

**REGENERATE OF DECANTER CAKE FROM PALM OIL MILL WASTE
EFFLUENT FOR THE REMOVAL OF HEAVY METAL IONS FROM
INDUSTRIAL WASTEWATER**

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UNIVERSITI TEKNIKAL MALAYSIA MELAKA

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**Laporan ini dikemukakan sebagai
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SUPERVISOR DECLARATION

“I hereby declare that I have read this thesis and in my opinion this report is sufficient in term of scope and quality for the award of degree of Bachelor of Mechanical Engineering (Thermal – Fluids)”.

Signature:

Supervisor: Mohd Haizal b. Mohd Husin

Date:

DECLARATION

“I hereby declare that the work in this report is my own except for summaries and quotations which have been duly acknowledged.”

Signature:

Author: Mohd Bakri b. Ismail

Date:

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ABSTRACT

The water pollution is a major problem to our environmental caused by several sources. The one of water pollution source came from industrial wastewater that contributed by several industries (manufacturing, semiconductor and etc). The assimilation of Pb (II) in the human body of relatively small amounts over a long period of time can lead to multifunctioning of certain organs and chronic toxicity. Therefore, the wastewater treatment is very important to reduce the concentration of heavy metal so that it can be less harmful. In the previous study, there are many ways to treat the wastewater such as precipitation, neutralization, ion exchange and adsorption processes. Adsorption method that uses decanter cake as the adsorbent was chosen as suitable method of wastewater treatment due to its capabilities and also low cost raw material. Decanter cake is a one of waste in palm oil mill waste from palm oil production industry. This research aim to reuse and regenerated decanter cake as a heavy metal ions removal from industrial wastewater. Pure decanter cake was drying at 110 °C in 12 hours than held to 200 °C, 400 °C, 600 °C and 760 °C under nitrogen atmosphere. The studies were emphasizing to adsorption capacities in term of contact time, heavy metal concentration and also adsorbent concentration by using Optical Emission Spectrophotometer (OES) for adsorption activities.

ABTRAK

Pencemaran air merupakan satu masalah utama kepada alam sekitar disebabkan oleh beberapa sumber. Salah satu sumber pencemaran air datang dari air sisa industri yang disumbangkan oleh beberapa industri (perkilangan, semikonduktor dan sebagainya). Asimilasi Pb (II) dalam tubuh manusia dalam jumlah yang kecil dalam jangka masa yang panjang boleh membawa kepada kitadakupayaan organ-organ tertentu dan ketoksikan yang kronik. Oleh itu, rawatan air sisa adalah sangat penting untuk mengurangkan kepekatan logam berat supaya ia menjadi kurang berbahaya. Dalam kajian sebelumnya, terdapat banyak cara untuk merawat air kumbahan seperti pemendakan, peneutralan, pertukaran ion dan proses penjerapan. Kaedah penjerapan yang menggunakan “decanter cake” sebagai adsorben telah dipilih sebagai kaedah yang sesuai rawatan air sisa kerana keupayaannya dan juga kos bahan mentah yang rendah. “Decanter cake” adalah satu sisa untuk sisa – sisa minyak kelapa sawit di industri pengeluaran minyak sawit. Tujuan penyelidikan ini adalah untuk menggunakan semula dan membangunkan semula “decanter cake” sebagai penyingkir ion logam berat daripada air sisa industri. “decanter cake” tulen dikeringkan pada 110 °C selama 12 jam dan kemudiannya dibiarkan pada suhu 200 °C, 400 °C, 600 °C dan 760 °C di bawah atmosfera nitrogen. Kajian ini menekankan kepada pembelajaran tentang kapasiti penjerapan dalam jangka masa sentuh, kepekatan logam berat dan juga kepekatan adsorben dengan menggunakan Spektrometer Pembebasan Optik (OES) sebagai aktiviti penjerapan.

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LIST OF ABBREVIATION

DC	Decanter Cake
POME	Palm Oil Mill Effluent
TGA	Thermogravimetry Analysis
XRD	X-Ray Diffraction
BET	Brunauer Emmett Teller
FFB	Fresh Fruit Bunches
MPOB	Malaysia Palm Oil Board
PDC	Pyrolysis Decanter Cakes
LPH	Liter Per Minute
GAC	Granular Activated Carbon
OES	Optical Emission Spectrophotometer
SEM	Scanning Electron Microscopic
FTIR	Fourier Transform Infra-Red
EDX	Energy Dispersive X-Ray

LIST OF SYMBOLS

Pb	Lead
Cd	Cadmium
Cu	Cooper
Hg	Mercury
Mn	Manganese
Ni	Nickel
Zn	Zinc
C	Carbon
N	Nitrogen
P	Potassium
K	Calcium
Mg	Magnesium
H ₂ O ₂	Hydrogen Peroxide
H ₂ O	Water
O ₂	Oxygen
Pb (NO ₃) ₂ .	Lead nitrate
AlO ₃ ,	Aluminum Oxide
SiO ₂	Silica Oxide
FeO ₂	Iron Oxide

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CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND

Malaysia is among of biggest producer of palm oil in the world that contributes 47% of global output. The processing of 1 tone of fresh fruits bunch produces 168 kg of crude palm oil and production of 140 kg fibre, 60 kg shell, 240 kg empty fruit bunch and 42 kg decanter cake (Zaki at al., 2010). The wastes from palm oil production also called Palm Oil Mill Effluent (POME). Besides that, the palm oil industry also generates large amount of palm shell, a large portion of it is either burned in the open air or was dumped in adjacent area to be mill, which contribute environmental and disposal problem within near areas. The one of the palm oil mill waste that can be reuse is decanter cake. The decanter cake is a potential raw material for production low cost adsorbent for heavy metal removal in wastewater.

1.2 WATER POLLUTION

Water is an essential element in the maintenance of all forms of life, and most living organisms can survive only for short periods without water. The supplying of good quality of water was very important because it is significant application in human daily life. The good water quality is able to protecting and preventing the human from critical illness that caused by water pollution and contamination in water supply. In other words, water is an essential resource that sustains life on earth.

Changes in the natural quality and distribution of water have ecological impacts that can sometimes be devastating.

Water pollution is caused by point and non-point sources. The point sources include sewage treatment plants, industries (manufacturing, semiconductor, textiles and etc), agro-based industries and animal farms. Non-point sources are defined as diffused sources such as agriculture activities and surface run-offs. The situation of water pollution in Malaysia is becoming more serious and need the drastic action by the government and community (Jacky, 2010). The industrial wastewater also contribute the major water pollution by discharge the heavy metal that dangerous to the human and life organism even exist in the small amount in wastewater

1.3 INDUSTRIAL WASTEWATER

The industrial wastewater is the one of water pollution resources that has many types of industries such as manufacturing, semiconductor and petro-chemical. Disposal of industrial wastewater has been always been a major environment issues. The pollutants and heavy metal in industrial wastewater are usually toxicity to human and environmental (Badmus at al., 2006). Table 1.1 show that the list of heavy metal from various industrial sources. However, the research only concerns the heavy metal of Pb (II).

Table 1.1: The list of heavy metal from industrial sources

Metal	Industrial sources
Pb	Storage batteries, insecticides, plastic water pipes
Cd	Electroplating, paint pigments, plastics, batteries
Cu	Printed circuits, pipe corrosion and metal plating
Hg	Pulp and paper, oil refining, rubber processing and fertilizer
Mn	Glass and ceramics, paint and varnish
Ni	Electroplating, zinc base casting and storage battery industries
Zn	Ceramics, textiles, fertilizers, pigments, steel production and batteries

(Source: Detox my child, 2006)

1.4 HEAVY METAL OF Pb (II)

In definition a heavy metal is a toxic metal. There is no standard definition assigning those metals as heavy metals. Most heavy metals have a high atomic number, atomic weight and the specific gravity bigger than 5.0. Some lighter metals and metalloids are toxic and dangerous for environmental. Heavy metals also include some metalloids, transition metals and basic metal (Anne, 2012).

Lead has environmental importance due its well-known toxicity and intensive use in industries such as storage battery manufacture, printing, pigment manufacturing, petrochemical, fuel combustion and photographic materials. The assimilation of Pb (II) in the human body of relatively small amounts over a long period of time can lead to multifunctioning of certain organs and chronic toxicity. In

water, Pb (II) tends to accumulate in aquatic organism through the food chain and also by direct utilization. It can damage practically all tissues, particularly the kidney, immune system and causes encephalopathy with the following symptoms such vertigo, insomnia, migraine, irritability, and even convulsions, seizures, and coma (Naseem, 2012).

The 6% of Pb (II) was used for the manufacturing of batteries. Such industries tend to pose a significant risk to their workers as well as to surrounding communities. There are the needs to treat the wastewater to reduce the concentration of toxic below the recommended release limit (Naseem, 2012). Adsorption is one of the methods that commonly used to remove heavy metal ions from aqueous solutions with relatively low metal ion concentrations. The efficiency of adsorption depends on the capability of the adsorbent to adsorb heavy metal ions from the solutions into the surfaces. The adsorption process could reduce the concentration of heavy metal in wastewater, thus reduce the negative impact to the environment.

1.5 PROBLEM STATEMENT

Heavy metals are among the most detrimental pollutants in source and treated water, and are becoming a severe health problem. Since the damaging effects of heavy metals in environment are known, many methods of treatment for industrial wastewater have been reported in literature. Amongst these methods are neutralization, precipitation, ion exchange and adsorption. For low concentration of metal ions in wastewater, the adsorption process is recommended for their removal.

In the other side, decanter cake are the major waste in crude palm oil industry even about 4-5 tons of decanter cake produced for every 100 tons of palm fresh fruit bunch processed. Currently, most of decanter cakes are disposed in the landfill or reuse as fertilizer. Due to their high organic content, decanter cake has potentially as absorbent for the regenerated and reuse as heavy metal ions removal from industrial wastewater.

1.6 OBJECTIVES

The objectives of this study are listed below:

- i. To regenerate decanter cake from Palm oil mill waste for the removal of heavy metal ions from industrial wastewater.
- ii. To reuse decanter cake from Palm oil mill waste for the removal of heavy metal ions (Pb^{2+}) from industrial wastewater.

1.7 SCOPES

- i. Regenerate, reuse and characterise the decanter cake from palm mill waste by heating treatment.
- ii. Study adsorption capacities of regenerated decanter cake for heavy metal ion Pb (II).

CHAPTER TWO

LITERATURE REVIEW

2.1 DECANTER CAKE

2.1.1 Decanter cake resource

Palm oil industries contribute of most of waste and effluent to the environment. More than 70% of fresh fruit bunches processed are released as effluent and waste during the milling process. The analysis conducted before found the 5.20 wt% of kernel and 23.52 wt% of oil had been produced then 71.28 wt% were lose as by product or waste from the fresh fruit bunch that were milled. Decanter cake is a solid waste produced from the three difference phase separation step of crude palm oil process. The production rate of decanter cake amount to 4 – 5 % weight of fresh fruit bunch processed. Fresh decanter cake contains over 70% moisture, while the dry matter contains oils, fibre and inorganic components (Dewayanto at al., 2010).

Many adsorbent were potentially to be prepared from agriculture waste since the raw material for making the adsorbent was available in low cost generally. Malaysia is among of biggest producer of palm oil in the world after Indonesia. The production in Malaysia contributes 47% amount of production of total global output. The processing of each 1000 kg of fresh fruits bunch produces 168 kg of crude palm oil and resulted in production of a40 kg fibre, 60 kg shell, 240 kg empty fruit bunch and 42 kg decanter cake (Zaki at al., 2010). Decanter cake is a potential raw material

for production low cost adsorbent for heavy metal ions removal. In this study, the transformation of decanter cake into low cost adsorbent of Pb (II) was being explored.

2.1.2 Decanter cake characterization

Thermogravimetry Analysis (TGA) measures the amount and rate of change in weight of a material as a function of temperature or time in controlled atmosphere. Measurement also used to determine the composition of materials and to predict their thermal stability in certain Temperature range. The proximate analysis using Thermogravimetry (TGA) of decanter cake carbonized at 500 °C were result that the adsorbent contained 4% moisture, 21% volatile, 23% fixed carbon, and 52% ash. The adsorbent was characterized by TGA Q 500 Instrument in the way to determine thermal properties and proximate analysis of decanter cakes produced. The samples were heated in nitrogen atmosphere from ambient temperature to 1000 °C at a heating rate of 5 °C / minute. The internal heating space then was switched into oxygen at 950 °C (Dewayanto at al., 2010).

X-Ray Diffraction analysis (XRD) can be used for examines crystalline the material structure including crystallite size, atomic arrangement, and disorders. The materials used will react by X-ray and then emitted in many directions. X-ray powder diffraction (XRD) is one of the most potential techniques for qualitative and quantitative analysis of crystalline compound for the solid adsorbent such decanter cake that in form of powder. This technique able to provides information that cannot be obtained in any other ways. The analysis includes types and nature of crystalline phase's, structural make-up of phases, rate of crystallinity, and amount of amorphous content such micros train & size and orientation of crystallites (Sam Iyengar, 2012).

Brunauer Emmett Teller (BET) analysis able to provides the precise specific surface area evaluation of decanter cake in form of powder by using the measure of nitrogen gas multilayer adsorption as a function of relative pressure using a fully

automated analyser. The technique studies external area and pore area evaluations of decanter cake particles to determine the total specific surface area in m^2/g yielding importance information during studying the effect of surface porosity and particle size in many applications. BET can also be employed to determine pore area and specific pore volume using adsorption and desorption techniques. This technique can characterize pore size of decanter cake particle distribution independent of external area due to size of the adsorbent sample (Ceram, 2012).

Chemical characterization in the scanning electron microscope (SEM) is performed non-destructively with energy dispersive X-ray analysis (EDX). Energy-dispersive X-ray spectroscopy (EDX) is an analytical technique used for the elemental analysis or chemical characterization of a sample. Chemical elements starting with the atomic number 6 (carbon) can be determined with this analysis method. It relies on the investigation of an interaction of some source of X-ray excitation and a sample. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing unique set of peaks on its X-ray spectrum (sensore electronic, 2012).

2.1.3 Decanter cake usage

The most common utilization of decanter cake is a fertilizer and animal nutrition sources due to presence of C, N, P, K and Mg. The decanter cake is source of nutrients for producing bio-compound fertilizer and also suitable for animal food (Dewayanto at al., 2010). In many applications, the local fertilizer manufactures usually mix decanter cake with inorganic fertilizer that follows MPOB formulation to increase the efficiency of nutrient that contributed by crops. It is estimated that about 0.4% of decanter cake could be produced for every tone Fresh Fruit Bunches (FFB) processed. Decanter cake obtain amount of nutrient and the boiler ash containing high percentage of potassium (Khalid at al., 2008). This product can be mixed with inorganic fertilizer to enrich the amount of nutrient content as the palm based bio-compound fertilizer.

Decanter cakes are the major wastes in crude palm oil industry which are currently disposed in the landfill or reuse as other applications. But on the other view, decanter cakes has potentially as a solid fuel same with charcoal, wood briquette, based on their calorific amount caused by the residual oil in decanter cakes. The initial finding of Thermogravimetric Analysis (TGA) and the heat of combustions by using oxygen bomb calorimeter methods for characterizing the different Pyrolysis Decanter Cakes (PDC). The absolute heat transfer value technique used to compare potential decanter cake with others commercial solid fuel types such as coconut charcoal, charcoal and charcoal briquette (Haizal at al., 2009).