial phosphate concentration in both synthetic and actual livestock wastewater, while second testing was applied for the final phosphate concentration in the filtrate. The analytical method used was USEPA[1] PhosVer 3 with Acid Persulfate Digestion. The phosphate detectable range was considered low which only from 0.06 to 3.50 mg/L. Therefore, the dilution on the testing sample was a must before measurement to avoid phosphate concentration of the sample exceeded the detectable range. A dilution factor of 100 was applied for every testing sample.

3.4.2 Scanning Electron Microscope (SEM)

The model of SEM used is Hitachi S-3400N. The basic principle of this technique is by scanning focused electron beam over the surface to create a detail image, while morphology and particle size of the substance can be identified when various signal produced from the interaction of electron with the sample (Robin Rajan, 2013). In this study, SEM analysis on struvite crystals produced from both actual and synthetic livestock wastewaters were conducted. In terms of sample preparation for SEM, only very little amount of the sample solid was required for analysis.

3.4.3 Energy-dispersive X-ray Spectroscopy (EDX)

EDX system is an attachment to SEM system. It can be conducted directly after SEM analysis. The basic principle of this technique is by using an electron beam to hit the testing sample in order to exciting an electron in the inert shell, while resulting in the ejection as well as formation of an electron hole in the electronic structure of the element (Nanakoudis, 2018). In this study, this technique was mainly to identify the compositions that exist in the sample solids produced from struvite crystallization in both synthetic and actual livestock wastewaters.

3.4.4 X-Ray Diffractometer (XRD)

The model of XRD used in this experiment is Shidmazu XRD-6000. XRD analyzes the detailed information of crystallographic structure, physical properties, and chemical composition of the sample. The analysis is non-destructive, and identifies based on the constructive interference of monochromatic X-rays and crystalline sample A unique "fingerprint" is provided by the X-ray diffraction pattern characteristics that generated in the typical XRD analysis (Science direct, 2016). The purity of products can also be studied by using X-ray diffraction (XRD), which utilize the diffraction angle and lattice spacing in crystals to identify the composition of crystalline materials (Dutrow, 1912). In this study, XRD was applied to analyse the crystalline states of struvite under atmospheric conditions, and to identify if the solids produced were the desired products.

3.5 Calculations

The recovery of soluble P was calculated as the absolute difference in concentration by the following equation:

$$\mathrm{Recovery}\ [\%] = \frac{\mathrm{C_{initial}} - \mathrm{C_{final}}}{\mathrm{C_{initial}}} \times 100\% \tag{3.1}$$

where $\mathrm{C_{initial}}$ is the ion concentration in the 0.5 L solution at the start of the experiment, $\mathrm{C_{final}}$ is the ion concentration in the 0.5 L solution after experiment, both could be measured by the spectrophotometer.

The estimation production of struvite based on molar removal of P was calculated as:

$$\mathrm{Yield}\left[\frac{\mathrm{mg}}{\mathrm{L}}\right] = (\mathrm{M_{initial}} - \mathrm{M_{final}}) \times \mathrm{MW_{struvite}} \times 1000\mathrm{mg/g} \tag{3.2}$$

where in this case, the $\mathrm{M_{initial}}$ is the initial phosphate concentration in mol/L, $\mathrm{M_{final}}$ is the final phosphate concentration in mol/L and $\mathrm{MW_{struvite}}$ is the molar weight of struvite = 245.41 g/mol.

3.6 Kinetics Study on Crystal Growth

According to Equations 2.19 and 2.20 as shown in Section 2.5.1.4, the first and second order kinetics equations were expressed as:

First order:

$$\ln\left(C - C_{eq}\right) = -kt + \ln(C_0 - C_{eq})$$

$$\ln\frac{C - C_0}{C_0 - C_{eq}} = kt$$

[y = mx]

Second order:

$$\frac{1}{C} = \frac{1}{C_0} + kt$$

[y = c + mx]

where in this example:

C = Mg^{2+} at any time, t

C_{eq} = Mg^{2+} at equilibrium

C_0 = Initial [Mg^{2+}] at time zero, (t = 0)

k = Reaction rate constant

t = Crystallisation time, minutes

3.7 Feasibility Study

In order to evaluate the feasibility of struvite crystallization in recovering the phosphate from the livestock wastewater, the product quality, operational issues and costs had to be considered, not only from the point of view of project benefits but also green chemistry. This section will identify the feasibility of struvite crystallization at practical scale meanwhile determine the more sustainable ways to develop struvite crystallization system.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Effects of Different Parameters on Phosphate Recovery

There were total 12 sets of experiment conducted in batch mode to study the parameter effects on the phosphate recovery performance of struvite crystallization. Only synthetic livestock wastewater was used in these cases. Each set of experiment was duplicated for more accurate outcomes. The discussions on optimum value of each parameter are in the Sections 4.1.1 to 4.1.3.

4.1.1 Effect of pH at Constant Mg: P ratio and Time

These experiments were conducted under various pH values at 5, 7, 10 and 12 (S1-S4) with Mg: P molar ratio of 1:1. pH adjustment was needed before crystallization begun, and stabilized the pH within 60 minutes.

4.1.1.1 Achieved Phosphate Recovery (S1-S4)

Figure 4.1 shows the phosphate recovery efficiency trend. The result showed that the performance of struvite crystallization in this study was decent in terms of phosphate recovery, where the best efficiency could be up to 56.7 % only. This might be due to the fact that the optimum conditions of Mg: P molar ratio had still not been applied. The trend of recovery efficiency well matched with the result obtained by Le Corre (2006) as well as Ali and Rajshahi (2005), in which the best recovery obtained fell in the range of pH 9 to 11, and could be observed that pH had very significant impact on the phosphate recovery rate. This was related to the solubility and supersaturation of the struvite. According to the research of Le Corre (2006), the struvite solubility dropped along with the increment of pH. This implied that the concentration of $\mathrm{PO_4^{3-}}, \mathrm{NH_4^+}$ and $\mathrm{Mg^{2+}}$ could exceed the struvite solubility easily, and hence achieved supersaturation state. In this case, the phosphate recovery was observed to rapidly increase with the pH raised from 7 to 10, and pH 10 was found to provide best performance. At pH 12, the amount of struvite produced was observed to decrease. The could be due to the evolution of free $\mathrm{NH_3}$ and the formation of $\mathrm{Mg(OH)_2}$ which might cause in the reduction of the available NH_4^+ and Mg^{2+} ions for struvite formation (Muryanto, 2017).

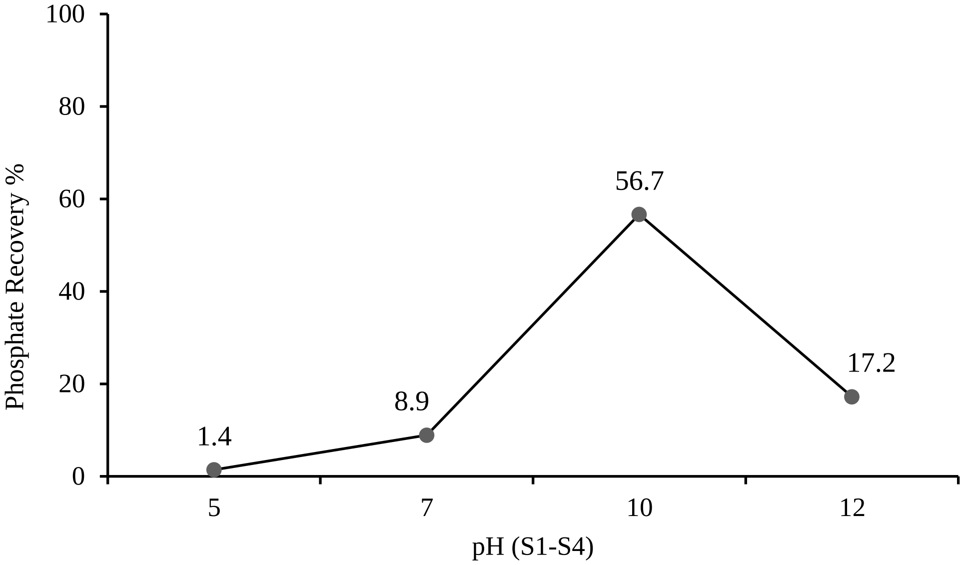


Figure 4.1: Phosphate Recovery Efficiency under different pH (S1-S4)

4.1.1.2 Production of Solids (S1-S4)

Figure 4.2 shows the production of solids at Mg: P ratio of 1.0 under various pH. The red colour line represents the theoretical struvite yield from the solution, and was calculated using Equation 3.2, while the blue bar indicates the actual solid yielded. Overall, it shows that the solids retrieved from the reactor were all lesser compared to the theoretical struvite yield. The main reason might be due to the fact of human error during the handling of filtration in retrieving the solids with the use of 102 qualitative filter paper. The pore size of this filter paper was too large from retrieving some fine particles, but most of the larger solids were able to be retrieved. Also, some solids were observed to have been stuck on the surface of reactor and magnetic stirrer. Undoubtedly, these were the contributors to the total error in solids yield measurements. The largest different between the actual solids produced and theoretical struvite yield could be up to 50 mg/L, and hence it was not easy to conclude any of these effects. At pH 5 and 7, the solids produced were actually quite insignificant. As mentioned in Section 4.1.1.1, the solution was not easy to reach the supersaturation state under low pH condition. The nucleation began late, and the growth rate was slow. Lesser struvite was produced and even in small crystal size, therefore it was hard to retrieve these fine particles. Nevertheless, both actual and theoretical struvite yields followed the same trend, and undoubtedly we could conclude that the pH 10 was the best pH for the struvite precipitation.

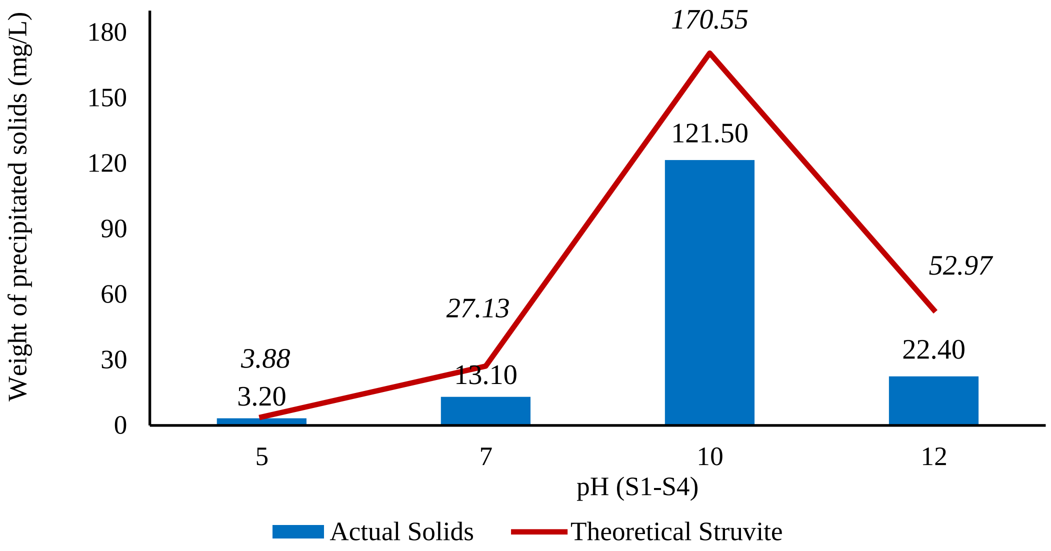


Figure 4.2: Weight of Products under different pH (S1-S4)

4.1.2 Effects of Mg: P ratio at Constant pH and Time

These experiments were conducted under various initial Mg: P molar ratios of 0.5, 1, 2 and 4 (S5-S8) at optimum pH 10 which was determined from the previous study. pH adjustment was needed before the crystallization begun, and the pH stabilized within 60 minutes. $MgSO_4 \cdot 7H_2O$ was the selected magnesium salt for the crystallization.

4.1.2.1 Achieved Phosphate Recovery (S5-S8)

The effect of the initial Mg: P molar ratio on phosphate recovery in synthetic livestock wastewater at pH 10 is shown in Figure 4.3. Within the expectation, the effect of Mg: P ratio was significant. The result implies that the higher the Mg: P molar ratio gave better phosphate recovery performance, where the best efficiency of 84.18 % was obtained at highest Mg: P molar ratio of 4:1. This was because of the supersaturation of the solution could be achieved by elevating the Mg: P molar ratio, and higher Mg: P molar ratio prevented inhibition of struvite formation and crystal growth. Overall, the recovery rate increased at directly proportional with approaching to linear form. Besides, shorter induction time was required if higher initial Mg: P molar ratio was introduced, which implied that the struvite nuclei began to form faster. However, in practical condition it was not recommended to have too high concentration of Mg^{2+} in struvite crystallization because this would lead to formation of others undesired magnesium salts. Also, the excessive amount of Mg^{2+} may lead to drug waste and serious secondary pollution (Daneshgar et al., 2018). However, the side effects were not obvious in this pure system as it was free of disturbance ions.

Liu et al. (2008) reported that the best Mg: P molar ratio for synthetic livestock wastewater was 1.5: 1 with phosphate removal of 92%, and it considered better than the result in the present study. Besides, Zhang, Jiang and Deng (2017) carried out the struvite crystallization using synthetic livestock wastewater with only Mg: P molar ratio of 1:1.4, but they successfully achieved a phosphate removal rate that greater than 90 %. One of the reason why the result of previous studies were better than the present study was that the solubility of $MgSO_4 \cdot 7H_2O$ was lower than the $MgCl_2$ that used by Liu et al. (2008) and Zhang, Jiang and Deng (2017). With lower solubility, Mg^{2+} dissolved slower in the solution, and more Mg^{2+} was needed to reach supersaturation. However, it was not recommended to have too high concentration of Mg^{2+} in the process. As Mg^{2+} was dissolved into the solution, it began to release proton when bonding happened between Mg^{2+} with the OH^- of water. Then, pH dropped and this leaded to more NaOH as pH adjustor needed for stabilizing the solution pH at desired pH 10. However, high concentration of Na^+ would reduce the activity of struvite ions, hence efficiency was reduced.

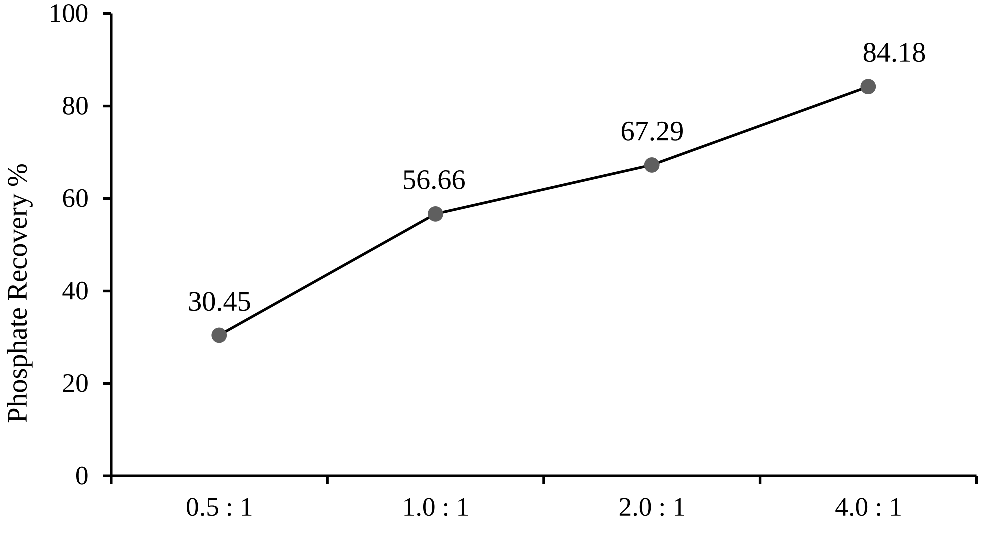


Figure 4.3: Phosphate Recovery Trend of Mg: P molar ratios (S5-S8)

4.1.2.2 Production of Solids (S5-S8)

Figure 4.4 shows the actual solids and theoretical struvite yield under various Mg: P molar ratios. Obviously, the trend of theoretical yield line (red line) shows the phosphate recovery performance could be improved by increasing the dosage of Mg^{2+} source. However, at molar ratio of 4:1, an error should occur as only 193.80 mg/L of solids were produced, and it was almost the same with 2:1 molar ratio which produced 192.60 mg/L. This could be due to the fact that poor handling during filtration and mass weighing leaded to solid losing. Other than this, both of the theoretical and actual yield were basically follow the similar trend. A low yield was observed at Mg: P of 0.5:1, where the explanation could be the supersaturation has not yet been established or level was still low. Come to the Mg: P at 1:1, it was found that there was about 30 % of different between actual and theoretical solid weight. Same as mentioned in Section 4.1.1.2, this was related to those human factors. However, the overall actual yield follows the trend of theoretical yield. This successfully proved that the higher Mg: P molar ratio could give better efficiency in terms of phosphate recovery. In this case, Mg: P molar ratio of 4:1 was the optimum molar ratio among the all.

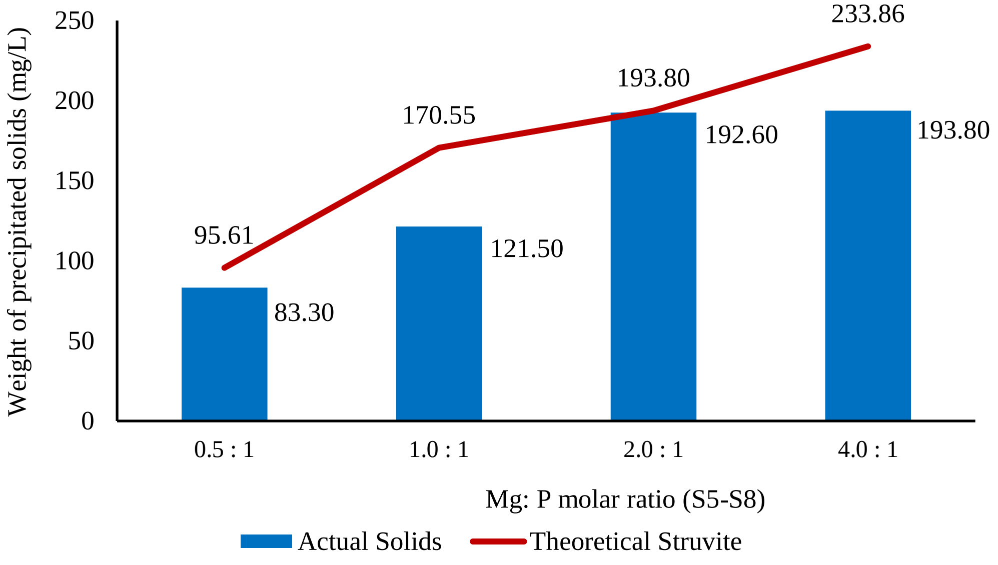


Figure 4.4: Weight of Products of Mg: P molar ratios (S5-S8)

4.1.3 Effects of Precipitation Time at Constant pH and Mg: P ratio

These experiments were conducted under different durations of 15, 40, 60 and 90 minutes (S9-S12) at optimum pH 10 with Mg: P molar ratio 4:1. pH adjustment was needed b crystallization begun, and stabilized the pH within the specific durations.

4.1.3.1 Achieved Phosphate Recovery (S9-S12)

Figure 4.5 shows the results at different precipitation time for struvite crystallization in synthetic livestock wastewater. It was found that the formation of struvite was rapid at the first 15 minutes. This was because of the concentration of PO_4^{3-}, NH_4^+ and Mg^{2+} reached the supersaturation state of solution. At 60 minutes where 84.87 % of recovery rate achieved, the reaction was considered to reach the equilibrium. In fact, the phosphate recovery rates were considered stable after 40 minutes since recovery rates were within the range from 80 % to 85 %. The result was basically in agreement with the previous literature studies. Shin and Lee (1998) observed that the phosphate, ammonia and magnesium concentrations in their struvite crystallization experiments were all reduced quickly within the first few minutes. However, they suggested that a precipitation time of at least 10 minutes to obtain better efficiency. Another research was from Çelen and Türker (2001). Their struvite crystallization process in an anaerobically digested wastewater was rapid and finished in just few minutes. Similarly, the reaction happened in this study was considered rapid but it was still slower as compared with the previous studies. The types of Mg^{2+} with lower solubility used in these experiments restricted the struvite activity which became one of the reasons. Precipitation time of 60 minutes was selected as best duration for struvite crystallization, as phosphate recovery at 90 minutes tended to stable and did not increase much. Last but not least, Grini (2018) reported that the effect of Mg: P molar ratios were more significant at low pH such as 7 and 8.

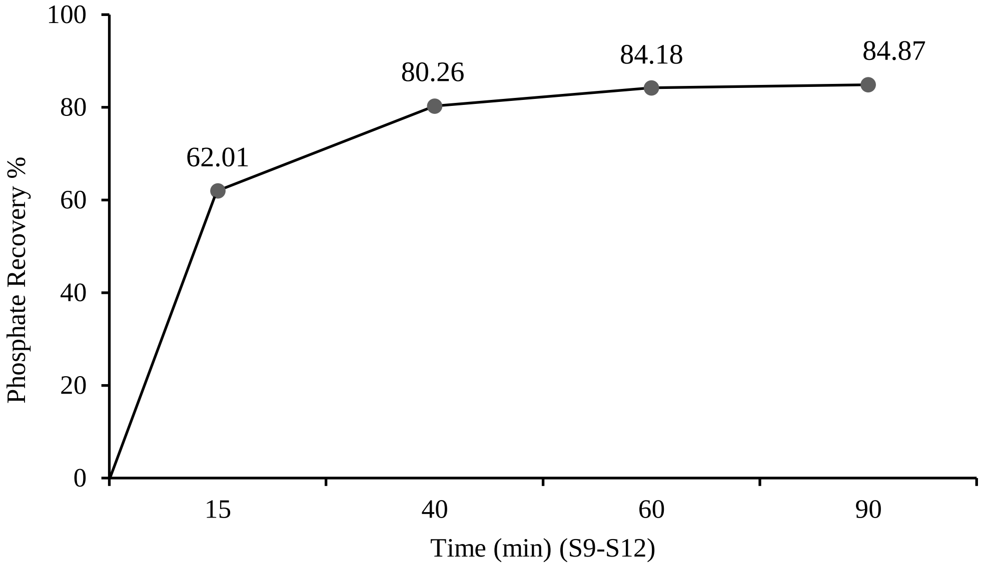


Figure 4.5: Phosphate Recovery Trend under Different Durations (S9-S12)

4.1.3.2 Production of Solids (S9-S12)

In terms of the theoretical struvite and actual solid produced, Figure 4.6 shows a similar growing trend from both of these. Same, as the filter paper was unable to retrieve all the solids produced, the actual solids retrieved were all lesser than theoretical struvite yield that estimated based on phosphate removal. Besides, there were similar actual solid amounts retrieved between 40 and 90 minutes. These should be due to the external errors that occurred during filtration and mass weighing. The 60 minutes of precipitation time was taken as optimum duration since the additional 30 minutes could not recover much phosphate during equilibrium. In addition, a previous study reported that the residual phosphate in the solution tended to increase after 60 minutes, and was perhaps due to the dissolution from the struvite precipitate (Shin and Lee, 1998). Hence, a precipitation time of 60 min was considered as the best duration to achieve maximum phosphate recovery. Therefore, the S11 with precipitation time of 60 minutes would be used for comparison with the result in the study of actual livestock wastewater (S13).

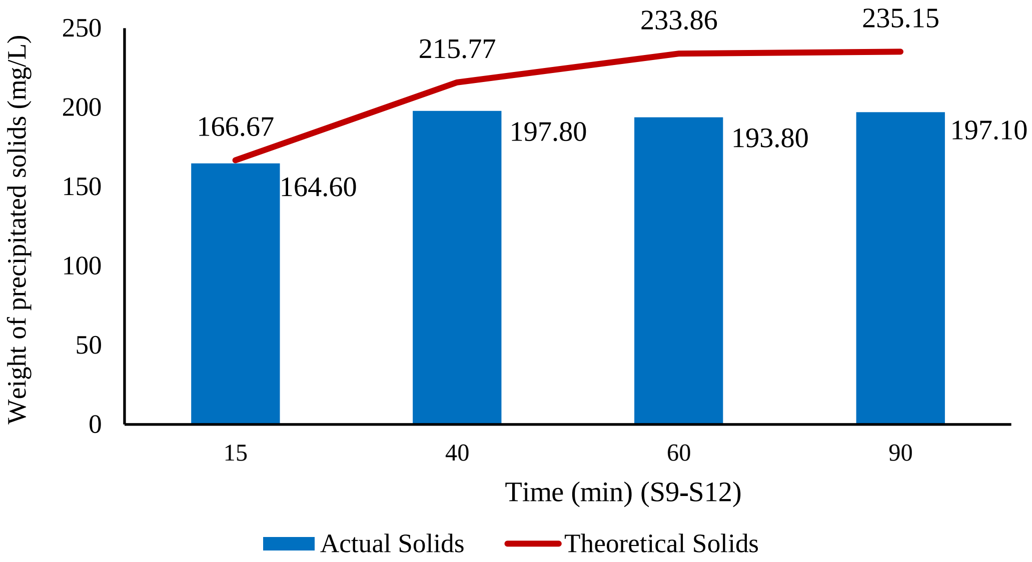


Figure 4.6: Weight of Products under Different Durations (S9-S12)

4.1.4 Actual Livestock Wastewater

These experiments (S13) considered the practically of struvite crystallization in recovering the phosphate. The optimum pH, Mg: P molar ratio and precipitation time were applied to obtain the possible maximum recovery efficiency in the actual livestock wastewater.

4.1.4.1 Achieved Phosphate Recovery (S13)

This experiment was conducted at optimum pH 10 and Mg: P molar ratio of 4:1 within 60 minutes of precipitation time. Figure 4.7 shows the comparison in terms of maximum phosphate recovery in both synthetic and actual solutions under the same optimum conditions. Obviously, the result shows that the phosphate recovery efficiency in actual solution was only 47.62 %, while in synthetic solution was up to 84.18 %. Thence, it was undoubted that some factors were limiting the efficiency of struvite crystallization in the actual wastewater. One of the factors might be the assumption made to the untested initial concentration of $\mathrm{NH_4^+}$ and $\mathrm{Mg^{2+}}$ in actual wastewater. Due to the restriction of resources, only phosphate initial concentration was measured using spectrophotometer. Therefore, the concentration of $\mathrm{NH_4^+}$ in the initial actual wastewater could only be assumed as 12 times to $\mathrm{PO_4^{3-}}$ and without any further concentration adjustment. Besides, the amount of $\mathrm{Mg^{2+}}$ added into the actual wastewater were based on the optimum Mg: P molar ratio of 4:1, and assumed absence of $\mathrm{Mg^{2+}}$ in the actual wastewater. However, assumptions might be deviated from realistic condition. It was perhaps the assumed initial $\mathrm{NH_4^+}$ concentration was too low for the solution to reach the supersaturation level, or it was too high that could affect the struvite activity, either of these would lead to lower recovery efficiency. In addition, certain concentration of $\mathrm{Mg^{2+}}$ might already exist in the actual wastewater. The only way to determine the suspicions above was to measure the initial concentration of $\mathrm{NH_4^+}$ as well as $\mathrm{Mg^{2+}}$. It could be identified that the assumptions made were unable to fulfil the ideal molar ratio of P: N: Mg (1: 12: 4) in this case.

Another factor that limited the phosphate recovery performance would be the presence of existing ions in actual wastewater, especially the calcium ions ($\mathrm{Ca^{2+}}$). According to the literature, calcium ions could form by-products with phosphate or carbonate ion especially at high pH level which favours the struvite crystallization. Formation of undesired calcium by-product affected the phosphate recovery by lowering the supersaturation degree (Le Corre et al., 2005). Some others ion like $\mathrm{Cu^{2+}}$ and $\mathrm{Zn^{2+}}$would also bring negative impact to phosphate recovery. The presence of other existing ions would be identified and discussed in the Section 4.4.2.

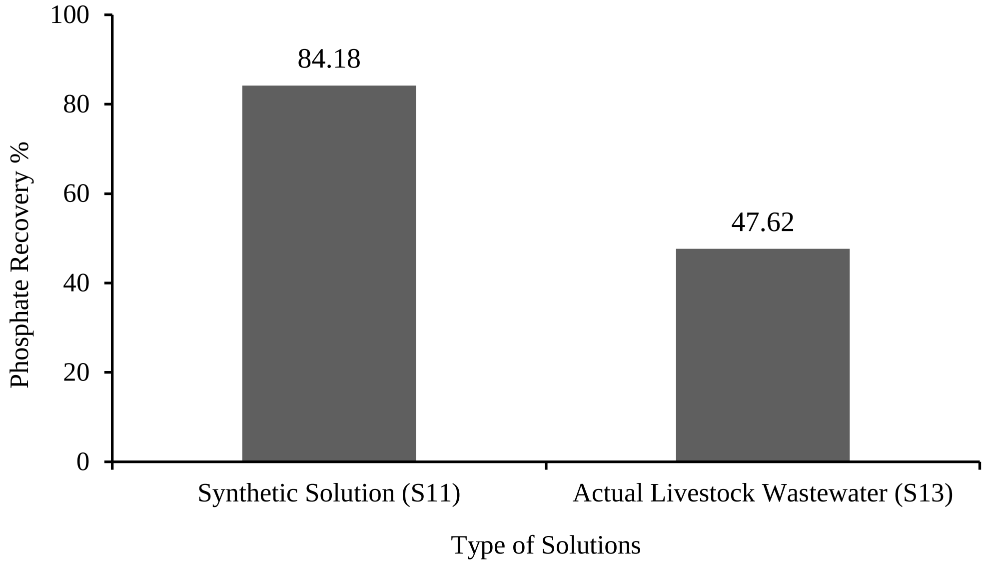


Figure 4.7: Phosphate Recovery of Different Types of Solution under same conditions (S11 & S13)

4.1.4.2 Production of Solids (S13)

The actual solids produced and theoretical struvite yield from both livestock wastewaters are shown in Figure 4.8. The estimated value of struvite yield was calculated as shown in Table 4.1. The struvite molecular weight is 245.41 g/mol. As mentioned in Section 4.1.4.1, external factor like the assumptions made that deviated the ideal molar ratio, and internal factors such as lower struvite activity with respect to the pure system could influence the crystallization efficiency in actual wastewater. Besides, it was observed that the actual weight of solids produced from synthetic and actual solutions were almost the same, which were 193.80 mg/L and 195.20 mg/L, and it was unusual as the phosphate recovery in actual wastewater was much lower compared in synthetic wastewater. On the others hand, as opposed to synthetic wastewater, the actual solid yielded in actual wastewater was 45 % higher than the theoretical struvite estimated. This obviously implied that the solids yielded in actual livestock wastewater consisted of undesired solids other than struvite only. In shorts, the purity of struvite was considerably low in the actual livestock wastewater.

In fact, it was hard to determine the composition of undesired solids that produced along with struvite, most probably they were suspended solids or organic matters. Although few times of pre-filtration were done before experiments begun, there were still some brown tiny impurities were observed in the actual wastewater. In alkaline conditions, suspended solids with negative charge would be adsorbed on the surface of the NH_4^+ and Mg^{2+}, which resulted in reduction of struvite activity (Suzuki et al., 2007). Also, Grini (2018) who used seawater as Mg^{2+} source in struvite crystallization studied the impact of suspended solids, and concluded that their impact was small, while both filtered and unfiltered reject water gave similar supersaturation. Apart from phosphate recovery, it was undeniable that the suspended solids would give large impact to the product purity. However, this depended on the concentration of suspended solids in individual.

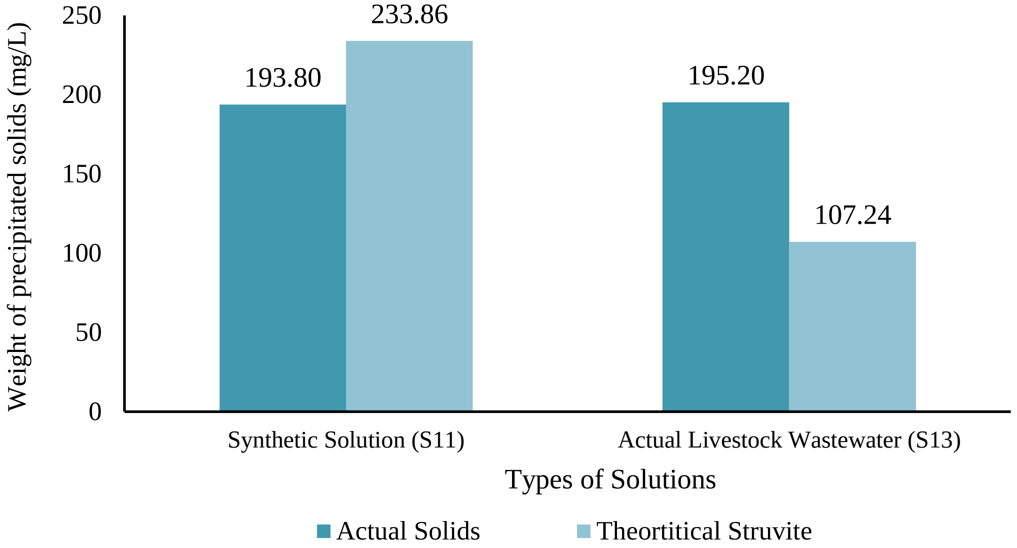


Figure 4.8: Yield Comparison on Actual Solids and Theoretical Struvite in Different Solutions (S11 & S13)

Table 4.1: Actual and Estimated Yield of Solids in Synthetic and Actual Livestock Wastewater

Set	**Wastewater**	**Initial Concentration (mg/L)**	**Final Concentration (mg/L)**	**Theoretical Struvite Yield (mg/L)**	**Actual Solids Yield (mg/L)**	**Different between Actual and Theoretical %**
11	**Synthetic**	107.5	17	233.86	195.80	16.27
13	**Actual**	87	45.5	107.24	195.20	45.06

4.1.5 pH Change at Different Mg: P molar ratios

Figure 4.9 illustrates the pH variation of different Mg: P molar ratios. The growth rate of the struvite was closely related to the pH change over the time. As crystallization proceeded, the pH of the solution tended to drop progressively due to the release H^+. Therefore, the rate of H^+ evolution indicated the formation rate of struvite (S. Muryanto, A.P.Bayuseno and E.Supriyo, n.d.). As shown in Figure 4.9, the pH curve of molar ratio 4:1 (red line) and 0.5:1 (black line) were reasonable, while pH curve of molar ratio 2:1 (blue line) and 1:1 (yellow line) show similar pH reduction rate, which implied that both possessing a similar crystal growth rate. Theoretically, the solution with larger molar ratio should gave greater and faster of pH reduction since the struvite formation was more efficient. On the others hand, there were pH rising trends at 30 and 40 minutes which were unusual, and poor handling and sensitivity of pH measurement were one of the major factors. As the overall pH reduction was only from 10 to 9.85 which considerably less, good sensitivity of pH meter was necessary in order to detect the insignificant pH drop from time to time, as well as good handling to prevent solution contamination. Besides, CO_2 from the air could be dissolved into the solution during the process. This leaded to the reduction of pH as well (Muryanto et al., 2017). Since few factors were identified that could lead to the pH reduction during the crystallization process, thus pH was unable to be a good indicator for growth rate study, unless a strict set-up of the experiment with minimize error was carried out. However, the result in this study was considered in good agreement with the theory, although some fluctuations in the pH curves were observed.

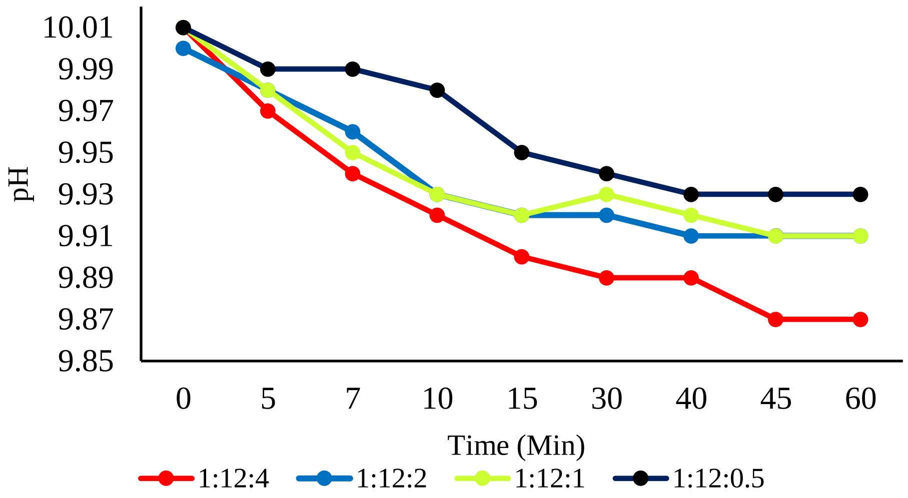


Figure 4.9: pH Change with Time at Various Mg: P molar ratios

4.2 Kinetics Study

It was important to study the speed of the struvite reaction. In order to study the kinetics, the initial, final and equilibrium concentrations of phosphate in the livestock wastewater were identified in Table 4.2. Due to the resource limitation, the concentrations of phosphate were only measured at 15, 40, 60 and 90 min, while the phosphate concentrations at 120 min was considered as equilibrium concentration in this case. Only synthetic livestock wastewater was conducted, and the optimum parameters pH 10 and Mg: P molar ratio of 4: 1 were adjusted precisely prior reaction begun. Based on literature, the struvite reaction always follows the first order reaction kinetics in order to determine the kinetics rate constant. The Equation 2.19 as shown in Section 2.5.1.3 that modified by Nelson, Mikkelsen and Hesterberg (2003) was used. Also, general second order reaction kinetics as shown in Equation 2.20 was studied as well to verify its applicability. Figures 4.9 and 4.10 show the fits of first and second order kinetics to the struvite reaction over the time.

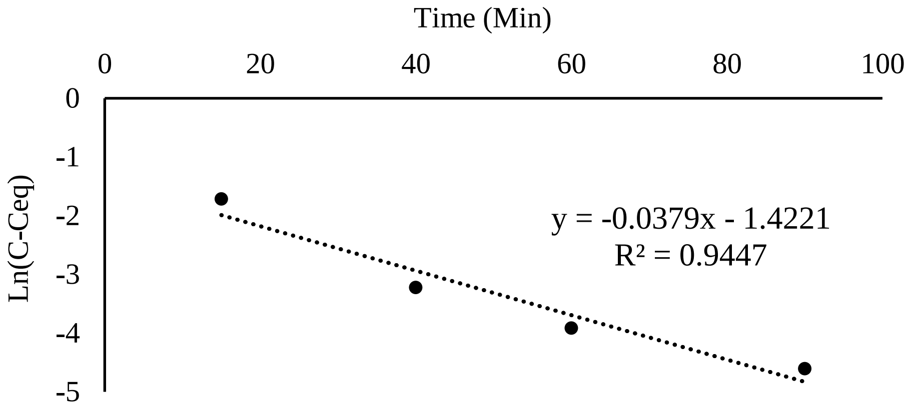


Figure 4.10: Fit of Linear First-order Kinetics Model over Time

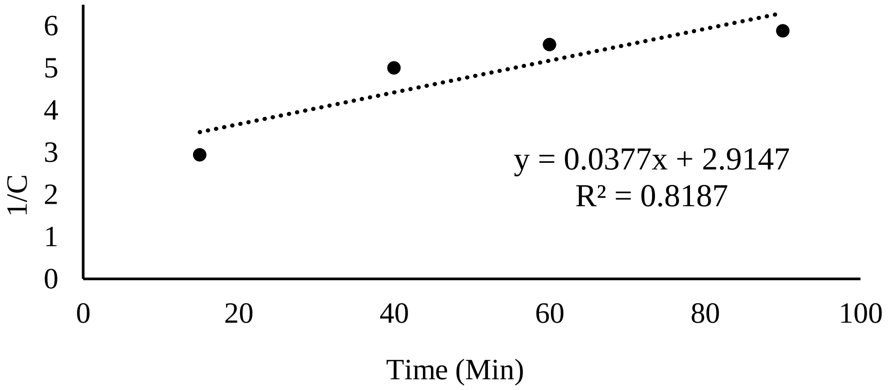


Figure 4.11: Fit of Linear Second-order Kinetics Mode over Time

Table 4.2: Phosphate Concentration in the Synthetic Solution over the Time

Time (min)	Concentration (mg/L)	Notes
0	104	Initial Concentration, C_O
15	34	Final Concentration 1, C
40	20	Final Concentration 2, C
60	18	Final Concentration 3, C
90	17	Final Concentration 4, C
120	16	Equilibrium Concentration, C_{eq}

Compare with the Figures 4.10 and 4.11, the first order kinetics model was reasonably fitted to the struvite reaction with the correlation coefficient R^2 of 0.9447; while the second order kinetics model was only 0.8187. These results matched well with the previous study of S. Muryanto, A.P.Bayuseno and E.Supriyo (n.d.). They studied both of the first and second order kinetics for the struvite crystallization, where their second order kinetics plot was always <0.90. Referring to Figure 4.10, the rate constant for struvite crystallization was found to be 2.274 h^{-1}. It was noticed that this value was lower than the rate constant as reported by Nelson, Mikkelsen and Hesterberg (2003), in which the value they obtained was 12.3 h^{-1} at pH 9 within 10 minutes. Besides, from the Figure 4.10, we able to see the rapid reaction rate occurred over the first 15 minutes, and phosphate removal rate was found to be 67 %, which from 104 to 34 mg/L. This implied that the first 15 minutes was the most crucial duration for the struvite formation as crystal nuclei began to develop and outgrowth. This was in agreement with the result illustrated by Figure 4.9 in Section 4.15, where the pH dropped significantly within first 15 minutes, clarified the close relationship between struvite growth rate and pH drop. On the others hand, the rate constant in this case was found lower with compared to the study of Nelson, Mikkelsen and Hesterberg (2003), but this was just because of the duration used in this case was 80 minutes longer, resulted in the overall rate constant was lower in comparison. Other than that, some factors which have been mentioned in Sections 4.1.1 to 4.1.5 could lead to lower rate constant in this case.

4.3 Phase Characterization

X-ray diffraction (XRD) can be used to study the purity of the products, by utilizing the lattice spacing and diffraction angle in the crystals to identify the compositions of the crystalline compounds. Four of the sample solids produced from different respective Mg: P molar ratios were analysed in order to study the Mg: P effects on the solid phase and purity of product. Samples from pH experiments (S1-S4) were not analysed because of no visible precipitants were observed at low pH condition (5 and 7), hence insufficient solid samples were retrieved for analysis. Figures 4.12 to 4.15 show the respective XRD patterns of samples from different Mg: P molar ratios. The black column bars in Figures 4.12 to 4.15 indicates the standard diffraction pattern of pure struvite which extracted from the XRD library in UTAR. Diffraction angle range used was 14° to 49°. Overall, the peaks of all molar ratios were almost identical in the way that the significant peak angles were the same along the X-axis (2-theta axis), at least for those significant peaks at 16°, 20.6° and 33°.

The different between the XRD pattern of samples and reference might be due to the fact that presence of co-precipitants in the sample. For instances, XRD pattern of all samples had a small extra peak at the 2 theta degree of about 44°, which was unable to observe in reference graph. It could not be ruled out that there were undesired co-precipitants, but since the peak intensity observed was not high, so that amount of co-precipitants should considerable less. One of the possible co-precipitants might be the struvite-K, since $\mathrm{KH_2PO_4}$ was one of the reagent used to synthesize the wastewater and it became source of $\mathrm{K^+}$. The ion replacement was possible because the ion radius of both $\mathrm{K^+}$ and $\mathrm{NH_4^+}$ were almost identical. However, the solubility of struvite-K was higher than struvite, which implied that the struvite with $\mathrm{NH_4^+}$ would have more preferable formation. Besides, the diffraction pattern of struvite-K was quite similar with struvite, as shown in Figure 4.16 which extracted from the result of Merino-Jimenez et al. (2017). Furthermore, the significant peaks at 2 theta degree of 16°, 20.6° and 33° of the sample with Mg:P molar ratio of 4:1, it was observed to have significant different with others in terms of peak intensities. This implies that the crystal size of struvite produced by molar ratio 4:1 was smaller, but at least the other small peaks gave similar intensities. The peak intensities are just the extent of crystallinity of the particular plane, and are not absolute, while the well-defined peak indicates the pure struvite produced from these experiments.

In fact, there were some errors in the XRD results since that only part of the solid was analysed with compared to the total precipitates including those that were unable to be retrieved. Within the expectation, the all XRD diffraction patterns indicate that the samples analysed were relatively pure struvite.

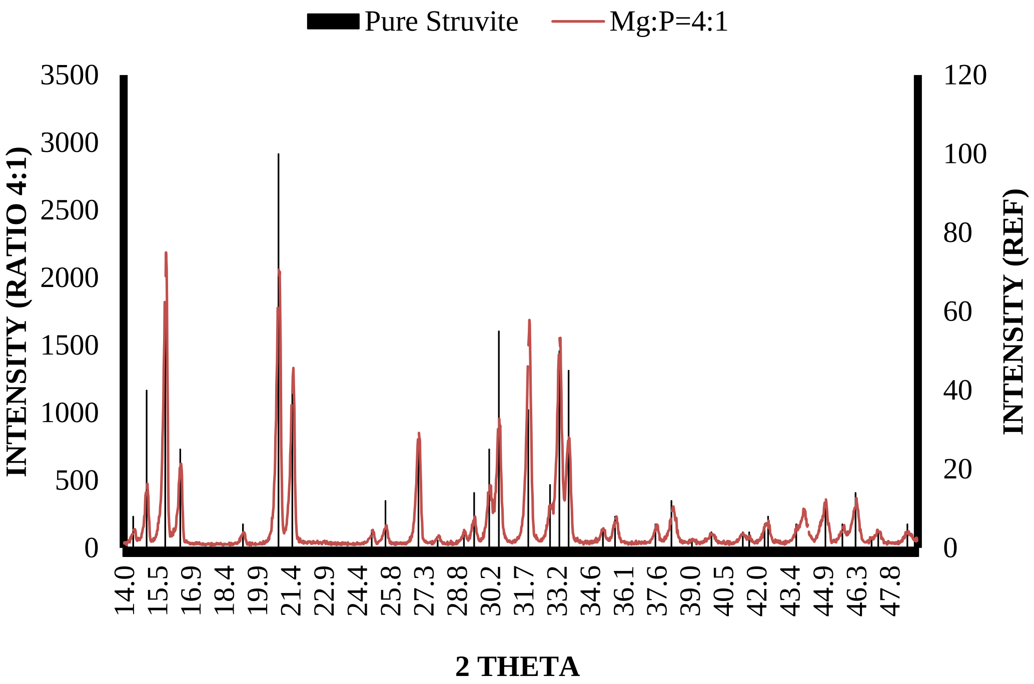


Figure 4.12: XRD Pattern of 4:1 Molar Ratio and Pure Struvite (S8)

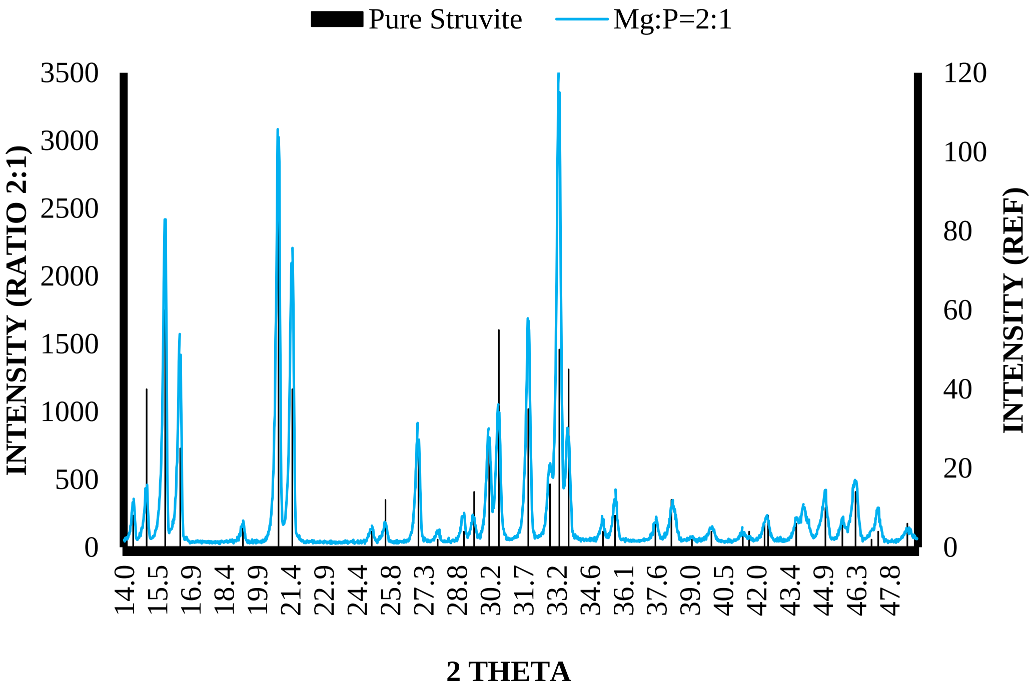


Figure 4.13: XRD Pattern of 2:1 Molar Ratio and Pure Struvite (S7)

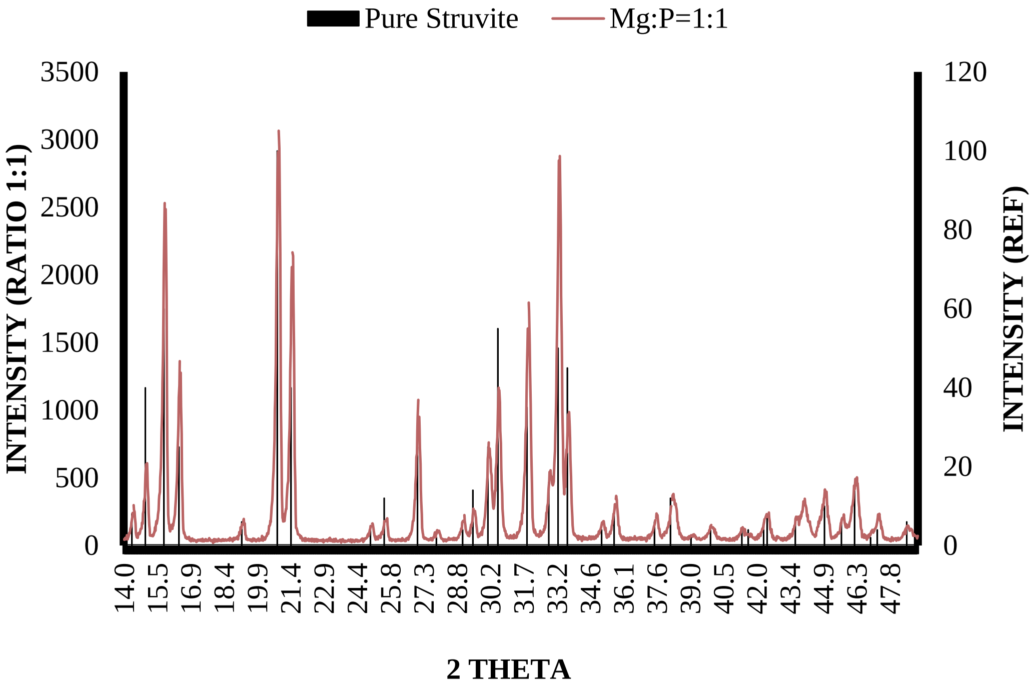


Figure 4.14: XRD Pattern of 1:1 Molar Ratio and Pure Struvite (S6)

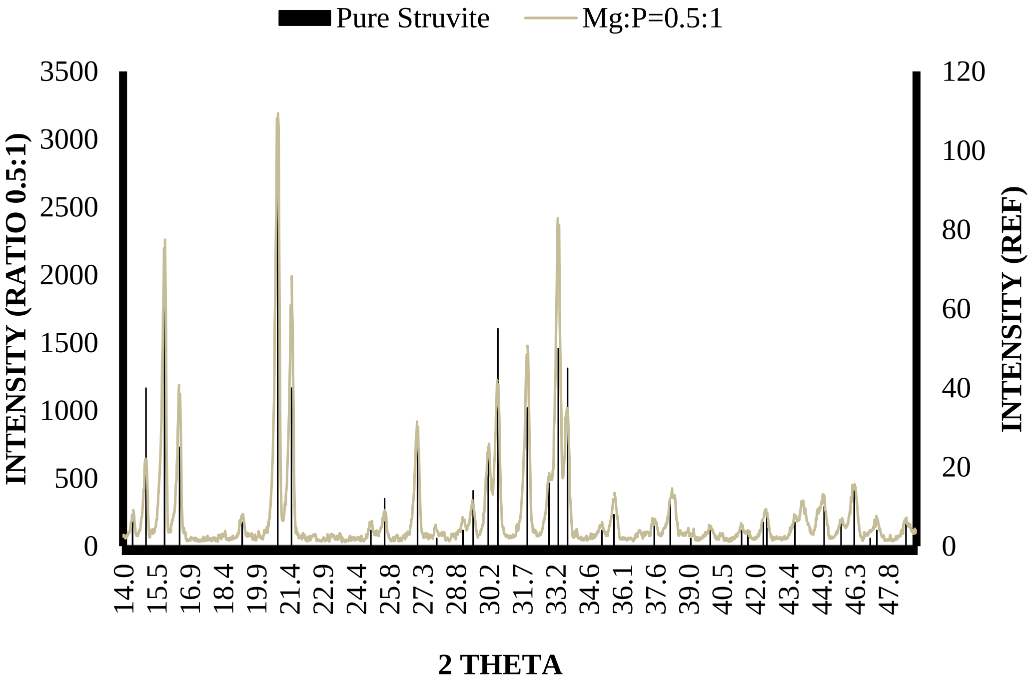


Figure 4.15: XRD Pattern of 0.5:1 Molar Ratio and Pure Struvite (S5)

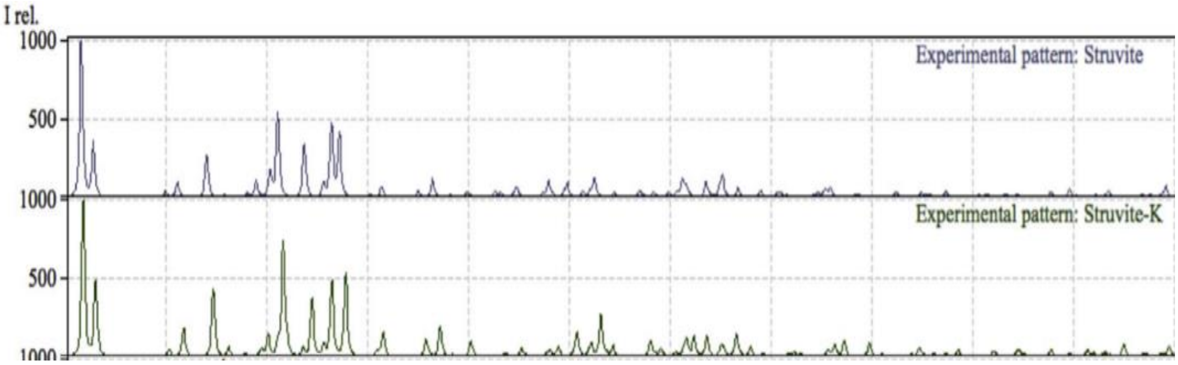


Figure 4.16: XRD Pattern of Struvite and Struvite-K (Merino-Jimenez et al., 2017)

4.4 Crystal Morphology

This section aims to study the crystal morphology of struvite produced from synthetic livestock wastewater under various Mg: P molar ratio condition (S5-S8). Also, the struvite produced from actual livestock wastewater (S13) under optimum conditions was tested as well. Crystal morphology study for different pH effects was unable to be carried out due to the insufficient solids produced at low pH for analysis.

4.4.1 Struvite Morphology in Synthetic Livestock Wastewater

Figure 4.17 shows the respective SEM images of struvite produced from synthetic livestock wastewater under various Mg: P molar ratio. As shown in figure, the struvite crystals were in white colours, with long rectangular shapes and some were hexagonal with rather smooth surface. The struvite crystal morphology in this case was in agreement with Maqueda (1994) who reported the similar morphology result (Maqueda, Pérez Rodríguez and Lebrato, 1994). From the Figure 4.17, similar sizes of the struvite crystal from different Mg: P molar ratio were observed, which implied that the effect of Mg: P molar ratio was insignificant to struvite morphology.

Figure 4.18 indicates the shapes of struvite (MAP) and possible co-precipitant to identify the components in the Figure 4.17. Basically, most of the solids crystal were observed to be struvite precipitate, although there were numbers of irregular, thin and long rod shape existed. Occasionally, some small crystal fragments occurred on the surface of struvite crystals. These might be due to the fact that formation of little amount of co-precipitants which were the extends of $\mathrm{KH_2PO_4}$ or $\mathrm{MgCl_2 \cdot 6H_2O}$. This could be further verified from the results of EDX analysis as shown in the Figure 4.19, at least $\mathrm{K^+}$ was detected, where the possible component to be formed could be struvite-K which was mentioned in Section 4.3. Otherwise, referring to the Perwitasari et al.

(2018), K^{+} was also possible to form sylvite (KCl) with Cl^{-} if both were existing in the solution simultaneously. However, it was observed from EDX results in Figure 4.19, if the amount of Mg^{2+} was high, Mg^{2+} tended to inhibit the K^{+} from forming struvite-K, which mean high Mg^{2+} condition favoured the formation of struvite. Overall, all the EDX results show the similar pattern with the results as reported by Perwitasari et al. (2018) and Muryanto (2017), at least for the significant component such as O, Mg and P.

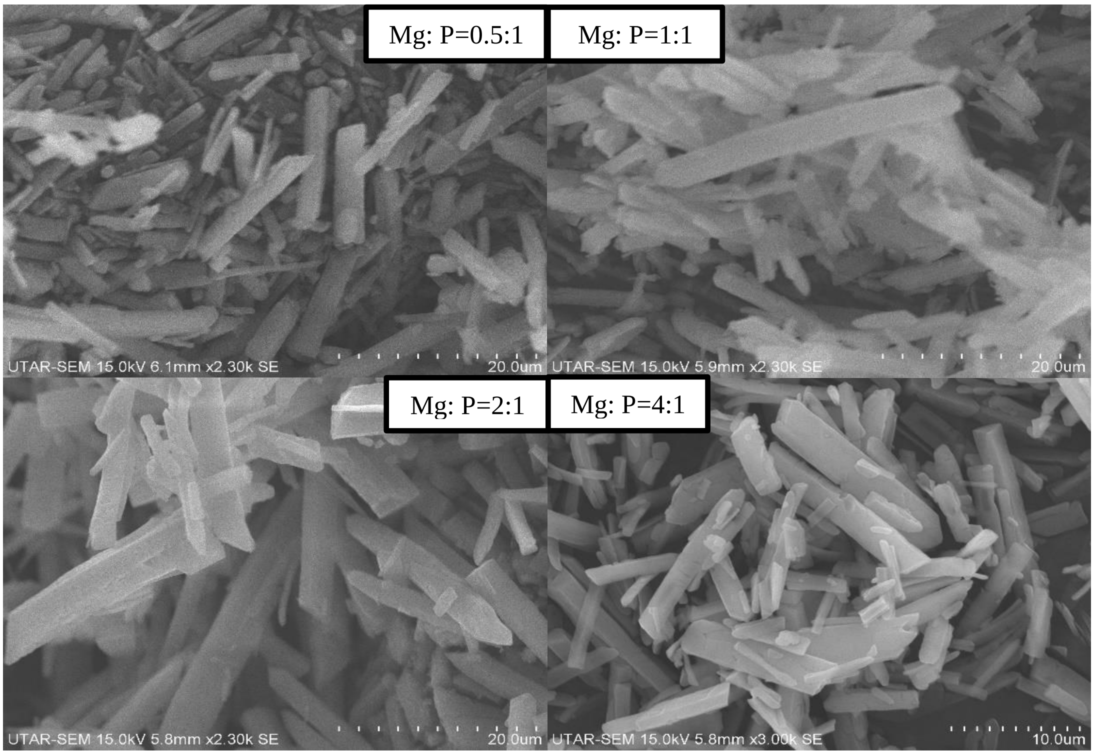


Figure 4.17: SEM Image of Struvite from Different Mg: P Molar Ratios (S5-S8)

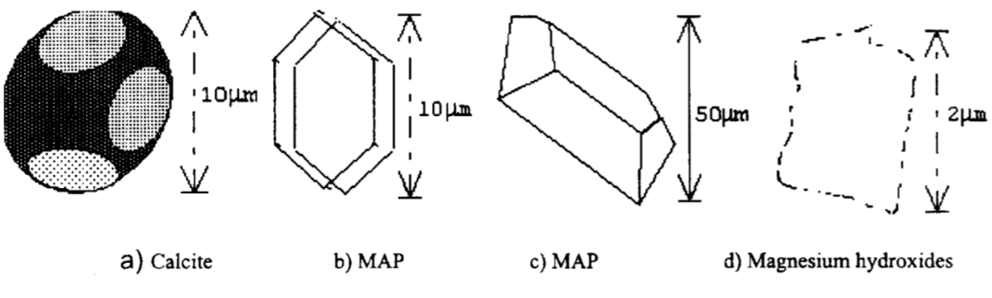
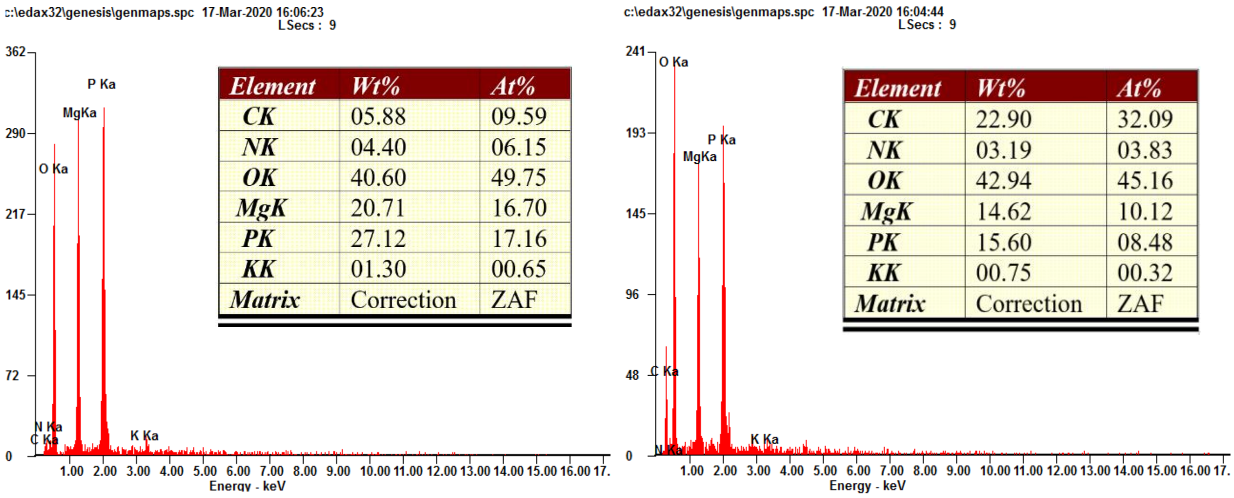


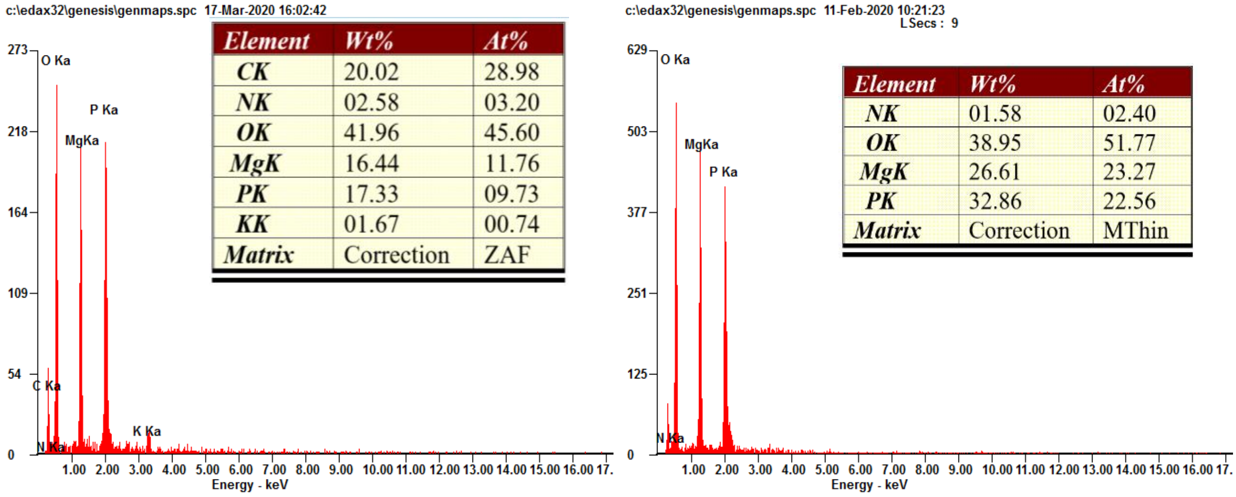
Figure 4.18: Comparison of Struvite and Related Crystal Morphology (Shin and Lee, 1998)



Element	Wt%	At%
CK	05.88	09.59
NK	04.40	06.15
OK	40.60	49.75
MgK	20.71	16.70
PK	27.12	17.16
KK	01.30	00.65
Matrix	Correction	ZAF

Element	Wt%	At%
CK	22.90	32.09
NK	03.19	03.83
OK	42.94	45.16
MgK	14.62	10.12
PK	15.60	08.48
KK	00.75	00.32
Matrix	Correction	ZAF

(a) Mg: P = 0.5:1 (S5) (b) Mg: P = 1:1 (S6)



Element	Wt%	At%
CK	20.02	28.98
NK	02.58	03.20
OK	41.96	45.60
MgK	16.44	11.76
PK	17.33	09.73
KK	01.67	00.74
Matrix	Correction	ZAF

Element	Wt%	At%
NK	01.58	02.40
OK	38.95	51.77
MgK	26.61	23.27
PK	32.86	22.56
Matrix	Correction	MThin

(c) Mg: P = 2:1 (S7) (d) Mg: P = 4:1 (S8)

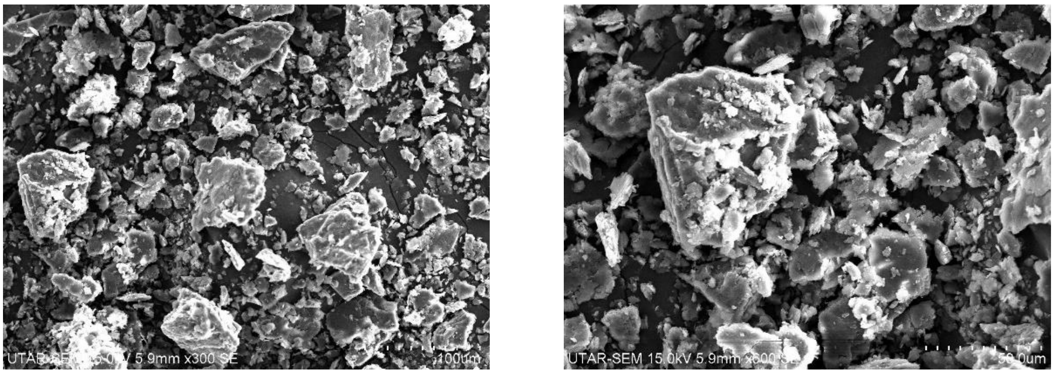
Figure 4.19: EDX Analysis of Struvite from Different Mg: P Molar Ratios (S5-S8)

4.4.2 Struvite Morphology in Actual Livestock Wastewater

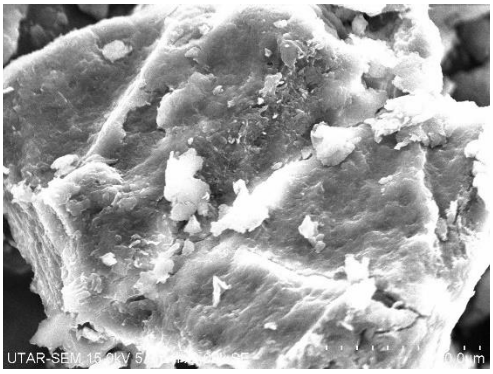
Figure 4.20 shows the SEM images of struvite yielded from the actual livestock wastewater under optimum parameter conditions, with 3 different magnifications provided. From the results, it was observed that the solid particle sizes in actual livestock wastewater were larger compared to synthetic livestock wastewater, however, it might be the extend of other impurities that existed in actual wastewater, with not just only formation of pure struvite. Instead of white powders, the solids produced from actual livestock wastewater were in brown colour after dried, which due to the presence of co-precipitants. Obviously, the most obvious different between the solids yielded from actual and synthetic wastewater was the shape of the crystals. Referring to the SEM images as shown in the Figure 4.20, instead of needle-like shape, the solids from actual wastewater were tended to amorphous with rough surface. With the presence of impurities during the crystallization, the nucleation process in actual wastewater was categorized as heterogeneous primary nucleation process where the struvite formed on the foreign surfaces such as TSS or others organic compounds. These constituents blocked the struvite crystal sites and inhibited its growth, and this became one of the reason of low phosphate recovery achieved in actual livestock wastewater. Besides, Ping et al. (2016) confirmed that lower phosphate removal rate with smaller struvite crystals were obtained if the TSS concentration was increased.

The particle size in actual livestock solution was found to be larger, but mostly it was because of the struvite grew and precipitated with others impurities. In fact, it was hard to determine the exact impurities that co-precipitated, however, it was undeniable that the Ca^{2+} was one of it. This was verified by EDX analysis in Figure 4.21. Le Corre et al. (2005) reported the negative impact brought by Ca^{2+} on the shape, purity and size of the struvite crystal. As higher concentration of the Ca^{2+} was introduced into the solution, the struvite crystal size tended to reduce and growth was inhibited, also leaded to formation of amorphous substance rather than pure struvite crystals. Figure 4.22 shows the SEM image obtain at Mg: Ca = 1:0 and 1:2 by Le Corre et al. (2005). From Figure 4.22 (ii), it was observed to be similar with Figure 4.20 here the particles mostly in amorphous and size was larger, as well were no longer in the coffin shape. These were because Ca^{2+} tended to represent Mg^{2+} to form calcium-phosphate salts such as tricalcium phosphate ($\mathrm{Ca_3(PO_4)_2}$), monenite ($\mathrm{CHPO_4}$) and etc (Grini, 2018).

In addition, a mistake was made in matching the element during the EDX analysis using computer. As circled (red colour) in the Figure 4.20, there was an unlabelled significant peak, where it could be estimated that was actually represented by the carbon (C). This could be identified by referring to the Figure 4.19 above, where the peak of N and C were located close. Also, livestock wastewater contained certain amount of organic matters which mainly composed of C. These C could form co-precipitants with Ca^{2+}, which called calcium-carbonate and it substantially reduce the purity of struvite product (Le Corre et al., 2005). Moreover, Capdevielle et al. (2016) conducted a study on the effect of organic matter such as colloids to the struvite crystallization. The result showed that organic matter gave positive to the crystal size, while brought negative effect to reaction kinetics. This was due to the mostly negative charge of colloids trapped on the ions like Mg^{2+}, NH^{4+}, Ca^{2+} and etc (Capdevielle et al., 2016). Complexes then would be formed which reduced the struvite purity and indirectly affected the phosphate recovery efficiency.

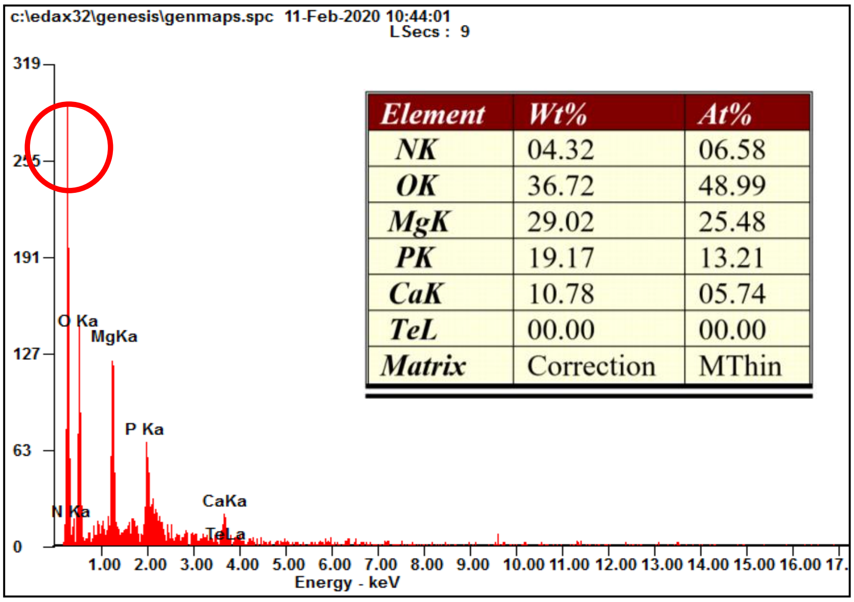


(a) Magnification 300x (b) Magnification 600x



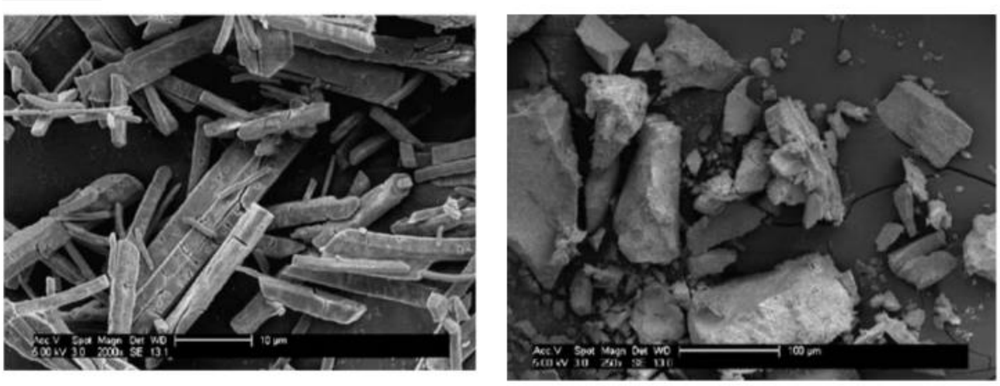
(c) Magnification 2.00kx

Figure 4.20: SEM Images of Struvite from Actual Livestock Wastewater (S13)



Element	Wt%	At%
NK	04.32	06.58
OK	36.72	48.99
MgK	29.02	25.48
PK	19.17	13.21
CaK	10.78	05.74
TeL	00.00	00.00
Matrix	Correction	MThin

Figure 4.21: EDX Analysis of Struvite from Actual Livestock Wastewater (S13)



(i) Mg: Ca at 1:0 (ii) Mg: Ca at 1:2

Figure 4.22: Effect of Ca^{2+} to Struvite Morphology (Le Corre et al., 2005)

4.5 Feasibility Study

Lab-scale struvite crystallization was carried out to determine the effects of each parameter on the phosphate recovery. Apart from this, it was important to assess the feasibility of this technique to the large-scale operation through few perspectives.

4.5.1 Effectiveness of Phosphate Recovery

Wastewater consists of different pollutants, as what intended in this study, the intensive discharge of phosphate rich livestock wastewater will be causing to eutrophication and other impacts to the environment. Besides, at many wastewater treatment facilities, struvite is a nuisance where it will deposit in the pipes, tanks and other mechanical equipment once it reaches the supersaturation threshold in the wastewater. Once happens, treatment plant will require costly down times for maintenance (Veolia, 2019). To date, struvite crystallization is one of the novel solutions to duel with these issues.

Struvite crystallization is not only treated as phosphate removal tools, as well it is used to recover the phosphate becomes struvite in the wastewater treatment. According to the results as discussed in the Sections 4.1 to 4.4, although in experiment where actual livestock wastewater was applied, the result achieved was not desired, these could not conclude that the struvite crystallization technique was unreliable. In fact, there were various factors that were restricting the performance of struvite crystallization in this study, which were all been mentioned in Sections 4.1 to 4.4, and the effects of these factors could be minimized by further improvements. On the others hand, Table 4.3 shows the efforts of various researchers to recover the phosphate from real livestock wastewater through struvite crystallization. Generally, all of the studies that are shown in Table 4.3 were able to achieve phosphate recovery rate of at least 85 %. It can be reasonably concluded that struvite crystallization is a promising tool with reliable phosphate recovery rate even under practical conditions.

Table 4.3: Effectiveness of Struvite Crystallization in Real livestock Wastewater

Samples	**Initial Phosphate Concentration**	**P: N : Mg Molar Ratio**	**pH**	**Reaction Time**	**Phosphate Recovery [%]**	**References**
Animal Manure Wastewater	60.01	1:63.5:1	8.09	4 hr	92.82	(Suzuki et al., 2007)
Animal Manure Wastewater	189.9	1:1:0.8	8.35	4 hr	96	(Zhang et al., 2009)
Animal Manure Wastewater	128	1:1:1.2	9	1 hr	98	(Muryanto and Bayuseno, 2014)
Anaerobic Bio-P Sludge	137.1	1:5.6:3	7.5	1 hr	85	(Grini, 2018)

4.5.2 Usefulness of Product

The product of struvite crystallization is important as an eco-friendly fertilizer source. Compared to chemical fertilizer, its major advantage is the slow release characteristic due to its low solubility. It can guarantee a slow but steady nutrient supply for a long period (Spuhler, 2019). Cheaper and natural source of P and N with the absence of heavy metals, pharmaceuticals compound as well as unpleasant odour make it becomes a high potential raw material for fertilizer. Moreover, it can be effectively taken up by plants and able to maintain the soil nutrient balance (Reza et al., 2019). By recovering the phosphate which is a limited resource in the Earth that is facing depletion, it can reduce the phosphate from mining, and this is really helpful in ensuring the agricultural sustainability. Other than the fertilizer sector, struvite can be treated as the source of PO_4^{3-} and Mg^{2+} during the microwave wastewater treatment in order to reduce the need of Mg^{2+} salts. The inputted struvite will dissociate into PO_4^{3-}, $NH^{4+}$and Mg^{2+} through a process called microwave irradiation, which are then recycled again into the wastewater influents for struvite crystallization (Cho, Lee and Ra, 2009). This can greatly reduce the production cost of struvite.

Struvite as a product of crystallization process helps in gaining additional profits if is treated as a fertilizer. Based on the online website called Alibaba (2020), the price of struvite fertilizer is about RM 1800/Metric Ton. However, the price of the struvite product is mainly based on the size of crystal and purity.

4.5.3 Operational Considerations

Although the struvite crystallization is considerably promising, there are still several design considerations such as formation of struvite crystal, pH elevation and the types of magnesium source use (Adnan, Koch and Mavinic, 2003).

In a denser wastewater condition where process happens, larger size of struvite crystal is required in order to settle successfully to enable harvesting. Several researchers reported that the size of crystal increased as time went. However, it would be more practical to use seeding material for commercial precipitation. A number of various seeding material are purposed for struvite crystallization, this including sand, quartz, magnesia clinker, pumice stone and bone charcoal (Durrant et al., 1999). However, additional cost is needed for the seeding materials. On the others hand, another issue occurs when the struvite forms successfully. According to Borgerding (1972), struvite formation was formed on the walls of the plant infrastructure. Retrieval of struvite is mostly impossible once the deposition has occurred. Some efforts can be performed involving mechanical cleaning using high pressure jet, acid washing, heat treatment and fluidization regime. However, the acid washing and heat treatment are not sustainable since they are time consuming and operational complex. Fluidization can be carried out by forcing air at the bottom into the reactor involving the use of some seeding. The pressurised influent flow must be sufficiently to achieve fluidization of the bed. However, the highly pressurized flow will be causing crystal breakage and this reduces the particle size (Seckler et al., 1996).

Apart from these, suitable process conditions such as pH and Mg^{2+} source are necessary for effective struvite formation. This requires the chemical dosing system to manipulate the pH and concentration of Mg^{2+} in the wastewater. Few suggestions that are currently in practice for chemical dosing system involve the metal salt precipitation and biological methods (Durrant et al., 1999). In terms of metal salt precipitation, the chemicals must be stored in a tank at the plant side. The tank is equipped with dosing apparatus and feed control system for the process. For the biological phosphorus removal system, it just takes the supplement of metal salts as an emergency measure in case the biological system fails (Durrant et al., 1999).

In terms of pH adjustment, normally caustic chemicals such as commercial grade sodium hydroxide (NaOH) is one of the good selection with the price of only RM 24.00/kg (Craftiviti, 2020). However, due to the large buffering capacity of supernatant or digester centrate, large amount of NaOH is needed for pH adjustment, and cost will be greatly increased. This always becomes one of the concerns to treatment system. The additional cost of NaOH can contribute up to 97% of the total chemical costs (Jaffer et al., 2002). Also, the ionic strength of the solution will be affected by the caustic chemical addition, so the dissolution ability of the struvite is increased as well (Fattah et al., 2010). Considering the dissolved CO_2 is always saturated in the wastewater, Cohen and Kirchmann (2004) proposed the method to raise the pH to alkaline level by removing the CO_2 from the wastewater, while this can reduce the dosage of caustic chemical use in struvite crystallization. Fattah et al. (2010) confirmed several advantages of CO_2 stripping. In addition to the larger struvite crystal is produced, this method can act as a heat exchanger to uniformly distribute the temperature to desired level for the process. Moreover, low caustic chemical usage leads to lower conductivity with lower ionic strength. This eventually results in better dissolve of Mg^{2+}, NH^{4+} and PO_4^{3-} which is good for the crystallization. Application of this method reduces the addition of caustic chemical up to 65 %, which implies about half of the operational cost can be saved. There is no doubt that CO_2 stripping can help in achieved process pH of 10 with the aid of little caustic chemical. Meanwhile, CO_2 stripping is aligned with sustainable development.

The type of magnesium salts is crucial as well in the struvite crystallization. There are various sources such as $MgCl_2$, $MgSO_4$, MgO and $Mg(OH)_2$. Since the unavailability of $MgCl_2$, $MgSO_4 \cdot 7H_2O$ was selected as the magnesium source in the present study. Among the all, $\mathrm{MgCl_2}$ is considered to have the best solubility, and hence shorter reaction time is required, but it will require higher pH of 8.5 or greater to perform effective struvite crystallization (Stratful, Scrimshaw and Lester, 2001). For the MgO and $\mathrm{Mg(OH)_2}$, although it is able to raise the solution pH and less expensive compared to $\mathrm{MgCl_2}$ and $\mathrm{MgSO_4}$, but they are less soluble in solution, which means lower crystallization rate can be obtained. Therefore, a more vigorous mixing of the reaction solution is needed, but this will reduce the crystalline size (Zeng and Li, 2006). To date, many studies have addressed alternative magnesium sources to make this process fully aligned with sustainable development. Some studies suggested using brine, bittern, by-product from salt manufacturing, or seawater (Quist-Jensen, Jørgensen and Christensen, 2016). The use of different kinds of $\mathrm{Mg^{2+}}$ sources mainly depends on the post-treatment of the wastewater treatment system with the consideration of heavy metals content and other undesired ions (Sakthivel, Tilley and Udert, 2012). Seawater as $\mathrm{Mg^{2+}}$ source is the most widely studied topic among the all suggestions above. It is a good $\mathrm{Mg^{2+}}$ source, however it requires additional seawater treatment such as nanofiltration, membrane distillation or membrane crystallization to concentrate $\mathrm{Mg^{2+}}$ by separating it from $\mathrm{Cl^-}$ that will create problems for the downstream of wastewater treatment. According to the analysis by Quist-Jensen, Jørgensen and Christensen (2016), they concluded that the treatment cost of either membrane distillation or membrane crystallization was higher than nanofiltration, but both of these techniques reduced the volume of seawater brine required, and this was able to beneficial from the green chemistry point of view. Also, the cost of membrane distillation and membrane crystallization could be eventually reduced by the method of low-grade heat in the wastewater treatment system (Quist-Jensen, Jørgensen and Christensen, 2016). Also, another study by Grini (2018) showed that the use of seawater as $\mathrm{Mg^{2+}}$ source gave an overall cost reduction of about 20 %.

Last but not least, cost feasibility shall be considered to ensure the overall project that is surplus in terms of profit. Molinos-Senante et al. (2011) applied a conventional cost analysis methodology called cost-benefit analysis (CBA) to determine the net profit by adding the internal benefit together with external benefit. Internal benefit involves those operational savings and sale of recovered phosphate minus internal costs such as investment value with respect to treatment system. On the others hand, external benefit is related to the difference between positive and negative externalities. However, it was difficult to perform cost feasibility study with respect to whole struvite crystallization system due to the information gap from online resources.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This report studied the effects of different parameters, including pH, Mg: P molar ratio and precipitation time on the performance of struvite crystallization. Among all the parameters, the effects of pH and Mg: P molar ratio were significant. The optimum pH value was observed to be 10. On the others hand, the higher Mg: P molar ratios gave better phosphate recovery efficiency, and it was found that Mg: P molar ratio of 4:1 was the best ratio in this study. In addition, 60 minutes of precipitation time was the best duration for maximum phosphate recovery efficiency. However, different maximum phosphate recovery efficiencies were achieved in both synthetic and actual livestock wastewaters, which were 84.18 % and 47.62 % under the same conditions. The XRD analysis results showed the struvite produced with different Mg: P molar ratios in the synthetic livestock wastewater was relatively pure, while there was only little difference in terms of peak intensity. The SEM analysis demonstrated that the effect of different Mg: P molar ratios in the synthetic livestock wastewater on surface morphology of struvite was insignificant, and most of the struvite crystals were present in coffin shape with white colour. In addition, amorphous crystals with brown colour were observed on the struvite produced from the actual livestock wastewater, indicating that the low purity that was mainly caused by co-precipitants. The EDX analysis demonstrated the presence of undesired C and Ca^{2+} in the actual livestock wastewater. Based on the all solids analysis, it could be concluded that the low phosphate recovery achieved in actual livestock wastewater might be due to the presence of impurities, such as foreign ions, TSS, organic matters, and etc. Another reason would be the wrong assumption made to the initial concentration of NH_4^+ and Mg^{2+} in the actual livestock wastewater due to the resource limitation. The feasibility study confirmed that the struvite crystallization is in fact cost feasible and environmental friendly for the phosphate recovery from the livestock wastewater.

5.2 Recommendations for Future Work

Throughout the whole study, several recommendations are provided for the improvements of the study. For a lab-scale struvite crystallization, the selection of Mg^{2+} source with high solubility is crucial for effective phosphate recovery, where $MgCl_2$ becomes the best choice. Apart from this, from the green chemistry point of view, the study of renewable sources like seawater which is an alternative source of Mg^{2+} can be studied as well. Besides, the study on the source of pH increment that is cost effective and eco-friendly can also be carried out. In addition, the range of pH conducted should be narrower in order to determine a more precise optimum pH for struvite crystallization. For better solid recovery during vacuum filtration, a membrane or fibre filter paper with fine pore size with just 0.2 µm can be considered, but the rate of filtration will certainly be slower. Struvite crystallization requires P: N: Mg molar ratio of 1:1:1, and hence accurate initial concentration measurements of each ion in the actual livestock wastewater must be carried out. Next, since different wastewater consists of different impurities, thus more types of wastewater can be conducted in the study to determine the feasibility of struvite crystallization in other wastewater conditions. In order to give a more practical result, it is recommended to build a lab-scale operation with continuous feed of wastewater and magnesium source, as well as pH auto-adjustment to provide better estimation of the parameters impacts on the struvite crystallization. In terms of economic feasibility study, an estimation of cost feasibility is recommended via cost estimation software that was applied by Le Corre et al. (2007) in the study.

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APPENDICES

Appendix I

The Table A.1 shows the actual data values of pH experiments (S1 to S4). Each set (S) of experiment required to be duplicated for accurate results. The initial phosphate concentration (IC) in synthetic wastewater was measured by spectrophotometry. The Mg: P molar ratios and precipitation time used were remained constant. After the experiment, the final concentration of phosphate (FC) in synthetic wastewater was tested by spectrophotometer, while the solids retrieved were weighted with electronic scale. Initial weight (IW) indicates the net weight of the filter paper, and the final weight (FW) represents the weight of filter paper contained with solids. The sample calculation of phosphate removed % and removed solid are shown in Appendix V. The duplicated result values of each set of experiment were taken as average value, and are shown in the Table A.2. The calculations of the average theoretical removed solid are shown in Appendix V as well.

Table A.1: Actual Data of pH Experiments (S1-S4)

Sets	**pH**	**P:N:Mg**	**Time (min)**	**IC (mg/L)**	**FC (mg/L)**	**Recovered P [%]**	**IW (mg)**	**FW (mg)**	**Actual Recovered Solid (mg)**
1	***5***	**1.12.1**	**60**	102	101	0.98	522.60	523.80	1.200
	5	**1.12.1**	**60**	108	106	1.85	533.00	535.00	2.000
2	***7***	**1.12.1**	**60**	128	116	9.38	523.10	528.10	0.005
	7	**1.12.1**	**60**	107	98	8.41	509.20	517.30	0.008
3	***10***	**1.12.1**	**60**	114	49	57.02	508.40	572.20	63.800
	10	**1.12.1**	**60**	119	52	56.30	494.00	551.70	57.700
4	***12***	**1.12.1**	**60**	115	96	16.52	523.10	534.60	11.500
	12	**1.12.1**	**60**	123	101	17.89	499.60	510.50	10.900

Table A.2: Average Results obtained from pH Experiments (S1-S4)

Sets	Average Recovered P [%]	Average Actual Recovered Solid (mg/L)	Average Theoretical Recovered Struvite (mg/L)
1	1.40	3.20	3.88
2	8.90	13.10	27.13
3	56.70	121.50	170.55
4	17.20	22.40	52.97

Appendix II

The Table A.3 provides the actual data values of Mg: P molar ratio experiments (S5 to S8). The duplicated result values of each set of experiment were taken as average value which are shown in the Table A.4. Same, the sample calculations of phosphate removed % and removed solid are shown in Appendix V.

Table A.3: Actual Data of Mg: P molar ratio Experiments (S5-S8)

Sets	pH	P:N:Mg	Time (min)	IC (mg/L)	FC (mg/L)	Recovered P [%]	IW (mg)	FW (mg)	Actual Recovered Solid (mg)
5	**10**	***1:12:0.5***	**60**	110	78	29.09	507.10	544.30	37.200
	10	***1:12:0.5***	**60**	132	90	31.82	505.10	551.20	46.100
6	**10**	***1:12:1***	**60**	114	49	57.02	508.40	572.20	63.800
	10	***1:12:1***	**60**	119	52	56.30	494.00	551.70	57.700
7	**10**	***1:12:2***	**60**	113	39	65.49	525.50	621.50	96.000
	10	***1:12:2***	**60**	110	34	69.09	495.70	592.30	96.600
8	**10**	***1:12.4***	**60**	110	17	84.55	503.70	604.50	100.800
	10	***1:12.4***	**60**	105	17	83.81	502.40	595.40	93.000

Table A.4: Average Results obtained from Mg: P molar ratio Experiments (S5-S8)

Sets	**Average Recovered P [%]**	**Average Actual Recovered Solid (mg/L)**	**Average Theoretical Recovered Struvite (mg/L)**
5	30.45	83.30	95.61
6	56.66	121.50	170.55
7	67.29	192.60	193.80
8	84.18	193.80	233.86

Appendix III

The Table A.5 provides the actual data information of precipitation time experiments (S9 to S12). The duplicated result values of each set of experiment were taken as average value and are shown in the Table A.6. Same, the sample calculations of phosphate removed % and removed solid are shown in Appendix V.

Table A.5: Actual Data of Precipitation Time Experiments (S9-S12)

Sets	**pH**	**P:N:Mg**	**Time (min)**	**IC (mg/L)**	**FC (mg/L)**	**Recovered P [%]**	**IW (mg)**	**FW (mg)**	**Actual Recovered Solid (mg)**
9	**10**	**1.12.4**	***15***	105	39	62.86	499.80	584.40	84.600
	10	**1.12.4**	***15***	103	40	61.17	509.20	589.20	80.000
10	**10**	**1.12.4**	***40***	105	18	82.86	498.50	604.50	106.000
	10	**1.12.4**	***40***	103	23	77.67	493.30	585.10	91.800
11	**10**	**1.12.4**	***60***	110	17	84.55	503.70	604.50	100.800
	10	**1.12.4**	***60***	105	17	83.81	502.40	595.40	93.000
12	**10**	**1.12.4**	***90***	109	15	86.24	502.40	605.50	103.100
	10	**1.12.4**	***90***	104	16	83.50	499.80	593.80	94.000

Table A.6: Average Results obtained from Precipitation Time Experiments (S9-S12)

Sets	Average Recovered P [%]	Average Actual Recovered Solid (mg/L)	Average Theoretical Recovered Struvite (mg/L)
9	30.45	83.30	95.61
10	56.66	121.50	170.55
11	67.29	192.60	193.80
12	84.18	193.80	233.86

Appendix IV

The Table A.7 provides the actual data information of actual livestock wastewater experiments (S13). The IW and FW values were higher in this case since several filter papers were used for vacuum filtration. The duplicated result values of each set of experiment were taken as average value which shown in the Table A.8. Same, the sample calculations of phosphate removed % and removed solid are shown in Appendix V.

Table A.7: Actual Data of Actual Livestock Wastewater Experiments (S13)

Sets	pH	P:N:Mg	Time (min)	IC (mg/L)	FC (mg/L)	Recovered P [%]	IW (mg)	FW (mg)	Actual Recovered Solid (mg)
13	**10**	**1.12.4**	**60**	91	46	49.45	1998.7	2104.8	106.1
	10	**1.12.4**	**60**	83	45	45.78	2011.1	2100.2	89.1

Table A.8: Average Results obtained from Actual Livestock Wastewater Experiments (S13)

Sets	Average Recovered P [%]	Average Actual Recovered Solid (mg/L)	Average Theoretical Recovered Struvite (mg/L)
13	47.62	195.20	107.24

Appendix V

Sample calculations that required to be obtained the results in Appendix I to IV are provided. The 1st set (not 2nd set from duplicated) of experiment S1 was used as sample calculation. The phosphate recovery (%) were obtained using Equation 3.1:

$$
\begin{aligned}
P\ Recovery\ [\%] &= \frac{C_{initial} - C_{final}}{C_{initial}} \times 100\% \\
&= \left(\frac{1.02 - 1.01}{1.02}\right) mg/L \times 100\% \\
&= 0.98\ \%
\end{aligned}
$$

The actual solid yield is basically the mass different between initial weight of filter paper and final weight after filtration:

$$
\begin{aligned}
\text{Actual Recovered Solid (mg)} &= \mathrm{W_i} - \mathrm{W_f} \\
&= (523.8 - 522.6)\mathrm{mg} \\
&= 1.2\ \mathrm{mg}
\end{aligned}
$$

while concentration unit $\mathrm{mg/L}$ is required:

$$
\text{Actual Recovered Solid (mg/L)} = \frac{1.2\ \mathrm{mg}}{0.5\ \text{L of deionized solution}} = 2.4\ \mathrm{mg/L}
$$

The average phosphate recovery (%) was obtained from the average value of initial and duplicated set (0.98 % and 1.85 % as shown in Table A.1), so the average value of phosphate recovery was **1.4 %.** Same for the actual solid recovered ($\mathrm{mg/L}$), the average was **3.2 mg/L** for S1. Then, the molar concentrations of initial and final phosphate in the synthetic solutions were calculated based on the given molar mass of phosphate = 94971.4 mg/mol:

$$
\mathrm{M_i} = 102\frac{\mathrm{mg}}{\mathrm{L}} \div\ 94971.4\frac{\mathrm{mg}}{\mathrm{mol}} = 0.00107\frac{\mathrm{mol}}{\mathrm{L}}\ \text{of}\ \mathrm{PO_4^{3-}}
$$

$$
\mathrm{M_f} = 101\frac{\mathrm{mg}}{\mathrm{L}} \div\ 94971.4\frac{\mathrm{mg}}{\mathrm{mol}} = 0.00106\frac{\mathrm{mol}}{\mathrm{L}}\ \text{of}\ \mathrm{PO_4^{3-}}
$$

The following Equation 3.2 could be used to calculate the theoretical recovered struvite (mg/L), with given struvite molar mass 245410 mg/mol:

$$\begin{aligned}\mathrm{Yield}\left[\frac{\mathrm{mg}}{\mathrm{L}}\right] &= (\mathrm{M}_{\mathrm{initial}} - \mathrm{M}_{\mathrm{final}}) \times \mathrm{MW}_{\mathrm{struvite}} \times 1000\mathrm{mg/g} \\ &= (0.00107 - 0.00106)\frac{\mathrm{mol}}{\mathrm{L}} \times 245410\frac{\mathrm{mg}}{\mathrm{mol}} \\ &= 2.58\ \mathrm{mg/L}\end{aligned}$$

The average value of theoretical recovered struvite (mg/L) could be obtained with the initial and duplicated set values of theoretical recovered struvite:

$$\begin{aligned}\text{Average Theoretical Struvite Recovered}\left(\frac{\mathrm{mg}}{\mathrm{L}}\right) &= \frac{2.58 + 5.17}{2} \\ &= \mathbf{3.88\ mg/L}\end{aligned}$$

Appendix VI

The figures of solution with respects to the struvite crystallization status are provided. Figure A.1 shows the initial and final appearance of synthetic wastewater after crystallization, while actual livestock wastewater is shown in Figure A.2. Also, Figure A.3 shows the solids (struvite) obtained from different types of livestock wastewater after filtration.

(a) Initial Solution (b) Final Solution

Figure A.1: Appearances of Experimental Synthetic Livestock Wastewater

(a) Initial Solution (b) Final Solution

Figure A.2: Appearances of Experimental Actual Livestock Wastewater

(a) Synthetic Solution (b) Actual Solution

Figure A.3: Solids Product Yielded from Different Solutions