

COMPARISON OF ACTIVATION
PROCESSES OF ACTIVATED CARBON IN
REMOVING POLLUTANTS FROM PALM OIL
MILL EFFLUENTS

KAVIRAJ A/L ANBARASAN

B. ENG. (HONS.) CIVIL ENGINEERING
UNIVERSITI MALAYSIA PAHANG

COMPARISON OF ACTIVATION PROCESSES OF ACTIVATED CARBON IN
REMOVING POLLUTANTS FROM PALM OIL MILL EFFLUENTS

KAVIRAJ A/L ANBARASAN

A thesis submitted in fulfilment of the requirements
for the award of the degree of
Bachelor of Civil Engineering (Hons.)

Faculty of Civil Engineering & Earth Resources
Universiti Malaysia Pahang

JUNE 2016

THESIS STATUS VALIDATION FORM

UNIVERSITI MALAYSIA PAHANG

DECLARATION OF THESIS AND COPYRIGHT

NAME : KAVIRAJ A/L ANBARASAN
DATE OF BIRTH : 30 MARCH 1992
IC NUMBER : 920330-10-6329

**TITLE: COMPARISON OF ACTIVATION PROCESSES OF ACTIVATED
 CARBON IN REMOVING POLLUTANTS FROM PALM OIL MILL
 EFFLUENTS**

ACADEMIC SESSION: 2015/2016

I declare that this thesis is classified as:

☐

CONFIDENTIAL (Contains confidential information under the Official Secret Act 1972)*

☐

RESTRICTED (Contains restricted information as specified by the organization where research was done)*

☒

OPEN ACCESS I agree that my thesis to be published as online open access (Full text)

I acknowledge that Universiti Malaysia Pahang reserve the right as follows:

1. The Thesis is the Property of Universiti Malaysia Pahang.
2. The Library of Universiti Malaysia Pahang has the right to make copies for the purpose of research only.
3. The Library has the right to make copies of the thesis for academic exchange.

Certified by:

(Student's Signature)

KAVIRAJ A/L ANBARASAN

DATE: 27 JUNE 2016

(Signature Of Supervisor)

DR. MIR SUJAUL ISLAM

DATE: 27 JUNE 2016

NOTES : *If the thesis is CONFIDENTIAL or RESTRICTED, please attach with the letter from the organization with period and reasons for confidentiality or restriction.

SUPERVISOR DECLARATION

I hereby declare that I have checked this thesis and in my opinion this thesis adequate in terms of scope and quality for the award of the Degree of Civil Engineering or Bachelor of Civil Engineering (Hons.).

Signature : _____

Name of Supervisor : DR. MIR SUJAUL ISLAM

Position : SENIOR LECTURER

Date : 27 JUNE 2016

STUDENT'S DECLARATION

I hereby declare that the work in the thesis is my own except for quotations and summaries which have been duly acknowledge. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

Signature : _____

Name : KAVIRAJ A/L ANBARASAN

ID Number : AA12167

Date : 27 JUNE 2016

Special dedication to:

My beloved father Anbarasan Rengan

My beloved mother Malaysia Ramasamy

My UMP lecturer

And to my friends Dexter Dudu, Mangaibagan and others...

Thank you for everything...

ACKNOWLEDGEMENTS

I am grateful and would like to express my sincere gratitude to my supervisor Dr. Mir Sujaul Islam for his germinal ideas, invaluable guidance, continuous encouragement and constant support in making this research possible. He has always impressed me with his outstanding professional conduct, his strong conviction for science, and his belief that a Degree program is only a start of a life-long learning experience. I appreciate his consistent support from the first day I applied to graduate program to these concluding moments. I am truly grateful for his progressive vision about my training in science, his tolerance of my naïve mistakes, and his commitment to my future career. I also sincerely thanks for the time spent proofreading and correcting my many mistakes.

My sincere thanks go to all my lab mates and members of the staff of the FKASA Environmental Laboratory, UMP, who helped me in many ways and made my stay at UMP pleasant and unforgettable. Many special thanks go to member engine research group for their excellent co-operation, inspirations and supports during this study.

I acknowledge my sincere indebtedness and gratitude to my parents for their love, dream and sacrifice throughout my life. I acknowledge the sincerity of my parents, who consistently encouraged me to carry on my higher studies. I cannot find the appropriate words that could properly describe my appreciation for their devotion, support and faith in my ability to attain my goals. My sincere thanks go to my friends who stood beside me along the research until I manage to finish this research.

ABSTRACT

Malaysia is the second leading exporter of palm oil in the world. In Malaysia and Indonesia, there are about 84% of world's palm oil exports are produced. Indisputably, the level of our environment is affected by the oil palm industry and its processing and it may lead to the rise of ecological pollution. There are many types of treatment to improve POME quality and one of them is by using activated carbon. The purpose of this study is to compare two activation process of activated carbon in removing pollutants from palm oil mill effluent (POME). Samples were taken from Kilang Kelapa Sawit Lepar Hilir, Kuantan, Pahang Darul Makmur. The activated carbons were produced in two different method which are physical activation (pyrolysis treatment) and chemical activation (acidic treatment). The water quality parameters also were conducted based on the standard methods. Among the water quality parameters that involved are pH, BOD, COD, Ammoniacal Nitrogen, Turbidity, Oil & Grease, Total Suspended Solids and Heavy Metals (Boron, Copper and Lead). After analysing the wastewater quality based on eight parameters, both of samples showed the improvement in removing wastewater pollutant due to its removal efficiency. The results obtained are compared with the limits in the Environmental Quality Act 1984. Among the two samples, chemically activated carbon gave the most effective results due to its highest removal efficiency except in oil and grease parameter. The results of percentages of removal for wastewater treatment using chemically activated carbon for COD, BOD, TSS, AN, Turbidity and Oil & Grease are ranged from 98.99 to 99.68% while for physically activated carbon the results are between 97.69 to 99.63%. From the result obtained, it showed that activated carbon have potentials to be used as a filter medium in removing wastewater pollutant. This study had also lead to many recommendations in order to improve the potential of activated carbon as a wastewater pollutant removal.

ABSTRAK

Malaysia adalah pengeksport kedua terbesar minyak sawit di dunia. Di Malaysia dan Indonesia, terdapat kira-kira 84% daripada eksport minyak sawit dunia dihasilkan. Tidak dapat dinafikan, tahap persekitaran kita dipengaruhi oleh industri kelapa sawit dan pemprosesan dan ia boleh membawa kepada kebangkitan pencemaran ekologi. Terdapat banyak jenis rawatan untuk meningkatkan kualiti POME dan salah satu daripada jenis itu adalah dengan menggunakan karbon yang diaktifkan. Tujuan kajian ini adalah untuk membandingkan dua proses pengaktifan karbon yang diaktifkan dalam mengurangkan bahan pencemar daripada sisa kilang minyak sawit (POME). Sampel telah diambil dari Kilang Kelapa Sawit Lepar Hilir, Kuantan, Pahang Darul Makmur. Karbon yang diaktifkan telah dihasilkan dengan dua kaedah yang berbeza iaitu pengaktifan fizikal (rawatan pirolisis) dan pengaktifan kimia (rawatan berasid). Parameter kualiti air juga dijalankan berdasarkan kaedah standard. Antara parameter kualiti air yang terlibat ialah pH, BOD, COD, Ammoniakal Nitrogen, kekeruhan, Minyak & Gris, Jumlah Pepejal Terampai dan Logam Berat (Boron, Kuprum dan Plumbum). Selepas menganalisis kualiti air kumbahan berdasarkan lapan parameter, kedua-dua sampel menunjukkan peningkatan dalam mengurangkan pencemar air sisa kerana kecekapan pemindahannya. Keputusan yang diperolehi akan dibandingkan dengan had dalam Akta Kualiti Alam Sekitar 1984. Antara dua sampel, karbon yang diaktifkan melalui kimia memberikan hasil yang paling berkesan kerana kecekapan penyingkiran tertinggi kecuali dalam parameter minyak dan gris. Keputusan peratusan penyingkiran untuk rawatan air sisa menggunakan karbon yang diaktifkan secara kimia untuk COD, BOD, TSS, AN, kekeruhan dan Minyak & Gris adalah antara 98.99-99.68% manakala bagi karbon yang diaktifkan fizikal keputusan adalah antara 97.69-99.63%. Daripada keputusan yang diperolehi, ia menunjukkan bahawa karbon yang diaktifkan mempunyai potensi untuk digunakan sebagai medium penapis dalam menghapuskan pencemar air sisa. Kajian ini juga telah membawa kepada banyak cadangan untuk meningkatkan potensi karbon yang diaktifkan sebagai penyingkiran air sisa bahan pencemar.

TABLE OF CONTENTS

	Page
TITLE PAGE	i
THESIS DECLARATION	ii
SUPERVISOR’S DECLARATION	iii
STUDENT’S DECLARATION	iv
DEDICATION	v
ACKNOWLEDGEMENTS	vi
ABSTRACT	vii
ABSTRAK	viii
TABLE OF CONTENTS	ix
LIST OF TABLES	xii
LIST OF FIGURES	xiii
LIST OF ABBREVIATIONS	xiv
 CHAPTER 1 INTRODUCTION	
 1.1 Background of Study	1
1.2 Problem Statement	5
1.3 Objectives	5
1.4 Scope of Study	6
1.5 Significance of Study	6
 CHAPTER 2 LITERATURE REVIEW	
 2.1 Introduction	8
2.2 Water Pollution	8
2.3 Types of Pollution	9
2.3.1 Point source pollution	9
2.3.2 Non-point source pollution	9
2.4 Causes of Pollution	9

2.5	Classifying Water Pollution	10
2.6	Palm Oil Mill Effluent (POME) and Treatment	11
2.7	Composition of POME	14
2.8	Activated Carbon	16
2.9	Characteristic of Activated Carbon	17
2.9.1	Adsorption Process	17
2.9.2	Differences between Adsorption and Absorption Process	19
2.9.3	Factors that affect Adsorption	20
2.10	Properties of Activated Carbon	21
2.10.1	Physical Properties	21
2.10.2	Chemical Properties	23
2.11	Types of Activated Carbon	24
2.11.1	Granular Activated Carbon (GAC)	25
2.11.2	Powdered Activated Carbon (PAC)	25
2.12	Method to Produce Activated Carbon	26
2.12.1	Carbonization	27
2.12.2	Physical Activation	28
2.12.3	Chemical Activation	29
2.13	Filter used for Activated Carbon Treatment Process	31

CHAPTER 3 METHODOLOGY

3.1	Introduction	32
3.2	Study Area	32
3.3	Flow Chart of the Methodology Study	34
3.3.1	Method to Produce Activated Carbon	36
3.3.2	Flow Chart of Water Quality Testing	39
3.4	Design of Bio-Sand Filter	40
3.5	Water Quality Parameters	41
3.5.1	pH	41
3.5.2	Chemical Oxygen Demand (COD)	41
3.5.3	Biochemical Oxygen Demand (BOD)	42
3.5.4	Total Suspended Solids (TSS)	43
3.5.5	Ammoniacal Nitrogen	43
3.5.6	Turbidity	43
3.5.7	Oil and Grease	44
3.5.8	Heavy Metals	44
3.6	Data Analysis	45

CHAPTER 4 RESULTS AND DISCUSSIONS

4.1	Introduction	46
4.2	Water Quality Results	47
4.2.1	pH	47
4.2.2	Chemical Oxygen Demand (COD)	48
4.2.3	Biochemical Oxygen Demand (BOD)	50
4.2.4	Total Suspended Solids (TSS)	51
4.2.5	Ammoniacal Nitrogen	52
4.2.6	Turbidity	53
4.2.7	Oil and Grease	54
4.2.8	Heavy Metals	55
4.3	Removal Efficiency (%)	55

CHAPTER 5 CONCLUSION AND RECOMMENDATION

5.1	Introduction	57
5.2	Conclusion	58
5.3	Recommendation	59

REFERENCES	60
-------------------	----

APPENDICES	65
-------------------	----

A Discharge Standard	65
----------------------	----

B Tabulated Data Analysis	66
---------------------------	----

C Process of Producing Activated Carbon	67
---	----

LIST OF TABLES

Table No.	Title	Page
1.1	2013 World palm oil productions	2
1.2	Parameters limits in respective standard discharge by the Malaysian Environmental Quality, 1984	3
2.1	Characteristics of palm oil mill effluent (POME)	13
2.2	The typical range of values for commercial activated carbons.	21
4.1	Characteristics of treated water sample	47
4.2	Results for pH	48
4.3	Results for COD	49
4.4	Results of BOD ₅	50
4.5	Results of Total Suspended Solids	51
4.6	Results of Ammoniacal Nitrogen	52
4.7	Results of Turbidity	53
4.8	Results of Oil & Grease	54
4.9	Results of Heavy Metals	55
4.10	Results of removal efficiency for all parameters	55

LIST OF FIGURES

Figure No.	Title	Page
1.1	2013 World palm oil production	2
2.1	Activated carbon adsorption diagram (Kvech, 1998)	18
2.2	Adsorption vs. Absorption (Dan Farrente, 1996)	19
3.1	Felda Palm Industries Sdn Bhd, Kilang Kelapa Sawit Lepar Hilir, Kuantan, Pahang Darul Makmur.	33
3.2	Wastewater sampling point.	33
3.3	Flow Chart of the Methodology	34
3.4	Flow chart process of producing Physically Activated Carbon from coconut shell.	36
3.5	Flow chart process of producing Chemically Activated Carbon from coconut shell.	37
3.6	Flow chart of variables that related in the experiment.	39
3.7	Testing Apparatus	40
4.1	Graph of pH against Water Samples	48
4.2	Graph of COD against Water Samples	49
4.3	Graph of BOD ₅ against Water Samples	50
4.4	Graph of TSS against Water Samples	51
4.5	Graph of AN against Water Samples	52
4.6	Graph of Turbidity against Water Samples	53
4.7	Graph of Oil and Grease against Water Samples	54

LIST OF ABBREVIATIONS

AC	Activated Carbon
AN	Ammoniacal Nitrogen
B	Boron
BOD	Biochemical Oxygen Demand
CACFS	Chemically Activated Carbon Filter System
CaCl ₂	Calcium Chloride
CO ₂	Carbon Dioxide
COD	Chemically Oxygen Demand
Cu	Copper
DO	Dissolved Oxygen
EQA	Environmental Quality Act
FFB	Fresg Fruit Bunches
FKASA	Fakulti Kejuruteraan Awam dan Sumber Asli
GAC	Granular Activated Carbon
IPA	Isopropyl Alcohol
MPOB	Malaysian Palm Oil Board
O&G	Oil and Grease
OPF	Oil Palm Fronds
OPT	Oil Palm Trunks
PAC	Powdered Activated Carbon
PACFS	Physically Activated Carbon Filter System

PKC	Palm Kernel Cake
POMS	Palm Oil Mill Sludge
POME	Palm Oil Mill Effluent
TSS	Total Suspended Solids
ZnCl ₂	Zinc Chloride

CHAPTER 1

INTRODUCTION

1.1 Background of Study

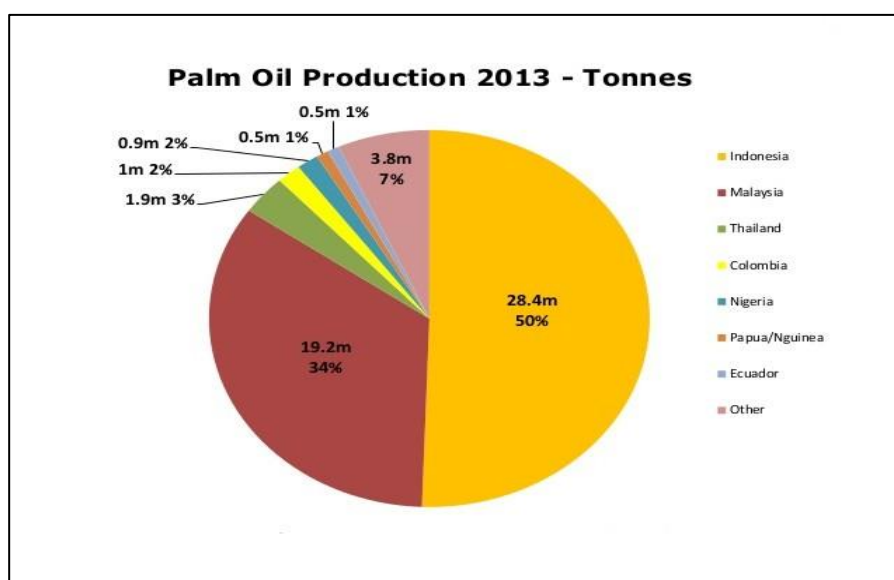
Water consists of two components of hydrogen and one component of oxygen. This compound also known as water is the most crucial substance to health. All plants and animals need water to survive. If there was no water there would be no life on earth. Fresh water is the vital element of environment and all living being. Contaminated water is dangerous to human health. Contaminated water from industrial sources contributes to contain of pollutants in wastewater. There is a water crisis today, but the crisis is not about having too little water to satisfy our needs. It is a crisis of managing water so badly that billions of people and the environment suffer badly (World Water Council, 2014).

Malaysia is the second leading exporter of palm oil in the world. In Malaysia and Indonesia, there are about 84% of world's palm oil exports are produced. In year 2013, the number of palm oil products exportation was rocketed to achieve 19.2 million tonnes. Table 1.1 and Figure 1.1 show the world palm oil production (MPOB, 2013).

Table 1.1: 2013 World palm oil productions

Countries	Tonnes (x10 ³)	% Share
Indonesia	28400	50
Malaysia	19200	34
Thailand	1900	3
Colombia	1000	2
Nigeria	900	2
Papua/Nguinea	500	1
Ecuador	500	1
Other	3800	7

Source: MPOB, 2013

**Figure 1.1:** 2013 World palm oil productions.

Indisputably, the level of our environment is affected by the oil palm industry and its processing and it may lead to the rise of ecological pollution. Moreover, the palm oil mill effluent (POME) causes negative impact to the environment. This industry has been causing the largest pollution load to rivers in whole country (Hwang et al. 1978). Physically POME is a dense brownish viscous liquid waste which is non-hazardous but has unpleasant smell which contains soluble materials that may have a major impact on the environment. The composition of POME are mainly water, oil,

suspended solid, dissolved solid and sand. In year 2008, almost 53 million tonnes of POME were generated in Malaysia (Phaik et al. 2010).

The palm oil industries should give importance towards the sustainability of environmental for future generation. Protection and management of water resources is necessary for sustainable environment. The regulation of effluent standard by the government stated under the Environmental Quality Act 1974, Revised 1984, provides the guidance for environmental management in general and water pollution control. In 1984, the Malaysia Environmental Quality stated standards for the palm oil mill effluents before discharging into streams that became strict as in Table 1.2 (Malaysian Environmental Quality, 1984). The final effluent samples have to satisfy the standard quality just then the results are obtained to be reported to the Department of Environment, Malaysia. Any difference in the expected quality of water resources may disturb the equilibrium of ecology (Murhekar Gopalkrushna, 2011).

Table 1.2: Parameters limits in respective standard discharge by the Malaysian Environmental Quality, 1984

Parameter	Units	Limits
Biochemical Oxygen Demand (BOD ₅)	mg/L	100
Chemical Oxygen Demand (COD)	mg/L	-
Suspended Solids	mg/L	400
Oil and Grease	mg/L	50
Lead (Pb)	mg/L	-
Copper (Cu)	mg/L	-
Boron (B)	mg/L	-
pH	-	5 - 9
Turbidity	NTU	-
Temperature	°C	45
Ammoniacal Nitrogen	mg/L	100

Source: Malaysian Environmental Quality, 1984

Coconut is the third most vital industrial yield in Malaysia after oil palm and rubber (Shafie, 2012). Coconut is known as a multipurpose plant species. Besides food aspect, coconut shell and husk are very favourable sources of activated carbon. In Malaysia, about 151,000 ha of land were used for coconut plantation in the year 2001 but this is gradually reducing every year due to competition with oil palm for land (Tan,

2008). Lately, a coconut industry revitalizing plan (2008–2015) was started to replant and rehabilitate the coconut plantation area (Sivapragasam, 2008).

Activated carbon is a type of carbon species that is prepared to have high porosity and very large surface area for adsorption (Ahmedna et al. 2000). Coconut shell is suitable for preparing micro porous activated carbon due to its natural structure and low ash content. Activated carbon can be prepared by physical activation or chemical activation. Coconut shell carbons have several advantages like high purity, high density. They are practically dust-free, since they are harder and more resistant to attrition (Elsheikh et al. 2003). There is a uniform pore structure distribution, with the majority of pores having size in the micro porous range. Activated carbon is used in gold purification, sewage treatment, metal extraction, water purification, gas purification, medicine, air filters in gas masks and respirators, filters uncompressed air and many other applications (Hammer, 2001).

Two-step process is involved in physical activation which needs carbonization material followed by activation at the high temperature in the presence of oxidizing gases such as carbon dioxide (CO_2) or steam. In the chemical activation process the carbon are soaked with dehydrating chemicals in a single step (Marsh et al. 2006). There are few types of activation processes such as acidic treatment, base treatment, impregnation, microwave treatment, ozone treatment, plasma treatment, biological modification and miscellaneous modification methods of activated carbon. Several modification methods are studied to increase the adsorption potential of activated carbon (AC) for diverse type of pollutants from wastewater and water. These methods have been found to modify the pore structure of carbon to certain extent. Commonly, acidic treatment of AC has been found favourable for the higher uptake of metal ions, while base treatment of AC favours in uptake of anionic species from aqueous solutions (Amit Bhatnagar et al. 2013).

Nowadays, water quality has become most wanted issue in this global. Most people require the best quality of water for their daily lives. Therefore, it needs treatment to make it safe for human and all living things in this world. There are many types of treatment that can improve water quality. To encounter the current problems

and challenges in POME treatment, it is suggested to use activated carbon to remove the pollutants. Activated carbon comes from different types of material such as saw dust, rice husk, wood, coconut shell and other but, this study was focused more on activated carbon from coconut shell. Furthermore, in this study was focused more on comparing the activation process between physical activation and chemical activation of activated carbon in removing pollutants from palm oil mill effluent.

1.2 Problem Statement

Due to the rapid growth and innovation of nowadays technology, there is suggestion to apply membrane separation technology for removing pollutants. However, the palm oil mill industry still do not apply and used the membrane technology to treat POME due to the high cost for installation of the membrane set up and maintenance. Furthermore, it requires highly skilled operators for the operation process. Furthermore, convectional biological treatments of anaerobic and facultative are applied in palm oil mill management. However this system requires appropriate maintenance and controlling such as quite a number of labour force and cost. In previous study, many types of activating processes were used to produce the activated carbon. The needs to identify the most effective and suitable activating process is crucial because it can produce best result and effectiveness of wastewater treatment.

1.3 Objectives

The main objectives of this study are as follows:

- i. To produce physically and chemically activated carbon.
- ii. To prepare the bio-sand water filter based on two types of activated carbon.
- iii. To obtain the most suitable and effective activation process in pollutants removal from palm oil mill effluents.

1.4 Scope of Study

Scope of study can be listed as follows:-

- i. Palm oil effluent samples were taken from oil palm industrial effluent at Kilang Kelapa Sawit Lepar Hilir, Gambang, Kuantan, Pahang Felda estate area.
- ii. The samples were analysed at FKASA Environmental Laboratory at Universiti Malaysia Pahang to determine their characteristics based on the water quality parameters such as Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), pH, Total Suspended Solids (TSS), Turbidity, Oil and Grease, Ammoniacal Nitrogen and Heavy Metals (Boron, Copper and Lead).
- iii. The activated carbon was produced using coconut shell by activation process.
- iv. The effluent samples were treated using activated carbon to identify their effectiveness and performances.

1.5 Significance of Study

Contrary to the past, our recent developed technological society has become indifferent to this miracle of life. Our natural heritage (rivers, seas and oceans) has been exploited, mistreated and contaminated. Thus, it is beneficial to our industry because it can improve water quality of the streams. When water quality is improved, it is safe for living things especially human being use the water to drinks, bath and so on. Other than that, there is a lot application of coconut shell as activated carbon such as gas purification, gold purification, metal extraction, water purification and so on.

This activated carbon do not required highly skilled operators to handle compare to the membrane separation technology. Coconut shell and husk is quite abundant in our country since coconut is the third most vital industrial yield in Malaysia. There are two types of carbon activation which are physical and chemical activation. In this study, both physical and chemical activation processes were compared in order

to identify the most suitable and effective activation process of activated carbon from coconut shell as wastewater pollutant removal.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

This literature review justifies all the important information and relevant data regarding this study and briefly discussed and supported with all articles reviews extracted from journals, e-book, references book, thesis, internet articles and other relevant sources.

2.2 WATER POLLUTION

Water pollution is a major global problem which needs frequent supervision globally. It has been stated that it is the current cause of deaths and diseases, and that it have cause for deaths of more than 14,000 people daily. Approximately 700 million Indians have no access to a proper toilet, and 1,000 Indian children die of diarrhoea sickness every day. Some 90% of China's cities suffer from water pollution, and almost 500 million people lack access to safe drinking water. In addition to the acute problems of water pollution in developing countries, industrialized countries continue to struggle with pollution problems as well. In the most recent national report on water quality in the United States, 45% of assessed stream miles, 47% of assessed lake acres, and 32% of assessed bay and estuarine square miles were classified as polluted (Wikipedia, 2015).

2.3 TYPES OF POLLUTION

Surface water and groundwater have often been studied and managed as separate resources, although they are interrelated. Sources of surface water pollution are generally grouped into two categories based on their origin (Wikipedia, 2015).

2.3.1 Point source pollution

Point source pollution is the contaminants that enter a channel through a discrete passage, such as a pipe or ditch. Examples of sources in this category include discharges from a sewage treatment plant, a factory, or a city storm drain. The U.S. Clean Water Act (CWA) defines point source for regulatory enforcement purposes. The CWA definition of point source was amended in 1987 to include municipal storm sewer systems, as well as industrial storm water, such as from construction sites (Wikipedia, 2015).

2.3.2 Non-point source pollution

Non-point source (NPS) pollution is the diffusion of contamination that does not originate from a single discrete source. NPS pollution is often accumulative effect of small amounts of contaminants gathered from a large area. The leaching out of nitrogen compounds from agricultural land which has been fertilized is a typical example. Nutrient runoff in storm water from "sheet flow" over an agricultural field or a forest is also cited as examples of NPS pollution (Wikipedia, 2015).

2.4 CAUSES OF POLLUTION

Many causes of pollution including sewage and fertilizers contain nutrients such as nitrates and phosphates. In excess levels, nutrients over stimulate the growth of aquatic plants and algae. Excessive growth of these types of organisms consequently clogs our waterways, use up dissolved oxygen as they decompose, and block light to deeper waters. This in turn, proves very harmful to aquatic organisms as it affects the

respiration ability of fish and other invertebrates that reside in water (Krantz and Kifferstein, 1997).

Pollution is also caused when silt and other suspended solids, such as soil, wash off ploughed fields, construction and logging sites, urban areas, and eroded river banks when it rains. Under natural conditions, lakes, rivers, and other water bodies undergo Eutrophication, an aging process that slowly fills in the water body with sediment and organic matter. When these sediments enter various bodies of water, fish respiration becomes Impaired, plant productivity and water depth become reduced, and aquatic organisms and their environments become suffocated.

Pollution in the form of organic material enters waterways in many different forms as sewage, as leaves and grass clippings, or as runoff from livestock feedlots and pastures. When natural bacteria and protozoan in the water break down this organic material, they begin to use up the oxygen dissolved in the water. Many types of fish and bottom-dwelling animals cannot survive when levels of dissolved oxygen drop below two to five parts per million. When this occurs, it kills aquatic organisms in large numbers which leads to disruptions in the food chain (Krantz and Kifferstein, 1997).

2.5 CLASSIFYING WATER POLLUTION

The major sources of water pollution can be classified as municipal, industrial, and agricultural. Municipal water pollution consists of waste water from homes and commercial establishments. For many years, the main goal of treating municipal wastewater was simply to reduce its content of suspended solids, oxygen-demanding materials, dissolved inorganic compounds, and harmful bacteria. In recent years, however, more stress has been placed on improving means of disposal of the solid residues from the municipal treatment processes. The basic methods of treating municipal wastewater fall into three stages which are primary treatment, including grit removal, screening, grinding, and sedimentation; secondary treatment, which entails oxidation of dissolved organic matter by means of using biologically active sludge, which is then filtered off; and tertiary treatment, in which advanced biological methods of nitrogen removal and chemical and physical methods such as granular filtration and

activated carbon absorption are employed. The handling and disposal of solid residues can account for 25% to 50% of the capital and operational costs of a treatment plant.

The characteristics of industrial waste waters can differ considerably both within and among industries. The impact of industrial discharges depends not only on their collective characteristics, such as biochemical oxygen demand and the amount of suspended solids, but also on their content of specific inorganic and organic substances. Control can take place at the point of generation in the plant; wastewater can be pre-treated for discharge to municipal treatment sources; or wastewater can be treated completely at the plant and either reused or discharged directly into receiving waters (Krantz and Kifferstein, 1997).

2.6 PALM OIL MILL EFFLUENT (POME) AND TREATMENT

Concomitant production of huge wastes always results from processing of oil palm fresh fruit bunches (FFB) primarily for palm oil. During processing in palm oil mills, more than 70% (by weight) of the processed FFB is usually left over as oil palm wastes (Prasertan, 1996). The wastes products from oil palm processing consist of oil palm trunks (OPT), oil palm fronds (OPF), palm oil mill effluent (POME), empty fruit bunches (EFB), palm press fibre (PPF), shell palm oil mill sludge (POMS), and palm kernel cake (PKC) (Singh, 2010).

POME consists of water soluble components of palm fruits as well as suspended cellulosic materials like palm fibre, fat, grease and oil residues (Agamuthu, 1995). However, among the wastes that are generated from processing of oil palm fruits, POME is considered the most harmful waste to the environment if discharge untreated (Rupani et al. 2010).

POME is a colloidal suspension originating from mixture of sterilizer condensate, separator sludge and hydro cyclone wastewater in a ratio of 9:15:1 respectively (Wu et al. 2010). About 2.5-3.0 tonnes of POME per tonnes of produced crude oil is obtained in the extraction processes. POME, when fresh, is a thick brownish colloidal mixture of water, oil and fine suspended solids (Borja & Bank, 1994). It is hot

(80-90oc) and possesses a very high Biochemical Oxygen Demand (BOD) which is non-toxic as no chemicals are added to the extraction process and also acidic with a PH of around 4.5 as it contains organic acids in complex forms that are suitable to be used as carbon sources. The suspended solids or particulate fraction of the effluent contribute with less than 50% to the total pollutant level (Md Din et al. 2006).

POME may vary considerable for different batches, days and factories, processing techniques and the age or type of fruit (Ng et al. 1987). The nature of POME may as well depend on the discharge limit of the factory, climate and condition of the palm oil processing. The raw or partially treated POME has an organic matter which is due in part to the presence of unrecovered palm oil. This highly polluting wastewater can cause pollution of water –ways due to oxygen level in rivers leads to anaerobic conditions and the release of noxious gases, particularly hydrogen sulphide (Ahmad et al. 2006). Thus, the natural ecology of the rivers is destroyed (Khalid & Wan Mustafa, 1992). Raw or untreated POME is characterized by high BOD often in the range of 25,000gm/l or higher as shown in Table 2.1.

Table 2.1: Characteristics of palm oil mill effluent (POME)

Parameter	POME (Average)	Range
pH	4.2	3.4 – 5.2
Oil and grease	4,000	-
Biochemical oxygen demand (BOD)	25,000	10,250 – 43,750
Chemical oxygen demand (COD)	51,000	15,000 – 100,000
Total solids	40,000	11,500 – 79,000
Suspended solids	18,000	5,000 – 54,000
Total volatile solids	34,000	9,000 – 72,000
Ammoniacal nitrogen (NH ₃ -N)	35	4 -80
Total nitrogen (T.N.)	750	180 – 1,400
Phosphorous (P)	180	-
Potassium (K)	2,270	-
Magnesium (Mg)	615	-
Calcium (Ca)	439	-
Boron (B)	7.6	-
Iron (Fe)	46.5	-
Manganese (Mn)	2.0	-
Copper (Cu)	0.89	-
Zinc (Zn)	2.3	-

*All values are in mg/L except pH

Source: MPOB, 2013

There are numerous advanced approaches that have been developed and used by palm oil mills for the treatment of POME. Usually convectional biological treatments of anaerobic and facultative digestion are used in palm oil mill management. The anaerobic and facultative ponds depend on bacteria to break down the organic matters into final products of carbon dioxide, methane, hydrogen sulphide and water. But, this convectional biological treatment system needs appropriate maintenance and monitoring such as increase the labour force and cost. The microorganisms are very sensitive to the surrounding temperature and pH and have to ensure a favourable environment for the microorganism to grow (Ahmad, 2003). This treatment also required large treatment area with a long treatment periods usually 80 to 120 days (Chan and Ahmad, 2009).

Moreover, biological treatment also generates vast amounts of biogas, which is corrosive and odorous. This biogas contains methane, carbon dioxide and trace amounts of hydrogen sulphide. These gases are corrosive and dangerous. Moreover, methane gas is more potent and fire hazard (Ahmad, 2003).

To encounter the current problems and challenges in POME treatment, it is suggested to apply membrane separation technology. This technology is in a state of rapid growth and innovation. There are several advantages to use membrane separation technology. It can be applied across a wide range of industries; the quality of the treated water is more consistent regardless of the influent variations; it can be used in a process to allow the recycling of selected waste streams within a plant; highly skilled operators would not be required when the plant can be fully automated (Cheryan and Rajagopalan, 1998) and the water reclaimed from this treatment could be reused in the mill. Thus, the primary advantages lie in the reduction of the cost for the water supply and its further treatment as well as in the effective elimination of the pollutant from the POME. However, the palm oil mill industry still does not apply and use the membrane technology to treat POME due to the high cost for installation of the membrane set up and maintenance. The cost for maintenance can be reduced by first pre-treating the POME to lower the concentration of the colloidal particles which can cause damage and fouling before applying it to ultrafiltration membrane.

Moreover, the operational time of membrane technology was lesser than other conventional treatment and the cost of the treatment can be reduced simultaneously. Hence, high cost in set up installation was only at the beginning to compare with the cost of treatment area and time consuming for conventional treatment which is more expensive.

2.7 COMPOSITION OF POME

Composition of POME depends mainly on raw material quality, season and the particular operations being used at any given time. As stated earlier, POME when fresh is a thick brownish colloidal mixture of water, oil and fine suspended solids. It is hot (80-90°C) and possesses high amounts of total solids (40,500g/l), very high BOD of

25,000gm/l, Chemical Oxygen Demand (COD) of 50,000gm/l, oil and grease of 4,000gm/l. POME is non-toxic, as no chemicals are added during extraction process (Khalid & Wan Mustafa, 1992). However, POME is low in PH because of the organic acids produced in the fermentation process; it is acidic with PH of about 4.5 as it contains organic acids in complex forms that are suitable to be used as carbon source (Md Din et al. 2006). POME consist of water soluble components of palm fruits as well as suspended materials like oil residues, short palm fibre, cell walls, organelles, a variety of carbohydrates ranging from cellulose to simple sugars, a range of nitrogenous compounds from proteins to amino acids, free organic acids and assembly of minor organic and mineral constituents (Ugoji, 1997).

Nutrients contains in POME are nitrogen, phosphorus, potassium, magnesium and calcium, which are all vital nutrients elements for plant growth. High content of A1 in POME as compared to chicken manure and composted sawdust was also stated (Muhrizal et al. 2006). According to Habib et al. (1997), toxic metals such as lead can also be found in POME (Habib et al.1997). However, the lead concentration are usually below sub lethal levels ($> 17.5 \text{ ug/g}$) and in their view lead is found in POME as a result of contamination from plastic and metal pipes, tanks and containers where lead is widely used in paints and glazing materials (James et al. 1996).

POME, despite its biodegradability, cannot be discharged without first being treated because it is acidic and contains residual oil that cannot be easily separated using conventional gravity-based systems. Basically, this oily mix needs a lot of oxygen before it can decomposed completely, and this phenomenon is called having high biochemical oxygen demand, and raw POME can sometimes have BOD of up to 100 times higher than that of domestic sewage. Because POME still contains a significant amount of organic matter even when treated, still imposes a demand on the environment. Microbes in water take in dissolved oxygen as they digest organic matter. This demand for oxygen known as BOD is usually measured in milligrams per litre (mg/l) and is normally used as an indication of the organic quality or the degree of organic pollution of water. Basically a higher BOD means poorer quality, and the inverse holds true as well.

Consequently, it has been observed that the microbial population increases in proportion to the amount of food available. In such conditions, the microbial action will consume dissolved oxygen faster than atmospheric oxygen can dissolve in the water. Apparently, fish and other aquatic organism might die because the water body has been depleted of its oxygen.

2.8 ACTIVATED CARBON

Nowadays activated carbon has been widely used and can be produced from any of carbonaceous source materials. Coconut shell is suitable for preparing microporous activated carbon due to its low ash content and good natural structure (Su Wei et al. 2006).

Activated carbon can be produced by chemical activation or physical activation. Physical activation is a simple process that produces activated carbon with steam or CO₂ as activation agent, which does not produce any wastewater. Through this approach, the overall production of an activated carbon from coconut shell is about 8% (by mass). Air activation is economically worth for its high yield, low energy cost and overall short activation time. However it is not frequently used since its high reactivity is very hard to control. But, its high reactivity can be controlled under certain condition. In the two step processes, activated carbon needs to be heated to high temperature twice through this much energy is to be consumed. Then it needs several hours to be cooled down to the room temperature from the high carbonization temperature before the charcoal is oxygenated. In chemical activation, issue production cost, concerning corrosion and wastewater treatment prohibited further development of this method (Su Wei et al. 2006).

Activated carbon is frequently used in water treatment systems as a filter, where water is channelled downwards through a stationary bed of activated carbon, leaving organic material to collect at the top of the bed. Activated carbon is similarly used to lower radon level in water (John, 2003).

2.9 CHARACTERISTIC OF ACTIVATED CARBON

Activated carbon has been explained in different ways by several authors. Activated carbon is known as porous carbon, which has been treated by oxidizing gases during or after carbonization in order to increase porosity. Activated carbon is an organic material constituted basically by a graphitic structure. Activated carbon is known as predominantly an adsorbent with a large internal pore volume and surface area (Marsh, 1989).

Activated carbon is the generic term used to describe a family of amorphous carbonaceous adsorbents with a highly crystalline form and well developed internal pore structure. In general terms, one can differentiate two types of carbon which are graphitizable and non graphitizable. Carbon is converted into graphite when it is burned to 3000°C in an inert atmosphere. Activated carbons belong to the second group –non-graphitizable carbon and are prepared from rich carbon materials that do not pass through a fluid phase during carbonization (Marsh, 1989).

A wide variety of commercial activated carbon products are available showing different characteristics depending on the starting material and activation method used in their production. Wood, coal, lignite, coconut shell and peat are the most important raw materials for the production of activated carbons, although other materials such as synthetic polymers or petroleum residues can also be used (Marsh, 1989).

2.9.1 Adsorption Process

Adsorption is the process by which activated carbon removes substances from water. Defined, adsorption is “the collection of substances onto the surface of adsorbent solids”. It is a removal process where certain particles are bound to an adsorbent particle surface by either chemical or physical attraction. Adsorption is often confused with Absorption, where the substance being collected or removed actually penetrates into the other solid (Reynolds and Richards, 1996).

The reason that activated carbon is such an effective adsorbent material is due to its large number of cavernous pores. These provide a large surface area relative to the size of the actual carbon particle and its visible exterior surface. An approximate ratio is 1 gram = 100 m² of surface area (Reynolds and Richards, 1996). Adsorption is a physicochemical phenomenon in which a solid, called adsorbent, retain in the walls a certain kind of molecules, called adsorbates, that are contained in a gas or liquid. Hence it is a separation and concentration process of one or more compounds of a system on a solid or liquid surface. The most employed adsorbents are silica, some synthetic resins and activated carbons.

There can be three types of adsorption attributed to the adsorbent-adsorbate attraction is electrical, Van der Waals or chemical. The first type is commonly called ion exchange because the ions of a substance are concentrated on the surface as a result of an electrostatic attraction. The Van der Waals adsorption also known as physical adsorption and takes place when the molecule is bound into the interphase usually at low temperatures. Most of organic compounds that are in water are adsorbed with activated carbons for this type of adsorption. The chemical adsorption is a reaction between the adsorbate and the adsorbent due to their chemistry and is characterized for being strong in the active point of the adsorbent (Reynolds and Richards, 1996).

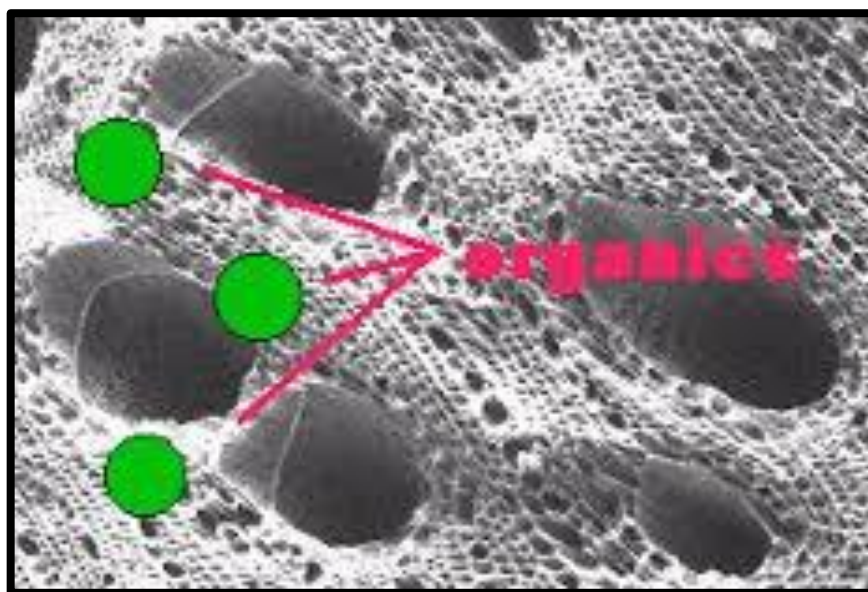


Figure 2.1: Activated carbon adsorption diagram (Kvech, 1998)

2.9.2 Differences between Adsorption and Absorption Process

Sorption reactions generally occur over a short period time, however if the adsorbed contaminant begins to be incorporated into the structure of the sorbent, a slow occurring reaction, known as absorption is that adsorption is the attraction between the outer surface of a solid particle and a contaminant, whereas absorption is the uptake of the contaminant into the physical structure of the solid (Dan Farrente, 1996).

This figure shows the primary differences between intraparticle absorption versus surface adsorption. The main difference being that some contaminant particles are attracted to the outer surface of the soil particles, while another has been actually incorporated into the particles' structure (Dan Farrente, 1996).

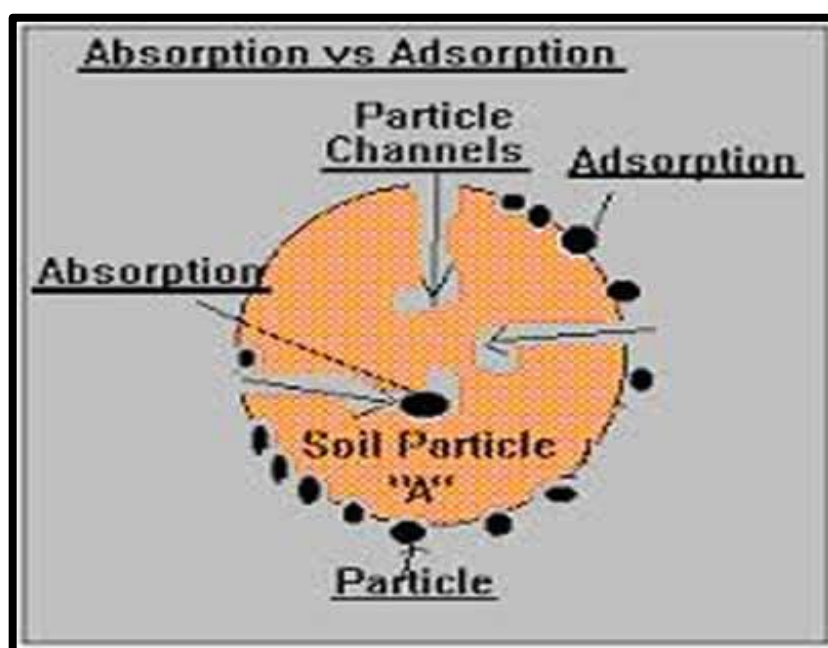


Figure 2.2: Adsorption vs. Absorption (Dan Farrente, 1996)

2.9.3 Factors that affect Adsorption

Adsorption is influenced by the properties of the carbon and the adsorbate as well as the conditions of the gas and liquid.

i) **Properties of the carbon**

A correct pore size distribution is necessary to facilitate the adsorption process by providing adsorption sites and the appropriate channels to transport the adsorbate. A relevant parameter is the pore volume estimated as the liquid volume of adsorbate adsorbed at a relative pressure. It is important to determine the micropore volume and microporous surface area due to the high relevance that have in the adsorption process.

ii) **Properties of the adsorbate**

Almost all kinds of organic molecules can be adsorbed. Otherwise, there is practically no adsorption of inorganic substances to the activated carbon surface, though there are some exceptions as silver salts or iodine.

Adsorption of organic compounds is stronger if its molecular weight is greater, provided that the size of the molecule is no greater than the pore size. The n-polar organic molecules are well adsorbed than the polar ones, as well as, the major part of organic molecules that have bound chlorine, bromine or iodine atoms. Adsorption increases in liquid medium where the solubility of the adsorbate decreases.

iii) **Properties related with the gas or liquid temperature**

In liquid phase when the pH decreases the adsorption increases generally. At high temperatures the solubility of the adsorbate is higher and the adsorption is more complicated, although, when the temperature goes up the viscosity is lower

and the adsorbate is moved easily inside the pores. Summing up, as the temperature increases so does the adsorption.

Table 2.2: The typical range of values for commercial activated carbons.

Properties	Value
Specific surface area, BET (m ² /g)	600 – 1500
Total pore volume (m ³ /g)	0.6 -1.8
Apparent density (g/cm ³)	0.3 -0.7
Granularity (mm) a: dust ; b: granular	0.05 – 0.1 (a) ; 0.1 – 2 (b)
Ash percentage (%)	2 -10
Uniformity coefficient (grain)	1.1 - 12

Source: KTH Chemical Science and Engineering

2.10 PROPERTIES OF ACTIVATED CARBON

The characterization of the active carbons requires information on both physical and chemical properties of the materials. On the physical side, one must obtain information such as moisture and ash content, as well as the pore structure and the size of the pores that determine how adsorption does take place. The chemical properties to have in consideration are the specific surface area and the surface chemistry.

2.10.1 Physical Properties

Generally activated carbons are stored under dry conditions if not it might adsorb considerable moisture. Actually they may adsorb as much as 25 to 30% moisture and still appear dry. For many purposes, the moisture content does not affect the adsorptive power, but obviously it dilutes the carbon. However, an additional weight of moist carbon is needed to provide the required dry weight.

The total amount of inorganic constituents will vary from one carbon to another depending on the source of materials and from activating agents added during manufacture. Ash content can lead to increase hydrophobicity and can have catalytic effects, causing restructuring process during regeneration. The inorganic material

contained in activated carbon is generally in the range between 2 and 10% as can be seen in Table 2.2.

A pore is a kind of cavity which is linked to the surface of a solid and allows the connection of fluids into, out of, or through a material. Basically, the pores are classified in three groups according to the International Union of Pure and Applied Chemistry (IUPAC) defining the diameter of the pore as:

- a) Micropores : $D < 2 \text{ nm}$
- b) Mesopores : $2 < D < 50 \text{ nm}$
- c) Macropores : $D > 50 \text{ nm}$

Activated carbon is a mixture of the three size pores and each one has different functions. The micropores are the most important ones due to their high surface area which gives them the higher adsorption capacity because of their smaller size; similar to the molecules that will be adsorbed.

The mesopores have a double function, at sufficiently high pressures condensation take place forming a meniscus and, secondly, serve as a step towards the micropores. The typical molecules retained in these pores are those ones where the sizes are between the micropores and macropores range.

Macropores are the big size pores and cannot be filled by capillary condensation. Their main function is to communicate the external surface of the activated carbon with the mesopores. Actually, the surface of the macroporous may be regarded as nonporous, though its importance lies in the liquid retention that may occur. For that reason one of the main functions of the macroporous is to ensure that the adsorbate arrives quickly to the smaller size pores located deeper in the activated carbon.

Activated carbons are widely known for the high specific surface area, which provides a well-developed porosity. The typical values ranged from $500 \text{ m}^2/\text{g}$ to $3000 \text{ m}^2/\text{g}$ and can be explained by the micropore structure (Reffasa, 2010). One can think that for a higher surface area, the adsorption characteristics as adsorbent will be

better because there will be more points where the adsorbates could be retained. However, depending on whether the adsorbate molecules size is bigger than some of the micropore size not all surfaces will be available for those molecules. At the same point the geometry of the adsorbate and the pore have to be taken into consideration as well.

2.10.2 Chemical Properties

The physical properties and the chemical composition of the starting material, as well as the methods and process conditions employed for activation, determine the pore size distribution and the adsorption properties of the activated carbon (Haimour et al. 2006). One of the parameters that differentiate one material from another is its composition, i.e. lignin, cellulose and halocellulose. Materials with a greater content of lignin as grape seeds or cherry stones develop activated carbon with a predominance of macroporous, while other raw materials characterized by having a higher content of cellulose as apricot stones or almond shells produce activated carbons with a predominantly microporous structure (Ioannidou et al. 2007). It is easier to carry on with the preparation of activated carbons having more cellulosic content instead of having high lignin content (Daud et al. 2004).

Furthermore of the porosity properties, the chemical surface characteristics of the solid develop specific surface complex which are also important in the adsorptive process. Activated carbons show a lack of specificity in molecules retention but will retain easily polar molecules, like hydrocarbons and dyes; while compounds like water, nitrogen and oxygen are not retained a lack in a retention process.

The chemistry of the carbons takes place essentially on the edges of the graphitic sheets where a variety of oxygen groups or other induced chemical groups is found. One of the most important and studied is the oxygen complex; those ones are formed by the reaction between the carbon and the oxygen as well as reaction with oxidizing agents. Other compounds as hydrogen, nitrogen, phosphorous or sulphide could be mixed with carbon to form superficial complex but in a less quantity. The surface chemistry of an activated carbon is related to the presence of heteroatoms

(oxygen, hydrogen, and nitrogen) within the carbon matrix resulting in superficial complex (Robert Considine et al. 2001).

Polar molecules are adsorbed weakly on the surface of the carbon, where the fixation of heteroatoms in the carbon create functional groups as carboxylic acids, lactones, etc which increases the affinity of polar molecules for the carbon surface. These heteroatoms found on an activated carbon surface are directly attributed to three factors: the starting material, method of activation and treatment conditions; and are chemically bonded to the carbon surface during the carbonization and activation, forming carbon- heteroatom structures (Robert Considine et al. 2001).

The surface chemistry of activated carbons determines its:

- a) Moisture content,
- b) Catalytic properties
- c) Acid-base character
- d) Adsorption capacity

The efficiency of a carbon for removing a given pollutant depends on both its adsorption capacity and its surface chemistry. Particularly, adsorption of substances with high polarity and low molecular weight will be very complicated and will take place easily if the carbon is impregnated with specific chemicals or are used properly the catalytic properties of the carbon.

2.11 TYPES OF ACTIVATED CARBON

Two types of activated carbon use which are, formed activated carbon (FAC) and granular activated carbon (GAC). Granular activated carbon usually used in water treatment and very useful for micro-pollutant removal. Whereas FAC is cylindrical in shape and results better in hydraulic condition and pore size distribution compared to GAC (John, 2003).

There are three types of activated carbon which are powdered activated carbon (PAC), granular form called granular activated carbon (GAC) and activated carbon fiber (ACF) (Accardio et al. 2003).

2.11.1 Granular Activated Carbon (GAC)

GAC is extremely porous adsorbent material which produced by heating organic matter, such as coal, wood and coconut shell, which is then crushed into granules. Negative ions from the water such as ozone, chlorine, fluorides and dissolved organic solutes can be removed by absorption onto the activated carbon, since the activated carbon is positively charged. The activated carbon must be changed from time to time as it may become saturated and unable to perform. Activated carbon is not useful in removing heavy metals. Activated carbon is frequently used in water treatment systems as a filter, where water is channelled downwards through a stationary bed of activated carbon, leaving organic material to collect at the top of the bed. Activated carbon is similarly used to lower radon level in water (Wikipedia, 2015)

Granular activated carbon: Those carbons show an average particle size between 1 to 5 mm. GAC can be divided into two categories which are chopped carbon (formless) and formed carbon with a specific form as cylindrical. The first type is obtained by milling and sieving while the second ones are a mixture of carbon and a binder. Furthermore, there also other forms of carbon adsorbents as activated carbon fibres, filters of activated carbon, monolithic structures, carbon membranes, etc. Those carbons are valuable for their hardness and particle size. Much of the operation cost is caused for the attrition during the regeneration and normal work (Wikipedia, 2015)

2.11.2 Powdered Activated Carbon (PAC)

Active carbons are made in the form of powders or fine granules which is less than 1.0 mm in size with an average diameter between 0.15 and 0.25mm. Thus they present a large surface to volume ratio with a small diffusion distance. PAC is made up of crushed or ground carbon particles, 95-100% of which will pass through a designated mesh sieve or sieve. Granular activated carbon is defined as the activated carbon being

retained on a 50-mesh sieve (0.297mm) and PAC material as finer material, while ASTM classifies particle sizes corresponding to an 80-mesh sieve (0.177 mm) and smaller as PAC. PAC is not commonly used in a dedicated vessel, owing to the high head loss that would occur. PAC is generally added directly to other process units, such as raw water intakes, rapid mix basins, clarifiers and gravity filters (Wikipedia, 2015).

2.12 METHOD TO PRODUCE ACTIVATED CARBON

Coconut shell is used for manufacturing a variety of including activated carbon. Coconut shell is carbonized by using methods like drum method, pit method, destructive distillation and others. Coconut shell based activated carbon is widely used in the production of refining and bleaching of vegetables oils and chemical solutions, water purification, recovery of solvents, recovery of gold and others. Coconut shell based activated carbon units adopt steam activation process to produce good quality activated carbon. Activated carbon is a non-graphite form of carbon which could be produced from any carbonaceous material such as coal, lignite, wood, paddy husk, coir pith, coconut shell, etc. (Bhavan, 2009). Steam activation and chemical activation are two commonly used processes for the manufacture of activated carbon. However coconut shell based activated carbon units is adopting the steam activation process to produce good quality activated carbon (Bhavan, 2009).

However, form other opinion, activated carbon is produced from coconut shell char using steam or carbon dioxide as the reacting gas in a 100 mm diameter fluidized bed reactor. The effect of process parameters such as reaction time, fluidizing velocity, particles size, static bed height, temperature of activation, fluidizing medium and solid raw material on activation is studied. The product obtained in the fluidized bed reactor is much superior in quality to the activated carbons produced by the conventional processes. Based on the experimental observations, the optimum values of process parameters are identified (Ahmed, 1997).

Method to produce activated carbon is first, separate and clean coconut shell from other materials, such as coconut fiber or soil, then dry it under the sun and next burn dried coconut shell at burning sink or drum at 300-500°C for 3-5 hours. After that,

soak charcoal in chemical solution (CaCl_2 or ZnCl_2 25%) for 12-18 hours to become activated charcoal then wash charcoal with distilled/clean water, spread on tray at room temperature to be drained, next, dry in oven at temperature 110°C for 3 hours and crush or refine activated charcoal in plastic (Food & Fertilizer Technology Center, 2004)

Other method to produce is first, clean up the coconut shell to remove other contaminants. After cleaning up, dry it with temperature of 105°C for one hour. Next, go through pyrolysis process where the dry coconut shells were placed inside furnace in 550°C for 2 hours. After that, take the burning coconut shell cleans it with distilled water and last, drying it inside the furnace again at temperature of 105°C for one hour. Then, then final product of activated carbon from coconut shell will produce (Masha Nur Salsabiela, 2006).

2.12.1 Carbonization

The first step is a thermal treatment of the raw material that implies dehydration and where most of the non-carbon elements as dust and volatile substances are eliminated by heating the source in anaerobic conditions. The aim of the carbonization stage is to conserve the carbonaceous structure of the material which is achieved by burning off the material in a range of temperatures from 400°C to 850°C (Juntgen, 1977).

The char is constituted when carbon atoms regroup themselves into sheets forming rigid and dense clusters of microcrystals, each one consisting on several layers of graphitic planes. Each atom inside one stack is bonded to four adjacent carbon atoms. Thus, the carbon atoms on the edges of the planes have a high adsorption potential available.

The internal structure is not homogeneous neither regular; leaving free interstices that constitute the porosity of the char. These interstices may be filled or blocked by disorganized carbon resulting from deposition and decomposition of tars making them not always accessible and reducing the porosity (Namanee et al. 2005). Pyrolysis of lignocellulosic materials in an inert atmosphere produces a non-

graphitizable char, because burning off polymeric cellulose or lignin, the typical composition of the raw materials used, during that step liberates most of the non-carbon elements mainly hydrogen, oxygen, and nitrogen in the form of gases and tars, leaving behind a rigid carbon skeleton (Moreno-Castilla et al. 2001).

i) Products and Their Characteristic of Carbonization

The primary products can be gas, liquid and solid depending on the process employed. The liquid, when formed, approximates to biomass in elemental composition with a slight higher heating value of 20-25MJ/Kg, and is composed of a very complex mixture of oxygenated hydrocarbons. The complexity arises from the degradation of lignin, and the broad spectrum of phenolic compounds. The liquid is often called oil, but is more like tar. This also can be degraded to liquid hydrocarbon fuels. The crude pyrolysis liquid is a thick black tarry fluid with up to 20% of water and viscosity as heavy oil. The solid products from pyrolysis process is char, which has limited application in developed countries for metallurgical and leisure use. An alternative approach to liquid products lies in grinding the char and slurry it with water with a stabilizer (Natural Resources and Environment, 1994).

2.12.2 Physical Activation

The objective of the activation process is to enhance the pore structure. The physical activation is the partial gasification of the char with steam, carbon dioxide and air, or a mixture of these, at temperatures around 1100- 1250K. Once the no desirable materials have been removed the char is accessible. The main change is an increase in pore volume making the crystallites become exposed to the action of the activating agent (oxidizing gases) for further development of porosity with increasing burn-off. The oxidizing gases employed, steam or CO₂, are reactive agents that reacts with the raw material and also remove volatile material from the solid.

The experimental information described in the literature on the gasification rate of different forms of carbon such as graphite, coke and chars show that, for a given

temperature, the reactivity with steam is larger than with carbon dioxide. However, when the effect of the activating agent on the development of porosity is analysed, the results do not show a clear tendency, for example for the graphite. Most important variables in the gasification process from the point of view of porosity development are:

- a) Activating agent
- b) The final burn-off reached
- c) The presence of inorganic impurities that catalyse or inhibit the gasification reaction

2.12.3 Chemical Activation

The term, chemical activation is referred to the pyrolysis of the starting material which have been previously added some chemical as phosphoric acid or zinc chloride that restrict the formation of tar; in this way, a carbonized product with a well-developed porosity may be obtained in a single operation. All the agents involved in the chemical activation have a common feature of being dehydrating agents that influence during the pyrolytic decomposition and inhibit the formation of tar increasing the yield of carbon.

The yield and properties of activated carbons depend on the impregnation conditions, such as impregnation ratio (weight of activating reagent/ weight of carbon precursor), time of pre-drying impregnated materials, as well as pyrolysis conditions, such as temperature, soaking time (period of time that the sample and chemical are in contact) and atmosphere. All these process variables vary with the type of carbon precursor and the activating agent.

The main impregnation condition is the chemical ratio, one of the most important parameter in the production of activated carbon by chemical activation. As said before, this parameter makes a relation between the agents as a function of the starting material involved. In the preparation of activated carbons, different ratios are studied in order to find out the effect on yield and other properties, though the typical ratios are 2:1 and 4:1.

There are two competing mechanisms of pore evolution in the carbon structure. The first one is the micropore formation, which starts with the addition of chemicals into the lignocellulosic structure that seems to be the cause of the creation of micropores, and the second one is the pore widening that is the result of the chemical effects inside the pores; therefore it starts acting when the chemical ratio is reasonably high (F. Rodriguez-Reinoso et al. 1996). The activated carbons can be obtained at low impregnation ratios were essentially microporous and when the amount of impregnation agent increases, the activated carbon becomes predominantly mesoporous (Gonzalez et al. 1995).

The pyrolysis temperature is also an important factor that must be studied in detail, depending on the raw material the optimum temperature can vary taking into account the wide range of available temperatures. Activation is usually a one-step process and the temperature range is commonly around 450-900°C. The optimum pyrolysis temperature for manufacturing activated carbon from lignocellulosic materials is 500°C (F. Suarez-Garcia et al 2002). In this temperature the maximum development of porosity is produced, though the carbonization of the material may be incomplete. By increasing the pyrolysis temperature, an increase in the mesopore volume corresponded to a decrease in microporosity and after a certain temperature, surface area decreased causing a contraction of the carbon porous structures (Haimour et al. 2006).

Pyrolysis time is referred to the amount of time that the sample is going to be burning off and is a critical parameter that affects the quality of activated carbon. The preparation of activated carbon by chemical activation the pyrolysis time more often used is 1 or 2 hours (Haimour et al. 2006). Generally, for a soaking time longer than 1 h led to a reduction in both surface area and total pore volume. The decrease in pore volume is referred essentially to a decrease in micropore volume, presumably due to collapse of the smaller pores.

2.13 FILTER USED FOR ACTIVATED CARBON TREATMENT PROCESS

Logically, to make the wastewater sample go through activated carbon, an apparatus like bio-filter is needed. A bio-filter is simply a layer of organic material, typically a mixture of compost and wood chips or wood shreds that support microbial population (David et al. 2006). Odorous air is forced through this material and is converted by the microbes to carbon dioxide and water. Key factor influencing bio-filter performance are the amount of time the odorous air spends in the bio-filter (contact time) and the moisture content of the filter material. The bio-filter reliance on microorganisms requires an appreciation of ecological concepts which must be considered in bio-filter design. It has been in household filters since the nineteenth century in the form of charcoal. 'Activated' carbon is very finely divided carbon which presents a large surface area of adsorption. It can be added to the water in powder form. Good mixing with the water is essential; the point of addition is either before any mixing and sedimentation tanks or just before the water passes on to rapid gravity filters, when the water is filtered the carbon is left on the top of the beds and is removed by backwashing. For effective use the dose must be adequate, the mixing thorough, and the time of contact long enough for the material to carry out its work (Twort et al. 1985).

Activated carbon filters can be used for the removal of tastes and organic impurities. They consist of a bed activated carbon in granular form and are used in a few waterworks after the rapid sand filters. Compared with dosing with powdered activated carbon, the used of carbon filter beds has the advantage that the ratio of carbon to water whilst in the filter is obviously many times greater than with a dose of powder. Much more favourable adsorption equilibrium should thus be obtained provided, of course, that the carbon remains active to the specific substances required to be removed. Carbon filters are generally the most effective of all methods of removing 'earthy' or 'mouldy' tastes or odours. They are also effective in removing a wide range of complex organic substances, for example pesticides and aromatic hydrocarbons, and their use will no doubt become more widespread under modern conditions of water supply (Twort et al. 1985).

CHAPTER 3

METHODOLOGY

3.1 INTRODUCTION

This chapter discussed on methodology which consist of study area, flow chart of methodology study, method to produce activated carbon, flow chart of water quality testing, design of rapid bio-sand filter, water quality parameters and data analysis. It can be said that, research methodology is defines the activity of study to achieve objectives stated in Chapter 1. Palm Oil Mill Effluent samples were taken and tested with eight parameters such as BOD, COD, Turbidity, Oil and Grease, Total Suspended Solid, pH, Ammonia Nitrogen and Heavy Metals (Boron, Copper and Lead).

3.2 STUDY AREA

This water quality testing was conducted in Fkasa Environmental Laboratory at Universiti Malaysia Pahang. However, the collection of palm oil mill effluent was taken at Felda Palm Industries Sdn Bhd, Kilang Kelapa Sawit Lepar Hilir, Kuantan, Pahang Darul Makmur. There are several ponds on the palm oil processing and each of them differs on its content of pesticide, microorganism, biological oxygen demand, chemical oxygen demand, dissolved oxygen and total suspended solid. The one that was taken is from the latest effluent which has been discharge from the operation mill. Effluent sample was preserved first in order to retain its existed compound and not degraded by the action of microbiology organism and bacteria. The sample was stored at 4°C to avoid biodegradation due to microbial action.



Figure 3.1: Felda Palm Industries Sdn Bhd, Kilang Kelapa Sawit Lepar Hilir, Kuantan, Pahang Darul Makmur.



Figure 3.2: Wastewater sampling point.

3.3 FLOW CHART OF THE METHODOLOGY STUDY

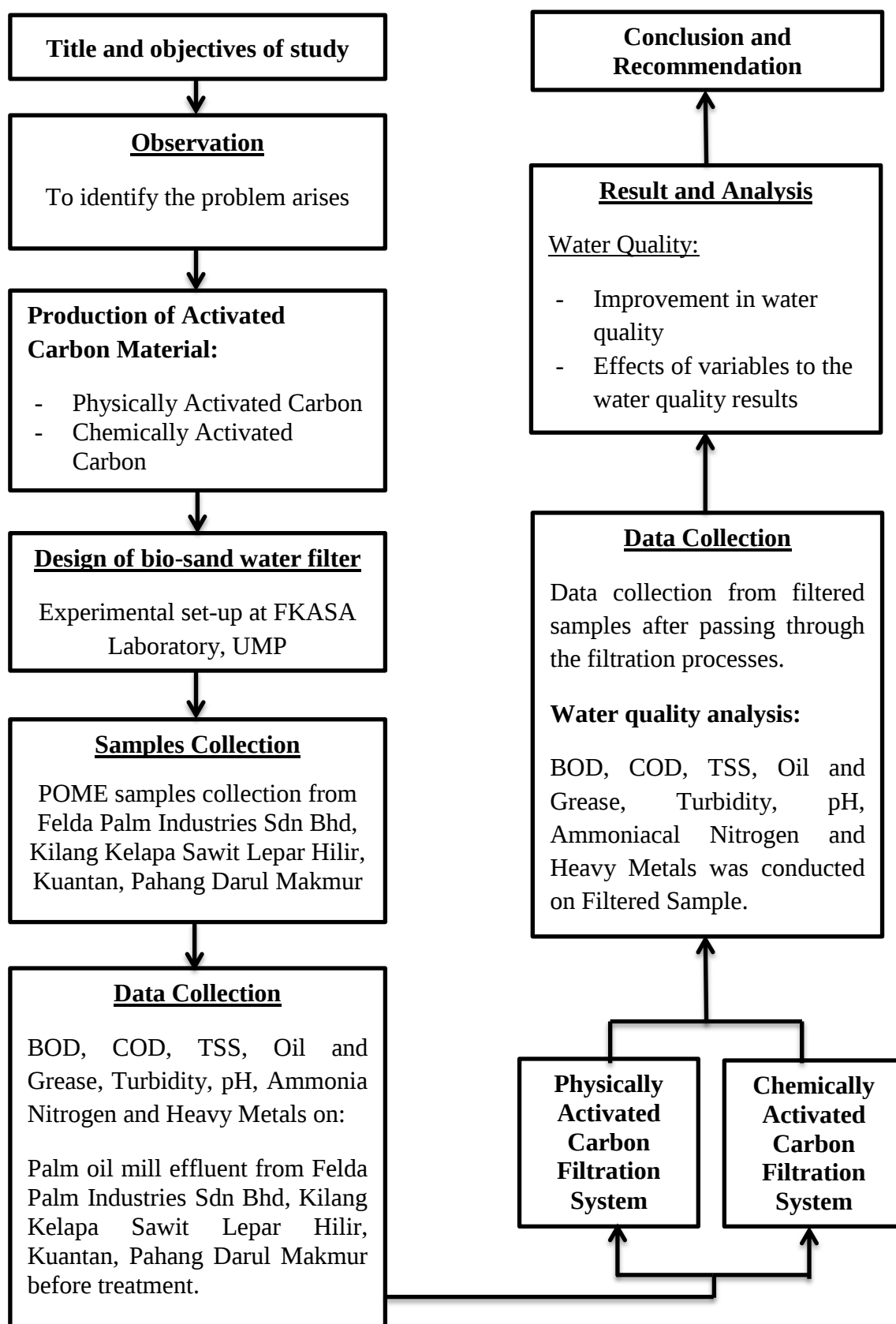


Figure 3.3: Flow Chart of the Methodology

The methodology of this study can be viewed from Figure 3.3 where it started with the identification of title and objectives of study before identifying the problem. After identifying the problem, the activated carbons were produced. Then the production of activated carbon, it was tested by running through the filtration process and the outflows of the POME samples were tested. After all the readings were recorded, the results were compared with initial reading to see the differences.

The wastewater samples at effluent from Felda Palm Industries Sdn Bhd, Kilang Kelapa Sawit Lepar Hilir, Kuantan, Pahang Darul Makmur was taken and tested using eight parameters. The eight tests that were conducted are BOD, COD, TSS, Oil and Grease, Turbidity, pH, Ammoniacal Nitrogen and Heavy Metals (Boron, Copper and Lead). After the wastewaters have been tested, the readings were recorded and set as initial reading before the wastewater samples undergo filtration process. Laboratory modified bio-sand filter was used as a testing material that was set up at FKASA Environment Laboratory. For this study there were two types of filtration system which are physically activated carbon filtration system and chemically activated carbon filtration system. Then, the result were analysed to come out with discussion, conclusion and recommendation based on the effectiveness of activated carbon in removing pollutants from palm oil mill effluent.

3.3.1 Method to Produce Activated Carbon

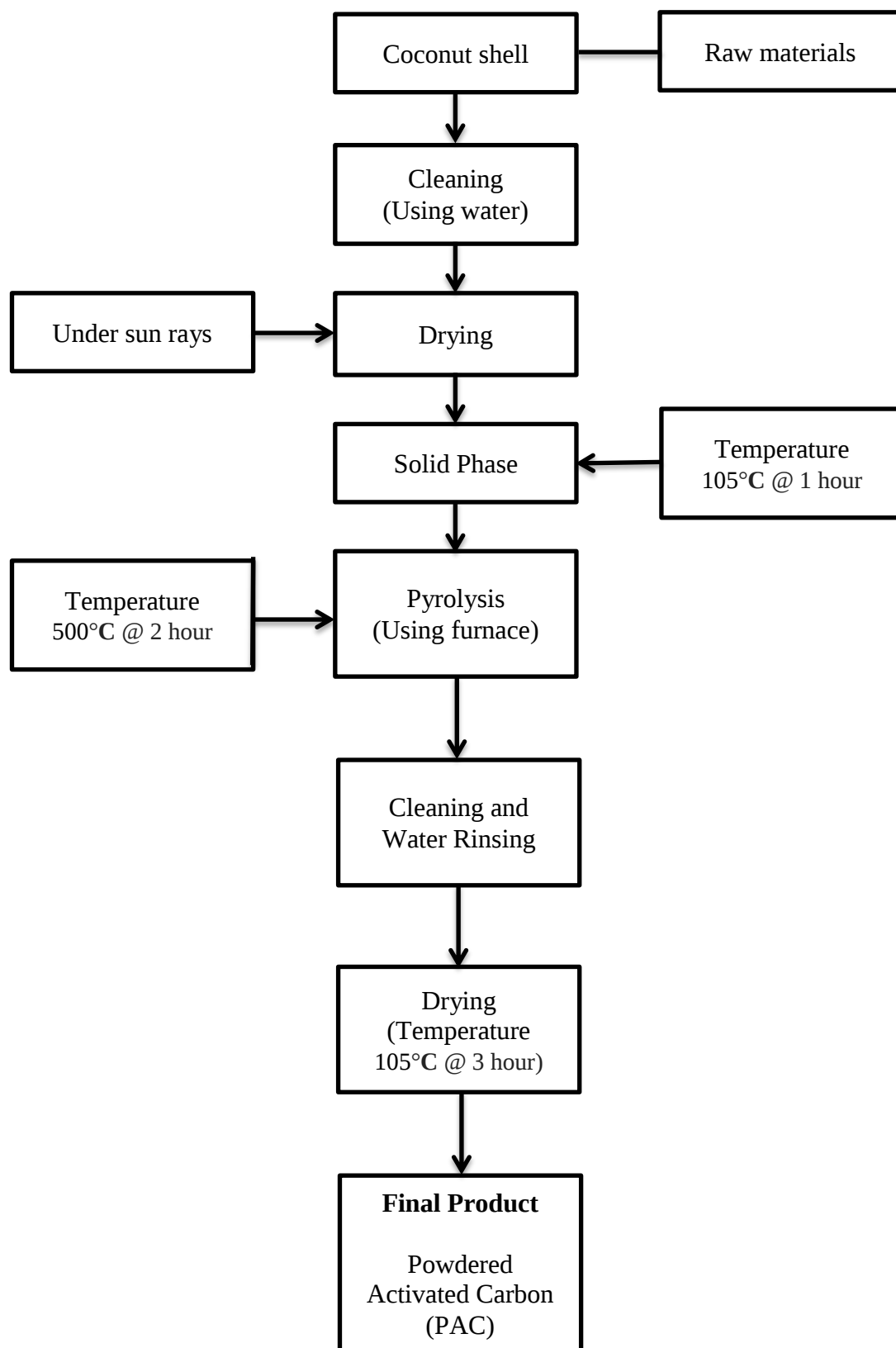


Figure 3.4: Flow chart process of producing Physically Activated Carbon from coconut shell.

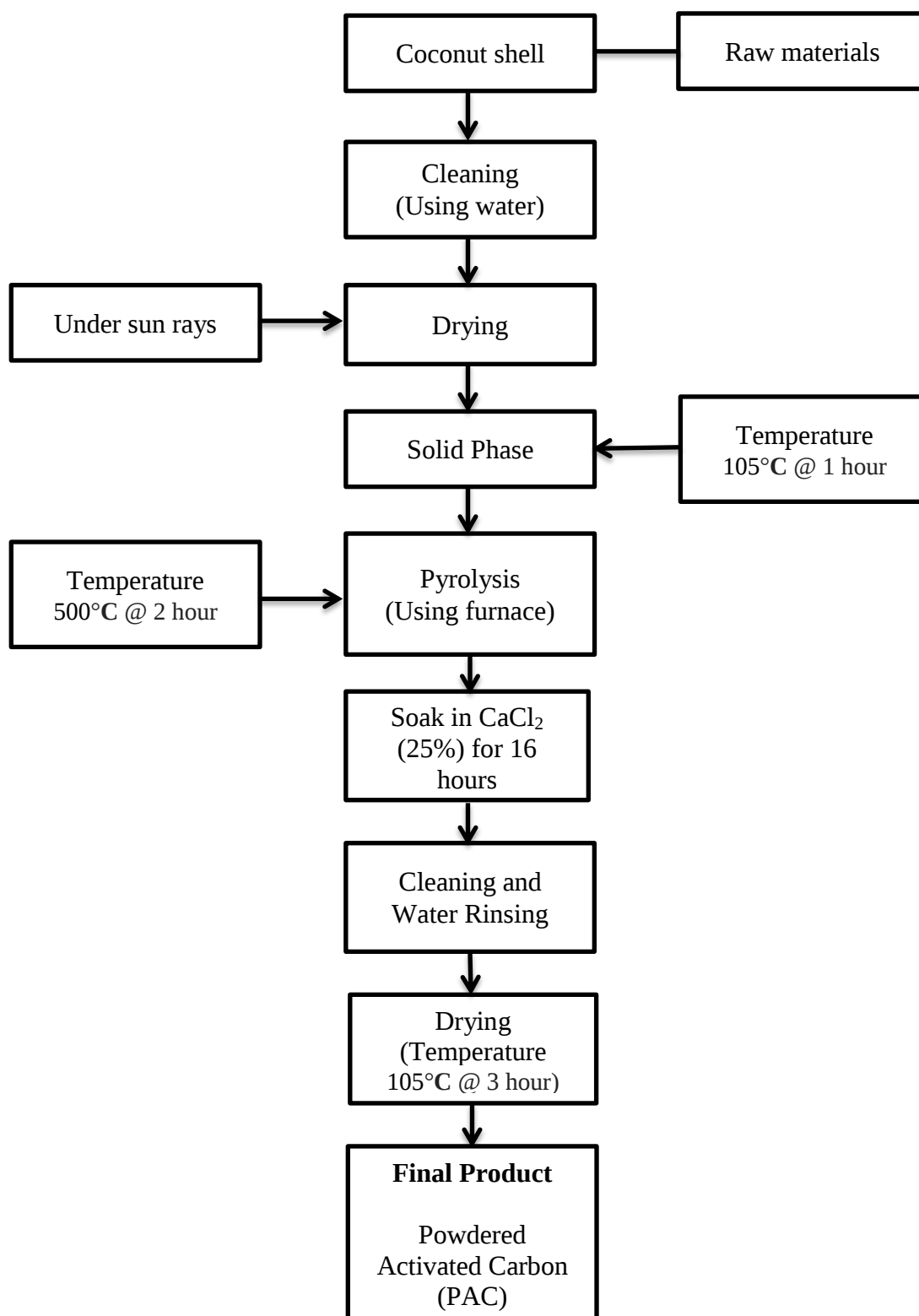


Figure 3.5: Flow chart process of producing Chemically Activated Carbon from coconut shell.

The first step in producing activated carbon was the collection of coconut shells. The coconut shells then were cleaned with water to reduce impurities. The clean coconut shells were dried under the sun rays until it completely dry. The dried coconut shells are called as solid phase. The dried coconuts were burned inside the furnace with 500°C about two hours. This process is called carbonization or pyrolysis process. After coconut shells burned through pyrolysis, the activation process will take place. Two activations process were involved in this study which are chemical and physical activation. In the physical activation, after pyrolysis process the coconut shells were cleaned with distilled water. This method was used to eliminate the impurities before the coconut shell are once again dry inside the oven with 105°C for three hours. Lastly, the final powdered product of activated carbon from coconut shell was produced.

In the chemical activation process, after pyrolysis process the coconut shell was soaked in aqueous CaCl_2 with the concentration of 25% for 16 hours. After that, the soaked coconut shell was cleaned with distilled water. This method was used to eliminate the impurities before the coconut shell are once again dry inside the oven with 105°C for three hours. Lastly, the final powdered product of activated carbon from coconut shell was produced.

3.3.2 Flow Chart of Water Quality Testing

There is only one variable in the experiment:-

- Types of activation process
 - Physical Activation – Pyrolysis Treatment
 - Chemical Activation – Acidic Treatment

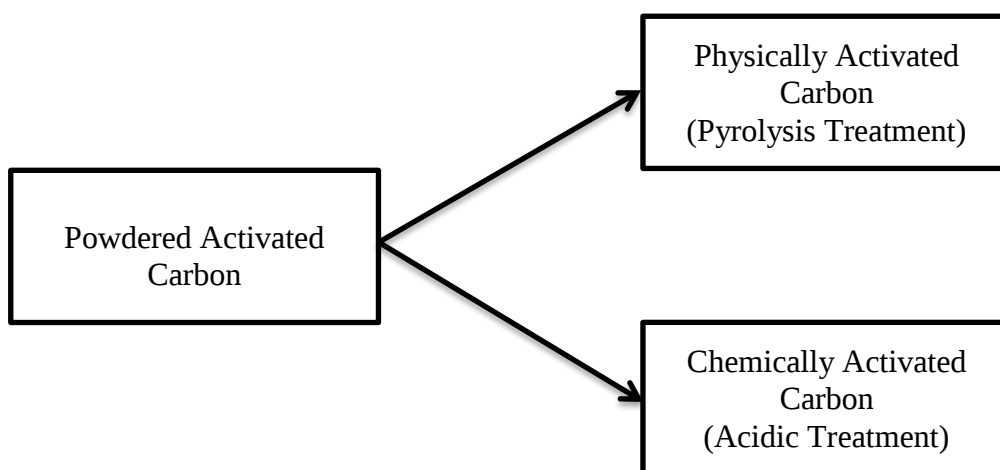


Figure 3.6: Flow chart of variables that related in the experiment.

In this study only two activation processes were used to compare the effectiveness of activated carbon in removing pollutants from POME which are physical and chemical activation process of Powdered Activated Carbon. Figure 3.6 is made to accomplish the objective which is to obtain the most suitable and effective activation process in removing pollutants from palm oil mill effluents.

3.4 DESIGN OF BIO-SAND FILTER

For the testing apparatus, the concept of rapid sand filter was used to design the testing apparatus. This apparatus was used for the filtration process of the effluent.



Figure 3.7: Testing Apparatus

The thickness of each layers are as below:

- i. Activated Carbon – 5.0 cm
- ii. Fine Sand – 15.0 cm
- iii. Course Sand – 2.5 cm
- iv. Gravel – 2.5 cm

The particle sizes of the elements in the testing apparatus are as below:

- i. Activated Carbon – 0.177 mm or less
- ii. Fine Sand – varies from 0.35 mm to 0.55 mm
- iii. Course Sand – varies from 0.60 mm to 2.5 mm
- iv. Gravel – varies from 5 mm to 7 mm

3.5 WATER QUALITY PARAMETERS

3.5.1 pH

The pH meter was calibrated. For calibration process each buffer solution were poured into 50 ml beaker respectively. Then, 'ON/OFF' button was pressed to start. 'CAL' button was pressed to calibrate. The displayed was prompted for Standard 1. After that, pH electrode was placed in one of the buffer. Then, 'READ' button was pressed to read the pH value, wait until the electrode has stabilized. The displayed was prompted for Standard 2 then the electrode was rinsed with the deionized water. Followed up with the placing of electrode in the second buffer then 'READ' button was pressed. Repeated these steps for the third buffer. When the reading was stable, the slope and A was appear, to save the calibration, press READ for a few second and hold.

To measure the sample, the sample was shook well, and then poured about 35 ml samples in 50 ml clean beaker. pH was determined without dilution until constant reading achieved. After that, pH electrode was placed in the beaker, then press 'ON/OFF' button and press 'READ' button. The displayed shows pH reading and temperature. After that, the pH reading was recorded to nearest 0.01 and temperature of the sample. Finally, press 'ON/OFF' button when finish.

3.5.2 Chemical oxygen demand (COD)

COD also was analysed using HACH DR 5000 Spectrophotometer method. The test needed reagents which are combination of sulphuric acid, potassium dichromate and distilled water. Also need additional chemicals powder which are argentum sulphate and mercuric sulphate. After that, 3 ml of the reagent was placed into a vial.

Next, 2 ml of the sample and the additional chemical powders were added into the vial. For the blank, 2 ml of the sample was replaced with distilled water. Then, the vials were refluxed for 2 hours. Finally, after the vials were cooled in room temperature, the samples were analysed using HACH DR 5000 Spectrophotometer to get the content of COD in the samples.

3.5.3 Biochemical oxygen demand (BOD)

BOD is a parameter which was used to analyse using DO meter YSI 5100. pH of all samples were checked before testing unless previous experience indicates that pH is within acceptable range. If samples containing caustic alkalinity or acidity, neutralize the sample to pH around 6.5 to 7.5 using 1N sodium hydroxide (NaOH) or sulphuric acid (H₂SO₄). After that, a measuring cylinder was used, mix 100ml sample and 400ml dilution water into clean beaker. If the sample contains material that react rapidly with DO, determine initial DO immediately after filling BOD bottle with diluted sample. If a rapid initial DO uptake is significant, the time period between preparing dilution and measuring initial DO is not critical but should not exceed 30 min. Then, BOD bottle containing sample and dilution water was incubated at 20°C. After 5 days incubation, samples were removed from incubator until it reaches room temperature. Then DO was determined in the sample dilutions and checked using DO meter.

$$\text{BOD} = \frac{\text{DO}_i - \text{DO}_t}{P}$$

DO_i – Initial Dissolved Oxygen

DO_t – Final Dissolved Oxygen

P – Dilution Factor

3.5.4 Total Suspended Solids

Weighed a filter paper and then placed on the filter apparatus. A 100 ml of sample was poured into a pump vacuum. After a few minutes, the filter paper was placed in an oven for one hour at 105°C. Then, the filter paper was weighed for the second time. After subtracting the both weight mass, the mass of the suspended solids was determined.

$$\text{TSS} = \frac{A - B}{C}$$

A – Weight of filter paper + Suspended Solids

B – Weight of filter paper

C – Volume of Sample

3.5.5 Ammoniacal Nitrogen

For Ammonia Nitrogen, hatch program DR 5000 Spectrophotometer. Then, two sample bottles were prepared, each 10 ml of distilled water and 10 ml of water sample. After that, Ammonia Salicylate Reagent Powder Pillow (cat.26532-99) was added to both bottle and then shook. Touch the timer icon or DR 5000 for three minutes. The bottles were left for three minutes reaction. After timer ‘beep’, Ammonia Cyanurate reagent (cat.26531-99) was added to same bottles and shook. Touch the timer icon for 15 minutes reaction. Lastly, after time ‘beep’, the reading was taken starting from distilled water that act as ‘blank’ for ‘zero’ set.

3.5.6 Turbidity

Turbidity is the amount of solid particles suspended in water that causes light rays shining through the water to scatter. Too much turbidity will make water cloudy or in the extreme case, muddy. Turbidity was measured accurately with a nephelometer (turbidimeter) in units called nephelometric turbidity units, or NTUs. Most states limit drinking water to a maximum of 5 NTUs, however usually drinking water is 1 NTUs or surrounding factor. Turbidity meter is easy to use by pour the water inside the bottles

and placed it into the turbidity meter and press button 'READ'. The value appeared with the units of NTU.

3.5.7 Oil and Grease

This test method is appropriate for the determination of Oil and Grease in all types of water and wastewater. For the procedure of Oil and Grease, the first step was wash and dry two conical flasks in oven for one hour. By using 500 ml of water sample, poured it into the conical flask. Put 2.5 ml of sulphuric acid 1:1 in the samples. After that, put 30 ml Hexane in sample then shook it rigorously for two minutes. Let until oil form a layer and after that, flow out water slowly until only oil is left in the conical flask. Put a small amount of isopropyl alcohol (IPA) to detect the oil visibly. Repeat the same steps three times then put it inside oven for two hour. Then let it cold in decicator for 30 minutes before finally take the readings.

3.5.8 Heavy Metals

The characteristic concentration check value is the concentration of element (in mg/L) that will produce a signal of approximately 0.2 absorbance units under optimum conditions at the wavelength listed. By using the characteristic concentration check, the operator can determine whether instrumental parameters are optimized and whether the instrument is performing up to specifications. Calibration of AAS was carried out by using an external calibration curve. The external calibration curve was prepared from solution of known concentrations of the sample element, which was also known as stock solution. High purity metal salts dissolved in high purity acids were used to make the stock solution. Working standards were diluted from the stock standard.

3.6 DATA ANALYSIS

Data that obtained from the experiment were analysed to determine the performance of treatment palm oil mill effluent with activated carbon. The data should be at least states the percentages of removal of wastewater pollutant. The formula for removal efficiency is shown in Equation 3.1. Microsoft Excel was used in tabulating data and also for analysis purposes.

$$\text{Percentage of removal (\%)} = \frac{(\text{Influent} - \text{Effluent})}{\text{Influent}} \times 100 \quad \dots\dots\dots (3.1)$$

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Introduction

Activated carbon criteria are evaluated by the performance of activated carbon in improving water quality and its ability to remove pollutant. To determine the possibility of objective achievement, this chapter have been discusses the results and finding of the study as described in the methodology. All the data and result obtained are analysed by in terms of percentages of removal and also literature reviews.

The water quality parameters tested are pH, biochemical oxygen demand (BOD₅), chemical oxygen demand (COD), total suspended solids, Ammoniacal Nitrogen, turbidity, oil and grease, and heavy metals. Palm oil mill effluent (POME) was acquired from local palm oil industry, Felda Palm Industries Sdn Bhd, Kilang Kelapa Sawit Lepar Hilir, Kuantan, Pahang Darul Makmur, was chosen for this study. Raw wastewaters from palm oil mill processing are selected for sampling. The point of sample collection was located at the position before the wastewater flows into the POME treatment plant. POME samples were collected and kept in containers which were closed tightly and transported to laboratory in order to prevent the wastewater from undergoing biodegradation due to microscopic organism action, POME was preserved at a temperature less than 4 °C, but above the freezing point.

This chapter shows the result of filtration using two different activated carbon filter system. The wastewater samples were taken on 22/03/2016. Meanwhile, for the various characteristics of activated carbon filter system used, all the characteristics are represented as CACFS (Chemically Activated Carbon Filter System) and PACFS

(Physically Activated Carbon Filter System). Percentage of removal was calculated using Equation 3.1 and characteristics of treated wastewater samples are shown in the Table 4.1.

Table 4.1: Characteristics of Treated Water Samples

Samples	Size	Treated Water samples
CACFS	Powdered	Powdered Chemically Activated Carbon
PACFS	Powdered	Powdered Physically Activated Carbon

4.2 Water Quality Results

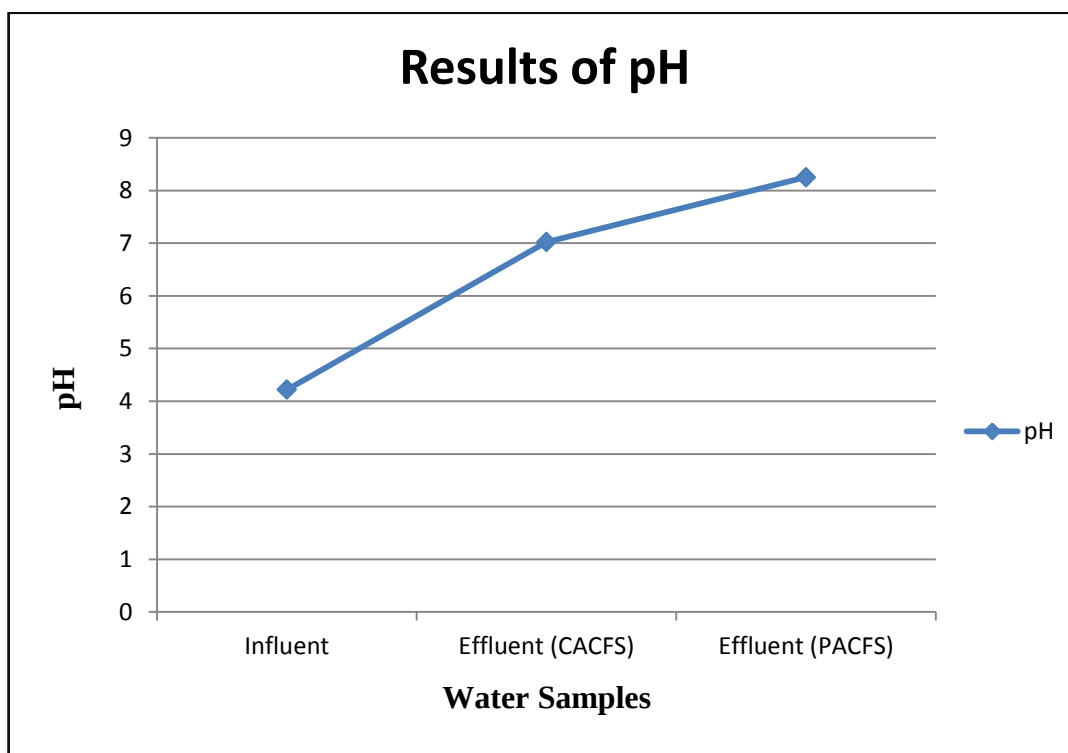
Based on the data collected, the graph of pH against water samples, COD against water samples, BOD against water samples, TSS against water samples, AN against water samples, Turbidity against water samples, and Oil & Grease against water samples.

4.2.1 pH

Results of pH are shown in Figure 4.1. According to Figure 4.1, it can be seen that pH value of both effluent of CACFS and PACFS are above the value of influent, it shows that after the treatment process the pH value have increased. All of effluent results are comply with limit, Environmental Quality Act (1984). The allowable limit is range from 5 to 9 pH value only. Both CACFS and PACFS are between the limit as in EQA (1984). The result from Figure 4.1 shows that the value of pH of CACFS is less than PACFS which means the value of pH for treated waste water is nearer to the neutral value if chemically activated carbon is used.

Table 4.2: Results for pH

Water Samples	pH
Influent	4.22
Effluent (CACFS)	7.02
Effluent (PACFS)	8.25
Limits	5.00 – 9.00

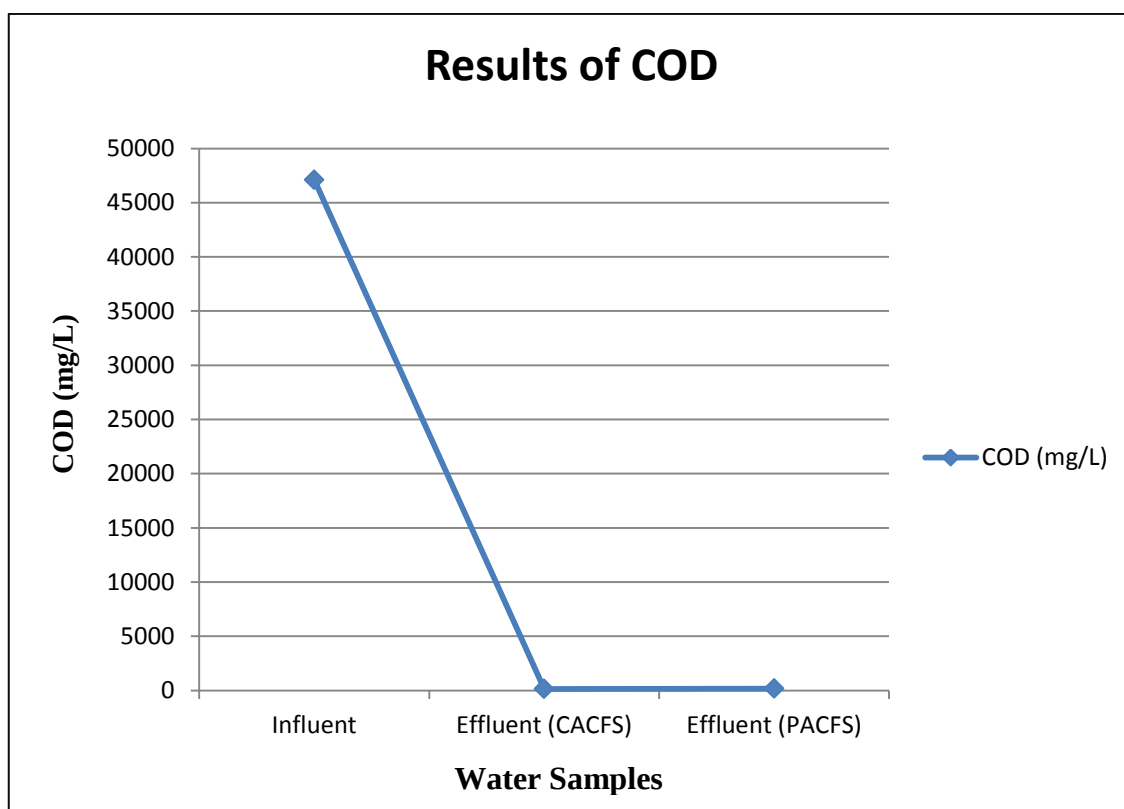
**Figure 4.1:** Graph of pH against Water Samples

4.2.2 Chemical Oxygen Demand

From Figure 4.2, it can be observed that both the effluents are under the influent values. It can be seen that all of these effluent (CACFS & PACFS) have effectively improve the quality of Chemical Oxygen Demand. CACFS shows the lowest concentration of COD values compared to PACFS. This indicates that CACFS is more effective compared to PACFS which means chemically activated carbon will improve the concentration of COD better than the physically activated carbon.

Table 4.3: Results for COD

Water Samples	COD (mg/L)
Influent	47 100
Effluent (CACFS)	149
Effluent (PACFS)	176
Limits	-

**Figure 4.2:** Graph of COD against Water Samples

4.2.3 Biochemical Oxygen Demand

The results of BOD₅ are plotted in Figure 4.3. The results indicate that all the effluents are under the influent value. However, the effluent of CACFS is complying with the limit, Environmental Quality Act 1984, whereas the effluent of PACFS does not comply with the limit, EQA (1984). The result from this Figure 4.3 explained that CACFS is most effective compare to PACFS which means the concentration of BOD is improved when activated carbon is activated chemically.

Table 4.4: Results of BOD₅

Water Samples	BOD ₅ (mg/L)
Influent	9552
Effluent (CACFS)	96.3
Effluent (PACFS)	127.4
Limits	100

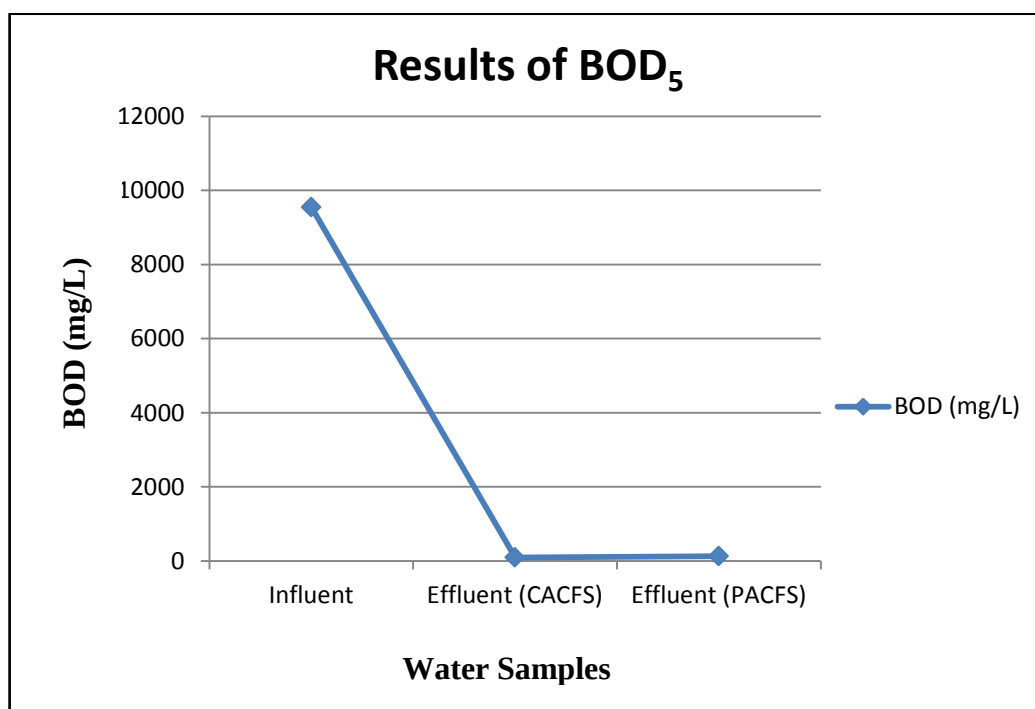


Figure 4.3: Graph of BOD₅ against Water Samples

4.2.4 Total Suspended Solids

From Figure 4.4 that has been plotted, it can be noticed that all two effluent have effectively improve the quality of TSS. However, the effluent values are not complying with the limit, Environmental Quality Act 1984. The result from this Figure 4.4 explained that CACFS is most effective compare to PACFS which means the concentration of BOD is improved when carbon is activated chemically.

Table 4.5: Results of Total Suspended Solids

Water Samples	TSS (mg/L)
Influent	149 700
Effluent (CACFS)	550
Effluent (PACFS)	643.5
Limits	400

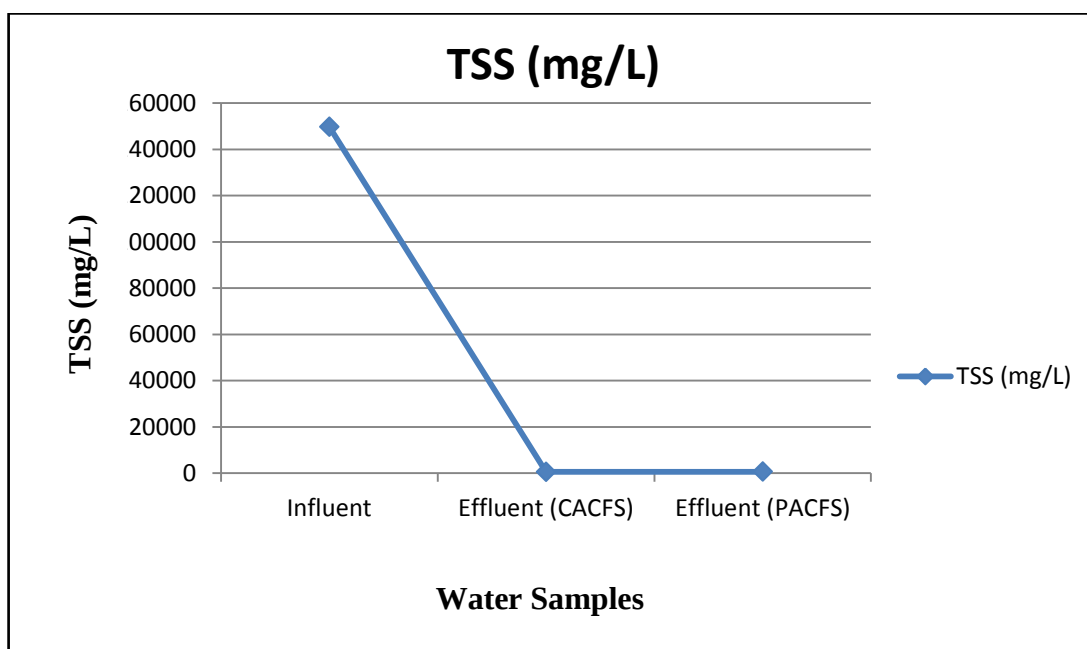


Figure 4.4: Graph of TSS against Water Samples

4.2.5 Ammoniacal Nitrogen

Results of Ammoniacal Nitrogen are represented in Figure 4.5 and from Figure 4.5, it can be seen that all of these effluents have effectively improve the quality of Ammonia Nitrogen. Both the effluents' Ammonia Nitrogen values are below the limit as in the EQA (1984). The results shows that CACFS is more effective compared to PACFS which means the concentration of BOD is improved when activated carbon is activated chemically.

Table 4.6: Results of Ammoniacal Nitrogen

Water Samples	Ammonia Nitrogen (mg/L $\text{NH}_3\text{-N}$)
Influent	26
Effluent (CACFS)	0.2
Effluent (PACFS)	0.6
Limits	100

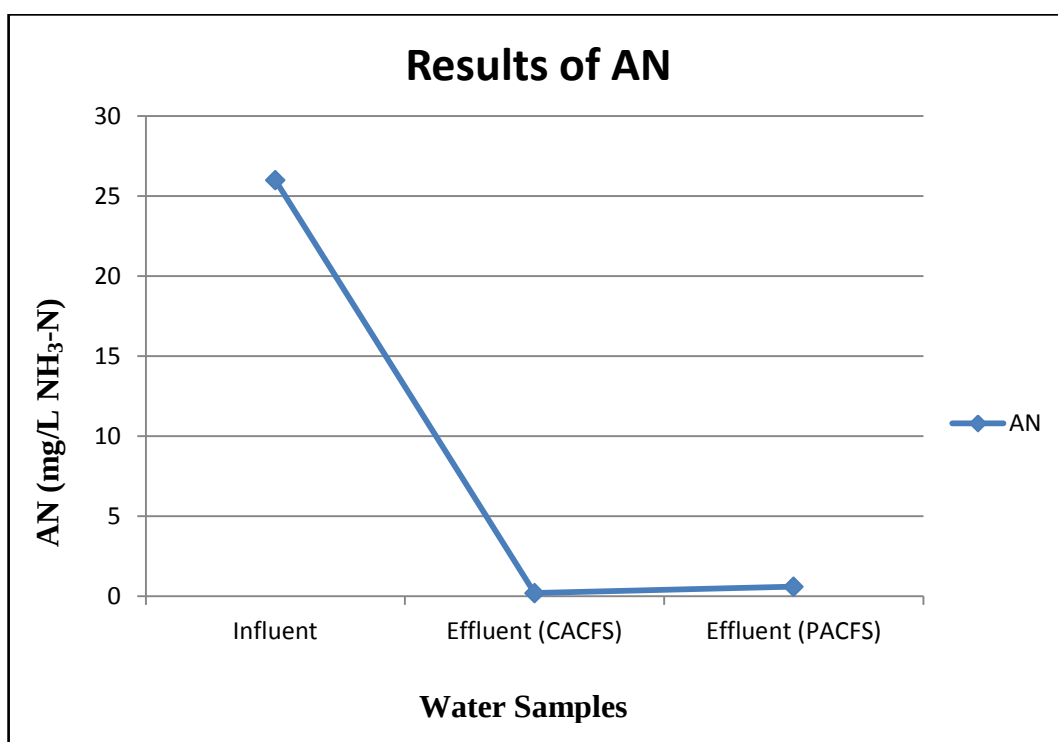


Figure 4.5: Graph of AN against Water Samples

4.2.6 Turbidity

Graph plotted at Figure 4.6 shows the result of turbidity. According to Figure 4.6, it can be seen that all of these effluents have effectively improve the quality of turbidity. The results from this Figure 4.6 also share the same condition with other parameters by shows that CACFS is more effective compared to PACFS which means the concentration of turbidity is improved when activated carbon is activated chemically.

Table 4.7: Results of Turbidity

Water Samples	Turbidity (NTU)
Influent	18800
Effluent (CACFS)	117
Effluent (PACFS)	153
Limits	-

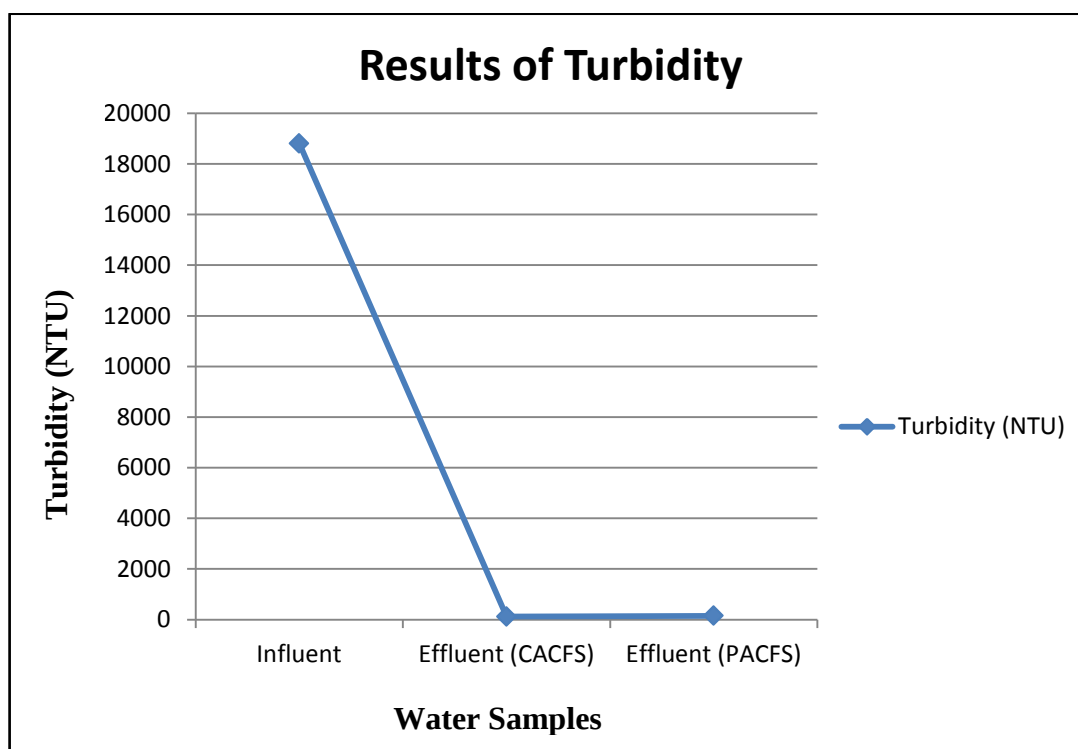


Figure 4.6: Graph of Turbidity against Water Samples

4.2.7 Oil and Grease

Results of Ammonia Nitrogen are represented in Figure 4.7 and from Figure 4.7, it can be seen that all of these effluents have effectively improve the quality of Oil and Grease. Both the effluents' Oil and Grease values are below the limit as in the EQA (1984). The results from this Figure 4.7 do not share the same condition with other parameters by shows that PACFS is more effective compared to CACFS which means the concentration of Oil and Grease is improved when activated carbon is activated physically.

Table 4.8: Results of Oil & Grease

Water Samples	Oil and Grease (mg/L)
Influent	4418
Effluent (CACFS)	19.4
Effluent (PACFS)	10.6
Limits	50

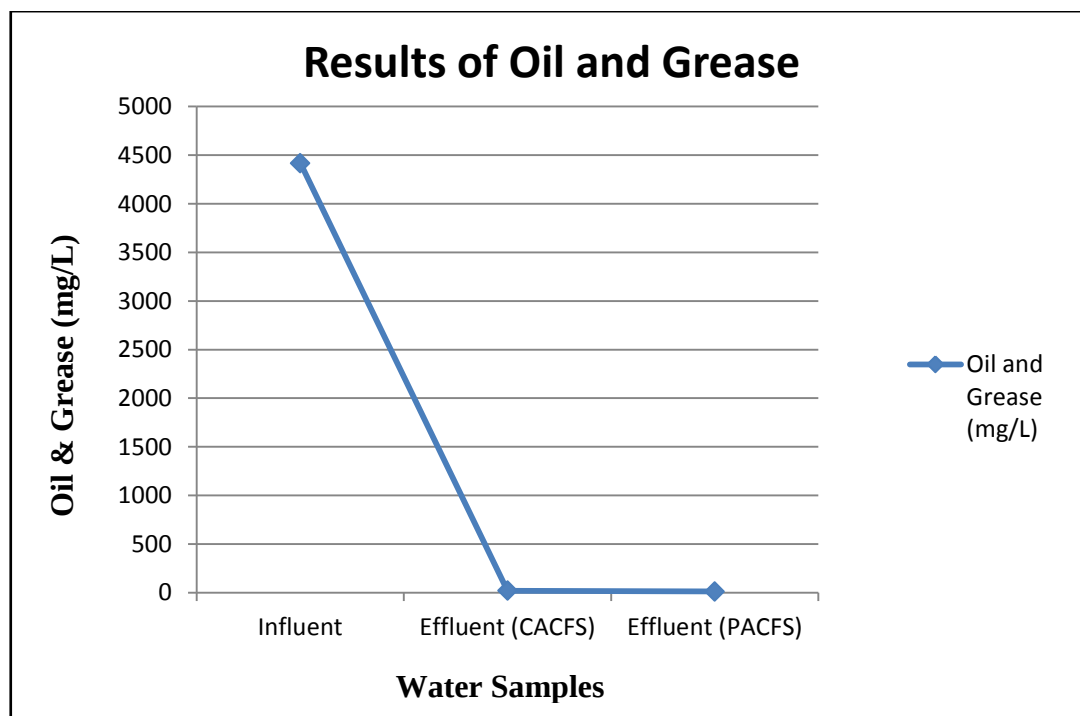


Figure 4.7: Graph of Oil and Grease against Water Samples

4.2.8 Heavy Metals

Results of Heavy Metals are represented in Table 4.9 and from Table 4.9, it can be seen that all of these heavy metals of water samples that were analysed did not contained any heavy metals such as Cu, Zn and B.

Table 4.9: Results of Heavy Metals

Water Samples	Heavy Metals (mg/L)		
	Copper (Cu)	Zinc (Zn)	Boron (B)
Influent	0	0	0
Effluent (CACFS)	0	0	0
Effluent (PACFS)	0	0	0
Limits	-	-	-

4.3 Removal Efficiency (%)

To calculate percentage of removal of each parameter a table have been tabulated for all parameters except pH. The formula for removal efficiency is shown in Equation 3.1.

Table 4.10: Results of removal efficiency for all parameters

Parameters	Percentage of Removal (%)	
	CACFS	PACFS
Biochemical Oxygen Demand	98.99	98.66
Chemical Oxygen Demand	99.68	99.63
Ammonia Nitrogen	99.23	97.69
Total Suspended Solids	99.63	99.57
Turbidity	99.38	99.19
Oil and Grease	99.56	99.76
Heavy Metals	0	0

Based on the Table 4.10 it shows that the results of percentages of removal for wastewater treatment using chemically activated carbon for COD, BOD, TSS, AN, Turbidity and Oil & Grease are ranged from 98.99 to 99.68% while for physically activated carbon the results are between 97.69 to 99.63%. Based on the removal efficiency we can able to conclude that Chemically Activated Carbon is very effective than the Physically Activated Carbon.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Introduction

Generally, this study had reached its objectives to determine the effectiveness of activated carbon and also to obtain the most suitable and effective activation process in removing pollutants from palm oil mill effluents. All of experiments are tested at UMP's Environmental Laboratory. All of the results have been recorded and tabulated by using eight parameters and all of the data have been analysed in terms of percentages of removal.

5.2 Conclusion

From this study, several conclusions can be drawn which are given as follows:

1. Productions of activated carbon from coconut shell have been successfully produced in two types, Chemically Activated Carbon and Physically Activated Carbon. Both activated carbons are produced in powdered size of 0.177 mm and below.
2. Production of bio-sand filter design has been successfully produced for the two types of activated carbon. Both the activated carbon filter systems were produced based on the specification needed.
3. For overall, the study indicates that the activated carbons produced are capable to improve water quality. This have been proved when the quality of all seven parameters, pH, COD, BOD, TSS, AN, Turbidity and Oil & Grease are improved. Total suspended solids (TSS) is the parameter that does not complying with the limits, Environmental Quality Act 1984. Quality of wastewater samples still improve due to its removal efficiency. However, for heavy metals parameter comparison could not be made because there is no presence of heavy metals in the palm oil mill effluent.
4. Generally, both of activated carbon filter system gives a good result in removing the wastewater pollutant from palm oil mill effluents but, chemically activated carbon filter system is more effective than physically activated carbon filter system. It has been proved with all the data that been analysed where chemically activated carbon give the highest percentage of removal compared to physically activated carbon filter system. The results of percentages of removal for wastewater treatment using chemically activated carbon for COD, BOD, TSS, AN, Turbidity and Oil & Grease are ranged from 98.99 to 99.68% while for physically activated carbon the results are between 97.69 to 99.63%.

5.3 Recommendation

All problems factor occur that affect the results because of several factors. The main factor is based on human behaviour that do not concern about a little mistakes that can cause bad results of experiment. Other than that, the quality of activated carbon produced is not as good as expected besides the water filter used to treat wastewater by using activated carbon is not suitable.

From the study conducted, it is suggested that a few recommendation must be taken into consideration stated below:

- a) The design of water filter should be improved. It is because the water filter used to treat wastewater form activated carbon can only accommodate up to 5cm thickness layer of activated carbon. Other than that, the design of the water filter used maybe not suitable to use in order to treat wastewater from activated carbon.
- b) The quantity of activated carbon to remove wastewater pollutant should be increased. Due to this study proves successfully that the percentages of removal are high when using activated carbon, the addition of activated carbon quantity should come into considerations.
- c) A proper production of activated carbon should be emphasized. Activated carbon are not let exposed to air for too long period of time. It is because the presence of air will disturb the characteristics of activated carbon. Other than that, do not burn coconut shell in a short period of time. The coconut shell should be burn under pyrolysis process within two hours.
- d) A proper backwash calculation for the filter system should be given important. Since the study proves that the activated carbon can able to increase the quality of wastewater. Furthermore, the filter system can able to accommodate up to 1 litre of sample only.

REFERENCES

- Accardio P. Sincero and Gregoria A. Sincero. 2003. *Physical and Chemical Treatment of Water and Wastewater*. Publisher: CRC Press.
- Agamuthu, P. 1995. Palm oil mill effluent and utilization. In: Sastry C.A et al. (eds). Waste treatment plant. *Narosa Publishing House, New Delhi*. pp. 338-360.
- Ahmad, A. L., S.Sumathi and B.H. Hameed. 2006. Coagulation of residue oil and suspended solid in palm oil mill effluent by chitosan, alum and PAC. *Chemical Engineering Journal*. **118**: 99-105.
- Ahmad, A. L., Ismail, S. and Bhatia, S. 2003. Water Recycling from Palm Oil Mill Effluent (POME) using Membrane Technology. *Desalination*. **157**(1-3): 87-95.
- Ahmed, J. 1997. Production of Activated Carbon from Coconut Shell Char in a Fluidized Bed Reactor. *Centralised Waste Management Facility*.
- Ahmedna, M. Marshall, W. E. & Rao, R.M. 2000. Production of granular activated carbons from select agricultural by-products and evaluation of their physical, chemical and adsorption properties. *Biosource Technology*. **71**: 113-123.
- Amit Bhatnagar, William Hogland, Marcia Marques and Mika Sillanpaa. 2013. An overview of the modification methods of activated carbon for its water treatment applications. *Elsevier Science & Technology Books*.
- Bhavan, K. 2009. Coconut Development Board, Ministry of Agriculture, India- Activated Carbon. <http://coconutboard.niin/activatd.htm> (10 October 2015).
- Borja, R., and Banks, C.J. 1994. Anaerobic digestion of palm oil mill effluent using an up-flow anaerobic sludge blanket reactor. *Biomass Bioenergy* **6**: 381-389.
- Caturla F., M. Molina-Sabio and F. Rodriguez-Reinoso. 1991. Preparation of activated carbon by chemical activation with ZnCl₂. *Carbon*. **29**: 999-1007.
- Chan, C.Y. and Ahmad, A. L. 2009. Sustainability of Palm Oil Industries: An Innovative Treatment via Membrane Technology. *Journal of Applied Sciences*. **9**(17): 3074 - 3079.
- Cheryan, M. and Rajagopalan, M. 1998. Membrane Processing of Oily Streams. Wastewater Treatment and Waste Reduction. *Journal of Membrane Science*. **151**(1): 13-28.
- Dan Ferrente. 1996. *Groundwater Pollution – Sorption Process*. Virginia Tech., Civil Engineering Department.
- Daud W.M.A. and W.S.W. Ali. Comparison on pore development of activated carbon produced from palm shell and coconut shell. *Bioresour. Technology*. **93**: 63–69.

- David, S, Kevin A J, and Nicolai R. 2006. Biofilter Design Information. *Agricultural and Biosystems Engineering Extension and Outreach Publications*.
- Dr. Hoehn, R.C. 1998. *Water and Wastewater Design*. Virginia Tech., Civil Engineering Department.
- Elsheikh A., Newman A., Al-Daffae H., Phull S. and Crosswell N. 2003. Characterization of activated carbon prepared from a single cultivar of Jordanian olive stones by chemical and physicochemical techniques. *Journal of Analysis & Applied Pyrolysis*. **30**: 1-16.
- Food & Fertilizer Technology Center. 2004. Processing of Coconut Shell into Activated Carbon/Charcoal. <http://www.agnet.org/library/pt/2004003> (10 October 2015).
- Gonzalez J.C., M.T. Gonzalez, Molina-Sabio, M. and Rodriguez-Reinoso. 1995. Porosity of activated carbons prepared from different lignocellulosic materials. *Carbon*. **33**: 1175 - 1188.
- Habib, M.A.B., Fatimah Yusoff, Siew-Moi Phang, K.J.Ang and Suhaila Mohamed. 1997. Nutritional values of chironomid larvae grown in palm oil mill effluent and algal culture. *Aquaculture*. **158**: 95-105.
- Haimour N.M. and S. Emeish. 2006. Utilization of date stones for production of activated carbon using phosphoric acid. *Waste Manage*. **26**: 651–660.
- Hammer MJ. 2001. *Water and wastewater technology*. 4th ed. Prentice-Hall Inc.
- Hwang T.K., Ong S.M., Seow C.C. and Tan H.K.. 1978. Chemical composition of palm oil mill effluents. *The Planter*. **54**: 643-648.
- I.A.W. Tan, A.L. Ahmad and B.H. Hameed. 2008. Optimization of preparation conditions for activated carbons from coconut husk using response surface methodology. *Elsevier Chemical Engineering Journal*. **137**(3): 462-470.
- Ioannidou O. and A. Zabaniotou. 2007. Agricultural residues as precursors for activated carbon production: a review. *Renew. Sust. Energ.*. **11**.
- James, R. 1996. Effects of lead on respiratory enzyme activity, glycogen and blood sugar levels of the teleost *Oreochromis mossambicus* (Peters) during accumulation and depuration. *Asian fisheries science. Metro Manila*. **9**: 87-100.
- John, C Geankoplis. 2003. *Transport Process and Separation Process Principles*. 4th ed. UK: Pearson Education Inc.
- Juntgen H. 1977. Carbon. *Chemical Engineering Journals*. **273**.
- Khalid, A.R. & Mustafa, W.A.W. 1992. External Benefits of Environmental Regulations; Resource Recovery and the Utilisation of Effluents. *The Environmentalist*. **12**(4): 277-285.

- Krantz, D and Kifferstein, B. 1997. Water Pollution and Society (online). <http://www.angelfire.com/wi3/waterpol/waterpollution.htm> (12 October 2015).
- Malaysia. 1994. Natural Resources and Environment. *The Research Progress of Biomass Pyrolysis Process*.
- Malaysia. 1984. *Environmental Quality Act and Regulations 1974 (Revised 1984)*. (Act 127).
- Marsh H. and Rodriguez-Reinoso F. 2006. Active Carbon. *Elsevier Science & Technology Books*.
- Masha Nur Salsabiela binti Menhat. 2008. *Pre-treatment of Water Using Activated Carbon from Kernel Palm*. Universiti Malaysia Pahang. Bachelor of Civil Engineering.
- Md. Din and Rohani, Zainal Abideen, Muzaaffar, Ahmad, Mohd. Azlan, Razak, Mohd. Fadhil, Ujang, Zaini, Loosdrecht, M.C.M. Van, Ismail, Mohd. Nasir and Husin, Aishah. 2006. Storage of polyhydroxyalkanoates. (PHA) in fed-batch mixed culture using palm oil mill effluent (POME). In: *4th Seminar on Water Management (JSPS- VCC), Johor*. pp. 119-127.
- Moreno-Castilla C., F. Carrasco-Marin, M.V. Lopez-Ramon and M.A Alvarez-Merino. 2001. Chemical and physical activation of olive-mill waste water to produce activated carbons. *Carbon*. **39**: 1415-1420.
- MPOB. 2013. Malaysian Palm Oil Statistics. Malaysia: Malaysian Palm Oil Board, Ministry of Plantation Industries & Commodities.
- Murhekar Gopalkrushna H. 2011. Assessment of Physico- Chemical Status of Ground Water Samples in Akot City. *Research Journal of Chemical Sciences*. **1**(4): 117-124.
- Muhrizal, S. J., Shamshuddin T., I. Fauziah and M.A.H Husni. 2006. Changes in iron-poor acid sulphate soil upon submergence. *Geoderma*. **131**:110-122.
- Namanea, A. Mekarziab, K. Benrachedib, N. Belhaneche-Bensemraa, and A. Hellala. 2005. Determination of the adsorption capacity of activated carbon made from coffee grounds by chemical activation with ZnCl₂ and H₃PO₄. *Journal of Hazardous Materials*. **119**: 189–194.
- Ng W.J., A.C.C Goh and J.H. Tay. 1987. Palm oil mill effluent (POME) treatment- an assessment of coagulants used to aid liquid-solid separation. *Biological Wastes*. **21**: 237-248.
- Onwueme I.C & Sinha T.D. 1991. Field crop production in tropical Africa. CTA (The Technical Centre for Agricultural and Rural Co-operation). *Ede, The Netherlands*. pp. 1–480

- Phaik E.P., Wei-Jin Yong and Mei F.C.. 2010. Palm oil Mill Effluent (POME) Characteristic in High Crop Season and the Applicability of High-Rate Anaerobic Bioreactors for the Treatment of POME. *Industrial & Engineering Chemistry Research*. **49**: 11732 - 11740.
- Pleanjai S. 2004. Environmental Evaluation of Biodiesel Production from PalmvOil in a Life Cycle Perspective. *The Joint International Conference on Sustainable Energy and Environment (SEE)*, pp.1-3.
- Prasertsan, S. and Prasertsan P. 1996. Biomass residues from palm oil mills in Thailand: An overview on quantity and potential usage. *Biomass Bioenergy*. **11**(5): 87-395.
- Reffasa A., V. Bernardeta, B. Davida, L. Reinerta, M. Bencheikh Lehocineb, M. Dubois, N. Batissec and L. Duclaux. 2010. Carbons prepared from coffee grounds by H_3PO_4 activation: Characterization and adsorption of methylene blue and Nylosan Red N-2RBL. *Journal of Hazardous Materials*. **175**: 779–788.
- Reynolds and Richards, T. Reynolds and P. Richards. 1996. *Unit Operation and Process in Environmental Engineering*. 2nd ed. Boston, MA, USA: PWS.
- Robert Considine, Renaud Denoyel, Phillip Pendleton, Russell Schumann and Shiao-Hui Wong. 2001. The influence of surface chemistry on activated carbon adsorption of 2- methylisoborneol from aqueous solution. *Colloids and surfaces A: Physicochemical and Engineering Aspects*. **179**: 271-280.
- Rodriguez-Reinoso F. and M. Molina-Sabio. 1992. Activated carbons from lignocellulosic materials by chemical and/or physical activation: an overview. *Carbon*. **30**: 1111- 1118.
- Rodriguez-Reinoso F., and M. Molina-Sabio. 1996. Development of porosity in combined phosphoric acid-carbon dioxide activation. *Carbon*. **34**.
- Rupani, P. F., Rajeev Pratap Singh, M. Hakimi Ibrahim and Norizan Esa. 2010. Review of Current Palm Oil Mill Effluent (POME) Treatment Methods: Vermicomposting as a Sustainable Practice. *World Applied Science Journal*. **11**(1): 70–81.
- Shafie S.M., T.M.I Mahlia, H.H. Masjuki, and A. Ahmad-Yazid. 2012. A review on electricity generation based on biomass residue in Malaysia. *Renewable Sustainable Energy Rev.*, **16**: pp. 5879-5889.
- Singh, R.P. 2010. Composting of waste from palm oil mill: a sustainable wastemanagement practice. *Reviews in Environmental Science and Bio/Technology*. **9**(4): 331–344.

- Sivapragasam A. 2008. Coconut in Malaysia-Current developments and potential for revitalization. *Paper Presented at the Second International Plantation Industry Conference and Exhibition (IPICEX2008)*. Shah Alam, Malaysia: 18-21 November.
- Solum M.S., R.J. Pugmire, M. Jagtoyen and F. Derbyshire. 1995. Evolution of carbon structure in chemically activated wood. *Carbon*. **33**: 1247-1254.
- Su Wei, Zhou Li and Zhou Yapeng. 2006. Preparation of Micropous Activated Carbon from Raw Coconut Shell by Two-Step Procedure. *Chinese Journal Chemical Engineering*. **14**(2): 266-269.
- Twort A C, Law F M and Crowley F W, (1985). *Water Supply*. 3rd ed. UK: Amazon.
- Ugoji E.O. 1997. Anaerobic digestion of palm oil mill effluent and its utilization as fertilizer for environmental protection. *Renew Energy*. 10: 291-294.
- Wikipedia. 2015. Activated Carbon. https://en.wikipedia.org/wiki/Water_pollution (30 September 2015).
- Wikipedia. 2015. Wastewater. <https://en.wikipedia.org/wiki/Wastewater> (30 September 2015)
- Wikipedia. 2015. Water Pollution. https://en.wikipedia.org/wiki/Water_pollution (30 September 2015).
- World Water Council. 2014. *World Water Vision Report*. Republic of Korea: World Water Council.
- Wu T.Y., Mohammad AW, Jahim JM and Anuar N. 2010. Pollution control technologies for the treatment of palm oil mill effluent (POME) through end-of-pipe processes. *Journal Environment Management*. **91**: 1467-1490.

APPENDIX A

DISCHARGE STANDARD

Table 1: Parameters limits in respective standard discharge by the Malaysian Environmental Quality, 1984

Parameter	Units	Limits
Biochemical Oxygen Demand (BOD ₅)	mg/L	100
Chemical Oxygen Demand (COD)	mg/L	-
Suspended Solids	mg/L	400
Oil and Grease	mg/L	50
Lead (Pb)	mg/L	-
Copper (Cu)	mg/L	-
Boron (B)	mg/L	-
pH	-	5 - 9
Turbidity	NTU	-
Temperature	°C	45
Ammoniacal Nitrogen	mg/L	100

Source: Malaysian Environmental Quality, 1984

APPENDIX B
TABULATED DATA ANALYSIS

Table 2: Results of the treated Palm Oil Mill Effluent based on the types of Activated Carbon

Parameter	Units	Influent	Effluent (CACFS)	Effluent (PACFS)
Biochemical Oxygen Demand (BOD ₅)	mg/L	9552	96.3	127.4
Chemical Oxygen Demand (COD)	mg/L	47100	149	176
Suspended Solids	mg/L	149700	550	643.5
Oil and Grease	mg/L	4418	19.4	10.6
Lead (Pb)	mg/L	0	0	0
Copper (Cu)	mg/L	0	0	0
Boron (B)	mg/L	0	0	0
pH	-	4.22	7.02	8.25
Turbidity	NTU	18800	117	153
Ammoniacal Nitrogen	mg/L	26	0.2	0.6

APPENDIX C

PROCESS OF PRODUCING ACTIVATED CARBON



Figure 1: Drying of coconut shell under the sunlight.



Figure 2: Burning the coconut shell at 500 °C in the furnace.

APPENDIX C (CONTINUED)

Figure 3: Cooling the burned coconut shell in the desiccator.

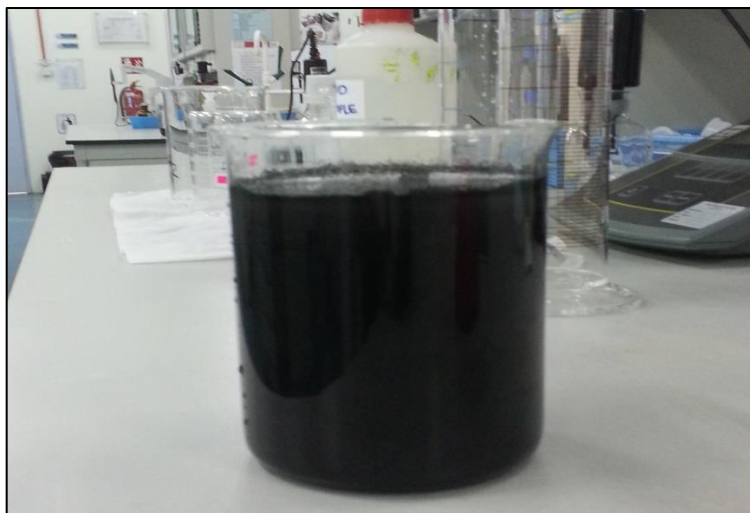


Figure 4: Soaking of carbon in CaCl_2 of 25% for 16 hours.

APPENDIX C (CONTINUED)



Figure 5: Activated carbon is produced.



Figure 6: Visible result after the filtration process.