INVESTIGATION OF FLUORIDE POLLUTANT REMOVAL FROM WASTEWATER

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INVESTIGATION OF FLUORIDE POLLUTANT REMOVAL FROM WASTEWATER

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A project report submitted in partial fulfilment of the requirements for the award of Bachelor of Mechanical Engineering with Honours

Lee Kong Chian Faculty of Engineering and Science
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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 **"INVESTIGATION OF FLUORIDE POLLUTANT REMOVAL FROM WASTEWATER"** was prepared by **KO SIN YEE** has met the required standard for submission in partial fulfilment of the requirements for the award of Bachelor of Mechanical Engineering with Honours at Universiti Tunku Abdul Rahman.

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ABSTRACT

Recently, the iron and steel, semiconductor and copper industries have discharged significant amount of wastewater that contains high amount of fluoride into the water system. Several methods can be used to remove fluoride from wastewater to fulfil the discharge requirements, such as reverse osmosis, electrocoagulation, and adsorption. Coagulation is one of the most commonly used method in the industry as it has simple and low operation cost. Response Surface Methodology (RSM) was applied to investigate the fluoride removal from wastewater by using three different coagulants (aluminium sulfate, ferric chloride, and PAC) under different pH and coagulant dosage. Two parameters including pH (3-11) and coagulant dosage (30 %v/v – 70 %v/v) were investigated and optimized to obtain the best response of fluoride removal. Poly Aluminium Chloride is found to have the highest fluoride removal, which is 96.5 % under the optimum condition of pH 7 and coagulant dosage of 50 %v/v (2500 mg/L). Aluminium sulfate has the same optimum condition as PAC, but aluminium sulfate has lower fluoride removal, which is 95 %. The sludge mass produced by PAC is 0.0672 g. This is lower than the mass of the sludge produced by aluminium sulfate, which is 0.5538 g. The optimum treatment condition of each coagulants were applied into real industrial wastewater. The result shows that PAC has the highest fluoride removal, 85.13 % with the lowest mass of sludge formation, 0.1364 g. By conducting this study, the coagulant that has high fluoride removal with low sludge formation can be found. Besides that, the treated wastewater will be able to protect the environment and contribute to the achievement of SDG 6. In addition, the fluoride in the wastewater produced by semiconductor, iron and steel, and copper industries can be removed.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS / ABBREVIATIONS

hr	hour
min	minutes
s	second
rpm	revolutions per minute
ppm	parts per million
g	gram
C_o	initial concentration of fluoride solution, mg/L
C_e	equilibrium concentration of fluoride solution, mg/L
A	pH
B	Coagulant Dosage, mg/L
L	litre
Cl^-	Chloride Ion
F^-	Fluoride Ion
OH^-	Hydroxide Ion
Al^{3+}	Aluminium Ion
HCl	Hydrochloric Acid
NaOH	Sodium Hydroxide
NaF	Sodium Fluoride
$FeCl_3$	Ferric Chloride
$Al_2(SO_4)_3$	Aluminium Sulfate
PAC	Poly Aluminium Chloride
DOE	Department of Environmental
CAGR	Compound Annual Growth Rate
NF	Nanofiltration
RO	Reverse Osmosis
RSM	Response Surface Methodology
SDG	Sustainable Development Goal
LH	Luteinizing Hormone
FSH	Follicle-Stimulating Hormone
TH	Thyroid Hormone

EL	Estrogen Level
ER/AR	Ratio of Estrogen Receptor to Androgen Receptor
ACAS	Activated Carbon of Avocado Seeds
CCD	Central Composite Designs
R	Coefficient of Correlation
R^2	Coefficient of Determination

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 General Introduction

Rapid grow of urbanization and industrialization has contributed to the large volume of water usage without proper management, which has caused the wastewater discharge issue. According to the report published by European Investment Bank in 2022, the wastewater production is estimated to grow by 24 % and 51 %. In addition to that, it is estimated that more than 80 % of the wastewater is released into the water system without proper treatment globally. As the wastewater production has grown, the untreated wastewater that is released will be the major problem to the countries in the future. Recently, government and people have paid attention to this issue as it will bring harmful effect to both environment and human. The market size of wastewater treatment has grown as the wastewater produced by industries increases from year to year. Figure 1.1 shows the water and wastewater treatment market size for 2022 to 2032. The market size of the water and wastewater treatment is estimated to expand at compound annual growth rate (CAGR) of 6.9 % after 10 years from 2023. One of the element that drives the growth of market is the growing trend of the reduction of freshwater resources (Water and Wastewater Treatment Market, 2023). Figure 1.2 shows the percentage of the untreated wastewater for different income level countries in 2015 and the predicted value for 2030. From the graph, it is shown that the high income countries will have lower percentage of untreated wastewater.

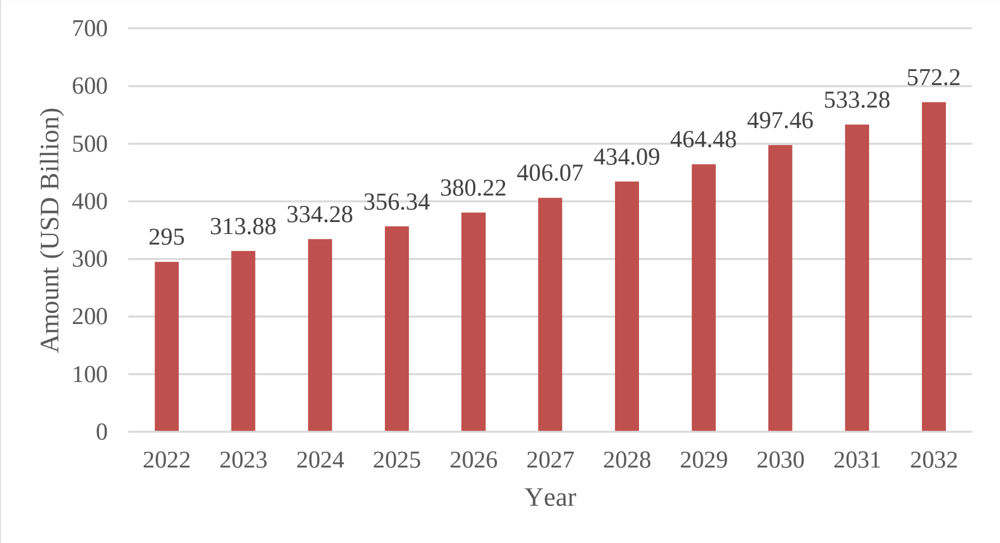

Figure 1.1: Graph of Water and Wastewater Treatment Market Size, 2022 to 2032 (Water and Wastewater Treatment Market, 2023).

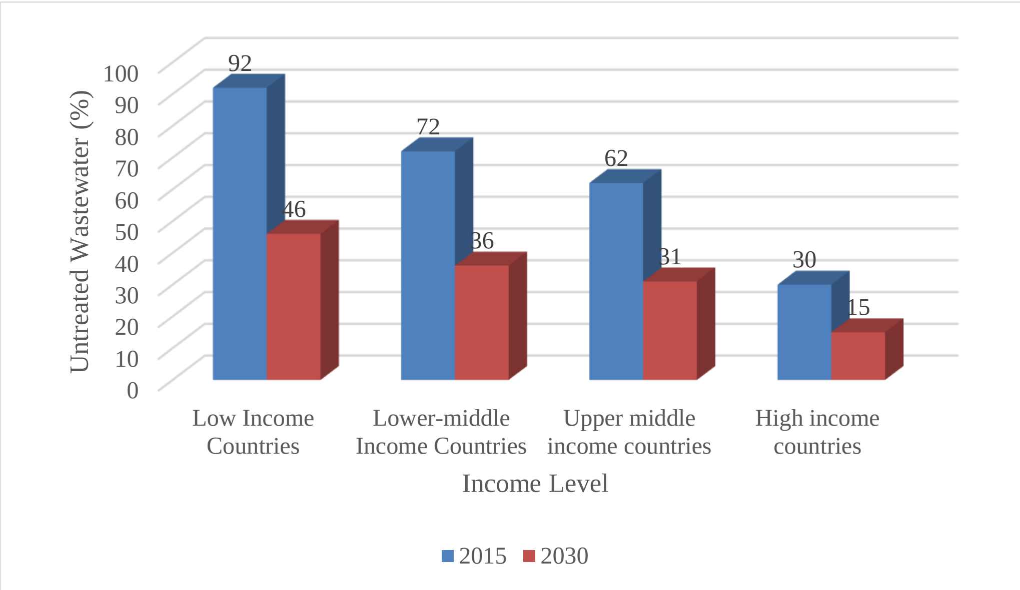

Figure 1.2: Percentage of Untreated Wastewater for Different Income Level Countries in 2015 and Aspirations for 2030 (50 % Reduction vs 2015 Baseline) (European Investment Bank, 2022).

There are a few pollutants that can be found in the wastewater which will cause environmental pollution. These pollutants include nitrogen, phosphorus, fluoride and more. The focus of this study is to remove the fluoride pollutant from the wastewater. As people are moving towards the digitalization era, the computers and electronic devices have become more common in daily life. The demand towards the electronic devices have become higher, which means the demand towards electronic chips and other component in the electronic devices also has increased. In the semiconductor industry, fluorine is used as the cleaning agent to remove particles and films on the surfaces of the vacuum chamber and process apparatus (Stockman, 2016). Besides that, the etching of semiconductor will use the hydrofluoric acid which will produce the fluoride wastewater. Other than that, the iron and steel, copper and zinc producing industries discharge fluoride wastewater in large volume as it is the chemical by-products that will be produced during the production process. The blast furnace is used in iron and steel production and the iron concentrates that consists of fluoride are produced during the ore mining, sintering and smelting processes. Meanwhile in copper smelting, the acidic wastewater with high concentration of fluoride is produced during the flue gas acid generation and extraction of rare metal. In the zinc smelting process, the fluoride is found in the zinc concentrates. Figure 1.3 shows the average percentage of the fluoride concentration in the water system for various countries.

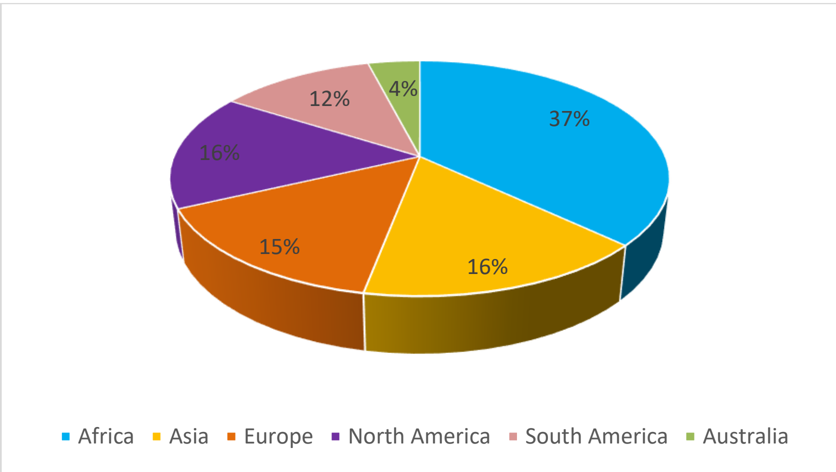

Figure 1.3: Average Percentage of Fluoride Concentration in Water System for Various Countries (Uddin, Ahemd and Naushad, 2019).

To protect the water bodies and human health, the fluoride concentration needs to be reduced to the allowed value before it is discharged. The government has set the rules and regulation based on this issue to solve the problem that is caused by wastewater that contains fluoride. The fluoride discharge limits are not more than 20 ppm if it will be discharged into public sewer system. If it is discharged into aquatic environment, the discharge limit is lower, which is not more than 5 ppm (Fluoride Removal from Industrial Wastewater Using Advanced Chemical Precipitation and Filtration, 2019). According to WHO, the concentration of fluoride in the drinking water must be between 0.5 to 1 ppm (Khatibikamala, et al., 2010). In Malaysia, the permitted fluoride concentration in industrial wastewater effluent is 2 ppm for Standard A and 5 ppm for Standard B (Department of Environment, 2010). If the wastewater is discharged into upstream of a water supply intake, it should follow the Standard A meanwhile, if it is discharged downstream, it should follow Standard B.

To be in line with the government policy, protect the environment and ensure the clean water supply in future, the fluoride pollutant in the wastewater must be removed or reduced before it is discharged. Few methods that have been used to remove the fluoride can be categorized into different types, which are physical processes (screening, filtration and membrane filtration). Besides that, chemical processes which includes chemical precipitation, ion exchange and adsorption are also widely used. The biological processes such as bioprecipitation and biosorption are also one of the method that will be chosen. In this study, physical processes and chemical processes will be used to remove the fluoride pollutant. Precipitation, coagulation and solid separation are mainly used in the past but the sludge produced by the precipitation process has caused another problem to the management (Diwani, et al., 2022). Researchers are putting effort to find the method that are efficient, low-cost and friendly to environment. As the resource of earth is reducing nowadays, researchers are moving towards biomass resources. Recently, people are using activated carbon and activated alumina to remove the fluoride in the wastewater. As the technology is not mature and the cost is considered high, more research studies are needed to be done.

1.2 Importance of the Study

Wastewater pollution is a global issue. If it is not treated and discharged properly, it will cause damage to the environment and human’s health. To ensure that the next generation still be able to use the clean and safe water resource, the treatment of wastewater is essential. In addition of that, a proper wastewater treatment will protect the environment from water pollution so that clean and reusable water will be available for next few decades.

After the fluoride removal from wastewater, the water can be reused in the manufacturing process and new water source is no longer required. By having a suitable method and coagulant to remove the fluoride pollutant in large scale, the factory is able to treat the wastewater to ensure that it fulfils the government requirement and reduce the harm to the environmental.

In a nutshell, by doing this study, the possible result will be:

- The fluoride pollutant can be removed from the wastewater
- Avoid water pollution that is caused by fluoride pollutant
- Protect the environment and water system
- To achieve the Sustainable Development Goal (SDG) 6, which is Clean Water and Sanitation
- Reuse the wastewater that is treated and save the water resource
- Find out the suitable material that will be able to remove fluoride

1.3 Problem Statement

To date, people are still doing research to find the most suitable method and coagulant to remove fluoride from wastewater. Some research studies show that the coagulant is able to reduce the concentration of fluoride to the required value but there will be by-product, which is sludge that will cause another problem. Besides that, some coagulant is only able to remove fluoride at specific temperature or pH value. To fulfil the government required value of fluoride removal, a few parameters are needed to be determined such as pH value and coagulant dosage to make sure that fluoride can be removed from the wastewater before it is discharged into the water bodies. In addition to that, the formation of sludge also needs to be minimized.

1.4 Aim and Objectives

The aim of this study is to investigate the material that can be used to remove the fluoride pollutant from wastewater. The objectives are stated below:

- To compare fluoride removal using different coagulants (aluminium sulfate, ferric chloride, and PAC)
- To determine the parameters (pH and coagulant dosage) of coagulant for fluoride removal using response surface methodology
- To minimize the sludge formation

1.5 Scope and Limitation of the Study

This study mainly focused on the physical and chemical method, which is also known as coagulation and flocculation to remove the fluoride pollutant from wastewater. Other than that, there are a few methods that can be used to remove fluoride, which includes biological method. But, as the time and resources are limited, this study will consider to use physical and chemical methods only.

1.6 Contribution of the Study

The contribution of this study includes the findings of the coagulant that has high fluoride removal with low sludge formation. By this, this finding will enhance the understanding of water treatment through coagulation. Besides that, the treated wastewater will help to protect the environment and contribute to the achievement of Sustainable Development Goal (SDG) 6. In addition, it helps the semiconductor, iron and steel, and copper industries to remove the fluoride from the wastewater.

1.7 Outline of the Report

There are some chapters included in this report, which are literature review, methodology and work plan, results and discussion, conclusions and recommendations.

Literature review will discuss the history of the water treatment and the pollutant that can be found in the wastewater, especially fluoride. Besides that, the effect of the untreated wastewater is also included in the literature review. There are some methods that can be used to perform fluoride removal. The coagulation and flocculation is the focus in this study. A few type of coagulants are introduced and the condition for the coagulation process are also discussed. In addition, the Response Surface Methodology (RSM) technique is also discussed in this section. A few researches have used RSM to optimize the study.

Methodology and work plan section will cover the steps of the experiment that were done to determine the performance of fluoride removal of each coagulants. There are two types of wastewater used, which are artificial wastewater and real industrial wastewater. The performance of each coagulant will be investigated by using both the artificial and real industrial wastewater. A few apparatus that were used in this experiment were introduced in this chapter. Besides that, the method to determine the final fluoride concentration is also written in this section.

Next, the result and discussion part will evaluate the fluoride removal and sludge formation by each coagulants. The effect of pH and dosage have been included in the discussion section. The result of the Scanning Electron Microscope (SEM) is included and discussed to support the result of the final fluoride concentration. The characteristic of the sludge formed were also determined by using the analysis. The three dimensional response surface and equation formed have been included in this section to predict the response and summarize the result obtained in this study.

Lastly, the chapter of conclusions and recommendations summarize all the findings of this study. This section verifies the achievement of the objective for this study. To improve the study conducted, some suggestions are stated to overcome the shortcomings of the study.

CHAPTER 2

LITERATURE REVIEW

2.1 Current Trend of Wastewater issue

In recent years, the issue of wastewater management has emerged as a critical global concern. As the rapid grow of urban population, the industrial activities will cause the increment of wastewater discharge. The environmental impact of untreated wastewater will affect aquatic ecosystems, human health and the environment.

2.1.1 Water Treatment in Human History

Water plays an essential roles in human history since the era of Neolithic, around 7000 B.C. Not only human need the water to survive, other living things such as animal and plants also need the water as basic needs. The first system that was used by the primitive human to get cleaner water was by letting the water to settle in vessels or wells to undergo decantation and improve the physical properties of the water. From time to time, more methods were expanded out such as filtering by using sand, exposing the water to sunlight or boiling it. The biggest breakthrough was done by the Greeks and Egyptians. The former used the carbon filters and the history of Egyptian can be tracked until 1500 B.C. when they explain how minerals and plants were used to do the facilitation of water’s precipitation and clarification. This technique is used until now and is known as flocculation.

The first two water treatment plants which used sedimentation and filtration through sand and carbon, were introduced into the operation on a large scale which aims to supply the modern cities with water in Glasgow in 1804 and in Paris in 1806. Human start to have new finding when a French bacteriologist demonstrated that the existence of numerous microscopic organisms that can transmit diseases are present in the water. This had shown that by only improving the physical aspects of water is not enough. From this time, human start to learn to use disinfectants. Chlorine was firstly used in 1908 and ozone was starting to be used too. When the water treatment had spread to the developed countries such as England, France, Germany, there was a finding showed that the life expectancy had increased by 10 to 15 years. The chlorine not only eliminates the microorganisms and it also prevents the proliferation of mould and algae at the same time (Navas, 2019). This is where the history of human treating the water started, from only improving the physical appearance to eliminate the microorganism that is invisible to the naked eyes.

With the improvement of human life and the revolution of industrial, water is no longer only used to keep living things alive, but is also used in manufacturing and industry. The water is used during the production process which is when creating the products or cooling the equipment. Large amounts of water are used in the food, paper and chemicals industries. According to EPA (2022), high-tech industry such as semiconductor uses considerable quantities of water to manufacture the products. The process of cleaning and rinsing silicon chips will uses up to billions of gallons of water per year. If there is large amount of water used in the industry, it also means that a large amount of wastewater is also being discharged from the industry. Usually, most of the wastewater will be discharged into the drainage system and the river nearby.

Industrial wastewater is the common by-product produced by the industrial, after the production process done and this process water has been used, it is considered as waste and need to be treated before it is discharged. Without treatment, the high concentration of impurities contained in the wastewater will causes the water pollution at that area. There are a few of impurities in the wastewater that will cause water pollution and threaten the balance of ecosystem. The wastewater usually contains high concentration of nitrogen, phosphorus, metals (lead, mercury) which depends on the type of wastewater and source of the wastewater. The common chemical pollutant that can be found in the wastewater is nitrogen, phosphorus, fluoride and more. Until now, there are more advanced technology that is used to remove the pollutant which includes reverses osmosis, membrane separation, adsorption, biosorption and more. As human has found that the resources of earth is decreasing from time to time, we have opt to use perpetual resource to save the resource. Now, people is doing more research to use the biomass to do the wastewater treatment and reduce the sludge produced during treatment process. Currently, the commonly used adsorption included coconut fibre and activated carbon. Activated carbon is the only adsorbent that is that is efficient in highly acidic condition (pH lower than 3.0) (Melidis, 2015).

2.1.2 Fluoride Pollutant in Wastewater

There are a few of pollutants that are found in the wastewater that caused the water pollution problem. Fluoride is one of the commonly found pollutants in the wastewater. Usually, fluoride can be found in the industrial wastewater from various sources, which includes fertilizer manufacturing plants, aluminium smelters, surface treatments facilities for copper, aluminium and stainless steel and more (CONCEPT_ENVIRO, 2016).

2.1.2.1 Fluoride in iron and steel metallurgy

The ore mining, beneficiation, sintering and smelting processes are some essential steps in the steelmaking industry. During those processes, the iron concentrates that is produced will contain fluoride. When the wastewater and sludge are discharged to the environment, the fluoride will be exposed to the environment. The fluorite and sodium fluoride are used to reduce the melting point of slag. The process of electro slag has emitted high amount of fluoride gases as high as 118.47 tons of fluoride for the annual gases emissions.

2.1.2.2 Fluoride in Copper Smelting

The generation of acidic discharge water with high level of fluoride solution is associated with the flue gas acid production. In addition to that, the process of metal extraction in the copper smelting process will also produce the acidic effluent water. The fluoride concentration can be exceeding 10,000 mg/L (Wan, et al., 2021). To treat this wastewater, lime neutralization is commonly used in the copper-smelting industry. However, there is disadvantages of the method which is inefficient fluoride removal and production of large amount of sludge.

2.1.2.3 Fluoride in Semiconductor

In the semiconductor process, the hydrogen fluoride is the main material needed to complete the etching. In another word, the hydrogen fluoride is also called as ‘etching gas’. The hydrogen fluoride will cut off the unwanted parts of the material. After that, the hydrogen fluoride will also use to clean up the impurity. The impurity will damage the circuit and affect the performance. The usage of fluoride-based acid in the semiconductor industry has generated significant quantities of wastewater that contains fluoride.

2.2 Effect of Fluoride Wastewater

The impact of the untreated fluoride wastewater has become significant environmental and public health concern. Fluoride will be beneficial in small quantities for dental health, but the excessive fluoride in water system will cause the negative effect to the environment and human health.

2.2.1 Effect to the Environment

The one of the main causes of the water pollution is the discharge of untreated wastewater. The excess of nutrients are released into the environment via untreated wastewater, which directly cause the fouling of natural ecosystems and disruption of aquatic life. According to Zelko (2018), the by-products of fertilizer production, which are hydrogen fluoride and silicon tetrafluoride gases were the main causes of the most noxious air pollution in central Florida in the 1970s. The discharged of the untreated wastewater will cause harm to the ecosystems that lives nearby the water bodies or organism that lives depends on the water. All the living things in the complex web (animals, plants, bacteria and fungi) will be affected. As water pollution will promote the algae growth in the water, the oxygen levels will reduced as the algae has cover the surface of water. No sunshine is able to shine through the water. Without oxygen, the plants and animals are suffocated and this creates “dead zones”. In addition to that, as industrial wastewater will usually contain the toxic chemicals and heavy metals, these harmful substances will reduce the organism’s life span and their ability to reproduce (Denchak, 2023). When the situation get worse and worse, the quality of organism living in the water will reduce and the species may face the risk of extinction.

As some process will introduce fluoride into the process, the industry will discharge the wastewater that has high concentration of fluoride. In Taiwan, the concentration of untreated wastewater from semiconductor industry can be as high as 500 to 2000 ppm (Ochoa-Herrera, et al., 2009). Fluoride content can be toxic to aquatic life. For wild fish population that lives in hard water, the rainbow and brown trout species were calculated to be 5.1 and 7.5 ppm respectively (Environmental Pollution, n.d.). If the level of fluoride in the water has exceed the value, the aquatic life will face the risk of losing their life as the fluoride will accumulate in the bone tissue. Not only aquatic life is affected by untreated wastewater, the mammal's lives are also affected by the fluoride in the wastewater. The fluoride may be taken into the bodies of the animals through vegetation, soil and drinking water. If the animals drink the water from the river that the untreated fluoride wastewater is discharged, the fluoride might flow into the bodies via water. The accumulation of the fluoride in their bodies (mainly in teeth and bones) will damage their health and productivity (Bunce, 1985). Health issues, including excessive salivation, nasal discharge, difficulty in breathing, seizures and even fatalities will occur with a range of 2.5 to 58 hr, were documented in buffalo calves following with the ingestion of 200-400 mg of sodium fluoride per kilogram of body weight. (Ranjan and Ranjan, 2015).

2.2.2 Effect to Human Health

The wastewater will cause many harmful effects if it is not treated and discharged properly. The microorganisms such as viruses, bacteria, protozoans may cause the water-borne diseases that will cause major public health problem. According to World Health Organization (2022), nearly 829,000 people are estimated to pass away because of diarrhoea due to unsafe drinking-water, poor sanitation and hand hygiene. In 2017, more than 220 million individuals needed preventive treatment as they suffered from schistosomiasis, which is one of the disease caused by the parasitic worms that is contracted through exposure to the untreated water. Not only microorganisms will cause the harmful effect on human and environment, the chemical substance in the water also will cause negative effect on human health. It can be toxic, corrosive and acidic. In other word, the wastewater treatment is essential to avoid it cause damage to human health and body.

Excess of fluoride in the wastewater will cause adverse effects on human health when it is discharged into body of water. The problems such as lipid metabolism disorder, myelosclerosis, dental and skeletal fluorosis are mainly caused by the fluoride in the water system (Wang, et al., 2021). If the fluoride wastewater is discharged into body of water without filtering out excess concentration of fluoride, it will flow into human body via drinking water. According to Brazier (2018), the 0.7 ppm concentration of fluoride is considered as the best for dental health. If the concentration is more than 4.0 ppm, it may be hazardous to human. Exposure to high concentration of fluoride during teeth developing time will cause problem of mild dental fluorosis. Other than teeth, the excessive fluoride may also cause harm to bone. The bone disease is known as skeletal fluorosis. The bones will having the risk of fractures as it will become hardened and less elastic from time to time. This is due to the fundamental component found in dental enamel and bones which is known as hydroxyapatite. The hydroxide ions are replaced by the fluoride and will forms harder compound which is known as fluorapatite. If fluoride is taken for a long period, the formation of fluorapatite is more significant, leading to more stiffer and brittle bone and teeth. As the fluoride concentration is up to 3.0 ppm, the dental fluorosis will converted to skeletal fluorosis. A study was done in India and it was found that more than 21 % of adolescent and 36 % of adult who lives at the area which the drinking water has fluoride concentration of 1.5 ppm will face the problem of dental fluorosis. The age range of 17-22 years are having the fastest spreading rate of dental fluorosis which is 77.1 %.

In addition, the fluoride wastewater problem also lead to the reproductive problem. The increasing exposure of fluoride will increase the luteinizing hormone (LH) level and follicle-stimulating hormone (FSH). This will also decrease the thyroid hormone (TH), reduce estrogen level (EL), and disturbed the ratio of estrogen receptor to androgen receptor (ER/AR). It is also observed that a reduced circulating testosterone concentration in a male patient that has the issue of skeletal fluorosis. The sodium fluoride (NaF) will damage the mouse germ cells and cause the increment in sperm abnormality and chromosomal aberrations in the primary testicular cells.

Not only the fluoride affect the male reproductive system, it also harms female reproductive system. It causes stromal congestion and ovarian follicles problem. Besides that, the blood vessels of female are also dilated (Ahmad, et al., 2022).

2.3 Treatment Used in Fluoride Removal

From previous statement, it is shown that the fluoride bring harms to not only environment, but also to human health if it is exposed more than the limit value. As people aware of this problem, more researches were done to find out the strategies to reduce the concentration of fluoride in wastewater. At early stage (1900-early 1970'S), people only focus on removing suspended particles, treating biodegradable substances, and removing the microorganisms. As time flows to early 1970's to about 1990s, the earlier tasks were continued with larger levels, with additional tasks, which are protecting the aesthetic value of the environment and decrease the harms towards human health (Rajasulochana and Preethy, 2016). The traditional method of fluoride removal has helped to remove the fluoride from wastewater to a certain extent. As a result, the treatment will also produce sludge that may cause another problem to the industry. In addition to that, cost is also another concern of the industry. Therefore, people is putting the effort in research to find the method that is low-cost and environmental-friendly. To fulfil the requirement, the new green technical methods are being introduced to the world. However, there are some limitations such as lacking of infrastructure, lacking of financial support, and low technical know-how that become barrier to some country to apply the new advanced technology. In summary, there are few pros and cons of each method in fluoride removal task.

2.3.1 Reverse Osmosis

Reverse osmosis (RO) has gained its popularity when the issue is about managing and treating wastewater from industrial processes. It works by filtering out the unwanted impurities from the wastewater. The working principle of reverse osmosis is identical with other water purification technology, such as ultrafiltration. The idea that differ them is the reverse osmosis applied pressure to overcome osmotic pressure. A tank is divided into two sections by a semi-porous membrane that only allows certain substances to flow through. The hydraulic pressure will push the water pass through the membrane and left some contaminants at another section. It will block the monovalent ions, multivalent ions, bacteria and more from passing through the membrane. It has better filtration effect as compared to microfiltration, ultrafiltration and nanofiltration. The most commonly used surface film for reverse osmosis is 150 μm (Dutta, Arya and Kumar, 2021). The pH and temperature will highly influence the membrane performance and thus affecting the fluoride removal. As reverse osmosis has the ability to remove all the ions, on the other hand, it becomes the major drawback of this method. Some minerals are essential for human body growth and metabolism, after reverse osmosis, all those needed minerals are removed. As result of this, the treated water needed to undergo re-mineralization. This makes the treatment process cost increase (Ahmad, et al., 2022). Figure 2.1 shows the membrane process characteristics for microfiltration, ultrafiltration, nanofiltration and reverse osmosis.

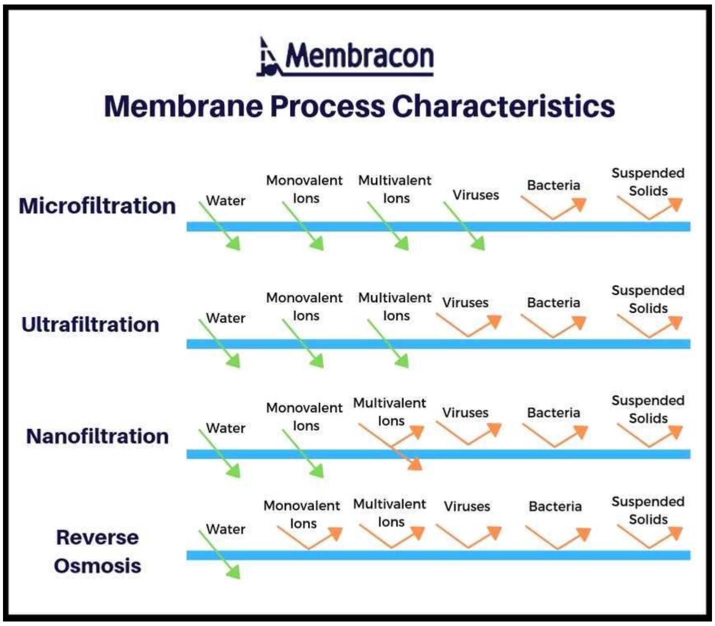

Figure 2.1: Difference between Microfiltration, Ultrafiltration, Nanofiltration and Reverse Osmosis (Atkinson, 2023).

Reverse osmosis will be used in the final polishing in fluoride removal process. According to Dolar, Košutić and Vučić (2011), the efficiency of fluoride removal has reached more than 96 % by reverse osmosis. The retention of fluoride is highly affected by the size exclusion and charge interaction mechanism. In size exclusion model, if the solute is larger than the pore size of the membrane, it is retained. The effective size for fluoride ion need to account of ionic size and hydration layers. As fluoride is dissolved in water, the ion is surrounded by water molecules and forms larger entity. The radius of hydrated ion will increase. The smaller ion will hold water molecules more strongly due to the high charge density. As a result, the fluoride ion will has higher retention as compared to other anions. Fluoride ion is strongly hydrated and the hydration shell will not detached easily, therefore it is not able to pass through membrane easily. The charge interaction mechanism happens between charged solute and charged membrane. The membrane function group charges will avoid the fluoride co-ions from passing the membrane (Shen and Schäfer, 2014). The interaction between the ions is shown in the Figure 2.2.

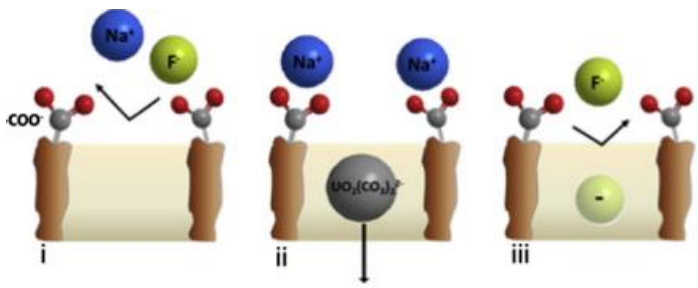

Figure 2.2: Charge Interactions of Fluoride Retention Mechanism in Reverse Osmosis / Nanofiltration (Shen and Schäfer, 2014).

2.3.2 Nanofiltration

Nanofiltration (NF) is another type of membrane filtration with different membrane pore size that can allow more type of substances (include monovalent ions) to flow through as compared to reverse osmosis. Nanofiltration applications not only includes water and wastewater treatment, but also other industrial applications such as separation of solute or chemical from solution, the pharmaceutical sector, and flavours (Abdel-Fatah, 2018). Currently, nanofiltration is significant in the field of separation technology for various applications. People are putting the effort to replace reverse osmosis with this technology in water purification, material extraction and more (Abdel-Fatah, 2018).

Nanofiltration has larger pore size than reverse osmosis membrane, ranging from 1 to 10 nm (Ismail and Matsuura, 2021). As it has this characteristics, it is used as softening membrane which aims to eliminate calcium and magnesium ions from water without adding sodium ions. Although nanofiltration is able to perform well in water treatment process, considering in another aspect, it will increase the energy requirements for water treatment for 60-150 %. To solve this, more permeable nanofiltration is required to reduce the pressure and energy requirements (Abdel-Fatah, 2018). But as the pressure is main force to drive the operation, reducing the pressure will affect the membrane performance. In addition, although it has superior quality of water treatment result, people are considering the implementation of nanofiltration because of the high cost associated with the operation. According to Abdel-Fatah (2018), for those smaller plants with plant capacity of 4000-8000 m^3/d, the membrane-related investment cost is the 20-30 % of the total investment cost. The proportion will increase to near 50 % when the plant size increases, which means the plant capacity has become 53000-125000 m^3/d (Abdel-Fatah, 2018). The process efficiency are affected by the pH and concentration of substance. Nanofiltration has the properties between reverse osmosis and ultrafiltration. It needs lower pressure as compared to reverse osmosis which makes the energy consumption is lower.

For fluoride removal, a study has been conducted and found that when initial fluoride concentration lower than 6 ppm, it is suggested to employ simple pass configuration with membrane type of NF270 or TR60. For concentration higher than 6 ppm, double-pass system with TR60 or NF270 membranes, simple pass with combination of membranes or the simple pass that utilize NF90 membranes is preferred (Tahaikt, et al., 2007). In addition, there are another study that has been done to compare the performance of two commercial nanofiltration membranes (NF5 and NF9). The retention of fluoride depends on the rate of hydration of fluoride ion. The fluoride retention is found to be 88 % and 75 % respectively for NF9 and NF5 (Nasr, et al., 2013).

2.3.3 Precipitation / Coagulation

Chemical precipitation or reagent coagulation is a method that work by precipitating the impurities from the purified water by the aid of precipitating agents, known as coagulants (Ojavan and Lee, 2014). It is the widely used technology that is used to eliminate the dissolved metals from the solutions. There will be chemical reaction between the metal ions and the precipitating reagent, which makes this process is categorized under chemical process. In industry, people will use calcium hydroxide (lime) or sodium hydroxide as the precipitant and forms metal hydroxides (Dahman, 2017). In addition to that, alum is also one of the most commonly used precipitant. This process is known as hydroxide precipitation.

The Nalgonda technique is learnt to be the best example of the fluoride removal by using the precipitation method. Nalgonda technique is commonly used in the developing countries such as India, Kenya and Tanzania for defluoridation of water. The aluminium salts, bleaching powder, and lime will be added into the fluoride wastewater in six consecutive steps. The steps are coagulation/flocculation, disinfection, filtration, rapid mixing, and sedimentation and lastly is sludge concentration (Ahmad, et al., 2022). This method is commonly used by industry is because of its outstanding advantages as compared to other method, such as simplicity of the process and low precipitant cost. However, it also has some limitation since it requires enormous amounts of chemicals to reduce the metal percentage in wastewater to prerequisite level before discharge. In addition, as there is chemical reaction between ions, there will be formation of solid form of solid substance that is known as sludge. The production of sludge will require post treatment to avoid environmental impacts that are brought by disposal of sludge (Dutta and Sharma, 2019).

According to Zewge (2016), the combined aluminium sulfate/ hydroxide is used as the coagulant to remove the fluoride and the removal efficiency has reached 93 %. Meanwhile for aluminium sulfate, that are a few research studies that have been done, which prove that it is able to reduce 40 % of fluoride concentration or over 1.4 mg F/L respectively (Yadav and Yadav, 2009 ; Hamamoto, Kishimoto and Ueki, 2015). Other than that, there are other coagulants that are used to remove the fluoride which are potassium hydroxide and calcium oxide, calcium hydroxide and hydroxyapatite(post treatment), with 88.7 %, 88.3 % and 94. 5% removal efficiency respectively (Diwani, et al., 2022; Melidis, 2015).

In order to improve the traditional coagulation process, some investigations are done onto the coagulation-ultrafiltration method to increase the fluoride removal. According to Qiu, et al. (2022), the chemical mechanical polishing (CMP) wastewater is used as a coagulant. There is SiO_2 ion (negatively charged) in the CMP wastewater that will adsorbed on the CaF_2 particles surface (positively charged). The CaF_2 is resulting from the addition of calcium salt in the fluoride containing wastewater. The electrostatic interaction takes place between the ion and particles surface. There is a research that has proven that the fluoride concentration can be reduced to lower than 10 mg/L by using the conventional coagulation-UF process (Qiu, et al., 2022).

2.3.4 Adsorption

Adsorption is a method that utilize the characteristic of some material to adsorb the ions of metal onto itself. The material provides a surface area for the metals to adsorb onto it and forms a substance layer by physiochemical interactions. In details, the adsorption process can be elaborated into three steps. First, the fluoride layer will accumulate across the surface of the adsorbent. After that, the fluoride ions will adsorb on the surface. And lastly, the adsorbed fluoride will shift into the inner surface of the adsorbed material as there are porous inside it. This is called intra-particle diffusion (Ahmad, et al., 2022). From these process, it can be said that the amount of ions adsorbed on the surface is depending on the porous inner surface of the material, and the efficiency of metal removal can be reflected from this characteristic. If it is able to adsorb large amount of metal ions, this means the efficiency of ion removal is high as the ions have been removed from the water. Other than that, the removal of the adsorbent is also depending on initial concentration of fluoride, type of adsorbent used and pH of the water. In addition, the existence of interfering ions and the time of contact will also affect the removal efficiency. (Ahmad, et al., 2022).

It has some advantages over other defluoridation method, which includes simpler design, operational process that is not complicated, choices of variety adsorbent and low setup cost (Ahmad, et al., 2022). However, there are some adsorbent that has higher cost and there is situation where the rural areas do not fulfil the adsorbent working condition. Some commonly used adsorbents includes active alumina, activated carbon, sawdust, fly ash, coconut coir pith and more (Dutta, Arya and Kumar, 2021). The use of activated alumina is efficient in fluoride removal but it can cause health effects too. Alumina is proven and acknowledged to be the most efficient adsorbent for defluoridation, this is because of the highly porous aluminium oxide has the high surface area (Ahmad, et al., 2022). As it is expensive and highly affected by the presence of co-ions in water, people are putting their effort to develop the modified alumina by impregnating the metal oxides recently (Bhatnagar, Kumar and Sillanpää, 2011). The modified alumina has shown significant performance in the fluoride removal process.

According to Dar and Kurella (2023), the removal rate of fluoride by activated charcoal can reach 94 % under an appropriate dosage of 2.0 g/ 100 mL, reaction time of 2 hr and the pH of 2. Other than that, the activated alumina has the maximum fluoride removal rate of 16.3 mg/L at the optimum pH range of 5-7 (Habuda-Stanić, Ravančić and Flanagan, 2014; He, et al., 2020). A study that use P/γ- Fe2O3 as adsorbent has shown that this adsorbent has removal efficiency of 99 % (Ahmadi, et al., 2019). According to Goswami and Purkait (2012), by using the acidic alumina adsorbent under the pH of 4.4, the fluoride removal rate will reach 94 %.

According to Srivastav, et al., (2013), a new adsorbent which is hydrous bismuth oxides (HBOs) is investigated to be used to remove fluoride from water. Three different ratio of 1:1, 1:2 and 1:3 (0.1 M Bi_2O_3 solution: 2 N NaOH) were prepared and designated as HBO_1, HBO_2 and HBO_3 precipitates respectively. After conducting the experiment, it was found that HBO_1 has the highest removal rate which is 65 % and followed by HBO_2 (27 %) and HBO_3 (33 %). The HBO_1 will give good performance under the condition of fluoride initial concentration 5-10 mg/L, 50 g/L dosage of HBO_1, and pH 4 (Srivastav, et al., 2013).

2.3.4.1 Activated Carbon

As adsorption technology has gained its popularity in the fluoride removal field, material such as alumina, activated carbon, bone charcoal and more are employed to remove the fluoride from wastewater. Activated carbon is the most commonly used adsorbent. As compared to other adsorbents, activated carbon is known for its superior porosity, outstanding surface area and adaptable surface chemistry. To improve the adsorption strength of activated carbon, modification has been done onto it. According to study conducted by Pang, et al. (2020), the activated carbon fibers modified with zirconium (Zr-ACF) adsorbents has been created by using the new drop-coating method. The maximum adsorption capability was reported to be 28.50 mg/L. The main mechanisms of fluoride retention were ion exchange and electrostatic attraction. According to the study conducted by Tefera, et al. (2020), the performance of activated carbon of avocado seeds (ACAS) was investigated. The highest adsorption capability was found to be 1.2 mg/g (1200 mg/L). The activated carbon derived from $CaCl_2$-Modified Crocus Sativus Leaves (AC-CMCSL) showed the highest adsorption capability of 2.01 mg/g (2010 mg/L) (Dehghani, 2018). La/Mg/Si-Activated Carbon was found to have rough and porous structure, uniformly modified through impregnation with La, Mg, and Si (Kim, 2020). As such, it was found to be suitable to be used to remove fluoride from water. Figure 2.3 shows the maximum adsorption capacities of the activated carbon-based materials.

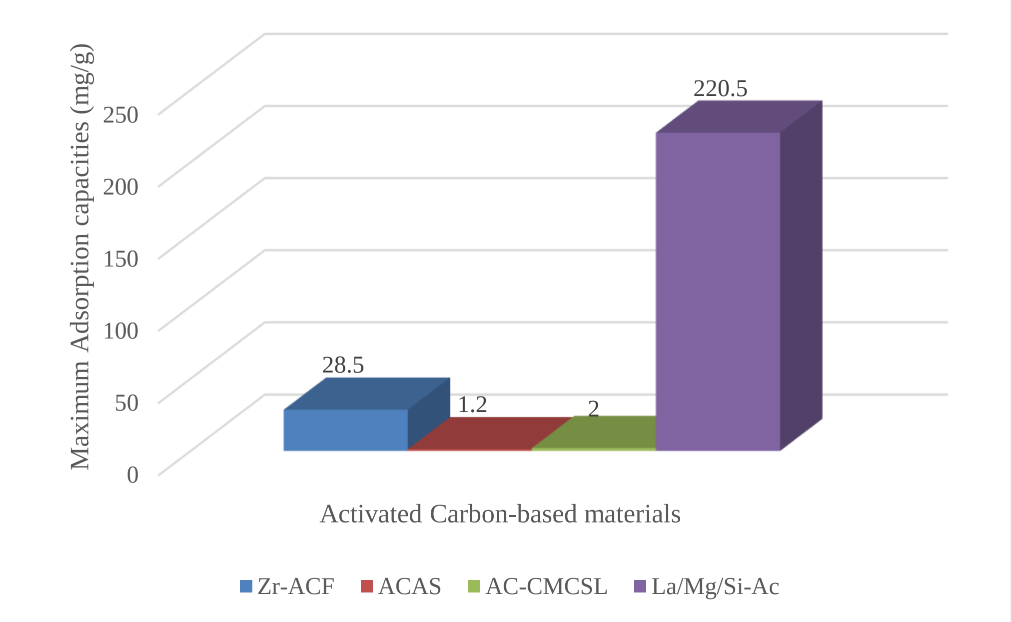

Figure 2.3: Maximum Adsorption Capacities (mg/g) for Activated Carbon-Based Material (Tolkou, et al., 2021)

2.3.5 Ion Exchange

Ion exchange is a defluoridation process that focus more on the exchange process of the ions. The unwanted ion will be exchanged with an ion that is added into the wastewater. Equation 2.1 shows the reaction for the process:

$$\text{Matrix-NR}_3 + Cl^- + F^- \leftrightarrow \text{Matrix-NR}_3 + F^- + Cl^- \text{ (Ahmad, et al., 2022)} \quad (2.1)$$

A liquid substance will be added to the wastewater to act as a resin to introduce chloride ion into the wastewater and remove fluoride ion. The chloride ions in the resin is exchanged and replaced with the fluoride ion. The process is continuous until every chloride ion in resin is replaced. The fluoride ion is able to replace the chloride ion as it has higher electronegativity, it tends to replace the chloride ion in the resin (Ahmad, et al., 2022). The efficiency of the ion exchange is depending on various factors, such as pH, temperature, initial concentration of adsorbent and adsorbate and the ion contact time. According to the study done by Meenakshi and Viswanathan (2007), the fluoride removal efficiency was compared between chelating Ceralite IRA400 (CER) and Resin FR10 (IND). As a result, it is found that the chelating resin is highly recommended for the fluoride removal. It is shown that ion exchange process has high potential of fluoride removal as high as 95 %. But, there is some limitation that limits the usage of resin and ion exchange process in wastewater treatment in industry, which are the high cost of resin. Although it is readily renewed, it may also cause the process to be uneconomical when the replace frequency is high. The used resin will tend to degrade with fouling smell after used for a period of time (Dutta, Arya and Kumar, 2021). The disposal of fluoride-loaded waste also cause an extra problem to be considered by the management level of factory.

2.4 Coagulation and Flocculation

Coagulation and flocculation processes are the most common method used in the wastewater treatment to ensure that the water discharge has fulfilled the local government requirement and to protect the environment. It is used to remove certain type of pollutant or substance that will harm human and environment. These methods are commonly used in industry as it provide high efficiency of substance removal and the cost is lower as compared to other method such as membrane filtration.

2.4.1 Coagulation and Flocculation Processes

Coagulation is the process of bringing insoluble materials by destabilizes the charges of particles. Coagulant that is having an opposite charge is added to the suspended solids to promote the formation of clumping of particles. The opposite charges will neutralizes the charge. The common coagulants that are used in industry includes iron or aluminium salts. The salts will hydrolyse the particles to form insoluble precipitates. Coagulation will be used when the aim is to remove fine particles from suspension. After the coagulation, the flocculation will be performed as the particles formed by coagulation process is not visible to naked eyes (Samanthi, 2017).

Flocculation is the process of formation of flocs. Initially, the flocs from coagulation process appears as a cloud. Flocculation process focuses on the joining the coagulated flocs to form large masses of flocs and converted it to become precipitate. The mixing in flocculation will increase the size of clumps until it can be seen with naked eyes. The intermicrofloc collisions between the contacted microflocs is done by the mixing. After that, the precipitate can be separated from the solution and removed easily. After the flocculation process is done, the water will undergo separation processes (Samanthi, 2017).

There are some difference between coagulation process and flocculation process although they are commonly used together in water treatment process. The detail differences between coagulation and flocculation are shown in the Table 2.1.

Table 2.1: Difference between Coagulation and Flocculation (Samanthi, 2017)

	Coagulation	**Flocculation**
Process Type	Chemical Process	Physical Process
Added Compounds	• Aluminium Salt (Aluminium Sulfate, Aluminium Chloride) • Iron Salt (Ferric Chloride, Ferric Sulfate) • Melamine Formaldehydes	Organic Polymer that is used to bridging and strengthening the flocs
Physical Mixing	No	Yes
Process	Clumping of particles	Settling of coagulated particles

2.4.2 Type of Coagulant in Fluoride Wastewater Treatment

Coagulant is a chemical that is used to remove the pollutant by helping the aggregation of small particles and dissolved substances into larger clumps, making them easier to be separated from the water. There are various type of coagulants that can be used with different properties and mechanisms of action. Some commonly used coagulants are aluminium salts and iron-based coagulants. The chemicals work by neutralizing the charge on the fluoride ions. The aggregation will be promoted and the pollutant can be removed via sedimentation or filtration.

2.4.2.1 Aluminium Salt

Aluminium salt-based coagulant is one of the most commonly used coagulants used in water treatment. Aluminium sulfate (alum) is the common coagulant used to form precipitation in water treatment. Alum is added to the water and forms aluminium hydroxide ($Al(OH)_3$). The aluminium hydroxide flocs will be formed when the acidic coagulant and natural alkaline water reacts. The flocs are insoluble under narrow bands of pH, therefore the pH control is essential to maintain the minimum levels of dissolved residue aluminium in clarified water. To control the pH, the sulphuric acid will be more economic as compared to excess aluminium sulfate. The excess coagulant used will causes more sludge production (Brandt, et al., 2017)

The pathway to form the Al-F complexes is different for coagulation process and adsorption process. In the coagulation process, the Al-F complexes will be formed after the Al^{3+} solution is added and formed the Al-F precipitates to remove fluoride. Meanwhile, for adsorption system, the fluoride will be adhered onto AlO_xH_y surfaces through mechanism that involves hydroxyl replacement and electrostatic interaction. Two main mechanisms that are involved in the fluoride removal by aluminium sulfate are adsorption and co-precipitation. Equation 2.2 and 2.3 describe the adsorption on $Al(OH)_3$ and co-precipitation process in fluoride wastewater treatment (Ozairi, et al., 2019).

$$Al_n(OH)_{3n(s)} + mF^-{}_{(aq)} \rightarrow Al_nF_m(OH)_{3n-m(s)} + mOH^-{}_{aq} \qquad (2.2)$$

$$nAl^{3+}_{(aq)} + (3n-m)OH^-_{(aq)} + mF^-_{(aq)} \rightarrow Al_nF_m(OH)_{3n-m(s)} \qquad (2.3)$$

From Equation 2.2 and 2.3, the fluoride ion will form solid when after the adsorption and precipitation process. After it form solid, the precipitate that contains fluoride can be removed from the wastewater.

According to Gong, et al. (2011), as the coprecipitate process occurred, the fluoride is removed from the wastewater and it formed the Al-F-OH complexes which can be seen as the sludge produced. According to Chen, et al. (2022), more than 92 % removal of fluoride is achieved by aluminium hydroxide within 2 hr. According to the study done by Ozairi, et al. (2019), the optimum pH to get maximum removal of fluoride is at pH 4 when the dosage of aluminium sulfate is 300 mg/L and initial fluoride concentration is 3 mg/L.

From the online shopping platform, 1 kg of aluminium sulfate powder is sold for RM 7.00 (Shopee.com, no date), which can be considered as cheaper as compared to other coagulant such as bentonite (RM 45 for 1 kg) (Shopee.com, no date). In another word, the coagulation method by aluminium sulfate can be as effective and affordable. However, as most of the water treatment uses the aluminium sulfate as coagulant, the aluminium concentration are expected to be high in the residue. The estimated disposal cost of residue at municipal landfills and Kualiti Alam was reported to be RM 0.06 and RM 1.58 respectively per cubic meter of water produced. In addition to that, the annual cost will exceed RM 10 billion if all the residue is sent to Kualiti Alam, which is doubled the revenue of provision of water supply industry (Study on the Current Issues and Needs for Water Supply and Wastewater Management in Malaysia, 2014). In summary, although the removal of fluoride from wastewater by aluminium sulfate is considered to be effective and low-cost, the trade-off will be the sludge disposal cost that will need to be borne by government and residents.

2.4.2.2 Iron Salt

Another alternative to remove the fluoride from wastewater without forming large amount of sludge is to use iron salt in coagulation process. The commonly used iron coagulants in wastewater treatment is ferric sulfate, ferrous sulfate and ferric chloride. Usually, people will opt for ferric sulfate as the ferric chloride will introduce the chlorine ions into the water and increase the corrosivity. According to Tarleton and Wakeman (2007), the most commonly used iron salt is ferric chloride ($FeCl_3$) and it has higher removal as compared to hydrated sulfate compound which is $Fe_2(SO_4)_3{\cdot}(H_2O)_8$. Although ferric chloride is corrosive, the high removal will be more significant. To solve the corrosivity issue, the pH of wastewater can be adjusted to neutral condition by adjusting the alkalinity. Ferric chloride is produced by the process of oxidation of ferrous chloride with chlorine. The price of ferric chloride is RM 26 for 500 g (Lazada.com, no date). It comes in dark brown powder form. As compare to aluminium sulfate, it has higher price. The advantages of using iron salt as compared to aluminium salt is it is able to produce a denser floc as compared to aluminium salt (Brandt, Johnson and Ratnayaka, 2017). Therefore, the settlement characteristics will improve.

2.4.2.3 Poly Aluminium Chloride (PAC)

Other than the hydrolysing metal salts (ferric salt and aluminium salt), the pre hydrolysed metal salt is also one of the choice of the water treatment coagulant. Poly aluminium chloride (PAC) is made up of aluminium, oxygen, hydrogen and chlorine. The production of raw materials differ it from the aluminium chloride. The aluminium chloride is made from the aluminium ash while PAC is made by mixing calcium powder with hydrochloric acid. Other than that, the application field is also different, the aluminium chloride is mainly used in industrial sewage and PAC has more extensive scope of application which are industrial sewage, domestic sewage and drinking water. PAC has better efficiency in separating the solid-liquid, sedimentation filtration and sludge dewatering performance. This means it shorten the settling time in the sedimentation tank. PAC not only shows good result in condensation and removal of turbidity, but also decolourization and removal of humus (Yolanda, 2022). Only half of the dosage of traditional aluminium salt is requires under the same external treatment conditions to achieve the best result.

PAC is an alternative solution to solve the problem of sludge production by the aluminium sulfate. The large production of sludge during the water treatment process will cause the increment of disposal cost and directly impact the operational cost of water treatment plant. According to Brandt, et al. (2017), there are a few coagulants, for instance the poly aluminium chloride (PAC), poly aluminium silicate sulphate (PASS) and poly aluminium chlorosulphate (PACS) are formulated as high basicity coagulants. With the high basicity from the coagulant, it does not depress the pH of the treated water as much as aluminium sulfate does and thus reduces the alkali dose needed for final pH correction. The flocs produced are stronger and easier to settle.

According to the study conducted by Zhang, et al. (2023), the PAC shows as the dosage increase, the fluoride removal efficiency will also increase up to 53.2 % and 65.1 % at the dosages of 0.8 mmol/L and 1.0

mmol/L. PAC has been used as an alternative to aluminium sulfate because of the high basicity characteristic it has. By using PAC, the amount of the lime required to maintain the optimum pH will be lesser. The PAC can be synthesized through different ways and some improvement can be done to improve the coagulation effect of the PAC. A study has been done by Zhou, et al. (2014) shows that the coagulation effect of PAC-IG (PAC-industrial grade) was better as compared to PAC-SCML (PAC produced by synthetic cryolite mother liquor) for low turbidity wastewater. But, when it was applied on high turbidity water, the PAC-SCML shows better performance as compared to PAC-IG. This may be because of the water insoluble CaF_2 and $CaSiF_6$ that can helps with the coagulating reaction for high turbidity water.

2.4.2.4 The Advantages and Disadvantages of Aluminium Sulfate and Ferric Chloride

Table 2.2: Advantages and Disadvantages of Aluminium Sulfate and Ferric Chloride (Alum and Ferric Chloride: Pros, Cons, and Substitutes, 2017).

	Advantages	Disadvantages
Aluminium Sulfate	• Low cost • Commonly used • Simple Operation • Low toxicity	• Need a lot to treat the wastewater • Produce high amount of sludge, cost of disposal of sludge become a new problem
Ferric Chloride	• No pH requirement • Simple Operation	• Corrosive • Fluctuate Price

2.4.3 Condition for Coagulation/ Flocculation

Coagulation and flocculation are the methods that are essential in removing the suspensions, organic and inorganic compounds to ensure that the water that will be discharged has fulfilled the requirement by government. In addition to that, the management also try to achieve other objective of treatment such as strong flocs, lower amount of sludge and lower water loss.

To obtain the optimum removal, the acidic pH values are preferred to enhance the charge neutralization mechanism. The optimum pH for ferric salts are found to be in the range of 3.7 to 4.2. For aluminium sulfate, the range are discovered to be 5.0 to 5.5 (Mahmood, Khan and Khan, 2014). From these studies, it can be concluded that the ferric salts and aluminium sulfate works better in acidic condition. To improve the removal, the water treatment by metal coagulants can be added with powdered activated carbon (Mahmood, Khan and Khan, 2014). The lower pH condition will create the chance for the increment presence of the positively charged particles to loose in the water and by this, they are able to react with the negatively charged colloids. The charge neutralization of ferric species and the complexation between the ferric species and organic compounds acts as the domain coagulation mechanisms in the acidic coagulation conditions (Cao, et al., 2011). After the reaction between the negative charge and positive charge, the mixture will be adjusted to alkaline condition. This is to ease the formation of flocs. According to Cao, et al. (2011), the growth time of the flocs will decrease when the pH is increased. This followed by the increment of the flocs diameter size.

2.5 Response Surface Methodology

Response surface methodology (RSM) is commonly used technique for modelling and analysing the problems where outcome of interest is influenced by multiple variables. It will be used to employ regression analysis onto the collective data and is useful when the relationship between the response and input variables is unknown. One of the experimental design technique is central composite designs (CCD), which is able to fit a full quadratic model. It is use when sequential experimentation is required because the design will include information from a correctly planned factorial experiment. CCD is the most common design used for the 2nd degree model. It consists of three sets of experimental runs: a factorial design (two levels for each factor), centre points (replicated experimental runs with median factor values), and axial point (experimental runs with factors at extreme values). After collecting the data, the mathematical model can be developed to represent the relationship of response function and the factor level. Some tests can be used to shows the significance of the model such as t and F-test, Parity plot and Pareto chart.

The fit quality of the model can be assessed through the Coefficient of Correlation (R) and the coefficient of Determination (R^2). The closer the value of R^2 to 1, the more reliable the predicted model will be.

2.6 Summary Table for Different Type of Coagulant/ Adsorbent, Condition and Performance

In summary, the coagulant and adsorbent are widely used to remove the fluoride from wastewater. Table 2.3 shows the condition and performance for each of the coagulant and adsorbent.

Table 2.3: Summary Table of Various Coagulant and Adsorbent

Coagulant / Adsorbent	**Condition**	**Performance**	**Reference**
Coagulation			
Combined Aluminium Sulfate/Hydroxide	pH range 5-9 80 mg alum/mg F, 5 mg aluminium hydroxide/mg F, lime =35 % of alum	Remove 93 % of fluoride	(Zewge, 2016)
Aluminium Sulfate	pH 7.0±0.5 8 g/kg soil Time 120 hr Temperature 20±5 °C	Reduce 40 % of fluoride concentration	(Yadav and Yadav, 2009)
Aluminium Sulfate	pH 7.0-8.2	Fluoride removal over 1.4 mgF/L	(Hamamoto, Kishimoto and Ueki, 2015)

Table 2.3: Continued

Potassium Hydroxide (KOH) and Calcium Oxide (CaO)	Start with pH 3 and after adding Cao, pH adjusted to 7.5	F is main constituents (88.7 %) in the precipitate	(Diwani, et al., 2022)
Calcium Hydroxide	pH 12.5	Removal efficiency 88.3 %	(Melidis, 2015)
Hydroxyapatite (Post Treatment)	4 hr contact time 4.0 g/L of HAP	Removal efficiency 94.5 %	(Melidis, 2015)
Poly Aluminium Chloride (PAC)	pH 6.5- 8.5 (Continuous)	Removal efficiency: 86.7% (Batch) 85.5% (Continuous)	(Dubey, et al., 2018)
PAC with mixture of sodium aluminate	3.0g/L of PAC pH 7	Removal efficiency 85.9%	(Goh, et al., 2018)
Adsorption			
P/γ- Fe_2O_3	pH 7 0.02 g/L dose 30 min contact time	Efficiency of 99 %	(Ahmadi et al., 2019)

Table 2.3: Continued

Acidic Alumina	pH 4.4 4.5 g/L dose 1.5 hr contact time	Removal rate of 94 %	(Goswami and Purkait, 2012)

CHAPTER 3

METHODOLOGY AND WORK PLAN

3.1 Material

The artificial wastewater, aluminium sulfate, ferric chloride and poly aluminium chloride were prepared by using the chemicals such as sodium fluoride (NaF), aluminium sulfate (Al_2SO_4), ferric chloride ($FeCl_3$) and poly aluminium chloride powder. Besides that, hydrochloric acid (HCl) and sodium hydroxide (NaOH) were also used to adjust the pH of the solution. In addition, the distilled water were also obtained in the laboratory.

3.1.1 Artificial Wastewater

An artificial wastewater will be used to simulate the real wastewater discharged from the industry factory. To prepare the stock solution of fluoride with concentration of 1000 mg/L, 1 L volumetric flask was filled with distilled water and mixed with 2.21 g of NaF. The volumetric flask was swirled gently to dissolve the reagent. To make it similar with real wastewater, the pH of the water sample was adjusted by adding the 3 N HCl or 1 N NaOH solutions based on the availability in the laboratory room. The fluoride ion in the wastewater caused the pH of wastewater to be having pH of 1 to 3 (Diwani, et al., 2022). In this experiment, the wastewater was adjusted to acidic condition (pH 2). A standard solution (100 mg/ L) was prepared by adding the stock solution with the distilled water (Fito, et al., 2019). By using the diluting formula, it was calculated that 20 mL of stock solution was diluted with 180 mL distilled water to form 200 mL standard solution.

3.1.2 Preparation of Aluminium sulfate

Aluminium sulfate is one of the most commonly used aluminium salt-based coagulants for fluoride removal with high removal based on the few studies in a few years ago. 31.65 g of aluminium sulfate was mixed with distilled water to prepare stock solution of 5000 mg/L. Aluminium sulfate with different concentration, which is in the range of 1500-3500 mg/L (30 % - 70 %v/v) was prepared by diluting stock solution with distilled water. For 1500 mg/L

(30 %v/v) concentration, 100 mL of sample was prepared by diluting 30 mL of stock solution with 70 mL of distilled water.

3.1.3 Preparation of Ferric Chloride

14.5 g of ferric chloride was dissolved in distilled water and the solution volume was increased to 1 L to get the 5000 mg/L concentration of stock solution. Different concentrations, which is in the range of 1500-3500 mg/L (30 % - 70 %v/v) were prepared from the stock solution. The dilution equation was used to find the volume of stock solution needed to prepare solution with different concentration. For 1500 mg/L (30 %v/v) solution, 30 mL of stock solution was added with 70 mL of diluted water.

3.1.4 Preparation of Poly Aluminium Chloride (PAC)

30 % Poly Aluminium Chloride used in this experiment is a light-yellow powder. 5 g of PAC was dissolved in the distilled water to form the stock solution of 5000 mg/L. The different concentration of PAC was prepared, which is in the range of 1500-3500 mg/L (30 % - 70 %v/v). For 1500 mg/L (30 % v/v), as indicated in the volume percentage, 30 mL of solution was added to 70 mL of distilled water to form 100 mL solution.

3.2 Apparatus

Some apparatus were also used to perform the experiment, including magnetic stirrer, analytical balance, oven and centrifuge. Other than that, some apparatus were used to measure the data of the solution. These apparatus include spectrophotometer and pH meter.

3.2.1 Magnetic Stirrer

To perform mixing, a magnetic stirrer and magnetic bar were used. The brand of the magnetic stirrer used was IKA RCT basic. The LED display screen would show the mixing speed and heating temperature. In this study, no heating was required. So, the display screen would only focus on the mixing speed. In this study, the solution will be mixed at the speed of 200 rpm for 1 min and 80 rpm for 30 min. With the display screen, the mixing speed was able to be tracked from time to time.

3.2.2 Centrifuge

To separate the solid and liquid from the mixture, a centrifuge machine was used. After rotating at rapid speeds, the centripetal force would separate substance and therefore the liquid can be separated out from the solid substance. The brand of the centrifuge machine used is Centurion. It can be used in the laboratory to perform separation process. The centrifuge process was done to separate the liquid and the flocs formed. The liquid would be used for testing for final fluoride concentration meanwhile the solid (the sludge) would be dried and weight to measure the amount of sludge produced by each coagulant. The centrifugation process would be done under the condition of 10000 rpm for 10 min for all the samples.

3.2.3 Spectrophotometer

To analysis the contaminant of fluoride in the water sample, the spectrophotometer would be used. The model is HACH DR3900 Laboratory Spectrophotometer. The wavelength range for this spectrophotometer is 320-1100 nm. It measures the intensity by utilizing the wavelength of the light source. In simple, the working principle of spectrophotometer is by splitting the light from the source into different wavelengths (which means it will have different colour). Specific wavelength will pass through the sample and the intensity will be measured. There are a few components that build up spectrophotometer, which are light source, monochromator, aperture, cuvette, photodetector, amplifier and the output display.

The absorbance of the chemical can be obtained from the amount of light it absorbs when all the light with different wavelength is passed through it. The spectrophotometer will measure the absorbance of the different wavelength by adjusting the monochromator. To measure the fluoride concentration, the spectrophotometer is adjusted to the wavelength of 570nm based on the standard methods for the examination of wastewater.

SPADNS reagent method was used for the measurement and analysis of fluoride. SPADNS 2 was used as reagent, which was able to remove interference from chlorine without arsenic. 2 mL of reagent was added to each sample cells that contained 10 mL of sample. For the control, 2 mL of reagent was added to distilled water. After mixing for 1 min, both the sample cells are inserted into the machine to get the reading of fluoride in the water sample. The distilled water was used as the reference solution, the absorbance of the other compounds would be zeroed out.

3.2.4 Analytical Balance

The analytical balance is used to determine the mass of the chemicals. It has high precision and advanced technology to perform specific tasks such as weighing material and quality control testing. The analytical balance (Vibra HT series) has the precision up to 0.0001 g.

3.2.5 pH meter

The solution's pH was determined by the pH meter (brand of Sartorius). It comes with a buffer solution which helps to stabilize the pH value. The digital screen on the pH meter makes the reading of result easier and more accurate as compared to traditional method, which is by using pH paper.

3.2.6 Oven

To compare the mass of sludge formed by each coagulants, the sludge was collected and dried at 80 °C overnight using Faithful Drying Oven WGL-65B.

3.3 Optimization of Experiment

To ensure that the experiment can be conducted smoothly and can be finished on time with accurate result, a planning should be done before performing the experiment. By this, the Design of experiments (DOE) has become essential. Multiple of input factors can be manipulated and DOE is able to determine the effect on desired output, which are final concentration of fluoride and sludge mass in this study. All the possible combinations of input factor will be listed out so that there is no missing possible combination of interactions.

In this work, the main objective of RSM is to maximize the fluoride removal of wastewater. The fluoride concentration (Y_F) is taken as the response variable meanwhile the solution pH (X_1) and the coagulant dosage (X_2, % v/v) are considered as the independent variables.

3.3.1 Aluminium Sulfate

For the aluminium sulfate, the input factor would be the pH value and the coagulant dosage. The pH value will be set to the range of pH 3-11. Meanwhile for the coagulant dosage, to find the most optimum dosage, the coagulant dosage of range 1500-3500 mg/L (30 % - 70 % v/v) is used. The output of the experiment will be the final concentration of fluoride in wastewater and the mass of the sludge produced by aluminium sulfate. After using the software developed by Stat-Ease, which is Design Expert, Table 3.1 is developed.

Table 3.1: pH and Coagulant Dosage Condition Obtained from Design Expert for Aluminium Sulfate

Run	pH	Coagulant Dosage (mg/L)	Coagulant Dosage (%v/v)
1	5	2000	40
2	9	2000	40
3	5	3000	60
4	9	3000	60
5	3	2500	50
6	11	2500	50
7	7	1500	30
8	7	3500	70
9	**7**	2500	50
10	7	2500	50
11	7	2500	50
12	7	2500	50
13	7	2500	50

3.3.2 Ferric Chloride

For the aluminium sulfate, the input factor would be the pH value and the coagulant dosage. The pH value will be set to the range of pH 3-11 which is from acidic to alkaline condition. Another factor to be studied is the most optimum dosage, so the coagulant dosage of range 1500-3500 mg/L (30 % -

70 % v/v) are used. The output of the experiment will be the final concentration of fluoride and the mass of the sludge produced by aluminium sulfate. After using the software developed by Stat-Ease, which is design expert, Table 3.2 is developed.

Table 3.2: pH and Coagulant Dosage Condition Obtained from Design Expert for Ferric Chloride

Run	**pH**	**Coagulant Dosage (mg/L)**	**Coagulant Dosage (%v/v)**
1	5	2000	40
2	9	2000	40
3	5	3000	60
4	9	3000	60
5	3	2500	50
6	11	2500	50
7	7	1500	30
8	7	3500	70
9	7	2500	50
10	7	2500	50
11	7	2500	50
12	7	2500	50
13	7	2500	50

3.3.3 Poly Aluminium Chloride (PAC)

To test the fluoride removal by PAC, the pH value will be set to the range of pH 3-11 to find the optimum pH value. To find the most optimum dosage, the coagulant dosage of range 1500-3500 mg/L (30 % - 70 % v/v) is used. The final concentration of fluoride and the mass of the sludge produced by aluminium sulfate were recorded after the experiment. To find the optimum combination of coagulant, Table 3.3 is developed which contains 13 set of experiments.

Table 3.3: pH and Coagulant Dosage Condition Obtained from Design Expert for Poly Aluminium Chloride

Run	pH	Coagulant Dosage (mg/L)	Coagulant Dosage (%v/v)
1	5	2000	40
2	9	2000	40
3	5	3000	60
4	9	3000	60
5	3	2500	50
6	11	2500	50
7	7	1500	30
8	7	3500	70
9	7	2500	50
10	7	2500	50
11	7	2500	50
12	7	2500	50
13	7	2500	50

3.4 Testing of fluoride removal by various coagulant

After done the preparation steps, the experiment were conducted by using three coagulants (aluminium sulfate, ferric chloride, and PAC). The experiments were separated into two sections, which were artificial wastewater and real industrial wastewater. The final fluoride for both the wastewater were collected and compared.

3.4.1 Artificial Wastewater

The experiment was conducted in 1000 mL beaker which contained 200 mL of artificial fluoride wastewater under continuous mixing condition at room temperature. To make conditions similar to real wastewater, 3 N HCl was added to the artificial wastewater so that the pH value was lower than 2. First, 100 mL of aluminium sulfate (start with 2000 mg/l, 40 %v/v) was added to beaker that contained 200 mL wastewater. The initial pH of artificial wastewater and aluminium sulfate were recorded. After HCl was added, the volume needed and final pH were recorded. The desired pH value for this set was pH 5 and it was adjusted by adding 1 N NaOH. The mixing process was done with speed of 200 rpm for 1 min and 80 rpm for 30 min. After the mixing process, the water sample was subjected to centrifugation with the speed of 10000 rpm for 10 min. The precipitate at the lower layer was collected and dried overnight in the oven with the temperature of 80 °C. The next set of experiment with different combination of pH and dosage (refer to Table 3.1) was done via same steps as above and final concentration and sludge mass were recorded. After completing the experiment sets that use aluminium sulfate as coagulants, the experiment sets were repeated using ferric chloride (refer to Table 3.2) and PAC (refer to Table 3.3). Figure 3.1, 3.2 and 3.3 show the mixing of coagulants with artificial wastewater.

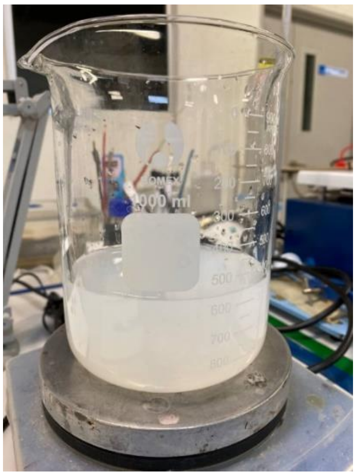

Figure 3.1: Mixing of Aluminium Sulfate and Artificial Wastewater

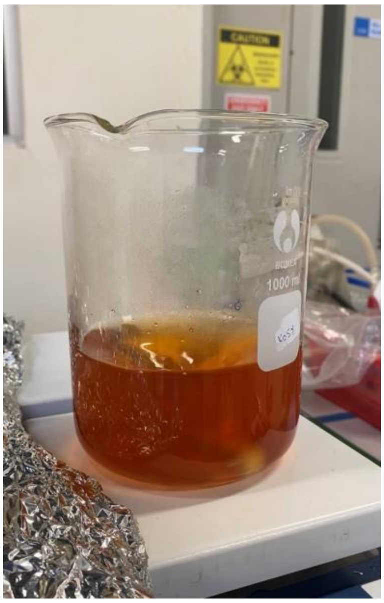

Figure 3.2: Mixing of Ferric Chloride and Artificial Wastewater

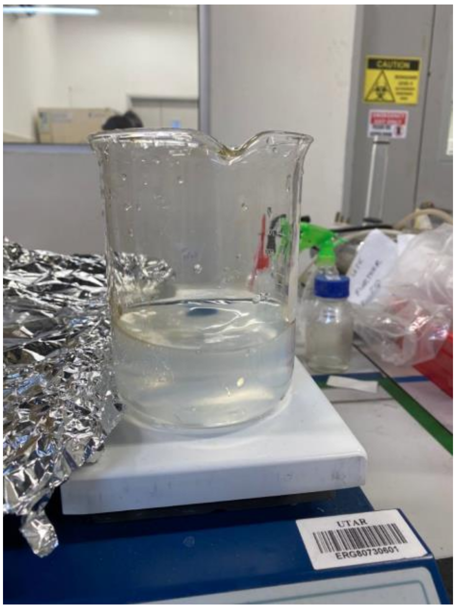

Figure 3.3: Mixing of PAC and Artificial Wastewater

3.4.2 Real Industrial Wastewater

After conducting the experiments for artificial wastewater, the data were collected and compared. The optimum condition for each coagulants was known. The optimum condition was applied onto the real industrial wastewater that was collected from the local semiconductor industry. Same procedures were done onto the real industrial wastewater, 200 mL of wastewater was mixed with 100 mL of coagulant. The initial fluoride concentration of wastewater was measured. As the wastewater was taken from the semiconductor industry, the pH of the wastewater was at the acidic condition. The pH of the solution was increased by using the 1 N NaOH to reach the desired pH value (pH 7 for PAC and Aluminium sulfate and pH 5 for ferric chloride). The wastewater and coagulant was mixed at same condition as artificial wastewater (refer Section 3.4.1). After that, the solution was allowed to settle for 30 min. The figure of settlement was shown in Appendix A. The final fluoride concentration was measured using the same equipment, which is spectrophotometer DR3900 based on the SPADNS method.

3.5 Flowchart of the Procedure

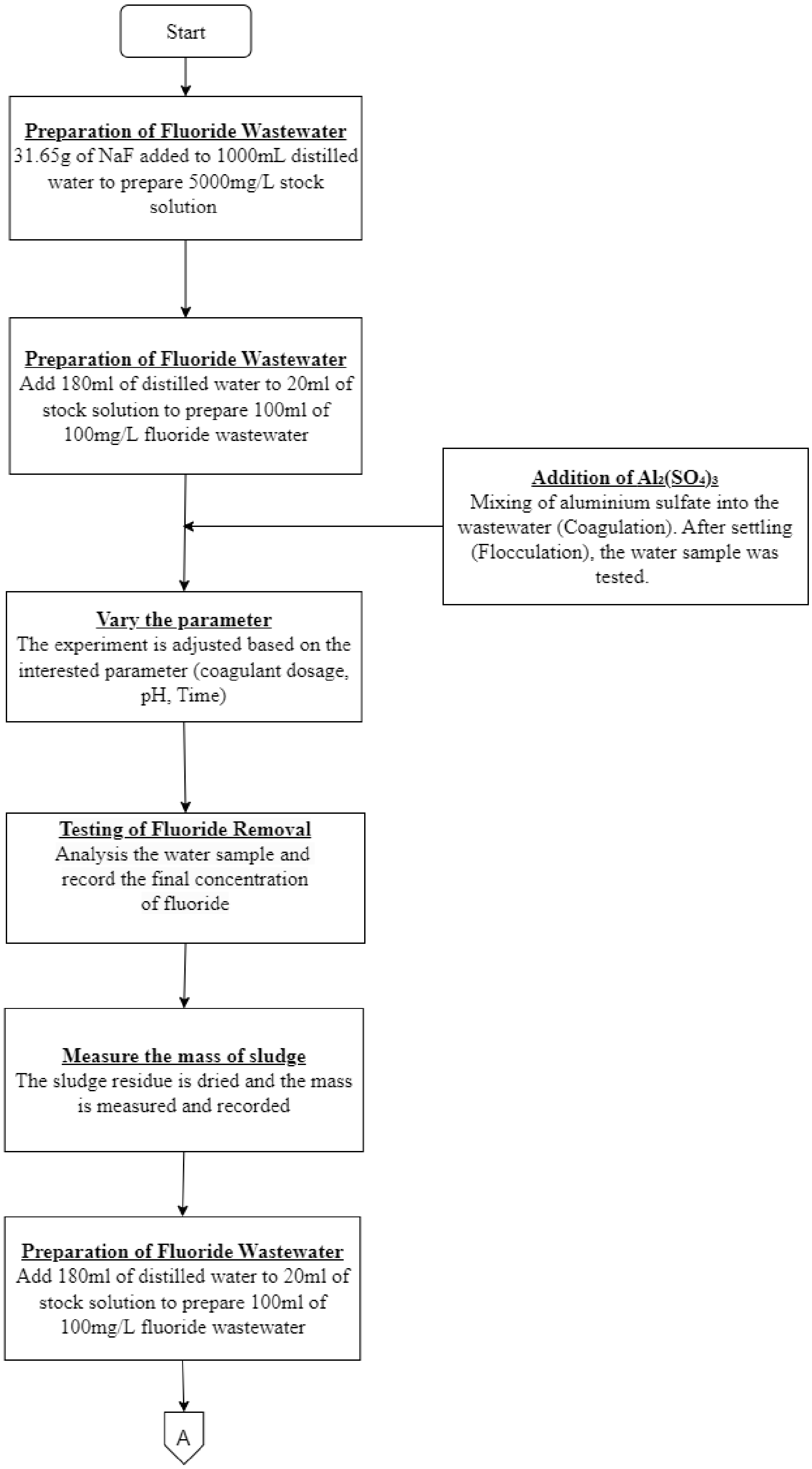

Figure 3.4: Flowchart of Experiment Procedure

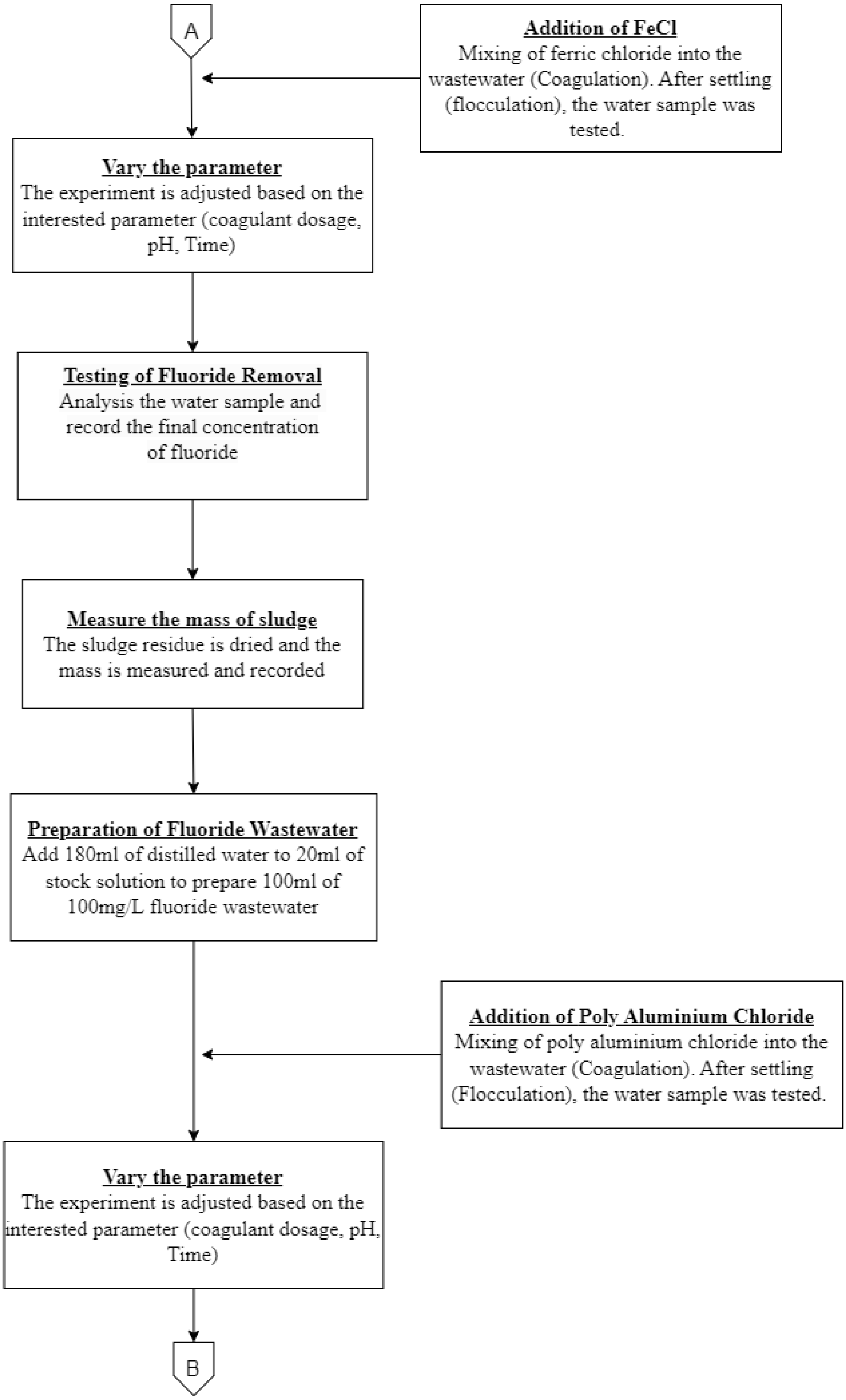

Figure 3.4: Continued

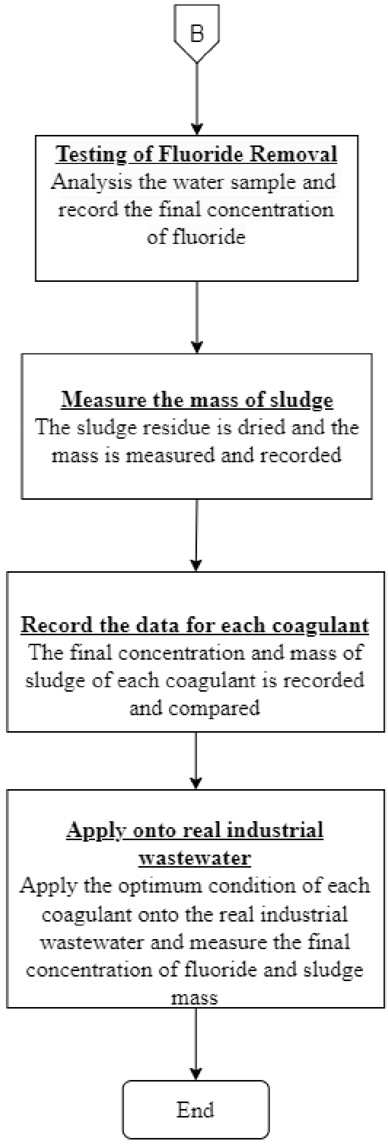

Figure 3.4: Continued

3.5.1 Fluoride Removal

The fluoride removal need to be calculated to compare performance of fluoride removal between the coagulants. The formula of fluoride removal is given as:

$$Percent\ fluoride\ removal\ (\%removal) = \frac{(C_O - C_e)}{C_o} \times 100 \quad (3.1)$$

where

C_o = initial concentration of fluoride solution, mg/l

C_e = final concentration of fluoride solution, mg/l

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Artificial wastewater

After conducting the experiment by using artificial wastewater, the data were collected and discussed. The coagulant that has highest fluoride removal and lowest sludge formation will be found. Besides that, the effect of pH and coagulant dosage on fluoride removal will be discussed.

4.1.1 Aluminium Sulfate

10 mL of water sample was tested with the spectrophotometer to find out final concentration of fluoride. The precipitate was dried in the oven with the temperature 80°C overnight to find out the sludge mass. Table 4.1 shows the result for the final concentration and sludge mass for different combination of pH and dosage.

Table 4.1: Final Concentration and Sludge Mass for Aluminium Sulfate

Run	pH	Coagulant Dosage (mg/L)	Coagulant Dosage (%v/v)	Fluoride Concentration (mg/L)	Fluoride Removal (%)	Sludge Mass (g)
1	5	2000	40	33.5	66.5	0.2000
2	9	2000	40	38.5	61.5	0.1451
3	5	3000	60	25.5	74.5	0.2288
4	9	3000	60	27	73	0.2217
5	3	2500	50	39	61	0.1270
6	11	2500	50	29.5	70.5	0.2120
7	7	1500	30	28	72	0.2167
8	7	3500	70	3.5	96.5	0.6100
9	7	2500	50	5	95	0.4419
10	7	2500	50	5	95	0.5538
11	7	2500	50	7	93	0.2420
12	7	2500	50	7	93	0.2348

Table 4.1: Continued

13	**7**	**2500**	**50**	**5**	**95**	**0.5579**

Table 4.1 shows that the coagulant dosage with 70 %v/v (3500 mg/L) and the pH value of 7 has the lowest final concentration value, which is 3.5 mg/L. However, as the dosage has increased, the sludge produced will also increase. The sludge produced is the heaviest among all the dosage, which is 0.6100 g. When there is more dosage of coagulant, more Al^{3+} ion is available to form the $AlF(OH)_3$. The $AlF(OH)_3$ is the white solid precipitate which is known as sludge. As the 70 %v/v has the highest sludge, it will not be the optimum condition for the fluoride removal. The experiment aims to find the condition that provides high removal and low sludge production. By this, the 50 %v/v coagulant dosage with the pH 7 will be the best choice. The final concentration of this combination is 5 mg/L and is considered acceptable as it is in the range of government requirement. The sludge produced is relatively low as compared to 70 %v/v, which is 0.5538 g. The fluoride removal for pH 7 and 50 %v/v is high, which is 95 %. Based on result in Table 4.1, it is shown that when coagulant dosage increases from 30 %v/v to 70 %v/v, the fluoride removal increases from 72 % to 96.5 % when the pH is fixed to 7. The results are in agreement with journal published by Dargahi, et al. (2016) that stated when the coagulant dose increase, the fluoride removal efficiency will become higher. Dargahi, et al. (2016) also stated that when the initial fluoride concentration was set at 3 mg/L, the highest fluoride removal was obtained by using 300 mg/L concentration, which was the highest concentration of aluminium sulfate.

4.1.2 Ferric Chloride

Table 4.2: Final Concentration and Sludge Mass for Ferric Chloride

Run	**pH**	**Coagulant Dosage (mg/L)**	**Coagulant Dosage (%v/v)**	**Fluoride Concentration (mg/L)**	**Fluoride Removal (%)**	**Sludge Mass (g)**
1	5	2000	40	44	56	0.5258

Table 4.2: Continued

2	9	2000	40	90.5	9.5	0.0057
3	5	3000	60	33.5	66.5	0.6079
4	9	3000	60	76	24	0.3765
5	3	2500	50	76.5	23.5	0.3625
6	11	2500	50	89.5	10.5	0.1134
7	7	1500	30	87	13	0.3559
8	7	3500	70	56	44	0.3893
9	7	2500	50	46.5	53.5	0.4589
10	7	2500	50	47	53	0.3979
11	7	2500	50	47	53	0.4196
12	7	2500	50	46.5	53.5	0.4766
13	7	2500	50	47	53	0.4315

As shown in the Table 4.2, the highest removal that can be achieved by ferric chloride is 66.5 %, which is 33.5 mg/L of fluoride concentration. The pH is adjusted to pH 5 and the coagulant dosage used is 60 %v/v, which is equivalent to 3000 mg/L. The mass of sludge produced is 0.6079 g.

In addition, Table 4.2 has highlighted that when ferric dosage used is higher, the fluoride removal will be higher. To prove the statement in quantitative form, at same pH (pH 5), the fluoride removal of 40 %v/v and 60 %v/v are compared. 40 %v/v dosage is able to achieve the fluoride removal of 63 % meanwhile for 60 %v/v dosage is able to achieve higher fluoride removal, which is 66.5 %. These results tally with the result in the thesis published by Kowalchuk in 2012. According to Kowalchuk (2012), as the ferric dosage increased, the final fluoride concentration will decrease for pH 5.5 and pH 7.5. In conclusion, it is agreed that the higher the dosage used, the higher the fluoride removal will be.

4.1.3 Poly Aluminium Chloride (PAC)

Table 4.3: Final Concentration and Sludge Mass for PAC

Run	pH	Coagulant Dosage (mg/L)	Coagulant Dosage (%v/v)	Fluoride Concentration (mg/L)	Fluoride Removal (%)	Sludge Mass (g)
1	5	2000	40	14	86	0.0317
2	9	2000	40	64.5	35.5	0.0038
3	5	3000	60	35	65	0.0235
4	9	3000	60	25	75	0.0305
5	3	2500	50	30	70	0.0269
6	11	2500	50	56	44	0.0131
7	7	1500	30	27.5	72.5	0.0275
8	7	3500	70	8.5	91.5	0.0397
9	7	2500	50	3.5	96.5	0.0535
10	7	2500	50	3.5	96.5	0.0549
11	7	2500	50	3.5	96.5	0.0672
12	7	2500	50	3.5	96.5	0.0572
13	7	2500	50	3.5	96.5	0.0551

Table 4.3 has shown that if the pH is adjusted to 7 and the coagulant dosage used is 50 %v/v (2500 mg/L), the fluoride removal will be the highest, which is 96.5 % and final fluoride concentration that can be achieved is 3.5 mg/L. The sludge produced by PAC is relatively lower as compared to aluminium sulfate and ferric chloride. The sludge mass produced is only 0.0535 g for pH 7 and 50 %v/v dosage. Among the mass of sludge produced, the highest value is only 0.0672 g. It is observed that the sludge produced by the PAC is the least as compared to aluminium sulfate and ferric chloride. The fluoride removal result is match with the result that is obtained by Dubey, et al. (2018) which found out that the 80 % dosage of PAC give better fluoride removal as compared to 100 % dosage. The residue fluoride for 100 % dosage is higher than 80 % dosage, which indicates that higher dosage does not promise higher fluoride removal. But, with optimal dosage, the fluoride removal effect is

better. In this study, with same pH, which is 7, the 70 %v/v dosage is able to achieve 91.5 % removal but the 50 %v/v dosage is able to reach 96.5 % removal, which is higher removal with lower concentration.

4.1.4 Effect of pH on fluoride removal

pH is one of the factor that will influence the fluoride removal in wastewater as it will change the surface change of adsorbents. According to Singh, Kaushik and Raghuvanshi (2008), in the acidic medium, the weakly ionized hydrofluoric acid are formed and thus reduces the availability of free fluoride for adsorption. By this, the fluoride removal in acidic medium will have lower efficiency. In alkaline condition, the competition of OH^- ions with the F^- ions will lower the adsorption of F^- ions onto the adsorbents. To investigate the effect of pH on the fluoride removal, different coagulant were added to the wastewater under different pH condition to find the optimum pH condition to be used.

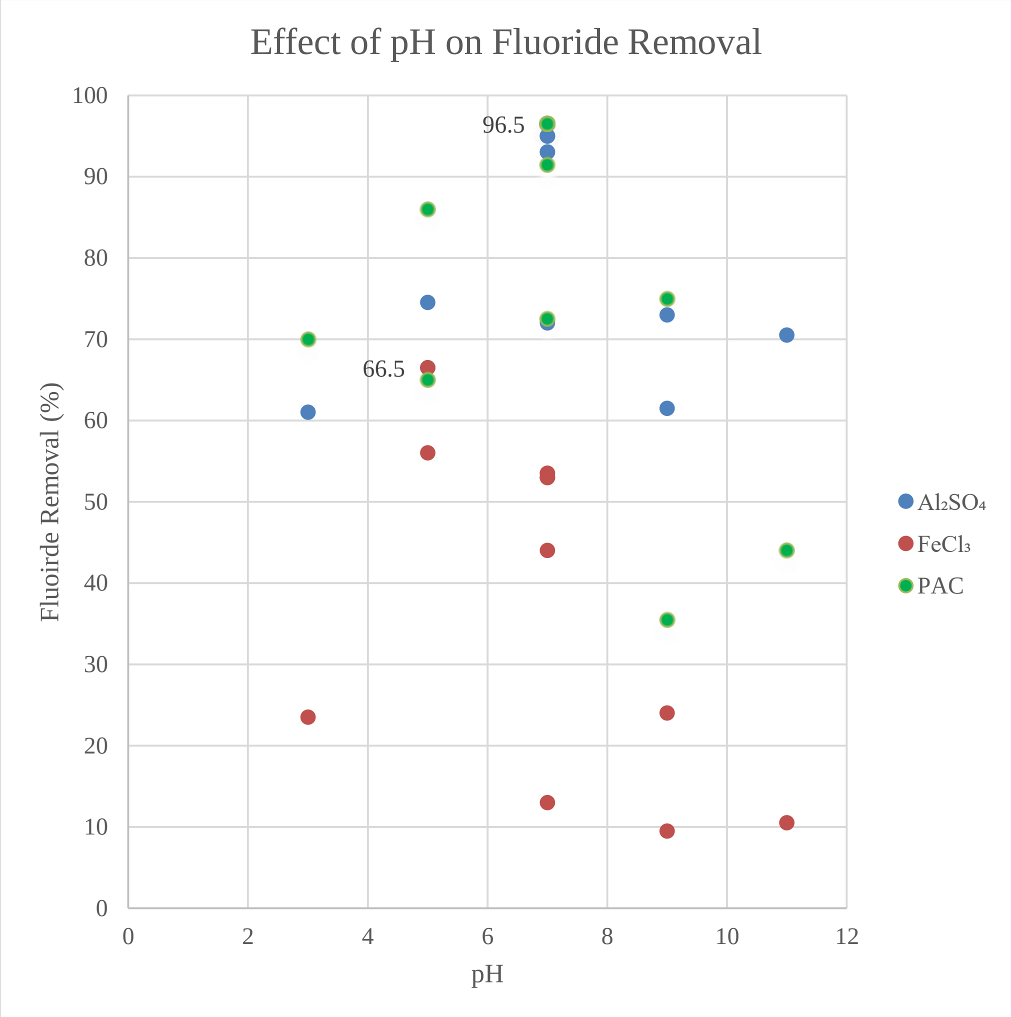

Figure 4.1: Fluoride Removal for pH Range from 3 to 11 by Different Coagulant

Figure 4.1 shows the fluoride removal at the pH range of 3 to 11 by using three different coagulants, which are aluminium sulfate, ferric chloride and poly aluminium chloride. Overall, the graph has shown that the PAC has higher fluoride removal as compared to aluminium sulfate and ferric chloride. The aluminium cations are more efficient in fluoride removal than iron cations. As discussed before, both aluminium sulfate and PAC achieved the highest fluoride removal, which is 96.5 % at pH 7. This is in agreement with the work published by Aoudj, et al. (2012) that stated the maximum fluoride removal occurred at the pH range of 6 to 7. The $Al(OH)_3$ flocs will adsorb the F^- ion strongly and is optimal in the range of 6-7. Under acidic condition (below pH 6), the dissolved aluminium species which includes Al^{3+}, $Al(OH)^{2+}$, and $Al(OH)_2^+$ are prevalent and the aluminium hydroxide tends to be soluble.

Meanwhile for alkaline condition, the $Al(OH)_4^-$ is the predominant species. The defluoridation is maximize by the high concentration of the hydroxyl-aluminium when the pH is between 6 to 8.

Ferric chloride has the lowest fluoride removal among the coagulants. The highest fluoride removal that is achieved by ferric chloride is 66.5 %, which is when the pH of solution is adjusted to 5.The result is agreed with the findings done by Kowalchuk (2012). At the pH of 5.5, by using the same ferric dose, the final concentration of fluoride is the lowest as compared to pH 7.5 and 9.5. By using Ferric dosage of 50 mg/L, the wastewater treated at pH 5.5 will achieve the final fluoride concentration of approximately 3.8 mg/L (Kowalchuk, 2012, pp.46). At the pH of 7.5, it has higher concentration, which is approximately 4.3 mg/L and at the higher pH, which is 9.5, it is approximately 5.4 mg/L (Kowalchuk, 2012, pp.46). This also shows that the lower the pH, the final concentration of fluoride will be higher. The ferric chloride will have better fluoride removal at acidic condition.

4.1.5 Effect of coagulant dosage on fluoride removal

The coagulant dosage has a significant effect on the fluoride removal of the wastewater. An optimum dosage is required to maximize the fluoride removal and reduce the sludge produced at the same time.

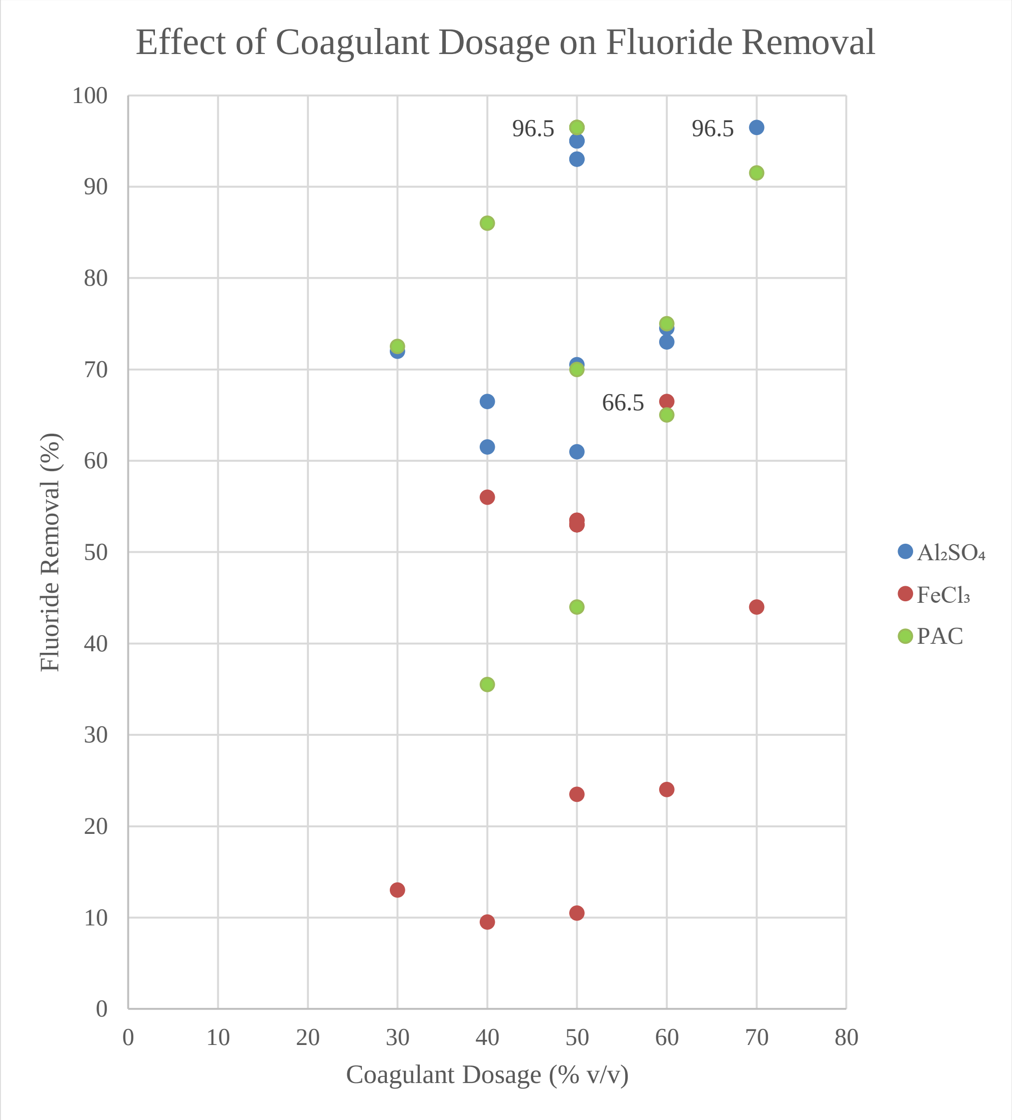

Figure 4.2: Fluoride Removal for Coagulant Dosage Range from 30 to 70 %v/v by Different Coagulants

Table 4.4: Fluoride Removal by Different Coagulants under Same pH and Dosage (pH: 7; Dosage: 50 % v/v)

Coagulant	**Fluoride Removal (%)**
Al_2SO_4	74.5
$FeCl_3$	66.5
PAC	65

Table 4.5: Fluoride Removal by Different Coagulants under Same pH and Dosage (pH: 5; Dosage: 60 % v/v)

Coagulant	Fluoride Removal (%)
Al_2SO_4	95
$FeCl_3$	53.5
PAC	96.5

Table 4.4 and 4.5 show the fluoride removal by different coagulants under fixed conditions. When the pH is fixed at 7 and dosage used is 50 %v/v, the fluoride removal for aluminium sulfate is highest (74.5 %) and PAC is the lowest (65 %). Meanwhile, when the pH is adjusted to 5 and the dosage used is 60 % v/v, the fluoride removal of PAC is the highest among coagulants, which is 96.5 %. In this condition, ferric chloride has the lowest fluoride removal, which is 53.5 %. The tables have shown that at different condition, the fluoride removal of the coagulants is different. Because of this, it is important to find the optimum condition for each coagulants to maximize the fluoride removal.

Figure 4.2 illustrates the effects of coagulants dosage on the fluoride removal by using aluminium sulfate (Al_2SO_4, $FeCl_3$, and PAC). There are two highest fluoride removal (96.5 %) observed, which are by using aluminium sulfate and PAC. For aluminium sulfate, the highest fluoride removal is achieved by using the coagulant dosage of 70 %v/v, meanwhile for PAC, by using only 50 %v/v, the maximum fluoride removal is achieved. Both PAC and aluminium sulfate have high ability to remove the fluoride but it depends on the external condition such as pH and coagulant dosage. Different dosage and pH will differ the fluoride removal. Under the same pH, aluminium sulfate has higher fluoride removal as compared to ferric chloride and PAC when the dosage is 70 %v/v. But, when the dosage is 40 %v/v, the PAC will has higher fluoride removal than the aluminium sulfate and ferric chloride. For the ferric chloride, it has the lowest fluoride removal as compared to aluminium sulfate and PAC. The highest fluoride removal it can achieved is 66.5 %, which is by using 60 %v/v.

4.1.6 Sludge Produced by Coagulants

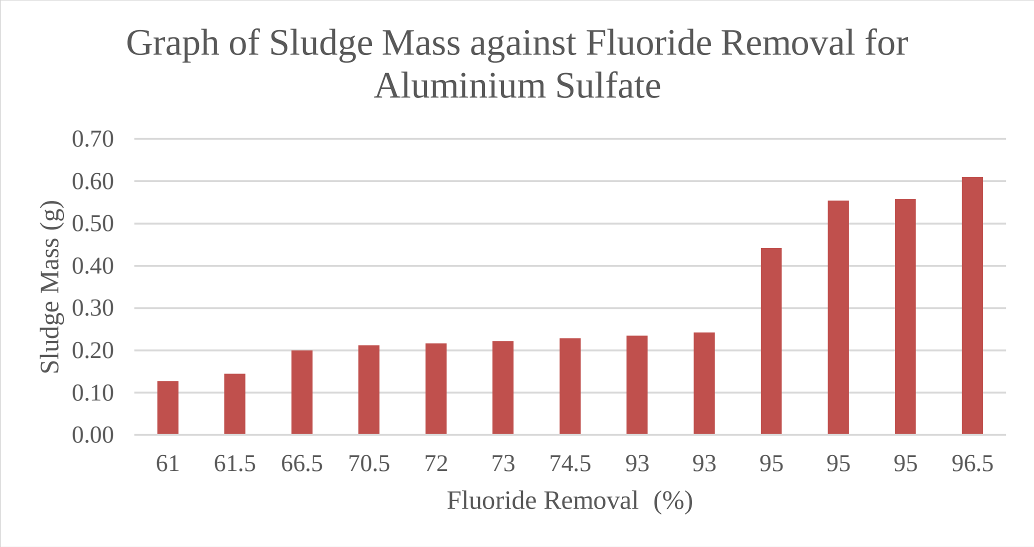

Figure 4.3: Sludge Produced by Aluminium Sulfate at Different Fluoride Removal

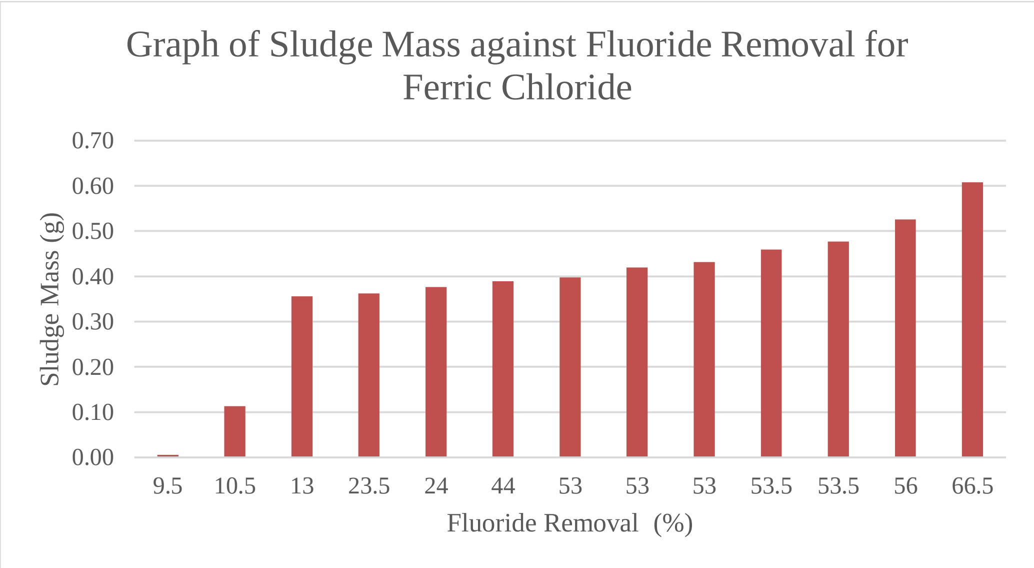

Figure 4.4: Sludge Produced by Ferric Chloride at Different Fluoride Removal

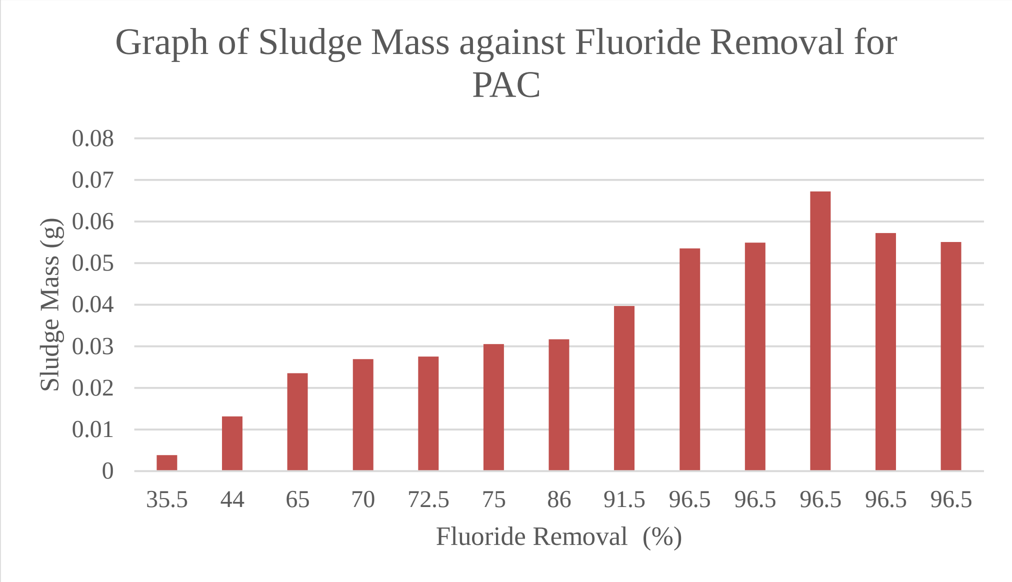

Figure 4.5: Sludge produced by PAC at Different Fluoride Removal

Based on the Figure 4.3, 4.4 and 4.5, the graphs are the graph for sludge mass produced by aluminium sulfate, ferric chloride and PAC respectively at different fluoride removal. The highest mass of sludge produced by aluminium sulfate is 0.61 g, which is when the fluoride removal is 96.5 %. For ferric chloride, the heaviest mass of sludge produced is 0.6079 g, which is near to aluminium sulfate but the fluoride removal is lower, which is only 66.5 %. This means that the ferric chloride will produced higher amount of sludge with lower fluoride removal. As such, ferric chloride will not be considered as effective coagulant to remove fluoride. For PAC, the highest sludge mass is 0.0672 g, which is the lowest among three coagulants. For the sludge with the mass of 0.0672 g, the fluoride removal has reached 96.5 %, which is same as aluminium sulfate. With the same fluoride removal, aluminium sulfate produced more sludge than the PAC. Overall, PAC has the lowest sludge production with high fluoride removal. It is an ideal coagulant as it has high fluoride removal with low sludge production.

According to Figure 4.3, 4.4 and 4.5, each of the graph unanimously shows that when the fluoride removal increased, the sludge mass produced will increased. When there is more fluoride removal, this means that more sludge precipitate are formed as more fluoride ions are removed from the wastewater.

For aluminium sulfate and PAC, the sludge is generated during the precipitate of aluminium hydroxide, which forms insoluble aluminium fluoride complexes. The addition of aluminium sulfate / PAC will introduce Al^{3+} ion in the fluoride wastewater. The ion will react with OH^- or Al-F complexes as shown in equation 4.1. The Al-F coprecipitation are mostly responsible for the fluoride removal from the wastewater.

$$Al^{3+} + 3OH^- \rightarrow Al(OH)_3 \quad (4.1)$$

Initially, when the solution is acidic, the Al-F complexes are dominant. The soluble species in the aqueous solution includes Al-F complexes, Al-OH complexes, Al^{3+} ion and free fluoride (Gong, et al., 2011). As the solution become more alkaline (more OH^-) is added, the Al species are precipitated at neutral pH. A new precipitate is formed, which is Al-F-OH. As the pH become higher, the concentration of OH^- will increase. More OH^- ions have dissolved in the solution and cause the competition between the OH^- and F^- ions to bond with Al^{3+} ions. This will leads to more aluminium-fluoride compounds forming and settling out of the solution. Consequently, the presence of colloidal aluminium species available for fluoride removal decreased, thus limiting the removal of fluoride. The fluoride involved in the hydrolysis of Al^{3+} and forms the insoluble precipitate of $AlF_2(OH)$, $AlF(OH)_2$ and AlF_3 as shown in Equation 4.2, 4.3 and 4.4 (Wan, et al., 2021).

$$AlF^{2+} + OH^- \rightarrow AlF_2(OH) \quad (4.2)$$

$$AlF(OH)^+ + OH^- \rightarrow AlF(OH)_2 \quad (4.3)$$

$$AlF^{2+} + 2OH \rightarrow AlF(OH)_2 \quad (4.4)$$

PAC has more aluminium species as compared to aluminium sulfate and thus it involves more complex mechanisms in fluoride removal. The polymeric aluminium species are highly positive charged and shows a stronger affinity for fluoride ions. In contrast, the polymeric aluminium exhibits a lower average charge density as compared to monomeric aluminium species. As a result, the aluminium polymer with higher degree of polymerization requires fewer hydroxyl or fluoride ions to achieve charge neutralization

(Dubey, Agarwal and Gupta, 2018). This is the reason PAC require lesser NaOH to maintain the alkalinity as compared to aluminium sulfate in this study. The polymeric aluminium has showed net structure and fluoride will be able to adsorb on both inner and outer region. The outer fluoride is bonded through ion exchange and charge neutralization, making it easily replaced by OH^- ions. Meanwhile, the inner fluoride is more stable as the removal is through sweep flocculation, and less likely to be displaced by hydroxyl ions (Dubey, Agarwal and Gupta, 2018). Figure 4.6 shows the mechanism for aluminium sulfate and PAC in the fluoride removal from wastewater.

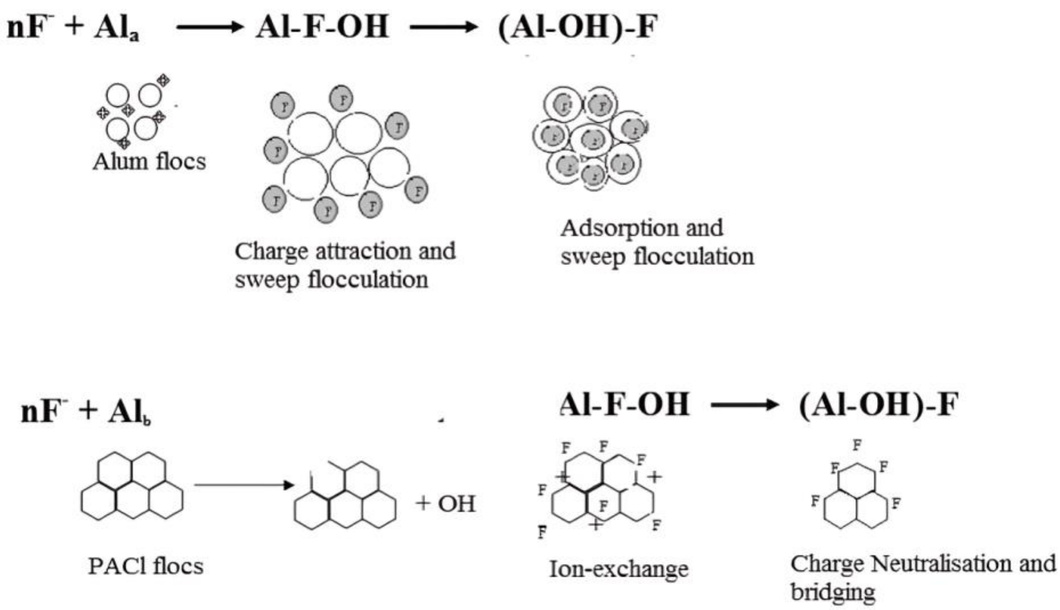

Figure 4.6: Mechanism for Aluminium Sulfate and PAC in Fluoride Removal (Dubey, Agarwal and Gupta, 2018)

4.1.7 SEM Analysis

SEM (Scanning Electron Microscopy) was used to compare the particle size and microstructure of the sludge for the three coagulants. Figure 4.7 shows the images of the sludge produced by aluminium sulfate, ferric chloride and PAC under same magnification factor, which is 40×. Overall, the particle size of the ferric chloride is the largest among three coagulants meanwhile PAC has the smallest particle size. When the particle size is smaller, the higher the fluoride removal will be. This is supported by the finding done by Schoeman and MacLeod (1987) that stated the external surface area of the smaller size particle would be larger than the larger particles. This expanded external surface area contributes to faster rate of adsorption as better access of internal adsorption site is given to fluoride ions.

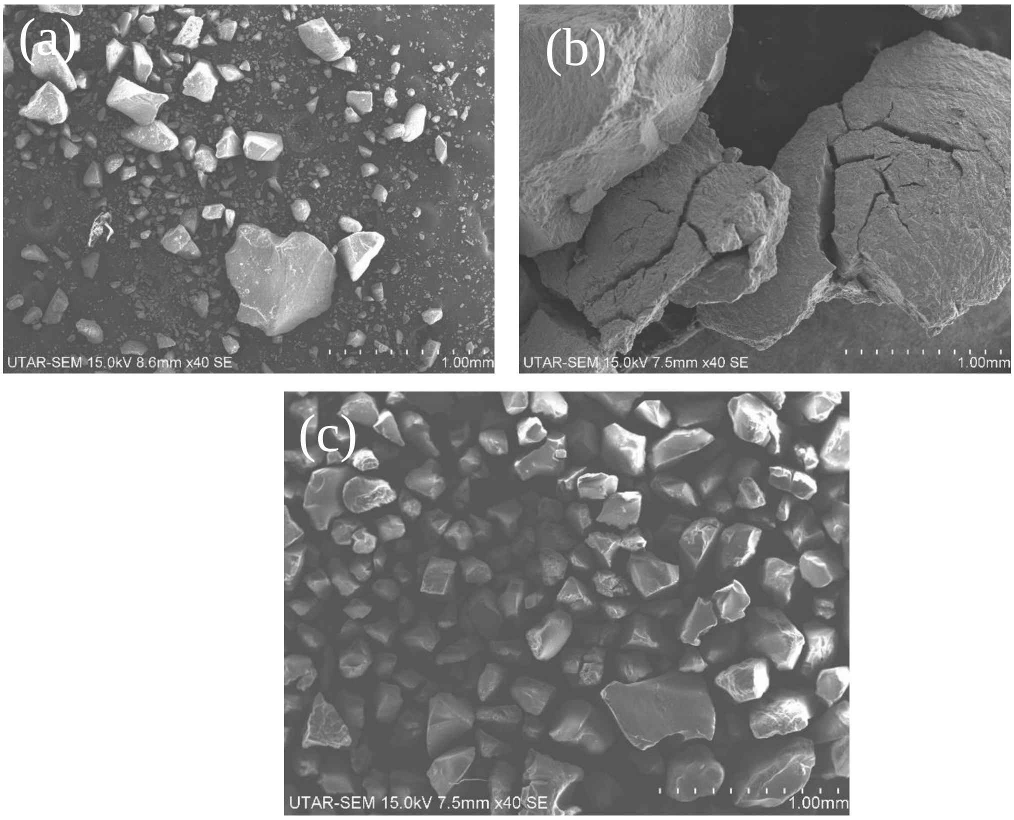

Figure 4.7: SEM Images Obtained at 40× Magnification of Sludge Precipitate in Artificial Wastewater of (a) Aluminium Sulfate, (b) Ferric Chloride and (c) PAC

4.1.8 Analysis of Fluoride Removal Using Response Surface Methodology

After the final fluoride concentration data was collected, it was imported to the Design Expert software to establish the correlation between variables and construct a model to predict and represent the performance of each coagulants under different conditions.

Based on Appendix E and F, fluoride removal of aluminium sulfate and ferric chloride are expressed as a reduced quartic model. The fluoride removal of PAC is expressed as Quadratic Model according to Appendix G. The P-values that less than 0.05 indicates that these models are significant. For aluminium sulfate (Appendix E), the term A (pH), B (Dosage), A^2, B^2, AB^2

and A^2B^2 are significant model terms. The software generated an equation that can be used to make prediction about the response at different conditions of the factor. Equation 4.1 is the predicted equation for the model.

$$y = 136.85 - 6.04A - 0.89B + 0.76AB - 2.54A^2 - 0.04B^2 \quad (4.1)$$

where
A = pH
B= Coagulant Dosage, % v/v

For ferric chloride (Appendix F), the term A, B, AB, A^2, B^2, A^2B, AB^2 and A^2B^2 are the significant model terms. An equation is generated to describe the model and the equation can be used to predict the response. Equation 4.2 is the predicted equation for the model.

$$y = 1846.37 - 325.89A - 74.29B + 13.66AB + 6.02A^2 + 0.73B^2 - 0.29A^2B - 0.13AB^2 + 0.003A^2B^2 \quad (4.2)$$

where
A = pH
B= Coagulant Dosage, % v/v

In addition, for PAC (Appendix G), the term A, AB, A^2 are the significant model terms. The F-value for this model is 6.74 and it implies that the model is significant and there is only 1.32% probability that this significant F-value could occur result from noise. An equation is formulated to represent the model, enabling the prediction of the response using this equation. Equation 4.3 is the predicted equation for the model.

$$y = 136.85 - 6.04A - 0.89B + 0.76AB - 2.54A^2 - 0.04B^2 \quad (4.3)$$

where
A = pH
B= Coagulant Dosage, % v/v

Table 4.6: Fit Statistics for Aluminium Sulfate

Std. Dev.	1.10	**R^2**	0.9980
Mean	80.50	**Adjusted R^2**	0.9940
C.V. %	1.36	**Predicted R^2**	NA
		Adeq Precision	38.9483

Table 4.7: Fit Statistics for Ferric Chloride

Std. Dev.	**0.2739**	**R^2**	0.9999
Mean	39.46	**Adjusted R^2**	0.9998
C.V. %	0.6940	**Predicted R^2**	NA
		Adeq Precision	250.1466

Table 4.8: Fit Statistics for PAC

Std. Dev.	11.29	**R^2**	0.8280
Mean	78.62	**Adjusted R^2**	0.7052
C.V. %	14.36	**Predicted R^2**	-0.1949
		Adeq Precision	7.8431

Table 4.6, 4.7 and 4.8 show the fit statistics value for three coagulants. The R^2 is used to measure the strength of the relationship between model and the dependent variables. The nearer the value to 1, the better the model fits the data. The value of 1 represent that the model predicts 100 % of the relationship. Figure 4.6 and 4.7 show that the R^2 value for aluminium sulfate and ferric chloride are 0.9980 and 0.9999 respectively, which means the model fit very well with the data. The R^2 value is 0.8280 for PAC, as shown in Table 4.8. This shows that the model fit the data, but does not as good as aluminium sulfate and ferric chloride do. Appendix J has shown the graph that shows the predicted versus actual data, and it is observed that the data do not lie on the line, but is near to the line.

4.1.9 3D Response Surface for Coagulants

Figure 4.8, 4.9 and 4.10 show the 3D Response Surface for aluminium sulfate, ferric chloride and PAC. The 3D Response Surface can be used to find the factor settings that will produce the desired response (maximum fluoride removal) and to model the relationship between the independent variables and response. For Figure 4.8, the highest fluoride removal by aluminium sulfate happens at the region of pH 7 and coagulant dosage of 50 %v/v. The 3D

Response Surface shows that the maximum fluoride removal will happen at optimum pH. The decrease or increase in pH value and coagulant dosage from the optimal level will reduce fluoride removal.

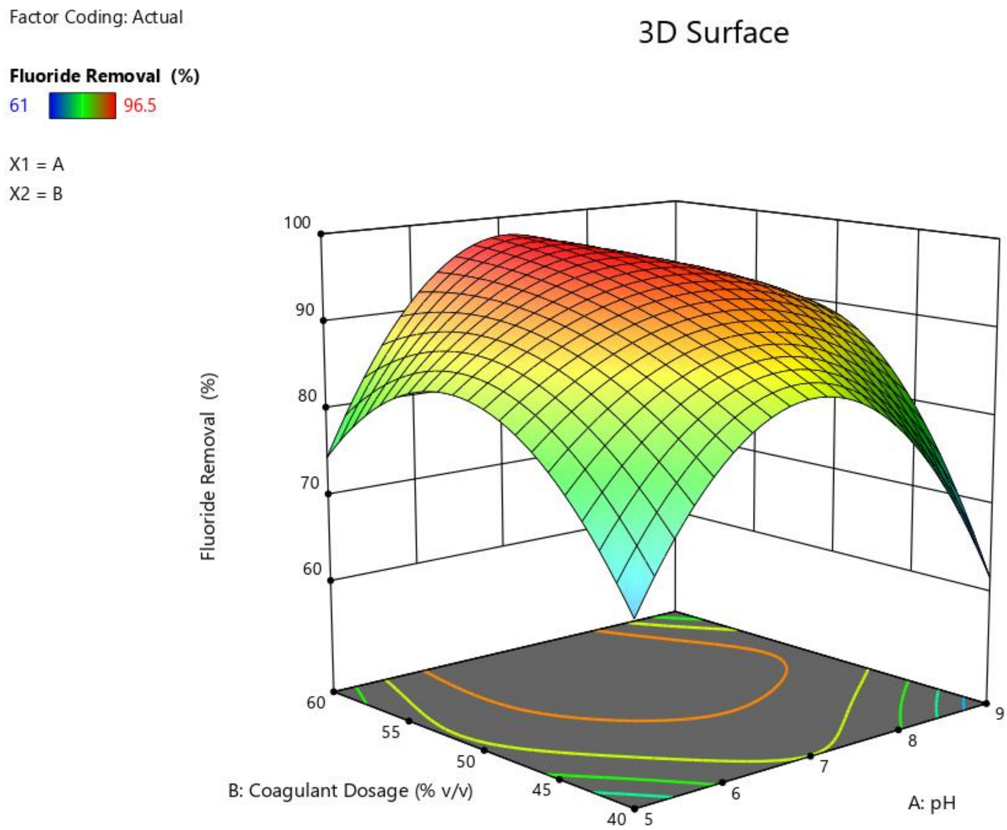

Figure 4.8: 3D Response Surface for Aluminium Sulfate

From Figure 4.9, the highest removal takes place at the region of pH 5 and coagulant dosage of 60 %v/v for the case of ferric chloride. The increment of pH will decrease the fluoride removal. In contrast, the surface response shows that the increment of coagulant dosage will increase the fluoride removal.

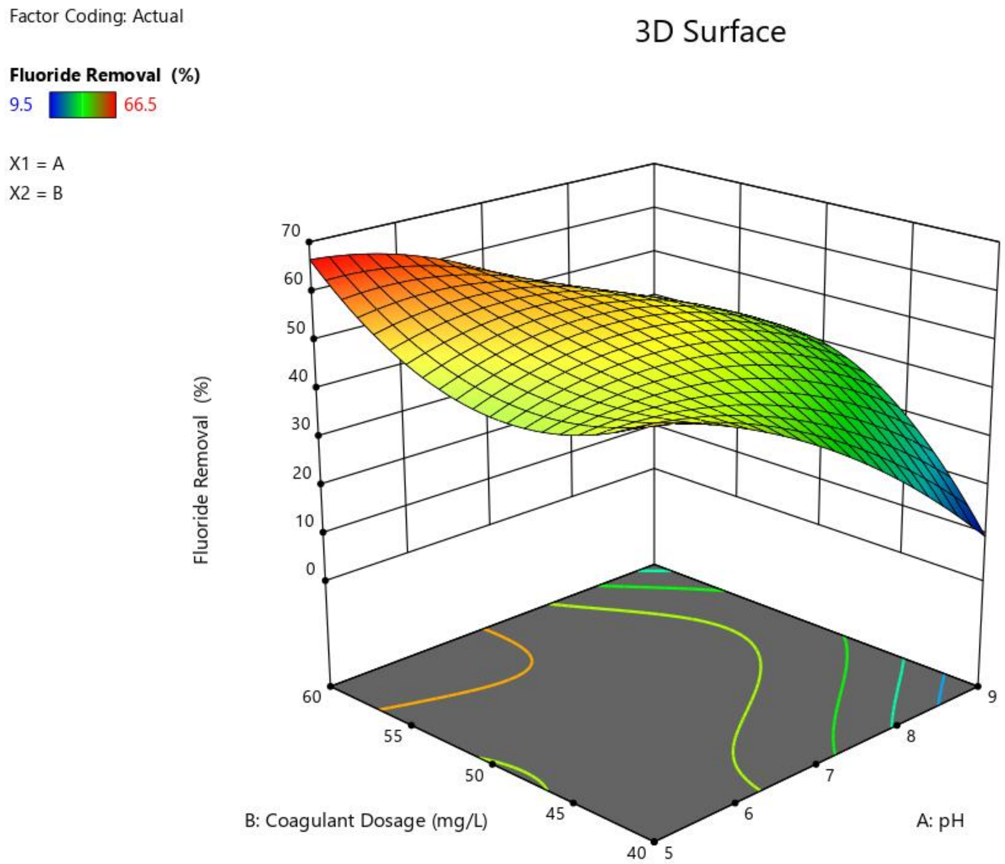

Figure 4.9: 3D Response Surface for Ferric Chloride

Figure 4.10 shows that the maximum fluoride removal is achieved when the pH is 7 and coagulant dosage of 50 %v/v. The increment of pH value and the coagulant dosage will lower the fluoride removal. As the R^2 of PAC model is lower as compare to aluminium sulfate and ferric chloride, the 3D surface response for PAC will not be as accurate as the 3D surface response for aluminium sulfate and ferric chloride do.

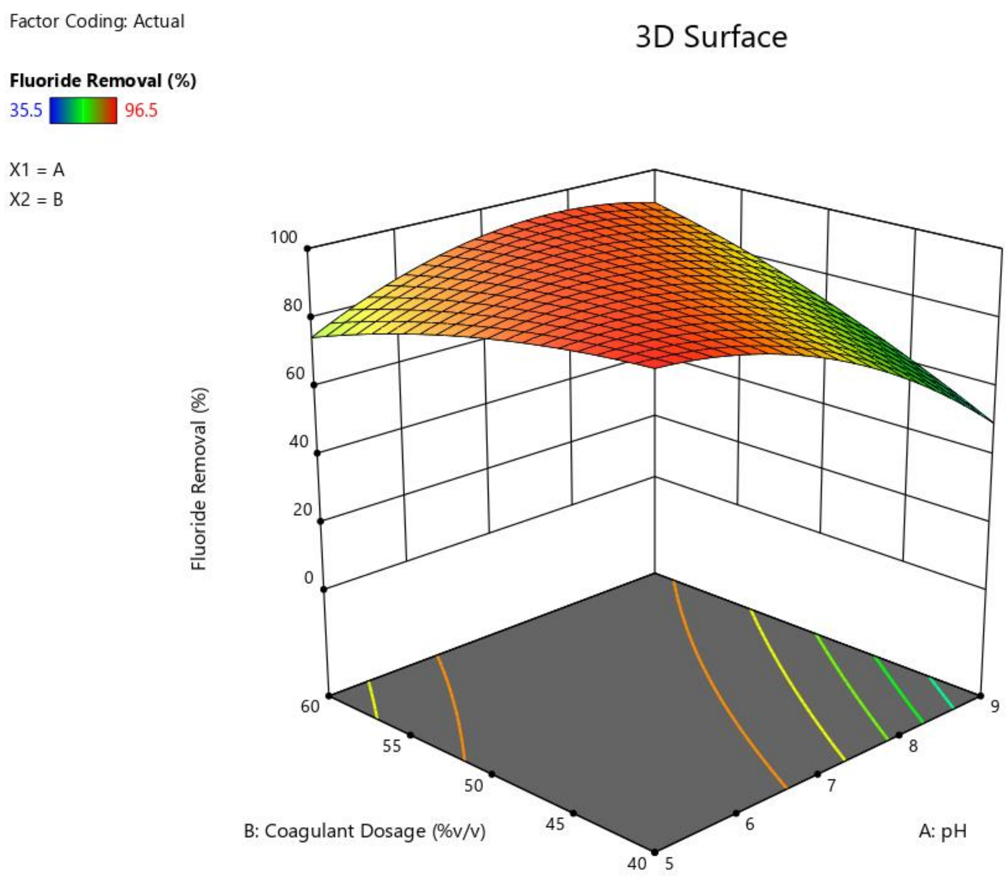

Figure 4.10: 3D Response Surface for PAC

4.2 Real Industrial Wastewater

Table 4.9: Fluoride Removal and Sludge Mass for Each Coagulant

Coagulant	PAC	$FeCl_3$	Al_2SO_4
Condition	pH 7	pH 5	pH 7
	50% v/v	60% v/v	50% v/v
Fluoride Removal (%)	85.13	73.97	74.66
Sludge Mass (g)	0.1364	0.4192	0.3234

Based on Table 4.9, PAC has highest fluoride removal among the coagulants used under their optimum condition. PAC is able to achieve the fluoride removal of 85.13 %, which is considered as high. Aluminium sulfate has lower fluoride removal than PAC, which is 74.66 % meanwhile ferric chloride is 73.97 %, the lowest fluoride removal. This result is agreed with the research result presented by Dubey, Agarwal and Gupta (2018) that stated PAC worked better because of the superiority of the main flocculation mechanism, particle bridging and over sweep floc mechanism of aluminium sulfate under the low turbidity suspensions.

PAC has the lowest sludge mass, which is only 0.1364 g and aluminium sulfate has the sludge mass of 0.3234 g, which is higher than PAC. Aluminium sulfate tends to form larger flocs as compared to PAC due to the denser structure resulting from charge neutralization, whereas the flocs produced through sweep floc mechanism are more loosely arranged (Jiao, et al., 2017). Ferric chloride produced the heaviest sludge mass (0.4192 g). This is because ferric chloride has higher charge density, which results in stronger attraction to negatively charged particles in the water (Liu, et al., 2021). The stronger attraction will lead to formation of larger and heavier flocs and thus caused the mass of sludge to increase. The detailed parameter were listed in Table 4.10 for aluminium sulfate, Table 4.11 for ferric chloride and Table 4.12 for PAC.

Table 4.10: Parameters of Experiment by using Aluminium Sulfate

Initial pH of Wastewater	2.58
Initial Concentration of Wastewater (mg/L)	73
pH of Aluminium Sulfate	3.05
Solution pH after adding NaOH	7.25
Volume of NaOH added (mL)	12
Final Concentration (mg/L)	18.5
Fluoride Removal (%)	74.66

Table 4.11: Parameters of Experiment by using Ferric Chloride

Initial pH of Wastewater	2.58
Initial Concentration of Wastewater (mg/L)	73
pH of Ferric Chloride	1.94
Solution pH after adding NaOH	5.19

Table 4.11: Continued

Volume of NaOH added (mL)	12.3
Final Concentration (mg/L)	19
Fluoride Removal (%)	73.97

Table 4.12: Parameters of Experiment by using PAC

Initial pH of Wastewater	2.58
Initial Concentration of Wastewater (mg/L)	74
pH of PAC	3.98
Solution pH after adding NaOH	7.14
Volume of NaOH added (mL)	2.5
Final Concentration (mg/L)	11
Fluoride Removal (%)	85.13

4.2.1 SEM Analysis

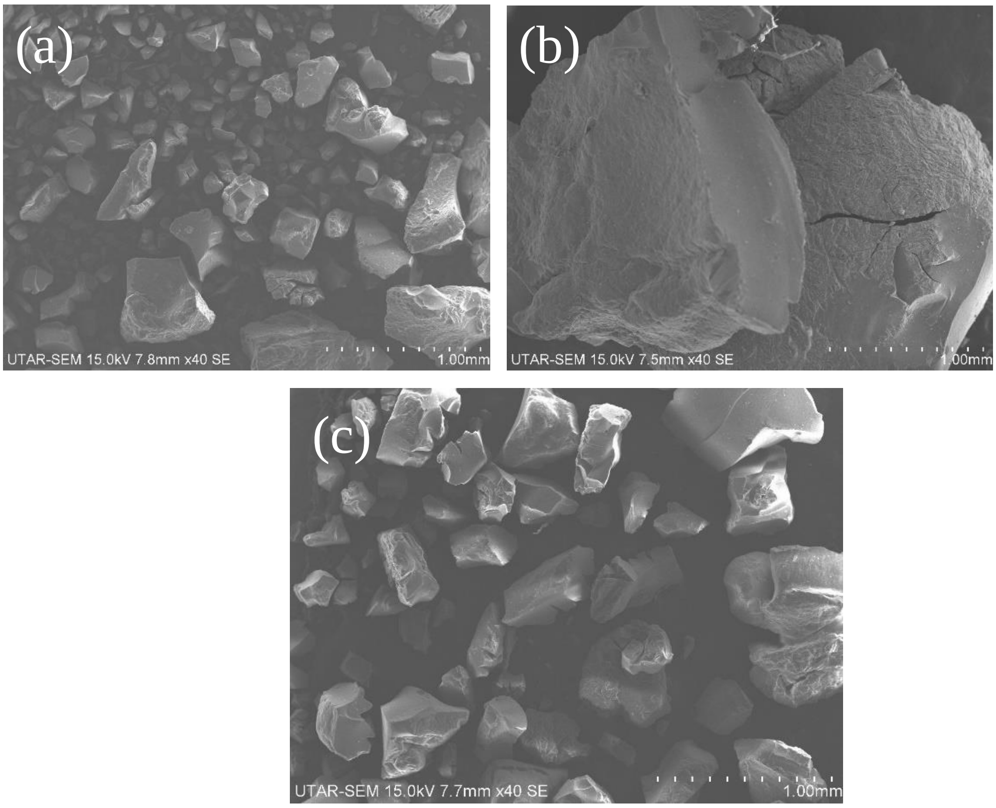

Figure 4.11: SEM Images Obtained at 40× Magnification of Sludge Precipitate in Real Industrial Wastewater of (a) Aluminium Sulfate, (b)Ferric Chloride and (c)PAC

The sludges produced by the coagulants after the wastewater treatment of real industrial wastewater were also collected and dried. After that, the sludge precipitates were also undergo the SEM analysis to investigate the microstructures. As there are other pollutant that present in the real industrial wastewater, the sludge produced will be different from the artificial wastewater that only contains fluoride pollutant. Based on Figure 4.11, the sludge precipitate of aluminium sulfate and PAC are almost identical in particle size. The particle size of sludge produced by ferric chloride is largest.

4.3 Summary of Result

Table 4.13 shows the summary of the result for artificial wastewater. From the table it is shown that the PAC has the highest fluoride removal (96.5 %) with the lowest sludge formation, which is 0.0672 g among three coagulants. The optimum condition for PAC is pH 7 and 50 %v/v coagulant dosage. It is shown that the PAC is the coagulant that is able to fulfil the objectives of this study.

Table 4.13: Summary Table for Artificial Wastewater

Coagulants	Fluoride Removal (%)	Sludge Mass (g)	Condition
Aluminium Sulfate	95	0.5538	pH 7 50 %v/v
Ferric Chloride	66.5	0.6079	pH 5 60 %v/v
PAC	96.5	0.0672	pH 7 50 %v/v

Table 4.14 shows the summary of result for real industrial wastewater. The condition used is the optimum condition obtained from experiment of artificial wastewater. From the table, it is shown that the PAC has the highest fluoride removal, which is 85.13 %. At the same time, PAC also has the lowest sludge formation (0.1364 g). This has concluded that PAC is the coagulant that has the highest fluoride removal with lowest sludge formation in this study.

Table 4.14: Summary Table for Real Industrial Wastewater

Coagulants	Fluoride Removal (%)	Sludge Mass (g)	Condition
Aluminium Sulfate	74.66	0.3234	pH 7 50 %v/v
Ferric Chloride	73.97	0.4192	pH 5 60 %v/v
PAC	85.13	0.1364	pH 7 50 %v/v

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In this study, the artificial fluoride wastewater was prepared and subjected to the coagulation process to remove the fluoride under different pH and coagulant dosage by using three coagulants, which are aluminium sulfate, ferric chloride and poly aluminium chloride (PAC). The characteristic of the sludge produced by the coagulants was characterized by using SEM. SEM analysis has shown that the sludge produced by ferric chloride has the largest particle size. In contrast, the sludge produced by PAC has the smallest particle size.

The effect of pH and coagulant dosage onto the fluoride removal in wastewater were investigated to find the optimum condition to maximize the fluoride removal and minimize the sludge formed. For aluminium sulfate and PAC, the optimum condition is found at pH 7 and 50 %v/v, meanwhile the optimum condition for ferric chloride is at pH 5 with concentration of 60 %v/v. It is found that the fluoride removal under the optimum condition for aluminium sulfate and ferric chloride is 95 % and 66.5 %, respectively. The fluoride removal of PAC is the highest among the coagulants, which is 96.5 %. After obtaining the optimum condition, it is applied into the real industrial wastewater. The result obtained is aligned with the artificial wastewater, which means PAC has the highest fluoride removal (85.13 %), followed by aluminium sulfate (74.66 %) and ferric chloride (73.97 %). Other than that, PAC has the lowest mass of sludge produced, which is 0.1364 g and ferric chloride has the highest mass (0.6079 g). In this study, PAC is the most effective coagulants in fluoride removal among the investigated coagulants as it has high fluoride removal with low sludge production. The objectives of the study have been achieved, which shows that PAC has the highest fluoride removal (85.13 %) and lowest sludge production (0.0672 g) under the condition of pH 7 and 50 %v/v. This result is found by using the RSM technique.

5.2 Recommendations for Future Work

Firstly, XRD analysis for the phase identification of the sludge can be performed. This can help to understand the composition of the sludge after the coagulation process.

In addition, more parameters can be investigated such as initial fluoride concentration, contact time and turbidity to find out the optimum condition to maximize the fluoride removal of each coagulants. These parameters have a significant impact on the fluoride removal. If more parameters are involved, the difficulty of analysis will be higher, thus, more details work are required. Furthermore, the involvement of more factors will increase the number of experiments to be conducted. As there are limited time and resource available to conduct the experiment and interpretation of data, more detailed study can be conducted in the future. In short, the following are the summarised recommendations that can be made to improve the study:

- XRD analysis with phase identification can be done to determine the composition of the sludge.
- Add more manipulated factors such as initial fluoride concentration, contact time and turbidity to determine the optimum condition for most effective coagulants to remove fluoride from wastewater.
- Increase the variety of the coagulants used as there are more coagulants that are introduced into the market such as highly polymerized zirconium coagulants (ZXC) and potassium ferrate (K_2FeO_4).

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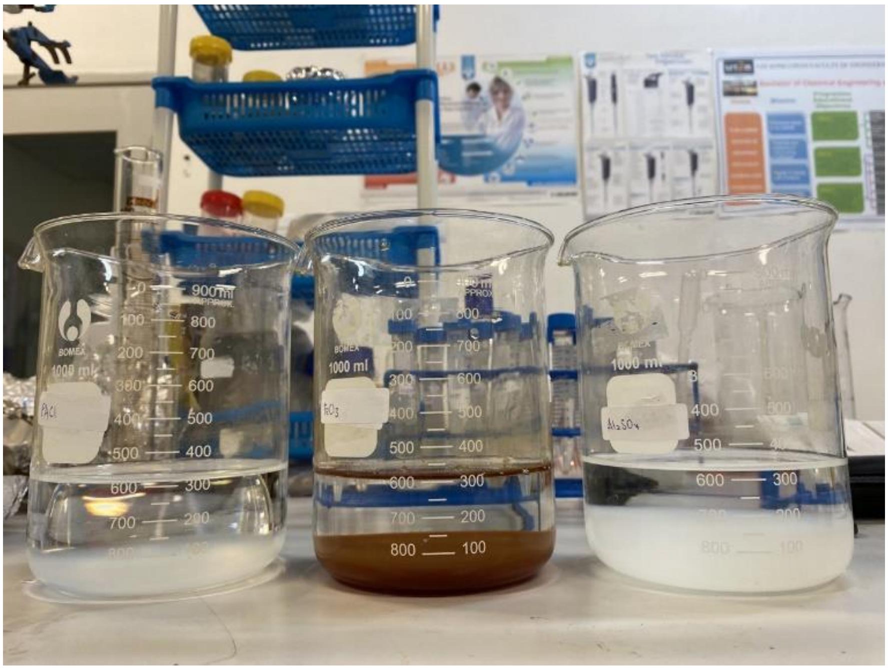
APPENDICES

Appendix A: Settlement of Real Industrial Wastewater after Treated with PAC (Left), Ferric Chloride (Middle) and Aluminium Sulfate (Right)



Appendix B: Parameter of Experiment for Artificial Wastewater with Aluminium Sulfate (pH 7; coagulant dosage 50 %v/v)

Initial pH of Wastewater	7.86
Initial pH of Aluminium Sulfate	2.96
pH after Adding HCl	1.99
HCl Volume used, mL	1.5
pH of Mixture of Wastewater and Aluminium Sulfate	7.40
NaOH Volume used, mL	16.4
Final Fluoride Concentration, mg/L	7

Appendix C: Parameter of Experiment for Artificial Wastewater with Ferric Chloride (pH 7; coagulant dosage 50 %v/v)

Initial pH of Wastewater	5.82
Initial pH of Ferric Chloride	1.93
pH after Adding HCl	1.95
HCl Volume used, mL	1.8
pH of Mixture of Wastewater and Ferric Chloride	6.82
NaOH Volume used, mL	18.5
Final Fluoride Concentration, mg/L	46.5

Appendix D: Parameter of Experiment for Artificial Wastewater with PAC (pH 7; coagulant dosage 50 %v/v)

Initial pH of Wastewater	7.62
Initial pH of PAC	4.05
pH after Adding HCl	1.94
HCl Volume used, mL	1.8
pH of Mixture of Wastewater and PAC	7.50
NaOH Volume used, mL	5.2
Final Fluoride Concentration, mg/L	3.5

Appendix E: ANOVA for Fluoride Removal by Aluminium Sulfate

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**	
Model	2396.20	8	299.52	249.60	<0.0001	Significant
A-pH	45.13	1	45.13	37.60	0.0036	
B-Coagulant Dosage	300.12	1	300.12	250.10	<0.0001	
AB	3.06	1	3.06	2.55	0.1854	
A^2	1156.29	1	1156.29	963.57	<0.0001	
B^2	141.43	1	141.43	117.86	0.0004	
A^2B	4.17	1	4.17	3.47	0.1359	
AB^2	42.67	1	42.67	35.56	0.0040	
A^2B^2	682.14	1	682.14	568.45	<0.0001	
Pure Error	4.80	4	1.20			
Cor Total	2401.00	12				

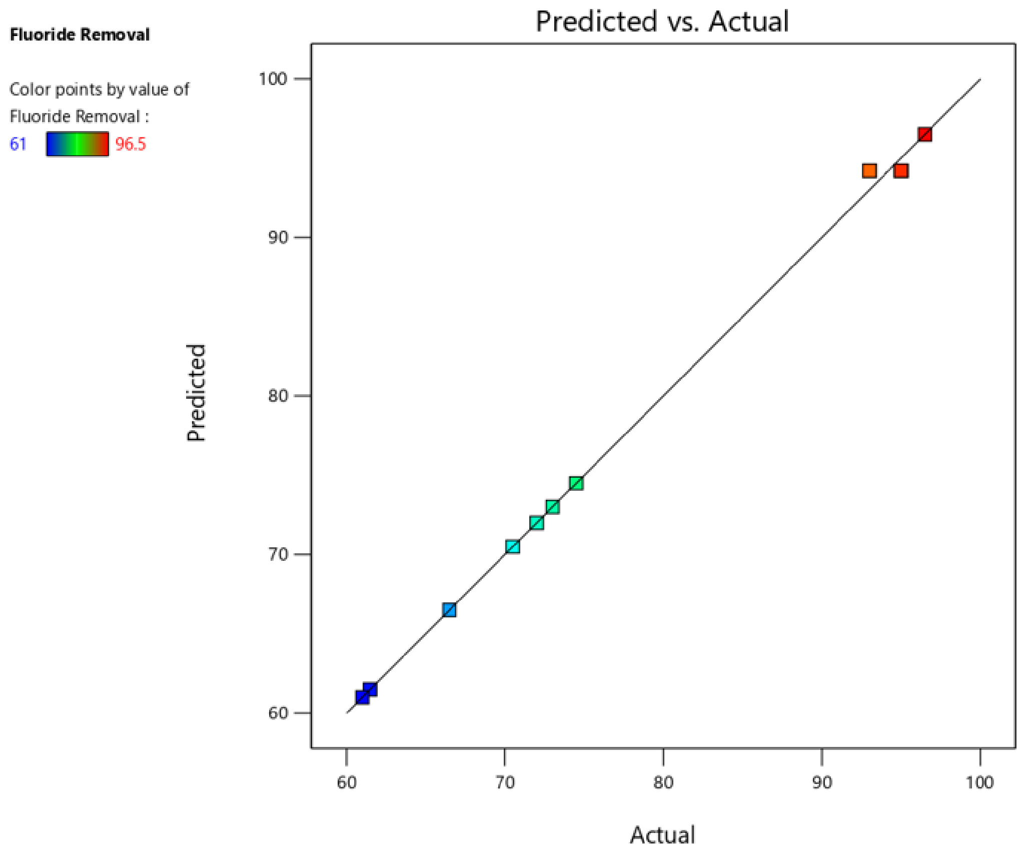
Appendix F: ANOVA for Fluoride Removal by Ferric Chloride

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**	
Model	4899.43	8	612.43	8165.72	<0.0001	Significant
A-pH	84.50	1	84.50	1126.67	<0.0001	
B-Coagulant Dosage	480.50	1	480.50	6406.67	<0.0001	
AB	4.00	1	4.00	53.33	0.0019	
A^2	1872.06	1	1872.06	24960.76	<0.0001	
B^2	871.56	1	871.56	11620.76	<0.0001	
A^2B	6.00	1	6.00	80.00	0.0009	
AB^2	962.67	1	962.67	12835.56	<0.0001	
A^2B^2	2.90	1	2.90	38.64	0.0034	
Pure Error	0.3000	4	0.0750			
Cor Total	4899.73	12				

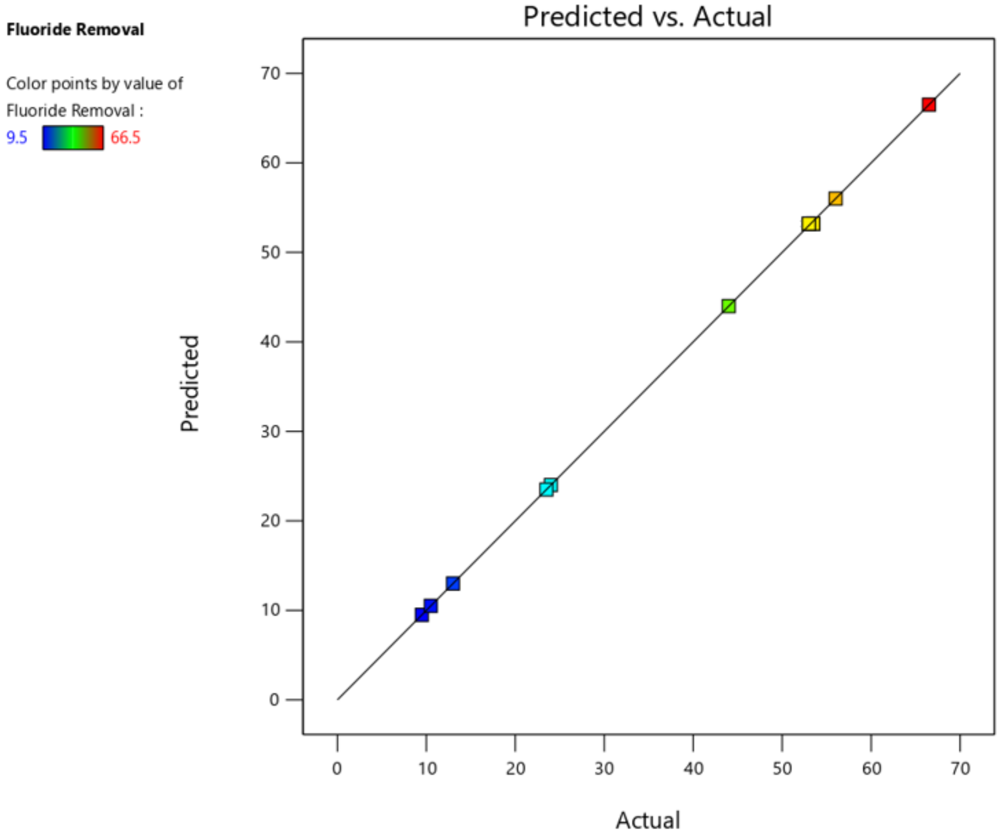
Appendix G: ANOVA for Fluoride Removal by PAC

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	4295.05	5	859.01	6.74	0.0132	significant
A-pH	713.02	1	713.02	5.60	0.0499	
B-Coagulant Dosage	266.02	1	266.02	2.09	0.1917	
AB	915.06	1	915.06	7.18	0.0316	
A^2	2374.07	1	2374.07	18.63	0.0035	
B^2	353.70	1	353.70	2.78	0.1397	
Residual	892.02	7	127.43			
Lack of Fit	892.02	3	297.34			
Pure Error	0.0000	4	0.0000			
Cor Total	5187.08	12				

Appendix H: Predicted vs Actual Graph for Aluminium Sulfate



Appendix I: Predicted vs Actual Graph for Ferric Chloride



Appendix J: Predicted vs Actual Graph for PAC