TREATMENT OF PULP AND PAPER MILL WASTEWATER USING *MORINGA OLEIFERA* VIA COAGULATION-FLOCCULATION TREATMENT PROCESS

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

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April 2020

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 **"TREATMENT OF PULP AND PAPER MILL WASTEWATER USING *MORINGA OLEIFERA* VIA COAGULATION-FLOCCULATION TREATMENT PROCESS"** was prepared by **CHUM CHINSON** has met the required standard for submission in partial fulfilment of the requirements for the award of Bachelor of Engineering (Honours) Chemical Engineering at Universiti Tunku Abdul Rahman.

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ABSTRACT

High levels of total suspended solids (TSS) and chemical oxygen demand (COD), as well as the presence of fibre in difficult-to-manage effluent from the pulp and paper (P&P) industries, remains a common concern due to its negative effects on the environment, especially on the surrounding waterbodies. Coagulation-flocculation is an important process in most wastewater treatment plants to remove a significant amount of suspended solids from the wastewater. At present, prolong exposure to residual amounts of common coagulants such as alum was found to be problematic as it can lead to several problems such as Alzheimer's disease or a huge volume of non-biodegradable sludge. Therefore, the objective of this project is to study the potential of a plant-based coagulant known as *Moringa oleifera* seed powder for the treatment of P&P wastewater. Alum is used as a benchmark coagulant for this study along with *M. oleifera* seed powder. Treatment efficiency was compared in terms of TSS and COD removal. The one-factor-at-a-time approach (OFAT) was used to screen the factors which affect the coagulation efficiency in this preliminary study. Each factor was investigated by adjusting its parameter trough jar tests: dosage (0, 0.5, 1.0, 1.5, 2.0, 2.5 g/L), pH (3, 5, 6.5, 8, 10), stirring speed (20, 40, 60, 80, 100 rpm) and settling time (0, 5, 10, 15, 20, 25 min). Dosage of 1.0 g/L, pH 6.5, stirring speed of 40 rpm and settling time of 20 min were determined as the optimum condition for treatment of P&P wastewater based on the OFAT approach. *M. oleifera* was able to achieve 85.59 and 29.62% whilst alum achieved 90.62 and 35.09% for TSS and COD removals respectively at optimum condition. The morphology, functional groups, crystallinity and thermal stability of coagulants were characterised using SEM-EDX, FTIR, XRD and TGA, respectively.

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LIST OF SYMBOLS / ABBREVIATIONS

$Al(OH)_3$	Aluminium hydroxide
$Al_2(SO_4)_3 \cdot xH_2O$	Alum
CH	Carbon Hydrogen bond
CH_2	Methylene
CH_2-N	Methyleneamino
C=O	Carbonyl group
CN	Carbon Nitrogen bond
COOH	Carboxyl group
CO_2	Carbon dioxide
COD	Chemical Oxygen Demand, mg/L
EDX	Energy-dispersive X-ray spectroscopy
EPA	Environment Protection Agency
FTIR	Fourier-transform Infrared Spectroscopy
H^+	Hydrogen ion
HCl	Hydrochloric acid
HCO_3^-	Bicarbonate ion
H_2O	Water
H_2SO_4	Sulphuric acid
NaOH	Sodium hydroxide
NH	Amide ion
OFAT	One-factor-at-a-time
OH^-	Hydroxyl ion
POME	Palm Oil Mill Effluent
P&P	Pulp and Paper
SEM	Scanning Electron Microscopy
SO	Sulphur monoxide
SO_4^{2-}	Sulphate ion
TGA	Thermogravimetric Analysis (TGA)
TSS	Total Suspended Solids, mg/L
FTIR	Fourier-transform Infrared Spectroscopy
XRD	X-ray Diffractometer

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CHAPTER 1

INTRODUCTION

1.1 General Introduction

A deluge of waste products from industries is discharged into the environment every day. United Nations' reports show that 1.5×10^6 m^3 of wastewater are generated every year. In many undeveloped countries, wastewater treatment plants could not be built due to the limitation of lands spaces and high construction cost. Therefore, approximately 70% of wastewater worldwide is released into natural water bodies without treatment. Water plays an important role in maintaining the ecosystem since it is essential to all living organisms on Earth. Any contamination in water sources will inevitably affect the nature of life.

In pulp and paper (P&P) industries, a huge amount of energy and chemicals are required during pulping, a process used to extract fibres from raw materials. Subsequently, these factories produce significant amounts of wastewater; therefore, the manufacturers are confronted with difficulties in observing environmental regulations. It was proven that a ton of product produces 20 000 to 60 000 gallons of wastewater (Pokhrel and Viraraghavan, 2004). In the United States, the P&P industry ranks third among other polluters; In Canada, 50% of the pollutants in waterbodies are from the P&P industry. Theen Seng Paper Manufacturing, a P&P company established since 1994 in Malaysia, produces 120 m^3 every day. Yet, there are more than twenty P&P mills in Malaysia (WEPA, n.d.).

In fact, the effluent should be sent for treatment before it is discharged into the river. Wastewater from the P&P industry contains a high amount of organic and inorganic solids. The untreated wastewater will cause water pollution and eventually lead to serious issues such as the depletion of oxygen in water sources. Ecosystems will be affected, and many aquatic organisms may go extinct due to the inability to adapt a polluted environment. Furthermore, the depth of rivers will reduce due to the accumulation and settling of solids from effluents, causing natural disasters such as flooding. Moreover, waterborne diseases among residents near polluted waterbodies are inevitable due to the consumption of polluted water. Therefore, it is important to treat the wastewater. At present, many wastewater treatment plants are equipped with advanced treatment technologies to improve the quality of the treated water. However, to prolong the lifespan of the equipment, pre-treatment plays an important role.

Coagulation-flocculation is commonly applied in the pre-treatment process. This process aims to remove a majority of the small particles and dirt through chemical and physical routes by changing the surface charges on the particles. Solids are usually suspended in wastewater due to the repulsion force among the particles. By destabilizing the particles’ charges, floc will be formed and settled at the bottom of the tank. Coagulation and flocculation will agglomerate the suspended particles including organic and inorganic matters, thereby reducing the COD of the effluent as well.

Certainly, coagulant must be added to aid and facilitate the process. Alum is usually dosed due to its high coagulating efficiency. Nevertheless, the usage of alum in wastewater treatment plants is suspected to be linked to the root cause of Alzheimer’s disease (arising from the residual aluminium found in treated water). Not only that, undeveloped countries could not afford the cost of importing chemical coagulants and disposal of non-biodegradable sludge. Thus, plant-based coagulant can be considered and studied for its potential to be utilized as a low cost and environmental friendly bio-coagulant with minimal operation skill for its application.

In the past, history has shown that native plants have been used as natural coagulants before. Yet, there is still a lack of scientific proof related to their efficiency. Therefore, chemical coagulants are much preferred in most of the industries today. Lately, the study of natural coagulants has gained attention due to the sustainability and impact of chemical coagulants on the environment. Today, many studies on different types of natural coagulants are available ranging from plant seeds to fruit waste (peels). The examples of plant seeds are *Phaseolus vulgaris* (Antan, Sciban, and Petrovic, 2010), *Cicer arietinum* (Gurumath and Suresh, 2019), *Parkinsonia aculeata* (Marobhe, Dalhammar, and Gunaratna, 2007), *Vigna unguiculata* (Marobhe, Dalhammar, and Gunaratna, 2007), okra extract (Al-Samawi and Shokralla, 1996) to list a few. The application of natural coagulants in wastewater treatment plants can reduce the presence of harmful chemicals in the environment. Among the natural coagulants available, seed powder of *M. oleifera* was proven to effectively remove TSS and COD while treating POME, wastewater from the tofu and jeans leaching industries. Moreover, seed powder is readily used and dosed into the wastewater without any pre-treatment steps. Thus, *M. oleifera* is studied to treat the effluent from the P&P industry.

In this study, the main aim is to evaluate the potential of using *M. oleifera* for the treatment of P&P mill wastewater. In order to determine the key factors and best conditions for the treatment, the one-factor-at-a-time (OFAT) approach was used. OFAT allows the study of a factor while keeping the other factors constant. An optimum point from each factor is selected and it will be kept constant in the subsequent study of another parameter.

1.2 Importance of the Study

At present, the quality of the water has dwindled due to the massive urbanisation of rural areas, development of industrial areas and other human activities. Increased production rate to meet the global demand for paper indirectly increases the volume and pollutants found in wastewater as well. Higher dosage of coagulant is needed to treat the wastewater (Asharuddin et al., 2019.). This will subsequently increase the expenses of the overall process. Apart from that, since most of the industries are using coagulant such as alum and ferric sulphate, excessive usage of these chemicals might affect the ecosystem. In contrast, plant-based coagulants are formed naturally and could greatly reduce the environmental impact caused by chemical coagulant. Therefore, the studies on plant-based coagulants are important as it has the potential to replace and reduce the usage of chemical coagulants.

1.3 Problem Statement

Wastewater released from the P&P industry has led to the formation of scum and unpleasant smell in the environment. Moreover, the effluents contain different pollutants that will physically and chemically change the conditions of the water system. The effluents produced depends on the chosen production pathway and the raw material used. Yet, generally, the produced wastewater contains high COD and different types of organic as well as inorganic compounds (Kamali and Khodaparast, 2015). Report shows that about 40 to 50 million metric ton of suspended solids is found in the effluent every year (Haddaway, 2014). Thus, the effluent must be treated before it is discharged to the environment.

1.4 Aim and Objectives

The aim of this study is to study the potential of utilising *M. oleifera* as a coagulant to treat pulp and paper mill wastewater in the coagulation-flocculation process. The objectives include:

(i) To investigate and identify the key factors which affect the performance of *M. oleifera* for the treatment of pulp and paper mill wastewater via the coagulation-flocculation process.

(ii) To establish the best condition for the treatment of pulp and paper wastewater using *M. oleifera* seed based on the one-factor-at-a-time approach (OFAT).

1.5 Scope and Limitation of the Study

The characteristics of wastewater from the P&P industry strongly depends on the production rate. The production will vary every month. When the production of a particular month is small, the volume of wastewater generated will be greatly reduced. As a result, the depth of the effluent will be different, giving rise to issues such as inconsistent sampling point during the collection of wastewater. Most of the solids will tend to remain at the lower part of the stream. Furthermore, rainfall is common in Malaysia. As a result, the rainwater will come into contact with the effluent from the process, thereby affecting the quality of the effluent (possible dilution). These will indirectly lead to inconsistent initial values of total suspended solids and chemical oxygen demand.

1.6 Contribution of the Study

Through this study, the discovery of an alternative natural coagulant is possible. This project will provide scientific evidence for the potential use of *M. oleifera* seed to treat pulp and paper mill wastewater. With this knowledge, the industry can anticipate the reduction of inorganic coagulant usage for wastewater treatment in the future.

1.7 Outline of the Report

This report consists of five chapters. Below is the brief description of each chapter:

Chapter 1:

The introduction briefly explains about the topic of this project. The pollution of water at the international level is described. The production of wastewater from the P&P industry is correlated to water pollution. The importance of the coagulation-flocculation process in the wastewater treatment plant is emphasised as well. The significance of the study on plant-based coagulants is explained. Additionally, the problem statement states the current problem faced by the P&P industry regarding wastewater generation and issues with sludge produced by alum. The aim and objectives of this study are listed. Moreover, the limitations of the study are elucidated. Last but not least, the contribution of the results obtained in this project is highlighted.

Chapter 2:

The literature review includes an overview of the P&P industry and its relevance in wastewater pollution. Then, the importance of wastewater treatment plants and details of coagulation process are enlightened under the topic of environmental impacts imposed by discharging the untreated wastewater into the natural water bodies, coagulation-flocculation process, types of coagulants, listing of studied natural coagulants and mechanism involved in the coagulation-flocculation process. Last but not least, literature review on the parameters that could affect coagulating activity is revealed towards the end of this chapter.

Chapter 3:

The materials, apparatus and equipment used are listed in this chapter. Other than that, the method used to prepare the natural coagulant is presented as well. The procedures of the experiment and the methods used to obtain the results of the treatment process are described. Furthermore, equipment used to characterise coagulants are listed and working principle is explained in detail.

Chapter 4:

This chapter discusses the results obtained from the experiments. The results obtained are related to the effects of several factors in the coagulation-flocculation process. The best condition is determined using the one-factor-at-a-time (OFAT) approach. Furthermore, characterisation of coagulants to explain the various mechanism which enabled the coagulation of colloids is discussed. The studied coagulants are compared in terms of TSS and COD removal efficiencies and the results obtained from characterisation.

Chapter 5:

Last chapter concludes the results and verifies the efficiency of the studied coagulants in removing the targeted pollutants. Recommendations are provided as well to further improve the efficiency of natural coagulant in the coagulation-flocculation process.

CHAPTER 2

LITERATURE REVIEW

2.1 Pulp and Paper

2.1.1 History of Papermaking

Circa 100 B.C., the Chinese started to investigate and study the physical properties of natural materials with a high content of fibres. The materials were heated, dried and pressed into different types of objects such as paper. Yet, this method was unreliable. In the early 2nd century, the Chinese inventor Cai Lun proposed the recipe to create and produce modern paper by using natural materials such as wood pulp. He planned to submerge and lose the heated fibres in warm water. Then, he mashed the fibres into pulp to press the liquid out from the pulp before drying it. However, this method could not manufacture paper in large quantities. Therefore, due to its scarcity, the papers were only used by the Chinese government or royal family. The usage of paper became much more common from the 3rd and 4th century onwards. Between the 3rd and 7th century, the popularity of paper arrived in Japan.

Slowly, the paper arrived in the Islamic region. In fact, the Islamic region was aware of the presence of paper in China. Yet, the method used to create papers was not known until the Battle of Talas which happened in 751 in modern-day Kyrgyzstan. The idea spread rapidly to the west, which included Baghdad, Egypt and Morocco. Inventors from the Islamic world successfully enhanced the production of paper by inventing new technologies, which could produce thicker sheets of paper. The new idea of paper production enables the paper to be used for art purposes and even bookmaking.

Paper then arrived in Europe in the 11th century. Majority of the European countries owned paper mills in the mid-17th century. In the 19th century, the Fourdrinier machine was invented in Frogmore, Hertfordshire, England in 1803. It allowed the paper to be produced in large rolls continuously. Ever since then, this steam-powered machine revolutionized the paper mills until today (History of Paper, 2020).

2.1.2 History of Paper Industries

The first paper mill was built in Frogmore, Hertfordshire in the year of 1803. Small machinery was found in this mill and it was powered with traditional methods such as manpower or animals. These powers were used later to mash the wood chips into pulp. However, slowly, steam was used as the power source with the purpose to increase the efficiency of the overall paper mill.

In the 19th century, most of the paper mills were built near rivers. There were non-integrated mills and fully integrated mills. Non-integrated mills were built far away from the water sources. These industries only received prepared materials to be pressed into the paper. On the other hand, integrated mills had raw wood chips as the raw materials. This is due to the existence of steam powered Fourdrinier machines in the industry, and steam could be easily obtained from the water sources nearby. Slowly, the technologies spread to the rest of the world. The enormous growth of paper mills in the early 20th century was proven by the massive reduction of forested areas, especially in Europe and the United States (History of Paper, 2020).

2.2 Global Statistics

Figure 2.1 shows the total paper consumption worldwide from 2005 to 2015. It clearly shows that paper consumption remained constant for ten years in Africa, Oceania and South America. It was observed that the consumption of paper in these three countries was low and remained below 25 000 metric ton for ten years. There are several reasons which could explain why the consumption of paper remained low in these countries. For example, most teenagers are not given the chances to study at schools in Africa. Education uses a lot of paper for printed textbooks, notes and exercise books. On the other hand, the consumption of paper reduced in Europe and North America which might be due to the development of technologies such as the invention of the smartphone. Notes could be saved in electronic devices instead of jotting down on papers. However, in Asia, paper consumption continues to increase dramatically within these ten years. This could be attributed to the rise of international trade that requires paperboards while exporting goods. Hence, the overall demand of paper worldwide has increased from 2005 to 2015.

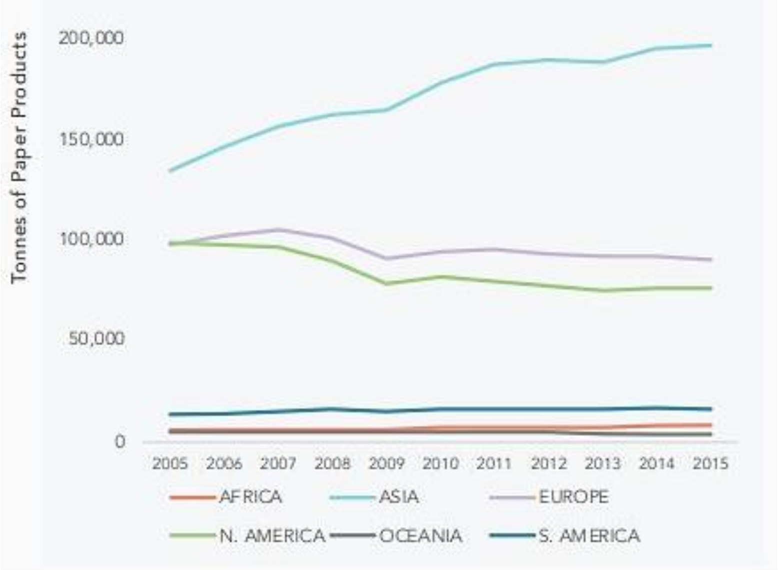
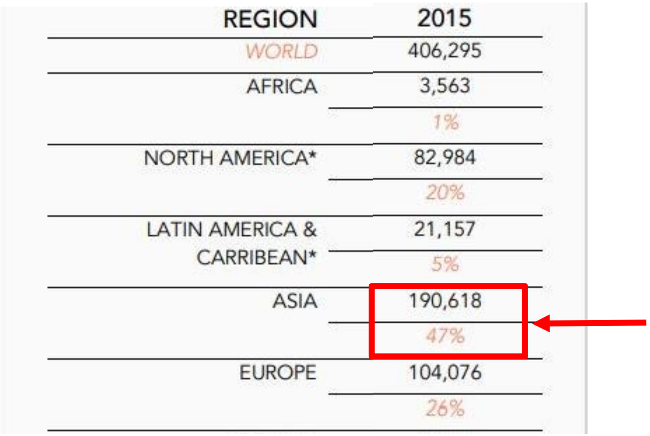


Figure 2.1: Metric Ton of Paper Products from Year 2005 to 2015 (Haggith et al., 2018).

Figure 2.2 shows the paper and paperboard production in 2015 and its contribution percentage to the world production. It is clear that Asia was responsible for 47% of the paper and paperboard produced worldwide in 2015. The consumption of paper in Asia was extremely high; therefore, the paper had to be produced in large scale in order to meet the high demand. Conversely, the low percentage of paper production (1%) in Africa was due to low demand in the country.



REGION	2015
WORLD	406,295
AFRICA	3,563
	1%
NORTH AMERICA*	82,984
	20%
LATIN AMERICA & CARRIBEAN*	21,157
	5%
ASIA	190,618
	47%
EUROPE	104,076
	26%

Figure 2.2: Paper and Paperboard Production in 2015 (Haggith et al., 2018).

2.2.1 Production of Paper in Malaysia

In Malaysia, there are more than 10 companies established for the production of paper. Figure 2.3 shows the locations of the paper industry in Malaysia and the majority of the companies are located in Peninsular Malaysia.

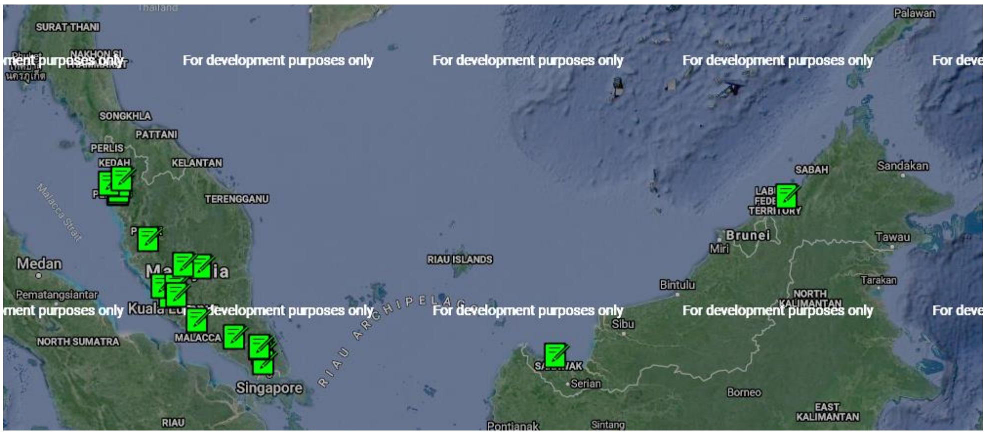


Figure 2.3: Locations of Paper Industries in Malaysia (IndustryAbout, 2018).

Table 2.1 shows the major producers of paper in Malaysia in 2012. By comparing the initial start-up and current capacity, the capacity of each and every factory has shown a significant increase, especially Muda Paper Mills Sdn. Bhd. and Nibong Tebal Paper Mill Sdn. Bhd. The massive development and growth of the paper industry clearly shows the high demand for paper in Malaysia.

Table 2.1: Major Producers of Paper in Malaysia (Malaysian Pulp and Paper Manufacturer Association, 2012).

Companies	Founded	Initial Startup Capacity (000MT)	Current Capacity (000MT)
Pascorp Paper Industries Berhad	1954	55	240
Muda Paper Mills Sdn. Bhd.	1964	3	480
Nibong Tebal Paper Mill Sdn. Bhd. (NTPM)	1975	2	105
Sabah Forest Industries Sdn. Bhd (SFI)	1982	150	165

Table 2.1 (Continued)

Genting Sanyen Paper and Packaging Group (GSPP)	1992	150	285
Malaysia Newsprint Industries Sdn. Bhd. (MNI)	1999	250	280

From Table 2.2, Malaysia produced approximately 7 737 000 metric ton of papers in 2015. Based on the statistic, the production of paper and paperboard had occupied about 57.89% of the total production. In Asia, Malaysia contributed about 2.19% on the total production of paper and paperboard in the year of 2015.

Table 2.2: Total Production of Paper in Malaysia and Asia (Food and Agriculture Organization of the United Nations, 2017).

Area	**Total Production of Paper (000MT)**
Malaysia	7737
Asia	190618

2.3 Paper and Pulp (P&P) Milling Process

Paper is a thin and flexible sheet of material which is comprised of cellulose pulp fibres that have been pre-treated in several stages. Basically, the production of pulp and paper consists of four main stages: preparation of raw material, pulping, bleaching and paper making. Commonly, any natural resources such as cotton or bamboo that contain fibre could be used to produce paper. However, the majority will obtain wood from plants and trees as raw materials (Condorchem Envitech, 2015).

Fibres of cellulose, which are the main materials used to produce paper must be extracted and separated from other components in the raw material. Cellulose is bound together by an organic polymer known as lignin. In the pulping process, either mechanical pulp or chemical pulp is employed to separate the fibres from lignin. Both the mechanical and chemical pulping methods could be applied to break the walls of lignin and release the fibres trapped inside. Mechanical and chemical pulping could achieve the yield of the pulp of about 90 to 95% and 40 to 50% respectively. However, the quality of paper made from chemical pulp will have better quality. Today, only 30% of the paper industry employs the method of mechanical pulping worldwide.

After the pulping process, the bleaching process is needed to remove the colour due to the presence of the leftover lignin in order to produce white pulp. Bleaching process could be carried out with the utilization of hydrogen peroxide, chlorine gas, chlorine dioxide or ozone. Then, the pulps are spread on a flat surface and dried in the pulp dryers through pressing. Heated steel rolls or hot air are employed to further remove the moisture of the pulp. Eventually, the pulps are passed through a roller operating under high pressure, known as calenders to produce papers (National Academy of Engineering, 1998). Figure 2.4 shows the four stages involved in the production of paper.

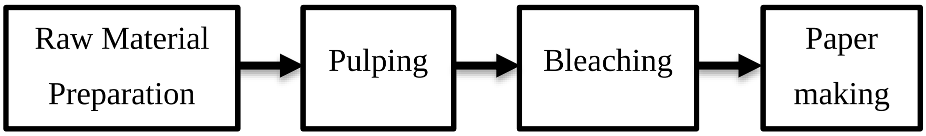


Figure 2.4: General Process of Producing Paper.

Each process involved in the production of paper requires high consumption of water. The quality of water used is essential to ensure the quality of the paper produced. Studies show that 2 000 to 18 000 L of fresh water and 2 000 to 2 500 kg of woods are needed in order to manufacture paper of approximately 1 000 kg. Water is used in the P&P industry for the washing of raw materials, pulping, cleaning of machines, heat exchanging and etc.

During the preparation of raw materials, the woodchips must be washed to remove all possible contaminants. Even though woodchips are mainly obtained from the inner part of the trees which are less likely to contain foreign substances, yet, it was found that excessive wear and tear as well as the breakdown of equipment occurred in the P&P industry are due to the foreign substances in the woodchips. Therefore, the washing of raw materials is important in order to minimize the damages on the equipment.

Among the processes, pulping consumes the highest amount of water because it involves the cooking and cleaning of fibres. The volume of the vessel could range from 20 to 60 ft^3 (57 to 170 m^3). The temperature of the vessel has to be maintained at a temperature of 170 ℃ and the pulp is heated for 2 to 4 h. A lot of steam will be needed to sustain the high energy required by the process in order to remove the lignin efficiently (Benjamin et al., 2012). Water is needed for the cleaning of pulp to wash the spent chemicals. Thus, pulping process uses around 40% of the water used in the P&P industry.

Other than the preparation of raw materials and pulping process, cleaning of machinery requires a large portion of water as well. The cleaning of machinery parts has to be carried out frequently to prevent blockage in the streams due to the accumulation of foreign substances. Besides, the accumulation of unwanted material will greatly reduce the volume of the vessel, leading to lower production of pulp.

The water used in providing utilities in the form of thermal energy and stock preparation occupies 10% of the total water used in the industry. Usually, cooling water or steam is supplied in the process to remove or provide heat energy. For instance, steam is used to recover the chemical used in the Kraft process. On the other hand, water is also used for stock preparation to mix and dilute the pulp uniformly. This is to ensure the consistency of the produced paper in terms of physical properties. Table 2.3 shows the consumption of water at each stage.

Table 2.3: Consumption of Water in P&P Industry (Olejnik, 2011).

Processes	**Percentage of water used (%)**
Pulping	40
Cleaning of Machinery Parts	35
Preparation of Raw Materials	15
Utilities	5
Stock Preparation	5

The consumption of water depends on the quantity and quality of paper produced at the end of the process. The volume of the effluent from the process is almost equivalent to the inlet feed. For instance, 15 to 30 m^3 of fresh water is needed to produce one ton of newsprint; at the end of the process, the effluent produced is approximately 12 to 25 m^3 (Olejnik, 2011). Table 2.4 shows the consumption of water for different types of paper production.

Table 2.4: Consumption of Water for different types of Paper Produced (Olejnik, 2011).

Types of Paper	**Volume of Water ($\frac{m^3}{\text{ton of paper}}$)**	
	Consumption	**Effluent**
Tissue	5 - 30	5 - 27
Newsprint	15 - 30	12 - 25
Packaging	6 - 45	5 - 40
Printing and Writing	10 - 50	8 - 45

2.4 Characteristics of P&P Mill Wastewater

In fact, the types of pollutants found in the wastewater depends strongly on the raw material, process employed in the industries and the types of products (Lenntech, n.d). Generally, the pollutants found in the effluent include naturally formed component and synthetic compounds that are produced due to the reactions that occur during the processes. For instance, wood components, organic matters, chemicals used, by-products formed such as chlorine dioxide, dioxin, furans etc. Table 2.5 shows the sources and the pollution intensity from different stages in the production of paper while Table 2.6 shows the examples of the pollutants.

Table 2.5: The Pollution Intensity from Each Processes (Saadia and Ashfaq, 2010).

Sources	**Pollution Intensity**
Preparation of Raw Materials	Less volume and pollutants
Digester (Pulping)	Less volume with high concentration of pollutants
Cleaning of Pulp	Less volume with high concentration of pollutants

Table 2.5 (Continued)

Bleaching of Pulp	Large volume with high concentration of pollutants
Cleaning of Machine	Volume depends on the cleaning frequency. It contains highest amount of solids

Table 2.6: Examples of Pollutants (Saadia and Ashfaq, 2010).

Pollutants	**Examples**
Suspended solids	Bark solids, fiber, dirt
Dissolved organic compound	Hemicellulose, cellulose, sugars, lignin,
Dissolved inorganic compound	Sodium hydroxide, Sodium sulphate, bleach chemicals
Microorganism	Coliform group
Toxic Chemicals	Resin, fatty acid, adsorbable organic halide (AOX)

One of the quantitative methods used to measure the quality of wastewater is by calculating its Total Suspended Solids (TSS). Wastewater from the P&P industry contains high amounts of total suspended solids. Research found that 90 to 240 kg of suspended solids will be produced per ton of paper manufactured (Kumar, Saha, and Sharma, 2015). TSS in the effluent from the P&P industry was found in the range between 1175 to 1976 mg/L (Singh, 2016; Tripathi, 2017). In the first stage, the washed bark particles enter the wastewater. Remnants of lignin and the loss of cellulose from the chemical pulping process are found in the effluent as well. Cleaning of machinery parts will further increase the content of total suspended solids as most of the solids will tend to stay in the vessel or pipe especially if the flow is slow (laminar flow).

Other than TSS, 500 to 1100 kg of COD is present in the effluent from the production of a ton of paper (Kumar, Saha, and Sharma, 2015). Based on the studies, wastewater from the P&P industry contained 2125 to 2720 mg/L of COD (Singh, 2016; Tripathi, 2017). The effluent has high COD due to the derivatives of lignin. Lignin is a polymer containing oxyphenylpropanoid units. Throughout the processes, lignin is broken down into different types of compounds. These compounds could not be digested easily by the microorganism. Furthermore, the chemicals that will be used at downstream such as chlorine will react with lignin to form highly toxic compounds. The toxic compounds that are present in the effluent are trichloroguicol, trichlorophenol, dichoroguicol tetrachloroguicol, dichlorophenol, and pentachlorophenol. These toxic compounds will lead to high COD values as well.

2.5 Impacts of Untreated Wastewater on Environment

In 1970, wastewater from the P&P industry was discharged into the environment without any treatment. Slowly, after the discovery of toxic components in the wastewater, wastewater treatment plants were built and developed to treat the wastewater. Figure 2.5 shows the volume of the wastewater being discharged into the environment.

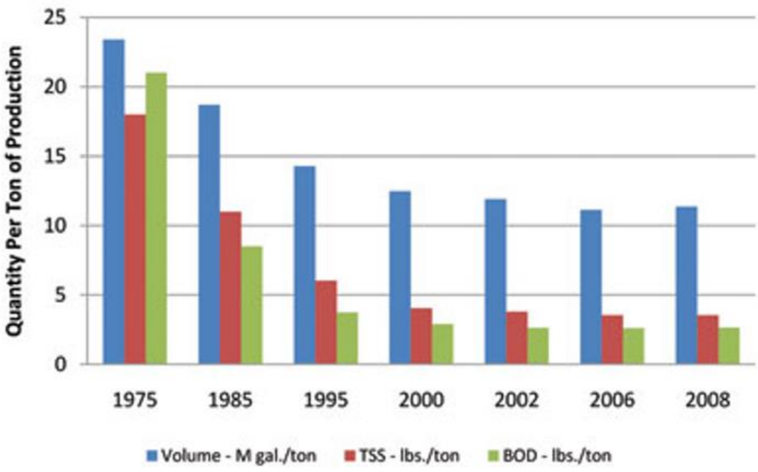


Figure 2.5: Statistic of P&P Mill Wastewater Discharge from 1975 to 2008 (Gunderson, 2012).

It shows a steady decrease in volume from 1975 to 2008. Initially, fresh water is required since the recycling and reutilization of water in the P&P industry can lead to negative impacts such as poor mechanical properties of paper and blockage of the machine due to the presence of irremovable impurities in water. However, new technologies such as membrane filtration, ion exchange process and granular activated carbon which could be utilised in the tertiary treatment have been studied in recent years in order to remove the impurities effectively. Since the aforementioned issue has been resolved, the industry is now trying to reuse treated water in the process. This will form a closed loop within the P&P process which can minimise the negative impacts on the environment.

Of the total surface covering the Earth, water covers 71% of it. Based on the estimation, there is a total of 1 386 million km^3 of water on Earth (USGS, 2018). The estimation data shows that it has about 11 million km^3, which is about 0.7% of the total water on Earth is usable. Furthermore, based on the statistic, the demand of water in global will increase from 3 500 to 5 500 km^3 within these fifty years (the year 2000 to 2050) (Willet et al., 2019). If the effluent with high TSS and COD from the P&P industry is discharged into the environment without any treatment, the quality of the usable water will definitely be affected. This will cause issues such as water scarcity, where the availability of freshwater will be greatly affected.

Moreover, if the TSS is too high, water tends to diffuse from their bodies, which will cause dehydration. This is due to the phenomenon where water will diffuse from an area of high concentration to low concentration. Moreover, effluent containing high content of organic matter and suspended solid will lead the depletion of dissolved oxygen in the water (Hubbe et al., 2016). This will cause the death of the living organism in the water system, thereby affecting the ecosystem. Additionally, the untreated organic matter will facilitate the growth of microorganism as well. The microorganism will cause various waterborne diseases to living beings when the polluted water is consumed.

COD measures the oxygen needed for the degradation of a compound in water. There are approximately more than 500 organic compounds present in the effluent from the P&P industry. High COD shows that the quality of water is low as the oxygen in the water is used to oxidise organic pollutants, leading to a lower concentration of oxygen is available to the aquatic ecosystem. Furthermore, organic compounds which are carcinogenic will show different effects on aquatic living organisms. For example, a carcinogenic compound was found to be capable of altering the reproduction of fishes by initiating gene mutation (Cabrera, 2017).

2.6 Coagulation-flocculation Process

Wastewater treatment is important in removing unwanted substances such as bacteria, colour, TSS or organic matters that might harm the environment. It is divided into three sections: primary, secondary and tertiary treatment. Primary treatment functions to remove all the large particles or solids; secondary treatment will reduce the majority of the COD while the tertiary treatment functions to remove nutrients or minerals present in the water. Figure 2.6 shows the general steps in a wastewater treatment plant.

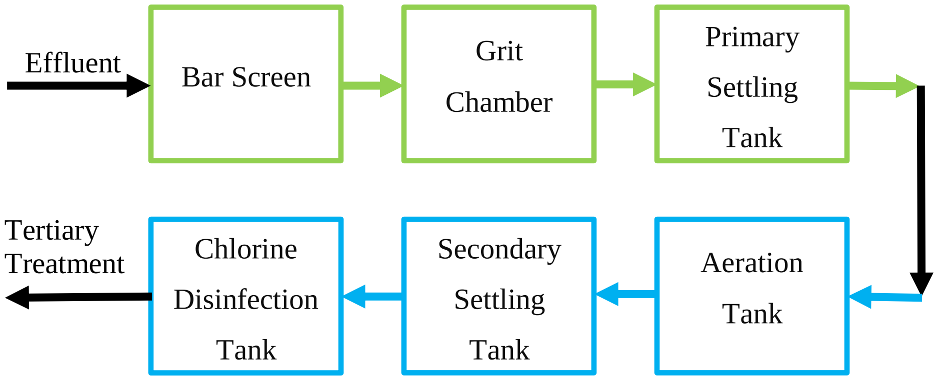


Figure 2.6: Wastewater Treatment Plant.

In primary treatment, the most important steps are coagulation and flocculation (Yongabi, 2010). Coagulation and flocculation are crucial steps as suspended solids might not be removed effectively during sedimentation or filtration. Basically, the process of coagulation and flocculation consists of two main steps: rapid mixing and slow mixing. Rapid mixing encourages the mixing of coagulant with the water to be treated; slow mixing promotes the formation of floc.

The significance of coagulation-flocculation is explained through the formula below. Equation 2.1 is derived based on Stokes law.

$$V = \frac{2gr^2(d_1 - d_2)}{9\mu} \tag{2.1}$$

where

V = velocity of settling particles, m/s

r = radius of the colloids, m

d_1 = density of colloids, m^3/kg

d_2 = density of liquid, m^3/kg

g = gravitational constant, m/s^2

μ = viscosity, kg/m s

According to Stokes law, the settling velocity decreases when the size of a colloid decreases. Since other constants always remain the same, the only way to speed up the velocity of colloids while settling is by increasing the particle sizes (Pillai, 1997). This can be done by using coagulants. Figure 2.7 shows a brief idea on how coagulation works: oppositely charged coagulant attracts the suspended solids and neutralizes the surface charge to form a microfloc.

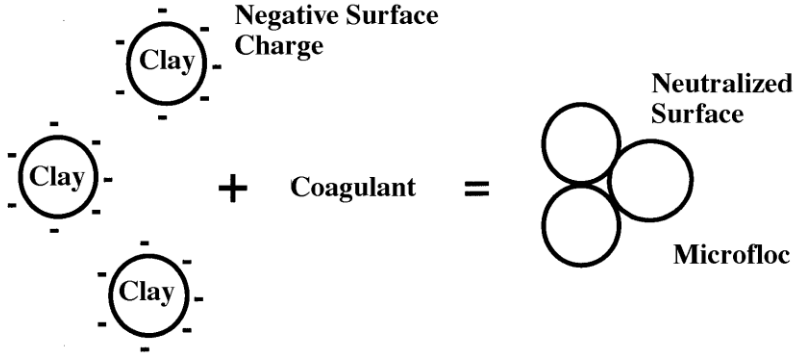


Figure 2.7: Function of a Coagulant in Coagulation Process (Pillai, 1997).

A colloid is normally in the size from the range of 10^{-3} to 1 μm. These colloids are very stable and will not settle through gravitational force. Stability of colloids comes from two significance forces: repulsive electrostatic force and Van der Waals attraction force. The repulsive force is responsible for maintaining the stability of particles, preventing the colloids from getting near to one another. Van der Waals force is created when the particles approach one another. Magnetic and electric fields will be formed due to the charges deposited on them. Their electrons will tend to rearrange themselves to achieve higher stability. Van der Waals forces must be stronger than the repulsive force in order to form floc. Thus, coagulation is very important to enhance the efficiency of sedimentation and shorten the time for the colloids to settle. Without coagulation, the colloids might take up to one year to settle. Filtration unit could not be used as well because the colloids are too small in size.

Coagulation is a chemical process whereby the coagulant is mixed into the wastewater to disrupt the charges on particles' surfaces. Colloids are very stable when the surface are charged. Repulsion occurs due to the similar charges on the surfaces. Destabilization, a process used to describe the neutralization of the charges, causing the particles to become unstable and eventually lead to the attraction and formation of flocs. Coagulation functions to reduce the suspended solids and organic matter that could be measured in terms of TSS and COD, respectively. By removing the particles, some of the microorganisms attached to the solids will be removed as well (Edogbanya, Ocholi and Apeji, 2013).

Coagulation process involves two steps: rapid and slow mixing. Rapid mixing allows the complete mixing of the coagulant in wastewater. Usually, the coagulant is dosed before a centrifugal pump. The rapid mixing is done in the impeller, where the rotational energy is converted into kinetic energy. Then, the solution is stirred gently to promote the formation of floc in a sedimentation tank (Nathanson, 2019).

Coagulation-flocculation process normally takes place in a clarifier in the P&P industry. Clarification is a process which holds wastewater for a specific period and allows the colloids to settle at the bottom of the tank. It aims to decrease the content of TSS and other pollutants that are small in sizes such as dirt, bark, fibres of cellulose and etc. At the same time, it targets to reduce the COD of the wastewater as well. Before the wastewater enters the clarifier, coagulant will be added to facilitate the settling process. Figure 2.8 shows a clarifier.

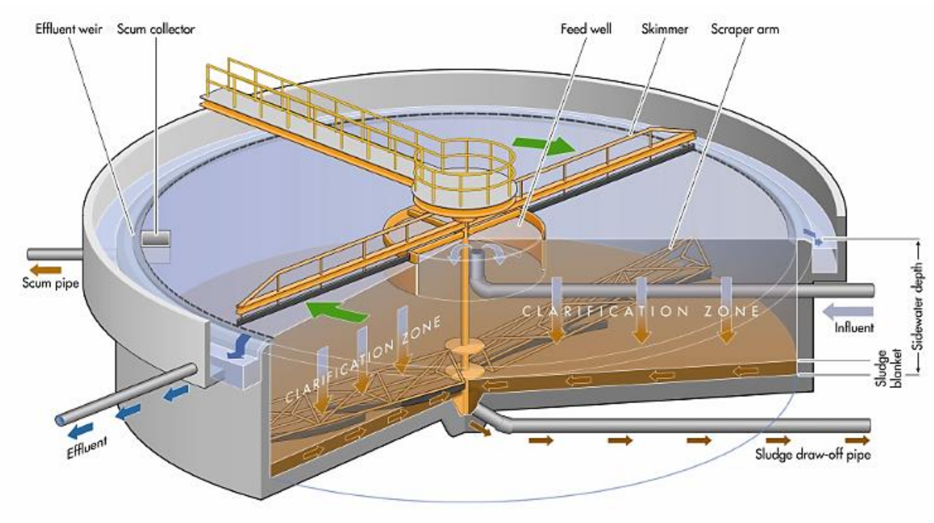


Figure 2.8: Clarifier (Voutchkov, 2017).

Before entering the clarifier, coagulants will be added into the wastewater. Aluminium and ferric salts are coagulants commonly used in the P&P industry (Prasath and Ansari, 2017). The influent and added coagulants will flow into the clarifier vertically and enter a feed well. The stream starts to flow radially at a lower velocity. This is to ensure that the effect of turbulence is reduced and the disturbance on the solids that have been settled at the bottom of the clarifier is minimised. The coagulants are mixed uniformly in the clarifier. Throughout the clarifier, the water flows horizontally while the solids move downwards due to gravitational force. The cleaner water will leave the clarifier through the pipe located at the surface of the clarifier (Voutchkov, 2017).

2.6.1 Coagulants

Coagulants are chemicals or substances with surface charges (opposite of pollutant particle’s surface charge) which promote destabilisation of suspended solids and the formation of floc. Therefore, the selection of coagulants depends on the pollutants found in the wastewater. There are two types of coagulants widely used in the industry: inorganic and organic based coagulants.

Inorganic coagulant such as alum or ferric salt is very commonly used in the industry (Oladoja, 2015). It is cost effective and versatile (applicable in a variety of wastewater) due to its high effectiveness (ChemTreat, 2020). Yet, it creates a high volume of sludge that is difficult to degrade (Maurya and Daverey, 2018). The non-biodegradable sludge produced is very sticky, especially when it is partially dewatered (ATS, 2017). These sticky sludges can be described as "biopolymer matrix". As the amount of water removed from it increases, it tends to stick on the surface of drying equipment (Peeters, Dewil, and Smets, 2014) until a maximum point is reached when it achieves its most viscous state. Further drying of sludge will lead to a drop in the viscosity as the concentration of the biopolymer is too high which prevents it from spreading out. Evidently, the drying of viscous sludge is challenging. Apart from this, study shows that metal coagulant-treated water has the potential of causing Alzheimer's disease in humans (Vijayaraghavan, Sivakumar and Kumar, 2011). Aluminium is known to degenerate neurofibrillary which causes the death of neuronal in the brain. It has been proven that the risk of getting Alzheimer's disease rises when the number of aluminium intake increases **(**Rondeau et al., 2008**).**

Alum functions differently in coagulating activity, depending on its dosage and pH of the environment. It was discovered that at low dosage, alum formed a precipitate, known as aluminium hydroxide (Brandt et al., 2017). This precipitate tends to sink to the bottom of the tank. At the same time, colloids or suspended solids are trapped in the precipitate; therefore, TSS in the wastewater reduces. The following chemical equations (2.2) and (2.3) show the reaction which occurs between alum and alkalinity of water:

$$\begin{aligned} Al_2(SO_4)_3 \cdot 14H_2O + 6HCO_3^- \\ \leftrightarrow 2Al(OH)_3 + 6CO_2 + 14H_2O + 3SO_4^{2-} \end{aligned} \tag{2.2}$$

$$Al_2(SO_4)_3 \cdot 14H_2O \leftrightarrow 2Al(OH)_3 + 8H_2O + 3H_2SO_4 \tag{2.3}$$

Contrarily, organic coagulants are made from repeating units with covalent bonds in between the units, forming a macromolecule. There are synthetic organic and natural polymeric coagulants. Synthetic organic coagulant is better than metal coagulant in some terms. Examples of synthetic organic coagulants are polyamine and polyethyleneimine. Polymers aid is used in the coagulation and flocculation process specifically to combat issues pertaining to slow floc formation at low temperature (Bolto and Gregory, 2007). In fact, a lesser dosage of organic coagulant is required in order to achieve certain efficiency. Synthetic polymeric coagulant will form larger floc; thus, the separation process is faster since larger floc is heavier. Most importantly, it produces lesser sludge; hence, the cost for treatment and disposal of sludge is lower (Renault et al., 2009). However, organic synthetic polymeric flocculants are expensive. Besides, some monomers will stay in the treated water and is irremovable. These monomers are toxic and carcinogenic. It has the potential to cause some serious diseases if the water containing its monomers is consumed (Vijayaraghavan, Sivakumar and Kumar, 2011).

Due to the pollution and health issues caused by inorganic and synthetic organic coagulant, natural polymeric flocculants are studied (Wei et al., 2018). Most natural coagulants originate from plants (seeds, fruit peels). It causes less harm to the environment as well as to the living organisms. Moreover, it is able to form flocs that have higher resistance towards shear force as compared to metal coagulant. Inorganic coagulants such as alum, made up of a single molecule, tends to attach to pollutants, whereas many natural polymeric coagulants link pollutants through their long polymeric chain. Additionally, based on the studies, natural coagulant only produces 20 to 30% of the sludge accumulated by alum after treatment (Sciban et al., 2009). However, natural coagulant dosed directly into the wastewater might not be as effective as metal coagulants. Natural coagulants need to be modified as it has a lower molecular weight, charge density and water solubility. With these characteristics, it is not able to coagulate colloids in the wastewater effectively. Table 2.7 shows the types of coagulants with their pros and cons.

Table 2.7: Types of Coagulants with their Advantages and Disadvantages.

Types of coagulant	Advantages	Disadvantages
Inorganic Coagulant	➢ High efficiency	➢ Forms non-biodegradable sludge ➢ Produces sticky sludge ➢ Causes health issue
Synthetic Organic Coagulant	➢ Lesser dose is required ➢ Formation of larger floc ➢ Produced less sludge	➢ Expensive ➢ Residual monomers can cause health issue
Natural Coagulant	➢ Environmentally friendly ➢ Formation of stronger floc	➢ Modification is required

2.6.1.1 Natural Coagulant

In the past, the method of aquaculture was used in treating wastewater before the coagulation and flocculation process was properly designed. Wetlands were developed and breeding of fish or cultivation of algae were done to remove the pollutants found in water. Water hyacinth is the most common plant in treating wastewater nowadays. Further study has been done on the utilization of aquaculture by cultivating the grass using domestic wastewater which at the same time, organic matter and suspended solids are removed from the stream. It is indeed an effective method in removing all the unwanted substances from wastewater.

To construct a wetland, large land is needed for the cultivation of aquatic plants and rearing of vertebrates in water. An area of 1 m^2 could only treat 1 m^3 of wastewater per day. Moreover, the cost used to construct the wetlands are high. Additionally, professional skills are needed. This will inevitably increase the overall cost of this technology. Therefore, it is difficult to be built in a country such as Africa.

Thus, natural coagulants were used to hasten the treatment of wastewater. Instead of constructing a wetland, natural coagulant is used to purify the wastewater. Its cost is much lower as compared to the use of aquaculture. Besides, native plants could be obtained easily due to plenty of sources. For example, *M. oleifera* seeds were used in Guatemala while peach and dried bean seeds were used in Bolivia. Furthermore, natural coagulant is easy to be prepared. The seeds are extracted and ground into powder to increase its surface area when it is in contact with the particles in the wastewater. Then, the powder is dosed into the untreated wastewater for clarification purpose (Yongabi, 2010).

Table 2.8 shows a few examples of natural coagulants that have been studied for the treatment of various types of wastewater. It is observed that a majority of natural coagulants which have been studied were plant-based coagulants derived from seeds and peels. Some examples include *M. oleifera* (Drumstick tree), *C. arietinum* (Chickpea), *Cassia obtusifolia* (Sicklepod), *Tamarindus indica* (Tamarind), *Musa* (Banana) and *Citrus sinensis* (Orange). The plant-based coagulants were tested for the treatment of wastewater ranging from Palm Oil Mill Effluent (POME), sewage water, municipal wastewater and wastewater from the chemical industry. A majority of the studies reported the performance of the natural coagulants based on TSS and COD removal efficiencies.

Table 2.8: Types of the Natural Coagulants that have been Tested on Various Wastewater.

Natural Coagulants		**Part**	**Types of wastewater**	**Optimal Conditions**				**Removal Efficiency (%)**		**Sources**
Scientific Name	**General Name**			**Dosage (mg/L)**	**pH**	**Stirring Speed (rpm)**	**Settling Time (min)**	**TSS**	**COD**	
Moringa oleifera	Drumstick tree	Seed	POME	6000	5	30	90	95	52	(Bhatia, Othman, and Ahmad, 2006)
Cicer arietinum	Chickpea	Seed	POME	2600	6.69	40	2400	-	90	(Lee et al, 2018)
Cassia obtusifolia	Sicklepod	Seed Gum	POME	1000	3	10	45	93	61	(Shak and Wu, 2014)
Tamarindus indica	Tamarind	Seed	Municipal Wastewater	14000	4	100	60	67	-	(Nurika, Mulyarto, and Afshari, 2007)
Musa	Banana	Peel	Municipal Wastewater	400	7.73	30	60	45	58	(Maurya and Daverey, 2018)
Citrus sinensis	Orange	Peel	Wastewater from Chemical Industry	8000	-	-	-	40	30	(Panchal, Sharma and Patel, 2017)

2.6.1.2 *Moringa oleifera* Seed

Moringa Oleifera, from the family of Moringaceae, has the potential to replace the common inorganic coagulant such as aluminium sulphate. *M. oleifera* is a tropical plant that could grow in a short period even under extreme conditions (Ali et al., 2009). It has high resistance to environments with low humidity and draught season (Camachoa et al., 2017). Initially, *M. oleifera* was mostly found in Northern India. However, today, it is cultivated throughout the tropical areas and is commonly found in countries such as Africa, Asia, or South America. Figure 2.9 shows a Moringa tree.

Figure 2.9: Moringa Tree (nurserylife, 2020).

The seed of *M. oleifera* is rich with proteins and lipids (Saa et al., 2019). It contains approximately 20 and 31% of protein and lipid respectively. However, lipid does not contribute to the coagulation-flocculation process (Nordmark, Przybycien, and Tilton, 2016). Most of the coagulating activity is done by the cationic and water-soluble protein contained in *M. oleifera* seeds. There are low (less than 12 kDa) and high molecular weight (12 – 14 kDa) compounds in the seed. Compounds with low molecular weight include a minority of proteins, terpenes, tannins, and alkaloids (Villasenor-Basulto et al., 2018). These components have less contribution to the coagulation of solids during wastewater treatment. Megersa et al. (2017) discovered that the compounds which are involved in the coagulating activity during treatment are the dimeric cationic proteins. These proteins have an isoelectric point at pH 10 or 11, indicating that the proteins tend to be positively charged ions at a wide range of pH (Camacho et al., 2017). Based on Camacho et al.'s work, dimer proteins contribute around 70% of the coagulating activity. However, proteins also exist in other forms in the *M. oleifera* seeds. For examples, chitin-binding protein and lectin (carbohydrate-binding protein). However, these compounds are proved to be effective for other functions an effective disinfectant for wastewater treatment.

The high content of water-soluble molecules in the seeds of *M. oleifera* allows it to be used as a primary coagulant for the treatment of wastewater (Al-Gheethi et al., 2017). These molecules, which include protein and carbohydrates could reduce the concentration of suspended solids and organic matter effectively. The efficiency of *M. oleifera* as a natural coagulant has been studied by using different types of wastewater such as wastewater from the tofu industry and jeans leaching industry. It was observed that *M. oleifera* successfully removed 85.72 and 88% of TSS and COD, respectively from the wastewater obtained from the tofu industry (Setyawati and Muyassaroh, 2017). On the other hand, it appeared that 83.69% of TSS was removed by the seeds from the wastewater in the jeans leaching industry (Rambe et al., 2017). Therefore, it has the potential to replace or reduce the usage of chemical coagulants in wastewater treatment in the future.

2.7 Mechanism in Coagulation-flocculation Process

2.7.1 Double Layer Compression

Coagulants are added into the water to increase the ionic strength. The ionic strength of the water depends on the concentration of ions existing in it. When the ions in the water increases, a gradient will not exist as the dispersion of the ions are being distributed evenly. The zeta potential is being compressed. The thickness of the diffused layer will become thinner. At this moment, the attractive force is stronger than the repulsive force. The colloids tend to attract each other and form floc eventually. Figure 2.10 shows the compression of zeta potential.

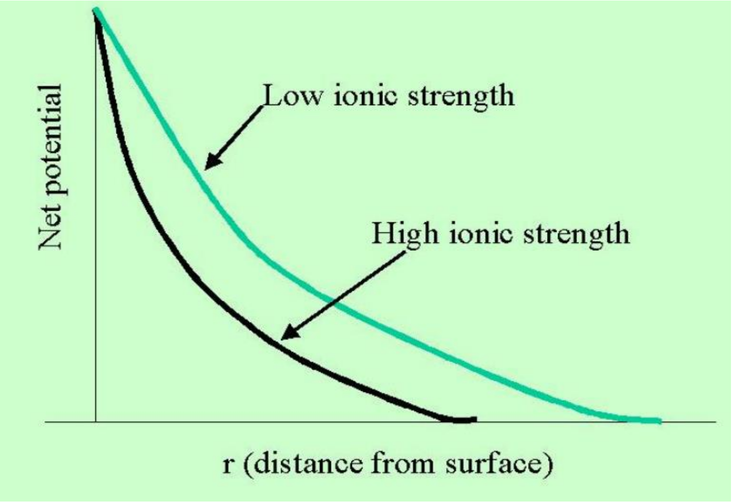


Figure 2.10: Compression of Zeta Potential (Binnie, Kimber, and Smethurst, 2002).

2.7.2 Sweep Flocculation

Sweep flocculation occurs when a metal salt is added in a specific quantity that exceeds its solubility in water after it dissociates, forming insoluble precipitate (Scholz, 2016). Colloids are trapped inside the precipitate and proceed to settle at the bottom of the tank when it becomes larger in size. The amount of metal salt to be added into the water is inversely proportional to the concentration of colloids. When the colloid concentration is high, the amount of metal salt needed is low. Colloids act as a centre point for the metal salt to precipitate on it once it has dissociated and form oxides or hydroxide compound in water. Conversely, if the concentration of colloids is low, then a higher amount of metal salt is needed. The colloids will be enveloped inside the precipitate formed by metal salts and settle together when the size has become larger and heavier.

2.7.3 Adsorption and Charge Neutralisation

The ions exist in water have a specific affinity towards the colloids’ surfaces. These ions are not being attracted due to the charges on their surfaces. This adsorption can occur in different ways: coordination bonding, Van der Waals force or ion exchange. The ions adsorbed on the surface will definitely reduce the charges on the colloids. This will allow the reduction of zeta potential, causing the attraction force to be stronger than the repulsive force, which will eventually lead to the agglomeration of the colloids. Through this mechanism, a lower dosage of coagulant is needed as compared to double layer compression. Its dosage depends on the concentration of colloids as well. The dosage of the coagulant is directly proportional to the colloid concentration. However, there is a limit for the dosage - if overdosing occurs, the charge on the surface of the colloid will be reversed.

2.7.4 Adsorption and Interparticle Bridging

Polymers are large in size and classified into anionic, cationic or non-ionic. Polymeric coagulants are inclined to attach to the colloid at one end, either by attraction due to opposite charge or Van der Waals forces in water. The tail will attach to another colloid, linking them together. By forming a bridge within the colloids, the floc will slowly grow in size. Figure 2.11 shows the mechanism of adsorption and interparticle bridging.

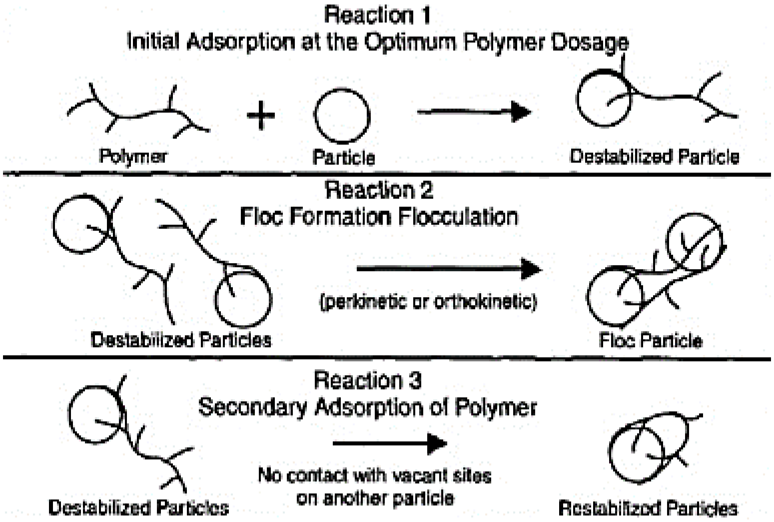


Figure 2.11: Adsorption and Interparticle Bridging (Binnie, Kimber, and Smethurst, 2002).

The dosing of these coagulants must not exceed the concentration of colloids. If the polymer is more than the colloids, there will be lesser available sites for attachment on the polymer; hence, bridging will not occur. When the polymer attaches its other end to the same particle, then the particle can be re-stabilized again. Also, the agitation force must not be too large as it might break the bridges that have been formed.

2.8 Factors affecting the Coagulation Process

2.8.1 Dosage

A low dosage of coagulant will result in a lower coagulating activity. There is a lack of active compound to destabilise the charges on the colloid and form bridges between them (Hussain, Ghouri and Ahmad, 2019). On the contrary, high dosage of coagulant increases the active site which neutralizes the charges on the colloids, thereby improving its coagulating efficiency (Wasewar, 2010).

From the study of treating POME with chickpea, Lee et al. (2018) stated increased of coagulant dosage above 0.7 g/L decreased the efficiency of COD removal. COD increased due to the increase of soluble organic compounds from chickpea. Nevertheless, TSS removal efficiency had increased. This might be due to the fact that when the dosage increased, the active component increased as well, which would eventually enhance the occurrence of destabilisation and bridging action.

Overdosing of natural coagulant can lead to the reversal of charges on colloid surface. When the charges on the surface of colloids are reversed, any addition of coagulant will increase the repulsion force instead of attraction force. Furthermore, the value of COD will also increase due to the dissociation of soluble compound from the natural coagulants in water. Rosmawanie et al. (2018) revealed that when the dosage of natural coagulants (*C. arietinum* and *M. oleifera*) were low, the efficiency of COD removal increased until it reached an optimum dosage (180 mg/L). Overdosing of both natural coagulants led to the reduction of efficiency in reducing COD value of the wastewater sample.

In addition, the study conducted to determine the coagulating activity of banana peel powder had shown that the TSS and COD removal percentage reduced when the dosage increased. According to Maurya and Daverey (2018) that the optimum dosage was 0.4 g/L. Overdosing of banana peel powder caused the TSS content and value of COD to increase, resulting in lower percentage removal. This phenomenon happened due to the restabilization of colloid particles in the wastewater sample.

The effect on TSS removal of overdosing could be proved through the experiment using powder ground from papaya seed as well. George and Chandrn (2018) reported that TSS removal increased until the dosage reached an optimum value. The charges on the colloids' surfaces were reversed due to the high concentration of positive charges contributed by the protein in papaya seed. Further increase of dosage did not lead to high removal of suspended solids due to the high repulsion force among the colloids.

2.8.2 pH

The initial pH of the wastewater will have different effects on COD and TSS. The low and high values of pH indicate the amount of H^+ and OH^- ions present in the wastewater. At low pH, the concentration of hydrogen is high. The bridging effect of the cationic polymeric coagulant might not be effective as positively charged H^+ ions will attract to the surface of colloid with the opposite charge, thereby producing floc with lower molecular weight. Neutralisation will be a preferred mechanism as hydrogen ions assist in neutralizing the charges on the surfaces of colloids. Conversely, when the concentration of OH^- ions is high, it will affect the bridging effect as well by occupying the active sites with positive charges on cationic polymeric coagulant. From the study of treating POME with chickpea, Lee et al. (2018) explained when pH increases from 4 to 6, there was an increase in efficiency of reducing COD and subsequently decreased from pH 6 to pH 8. On the contrary, TSS removal efficiency decreased significantly from pH 4 to 8.

In addition, pH could affect the solubility of the active compounds such as proteins and carbohydrates in the natural coagulant. Studies show that the solubility of macromolecules in the chickpea increased when the pH value was higher than 4. Higher content of protein and active components were found in the solution when the pH was increased (Moure et al., 2006). This might be due to the reason that the COD value rose after the value of pH exceeded 6. However, the increase of pH will also cause the changes in the charges on the functional groups. Any reversal of charges on the surface of the coagulant will cause a significant effect on the coagulating activity. As the negative impacts of the high pH on the active components were considered, the optimum pH value of the solution was set at 6 or 7.

Furthermore, the effectiveness of a particular coagulant depends much on the point of charge. If the pH of the environment is lower than the point of charge, then the coagulant tends to be positively charged. In contrast, the coagulant will tend to be an anionic polymer if the pH is higher than the point of charge (Weng et al., 2013). For instance, Figure 2.12 shows a graph of zeta potential of a natural coagulant. Any pH value that is lower than 2.78 will cause the coagulant to carry positive charges. Contrarily, coagulant will be a negative-charged carrier if the environment has a pH more than 2.78.

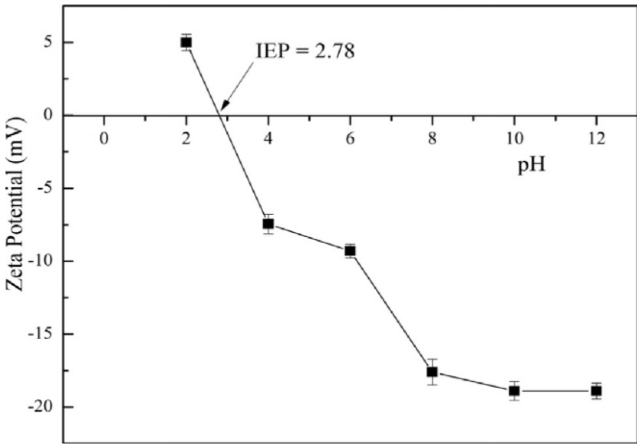


Figure 2.12: Point of Charge (Choudhary, Ray and Neogi, 2019).

2.8.3 Stirring Speed

Stirring speed will exert forces to bring the colloids and coagulant together. The forces exerted on the particles is directly proportional to the speed of the stirrer. The stirring speed is adjusted for different purposes. For instance, the stirring speed must be high during the mixing of coagulating agent and the wastewater sample to enhance the formation of floc (rapid mixing) while slow mixing rate should be used when the floc starts to form (slow mixing) (Mohammed, Al-Gheethi and Kassim, 2017). In brief, the rate of slow mixing must neither be too low nor too high. If the stirring speed is too low, the colloids will take a longer time to agglomerate and coagulate at the bottom of the beaker. In contrast, when the stirrer rotates at an extremely high speed, it might break the floc that has been formed previously.

In the study of POME treatment with chickpea done by Lee et al. (2018), when the stirring speed was increased from 140 to 200 rpm, the efficiency of removing TSS reduced which might be due to the high force that broke the bonding of the floc molecules. Apart from that, in the research using papaya seed, George and Chandrn (2018) proved that TSS removal increased when the stirring speeds were increased from 40 to 80 rpm. Any speed that is above 80 rpm decreased the efficiency of TSS removal as it showed an increase of TSS when the mixing speed is above 80 rpm.

In addition to that, study was done by Subramonian, Wu and Chai (2014) to investigate the coagulating potential of *C. obtusifolia* seed gum. When the stirring speed was increased, the efficiency of removing TSS increased as well. However, when the speed was more than 30 rpm, it showed a significant decrease in the TSS removal efficiency. This might be due to the turbulent flow of the fluid created by the high speed of magnetic stirrer caused the breakage of floc.

Besides, the stirring speed will affect the efficiency of COD removal as well. At lower stirring speed, the value of COD will decrease with the TSS content in the wastewater sample. However, the efficiency of COD will reduce when the floc that is formed previously started to break at higher stirrer speed. For instance, the COD removal efficiency increased until the stirring speed was set higher than 10 rpm in the study of *C.obtusifolia* as natural coagulant.

2.8.4 Settling Time

Colloids require some time to settle at the bottom of the beaker. Larger floc will settle faster due to high density, followed by floc with moderate and small sizes. Therefore, TSS removal will increase as time increases. However, TSS removal will remain constant after a certain period of time. This is due to the majority of solids with high densities are removed, leaving particles with small sizes. Thus, a longer time is needed for the coagulant to bind the particles that stay far away from one another, causing a lower rate of coagulation.

According to Mohd-Asharuddin et al. (2018), the utilization of cassava peel waste as a natural coagulant showed that at the first 30 min, 23.19% of the TSS was settled down. The removal of TSS increased slowly in the subsequent period as most of the active components were used. Patel and Vashi (2012) demonstrated similar results when Surjana seed powder, Maize seed powder and Chitosan were used as the natural coagulants. Three of the natural coagulants showed a similar trend of graph. The study deduced that small colloids settled quickly at the first 5 min. A small increment of the settled floc was observed in the next 15 min. After 20 min, the removal of TSS continues to increase but the increment was not obvious. Similarly, when *C.obtusifolia* gum was used, the TSS removal percentage increased with the settling time as well until the coagulating agent had been fully utilised, resulting in a constant removal rate.

At the same time, the manipulation of settling time will affect the COD value of the wastewater sample. The colloids will be removed effectively at the beginning of the experiment. Therefore, a lower value of COD will be obtained. However, when the available coagulating agent has been used up, the remaining colloids in smaller sizes could not be removed anymore. The TSS content in the wastewater will remain constant, resulting in a constant value of COD value. This can be proven when *C. obtusifolia* gum was used as the natural coagulant. Based on the study done by Subramonian, Wu and Chai (2014), after 1 min of settling time, the COD removal percentage remained unchanged, indicating that the settling time is no longer affecting the value of COD of the wastewater sample.

2.9 Summary

Globally, paper is in high demand for different purposes. Owing to the growing numbers in production, P&P mill effluent are generated in tremendous amount as well. Generally, the coagulation-flocculation process plays an important role at the primary stage of wastewater treatment to manage the highly polluted effluent generated by the P&P industry. To improve the treatment process in terms of sustainability and environmentally friendliness, the usage of common inorganic coagulant should be reduced by introducing potential natural coagulants. The treatment performance is dependent on various factors ranging from the properties of coagulant, coagulation dosage, medium pH, stirring speed and settling time.

CHAPTER 3

METHODOLOGY AND WORK PLAN

3.1 Materials

Alum, sodium hydroxide (NaOH), hydrochloric acid (HCl) and COD reagents were purchased from Sigma-Aldrich. Moringa seeds were obtained from India. Wastewater from the P&P industry was collected from MUDA Paper Mills, Kajang, Selangor (Figure 3.1). The wastewater was kept in a 2.5 L bottle. The quality of wastewater in terms of TSS, COD and pH were measured and listed in Table 3.1.

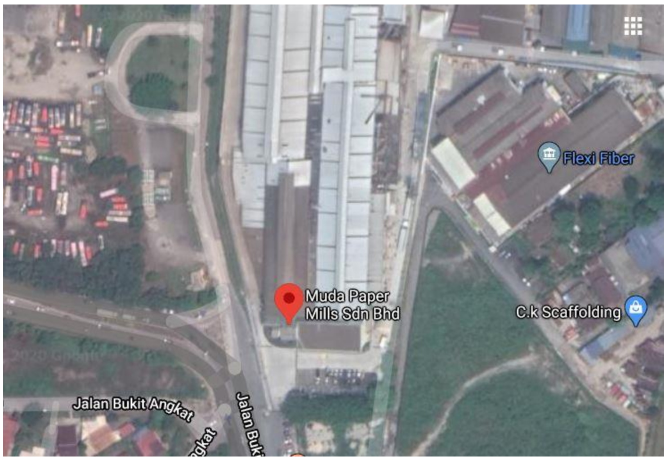


Figure 3.1: Location of Muda Paper Mills.

Table 3.1: Characteristic of Wastewater from MUDA Paper Mills, Kajang.

Parameters	**Units**	**Range**
pH	-	6.2 - 6.9
Total Suspended Solids (TSS)	mg/L	750 - 3270
Chemical Oxygen Demand (COD)	mg/L	2870 - 4590

3.2 Preparation of Coagulant

Firstly, the shells of the *M. oleifera* seeds were removed. The inner seeds are ground into powder by using a pestle and mortar. The resultant powder was then sealed in polythene sample bags to avoid contamination. *M. oleifera* seed powder was prepared daily to prevent degradation of quality over time. Figure 3.2 and 3.3 show *M. oleifera* seed powder and alum respectively.

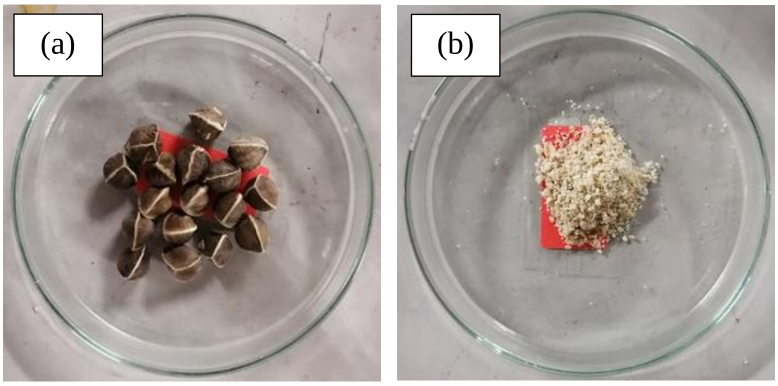


Figure 3.2: (a) Shelled and (b) Unshelled *M. oleifera* Seed Powder.

Figure 3.3: Alum.

3.3 Coagulation-flocculation Process

Jar Test (Figure 3.4) was carried out to perform and understand the process of coagulation. The beakers are prepared and filled with 300 mL of wastewater. 1 mL of water samples was collected at a depth of 2 cm from the top of the beakers. pH was measured before the coagulation-flocculation process. The wastewater pH was adjusted using 1M HCl or 1M NaOH. The wastewater was stirred at 150 rpm for 2 min. Then, coagulant was added and stirred again at 150 rpm for 3 min (rapid mixing). Later, the mixing speed was changed to 20 rpm and it was stirred for 10 min (slow mixing). After 15 min of slow mixing, the beakers are moved to a flat surface to allow the floc to settle at the bottom of the beakers. The beakers were left for 15 min.

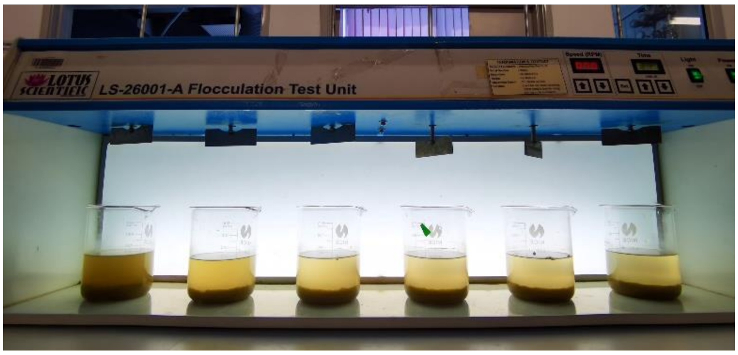


Figure 3.4: Effect of *M. oleifera* Seed Powder Dosage on TSS and COD Removal (from sequence of left to right: 0, 0.5, 1.0, 1.5, 2.0 and 2.5 g/L).

Again, 1 mL of water samples was collected at a depth of 2 cm from the top of the beakers and diluted with a factor of 10. TSS and COD before and after the coagulation-flocculation process were analysed. The final values of pH were taken. Finally, the floc was dried and kept for analysis.

3.4 Studied Parameters

The parameters were studied by changing the particular values and set the other parameters as constant. Dosage of natural coagulant was varied among 0.5, 1, 1.5, 2 and 2.5 mg/L. For the study of pH, before the coagulant was dosed, it was altered by manipulating the volume of 1 M HCl or 1 M NaOH added into the wastewater. Other than the ambient pH, it was also varied from the range of 3, 5, 7 and 9. In addition, the stirring speed (slow mixing) was manipulated from 20, 40, 60, 80 and 100 rpm. The effect of settling time was studied by varying the time from 5, 10, 15, 20 and 25 min.

3.5 Analytical Methods

Initial and final values of TSS and COD were taken to determine the efficiency of coagulating activity. Samples were collected from 2 cm below the surface of untreated and treated wastewater. TSS and COD were measured using HACH Spectrophotometer (HACH DR3900). The efficiency of TSS and COD removal were calculated by using the formulas below:

$$\text{TSS Removal (\%)} = \frac{(TSS_{initial} - TSS_{final})}{TSS_{initial}} \times 100\% \qquad (3.1)$$

$$\text{COD Removal (\%)} = \frac{(COD_{initial} - COD_{final})}{COD_{initial}} \times 100\% \qquad (3.2)$$

3.6 Characterisation of Coagulants

Zeta potential was measured to quantify the magnitude of the potential difference of layers between colloids (solids) and liquid at different pH of the wastewater. It was measured using Particle Size Zeta Potential Analyser (nano partia SZ-100V2 series). Surface morphology of different coagulant was studied under an electron scanning microscope (Hitachi S-3400N). To ensure proper insertion of both coagulants on sample holders, alum and *M. oleifera* seed powder were adhered on double-sided adhesive tapes. Samples were coated with a thin layer of gold and platinum before undergoing analysis. FTIR spectrophotometer (Nicolet IS10) was used to examine the functional groups that exist in coagulants, which contribute to the coagulation process. Methanol was used to clean surface of the stage where samples were supposed to be placed in order to prevent contamination. The spectra of both coagulants were collected from the range of 500 to 4000 cm^{-1}. X-ray diffraction was a technique used to identify the unknown components in the samples using X-ray Diffractometer (Shidmazu XRD-6000). Alum and *M. oleifera* seed powder were and scanned from 5° to 50° at the rate of 2° per minute. Thermal stability of different coagulant was determined by monitoring weight loss due to decomposition of components contained inside the samples using a Thermogravimetric Analyser (STA80000). Alum and *M. oleifera* seed powder were heated from room temperature to 600 ℃ with a rate of 10 ℃ per minute.

3.7 Summary

Jar test experiment was carried out to determine the coagulating efficiency of both coagulants, alum and *M. oleifera*. Spectrophotometer was used to determine TSS and COD values. These values were then substituted into the formula to investigate the efficiency. Characterisations were done by using SEM-EDX, FTIR, XRD and TGA to determine the properties of alum and *M. oleifera* seed that allow coagulation of colloids in the wastewater sample.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Effect of Parameters on TSS and COD Removal

4.1.1 Effect of Coagulant Dosage

The dosage of coagulant contributes significantly to the performance of coagulating activity. To study the effect of dosage, the coagulants were dosed at 0.5, 1.0, 1.5, 2.0 and 2.5 g/L. The effect of alum and *M. oleifera* seed powder dosage on the efficiencies of TSS and COD removal are shown in Figure 4.1 and 4.4 respectively. It was observed that the dosage had a significant effect on TSS and COD removal to different extents.

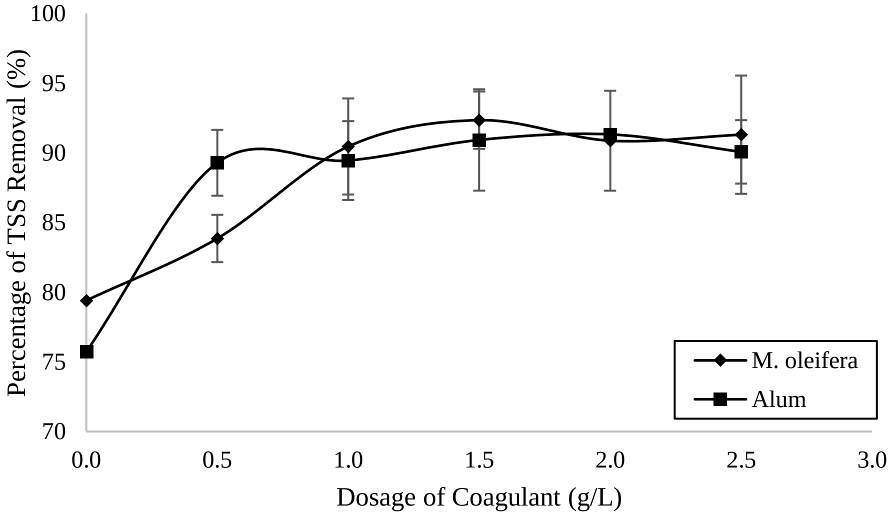


Figure 4.1: Effect of Dosage on TSS Removal.

The efficiency of TSS removal increased from 0 to 0.5 and 1 g/L for alum and *M. oleifera* seed powder, respectively. Further increase in dosage did not show any significant changes in the removal efficiency. However, COD removal efficiency exhibited different trends for coagulants. As the alum dosage increased, COD removal increased as well. Conversely, the COD removal rate decreased dramatically when the dosage of *M. oleifera* seed powder increased from 0.5 to 2.5 g/L.

When the dosage was 0 g/L, the supernatant of wastewater remained unclear. Figure 4.2 and 4.3 show the untreated and treated wastewater. From Figure 4.3, it can be seen that clearness increased with the addition of *M. oleifera* seed powder. By increasing the dosage to 0.5 g/L, higher TSS removal was observed. However, low coagulant dosage contributed lesser coagulating agent in the wastewater. Thus, there was an insufficient protein that could neutralise the negative charges on the colloids, leading to inefficient coagulating activity (Saritha, Srinivas, and Vuppala, 2017). The concentration of soluble protein increased when the dosage of *M. oleifera* seed powder increased to 1 mg/L. The rise in the concentration of coagulating agent effectively increased the probability of collision between colloids and coagulant. As a result, more particles were neutralised and destabilised (Lee et al., 2018).

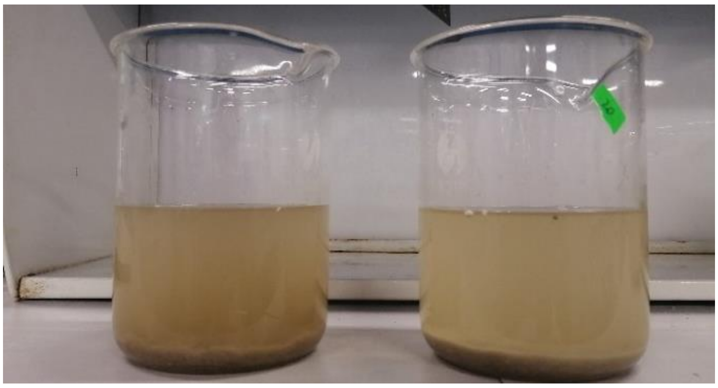


Figure 4.2: Untreated (left) and Treated (right) Wastewater (Side View).

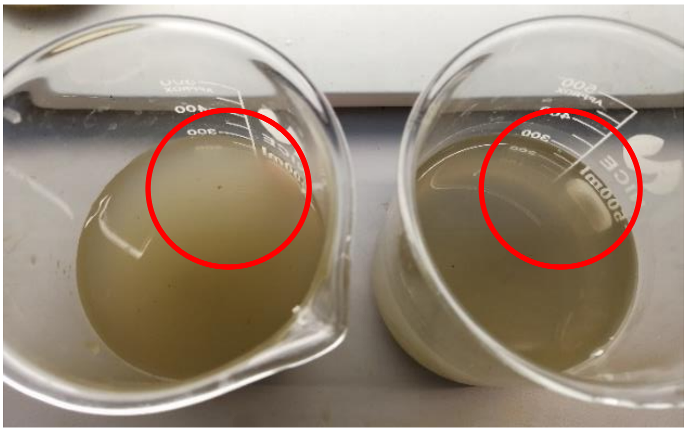


Figure 4.3: Untreated (left) and Treated (right) Wastewater (Top View).

Conversely, it is noteworthy that the efficiency of TSS removal remains constant after the optimum dosage of coagulant. This is due to the fact that most of the charges on the colloids' surfaces were neutralised at the optimum dosage (Hendrawati et al., 2016). The insignificant changes in the removal rate of TSS indicated that alum and *M. oleifera* seed powder have wide range of dosage for the optimum coagulating performance.

Figure 4.4 shows a positive impact of increasing alum dosage while negative impact of increasing *M. oleifera* seed powder on COD removal efficiency. The sweep flocculation caused by the high dose of alum in wastewater led to a high content of organic and inorganic matter suspended in the thick precipitate and settled at the bottom of the beaker. Thus, COD removal increased when the dosage of alum increased. On the other hand, the coagulating activity of *M. oleifera* seed powder was brought by the soluble protein. The higher the dosage, the higher the amount of protein dissolved in the water. These proteins are organic compound. At higher dosage, some of the protein surfaces did not attach or adsorb to any colloids; therefore, no floc was formed and the protein remained in the water instead of settling to the bottom due to its low molecular weight. Thus, it contributed to high COD and reduce the removal rate eventually (Lee et al., 2018).

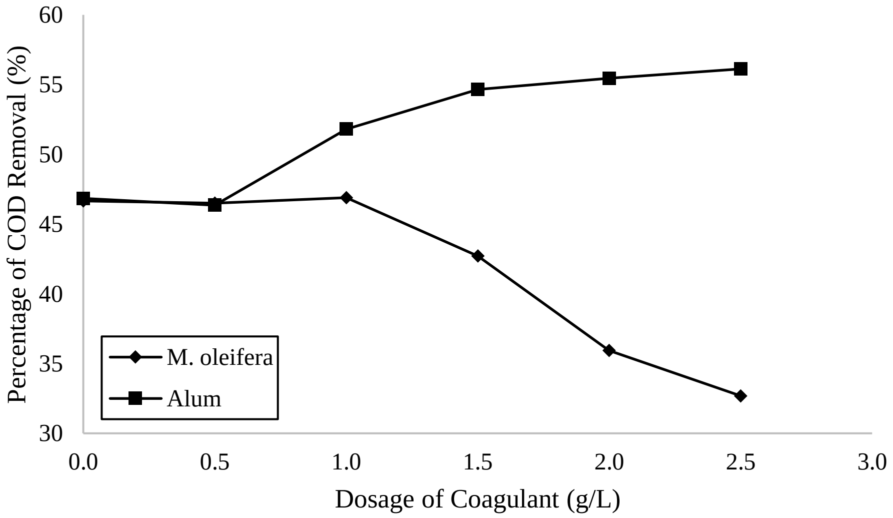


Figure 4.4: Effect of Dosage on COD Removal.

Rosmawanie et al. (2018) and Gardea et al. (2017) reported similar results for the application of *M. oleifera* to treat wastewater from the public market and coffee fermentation process. TSS values will decrease with the increased dosage of coagulant, then remain unchanged over a dosage range and subsequently increase when overdosing occurs. Through this study, it can be inferred that the optimum dosage of alum and *M. oleifera* seed powder are 0.5 and 1.0 g/L, respectively.

4.1.2 Effect of Initial pH of Wastewater

The effect of pH was studied by varying the initial pH between 3, 5, 9 and 11 other than the ambient pH, which was around 6.5. The optimum pH for both coagulants was at 6.5. At this pH, carboxylate ions were produced from amino acids contained in *M. oleifera* seed powder (Hendrawati et al., 2016). At the same time, protons were released. It tends to attract and neutralise the negative charge on the surfaces of colloids. As a result, the colloids coagulate. Based on Figure 4.5, the TSS removal increased when the pH increased from pH 3 to 10.

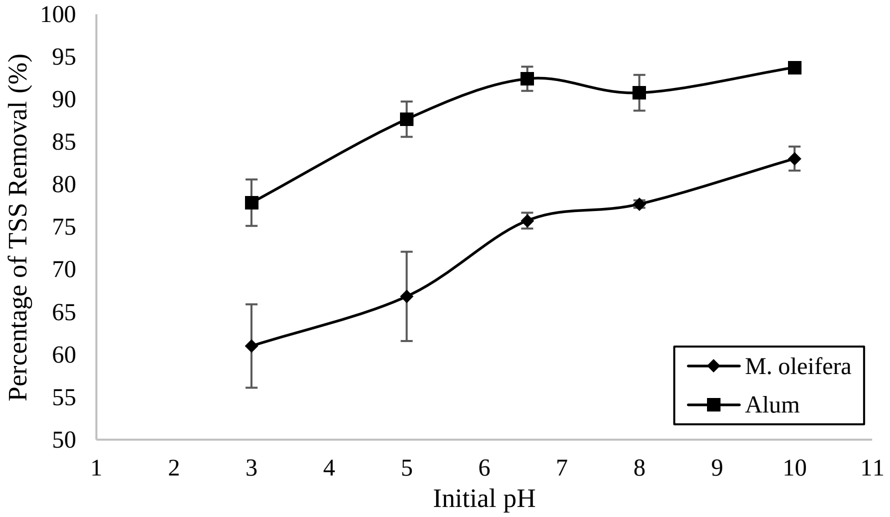


Figure 4.5: Effect of pH on TSS Removal.

The concentration of H^+ and OH^- ions is high at low and high pH respectively. An excessive amount of both ions present in the wastewater will result in different impacts. A high concentration of H^+ ions will assist in neutralising the negative charges on the colloids' surfaces, thereby increasing

TSS removal. Contrarily, OH^- ions tend to compete with the colloids to adsorb on the surface of the coagulating agent that carries positive charges, reducing the amount of active site available for coagulation-flocculation. Thus, at high pH, the efficiency appears to be lower.

The effect of H^+ and OH^- ions depends on the preparation steps. When the coagulant was dosed and pH was adjusted at the same time, the addition of acid or alkali directly affected the active components extracted from *M. oleifera* seed powder. However, when acid or alkali was added without any dosage of coagulant, H^+ and OH^- ions would only affect the charges on the colloids' surfaces. This was proved by the zeta potential analysis (Figure 4.6). Higher pH of the wastewater had lower zeta potential. Thus, the more negatively charged surfaces tend to adsorb to the coagulants.

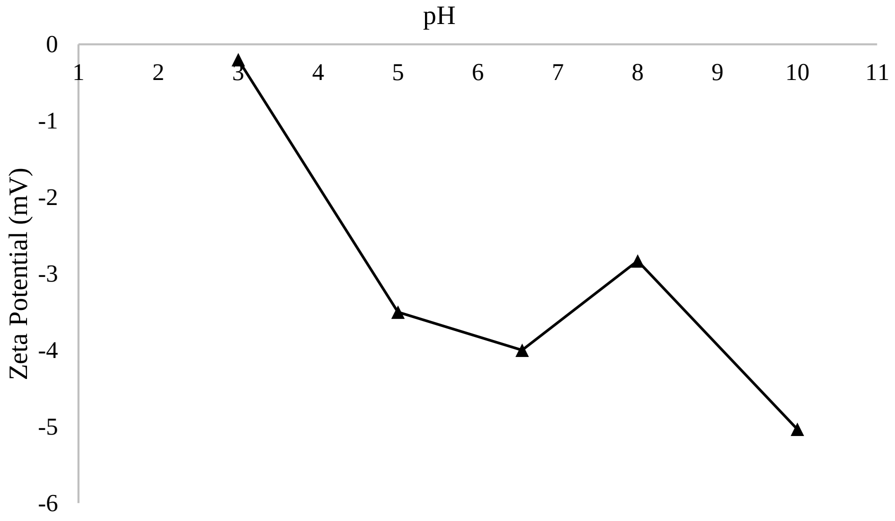


Figure 4.6: Zeta Potential of Wastewater at different pH.

In addition, pH affects protein solubility in the *M. oleifera* seed powder. The solubility of protein is low below pH 4 and gradually increase after pH 4 (Lee et al., 2018). Therefore, TSS removal efficiency was high as the pH increased. Similar phenomena occurred when alum was used as a coagulant.

On the other hand, Figure 4.7 shows when initial pH was adjusted from acid to basic range, COD removal increased as well. However, there was a sharp decline in efficiency when *M. oleifera* was used at pH 6.5. Researchers reported that protein of the seeds in soluble at this pH. Therefore, at this pH, high concentration of coagulating or non-coagulating protein accumulated in the wastewater. The efficiency increased when the pH was in the basic range, indicating that the solubility of non-coagulating protein was lower than it was at pH 6.5.

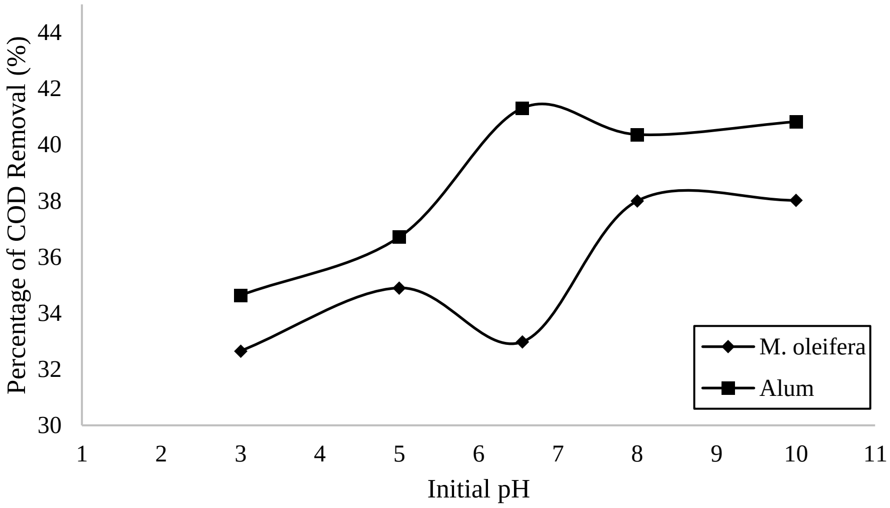


Figure 4.7: Effect of pH on COD Removal.

Based on Figure 4.8, the final pH of wastewater did not deviate much from the initial pH when *M. oleifera* seed powder was used as coagulant. However, there was a great reduction of pH value when the initial pH was in the basic range. The high concentration of OH^- ions, which were not bound on the surface of the colloids in the wastewater, might have attached to the coagulating protein. Therefore, the final pH decreased.

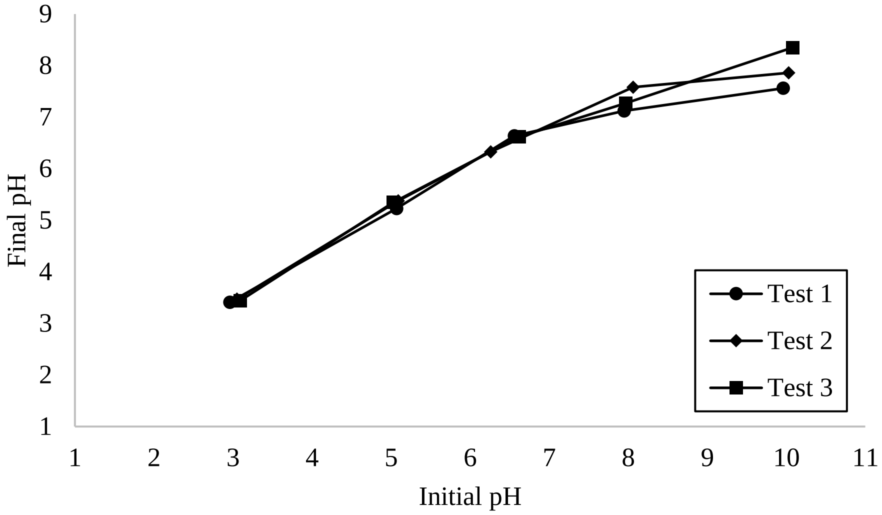


Figure 4.8: Effect of *M. oleifera* Seed Powder on the Final pH of Wastewater.

Conversely, when alum was dosed into the wastewater, the final pH dropped drastically as compared to the initial pH. This is due to the formation of sulphuric acid as shown in equation 2.2 and 2.3 (Hendrawati et al., 2016). Based on Figure 4.9, when initial pH increased, the pH dropped significantly especially when it was in the basic range. Formation of sulphuric acid reduced the final pH. Hypothetically if the alkalinity in the water is sufficient to neutralise sulphuric acid, the pH of the wastewater will not differ much from the initial pH. This can be inferred that the wastewater from the P&P industry does not have high alkalinity. Therefore, the final pH dropped when sulphuric acid was formed.

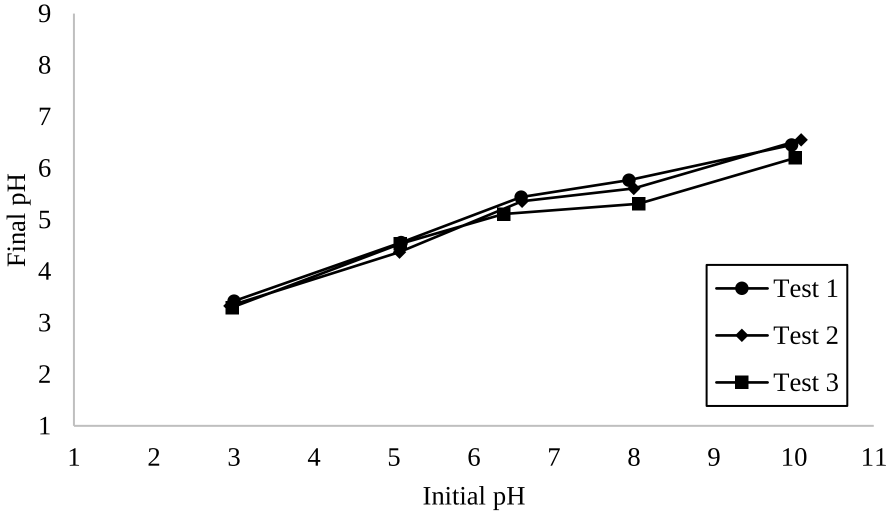


Figure 4.9: Effect of Alum on the Final pH of Wastewater.

Besides, the deviation of final pH from initial pH was related to the dosage of alum. pH was significantly affected when the dosage was high. From Figure 4.10, the final pH was 6.52 and 4.81 at the dosage of 0.5 g/L and 2.5 g/L, respectively. Therefore, different amounts of alum added into the wastewater has a significant effect on the pH to different extents (Abdulwahab et al., 2016).

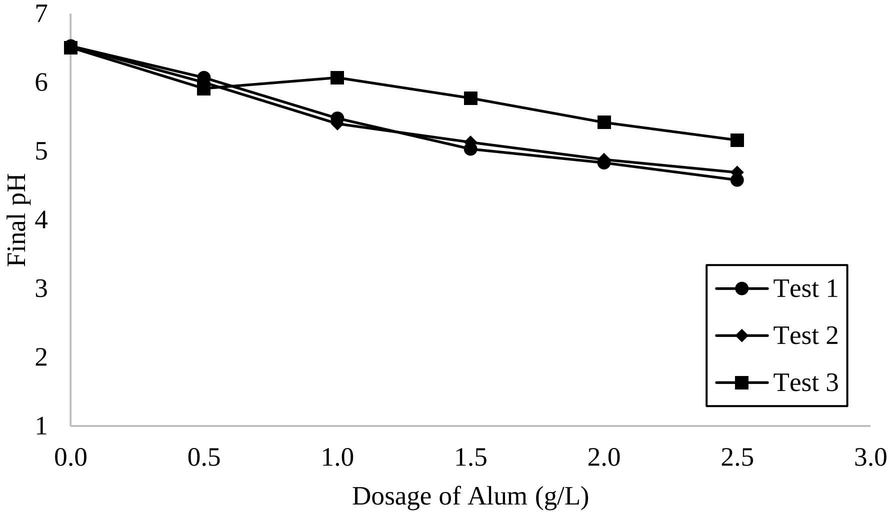


Figure 4.10: Effect of Alum Dosage on Final pH of Wastewater.

Similar results were reported by the researcher using *M. oleifera* to treat synthetic kaolin solution (Pritchard et al., 2010). The optimum pH was found to be around pH 6.5 when *M. oleifera* and alum were used. However, by comparing the effect of coagulant on the final pH, *M. oleifera* seed is better than alum. At the same time, it fulfils the requirement by EPA, which mentioned that the final pH of treated water should be in between 6.0 to 8.0 (The Daily Star, 2015).

4.1.3 Effect of Stirring Speed

The stirring speed was manipulated at 20, 40, 60, 80 and 100 rpm. Both of the coagulants exhibited the same trend for TSS removal. The graph of TSS removal against stirring speed was plotted in Figure 4.11. The TSS removal increased from 20 to 40 rpm. The purpose of stirring is to allow the particles of the same size to agglomerate and form larger particles that have sufficient density to settle with the aid of gravitational force. At 20 rpm, particles could come into contact and coagulate. However, the force was not sufficient to allow the maximum collision between colloids. When the speed was increased to 40 rpm, the efficiency of TSS removal increased. This proved that the colloids had a higher probability to collide with each other, forming denser floc. The maximum efficiency of TSS removal was achieved when stirring speed was 40 rpm for both coagulants. The efficiency decreased when the adjusted speed was higher than 40 rpm. TSS removal declined gradually from the stirring speed of 60, 80 and 100 rpm. When the speed increased, the shearing force acted on the colloids increased as well. The floc will never return to its original size when the high shear rate was applied and broke the large particles (Fitzpatrick, Fradin, and Gregory, 2004). The stirring speed of 60 rpm applied shearing force that was too high; as a result, the floc broke apart. Subsequent increased of stirring speed led to a shearing force that was even greater than before. Therefore, the efficiency of TSS removal showed a great reduction when the used of stirring speed was greater than 40 rpm. Therefore, lower speed should be utilised to reduce the force acted on formed floc at the initial stage (Muhammad et al., 2015). The speed should be high enough to allow the particles to coagulate but not to break the floc apart.

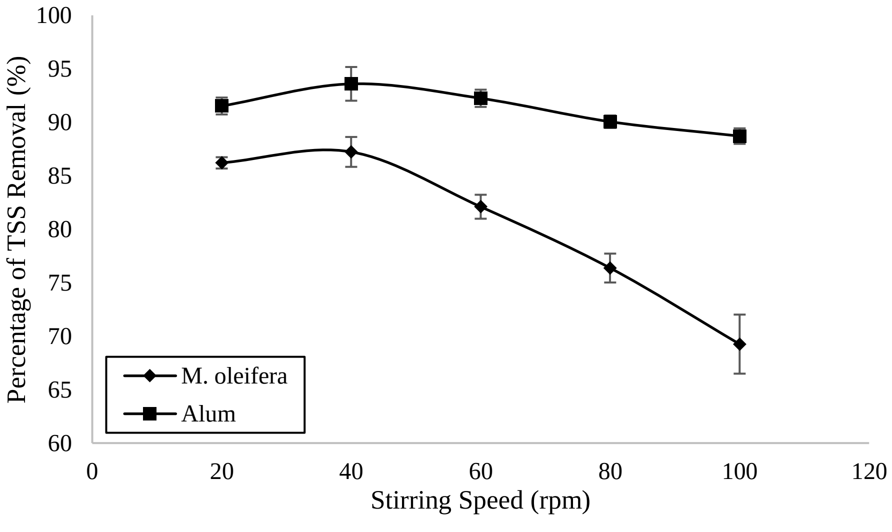


Figure 4.11: Effect of Stirring Speed on TSS Removal.

On the other hand, both coagulants showed different extents in removing COD when stirring speed was varied as shown in Figure 4.12. *M. oleifera* seed powder reduced COD as agitation speed increased from 20 to 40 rpm, indicating that organic matters were removed when suspended solids coagulated. Nevertheless, the rising of COD was observed as soon as stirring speed of 60 rpm and above was set, leading to a great reduction of COD removal. This was due to the surge of protein concentration in the wastewater. Greater stirring speed caused a high yield of protein extracted from *M. oleifera* seed powder (Kim and Lee, 2014). Conversely, mixing speed did not significantly affect the COD removal when alum was used as a coagulant. However, there was a drastic reduction in COD removal at 100 rpm. At this speed, most of the floc had been broken and the colloids are dispersed in the wastewater instead of coagulating. Therefore, most of the inorganic and organic matter remained in the supernatant of wastewater.

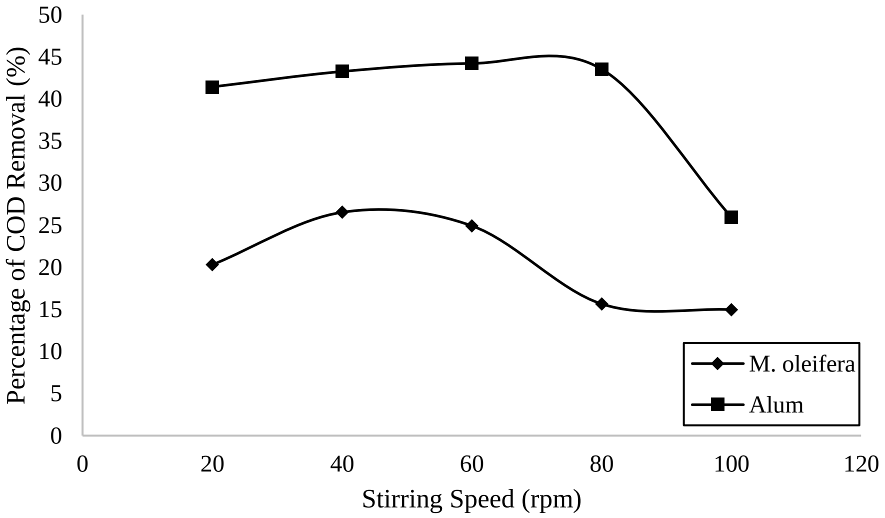


Figure 4.12: Effect of Stirring Speed on COD Removal.

The optimum stirring speed was 40 rpm while treating wastewater from the P&P industry using *M. oleifera* seed powder and alum. Sanchez-Martin, Beltran-Heredia and Peres (2012) and Muhammad et al. (2015) reported similar results when *M. oleifera* seed and watermelon seeds as natural coagulant respectively. Both of these researches used natural coagulants to treat river water. The results showed that the content of suspended solids decreased as agitation speed increased. However, when it reached maximum efficiency, it started to decline as the mixing speed was too high and solids could not coagulate.

4.1.4 Effect of Settling Time

To study the effect of settling time, the wastewater sample was collected at every 5 min interval. Flocs require adequate time to settle at the bottom of the beaker (Teh, Wu, and Juan, 2014). Nevertheless, when most of the flocs have settled, no significant changes on TSS was observed as the colloids that remain in the supernatant were not coagulated.

Figure 4.13 shows the TSS removal at different settling time. Alum and *M. oleifera* seed powder showed the same trend of graphs. At the first 5 min, maximum efficiency of TSS removal was achieved when alum is used. The efficiency remained constant after 5th min as most of the coagulated colloids with large densities settled at the bottom of the beaker, leaving the suspended solids behind. In the experiment using *M. oleifera* as coagulant, the result showed that the efficiency increased when settling time increased. This indicates that the flocs formed by *M. oleifera* require a longer time to settle (20 min). Furthermore, it is noteworthy that the initial TSS removal efficiency of alum was higher than that of *M. oleifera* seed powder. Therefore, it can be inferred that flocs formed by alum require lesser time to settle.

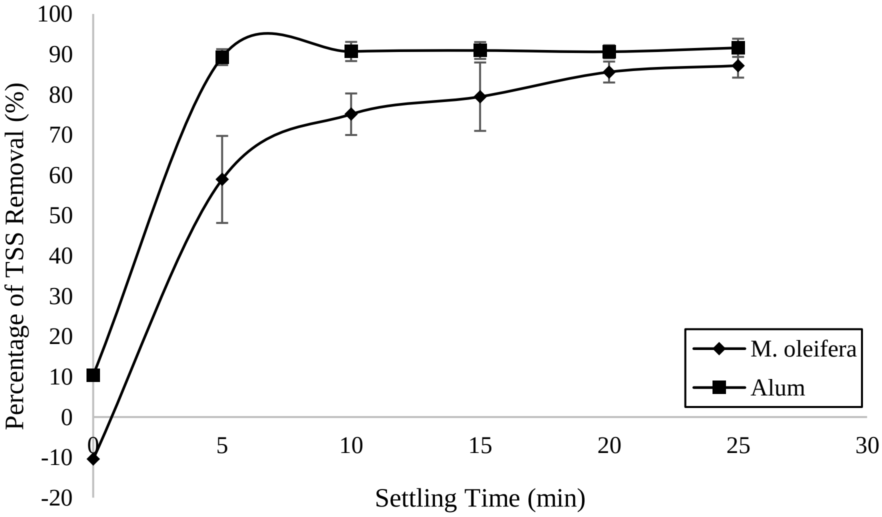


Figure 4.13: Effect of Settling Time on TSS Removal.

From Figure 4.14, it was observed that alum reduced COD gradually as settling time increased. On the other hand, *M. oleifera* seed powder reduced COD until 20th min. Increased of COD after 20th min indicated that soluble protein was continuously extracted from *M. oleifera*. This was proven when the extraction time was studied. The longer the extraction time, the more soluble protein are extracted. However, the efficiency of removing COD dropped because not all extracted protein was involved in coagulating activity (Jung et al., 2018).

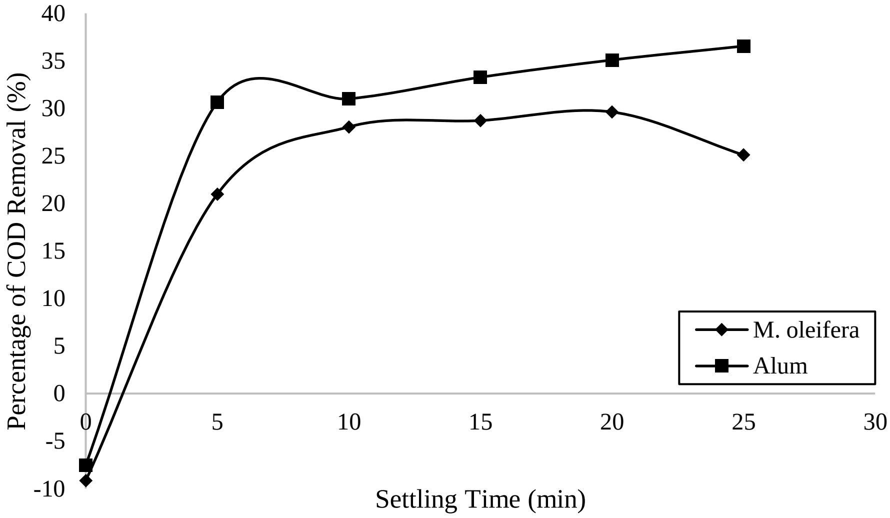


Figure 4.14: Effect of Settling Time on COD Removal.

The optimum settling time when alum and *M. oleifera* seed powder was used is 5 and 20 min, respectively. In fact, settling time depends on the types of natural coagulants. Variety of natural coagulants results in floc of different densities. For example, according to Marobhe, Dalhammar and Gunaratna (2007), coagulated colloids formed by protein extracted from *Vigna Unguiculata* and *Parkinsonia Aculeata* required two hours to settle. Nevertheless, the amount of suspended solids will eventually remain unchanged after a period of time for all coagulants.

4.2 Characterisation of Coagulating Activity

4.2.1 SEM-EDX

Figure 4.15 and 4.16 show the SEM images of Alum and *M. oleifera* seed powder. A crystalline structure was observed for alum. SEM images of alum showed minimal or no pores on the surface of alum. Instead, a multi-layered surface was evident. Solids of different sizes were well dispersed on its rough surface. The surface of alum did not exhibit any unique appearance as it was dissolved and dissociated when dosed into the wastewater.

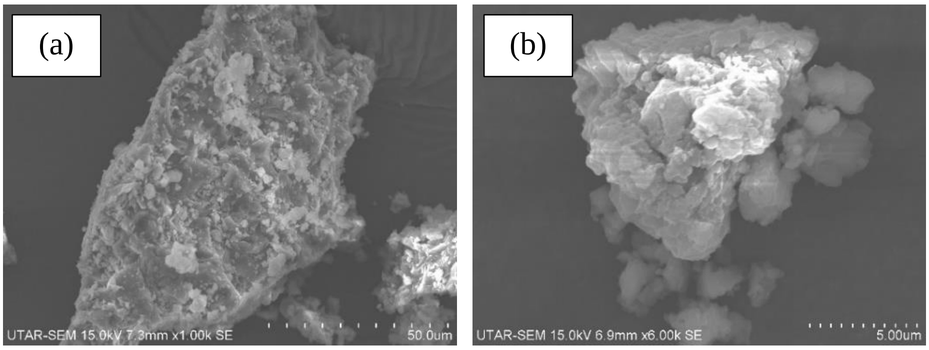


Figure 4.15: SEM images of Alum.

Unlike alum, *M. oleifera* seed powder did not have a crystalline shape. It had a compact but porous structure. Furthermore, pores were distributed evenly on the surface. Due to the presence of different components such as protein, fatty acid and carbohydrate in *M. oleifera* seed powder, it exhibited high porosity. Moreover, deformation of plant tissue contributed to the porosity observed on the surface as well. The irregular shape with high porosity led to high surface area exposed to the solvent. Coagulating agents could be extracted easily from the inner side of *M. oleifera* seed powder (Araujo et al., 2013; Kebede et al., 2018). Simate et al. (2012) has suggested that compact but porous structures are ideal attributes for the coagulation of particles through bridge aggregation.

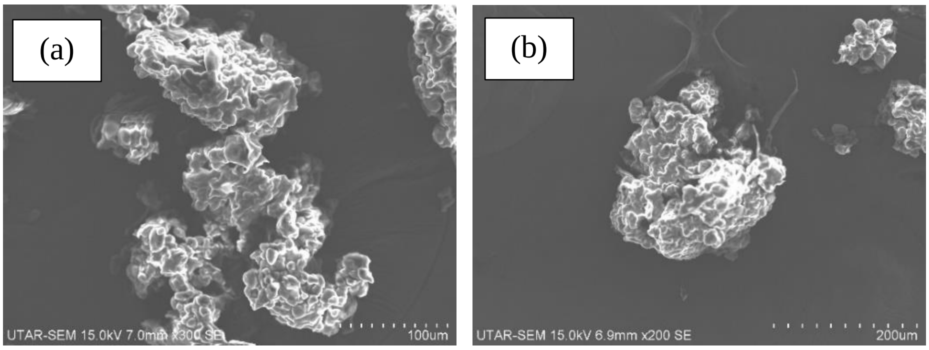


Figure 4.16: SEM image of *M. oleifera* Seed Powder.

EDX analysis was done on alum and *M. oleifera* seed powder. Result shows that aluminium (12.88 wt%), sulphur (21.14 wt%) and oxygen (63.01

wt%) are the main elements found in alum. Alum, as known as aluminium sulphate has the chemical formula of $Al_2(SO_4)_3$. Moreover, alum is an inorganic coagulant. Therefore, the result is valid. On the other hand, *M. oleifera* seed contains mainly organic compound. Thus, EDX result showed a high percentage of carbon and oxygen. Carbon indicates the carbon chain of an organic compound while oxygen attached to the carbon chain as functional groups. EDX analysis showed that carbon occupied 74.68 wt% of *M. oleifera* seed powder. This further proved that *M. oleifera* seed comprises of protein, fatty acid and carbohydrate.

4.2.2 FTIR

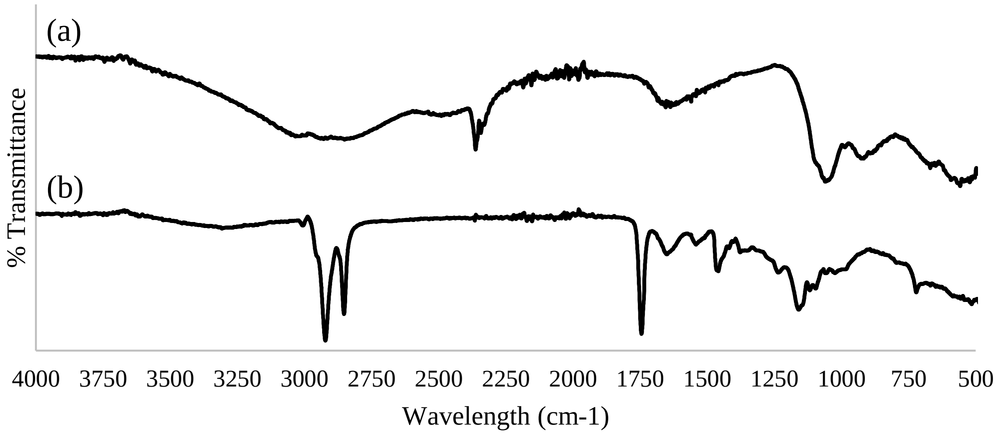


Figure 4.17: FTIR Spectrum of (a) Alum and (b) *M. oleifera* Seed Powder.

FTIR spectrum of alum is shown in Figure 4.17(a). The peak at 669.12 cm^{-1} is possibly due to bending vibration of the water molecule (H_2O). Water was absorbed, polymerized and crystallized in the powder of alum (Zhou et al., 2014). Peaks at 1654.44 and 1636.89 cm^{-1} could be attributed to the presence of hydroxyl (OH) bond involved in the bending vibration of H_2O while the peak at 2850.28 cm^{-1} related to the stretching of OH bond. Furthermore, peaks of 2489.76, 2362.37 and 2343.02 cm^{-1} were assigned to the vibration of water molecules having asymmetry stretching and bonded with aluminium. The signal at 1060.71 cm^{-1} corresponded to the bond vibration of SO in alum (Lal and Garg, 2017). Additionally, there was a peak at 557.62 cm^{-1} which could be shown as a result of bending vibration of Al-OH.

FTIR spectrum of *M. oleifera* seed powder is shown in Figure 4.17(b). The broad peak 3306.24 cm^{-1} is possibly due to hydroxyl (OH) and amide (NH) bond vibration of the hydroxyl group and amino group respectively (Araujo et al., 2010). Hydroxyl group present in the macromolecules such as proteins, lipids and carbohydrate in *M. oleifera* seed powder. On the contrary, the vibration of amide bond was due to the presence of protein. Besides, the peaks at 2921.16 and 2851.99 cm^{-1} represented the symmetrical and asymmetrical stretching of alkane (CH) bonded to the amino group. Band appearing at 1117.07 cm^{-1} indicated CH_2-N groups. CH_2 are commonly found in a long chain of fatty acid; therefore, this proves the presence of lipid. The content of lipid in *M. oleifera* could be further verified with the peak appearing at 1743.90 cm^{-1}.

The presence of protein could be proved by different peaks in the FTIR spectrum. The peak at 2067.25 cm^{-1} was assigned to the vibration of amide (NH) bond while peak at 1648.08 cm^{-1} corresponded to carbonyl group (C=O). The absorbance band at 1457.68 cm^{-1} is possibly due to the vibration of carboxylic groups (Lal and Garg, 2017). A peak at 1540.98 cm^{-1} represented the stretching of CN or the deformation of the NH bond which affirmed the existence of protein (Araujo et al., 2013). The peaks from 600 to 1230 cm^{-1} was associated with CN stretch primary amines, C-C-N bend amine and N-C=O bend amide (Kebede et al., 2018).

4.2.3 XRD

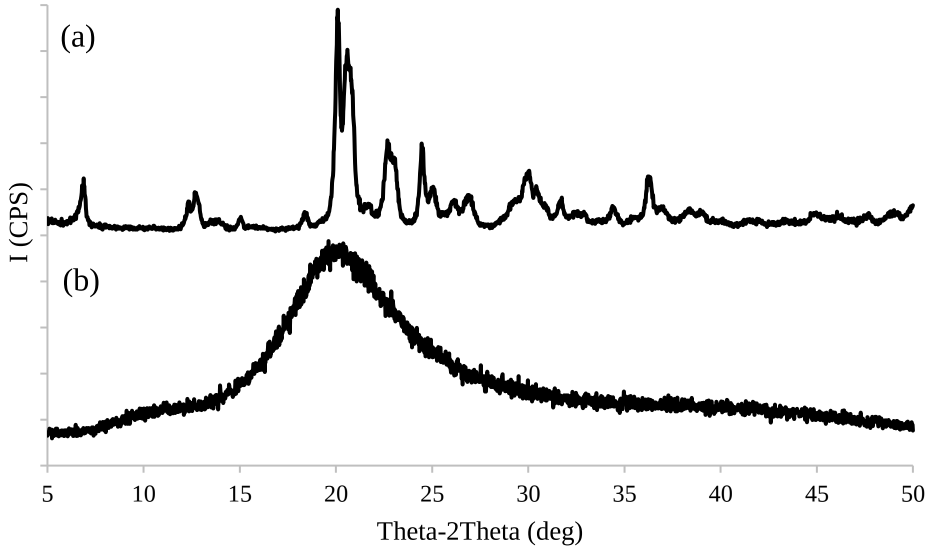


Figure 4.18: X-Ray Diffraction of (a) Alum and (b) *M. oleifera* Seed Powder.

Figure 4.18(a) shows the X-ray Diffraction of alum. The spectrum showed several peaks especially peaks at 20.1017, 20.54 and 22.68°, indicating that alum has crystallite shape. The peaks match the lattice plane (104) of aluminium sulphate (Nila and Radha, 2018). Furthermore, the peak at 20.1017° had the highest area under the graph. This proves alum has an abundance of lattice plane (104).

Figure 4.18(a) shows the X-ray Diffraction of *M. oleifera* Seed Powder. The peak was not sharp and it exhibited a broad range of peak. A broad peak indicates that the sample was amorphous and did not have specific shapes. The amorphous peak was probably due to the high percentage of protein and oils presence in *M. oleifera* seed. Protein diffracted X-ray at the peak of 20.14° (Zakaria, Mansor and Shahrin, 2018). Yet, at the same time, the amorphous peak was shown attributed to complex constituents which surrounded the protein. These constituents could be oils or carbohydrates (Araujo et al., 2010).

4.2.4 TGA

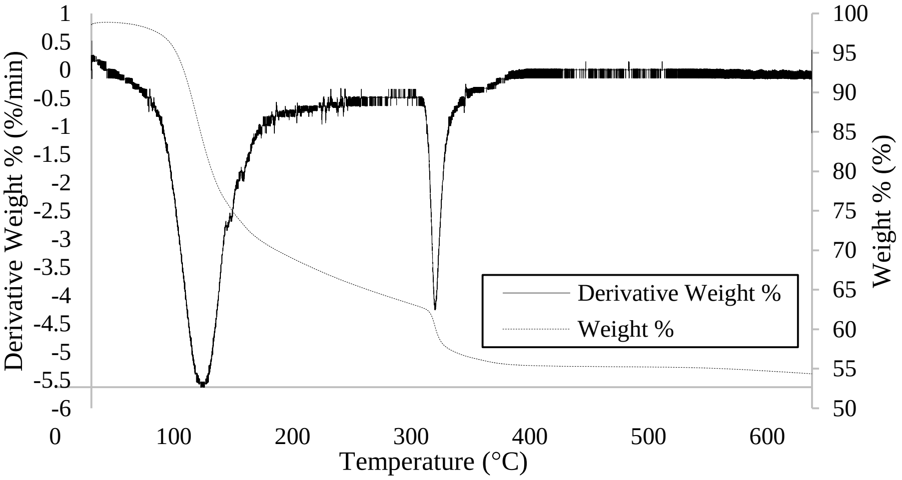


Figure 4.19: TGA of Alum.

Figure 4.19 shows the thermogravimetric analysis of alum. The weight of alum powder started to drop dramatically after 100 ℃ and remained constant again after 400 ℃. From the derivative curve, two significant peaks were found. The first peak appeared between 100 to 150 ℃. This peak was due to the removal of water molecule from alum powder, leading to a sharp decline of weight. The second peak was in the range of 300 to 350 ℃. Salt in anhydrous alum started to decompose (Souza et al., 2019).

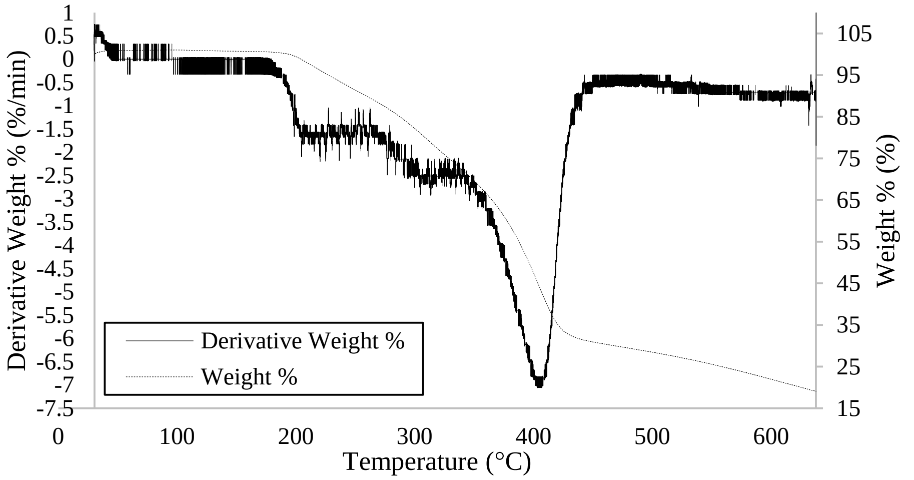


Figure 4.20: TGA of *M. oleifera* Seed Powder.

On the other hand, Figure 4.20 shows the thermogravimetric analysis of *M. oleifera* Seed Powder. The reduction of weight took place at three different stages. From the temperature of 100 to 150 ℃, the weight did not show a substantial decline in weight. At this range, water was removed from the samples. However, the powder of *M. oleifera* seed was dried at 80 ℃ overnight before TGA was carried out. Since most of the water had been removed from the sample; therefore, the derivative curve in this range did not show a significant change of weight. The second peak appeared from 180 to 350 ℃. Approximately 25% of the weight loss was observed. Loss of weight at this range of temperature was attributed to protein decomposition. An intense dropped was shown at a temperature of 350 to 450 ℃. The oil contained in the seeds started to decompose at this temperature as fatty acid has a high boiling point (Araujo et al., 2013).

By comparing both alum and *M. oleifera* seed powder, alum has lower thermal stability. After 350 ℃, alum was nearly decomposed while the oil (high boiling point) remained in *M. oleifera* seed powder, indicating that *M. oleifera* is much more stable than alum at high temperature. Tunggolou and Payus (2017) showed that *M. oleifera* achieved better coagulation rate at higher temperature as proteins are active at high temperature. Studies were done to treat POME which commonly discharged at 80 to 90 ℃ and it was proven that performance of alum was lower than *M. oleifera* (Othman, Ahmad and Bhatia, 2008; Ismail et al., 2014). Therefore, *M. oleifera* is preferred when wastewater is discharged at high temperature since alum is temperature-sensitive.

4.3 Summary

M. oleifera seed powder worked best at the dosage of 1 g/L, pH 5, agitation speed of 40 rpm and settling time of 20 min. Based on the results from SEM and XRD, alum had a regular shape. On the other hand, *M. oleifera* seed powder had an irregular shape, amorphous nature and porous were found on the surface. EDX analysis and FTIR spectrum showed that *M. oleifera* seed powder contained a high percentage of organic compound whilst alum comprised of inorganic compounds. Other than that, TGA results revealed that *M. oleifera* is preferable when discharged wastewater has a high temperature.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In this study, common inorganic (alum) and natural coagulants (*M. oleifera*) were prepared. OFAT approach was used to study the effects of different parameters and the optimum condition for the best coagulating performance was determined. Dosage (0, 0.5, 1.0, 1.5, 2.0, 2.5 g/L), pH (3, 5, 6.5, 8, 10), stirring speed (20, 40, 60, 80, 100 rpm) and settling time (0, 5, 10, 15, 20, 25 min) were the four studied parameters. The efficiency of coagulating activity was compared in terms of TSS and COD removals. The optimum condition for *M. oleifera* seed powder was the dosage of 1 g/L, pH 6.5, stirring speed of 40 rpm and settling time of 20 min. At this condition, *M. oleifera* seed powder could achieve TSS and COD removal of 85.59% and 29.62% respectively. Conversely, alum achieved TSS and COD removal efficiency of 90.62 and 35.09% respectively. *M. oleifera* seed powder required higher dosage and longer settling time in order to exhibit similar coagulating performance as alum.

Alum and *M. oleifera* seed powder were characterised using SEM-EDX, XRD, FTIR and TGA. SEM depicted that alum had a regular shape. *M. oleifera* seed powder had irregular morphology and high porosity on the surface, enabling the extraction of protein from the inner side. EDX analysis demonstrated that alum contained inorganic elements such as aluminium, oxygen and sulphur. On the other hand, *M. oleifera* seed powder mostly comprised of carbon and oxygen element. The high percentage of carbon was the evidence to prove the existence of organic compound such as protein, fatty acid and carbohydrate in *M. oleifera* seed. The crystallinity of both coagulants could be determined through XRD as well. XRD spectrum showed a sharp peak, indicating high crystallinity of alum while a broad peak for *M. oleifera* seed powder, proving that the surface was amorphous. Amorphous nature was attributed to the presence of macromolecules in *M. oleifera* seed powder. Additionally, FTIR analysis showed the vibration of functional groups such as OH, Al-OH, SO bonds in alum. Conversely, FTIR analysis indicated the presence of OH, NH, CH, CH_2-N, C=O, COOH, CN, C-C-N and N-C=O in *M. oleifera* seed powder. It is noteworthy that most of the functional group involved carbon elements. This again confirmed the presence of organic compounds in *M. oleifera* seed powder. On the other hand, based on the result from TGA, alum had lower thermal stability than *M. oleifera* seed.

In conclusion, the listed aims and objectives were achieved. This project verified the effects of different parameters on the coagulating performance of both inorganic and plant-based coagulant. Moreover, based on the result, it could achieve a maximum TSS and COD removal efficiency of 96.03 and 56.12%. Therefore, *M. oleifera* could reduce the usage of common coagulant, alum which is widely used in most of the industries today and has the possibility to impose harm to the environment.

5.2 Recommendations for future work

The procedures were followed to achieve the objectives of this study. However, the deviation of the result obtained led to repetitive of the experiments causing the problems such as wastage of raw materials and consumption of time. Due to unexpected events, the research could not be studied in details. Improvement could be done in order to obtain a much accurate results in determining the coagulating potential of *M. oleifera* seed.

(i) Further investigation on protein extraction from *M. oleifera* should be studied in order to improve the coagulating performance. Amount of protein extracted varies with the extracting solvent used. The solvent that will lead to a high yield of protein from *M. oleifera* could be studied. Greater concentration of coagulating agent will result in better efficiency of TSS and COD removal.

(ii) Different approaches such as Taguchi method, three factorial method or design of experiment (DOE) should be applied to obtain the efficiency of the coagulation-flocculation process. The interaction between factors could not be studied when OFAT is applied. As a comparison, DOE method is better than

OFAT as the interaction between parameter could be evaluated (Abou-Taleb and Galal, 2018).

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APPENDICES

APPENDIX A: Preparation of Hydrochloric Acid

Given:

Concentration of HCl = 37%

Specific gravity of HCl = 1.19 g/mol

Molecular weight of HCl = 36.5 g/mol

Targeted molarity = 1 M of HCl

Targeted volume = 100 mL = 0.1 L

Density of HCl:

$$\frac{37\ mL\ HCl}{100\ mL\ sol} \times\ 1.19\ \frac{g\ HCl}{mL\ HCl}\ =\ 0.4403\ \frac{g}{mL}\ =\ 440.3\ \frac{g}{L}$$

Initial Molarity of HCl:

$$\frac{440.3\ \frac{g}{L}}{36.5\ \frac{g}{mol}}\ =\ 12.0630\ \frac{mol}{L}\ =\ 12.0630\ M$$

Required volume to prepare 1 M of HCl in 100 mL solution:

$$\begin{aligned} M_1V_1 &= M_2V_2 \\ \left(12.0630\ \frac{mol}{L}\right)V_1 &= (1\ \frac{mol}{L})(0.1\ L) \\ V_1 &= 8.2898\ mL \end{aligned}$$

∴ To prepare 100 mL of 1 M HCl, a volume of 8.2898 mL stock solution with concentration of 37% is needed.

APPENDIX B: Preparation of Sodium Hydroxide

Given:

Molecular weight of NaOH = 39.997 g/mol

Targeted molarity = 1 M of HCl

Targeted volume = 100 mL = 0.1 L

Mass Concentration of NaOH:

$$1\ \frac{mol}{L} \times 39.997\ \frac{g}{mol} = 39.997\ \frac{g}{L}$$

Required mass to prepare 1 M of NaOH in 100 mL solution:

$$0.1\ L \times 39.997 \frac{g}{L} = 3.9997\ g$$

∴ To prepare 100 mL of 1 M NaOH, 3.9997 g of NaOH pellets is needed.

APPENDIX C: Raw Data

Average pH = 6.5

Stirring Speed (rpm) = 20

Settling Time (min) = 15

Table C.1: Effect of Dosage (Alum) on Coagulation Process.

Dosage (g/L)	**Test**	**TSS (mg/L)**		**Reduction (%)**		**COD (mg/L)**		**Reduction (%)**	**pH**	
		Initial	**Final**	**Sample**	**Average**	**Initial**	**Final**		**Initial**	**Final**
0	1	2533	432	82.95	75.73	5333	2835	46.84	6.44	6.53
	2	925	318	65.62					6.26	6.53
	3	1988	425	78.62					6.41	6.51
0.5	1	2299	223	90.30	89.28	5333	2861	46.35	6.23	6.07
	2	1021	137	86.58					6.26	6.00
	3	1052	95	90.97					6.57	5.91
1.0	1	1847	180	90.25	89.44	5333	2571	51.79	6.2	5.48
	2	1034	85	91.78					6.27	5.40
	3	1438	197	86.30					6.39	6.07

Table C.1 (Continued)

1.5	1	1589	146	90.81	90.92	5333	2419	54.64	6.32	5.03
	2	1170	63	94.62					6.25	5.13
	3	1098	139	87.34					6.4	5.77
2.0	1	2003	167	91.66	91.32	5333	2376	55.45	6.14	4.83
	2	1017	88	91.35					6.31	4.88
	3	1559	141	90.96					6.39	5.42
2.5	1	1532	192	87.47	90.07	5333	2340	56.12	6.2	4.58
	2	1062	88	91.71					6.24	4.69
	3	2104	189	91.02					6.4	5.16

Table C.2: Effect of Dosage (*M. oleifera*) on Coagulation Process.

Dosage (g/L)	**Test**	**TSS (mg/L)**		**Reduction (%)**		**COD (mg/L)**		**Reduction (%)**	**pH**	
		Initial	**Final**	**Sample**	**Average**	**Initial**	**Final**		**Initial**	**Final**
0	1	2709	441	83.72	79.40	4321.5	2305	46.66	6.88	6.79
	2	1721	414	75.94					6.7	6.75
	3	1822	391	78.54					6.83	6.82

Table C.2 (Continued)

0.5	1	2689	382	85.79	83.85	4321.5	2312	46.50	6.91	6.72
	2	2169	365	83.17					6.74	6.76
	3	1635	284	82.61					6.83	6.83
1.0	1	3222	181	94.38	90.45	4321.5	2295	46.89	6.9	6.71
	2	1734	190	89.04					6.73	6.83
	3	1616	195	87.93					6.82	6.82
1.5	1	3061	162	94.71	92.34	4321.5	2476	42.71	6.92	6.71
	2	1729	156	90.98					6.75	6.78
	3	2055	178	91.34					6.83	6.82
2.0	1	2568	137	94.67	90.87	4321.5	2769	35.93	6.89	6.7
	2	1916	184	90.40					6.72	6.78
	3	1589	198	87.54					6.84	6.85
2.5	1	3277	130	96.03	91.30	4321.5	2909	32.69	6.94	6.7
	2	1755	175	90.03					6.77	6.74
	3	1595	194	87.84					6.83	6.83

Optimum Dosage (g/L) = 1.0

Stirring Speed (rpm) = 20

Settling Time (min) = 15

Table C.3: Effect of Initial pH of Wastewater on Coagulation Process (Alum).

pH	**Test**	**TSS (mg/L)**		**Reduction (%)**		**COD (mg/L)**		**Reduction (%)**	**pH**	
		Initial	**Final**	**Sample**	**Average**	**Initial**	**Final**		**Initial**	**Final**
3.0	1	1060	202	80.94	77.85	3717.5	2430	34.63	3.00	3.42
	2	1032	250	75.78					2.95	3.33
	3	829	192	76.84					2.98	3.3
5.0	1	959	138	85.61	87.67	3717.5	2353	36.70	5.09	4.56
	2	1250	128	89.76					5.07	4.37
	3	800	99	87.63					5.08	4.53
6.5	1	1045	84	91.96	92.41	3717.5	2182	41.30	6.59	5.44
	2	871	76	91.27					6.6	5.36
	3	1018	61	94.01					6.37	5.11

Table C.3 (Continued)

8.0	1	1002	78	92.22					7.94	5.77
	2	816	95	88.36	90.77	3717.5	2217	40.36	8.00	5.61
	3	762	63	91.73					8.06	5.31
10.0	1	1142	78	93.17					9.97	6.45
	2	1146	64	94.42	93.75	3717.5	2200	40.82	10.09	6.55
	3	885	56	93.67					10.02	6.20

Table C.4: Effect of Initial pH of Wastewater on Coagulation Process (*M. oleifera*).

pH	**Test**	**TSS (mg/L)**		**Reduction (%)**		**COD (mg/L)**		**Reduction (%)**	**pH**	
		Initial	**Final**	**Sample**	**Average**	**Initial**	**Final**		**Initial**	**Final**
3.0	1	938	331	64.71					2.96	3.41
	2	1432	638	55.45	61.00	4583.5	3087	32.65	3.05	3.47
	3	1268	471	62.85					3.09	3.44
5.0	1	821	309	62.36					5.07	5.23
	2	1300	448	65.54	66.84	4583.5	2984	34.90	5.09	5.38
	3	1099	301	72.61					5.03	5.35

Table C.4 (Continued)

6.5	1	944	229	75.74	76.04	4583.5	3072	32.98	6.56	6.64
	2	1441	356	75.29					6.26	6.33
	3	1392	319	77.08					6.62	6.62
8.0	1	979	223	77.22	77.69	4583.5	2842	37.99	7.95	7.12
	2	1529	335	78.09					8.06	7.58
	3	1331	296	77.76					7.97	7.27
10.0	1	975	179	81.64	83.03	4583.5	2841	38.02	9.96	7.56
	2	1564	266	82.99					10.03	7.86
	3	1326	206	84.46					10.08	8.35

Optimum Dosage (g/L) = 1.0

Optimum pH = 6.5

Settling Time (min) = 15

Table C.5: Effect of Stirring Speed on Coagulation Process (Alum).

Stirring Speed (rpm)	Test	TSS (mg/L)		Reduction (%)		COD (mg/L)		Reduction (%)	pH	
		Initial	Final	Sample	Average	Initial	Final		Initial	Final
20	1	1070	81	92.43	91.52	3554	2082	41.42	6.63	5.30
	2	877	78	91.11					6.62	5.22
	3	858	77	91.03					6.56	5.21
40	1	1117	57	94.90	93.59	3554	2017	43.25	6.72	5.24
	2	968	79	91.84					6.67	5.19
	3	1073	64	94.04					6.64	5.25
60	1	1041	88	91.55	92.24	3554	1983	44.20	6.57	4.99
	2	1082	86	92.05					6.63	5.05
	3	1367	94	93.12					6.58	5.06

Table C.5 (Continued)

80	1	1083	113	89.57	90.05	3554	2007	43.53	6.54	5.13
	2	957	89	90.70					6.53	5.08
	3	999	101	89.89					6.71	5.06
100	1	844	102	87.91	88.71	3554	2632	25.94	6.58	5.17
	2	979	109	88.87					6.50	5.16
	3	919	98	89.34					6.55	5.24

Table C.6: Effect of Stirring Speed on Coagulation Process (*M. oleifera*).

Stirring Speed (rpm)	**Test**	**TSS (mg/L)**		**Reduction (%)**		**COD (mg/L)**		**Reduction (%)**	**pH**	
		Initial	**Final**	**Sample**	**Average**	**Initial**	**Final**		**Initial**	**Final**
20	1	855	123	85.61	86.20	3244.5	2586	20.30	6.65	6.71
	2	823	110	86.63					6.65	6.74
	3	880	120	86.36					6.63	6.74
40	1	889	120	86.50	87.23	3244.5	2384	26.52	6.79	6.81
	2	1084	121	88.84					6.67	6.83
	3	1047	143	86.34					6.69	6.83

Table C.6 (Continued)

60	1	1031	172	83.32	82.10	3244.5	2436	24.92	6.57	6.73
	2	899	163	81.87					6.59	6.75
	3	953	180	81.11					6.56	6.83
80	1	983	242	75.38	76.37	3244.5	2737	15.64	6.62	6.85
	2	1041	230	77.91					6.54	6.81
	3	889	215	75.82					6.6	6.78
100	1	960	267	72.19	69.25	3244.5	2759	14.96	6.63	6.76
	2	838	279	66.71					6.63	6.75
	3	835	260	68.86					6.62	6.71

Optimum Dosage (g/L) = 1.0

Optimum pH = 6.5

Optimum Stirring Speed (rpm) = 40

Table C.7: Effect of Settling Time on Coagulation Process (Alum).

Settling Time (min)	**Test**	**TSS (mg/L)**		**Reduction (%)**		**COD (mg/L)**		**Reduction (%)**	**pH**	
		Initial	**Final**	**Sample**	**Average**	**Initial**	**Final**		**Initial**	**Final**
0	1	1045	674	35.50	10.42	2867	3083	-7.53	6.49	4.78
	2	967	819	15.31					6.50	4.79
	3	767	917	-19.56					6.49	4.95
5	1	1045	95	90.91	89.29	2867	1988	30.66	6.49	4.78
	2	967	98	89.87					6.50	4.79
	3	767	99	87.09					6.49	4.95
10	1	1045	78	92.54	90.69	2867	1978	31.01	6.49	4.78
	2	967	82	91.52					6.5	4.79
	3	767	92	88.01					6.49	4.95

Table C.7 (Continued)

15	1	1045	81	92.25	90.94	2867	1913	33.28	6.49	4.78
	2	967	77	92.04					6.50	4.79
	3	767	88	88.53					6.49	4.95
20	1	1045	86	91.77	90.62	2867	1861	35.09	6.49	4.78
	2	967	84	91.31					6.50	4.79
	3	767	86	88.79					6.49	4.95
25	1	1045	70	93.30	91.60	2867	1819	36.55	6.49	4.78
	2	967	73	92.45					6.50	4.79
	3	767	84	89.05					6.49	4.95

Table C.8: Effect of Settling Time on Coagulation Process (*M. oleifera*).

Settling Time (min)	**Test**	**TSS (mg/L)**		**Reduction (%)**		**COD (mg/L)**		**Reduction (%)**	**pH**	
		Initial	**Final**	**Sample**	**Average**	**Initial**	**Final**		**Initial**	**Final**
0	1	756	909	-20.24	-10.42	3447	3763	-9.17	6.50	6.65
	2	825	1063	-28.85					6.51	6.76
	3	1228	1009	17.83					6.54	6.47

Table C.8 (Continued)

5	1	756	381	49.60	58.95	3447	2724	20.97	6.50	6.65
	2	825	359	56.48					6.51	6.76
	3	1228	359	70.77					6.54	6.47
10	1	756	202	73.28	75.13	3447	2480	28.05	6.50	6.65
	2	825	238	71.15					6.51	6.76
	3	1228	234	80.94					6.54	6.47
15	1	756	215	71.56	79.47	3447	2457	28.72	6.50	6.65
	2	825	178	78.42					6.51	6.76
	3	1228	142	88.44					6.54	6.47
20	1	756	127	83.20	85.59	3447	2426	29.62	6.50	6.65
	2	825	122	85.21					6.51	6.76
	3	1228	143	88.36					6.54	6.47
25	1	756	116	84.66	87.18	3447	2582	25.09	6.50	6.65
	2	825	112	86.42					6.51	6.76
	3	1228	117	90.47					6.54	6.47

APPENDIX D: Coagulating Potential of Alum and *M. oleifera*

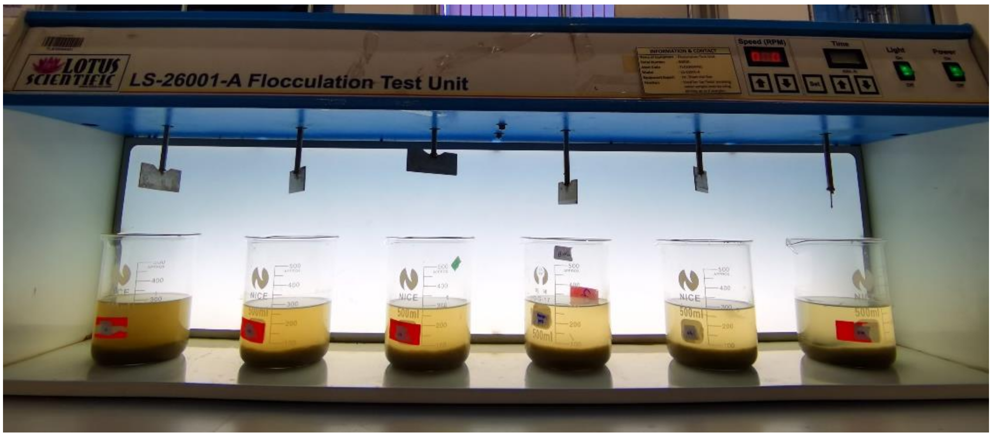

Figure D.1: Effect of Alum Dosage on Coagulating Activity (from sequence of left to right: 0, 0.5, 1.0, 1.5, 2.0, 2.5 g/L).

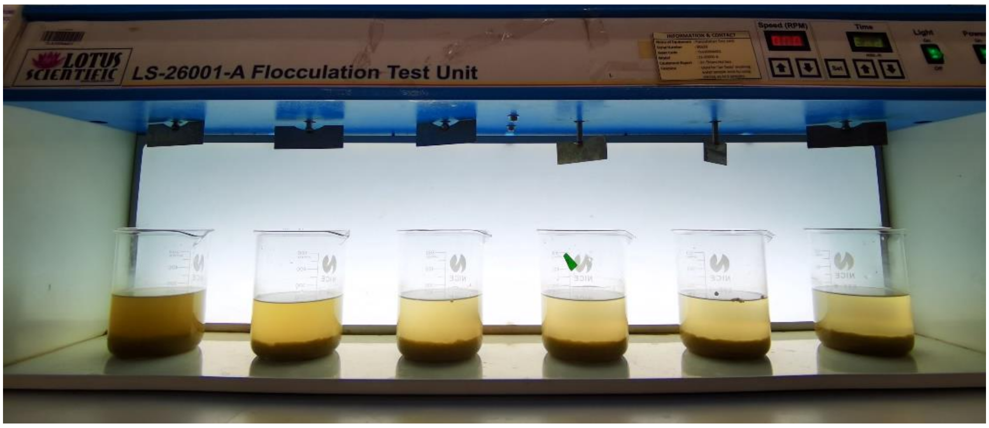

Figure D.2: Effect of *M. oleifera* Seed Powder Dosage on Coagulating Activity (from sequence of left to right: 0, 0.5, 1.0, 1.5, 2.0, 2.5 g/L).

APPENDIX E: FTIR Spectrum

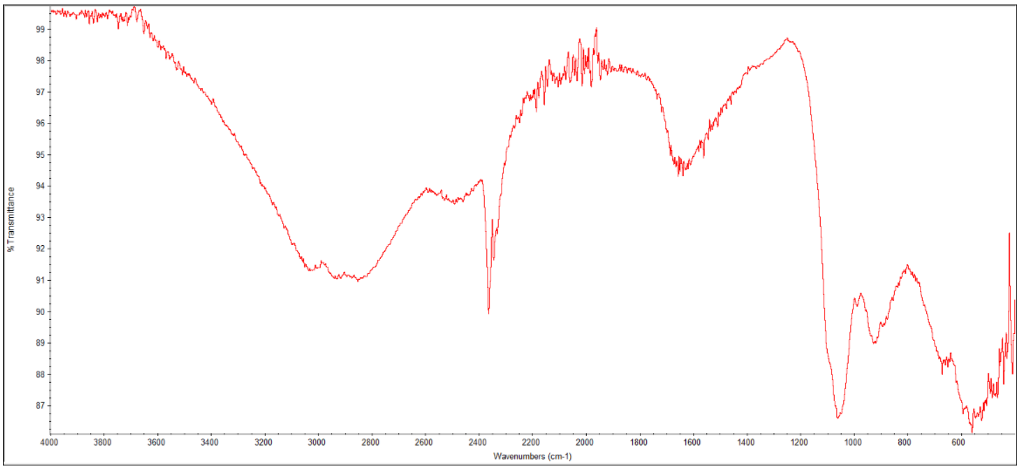

Figure E.1: FTIR Spectrum of Alum.

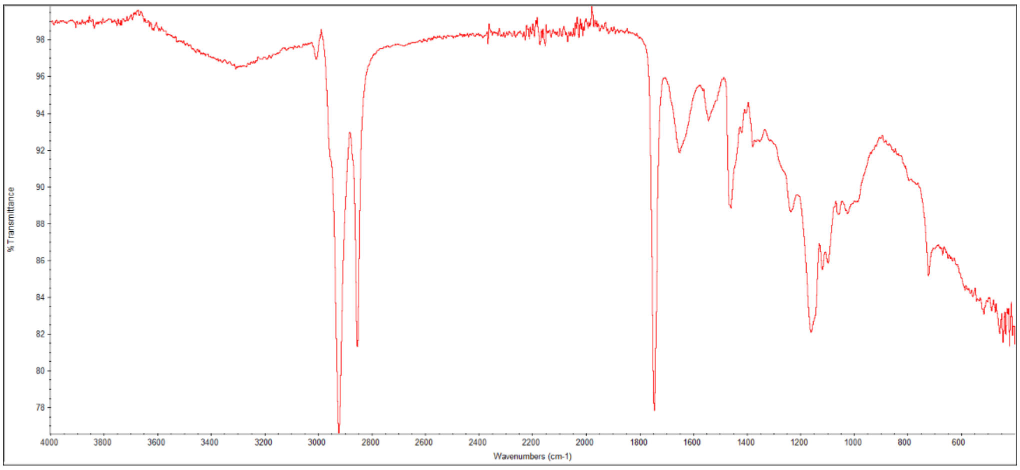

Figure E.2: FTIR Spectrum of *M. oleifera* Seed Powder.

APPENDIX F: TGA Spectrum

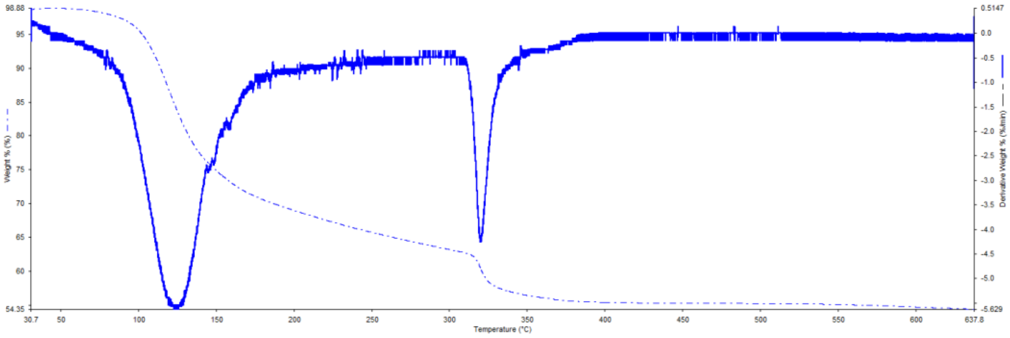

Figure F.1: TGA of Alum.

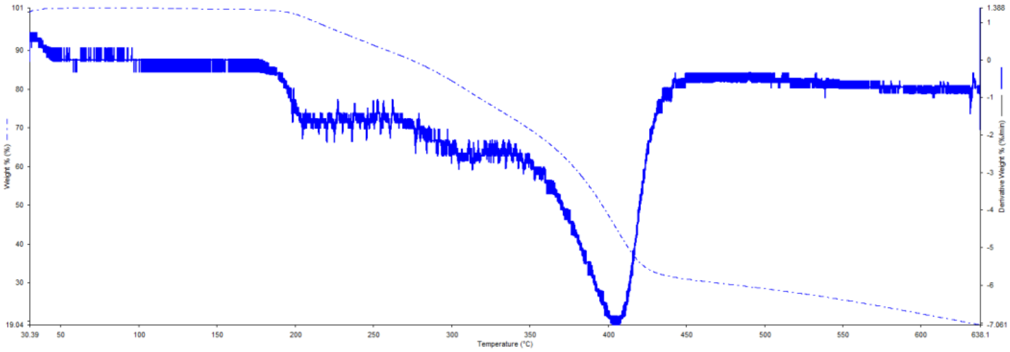

Figure F.2: TGA of *M. oleifera* Seed Powder.

APPENDIX G: EDX Analysis

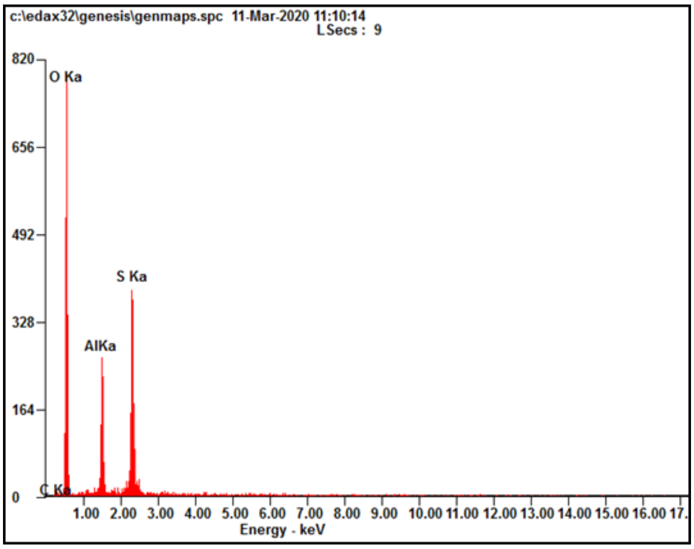

Figure G.1: EDX Mapping of Alum.

Table G.1: Elements in Alum.

Elements	**Wt %**	**At %**
O	63.01	74.00
Al	12.88	08.97
S	21.14	12.39

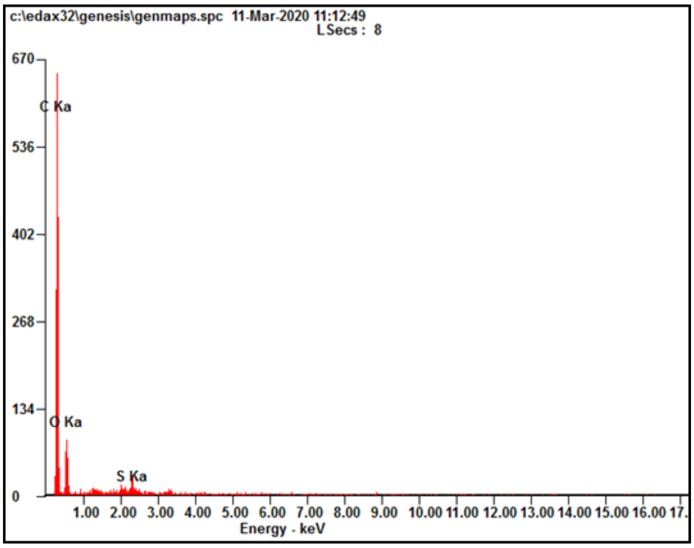

Figure G.2: EDX Mapping of *M. oleifera* Seed Powder.

Table G.2: Elements in *M. oleifera* Seed Powder.

Elements	**Wt %**	**At %**
C	74.68	80.20
O	23.81	19.20