Investigation of *Moringa Oleifera* as Potential Green Coagulant for Removal of Phenol from Aqueous Solution

by

Thanushya Krishnan

Dissertation submitted in partial fulfillment of

the requirements for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

August 2012

Universiti Teknologi PETRONAS,

Bandar Seri Iskandar,

31750 Tronoh,

Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

Investigation of *Moringa Oleifera* as Potential Green Coagulant for Removal of Phenol from Aqueous Solution

by

Thanushya Krishnan

A project dissertation submitted to the

Chemical Engineering Programme

Universiti Teknologi PETRONAS

in partial fulfillment of the requirement for the

BACHELOR OF ENGINEERING (Hons)

(CHEMICAL ENGINEERING)

Approved by,

DR. USAMA MOHAMED NOUR ELDEMERDASH
Senior Lecturer in Chemical Engineering
Universiti Teknologi PETRONAS

(DR USAMA ELDEMERDASH)

Universiti Teknologi PETRONAS

Tronoh, Perak

August 2012

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

THANUSHYA KRISHNAN

ABSTRACT

Highly water-soluble phenols have not satisfactorily been removed by current physical or chemical treatment of water thus a new approach using coagulation with a natural coagulant was investigated in this study. The need for alternative coagulant was crucial because conventional coagulant produce high amount of sludge which is non-biodegradable. The seed powder of a pan tropical tree, *Moringa Oleifera* was tested as a natural coagulant for phenol removal in wastewater treatment. Natural coagulants are more environmental friendly and produce lesser amount of sludge. The use of this coagulant was assisted by coagulants aids like bentonite and lime.

Phenol contaminated wastewater was treated using the enhanced coagulation method. The experiments had been carried out by varying few parameters like dosage of coagulant (*Moringa Oleifera*), pH, temperature and effect of coagulant aids (lime and bentonite). Series of jar test had been conducted with 3 minutes of rapid mixing at 200 rpm, followed by 30 minutes of slow mixing at 45 rpm and 1 hour of settling process. Afterwards, the solution was tested for phenol level, Chemical Oxygen Demand (COD) and amount of sludge produced.

The optimum condition for the process was at 4000ppm of *Moringa Oleifera,* pH 11 at room temperature and lime as coagulant aid at 2000ppm. The phenol removal percentage was 77%, COD reduction percentage was 70% and 0.7324g sludge was produced at the optimum condition.

ACKNOWLEDGMENT

The accomplishment of this project was dependent on many others apart from effort and hard work from me. I would like seize this opportunity to show my gratitude to the people who have been actively involved in assisting me to complete this project efficiently and effectively.

Firstly, I would like to express my utmost gratitude to my supervisor, Dr Usama Eldemerdash for his time and effort. His insightful ideas and constructive comments on my project were valuable and very much appreciated. He has encouraged and guided me along the way. Above all, his constant support was a drive towards the successful completion of the project.

Furthermore, I am very grateful for all the support from the lab technicians during the research and experimental works. The research wouldn't have been accomplished effectively without their guidance and persistent help. They were very kind and resourceful.

Lastly, I am extremely thankful to my family and friends for their tremendous support and encouragement. All of their contributions were a vital key for the success of the project.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

1.1 Background

Today, many countries trying to solve environmental problems originated from industrial wastes. Most of the industries contribute toxic compounds including phenols, to the treatment facilities or directly to receiving bodies, which causes important environmental and technical problems. Phenol is pollutant of high priority concern because of their toxicity even in low concentration and possible accumulation in the environment. Phenol is classified as hazardous pollutants because of their potential harm to human health(Banat, Al-Bashir, Al-Asheh, & Hayajneh, 2000). Phenols are present in waste water of various industries, such as refineries, coking operation, coal processing and manufacture of petrochemicals (Ozbelge, Ozbelge, & Baskaya, 2002).Phenols are widely used for the commercial production of a wide variety of resins including phenolic resins, which are used as construction materials for automobiles and appliances, epoxy resins and adhesives, and polyamide for various applications(Fang & Chan, 1997). Malaysia has strict restrictions on allowable phenol concentration in wastewater discharged to the environment. Thus it is essential for wastewater to be treated for phenol before discharge. At present there are many researchers working on for the most effective method of phenol removal with the least cost and ease of handling. This study focuses on coagulation method because of its ability to handle large amount of wastewater at a continuous process which leads to cost savings and better efficiency.

1.2 Problem Statement

Traditional coagulant and coagulant aid produces significant amount of sludge. High amount of sludge is undesired in coagulation method. Thus a new coagulant is proposed to further enhance the coagulation results. Natural coagulant will be tested as primary coagulant for phenol removal in this research. Natural coagulant has been proven to produce one fifth of sludge produced by chemical coagulants.

Natural coagulant is preferred because it is more eco-friendly and it is biodegradable thus does not impose negative effects to the environment. Biodegradable sludge is given priority due to the fact that it biodegrades after some time without leaving any chemical residue in the environment that might cause harm to the nature.

Application of coagulation in phenol removal requires several parameters to be investigated in detail. The parameters include pH, temperature, dosage of coagulant and also the effect of coagulant aid. Coagulation gives best result only at optimum condition. Even though, coagulation process is frequently employed in industries but very little data is available on the optimum operating condition. Moreover, the optimal condition for different coagulant and contaminant might differ. The optimization of the above mentioned parameters are vital to enhance the coagulation results. Thus this research focuses on finding the optimum condition for highest removal of phenol.

1.3 Objective

This study focuses on the following objectives:

1) To investigate the efficiency of coagulation process as treatment for phenol containing wastewater
2) To synthesis a natural coagulant that produce lesser and biodegradable sludge
3) To study the effect of pH, temperature, coagulant dose and coagulant aid dose (lime or bentonite) for higher phenol removal and Chemical Oxygen Demand (COD) reduction.

1.4 Scope

This research focuses on using coagulation method in phenol removal which is one of the major contaminants from several industries. The scope of this study is using alternative for coagulant and coagulant aid with emphasis on the performance attribute.

1.5 Relevancy of the Project

The research is significant and pertinent because discharging untreated phenol containing wastewater to the environmental may cause detrimental effect to the ecosystem and also to people who are been exposed to it. Phenol has been the priority pollutant in waste water treatment for many years. Many researches have previously done different kinds of treatment for phenol removal including coagulation. Thus this research is to done further to investigate the suitability of a natural coagulant for phenol removal and COD reduction. Natural coagulant is more preferred in this project because of its green nature.

1.6 Feasibility of the Project

It is feasible to complete the project in the given time frame with proper scheduling. The Gantt chart for the project can be referred at page 21.

CHAPTER 2

LITERATURE REVIEW

2.1 Background

Environmental Quality Act 1974 is established to ensure Malaysia's abundant natural resources are protected and preserved. Its main purpose it to prevent, abate and control pollution and further enhancing the quality of the environment in the country. Pollution, as acknowledged in the legislation includes the direct and indirect alteration of quality of the environment or any part of it by means of a positive act or act of commission(Abdullah, 1995).

According to the Environmental Quality (Sewage and Industrial Effluent), the effluents from the wastewater treatment can be categorized into two, which are Standard A and Standard B (refer to appendix 1). Standard A criteria applies only on to the area located upstream of drinking water supply off-takes and meanwhile Standard B applies for inland water. In other words, Standard A will be applicable if the downstream of the river is used for human activities and vice versa for Standard B. Thus this explains why Standard A appears to be much more strict compared to Standard B. According to the table in appendix, allowable phenol concentration in Standard A is 0.001 mg/l while in Standard B is 1.0mg/L.

Currently there are many technologies available for phenol removal. The technologies can be divided to three categories physical, chemical and biological. Physical treatment includes sedimentation, filtration and flotation. Chemical treatment on the other hand includes ion exchange and adsorption. This treatment method is considered more efficient to remove impurities and it is also more expensive. Example of biological treatment is activated sludge treatment, aerobic and anaerobic digestion Due to limitations of each unit operations, coagulation a combined process of physical-chemical method will be used in this study for higher removal of phenol. Before going further on this method, the characteristic of phenol is studied for a better understanding.

2.2 Phenol as Pollutant

2.2.1 Physical and Chemical Properties of Phenol

Phenol is also called as phenic acid or carbolic acid. Phenol was first isolated from coal tar in 1834 by the German chemist Runge. It is an aromatic compound. Its chemical formula is C_6H_5OH and its structure is that of a hydroxyl group (-OH) bonded to a phenyl ring (Figure 1). At ambient temperature and pressure it is a hygroscopic crystalline solid. When pure, solid phenol is white but is mostly colored due to the presence of impurities. Phenol is very soluble in ethyl alcohol, in ether and in several polar solvents, as well as in hydrocarbons such as benzene. In water it has a limited solubility and behaves as weak acid. As a liquid, phenol attacks rubber, coatings, and some forms of plastic. Hot liquid phenol attacks aluminum, magnesium, lead, and zinc metals. It is characterized by a typical pungent sweet, medicinal, or tar-like odour. It is a combustible compound.

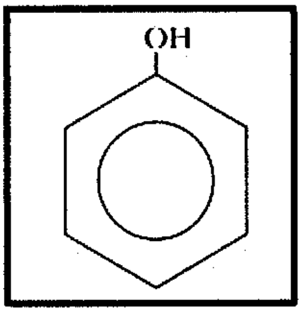


Figure 1: Chemical Structure of phenol

2.2.2 Effects of Phenol on Environment and Human Health

Phenol and its derivatives in industrial effluents pose significant environmental risks due to slow degradability (Ramakrishnan & Namasivayam, 2011). Furthermore, phenol's presence in natural waters can lead to further to formation of substituted compounds during disinfection and oxidation process.

Phenol presence in water may cause damage to the aquatic life and also the ecosystem. This is because phenol is a weak acid, and a high concentration of phenol can cause the water and land to be acidic which will not be suitable environment to live in for the plants and animals.

Exposures to phenol for humans can occur in the workplace, from environmental media, from contaminated drinking water or foodstuffs, or from use of consumer products containing phenol. Short-term effects reported include respiratory irritation, headaches, and burning eyes. Chronic effects of high exposures included weakness, muscle pain, anorexia, weight loss, and fatigue. Effects of long-term low-level exposures included increases in respiratory cancer, heart disease and effects on the immune system

2.2.3 Removal of phenol

Several treatment technologies are available for the reduction of all levels of initial phenols concentration in phenolic wastes. They are classified as solvent extraction for high levels of phenols (above 500 ppm), physico-chemical and biological treatments for intermediate levels of phenols (5–500 ppm), ozonation and carbon adsorption for low levels of phenols.

Many synthetic resins and low-cost natural adsorbents have also been examined for the removal of phenols (Ahmaruzzaman, 2008; Lin & Juang, 2009).However, highly water-soluble phenols have not satisfactorily been removed by current physical or chemical water treatment techniques.

Coagulation process may be a more suitable solution to achieve higher degree of liquid-solid separation with efficient removal of phenol from the wastewaters (Ozbelge et al., 2002).

2.3 Coagulation Process

In industrial waste water different compounds are present like suspended solids, colloidal solids and dissolved solids. Suspended solids have a diameter larger than 10^{-}

^{6}m, colloidal solids between 10^{-9}m and 10^{-6}m and dissolved solids smaller than 10^{-9}m.This material must be removed prior to discharge. Because of the nature of the colloidal suspension these particles will not sediment or be separated with conventional physical methods (such as filtration or settling) unless they are agglomerated through coagulation

Coagulation process is a physicochemical used to separate suspended and colloidal solids from the waste water. Coagulation is the one of the most popular unit operations in water and waste water treatment units. (Zonoozi, Moghaddam, & Arami, 2008). Coagulation is frequently applied to process in the primary purification of industrial waste water and in some cases in secondary and tertiary treatment. (Mondal, 2008).It is the main component of wastewater treatment units and the applications include wastewater treatment, recycling and removal of pollutants (Gupta, Saleh, Nayak, & Agarwal, 2012)

Coagulation, flocculation and clarification, followed by rapid gravity sand filtration, are the key steps in conventional waste water treatment systems. Conventional treatment (coagulation, sedimentation and sand filtration), as illustrated in Figure 2, has several distinct stages.

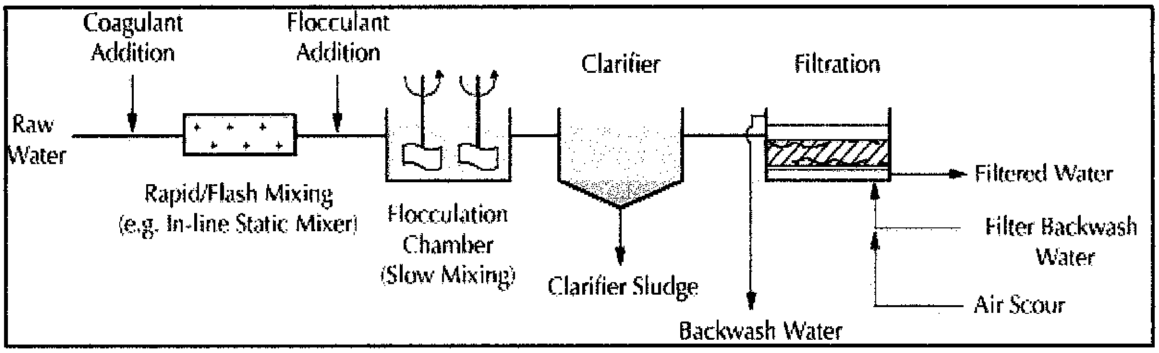


Figure 2: Conventional Coagulation, Sedimentation and Filtration

The coagulation process includes the dosing of a coagulant in water, resulting in the destabilization of water. It occurs in several steps intended to overcome the forces that stabilizes the suspended particles, allowing particle collusion and growth of floc.

The first step in the coagulation process is destabilizing the particle charges in the water. Coagulant of opposite charges added to neutralize the negative charge on the dispersed non-settlable solids. Once the charge is neutralizes, the smaller particles are capable of sticking together to form a slightly larger particles. Rapid mixing after coagulant dosing is an important design parameter. It ensures the coagulant is properly dispersed in the water and promotes particle collision that is needed to achieve good coagulation.

Depending on the type of colloidal suspension that should undergo coagulation different destabilization mechanisms can be employed such as:

- Repression of the double layer
- Neutralization of colloid charge by adsorption of counter ions on the surface of the colloid
- Bridging of colloidal particles via polymer addition
- Entrapment of colloidal particles by sweeping floc

The addition of certain chemicals into the raw water causes particles to destabilize and allows agglomeration and floc formation to occur. The general terms for chemicals used for this purpose are:

- coagulants, which assist the destabilization of particles (particularly colloidal sizes)
- flocculants (also known as flocculant aids or coagulant aids), which assist in the joining and enmeshing of the particles together

2.3.1 Types of Coagulants

Figure 3 shows how the chemical coagulants works, these colloids are negatively loaded so they repel each other and they cannot make contact; it's the reason for the use of coagulants

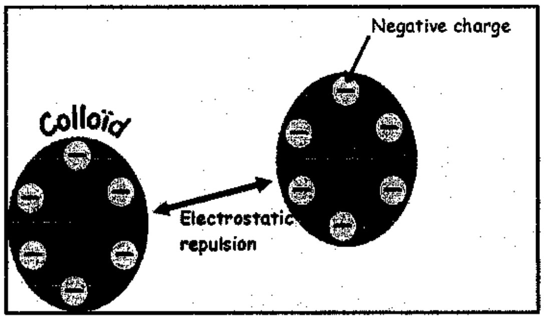


Figure 3: How Coagulants Works

There is vast selection of coagulant to choose from organic or inorganic types.

Coagulation is mainly induced by inorganic metal salts. The most common additives are aluminium sulphate (generally known as alum), ferric chloride and ferric sulphate (Renault, Sancey, Badot, & Crini, 2009). Using these chemical substances may have several environmental consequences such as:

i. an increase in metal concentration in water (which may have human health implications)
ii. production of large volumes of (toxic) sludge
iii. dispersion of acrylamide oligomers which may also be a health hazard

For these reasons, alternative coagulants have been considered for environmental applications (Bolto& Gregory, 2007).

Natural or organic coagulants are more environmental friendly. Even the sludge produced is biodegradable thus there aren't any toxic sludge problem. Organic polymers can be plant bases polymers like starch, guar gum, tannin and *Moringa Oleifera* or animal based like chitosan. (Verma, Dash, &Bhunia).

Moringa Oleifera as Coagulant

For this study organic coagulant *Moringa Oleifera* seed is chosen because it is environmentally friendly and biodegradable unlike some inorganics coagulants like alum and polyaluminium chloride (PAC) that cause hazards to humans and the environment.

Moringa Oleifera Lam (*M. oleifera*) is a multipurpose tree native to Northern India that now grows widely throughout the tropics even in Malaysia. It is among the 14 species of trees that belong to the genus *Moringaceae* (syns. *Moringa pterygosperma, Gaertn.*) It is a fast growing, aesthetically pleasing small tree adapted to arid, sandy conditions. The species is characterized by its long, drumstick shaped pods that contain its seeds. Virtually every part of the tree is beneficial in some way; within the pods are possibly the best part of the tree which is the seed.(Ashmawy, Moussa, Ghoneim, & Tammam, 2012). The seeds contain up to 40% by weight of quality edible oil (greater than 80% unsaturated fatty acid content) (Mohammed, Lai, Muhammad, Long, & Ghazali, 2003). The seeds yield proteins capable of acting as effective coagulants in water and wastewater treatment. The active components of the *M. Oleifera* seed has been proven to be effective coagulant at removing suspended material, generate reduced sludge volumes, soften hard waters and act as effective adsorber of cadmium(Bhuptawat, Folkard, & Chaudhari, 2007). The volume of sludge produced by extract of *M. Oleifera* is 5 times less than that produced by alum (Katayon et al., 2006).However this technology has not been adapted to any treatment plant yet.

The solution of *Moringa Oleifera* acts as cationic polyelectrolyte during treatment (Sutherland, Folkard, Mtawali, & Grant, 1994).This novel coagulant is competitive with other traditional coagulants, such as alum or tannin-derived products. (J Beltrán-Heredia, Sánchez-Martín, Muñoz-Serrano, & Peres, 2012)

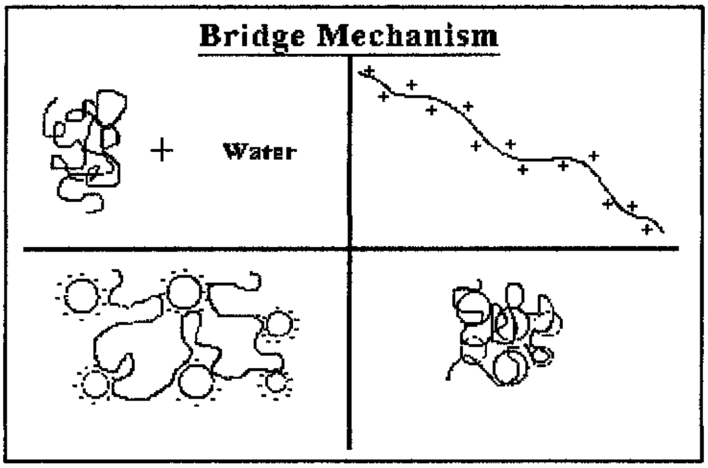
Figure 4: ***Moringa Oleifera***

Characterization studies on *Moringa Oleifera* were done using Energy-dispersive X-ray spectroscopy (EDX), Field emission scanning electron microscope (FESEM), Fourier Transform Infrared Spectroscopy, FTIR and BET. The results are attached in the appendix.

2.3.2 Coagulant Aid Mechanisms and Types

Coagulants aids add density to slow settling flocs as well as toughness to the flocs so that they will not break during the mixing and the settling process. Aggregation of suspended solids with coagulant aid mainly by either bridging or patch mechanism.

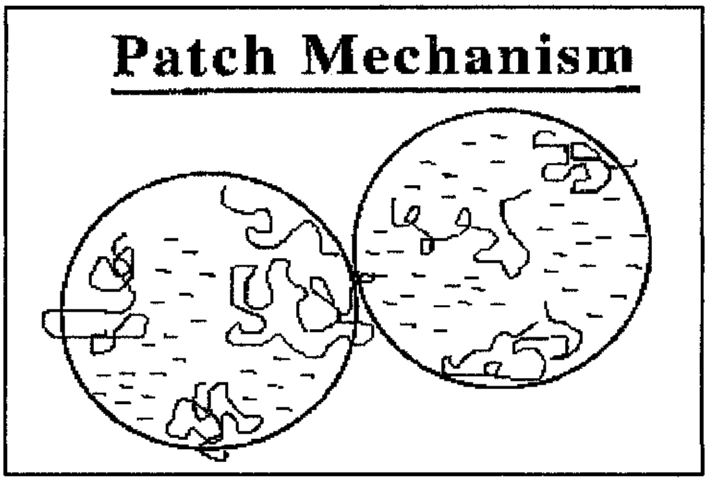
Destabilization by bridging occurs when segments of a polymer chain adsorb more than one particle, thereby linking the particles together. The coagulant aid will adsorb on the surface in a series of loops (segments extending in the solution) and trains (segments adsorbed on the surface).



(Sharma, Dhuldhoya, & Merchant, 2006)

Figure 5: Bridge Mechanism

Patch mechanism involves uneven distribution of charges resulting from the adsorption of discrete patches on the surface. A highly cationic coagulant aid is adsorbed on the negative particle surface in a flat conformation.



(Sharma et al., 2006)

Figure 6: Patch Mechanism

Several coagulant aids like bentonite and lime will be experimented and the results will be compared to choose the best type.

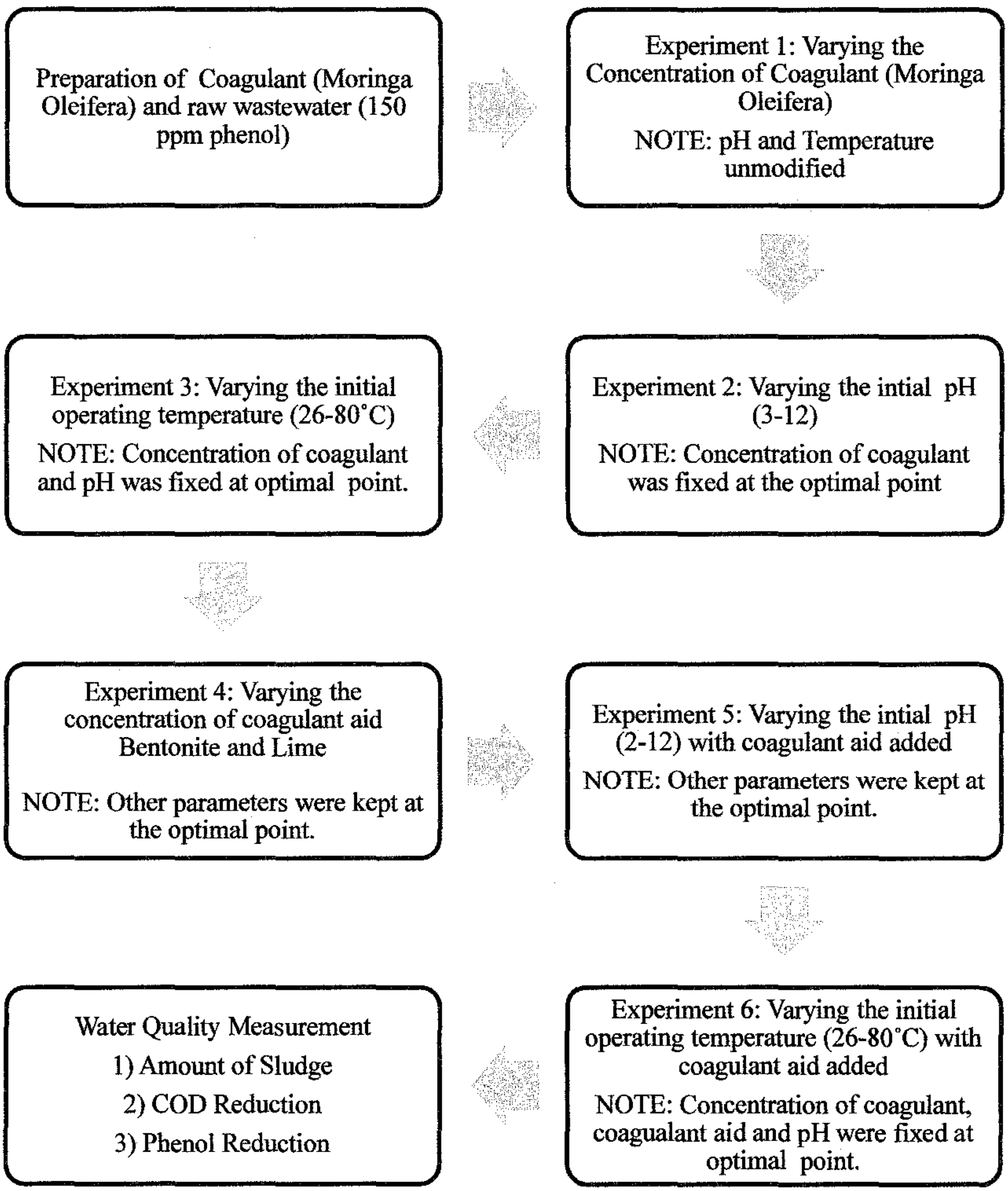
Bentonite consists essentially of clay minerals of the smectite (montmorillonite) group and has a wide range of industrial applications including clarification of edible and mineral oils, paints, cosmetics, and pharmaceuticals(Christidis, 1998). The abundance of bentonite in most continents of the world and its low cost make it a strong candidate as a coagulant for the removal of many pollutants from wastewaters. Research studies have shown its ability to bind and remove pathogenic viruses, pesticides, herbicides, and other toxins(Hartman & Martin, 1984; Lipson & Stotzky, 1985). Other studies were carried out to investigate the possible use of natural bentonite as an effective adsorbent for the removal of rare earth elements and heavy metals from aqueous solutions(Chegrouche, Mellah, & Telmoune, 1997; Mellah & Chegrouche, 1997). The aim of this work was to investigate experimentally, the potential of natural bentonite to act as coagulant aid to remove phenol in aqueous solution.

The use of lime in wastewater treatment was introduced long ago. Lime, as a general term, includes quicklime (CaO), hydrated lime [$Ca(OH)_2$], and dolomitic lime as defined by the National Lime Association, NLA, 1999(Semerjian & Ayoub, 2003). Historically, lime has been used in treating wastewaters for a multitude of reasons. It has the inherent advantage of making no contribution to an increase in salinity, as is the case when alum or iron salts are employed (Dziubek & Kowal, 1986). Moreover, apart from its positive economic impact in terms of chemical cost and energy requirements, lime effectively acts as a precipitant for phosphates, many trace metals, and bacteria, and as a coagulant for the removal of suspended and colloidal material in municipal wastewater. In this research work, lime ($CaOH_2$) will be tested as coagulant aid for the removal of phenol.

CHAPTER 3

METHODOLOGY

3.1 Summary of Project Works



3.2 Experiment Procedure

The methodology of this project is mostly experiment that was conducted using the jar test apparatus.

The coagulation and floc formation process was simulated. The jar test apparatus consists of six paddle stirrers and 6 jars filled with sample. Refer figure 7 below. To each jar a certain dose of coagulant was added during rapid mixing and coagulant aid was added during slow mixing. After rapid mixing at 200 rpm for 3 minutes, a slow stirring at 45 rpm for 30 minutes and a settling period of one hour, the sample was measured for Chemical Oxygen Demand (COD), phenol contaminant level and amount of sludge produced.

COD was measured using HACH Digital Reactor (DR 5000). Phenol level was measured using UV-Vis Spectrophotometer. After settling period, Total Suspended Solid (TSS) apparatus was used to collect the sludge. The sludge was then dried in the oven at 105°C for 24 hours to remove the moisture content before being weighed.

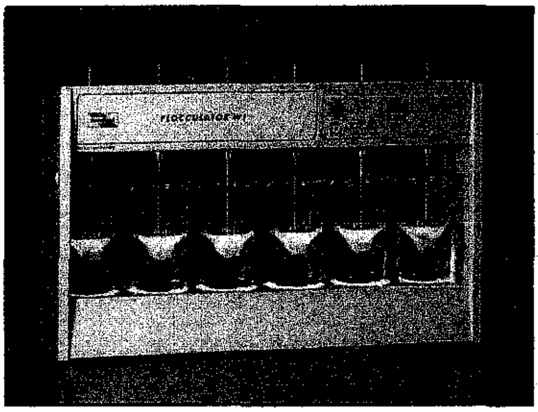


Figure 7: Jar Test Apparatus

There were several parameters that were manipulated in this experiment such as:

1) Optimum Coagulant Dose *Moringa Oleifera* (1000-6000ppm)
2) Optimum pH (pH3-12)

3) Temperature effect (26°C -80°C)
4) Optimum Coagulant aid dose, Lime and Bentonite (250-2500ppm)
5) Optimum pH with coagulant aid Lime and Bentonite (pH 2-12)
6) Optimum temperature with coagulant aid Lime and Bentonite (26°C -80°C)

3.2.1 Coagulant Preparation

Moringa Oleifera was obtained from Ipoh market and the tree is planted in Perak. The seeds were removed and dried. The seed wings and coat were removed manually, good quality seeds were then selected, and the kernel was grounded to a fine powder. Refer figure below.

Figure 8: *M.Oleifera* Seeds

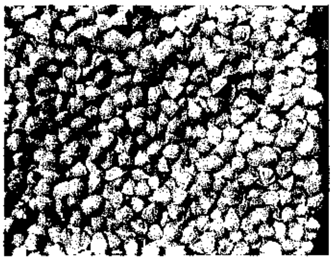


Figure 9: Seed Kernel after Wings and Coat Removed

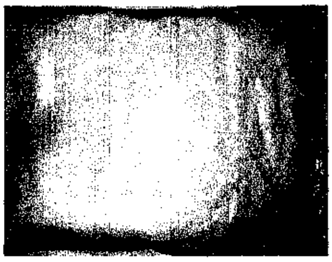


Figure 10: Seed Kernel Powder

1.2 grams of the seed powder was added to 300ml tap water and it was stirred for 1 hour to extract the active ingredient. The resulting suspension was filtered through a filter paper and the filtrates give a stock solution of approximate 4000 mg/l. The mass of seed powder varies according to the dosage that needs to be added. The solution had a pH of 6.5. The stock solution was prepared fresh for use as and when needed, since deterioration sets in if stored for more than two days at room temperature.

3.2.2 Raw Wastewater Preparation

Wastewater had to be prepared before conducting the experiment. According to literature, the standard phenol contaminant level in wastewater is in the range of 50ppm to 350 ppm. Throughout the experiment, 150ppm concentration of phenol was chosen to be the initial of concentration of wastewater. Wastewater was prepared by mixing 140 ml of 1070 ppm phenol with 1L of distilled water to produce 150ppm phenol. This is because the main focus in this study is only on phenol removal in wastewater.

3.2.3 Optimum Coagulant Dose

To study the effect of coagulant dosage on phenol removal by dosing different amounts of *Moringa Oleifera* seed solution into the wastewater sample. The sample at room temperature, initial pH 6.5 and with different dosage of coagulant was stirred in jar test at 200 rpm for 3minutes, then 30 minutes at 45 rpm and settling time for an hour. The sample water after test was tested for COD reduction, phenol removal percentage and amount of sludge produced. The coagulant dosage with the highest COD reduction and highest phenol removal percentage was chosen as optimum dosage. The following equations will be used:

$$COD\,\text{Re}moval\,Rate = \left(1 - \frac{C}{C_o}\right) \times 100$$

Where :

C = final COD value

C_o = Initial COD value

$$\text{Phenol Re}moval\,Rate = \left(1 - \frac{C_{phenolFinal}}{C_{phenolInitial}}\right) \times 100$$

Where :

$C_{phenolFinal}$ = Final Phenol Concentration

$C_{phenolInitial}$ = Initial Phenol Concentration

3.2.4 Optimum pH

pH plays an important role in the coagulation process. Thus pH must be controlled to establish optimum condition for coagulation. The pH was varied using 1M hydrochloric acid and 1M sodium hydroxide. The pH that was tested was3, 5, 7, 9, 11 and 12. The experiment was repeated at room temperature with optimum coagulant dose. The pH with most COD reduction and highest phenol removal percentage was chosen as optimum pH.

3.2.5 Temperature Effect

Temperature control is vital in this experiment. Temperature effects the floc formation. Temperature was varied 30°C, 40°C, 50 °C, 60°C, 70°C and 80°C at optimum coagulant dose and optimum pH. The temperature with most COD reduction and highest phenol removal percentage was chosen as optimum temperature.

3.2.6 Optimum Coagulant aid dosage

Different coagulant aids like bentonite and lime was experimented. Each coagulant aid was repeated using different dosage while keeping optimum coagulant dose, optimum pH, and optimum temperature constant. The coagulant aid with the most COD reduction and highest phenol removal percentage was chosen as the best coagulant aid at the optimum dose. The experiment was repeated for optimum pH and optimum temperature for optimum dosage of coagulant aid (Lime and Bentonite) with optimum coagulant dosage.

3.3 Chemicals

1) Moringa Oleifera
2) 1 M Sodium Hydroxide, Merck
3) 1 M Hydrochloric Acid, Merck
4) 250-2500 ppm Bentonite, R&M Chemicals
5) 250-2500 ppm Lime, R&M Chemicals
6) 1070 ppm Phenol, Merck

3.4 Equipment & Tools

1) Jar test Apparatus, FC6S-VELP (Scientifica)

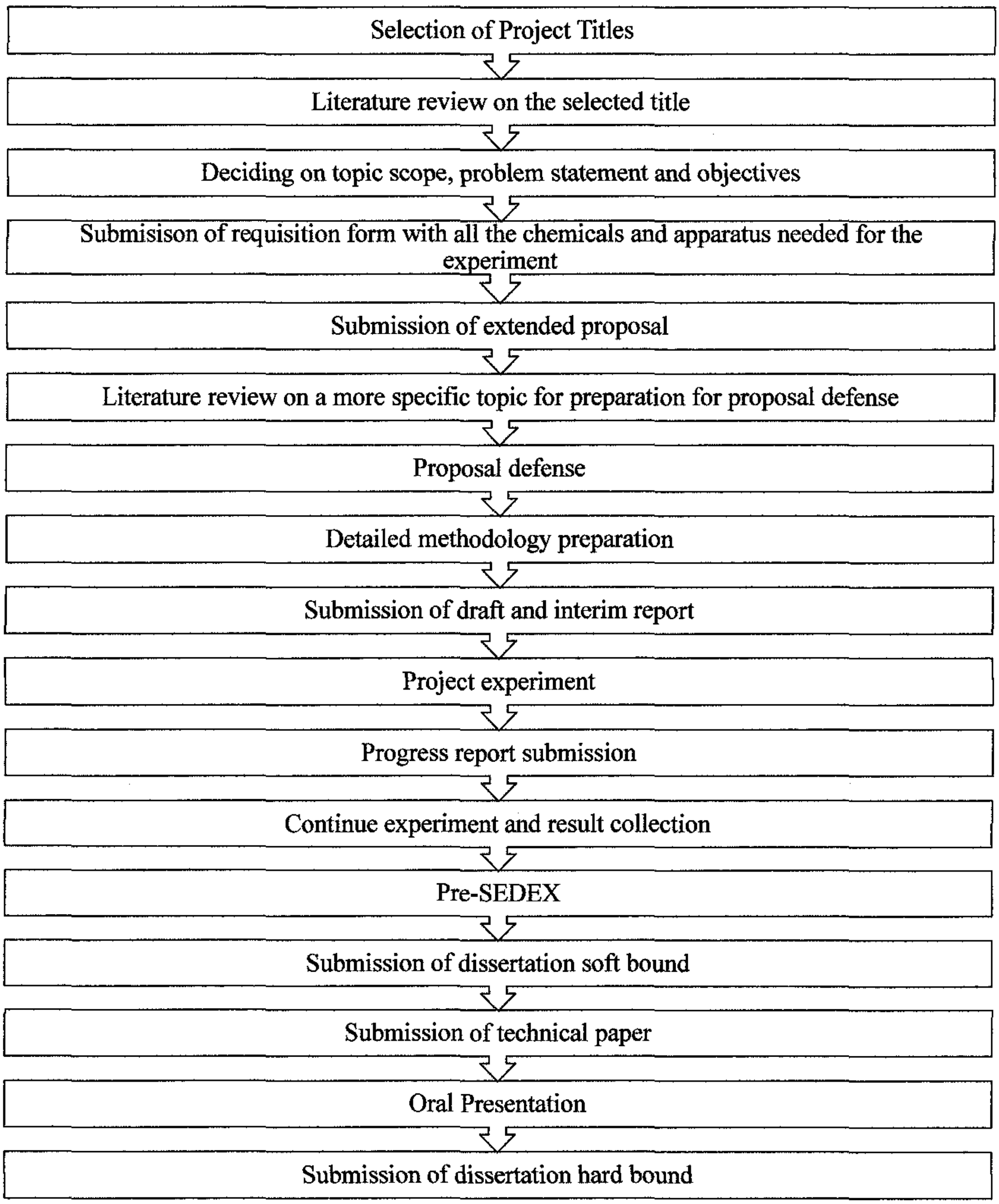
2) Total Suspended Solid Apparatus (TSS)
3) Whatman 41 Filter Paper 150mm
4) Oven
5) UV-Vis Spectrophotometer
6) HACH Digital Reactor(DR 5000) Spectrophotometer for high range COD (0-1500ppm)
7) Thermometer
8) pH meter, Eutech Std. Bench pH Meter Model 510
9) Heater
10) Stirrer

3.5 Key Milestone

Project Activity	Date
Completion of Preparation of Coagulant	30th May 2012
Optimum Coagulant, pH & Temperature	10th July 2012
Experiment with coagulant aid Lime and bentonite	17th July 2012
Optimum pH for coagulant and coagulant aid (Lime and Bentonite)	24th July 2012
Optimum temperature for coagulant and coagulant aid (Lime and Bentonite)	29th July 2012
Optimum condition for best performance	31st July 2012

3.6 Project Flow Chart

Project Flow Chart



3.7 Gantt Chart

Semester	2012 (Jan)														2012 (May)														
Activities	1	2	3	4	5	6	7	8	9	10	11	12	13	14	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Literature Review																													
Deciding topic scope, problem statement and objectives																													
Submission of requisition form																													
Submission of extended Proposal																													
Continue reading on the topic																													
Proposal Defense																													
Preparation for experiment																													
Submission interim report draft																													
Submission of interim report																													
Project Experiment starts																													
Submission of progress report																													
Experiment continues																													
Pre-EDX																													
Submission of draft report																													
Submission of dissertation soft bound																													
Submision of technical paper																													
Oral Presentation																													
Submission of Project Dissertation Hard Bound																													

CHAPTER 4

RESULTS & DISCUSSION

The research focuses on the optimum condition for the highest phenol removal percentage as phenol is the pollutant of main concern. In this study, coagulation method was tested on phenol contaminated wastewater. Natural coagulant was synthesized and experimented as potential green coagulant for phenol removal. Phenol contaminated wastewater is not visible to the eye because phenol is colorless but it gives off a distinct stinging smell. However, phenol concentration can be measured using UV-Vis Spectrophotometer. It measures the absorbance of phenol molecules in the wastewater. After each of the experiment the sample was tested for phenol removal percentage. The initial concentration of phenol throughout the research was 150ppm.

Chemical oxygen demand, COD is a vital test for assessing the quality of effluents and wastewater prior to discharge. The COD test is commonly used to directly measure the amount of organic pollutants found in wastewater. The initial COD measurement for 150ppm phenol in wastewater is 250ppm. The regulation for discharge in Standard A and Standard B is 50 and 100 ppm respectively. Thus for each experiment the reduction in COD was also tested. A sample of waste water containing organic material is placed in contact with a very strong inorganic oxidant, a mixture of dichromate and sulphuric acid with silver sulphate as a catalyst. The temperature is increased to the point of ebullition of the mixture which is at 150°C, resulting in an increase of the oxidation rate. After two hours (the standard duration of the test) oxidation of the organic compounds is virtually complete. Then the sample is tested in the HACH Digital Reactor, DR-5000 reactor for the COD level.

High production of sludge is undesirable in coagulation method. This is due to the difficulty in disposal of large amount of sludge. Throughout the research the amount of sludge produced was also measured.

The optimum condition is when phenol and COD removal percentage was the highest. So for each experiment to determine the best condition for dosage, pH or temperature the result on phenol and COD reduction was given the highest priority.

4.1 Determination of Optimum Coagulant Dosage

In this research, *Moringa Oleifera* was tested as a coagulant for removal of phenol in wastewater. Different dosage of *Moringa Oleifera* (1000-6000ppm) was added into the wastewater sample to determine the optimum dosage. The pH was unmodified so it was around 6.5 and experiment was conducted in room temperature. The dosage which gives highest phenol removal percentage and the most COD reduction will be chosen as the optimum dosage.

The results are tabulated below:

Table 1: Effect of *Moringa Oleifera* Dosage at pH 6.5 & Room Temperature

Moringa Oleifera **Concentration (ppm)**	**Phenol Concentration (ppm)**		**Phenol Removal Percentage (%)**	**COD (ppm)**		**COD Removal Percentage (%)**	**Amount of sludge (g)**
	Initial	**Final**		**Initial**	**Final**		
1000	150	148.3534483	0.930773706	250	248	0.8	0.48
2000	150	137.4051724	8.318789994	250	230	8	0.46
3000	150	136.887931	8.667830134	250	220	12	0.54
4000	150	107.5775862	28.44677138	250	189	24.4	0.59
5000	150	126.5431034	15.64863293	250	201	19.6	0.55
6000	150	147.1465517	1.745200698	250	241	3.6	0.48

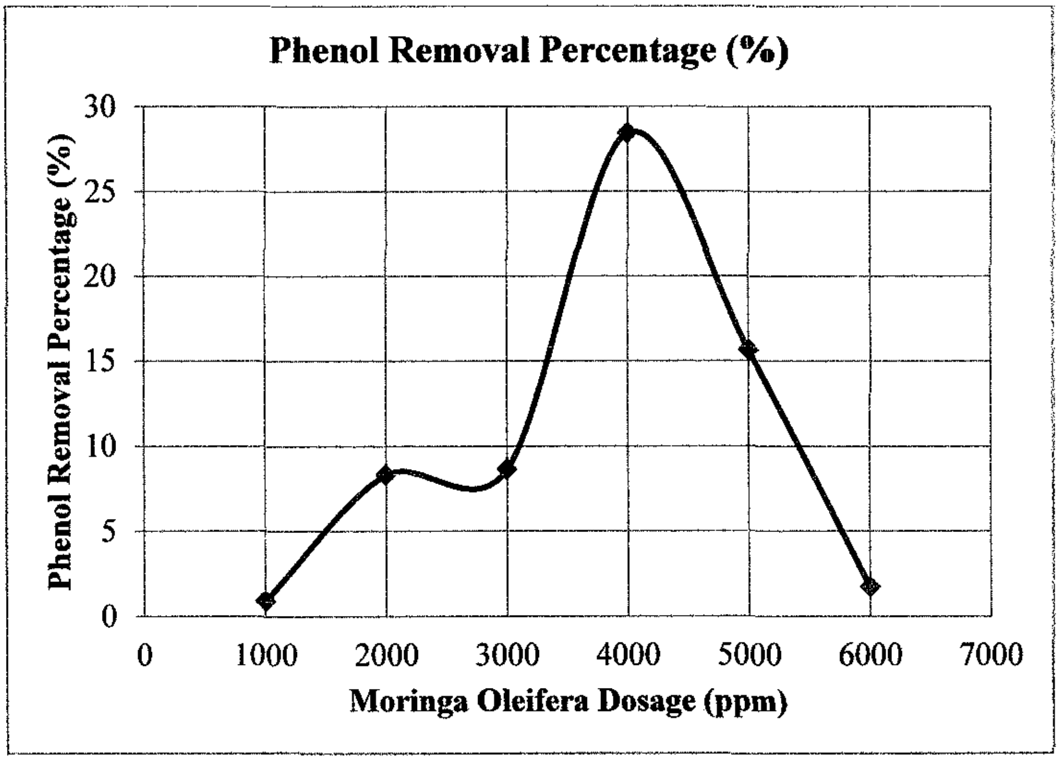


Figure 9: Phenol Removal Percentage (%) vs. *Moringa Oleifera* dosage (ppm)

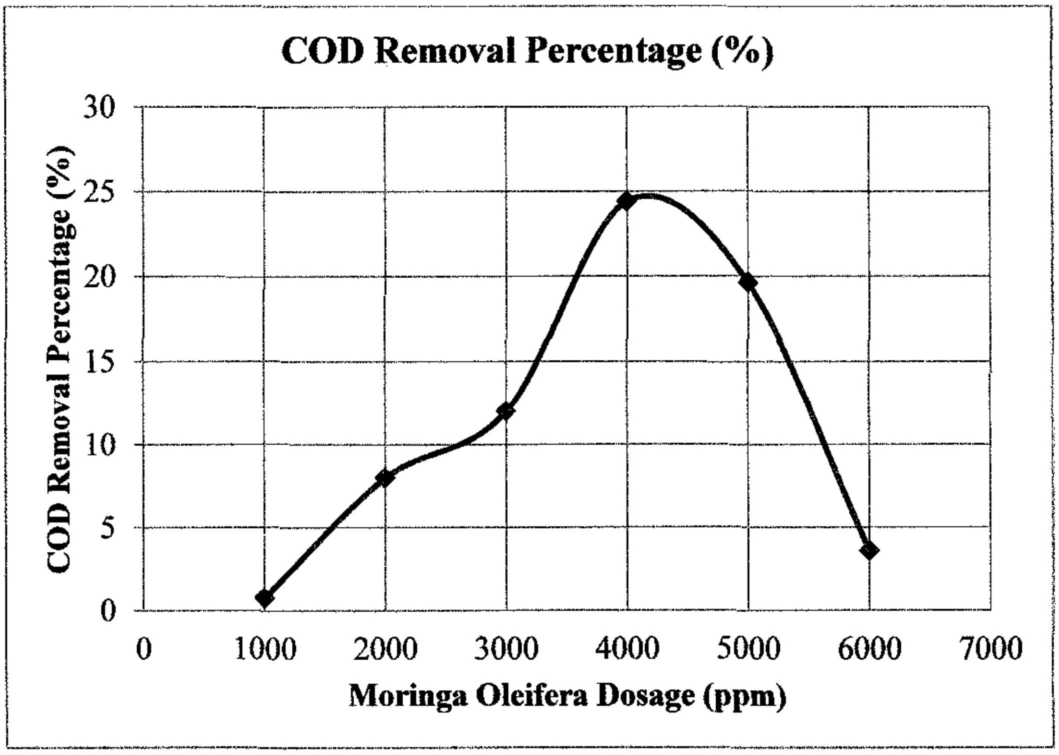


Figure 10: COD Removal Percentage (%) vs. *Moringa Oleifera* dosage (ppm)

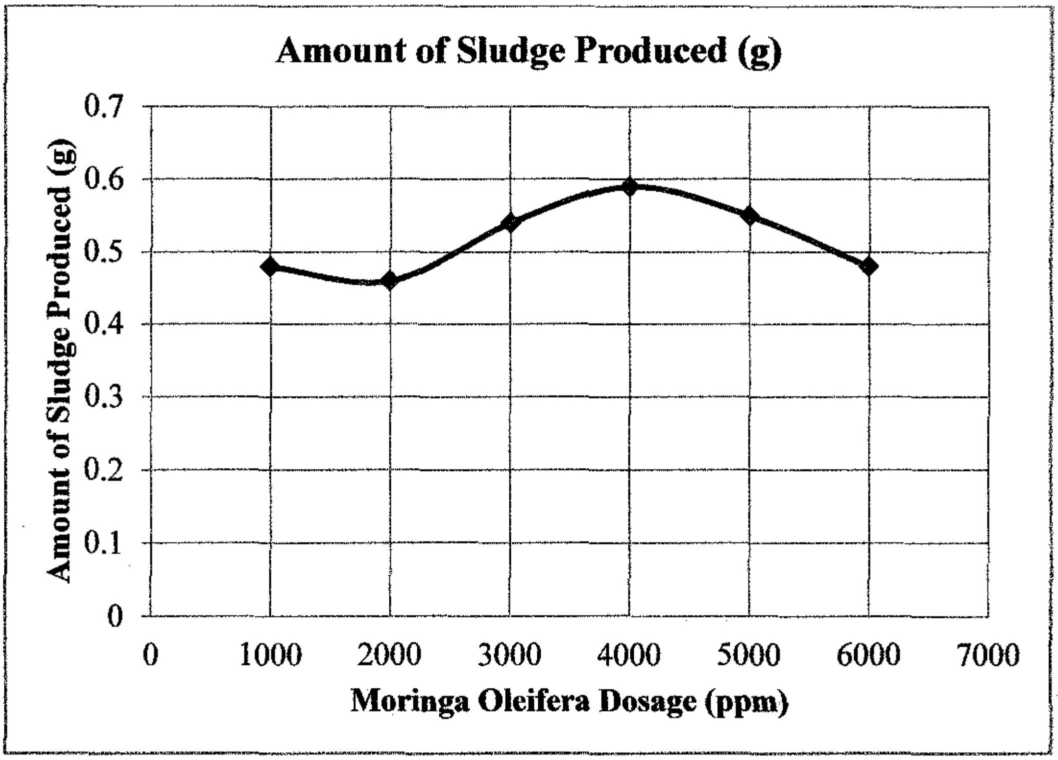


Figure 11: Amount of Sludge Produced (g) vs. *Moringa Oleifera* dosage (ppm)

The *Moringa Oleifera* seed kernels contain significant quantities of several water molecules and soluble proteins in solution carry a positive charge. Proteins are considered to act in a manner similar to synthesis of positively charged polymer coagulants. When added to raw wastewater to bind the colloids predominantly are negatively charged particles that make it rough murky waters. Under adequate agitation these particles then grow in size to form flakes, which can be solved by gravity or be removed by filtration. Coagulation activity is present in shelled seeds but only after the pods are dry. The active agents in coagulation with *Moringa* are water soluble cationic proteins. In previous studies, they found that the shelled *Moringa* seeds contain 55% carbon, 8.5% hydrogen and 6% nitrogen. The remaining 31% consists of oxygen and trace elements. The shelled *Moringa* seeds contain about 37% proteins, , whereas there is close to 35% of lipids in the shelled seeds, carbohydrates (as oligosaccharides) represent 5% of the shelled seeds. The carbohydrates content is very low whereas the high lipids content explains why *Moringa* seeds can be used as a source of vegetable oil. The lipids are not soluble in water (Ndabigengesere, Narasiah, & Talbot, 1995).

According to EDX results obtained in *Moringa* seed powder, 63.11 wt % is $CaCO_3$, it is the main element. The dissociation equation of this element is as below:

$$CaCO3\ (s) <=> Ca^{2+}\ (aq) + CO_3^{2-}\ (aq)$$

Phenol on the hand is also soluble in the water and the equation is as below:

$$C_6H_5OH\ (aq) + H_2O <=> C_6H_5O^-(aq) + H^+(aq)$$

The positively charged ions in *Moringa Oleifera* which mostly contains Ca^{2+}aids in coagulation as it will agglomerate with negative charged colloids in phenolic wastewater which is $C_6H_5O^-$. This causes the flocs to become bigger and eventually sediment at the bottom. This is what speculated that is happening during the coagulation process.

In coagulation process, coagulant dosage is one of the critical parameter in determining the effectiveness of the process. Basically, insufficient dosage or overdosing would result in the poor performance in flocculation. Apart from desire to achieve a better performance on phenol removal, the additional goal was also to achieve the minimum optimal dosage to minimize the cost on coagulant as well as to reduce the amount of sludge produced. High dosage of coagulant leads to more cost on purchase of coagulant. It is desired for the coagulation process to be cost efficient. Large production of sludge contributes to the handling and disposal problems afterward. This might also lead to increase in cost. Based on research done by others it is stated that the wastewater should be dosed at its optimal point so that the destabilization process of the colloidal particles can be effectively done and subsequently flocculate with each other and settle down at the bottom. But nevertheless, if the coagulant dosage goes beyond the optimum point, there is a possibility that the reverse process or restabilization phenomenon will take place. This theory is agreed by Hassan et.al. (Hassan, Ariffin, Tan, & Noor, 2009). They confirm that if the coagulant dosage is beyond the optimum point, the poor performance occur due to fact that the excess of coagulant have been absorbed onto the colloidal surface. As a result, the formation of inter-particle bridging is unable to be established due to the unavailability of site surface. Furthermore, the colloidal particles which have been surrounded by the coagulant will be positively charged and may repel each other. As the dosage increases, the electrical conductivity of the final solution will increase too (Malakootian &Fatehizadeh).

As mentioned, the optimum dosage will be the dosage of *Moringa Oleifera* with the highest removal percentage of phenol and COD. In Figure 11 and 12 at 4000ppm dosage of coagulant, phenol and COD reduction was the highest which is 28.4% and 24.4% respectively. Although the amount of sludge produced is highest at 4000ppm but the amount is still manageable, it is only 0.59g. Moreover 4000ppm is the minimum optimum dosage so the cost on coagulant will be the least. Thus the optimum *Moringa Oleifera* dosage is 4000ppm at unmodified pH 6.5 and at room temperature.

4.2 Determination of Optimum pH

Because coagulation process is strongly pH dependent, the pH effect in coagulation unit was investigated next. The experiment focuses on determining the optimum pH for the coagulation process with *Moringa Oleifera.* The pH was varied from pH 3-12. To make the solution more acidic less than pH 7, drops of 1M of hydrochloric acid were added to achieve the desired pH. To make the solution alkaline droplets of 1M sodium hydroxide was added till desired pH was achieved. This experiment was conducted at room temperature with optimum *Moringa Oleifera* dosage 4000ppm.

The results of effect of pH are tabulated below:

Table 2: Effect of pH at Room Temperature and 4000ppm *Moringa Oleifera*

pH	Phenol Concentration (ppm)		Phenol Removal Percentage (%)	COD (ppm)		COD Removal Percentage (%)	Amount of sludge (g)
	Initial	Final		Initial	Final		
3	150	147.8362069	1.279813845	250	240	4	0.5368
5	150	139.387931	6.980802792	250	239	4.4	0.5511
7	150	135.4224138	9.656777196	250	234	6.4	0.5905
9	150	126.6293103	15.59045957	250	224	10.4	0.6304
11	150	99.81896552	33.68237347	250	156	37.6	0.652
12	150	128.4396552	14.36881908	250	210	16	0.6184

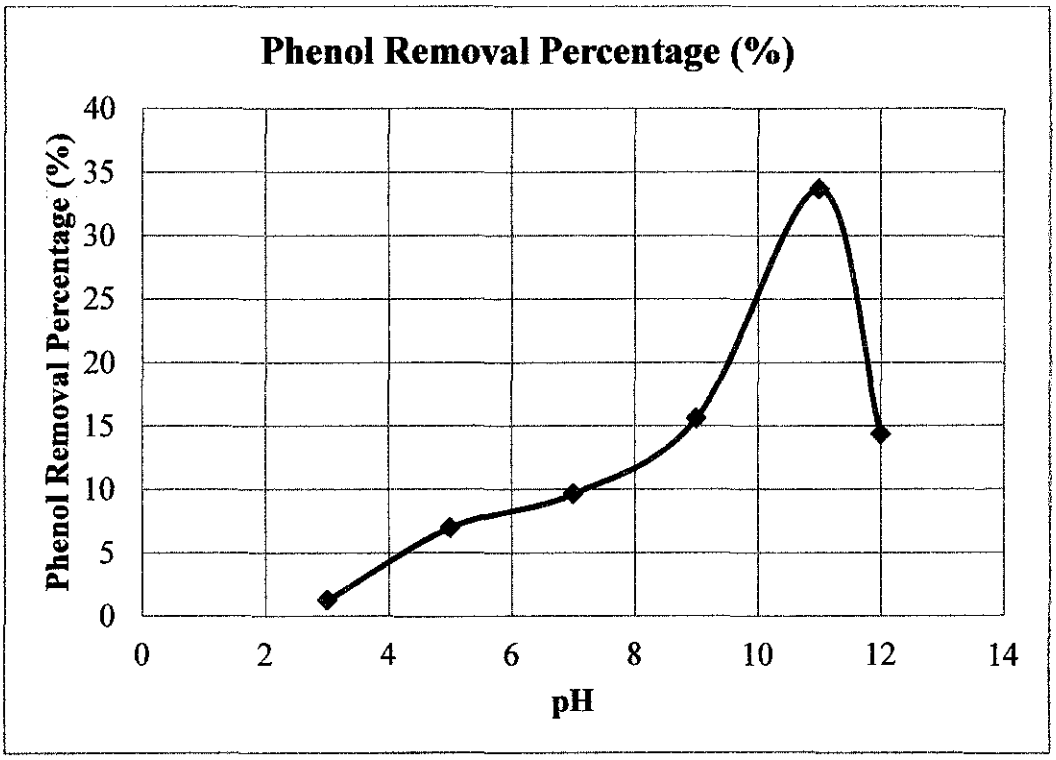


Figure 12: Phenol Removal Percentage (%) vs. pH

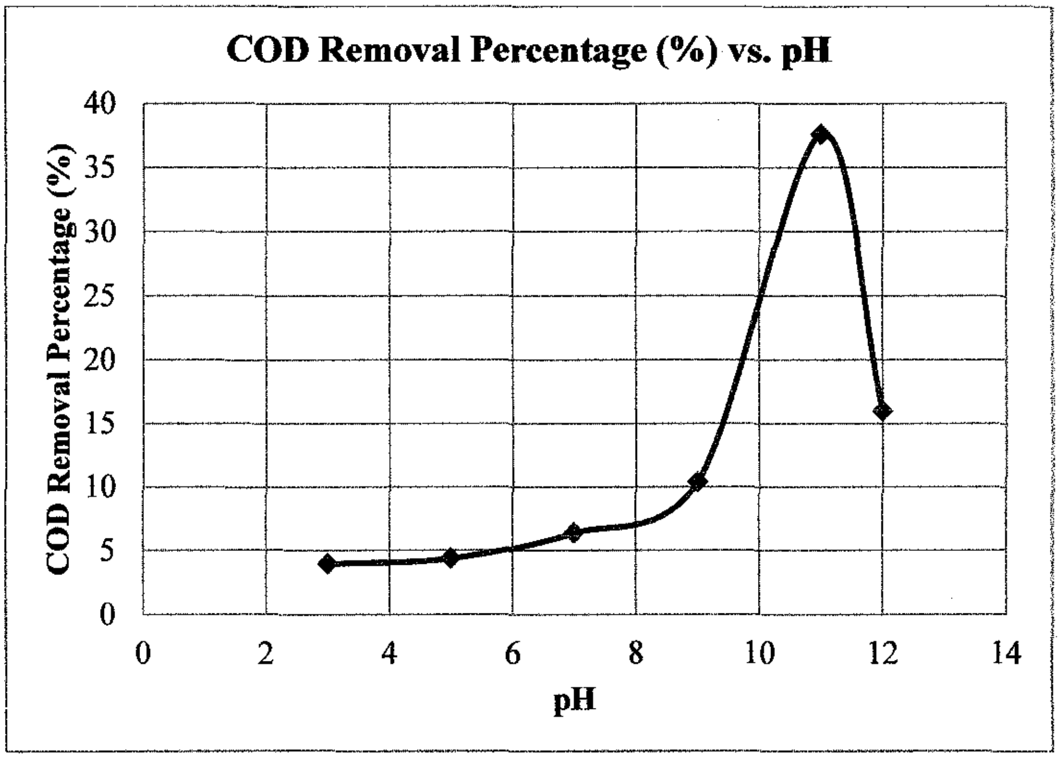


Figure 13: COD Removal Percentage (%) vs. pH

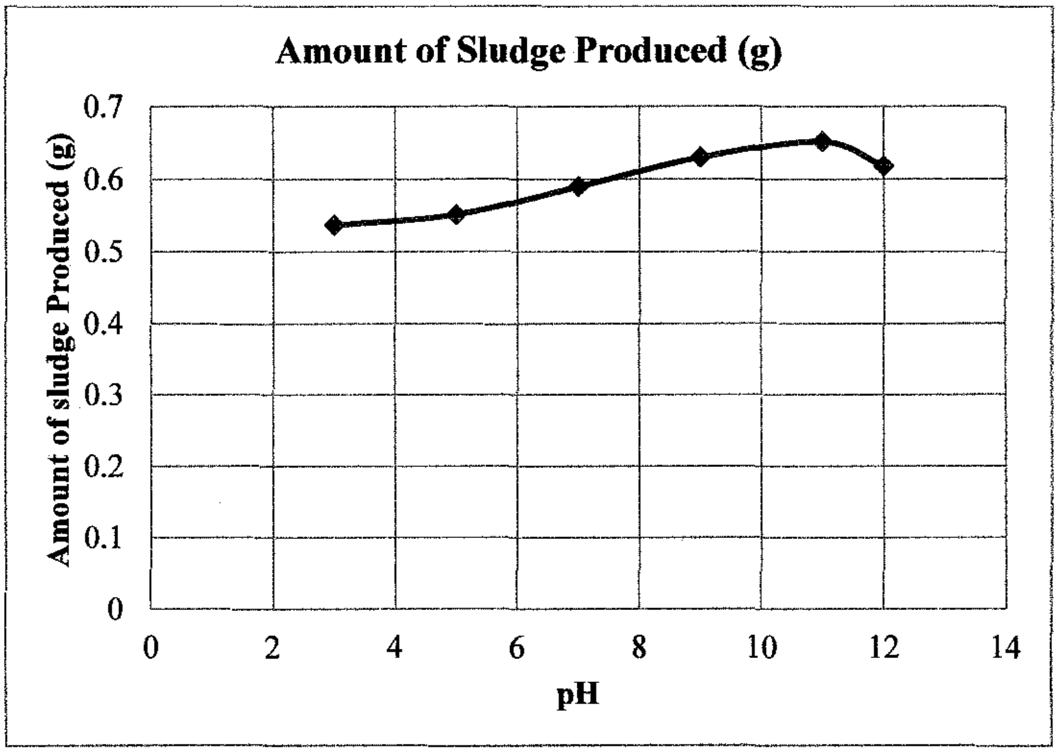


Figure 14: Amount of Sludge Produced (g) vs. pH

Variation of pH plays a major role in coagulation process. The pH will not only affect the surface charge of coagulants, but also the affects the stabilization of suspension (Hassan et al., 2009). Besides, the solubility of *Moringa Oleifera* in aqueous solution is influenced by pH value. Therefore, the study of pH was essential to determine the optimum pH condition of the treatment. The stability of colloidal agglomeration depends on the forces that hold the particles in a suspension form. Even more, at the optimal pH, the coagulation process is more efficient since the pH is adjusted to the iso-electric point, which enables these colloids to stick together (Klimiuk, Filipkowska, & Korzeniowska, 1999).

As stated earlier the optimum pH will be the pH with the highest removal percentage of phenol and COD. In Figure 14 and 15 at pH 11, phenol and COD reduction was the highest which is 33.7% and 37.6% respectively. Although the amount of sludge produced is highest at pH 11 but the amount is still manageable, it is only 0.652g. At lower pH, the efficiency of process was low this can be proved by observing Figure 14, 15 and 16. In Figure 14 and 15, at acidic condition the phenol removal percentage and COD reduction was the least which leads to lesser production of sludge because the colloids doesn't agglomerate and sediment. This might be perhaps due to the fact acidic environment is not a suitable condition for *Moringa* as coagulant. Thus the optimum pH is pH 11 at room temperature with 4000ppm of *Moringa Oleifera* dosage as primary coagulant.

4.3 Determination of Optimum Temperature

The next experiment focuses on determining the optimum temperature for the coagulation process with *Moringa Oleifera.* The temperature was varied from 26°C-80°C. This experiment was conducted at optimum pH, pH 11 and with optimum *Moringa Oleifera* dosage 4000ppm.

The results of effect of temperature are tabulated below:

Table 3: Effect of Temperature at pH 11 with 4000ppm *Moringa Oleifera*

Temperature (°C)	Phenol Concentration (ppm)		Phenol Removal Percentage (%)	COD (ppm)		COD Removal Percentage (%)	Amount of sludge (g)
	Initial	Final		Initial	Final		
26	150	99.81896552	33.68237347	250	156	37.6	0.652
30	150	101.5431034	32.51890634	250	158	36.8	0.65
40	150	134.3017241	10.41303083	250	238	4.8	0.5911
50	150	142.0603448	5.177428738	250	240	4	0.5305
60	150	147.2327586	1.687027341	250	244	2.4	0.4804
70	150	148.0948276	1.105293775	250	245	2	0.4525
80	150	150	151.5431034	-1.221640489	250	246	1.6	0.3984

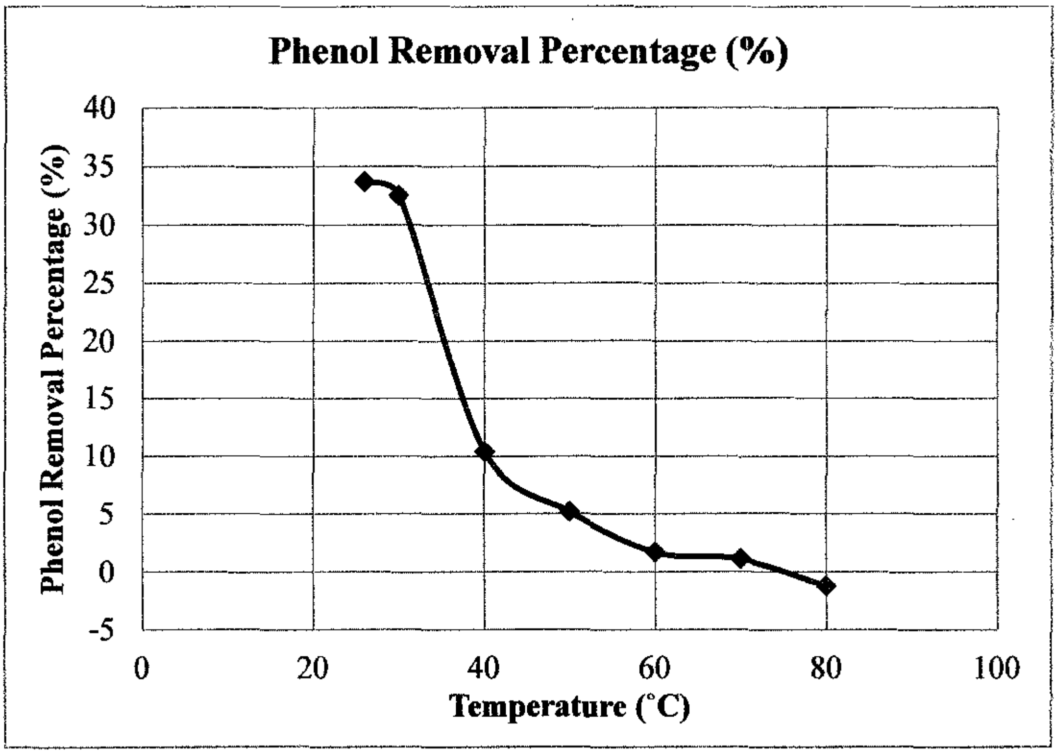


Figure 15: Phenol Removal Percentage (%) vs. Temperature (°C)

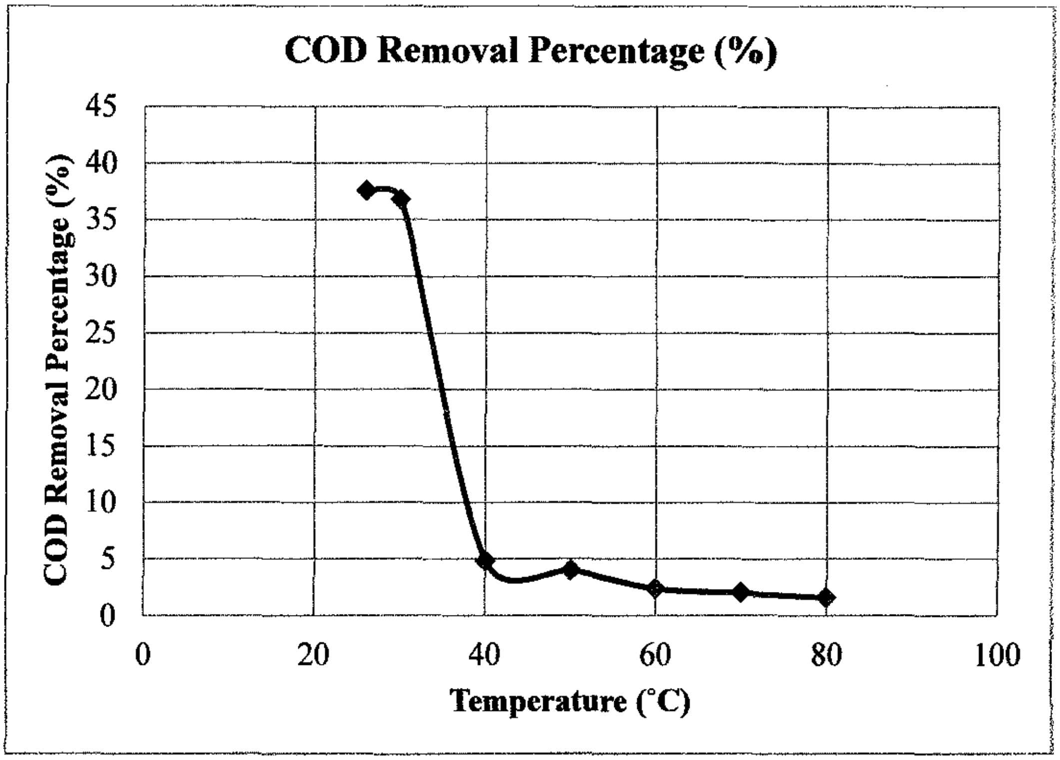


Figure 16: COD Removal Percentage (%) vs. Temperature (°C)

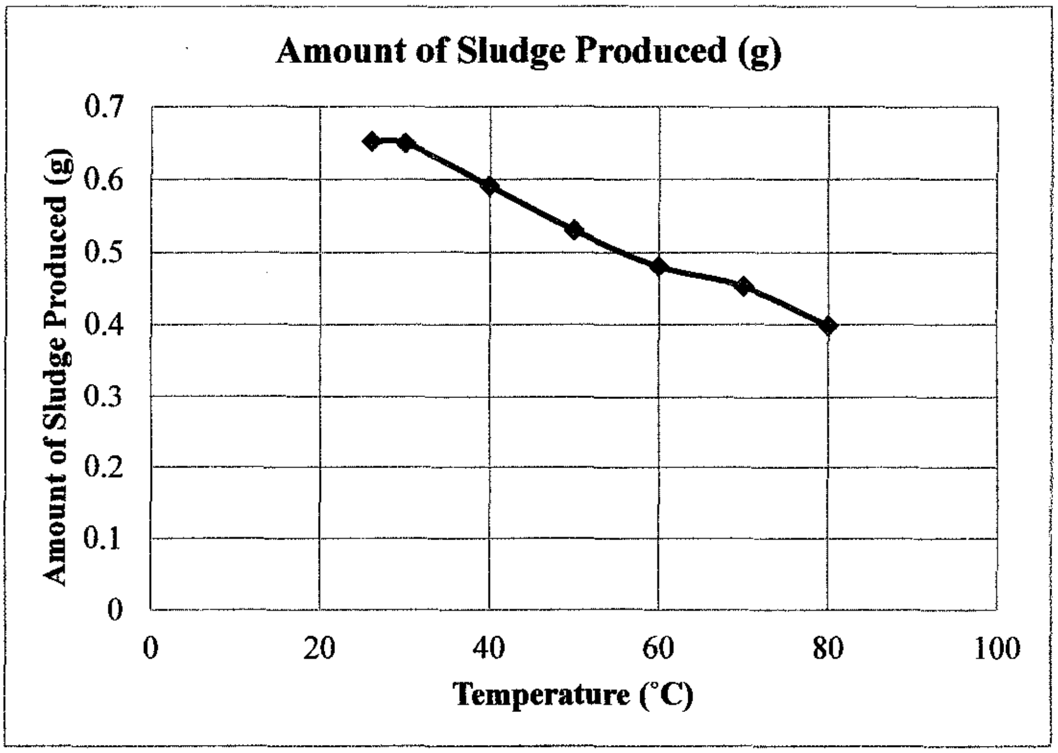


Figure 17: Amount of Sludge Produced (g) vs. Temperature (°C)

From Figure 17 and 18, it shows that by increasing temperature from 26°C to 80°C, both the phenol removal percentage and COD reduction percentage kept on decreasing. From observation done during the experiment, the amount sludge forming at the bottom of the beaker was decreasing as the temperature increases. Therefore, it can be assumed that that at higher temperature, there is a possibility that the formed precipitate re-dissolves in the solution. This statement can be strongly supported by looking at Figure 19 which shows the amount of sludge produced at different temperatures. At higher temperature, the amount of sludge produced kept decreasing.

The temperature effect may be due to the destabilization of charge on the suspended solids in wastewater. Once the temperature of wastewater is increased with the addition of the coagulant, the floc particles size was smaller compare to the size of floc particles at the room temperature of 26°C. This might be due to the particle transport processes or particle collision rates and through the effect on viscosity (concentration) in wastewater. The floc strength becomes weaker with the increase of temperature and the 'macrofloc' can be easily broken (Othman, Bhatia, & Ahmad, 2008). Thus the optimum temperature is room temperature, 26°C at pH 11 with 4000ppm of *Moringa Oleifera* dosage as primary coagulant.

4.4 Determination of Best Coagulant Aid and Optimum Coagulant Aid Dosage

After obtaining the optimum condition with primary coagulant *Moringa Oleifera*, the next experiments focused on the best condition with the addition of coagulant aid. Coagulant aid was added during the slow mixing to add density to flocs and speed up the coagulation process by making the flocs agglomerate and settle faster. Coagulant aid also enhances the toughness and settleability of the floc during the experimental works. Therefore, throughout the study the choice of coagulant aid was bentonite and lime. The purpose of choosing these coagulant aids are because they are easily available and has been proven to be excellent coagulant aids.

4.4.1 Lime as Coagulant Aid

In this experiment, lime was tested as a coagulant aid for removal of phenol in wastewater. Different dosage of lime was added into the wastewater sample to determine the optimum dosage. The pH of solution was pH11 and experiment was conducted in room temperature. The dosage which gives highest phenol removal percentage and the most COD reduction will be chosen as the optimum dosage.

Table 4: Effect of Lime Dosage at ph11, Room Temperature with *Moringa Oleifera* 4000ppm

Lime, $CaOH_2$ Concentration (ppm)	Phenol Concentration (ppm)		Phenol Removal Percentage (%)	COD (ppm)		COD Removal Percentage (%)	Amount of sludge (g)
	Initial	Final		Initial	Final		
250	150	105.8534483	29.61023851	250	200	20	0.4182
500	150	100.9396552	32.92611984	250	214	14.4	0.5371
750	150	92.6637931	38.51076207	250	205	18	0.5303
1000	150	83.78448276	44.5026178	250	135	46	0.6252
1500	150	70.59482759	53.40314136	250	105	58	0.6245
2000	150	35.1637931	77.31239092	250	74	70.4	0.7324
2500	150	65.59482759	56.77719604	250	96	61.6	0.7365

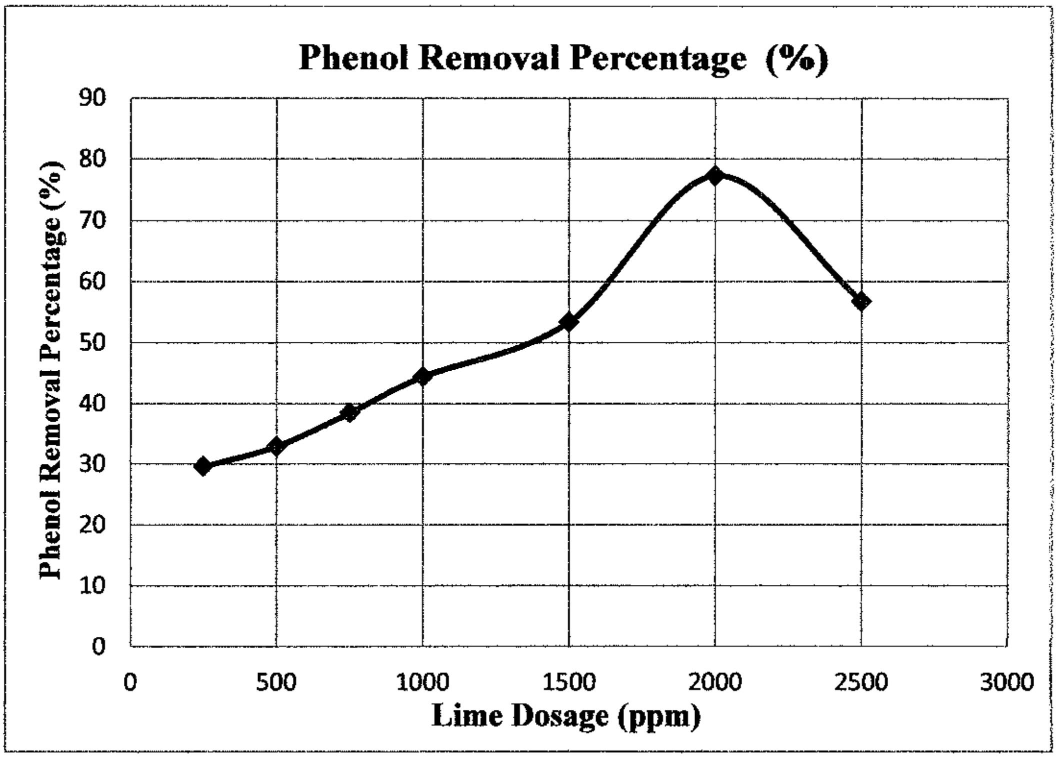


Figure 18: Phenol Removal Percentage (%) vs. Lime Dosage (ppm)

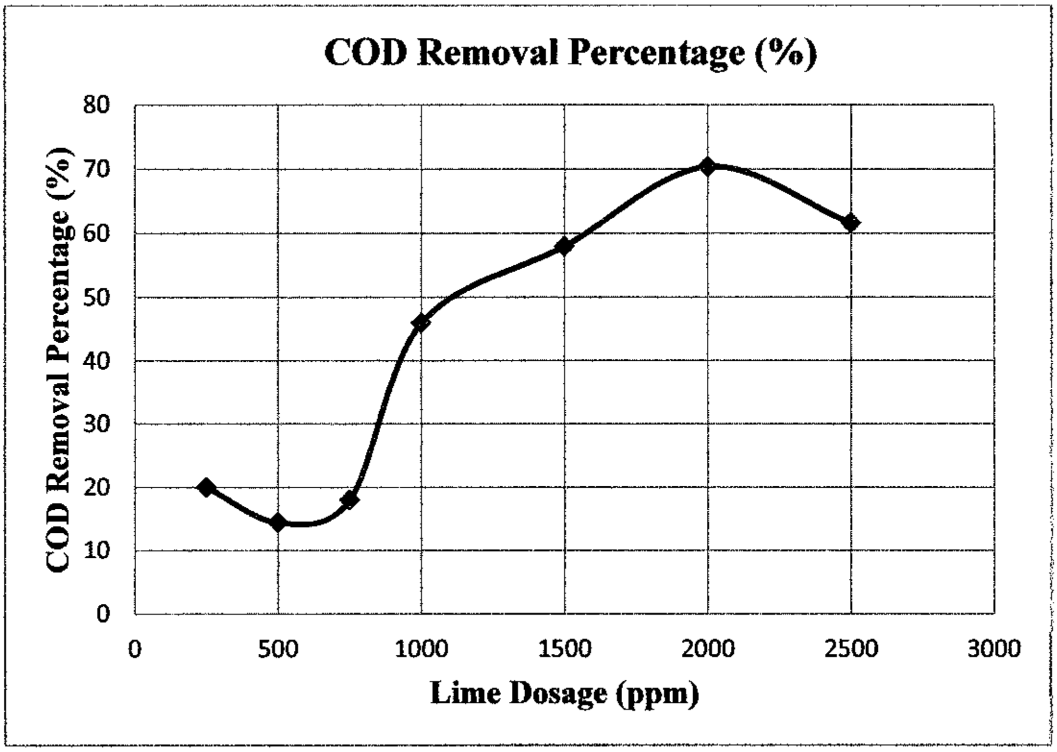


Figure 19: COD Removal Percentage (%) vs. Lime Dosage (ppm)

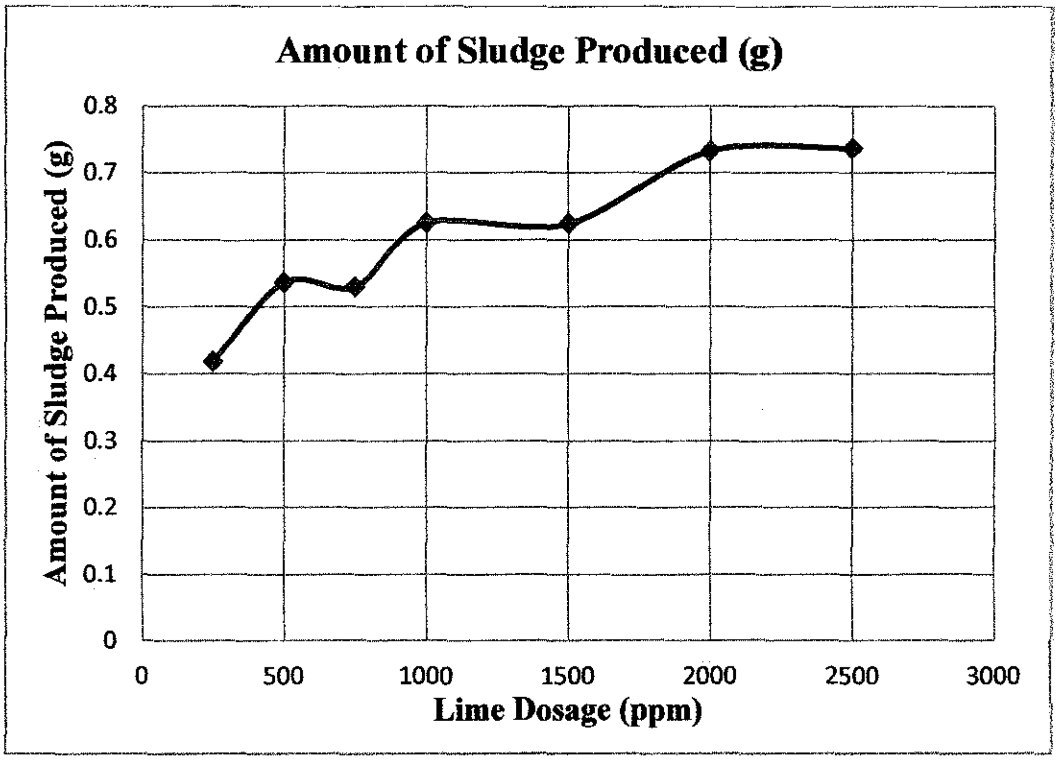


Figure 20: Amount of Sludge Produced (g) vs. Lime Dosage (ppm)

In figure 20 and 21, it's clearly shown that at 2000ppm of lime as coagulant aid the phenol removal percentage and COD reduction percentage was the highest. Thus the optimum coagulant aid lime dosage is 2000ppm at pH11, at room temperature with *Moringa Oleifera* as primary coagulant at 4000ppm.

4.4.2 Bentonite as Coagulant Aid

In this experiment, bentonite was tested as a coagulant aid for removal of phenol in wastewater. Different dosage of bentonite was added into the wastewater sample to determine the optimum dosage. The pH of the solution was pH11 and experiment was conducted in room temperature. The dosage which gives highest phenol removal percentage and most COD reduction will be chosen as the optimum dosage.

Table 5: Effect of Bentonite Dosage at ph11 & Room Temperature with *Moringa Oleifera* 4000ppm

Bentonite Concentration (ppm)	Phenol Concentration (ppm)		Phenol Removal Percentage (%)	COD (ppm)		COD Removal Percentage (%)	Amount of sludge (g)
	Initial	Final		Initial	Final		
250	150	99.81896552	33.68237347	250	156	37.6	0.652
500	150	108.2672414	27.98138453	250	169	32.4	0.539
750	150	118.8706897	20.82606166	250	223	10.8	0.546
1000	150	124.2155172	17.21931355	250	236	5.6	0.5355
1500	150	126.4568966	15.70680628	250	249	0.4	0.5429
2000	150	128.6982759	14.19429901	250	270	-8	0.7318
2500	150	129.9051724	13.37987202	250	289	-15.6	0.874

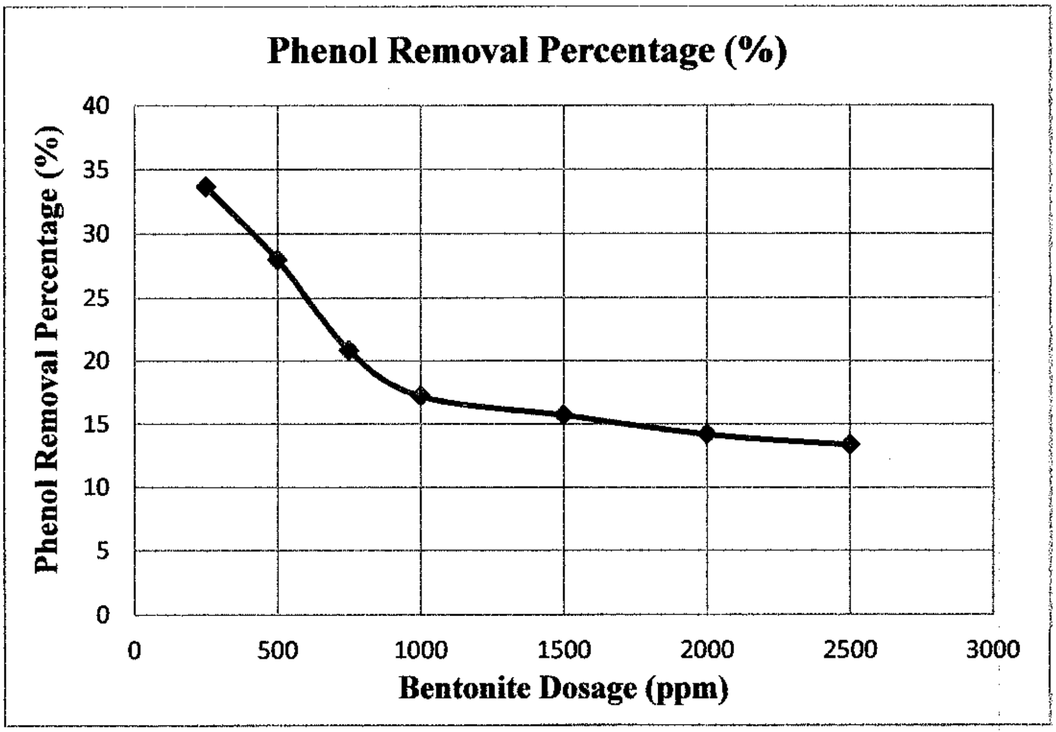


Figure 21: Phenol Removal Percentage (%) vs. Bentonite Dosage (ppm)

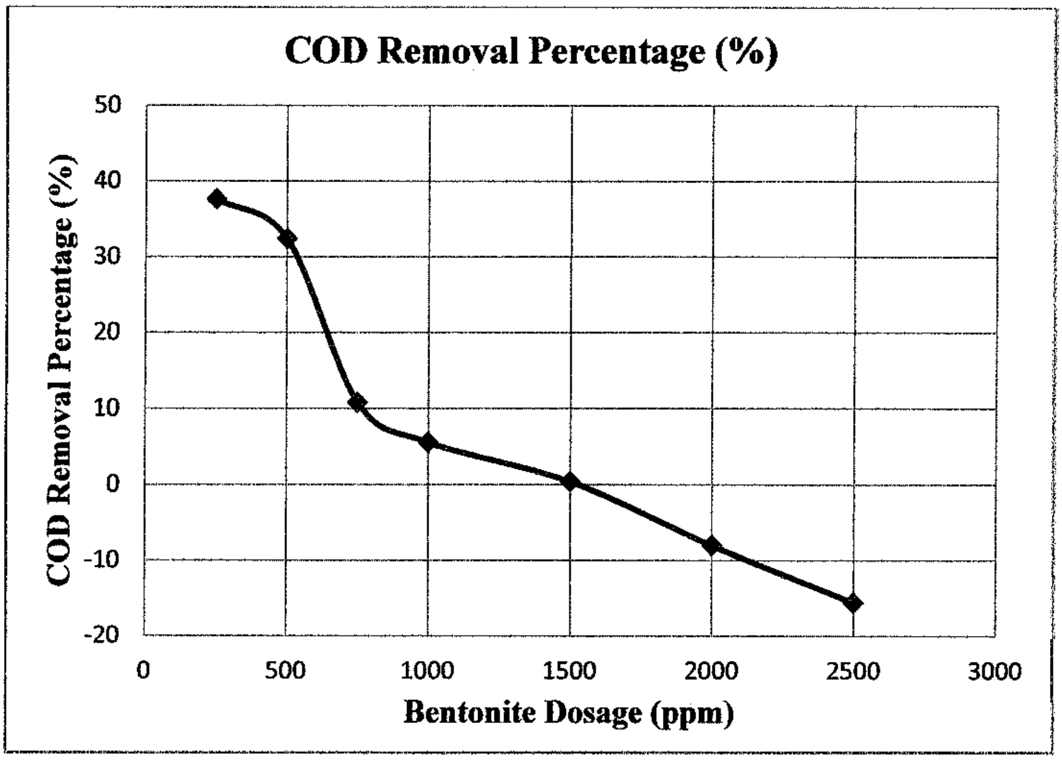


Figure 22: COD Removal Percentage (%) vs. Bentonite Dosage (ppm)

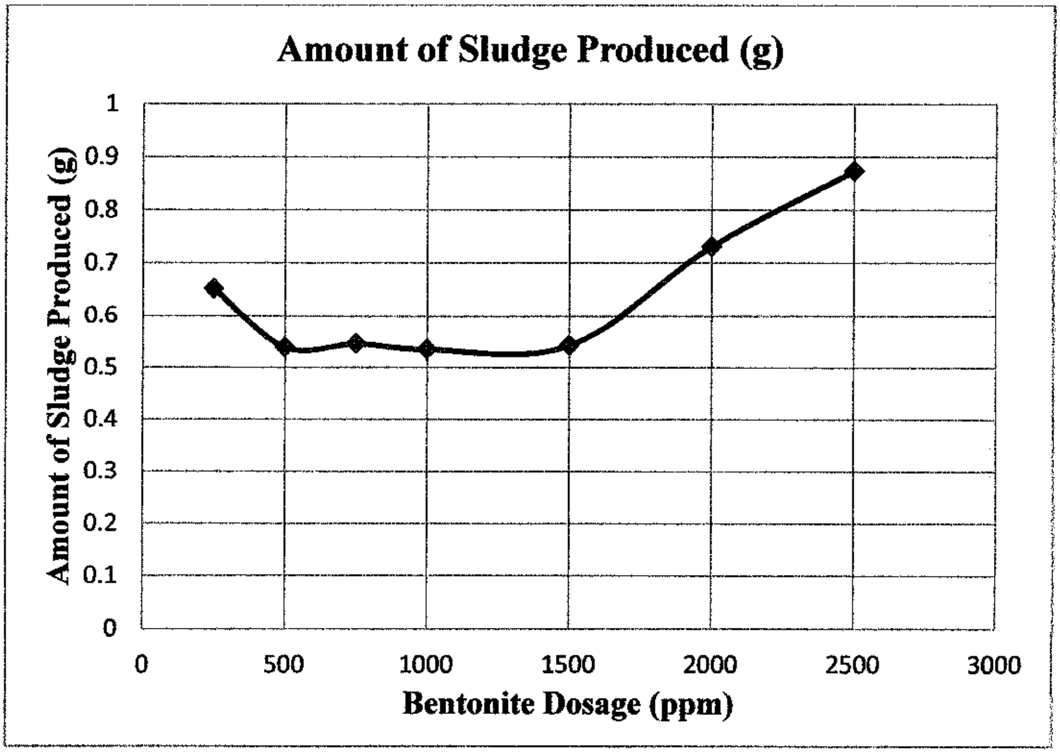


Figure 23: Amount of Sludge Produced (g) vs. Bentonite Dosage (ppm)

In figure 23 and 24, it's clearly shown that at 250ppm of bentonite as coagulant aid the phenol removal percentage and COD reduction percentage was the highest. Thus the optimum coagulant aid bentonite dosage is 250ppm at pH 11, at room temperature with *Moringa Oleifera* as primary coagulant at 4000ppm. From the data above, can be concluded that lime is a better choice of coagulant aid compared to bentonite in removal of phenol with *Moringa Oleifera* as primary coagulant. The performance of these two coagulant aids depends on surface area as well as the exchange capacity.

Lime is a coagulant aid used to increase the alkalinity of the water. The increase in alkalinity results in an increase in ions (electrically charged particles) in the water, some of which are positively charged. These positively charged particles attract the colloidal particles in the water, forming floc. This helps the flocs to agglomerate and settle faster. Bentonite is a type of clay used as a weighting agent in water high in color and low in turbidity and mineral content. Perhaps that is the reason the performance of bentonite on phenol removal was poor. This type of water usually would not form floc large enough to settle out of the water. The bentonite joins with the small floc, making the floc heavier and thus making it settle more quickly.

4.5 Determination of Optimum pH for Lime and Bentonite

After obtaining the optimum dosage of lime and bentonite as coagulant aid, the experiment continued to determine the optimum pH for lime and bentonite.

4.5.1 Lime as Coagulant Aid

In this experiment, the effect of pH was tested with lime as coagulant aid. The pH of solution was varied from pH 2-12 by using drops of 1M sodium hydroxide and 1 M of hydrochloric acid. The pH with the highest phenol removal and COD reduction will be picked as the optimum pH.

Table 6: Effect of pH for Lime Dosage 2000ppm at Room Temperature with *Moringa Oleifera* 4000ppm

pH	Phenol Concentration (ppm)		Phenol Removal Percentage (%)	COD (ppm)		COD Removal Percentage (%)	Amount of sludge (g)
	Initial	Final		Initial	Final		
2	150	123.3534483	17.80104712	250	223	10.8	0.5341
4	150	122.6637931	18.26643397	250	212	15.2	0.5399
7	150	121.112069	19.31355439	250	203	18.8	0.5162
9	150	62.23275862	59.04595695	250	80	68	0.697
11	150	35.1637931	77.31239092	250	74	70.4	0.7324
12	150	49.04310345	67.94648051	250	140	44	0.634

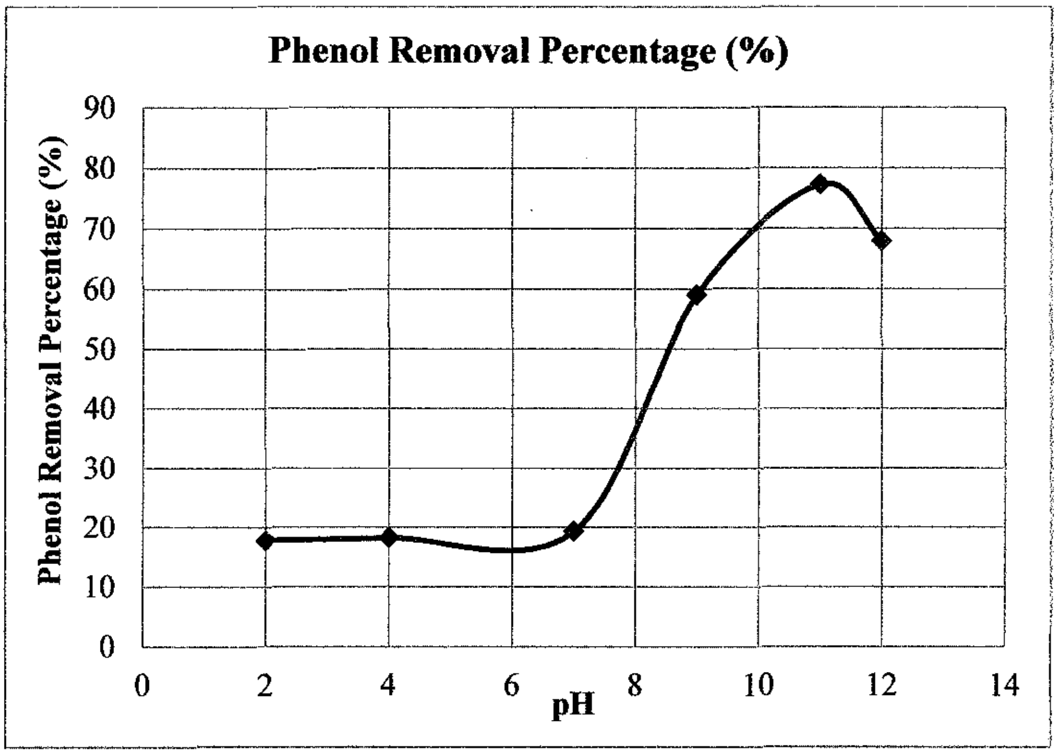


Figure 24: Phenol Removal Percentage (%) vs. pH

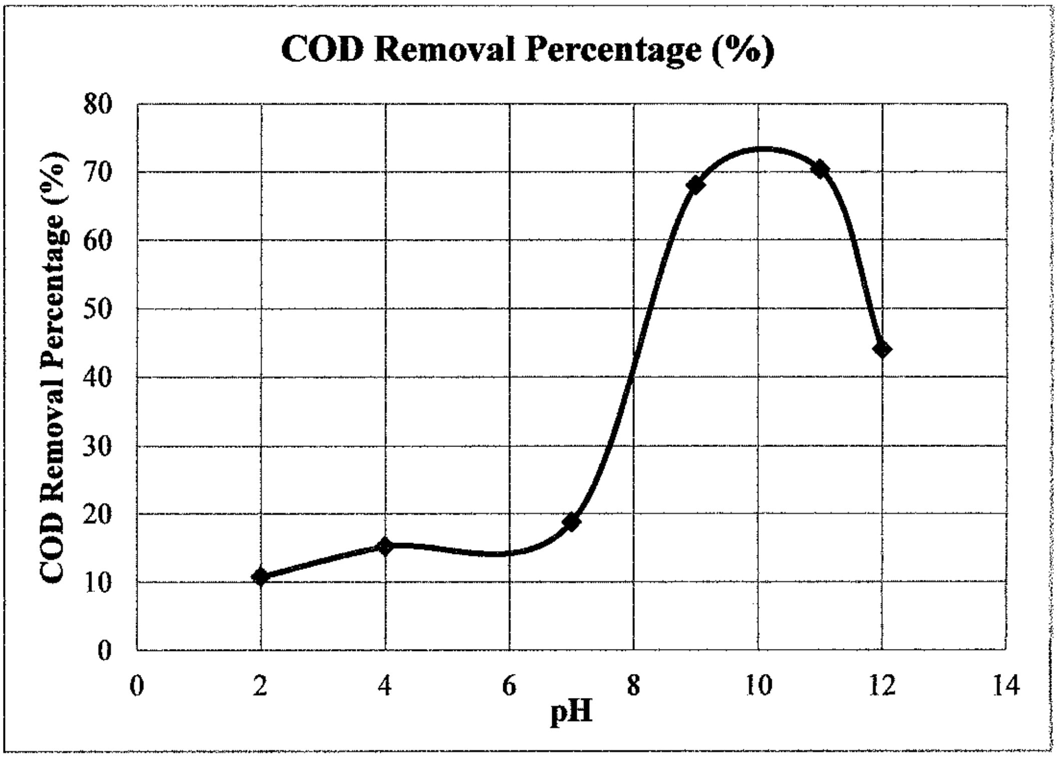


Figure 25: COD Removal Percentage (%) vs. pH

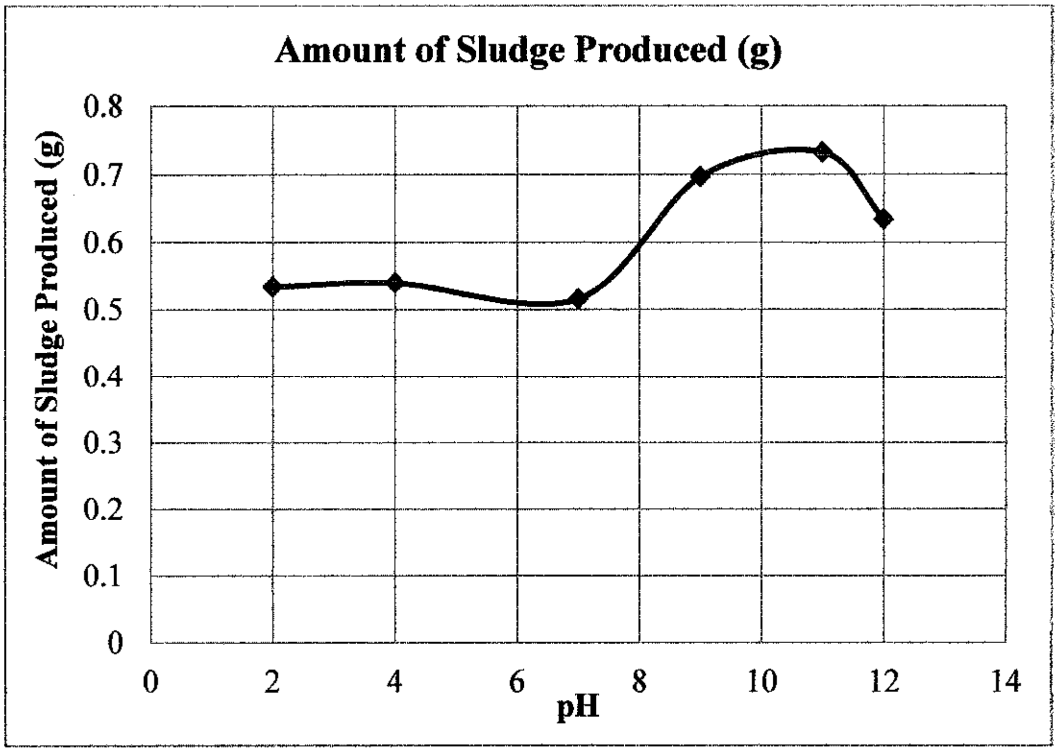


Figure 26: Amount of Sludge Produced (g) vs. pH

From Figure 26 and 27 it shows that the highest phenol removal percentage is at pH11 and most COD reduction is at pH9. After considering the both condition, it can be concluded that pH11 is the optimum pH for lime as coagulant aid.

4.5.2 Bentonite as Coagulant Aid

In this experiment, the effect of pH was tested with bentonite as coagulant aid. The pH of solution was varied from pH 2- 12 by using drops of 1M sodium hydroxide and 1 M of hydrochloric acid. The pH with the highest phenol removal and COD reduction will be picked as the optimum pH.

Table 7: Effect of pH for Bentonite Dosage 250ppm at Room Temperature with *Moringa Oleifera* 4000ppm

pH	Phenol Concentration (ppm)		Phenol Removal Percentage (%)	COD (ppm)		COD Removal Percentage (%)	Amount of sludge (g)
	Initial	Final		Initial	Final		
2	150	117.2327586	21.93135544	250	194	22.4	0.5379
4	150	109.387931	27.22513089	250	189	24.4	0.6193
7	150	78.35344828	48.16753927	250	120	52	0.8564
11	150	99.81896552	33.68237347	250	156	37.6	0.652
12	150	101.7155172	32.40255963	250	188	24.8	0.7465

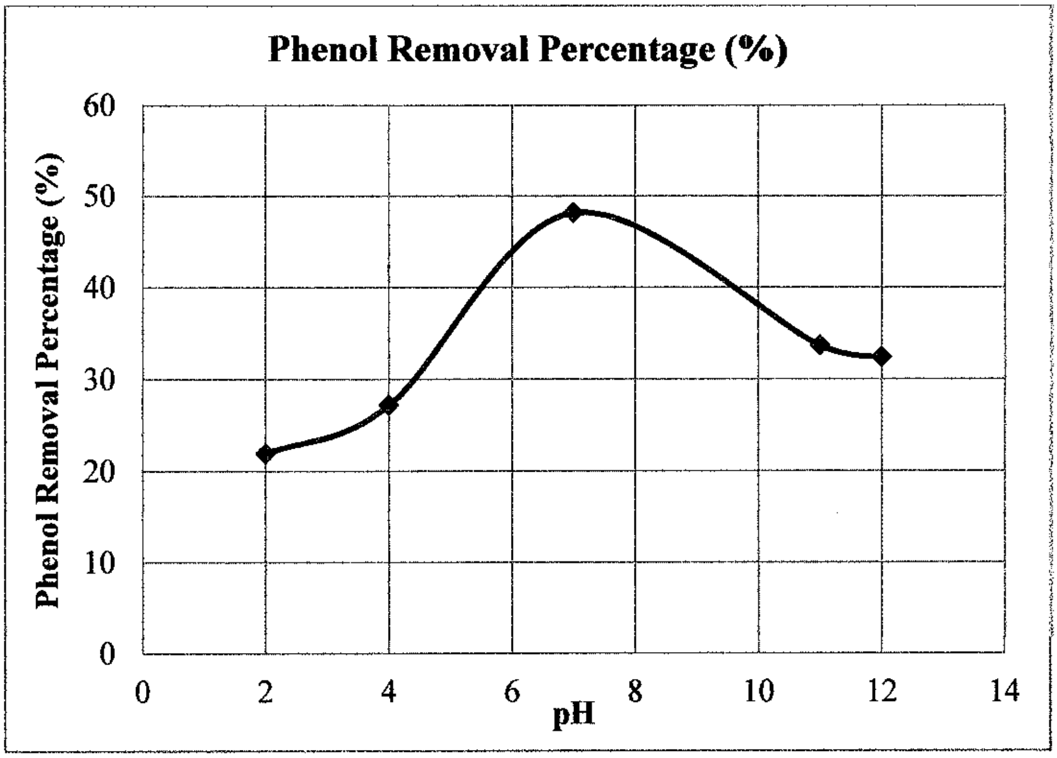


Figure 27: Phenol Removal Percentage (%) vs. pH

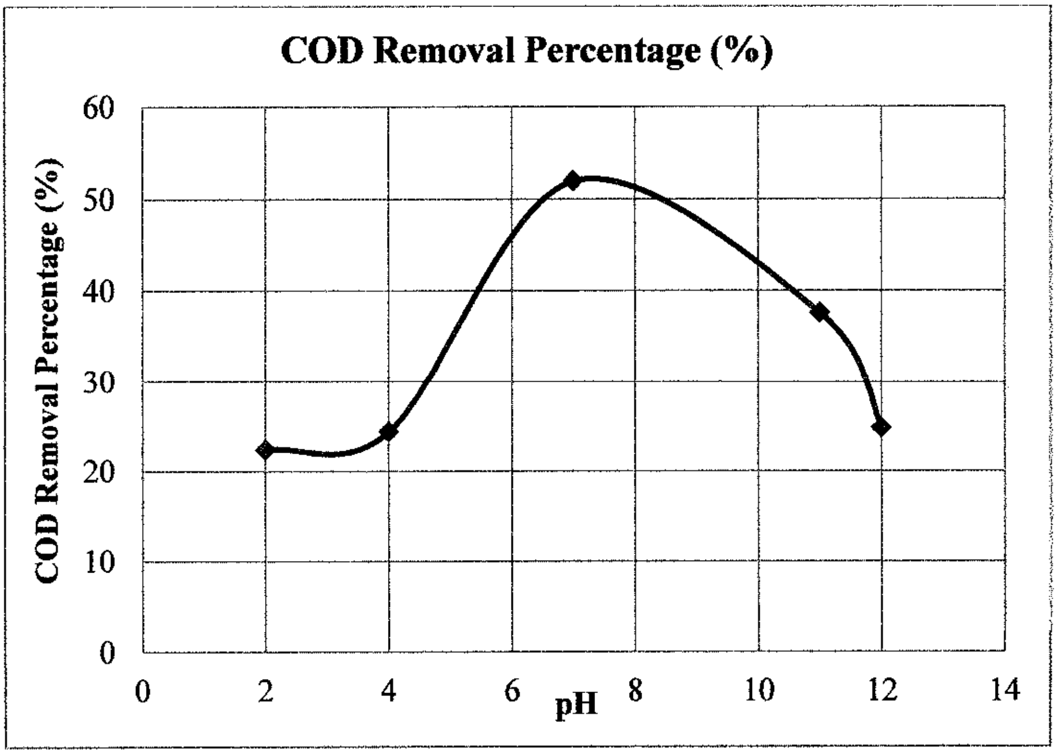


Figure 28: COD Removal Percentage (%) vs. pH

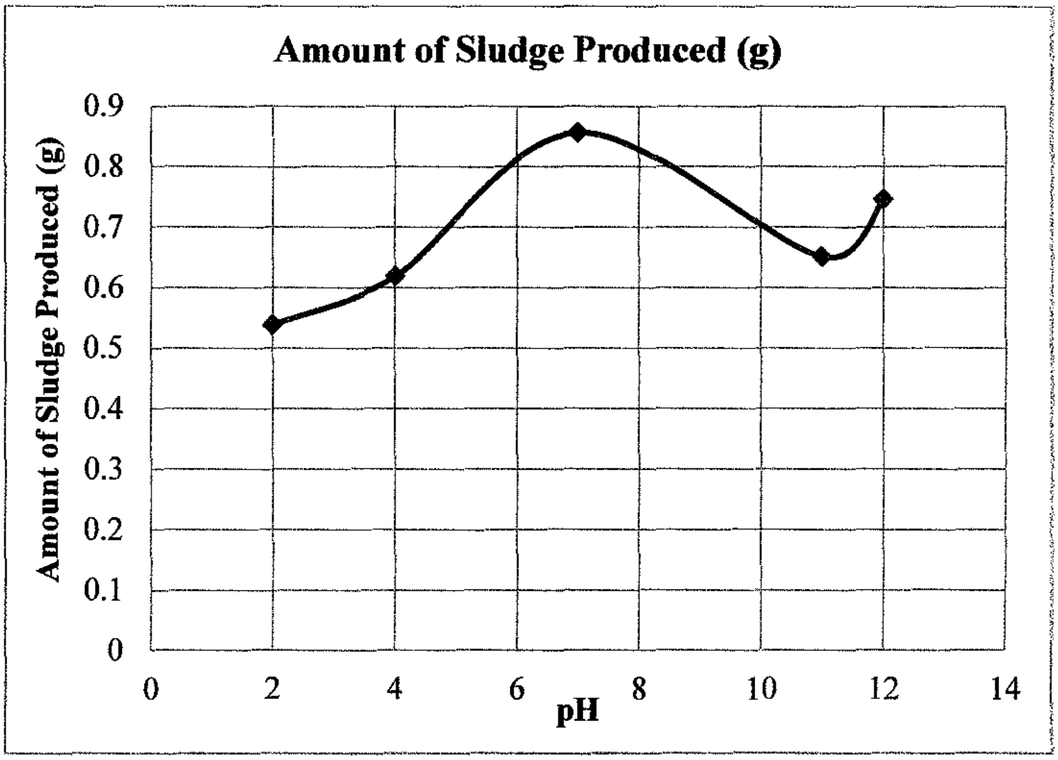


Figure 29: Amount of Sludge Produced (g) vs. pH

From Figure 29 and 30 it shows that the highest phenol removal percentage and most COD reduction is at pH7. Thus pH 7 is the optimum pH for bentonite as coagulant aid.

4.6 Determination of Optimum Temperature for Lime and Bentonite

After obtaining the optimum dosage of lime and bentonite as coagulant aid and also the optimum pH, the experiment continued to determine the optimum temperature for lime and bentonite as coagulant aid.

4.6.1 Lime as Coagulant Aid

In this experiment, the effect of temperature was tested with lime as coagulant aid. The temperature of solution was varied 30°C-80°C. The temperature with the highest phenol removal and COD reduction will be picked as the optimum temperature.

Table 8: Effect of Temperature for Lime Dosage 2000ppm at pH 11 with *Moringa Oleifera* 4000ppm

Temperature (°C)	Phenol Concentration (ppm)		Phenol Removal Percentage (%)	COD (ppm)		COD Removal Percentage (%)	Amount of sludge (g)
	Initial	Final		Initial	Final		
30	150	36.88793103	76.14892379	250	78	68.8	0.7324
40	150	105.4224138	29.90110529	250	150	40	0.5399
60	150	121.112069	19.31355439	250	197	21.2	0.5162
80	150	131.1982759	12.50727167	250	216	13.6	0.697

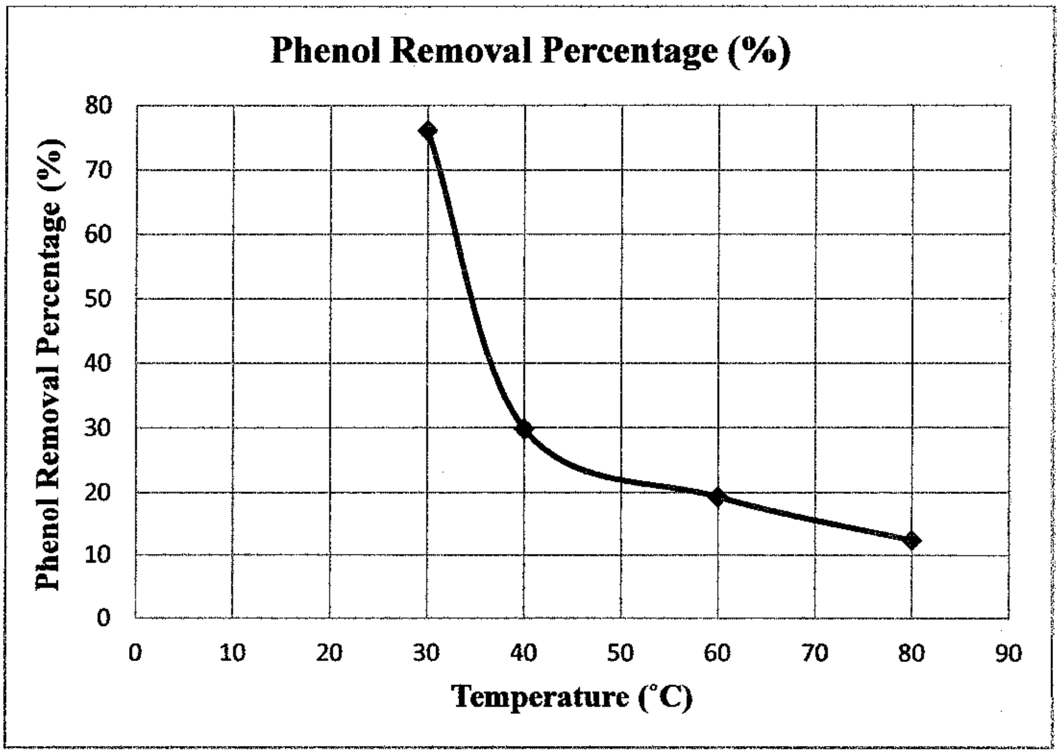


Figure 30: Phenol Removal Percentage (%) vs. Temperature (°C)

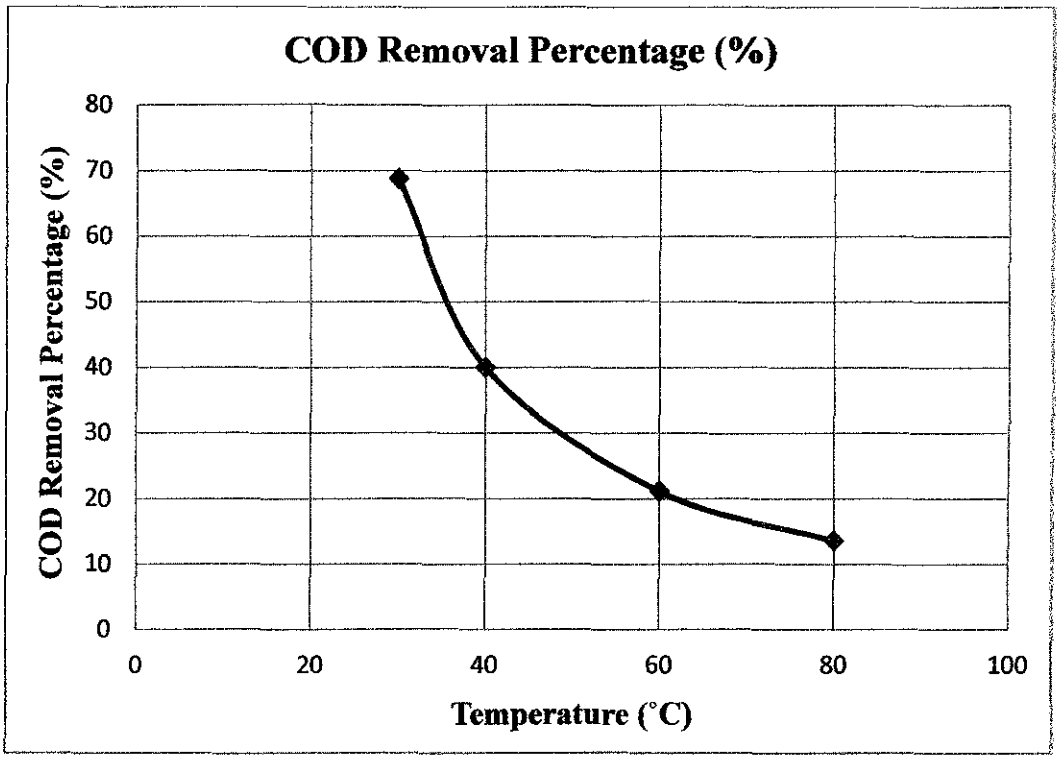


Figure 31: COD Removal Percentage (%) vs. Temperature (°C)

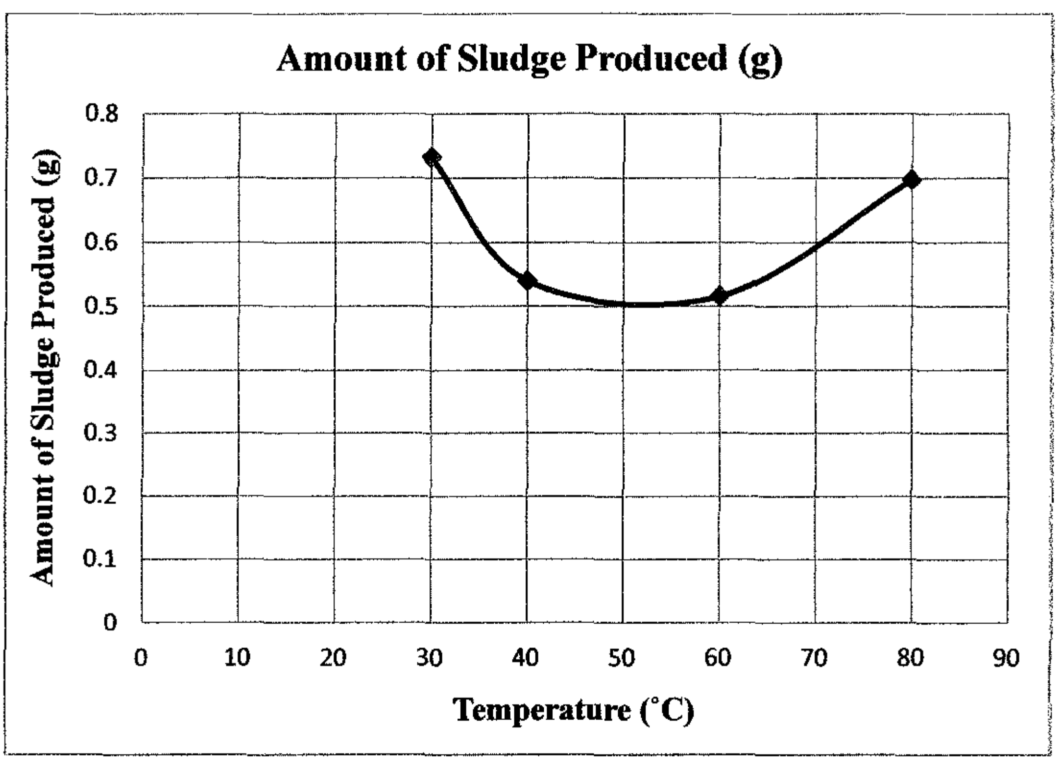


Figure 32: Amount of Sludge Produced (g) vs. Temperature (°C)

From Figure 32 and 33, it shows that as temperature increases the performance percentage decreases. This is very much similar with the result obtained for coagulant. Thus the optimum temperature is room temperature for lime as coagulant aid.

4.6.2 Bentonite as Coagulant Aid

In this experiment, the effect of temperature was tested with bentonite as coagulant aid. The temperature of solution was varied 30°C-80°C. The temperature with the highest phenol removal and COD reduction will be picked as the optimum temperature.

Table 9: Effect of Temperature for Bentonite Dosage 250ppm at pH 7 with *Moringa Oleifera* 4000ppm

Temperature (°C)	Phenol Concentration (ppm)		Phenol Removal Percentage (%)	COD (ppm)		COD Removal Percentage (%)	Amount of sludge (g)
	Initial	Final		Initial	Final		
30	150	79.21551724	47.5858057	250	127	49.2	0.8564
40	150	101.0258621	32.86794648	250	156	37.6	0.6193
60	150	107.8362069	28.27225131	250	180	28	0.614
80	150	119.2155172	20.59336824	250	204	18.4	0.552

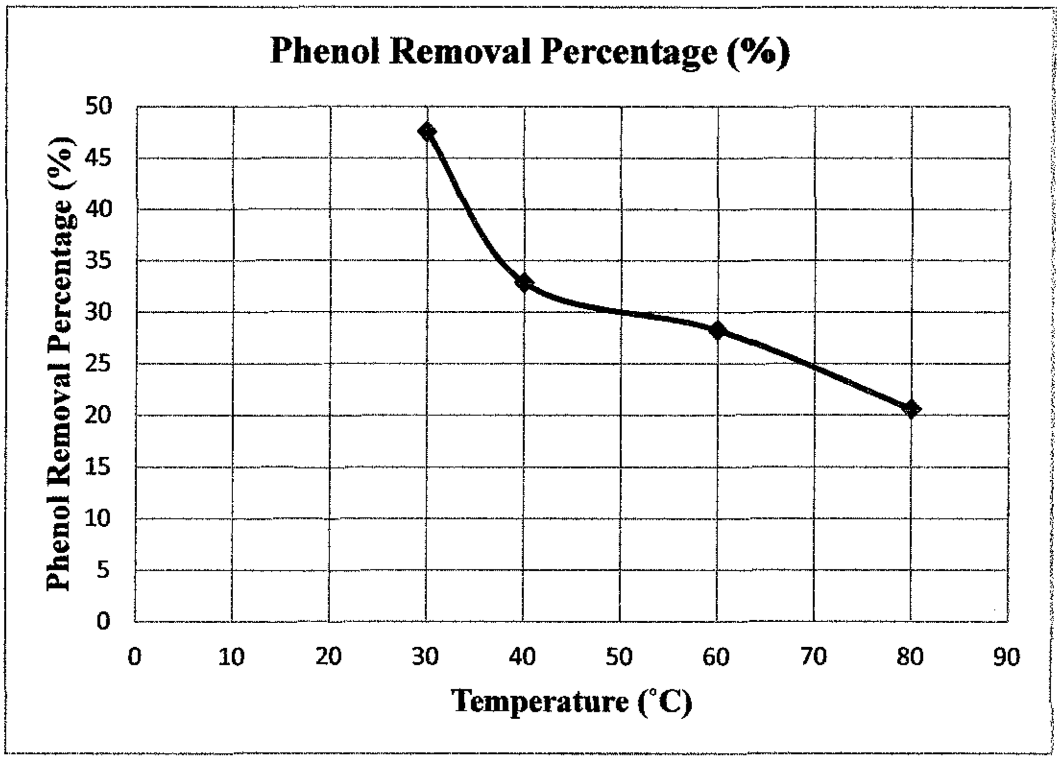


Figure 33: Phenol Removal Percentage (%) vs. Temperature (°C)

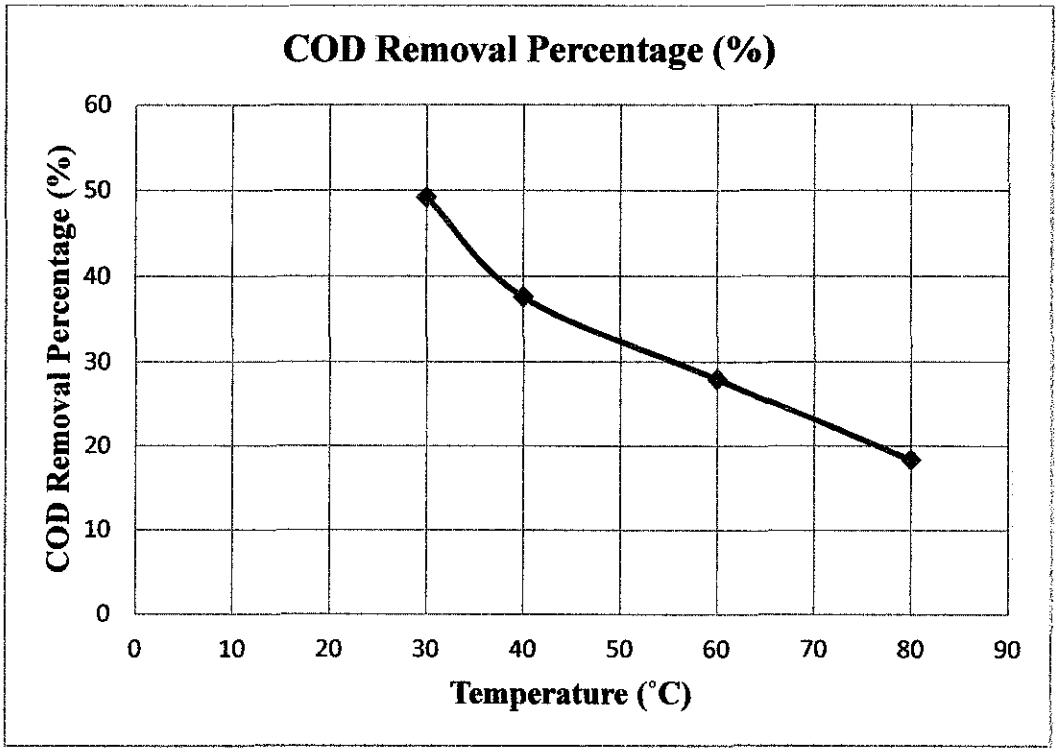


Figure 34: COD Removal Percentage (%) vs. Temperature (°C)

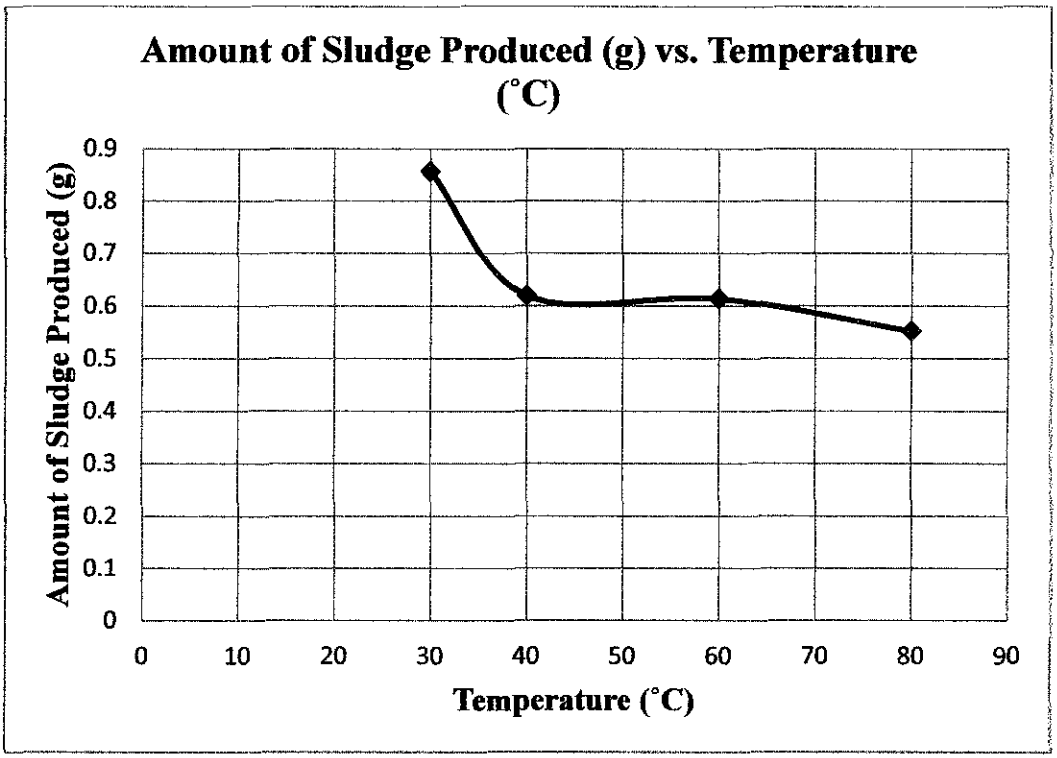


Figure 35: Amount of Sludge Produced (g) vs. Temperature (°C)

From Figure 35 and 36, it shows that as temperature increases the performance rate decreases. This is very much similar with the result obtained for coagulant. Thus the optimum temperature is room temperature for bentonite as coagulant aid.

CHAPTER 5

CONCLUSIONS & RECOMMENDATION

5.1 Conclusions

Phenol is a priority pollutant in wastewater as it was pointed out in the earlier chapters. Industries such as oil refineries, coking operation and petrochemicals contribute phenolic wastewater to the environment. Stringent rules have been set to ensure that the amount of phenol released to the environment is under the allowable concentration. There are varieties of treatment methods to treat phenolic wastewater. However, coagulation method is preferred compared to other methods because it is economically feasible, can handle large amount of wastewater and it is a continuous process. In any industry, cost plays a vital role thus every operation has to be cost effective. Despite the fact that coagulation process will produce sludge that needed to be treated later but if the coagulation process works efficiently at the optimum condition, it may ease the utilization or disposal of the sludge. Furthermore, natural coagulants were more preferred because of their lesser production of sludge and biodegradable sludge nature thus sludge disposal would not be a problem in this case.

The coagulation method is only applicable at certain coagulant dosage, pH of solution, temperature and also effects of the coagulant aids. The optimum conditions are stated below:

i. The optimum dosage of *Moringa Oleifera* as primary coagulant is 4000ppm
ii. The optimum pH of solution is at pH 11. The alkaline solution increases the number of ions in the solution; some of them are positively charged thus it aids the coagulation process.
iii. The optimum temperature is at room temperature is at 26°C, suggesting that the flocs re-dissolves at higher temperature.

iv. Lime performed better as coagulant aid compared to bentonite. The optimum dosage of lime is 2000ppm

v. The optimum pH remains pH 11 even after the addition of lime as coagulant aid

vi. The optimum temperature also remains at room temperature after adding lime as coagulant aid.

At the above stated optimum conditions the phenol was reduced from 150ppm to 35ppm thus the removal percentage was 77%. The COD on the other hand was reduced from 250ppm to74ppm thus the reduction percentage is 70.4%. The amount of sludge produced is around 0.7324g which is considered a very small amount.

In a nutshell, this research was a success; it has proven that natural coagulant *Moringa Oleifera* can be used as primary coagulant in removal of phenol in wastewater treatment. Moreover the amount of sludge is very small thus it makes this is a huge advantage because the big downside of coagulation process is the large production of sludge. Besides that, using a natural coagulant leads to formation of biodegradable sludge thus sludge handling has become way more simple.

5.1 Recommendation

A combination of process for phenol removal would be an option. For instance using advanced oxidation process like Fenton Oxidation. Some research on the degradation of phenolic compounds with advanced oxidation processes (AOPs) has already been published. Many studies have been developed on the degradation of phenolic compounds by different AOPs like O_3, O_3/H_2O_2, UV, UV/O_3, UV/H_2O_2, O_3/UV/H_2O_2, Fe^{2+}/H_2O_2 and photocatalysis (Esplugas, Gimenez, Contreras, Pascual, & Rodriguez, 2002). The Fenton reagent is found to be the fastest one for phenol degradation. Fenton process involving a mixture of ferrous ion and hydrogen peroxide generates hydroxyl radicals (•OH) at room temperature(Walling, 1975). The equation below shows the Fenton process:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + {}^{-}OH$$

The major advantage of Fenton process is that the reagent components are safe to handle and environmentally benign. Therefore a combination of coagulation process with Fenton oxidation will lead to even higher phenol removal percentage from wastewater.

REFERENCES

1. Abdullah, A. R. (1995). Environmental pollution in Malaysia: trends and prospects. *TrAC Trends in Analytical Chemistry, 14*(5), 191-198.
2. Ahmaruzzaman, M. (2008). Adsorption of phenolic compounds on low-cost adsorbents: A review. *Advances in Colloid and Interface Science, 143*(1-2), 48-67.
3. Ashmawy, M. A., Moussa, M. S., Ghoneim, A. K., & Tammam, A. (2012). Enhancingthe Efficiency of Primary Sedimentation in Wastewater Treatment Plants with the Application of MoringaOliefera Seeds and Quicklime. *Journal of American Science, 8*(2).
4. Banat, F. A., Al-Bashir, B., Al-Asheh, S., & Hayajneh, O. (2000). Adsorption of phenol by bentonite. *Environmental pollution, 107*(3), 391-398.
5. Bhuptawat, H., Folkard, G. K., & Chaudhari, S. (2007). Innovative physico-chemical treatment of wastewater incorporating Moringa oleifera seed coagulant. *Journal of hazardous materials, 142*(1-2), 477-482.
6. Bolto, B., & Gregory, J. (2007). Organic polyelectrolytes in water treatment. *Water research, 41*(11), 2301-2324.
7. Chegrouche, S., Mellah, A., & Telmoune, S. (1997). Removal of lanthanum from aqueous solutions by natural bentonite. *Water research, 31*(7), 1733-1737.
8. Christidis, G. E. (1998). Physical and chemical properties of some bentonite deposits of Kimolos Island, Greece. *Applied Clay Science, 13*(2), 79-98.
9. Dziubek, A. M., & Kowal, A. L. (1986). *Effect of pH and magnesium on colour and turbidity removal from aqueous solutions.*
10. Esplugas, S., Gimenez, J., Contreras, S., Pascual, E., & Rodriguez, M. (2002). Comparison of different advanced oxidation processes for phenol degradation. *Water research, 36*(4), 1034-1042.
11. Fang, H. H. P., & Chan, O. C. (1997). Toxicity of phenol towards anaerobic biogranules. *Water research, 31*(9), 2229-2242.

12. Gupta, V. K., Saleh, T. A., Nayak, A., & Agarwal, S. (2012). Chemical Treatment Technologies for Waste-water Recycling an Overview. *RSC Advances,*
13. Hartman, W. A., & Martin, D. B. (1984). Effect of suspended bentonite clay on the acute toxicity of glyphosate toDaphnia pulex andLemna minor. *Bulletin of environmental contamination and toxicology, 33*(1), 355-361.
14. Hassan, A., Ariffin, M., Tan, P. L., & Noor, Z. Z. (2009). Coagulation and flocculation treatment of wastewater in textile industry using chitosan. *Journal of Chemical and Natural Resources Engineering, 4*(1), 43-53.
15. J Beltrán-Heredia, J., Sánchez-Martín, J., Muñoz-Serrano, A., & Peres, J. A. (2012). Towards overcoming TOC increase in wastewater treated with Moringa oleifera seed extract. *Chemical Engineering Journal.*
16. Katayon, S., Noor, M. J., Asma, M., Ghani, L. A., Thamer, A. M., Azni, I., et al. (2006). Effects of storage conditions of Moringa Oleifera seeds on its performance in coagulation. *Bioresource technology, 97*(13), 1455-1460.
17. Klimiuk, E., Filipkowska, U., & Korzeniowska, A. (1999). Effects of pH and coagulant dosage on effectiveness of coagulation of reactive dyes from model wastewater by polyaluminium chloride (PAC). *Polish Journal of Environmental Studies, 8*, 73-80.
18. Lin, S. H., & Juang, R. S. (2009). Adsorption of phenol and its derivatives from water using synthetic resins and low-cost natural adsorbents: A review. *Journal of Environmental Management, 90*(3), 1336-1349.
19. Lipson, S. M., & Stotzky, G. (1985). Specificity of virus adsorption to clay minerals. *Canadian journal of microbiology, 31*(1), 50.
20. Malakootian, M., & Fatehizadeh, A. Color Removal From Water By Coagulation/caustic Soda And Lime. *Iranian Journal of Environmental Health Science & Engineering, 7*(3).
21. Mellah, A., & Chegrouche, S. (1997). The removal of zinc from aqueous solutions by natural bentonite. *Water research, 31*(3), 621-629.
22. Mohammed, A. S., Lai, O. M., Muhammad, S. K. S., Long, K., & Ghazali, H. M. (2003). Moringa oleifera, potentially a new source of oleic acid-type oil for

Malaysia. *Investing in Innovation: Bioscience and Biotechnology, Universiti Putra Malaysia Press, Serdang Press, Selangor, Malaysia, 3*, 137-140.

23. Mondal, S. (2008). Methods of dye removal from dye house effluent-an overview. *Environmental Engineering Science, 25*(3), 383-396.
24. Ndabigengesere, A., Narasiah, K. S., & Talbot, B. G. (1995). Active agents and mechanism of coagulation of turbid waters using Moringa oleifera. *Water research, 29*(2), 703-710.
25. Othman, Z., Bhatia, S., & Ahmad, A. L. (2008). Influence Of The Settleability Parameters For Palm Oil Mill Effluent (Pome) Pretreatment By Using Moringa Oleifera Seeds As An Environmental Friendly Coagulant.
26. Ozbelge, T. A., Ozbelge, O. H., & Baskaya, S. Z. (2002). Removal of phenolic compounds from rubber-textile wastewaters by physico-chemical methods. *Chemical engineering and processing, 41*(8), 719-730.
27. Ramakrishnan, K., & Namasivayam, C. (2011). Zinc chloride-activated jatropha husk carbon for removal of phenol from water by adsorption: equilibrium and kinetic studies. *Toxicological & Environmental Chemistry, 93*(6), 1111-1122.
28. Renault, F., Sancey, B., Badot, P. M., & Crini, G. (2009). Chitosan for coagulation/flocculation processes-An eco-friendly approach. *European Polymer Journal, 45*(5), 1337-1348.
29. Semerjian, L., & Ayoub, G. M. (2003). High-pH Magnesium Coagulation-Flocculation in Wastewater Treatment. *Advances in Environmental Research, 7*(2), 389-403.
30. Sharma, B. R., Dhuldhoya, N. C., & Merchant, U. C. (2006). Flocculants an ecofriendly approach. *Journal of Polymers and the Environment, 14*(2), 195-202.
31. Sutherland, J. P., Folkard, G. K., Mtawali, M. A., & Grant, W. D. (1994). *Moringa oleifera as a natural coagulant.*
32. Verma, A. K., Dash, R. R., & Bhunia, P. A review on chemical coagulation/flocculation technologies for removal of colour from textile wastewaters. *Journal of Environmental Management, 93*(1), 154-168.
33. Walling, C. (1975). Fenton's reagent revisited. *Accounts of Chemical Research, 8*(4), 125-131.

34. Zonoozi, M. H., Moghaddam, M. R. A., & Arami, M. (2008). Removal of Acid Red 398 dye from aqueous solutions by coagulation/flocculation process. *Environmental Engineering and Management Journal,* 7(6), 695-699.

APPENDIX

Appendix 1: Parameter Limits of Effluent of Standards A and B

Third Schedule

Environmental Quality Act 1974

Environmental Quality (Sewage & Industrial Effluent) Regulations 1979

(Regulation 8(1), 8(2), 8(3))

PARAMETER LIMITS OF EFFLUENT OF STANDARDS A AND B

Parameter	Unit	Standard A	B
(1)	(2)	(3)	(4)
(i) Temperature	°C	40	40
(ii) pH Value		6.0 - 9.0	5.5 - 9.0
(iii) BOD5 at 20°C	mg/l	20	50
(iv) COD	mg/l	50	100
(v) Suspended Solids	mg/l	50	100
(vi) Mercury	mg/l	0.005	0.05
(vii) Cadmium	mg/l	0.01	0.02
(viii) Chromium, Hexavalent	mg/l	0.05	0.05
(ix) Arsenic	mg/l	0.05	0.10
(x) Cyanide	mg/l	0.05	0.10
(xi) Lead	mg/l	0.10	0.5
(xii) Chromium, Trivalent	mg/l	0.20	1.0
(xiii) Copper	mg/l	0.20	1.0
(xiv) Manganese	mg/l	0.20	1.0
(xv) Nickel	mg/l	0.20	1.0
(xvi) Tin	mg/l	0.20	1.0
(xvii) Zinc	mg/l	1.0	1.0
(xviii) Boron	mg/l	1.0	4.0
(xix) Iron (Fe)	mg/l	1.0	5.0
(xx) Phenol	mg/l	0.001	1.0
(xxi) Free Chlorine	mg/l	1.0	2.0
(xxii) Sulphide	mg/l	0.50	0.50
(xxiii) Oil and Grease	mg/l	Not detectable	10

Appendix 2: *Moringa Oleifera* EDX Results

Energy-dispersive X-ray spectroscopy (EDX) is used for the elemental analysis or chemical characterization of a sample. It relies on the investigation of an interaction of some source of X-ray excitation and a sample.

Spectrum processing:

No peaks omitted

Processing option: All elements analyzed (Normalised)

Number of iterations = 4

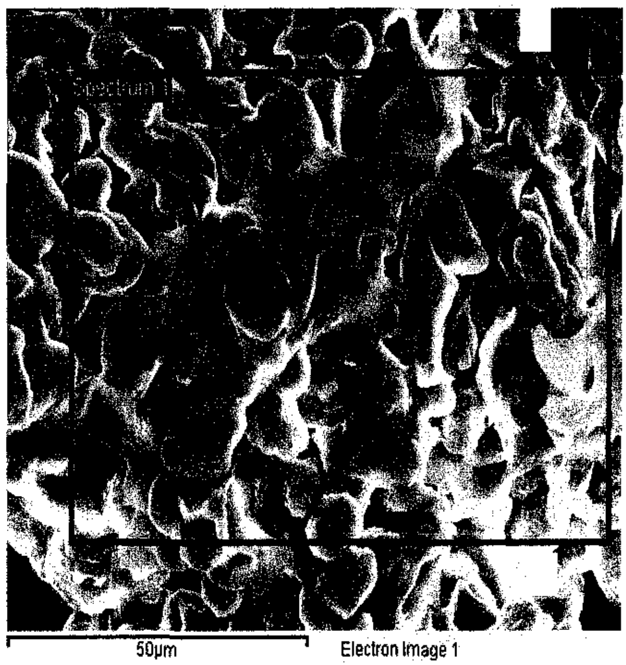
Standard:

C CaCO3 1-Jun-1999 12:00 AM

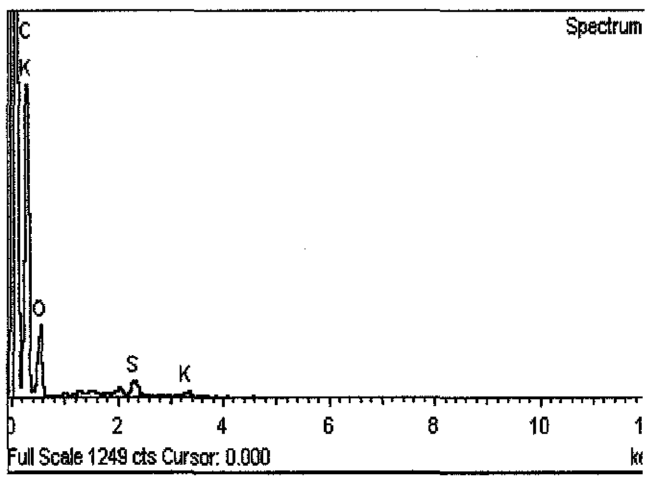
O SiO2 1-Jun-1999 12:00 AM

S FeS2 1-Jun-1999 12:00 AM

K MAD-10 Feldspar1-Jun-1999 12:00AM



Element	Weight%	Atomic%
C K	63.11	70.28
O K	34.33	28.70
S K	1.87	0.78
K K	0.70	0.24
Totals	100.00	



Appendix 3: ***Moringa Oleifera*** **FESEM Results**

Field emission scanning electron microscope (FESEM), equipment that allows the observation and characterization of materials using high-resolution RX energy dispersive spectrometry. It offers quantitative and qualitative chemical analysis and simultaneous surface distribution of chemical elements (up to 32) and linear profile chemical analysis. It is equipped with a detector for determining crystallographic textures (EBSD).

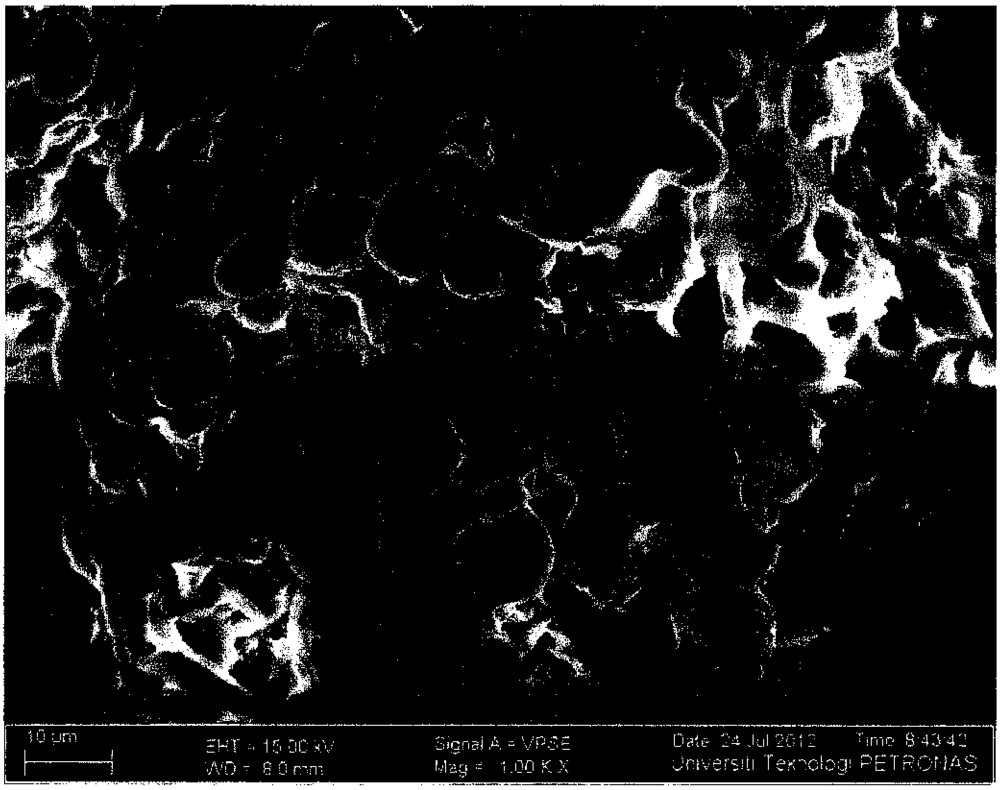


Figure 1 of *Moringa Oleifera* in FESEM

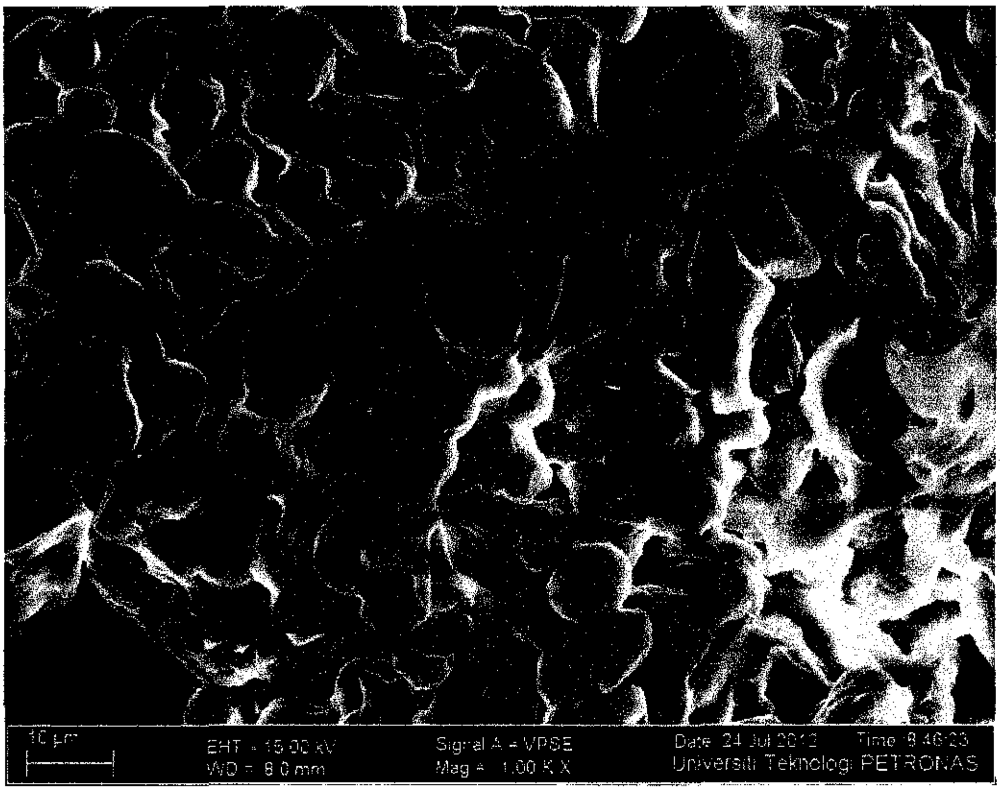


Figure 2 of *Moringa Oleifera* in FESEM

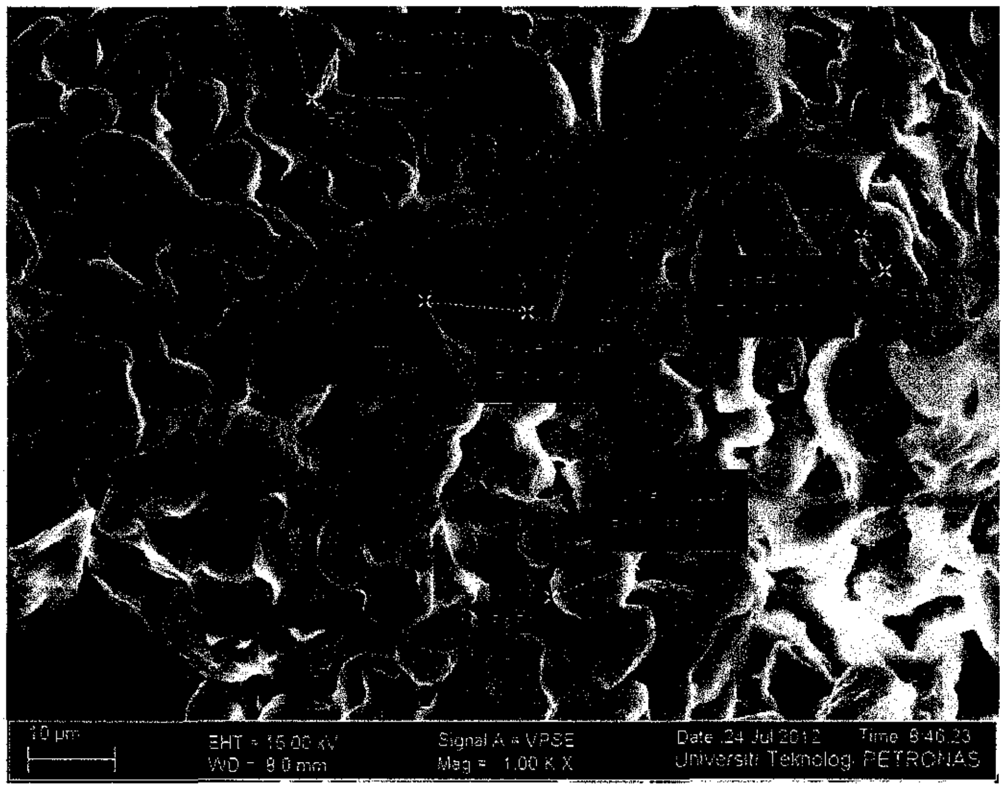


Figure 3 of *Moringa Oleifera* in FESEM

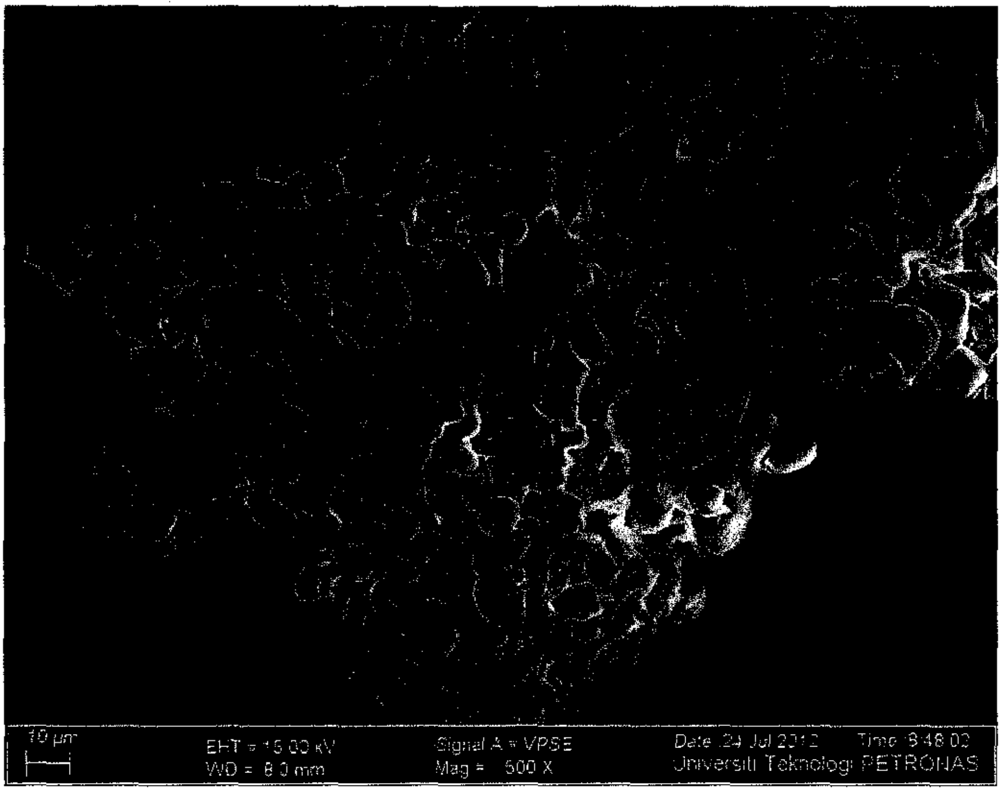


Figure 4 of *Moringa Oleifera* in FESEM

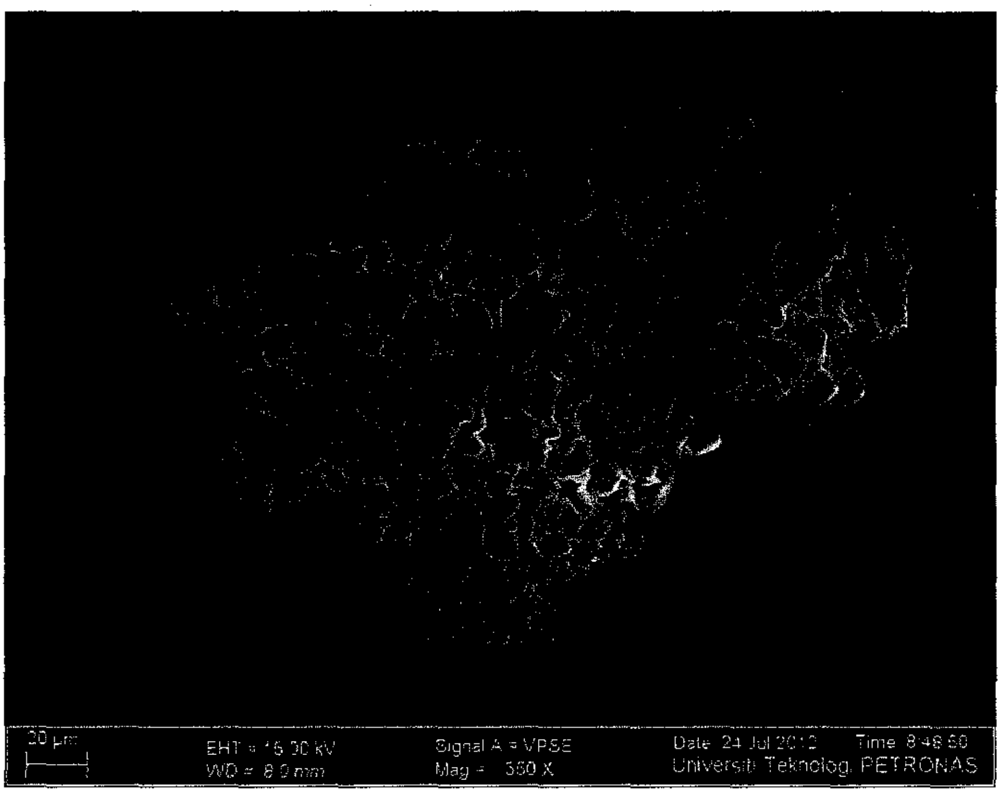
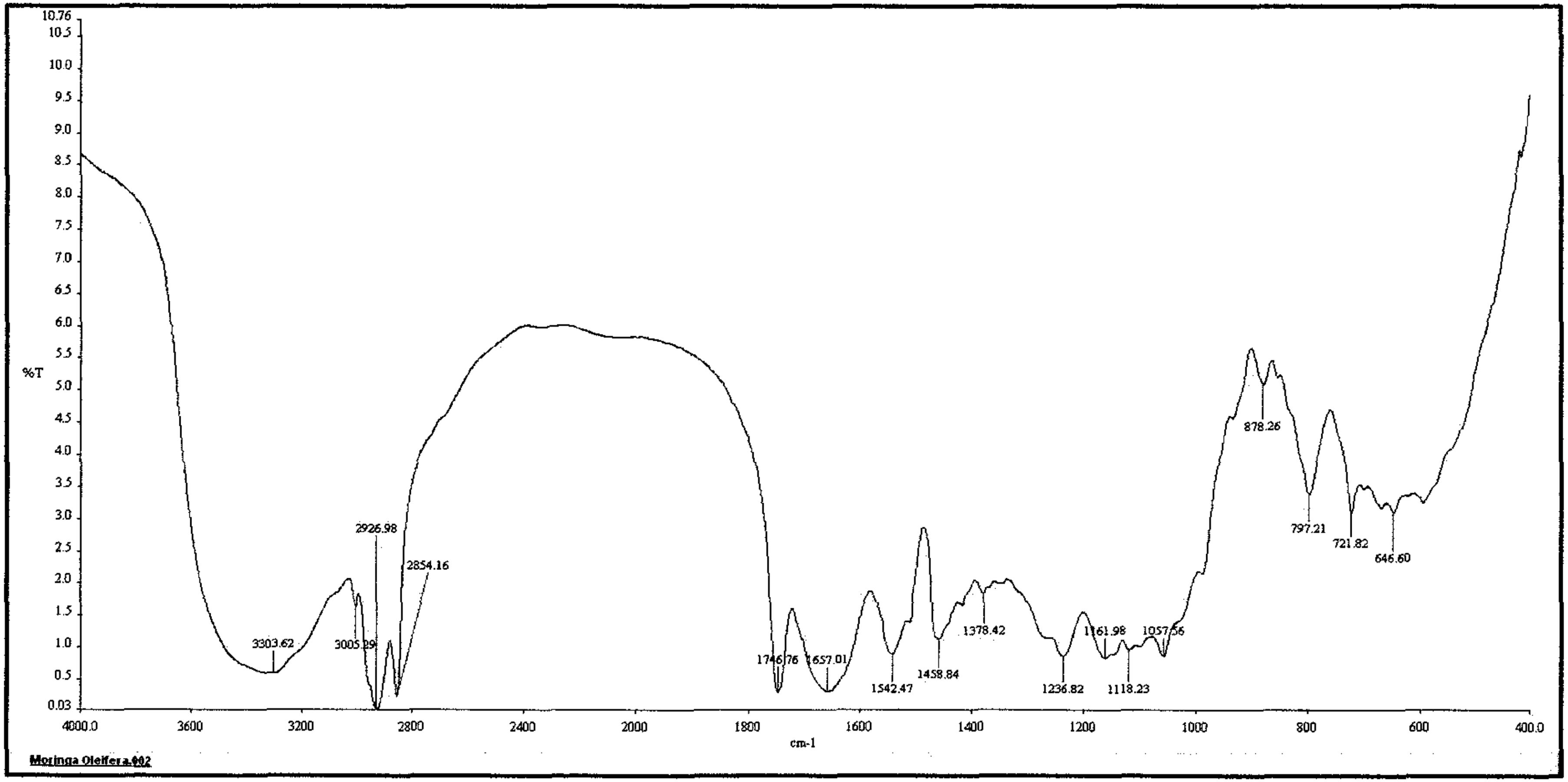


Figure 5 of *Moringa Oleifera* in FESEM

Appendix 4: *Moringa Oleifera* Fourier Transform Infrared Spectroscopy, FTIR Results

Table 10: FTIR Peaks and Functional Group Identification

FTIR Peaks (cm^{-1})	Functional Group
3303.62	Alkynyl C-H Stretch
2926.98 & 2854.16	Alkyl C-H Stretch
2926.98 & 2854.16	Carboxylic Acid O-H Stretch
1746.76	Ester C=O Stretch
1657.01	Amide C=O Stretch



Appendix 5: *Moringa Oleifera* BET Results

The most widely used technique for estimating surface area is called BET method (Brunauer, Emmett and Teller, 1938).

Summary Report

Surface Area

Single point surface area at P/Po = 0.250010302: 0.3547 m^2/g

BET Surface Area: -1.5761 m^2/g

Langmuir Surface Area: -0.4717 m^2/g

BJH Adsorption cumulative surface area of pores between 17.000 Å and 3000.000 Å width: 0.433 m^2/g

BJH Desorption cumulative surface area of pores between 17.000 Å and 3000.000 Å width: 0.1426 m^2/g

Pore Volume

Single point adsorption total pore volume of pores less than 1389.890 Å width at P/Po = 0.985877014: 0.000618 cm^3/g

Single point desorption total pore volume of pores less than 691.238 Å width at P/Po = 0.971190215: 0.000546 cm^3/g

BJH Adsorption cumulative volume of pores between 17.000 Å and 3000.000 Å width: 0.000773 cm^3/g

BJH Desorption cumulative volume of pores between 17.000 Å and 3000.000 Å width: 0.000649 cm^3/g

Pore Size

Adsorption average pore width (4V/A by): -15.6884 Å

Desorption average pore width (4V/A by): -13.8563 Å

BJH Adsorption average pore width (4V/A): 71.411 Å

BJH Desorption average pore width (4V/A): 181.967 Å

Appendix 6: Phenol Calibration Curve Using UV-Vis Spectrophotometer

UVProbe - [Photometric]

File Edit View Graph Operations Instrument Tools Window Help

Standard Table - [Active]

	Sample ID	Type	Ex	Conc	WL269.5	Wgt.Factor
1	Std1	Standard		50.000	0.561	1.000
2	Std2	Standard		100.000	1.141	1.000
3	Std3	Standard		150.000	1.719	1.000
4	Std4	Standard		200.000	2.323	1.000
5	Std5	Standard		250.000	2.878	1.000
6