TREATMENT OF LANDFILL LEACHATE BY PALM OIL WASTE CARBON COPPER-OXIDE NANO COMPOSITE

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By

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ABSTRAK

Pelupusan air larut lesap dalam tanah mengandungi sejumlah besar bahan cemar organik dan tidak organik yang berbahaya dan membawa kesan yang luar biasa ke arah persekitaran terutamanya di permukaan air, air bawah tanah dan udara. Pelupusan air larut lesap perlu dirawat untuk mengelakkan dari pencemaran komposisi berbahaya yang lahir dari proses larut lesap. Dalam kajian ini, kaedah rawatan yang telah dibincangkan adalah proses fizikal kimia penjerapan. Oleh itu, daun kelapa sawit digunakan sebagai prekursor untuk menghasilkan rawatan penjerapan dalam penyingkiran COD, warna dan logam berat dari air larut lesap. Kadar keberkesanan penjerapan telah dikaji berdasarkan kesan nisbah, suhu dan masa pengkarbonan yang diresapi dengan menggunakan H_3PO_4. Untuk menilai kadar penjerapan, ia dapat diperoleh daripada ujian nombor iodin di mana nisbah yang dilaraskan optimum ialah 1: 3 pada 400^oC selama 1 jam. Dos dan masa kontak diperiksa di mana kadar dos optimumnya adalah 0.6g pada 30 minit. Nanocomposite karbon diaktifkan dengan tembaga oksida telah dikaji dalam kajian ini untuk menentukan prestasi dalam kadar penjerapan. Kedua-dua Langmuir dan Freundlich Isotherms digunakan untuk menggambarkan penjerapan COD, warna dan logam berat.

ABSTRACT

Landfill leachate contains large amount of organic and inorganic contaminants which is it hazardous and bring a tremendous impact towards the environment in surface water, groundwater and air. The landfill leachate needed to be treated to avoid from contamination of these hazardous composition born from the leaching process. In this studies, the treatment method that have been discussed was chemical physical process of adsorption. Thus, oil palm frond was used as precursor to produce the adsorption treatment in COD, colour and heavy metals removal from landfill leachate. The effectiveness of adsorption rate was studied based on the effects of impregnated ratio, temperature and time of carbonization by using H_3PO_4. In order to examine the adsorption rate was gained from iodine number test where the optimum impregnated ratio was 1:3 at 400^oC for 1 hour respectively. The dosage and contact time was examined where the optimum dosage rate is 0.6g at 30 minutes. The activated carbon nanocomposite with Copper oxide was studied in this research to determine the performance in adsorption rate. Both Langmuir and Freundlich Isotherms could be used to describe the adsorption of COD, colour and heavy metals.

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LIST OF ABBREVIATIONS

AC	**A**ctivated **C**arbon
Can	**A**ctivated **C**arbon/CuO
OPF	**O**il **P**alm **F**rond
OPFAC	**O**il **P**alm **C**arbon **A**ctivated **C**arbon
SEM	**S**canning **E**lectron **M**icroscope
ICP	**I**nductive **C**ouple **P**lasma
PBSL	**P**ulau **B**urung **S**anitary **L**andfill
COD	**C**hemical **O**xidation **D**emand
BOD	**B**iochemical **O**xidation **D**emand
EQA	**E**nvironmental **Q**uality **A**ssessment

NOMENCLATURES

RL	A dimensionless equilibrium parameter
Co	Initial concentration (mg/L)
Ce	Final concentration (mg/L)
Qe	Equilibrium adsorption capacity (mg/g)
K_L	Langmuir adsorption constant (L/mg)
Qm	Maximum adsorption capacity (mg/g)
K_F	Freundlich constant (L/g)
nF	Heterogeneity factor of adsorption sites (dimensionless)
Ce	Dye concentration at equilibrium (mg/L)
Co	The highest initial dye adsorption concentration

CHAPTER 1

INTRODUCTION

1.1 Background of study (leachate)

A leachate is any liquid that drains or ‘leaches’ from a landfill in the course of liquid percolates or passing through permeable material, extracts dissolved and suspended material, or any other component of the material through become contaminated. However, it varies widely in composition regarding the age of the landfill and the type of waste that it contains. These substances which migrates in water surface and rock ambient create major hazardous pollution towards the quality of surface water and groundwater.

1.2 Pulau Burung Sanitary Landfill

PBSL is located at Byram reserves, Nibong Tebal, Pulau Pinang. It has an area of 62.4 ha of which 33 ha are currently operational receiving about 1,800 tonnes of municipal and non-hazardous industrial solid waste daily. On average, about 600 tonnes of incoming MSW are from Penang Island and the mainland. This site has a natural marine clay liner because of the landfill is sited near to sea shore. In the first 10 years of operation from early 1980s until 1990s, the waste disposed without appropriate management and no leachate control. In 1991, PBSL started operation as a semi-aerobic system complying with level II sanitary landfill standards by establishing a controlled tipping technique. In 2001, PBLS was upgraded to level III sanitary landfill by employing controlled tipping with leachate recirculation. In 2012, the operation of PBSL has been awarded to private concessionaire to ensure smooth and effectiveness of daily operation and management at the landfill.

In terms of engineered landfill system, PBSL has adapted Fukuoka method which enable ambient flows into the waste body by natural means through the leachate collection pipes which improves the waste stabilization process and increase the leachate quality due to enhancement of the micro-organism activities in the waste. Fukuoka method was a proven technology that have been tested in many countries including Japan, Malaysia, Iran and China. This method have several advantages such as enhanced aerobic biodegradation of organic matter, reduced methane generation, reduced contamination load if leachate and cost effectiveness in comparison to aerobic landfill.

1.3 Problem statement

Water scarcity and pollution are in the equivalent rank to the climate change as the most urgent environmental issue for the 21th century (Foo and Hameed, 2009). The percolation of leachate generation from the landfill into surface water and groundwater contains high organic matter and hazardous compounds that causes significant negative threat to the environment. The contamination produced from the external exposure and toxicity of the waste that emits within a landfill depending on both dissolved and suspended material. The leachate formation from the water balance infiltration entering the pores within the landfill and extract various contaminants producing moisture content sufficiently high to initiate the liquid flow induced by the precipitation, irrigation, surface runoff, gravity force, refuse decomposition, groundwater intrusion and initial moisture content present within the landfill. Therefore, the landfill leachate need to be treated to avoid from the contamination of the surface water and groundwater.

Adsorption process is recognized as the most efficient and favourable fundamental approach in the wastewater treatment method. However, commercially available activated carbon (mostly made of charcoal, wood, etc.) is quite expensive.

Thus, many low-cost raw materials from various agricultural by-products or wastes, such as rice husk, coconut shell, nut shell and oil palm shell was introduced. This study was carried out to analyse OPFAC with nano copper-oxide as low-cost adsorbent to treat pollutant in leachate.

1.4 Objectives

The purpose of this research is to study the ability of oil palm frond activated carbon with Copper Oxide nano-composite in eliminating the pollutant in wastewater of landfill leachate in terms of COD, colour and heavy metals. The objectives are as following:

i) To determine the chemical and biological properties of leachate.

ii) To determine the effect of contact time and dosage on the sorption of pollutant by OPFAC.

iii) To study the effect of copper nano composite in removing the targeted pollutant.

1.5 Scope and limitation of study

For this study, the only wastewater sample from Pulau Burung sanitary landfill leachate was used for the research. This experiment was conducted in the Environmental Laboratory 1, School of Civil Engineering USM Engineering Campus.

The characteristics of the landfill leachate that were considered in this study are BOD, COD, pH, colour and turbidity. Meanwhile, the parameter for the treated leachate tested colour removal and COD only.

Other than that, the OPFAC only used as adsorbent in order to treat the landfill leachate.

1.6 Thesis organization

Chapter 1: Introduction – this chapter gives an overview of the thesis, followed by the problem statement to identify, and understand why this research was carried out and its relevance to current times followed by the objectives of this research in order to set the desired target of work and finally the justification of this research.

Chapter 2: This chapter include the review of the previous study that have been done on the adsorption of activated carbon. The preparation of the activated carbon, the chemicals used, the image of the SEM and the way to calculate the adsorption isotherm.

Chapter 3: The overall methodology has been applied in this study with details. The brief description of the experiments was performed in order to determine the performance of the adsorption of Oil Palm activated carbon and their efficiency in order to treat COD, colour and heavy metal from landfill leachate.

Chapter 4: The preliminary studies on the effect of impregnation ratio, time and carbonization time was presented in this chapter to determine the optimum ability of active carbon. The result of different dosage used and the time contact for a fixed volume of leachate sample. Finally, the efficiency of these adsorbents was examined by a series of adsorption isotherms.

Chapter 5: Conclusion is drawn based on the results gained from the experiments work.

CHAPTER 2

LITERATURE REVIEW

2.1 Generation of leachate

Leachate generated in landfill contains large amounts of organic and inorganic contaminants which it has great impact on soil permeability, surface water, groundwater, and air. The leachate composition varies most likely depending on the age of the landfill and the nature of solid waste. Chemically bound water which is present in solid waste constituents, along with water from external sources, causing it to produce a really very high dissolved and suspended solid content together with both organic and inorganic. Landfill leachate can be describe as a dark coloured liquid, with a strong smell.

Typically, the characteristic of the landfill leachate can be best represented by chemical oxygen demand (COD), total organic carbon (TOC), biochemical oxygen demand (BOD), BOD/COD ratio, pH, suspended solids (SS), ammonium nitrogen (NH_3-N), total Kjeldahl nitrogen (TKN), bacterial count, turbidity or heavy metals content, which provided a prerequisite insight into the prediction of future trends of leachate quality and the design and operation of leachate management facilities (Foo and Hameed., 2009).

More precisely, it is a soluble organic and mineral compound formed when water infiltrates into the refuse layers, extracts a series of contaminants and instigates a complex interplay between the hydrological and biogeochemical reactions that acts as a mass transfer mechanisms for producing of moisture content sufficiently high to initiate the liquid flow, induced by the gravity force, precipitation, irrigation, surface runoff, rainfall, snowmelt, recirculation, liquid waste co-disposal, refuse decomposition, groundwater

intrusion and initial moisture content present within the landfills (Foo and Hameed, 2009).

2.2 Leachate treatment

There are a range of technologies available to treat landfill leachate in different ways. These include:

I. Biological Treatment – This is usually the first step in treating landfill leachate. It involves using many different filters to remove nitrogen and other biological compounds from the wastewater.

II. Chemical-Physical Processes – Wet oxidation processes can be used if it is possible to oxidize organic compounds. This includes activated carbon adsorption, precipitation, flocculation and ion exchange processes among others.

There are many methods of leachate treatment such as (Ragharb et al., 2013);

I. Aerobic Biological Treatment such as aerated lagoons and activated sludge.

II. Anaerobic Biological Treatment such as anaerobic lagoons, reactors.

III. Physiochemical treatement such as air stripping, pH adjustment, chemical precipitation, oxidation, and reduction.

IV. Coagulation using lime, alum, ferric chloride, and land treatment.

V. Advanced techniques such as carbon adsorption, ion exchange.

2.2.1 Adsorbent

Activated carbon (AC) products are produced from organic materials that are rich in carbon. The choice of precursor is largely dependent on its availability, cost and purity. The pre-cursor and the method used for activation largely determine the adsorption properties of the AC (Kalderis et al., 2008). AC is a widely used adsorbent in the treatment of wastewater and drinking water because it possesses desirable physiochemical properties including good mechanical strength, chemical stability in diverse media, and large pore size distribution in addition to its extensive specific surface area (Salman et al.,2011). The most important characteristic of an activated carbon is its absorption capacity which highly influenced by the preparation conditions (Salman., 2013).

Activated carbon adsorption aim is to ensure final polishing level by removing toxic heavy metals or organics and support microorganisms. Other materials, tested as adsorbents, have given treatment performances close to those obtained with activated carbon. (Abdulhussain et al., 2009).

In adsorption processes, adsorbents with high specific surface areas are needed. Small pores, such as micropores and mesopores, result in a large specific surface area responsible for adsorption. Pore size, pore distribution and surface area, as well as pore surface chemistry, are the major factors in the adsorption process (Givianrad et al., 2013). Activated carbon has attracted as one of the best adsorbent materials due to its capacity to remove unpleasant tastes, odors, color and various chemicals from water. Although activated carbon efficiently removes majority of organic contaminants, it is less effective in removing many heavy metals and micro-organisms in water (Jayaweera et al., 2018).

2.2.2 Adsorbate

Landfill leachate is a complex liquid that contains excessive concentrations of biodegradable and non-biodegradable products including organic matter, phenols, ammonia nitrogen, phosphate, heavy metals, and sulfide. If not properly treated and safely disposed, landfill leachate could be an impending source to surface and ground water contamination as it may percolate throughout soils and subsoils, causing adverse impacts to receiving waters. Lately, various types of treatment methods have been proposed to alleviate the risks of untreated leachate. However, some of the available techniques remain complicated, expensive and generally require definite adaptation during process. (Kamaruddin et al., 2013).

2.3 Activated carbon

2.3.1 Activated carbon from oil palm waste

Oil palm (*Elaeis guianensis*) grows well in wet, humid parts of tropical Asia. Since, Malaysia is one of the largest producer of palm oil in the world and also oil palm frond (OPF) is a horticultural waste that is usually discarded in fields and not being utilized completely. As an activated carbons are mostly solids with their wide surface area and pore volume. They are composed of a fundamental structure composing of dense aromatic circles. Pores in the carbon cause an increase in the surface area after activation (Altintig and Kirkil, 2016).

2.3.2 Chemical activation

Chemical activation has been shown as an efficient method to obtain carbons with high surface area and narrow micro-pore distribution (Muzakkir et al., 2007). Utilization of activated carbon (AC) by adsorption process is a very popular and effective way to

deal with these toxic and hazardous organic micro-pollutants in wastewater (Njoku et al., 2014). The most commonly used activating agents are $ZnCl_2$, H_3PO_4, KOH, K_2CO_3, etc. Then impregnated material is heated in the absence of oxygen (Sahin et al., 2015).

2.3.3 Activated carbon nanocomposite

Ionic copper for waste and wastewater treatment (INC) was used as bacterial regulator for biological waste in municipal wastewater treatment plants. A mineral-based bacteria regulator that suppresses anaerobic bacteria growth and encourages aerobic bacteria and biomass digestion to prevent and reverse toxicity and anoxic conditions arising from oxygen depletion. It effective against bacteria problem whether in aerobic and anaerobic producing bacteria.

These nano copper proprietary technology uses the most effective form of copper. It does not evaporate, precipitate out, nor is it affected by sunlight or temperature. Once inside the cell of the microorganism, ionic copper reacts with sulphur containing amino acids in the proteins used for photosynthesis (the process of converting light and nutrients into usable food and energy). As a result the target organism can no longer perform photosynthesis which leads to cell lyses (disintegration) and death. Even if the cell manages to live for a short time, the reproduc3on process is hampered by the presence of copper ions and the spread of the micro-organism is stopped. Most undesirable microorganisms are killed at low copper ion concentra3ons whereas important beneficial bacteria being more tolerant to copper will survive.

However, according to the figure 2.1 showed that the CuSO4 has never been used in this application of water and wastewater treatment simply because it precipitates quickly in this harsh environment unlike nano ionic copper where they penetrate cell walls and either disrupt reproduction or kill the organism outright.

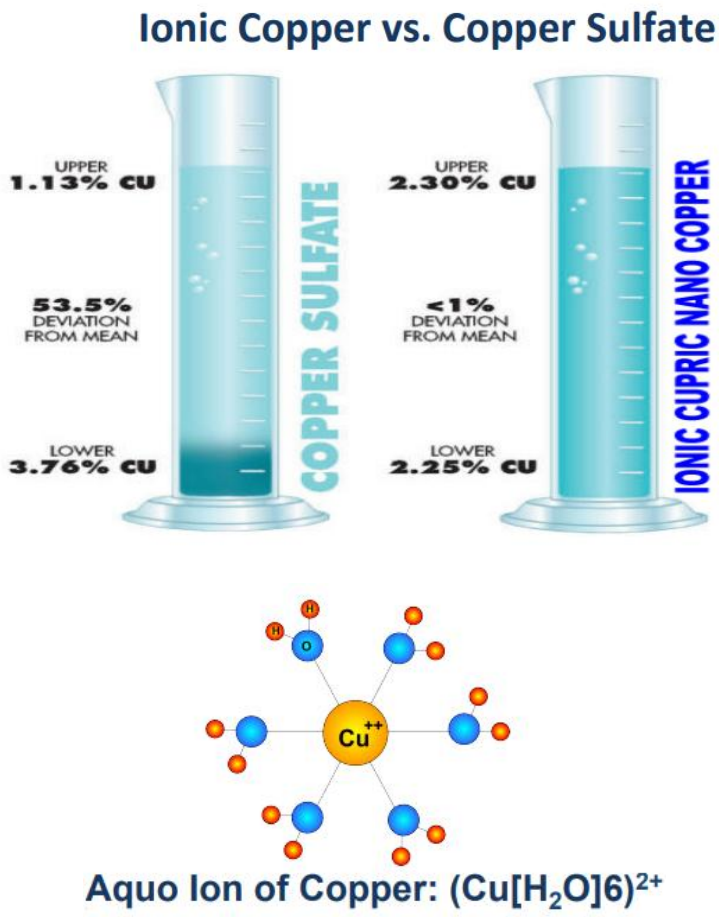

Figure 2.1 : The difference of $CuSO_4$ and ionic cupric nano copper (Kamaruddin., 2015)

2.3.4 Surface characterization by Iodine number test

Iodine test is a test method that covers the relative adsorption capacity for its simplicity and a rapid assessment of activated carbon quality by the adsorption of iodine from aqueous solution (Sahin et al., 2015). It is a measure of the micropore content of the activated carbon and is obtained by the adsorption of iodine from solution by the activated carbon sample. The micropores are responsible for the large surface area of activated carbon particles and are created during the activation process. (Ekpete and Horsfall., 2011).

2.4 Factors effect in activated carbon process

The most important characteristic of an activated carbon is its adsorption uptake or its removal capacity which is highly influenced by the preparation conditions. Besides, the activated carbon yield during preparation is also a main concern in the activated carbon production for economic feasibility (Jasim M, 2014). Heating rate, impregnation ratio and activation temperature are all sensitive conditions for the surface area development. Increasing the impregnation ratio can increase the surface area initially and then decrease the surface area (Patil and Kulkarni, 2012).

2.4.1 Effect of activation

Phosphoric acid as an activating agent was found to be very efficient in the production of activated carbons with high porosity and the impregnation ratio has a significant influence on porosity development (Chen et al., 2017) .

2.4.2 Effect of impregnation ratio

Phosphoric acid acts as catalyst on the one hand promoting bond cleavage reactions, on the other hand facilitating crosslinking via cyclization, condensation, and being able to combine with organic species to form phosphate linkages, such as phosphate and polyphosphate esters (Yorgun and Yildiz, 2015). The more the phosphoric acid was used, the larger the amounts of polyphosphates are formed and retained in activated carbon in the form of insoluble metal phosphates, or physically entrapped, even though phosphoric acid is removed after reaction by leaching with ample usage of fresh water to recover the reagent. (Mi et al., 2015).

2.4.3 Effect of carbonation temperature

The carbonization was done using the box-type resistance furnace at a temperature of 400^{o}C for 1 hour. The paste was then transferred into a crucible. The crucible was placed in the furnace where it was heated at a temperature of 400°C for 1 hr. It was allowed to cool and washed with distilled water until a neutral pH was obtained, oven-dried at 100°C for 12hrs (Ekpete et al., 2017). Precautionary measures are usually taken when choosing a temperature due to the fact that above certain temperatures the sample will completely change to ash. Temperatures within the range of 200–1100°C have been in constant use for preparation of activated carbon which is also dependent on the method of activation. ACs with high surface area can be obtained at lower temperatures, compared to the temperatures required for physical activation (Kalderis et al., 2008). The activating agents act as dehydrating agents that inhibit the formation of tar as well as volatile substances during the process, which helps to enhance the yield of porous carbon and to decrease the activation temperature and activation time compared with the physical activation method (Kumar and Jena, 2016).

2.4.4 Effect of carbonisation time

The excessive time that led to the contraction and collapse of pores, thus the surface area and pore volume became smaller (Wang et al., 2011). The prolongation of activation time beyond 1 hour led to a pronounced reduction in porosity development (Castro et al., 2000). A shorter activation time can reduce the energy consumption and improve economy of the production process and should be accepted in preparing activated carbon (Mi et al., 2015).

2.5 Absorption isotherm

2.5.1 Langmuir and Freundlich adsorption isotherm

The Langmuir equation assumes that the surface of adsorbent is energetically homogeneous whereas, the Freundlich equation accounts for a multisite adsorption isotherm for heterogeneous surfaces and is characterized by the heterogeneity factor 1/n. (Bhatt A.S et al., 2012).

Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform approaches of adsorption with no transmigration of adsorbate in the plane of the surface (Weber and Chakravorti., 1974). As for Freundlich model, this model is applied to describe the heterogeneity of the adsorbent adsorbate interaction and also suggests that sorption energy will exponentially decrease upon completion of the sorption centers of the adsorbent. (Rugayah et al., 2014)

Langmuir isotherm constants (Q and b) can be obtained by plotting 1/(x/m) against 1/Ce. The Freundlich isotherm constants were achieved by plotting log (x/m) against log (Ce). Based on the table below, these equations were used in adsorption isotherm.

A dimensionless equilibrium parameter RL (separation factor) could be used to express the characteristics of the Langmuir isotherm (Isa et al., 2007) described to evaluate the Langmuir favourable adsorption. When all the values of RL are in the range $0 < R L < 1$.

$$RL = \frac{1}{1+KLC_o} \qquad \text{Equation 2.1}$$

Table 2.1 : Equilibrium model equations; x and y values, slope and intercept for the isotherm equations (Bhatt A.S et al., 2012).

Langmuir isotherm		
Non linear	Linear	Slope and intercept
$Qe = \frac{Q_m K_L C_e}{I + K_L C_e}$	$\frac{Ce}{Qc} = \left(\frac{1}{Q_m}\right) C_e + \left(\frac{1}{K_L Q_m}\right)$ $y = \frac{C_e}{Q_e}$, $x = C_e$	$Slope = \frac{1}{Q_m}$ $Intercept = \frac{1}{Q_m K_L}$
Freundlich isotherm		
Non- linear	Linear form	Slope and intercept
$Qe = K_F C_e^{\frac{1}{nF}}$	$\ln(Q_e) = \ln(K_F) + \left(\frac{1}{n_F}\right) \ln(C_e)$ $y = \ln Qe$, $x = \ln Ce$	$Slope = \frac{1}{N_F}$ $Intercept = \ln K_F$

2.6 Instrumentation

2.6.1 Surface of adsorbent (SEM)

The SEM was used to identify the porous structure and external surface of the AC. The size and distribution of the pores for the samples were prepared under different conditions as shown in micrograph from SEM (Anisuzzaman et al, 2014). The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition, and other properties such as electrical conductivity (Das D. et al., 2015). Before activation process, pore structure is covered by impurities and tar. The impurities decrease after activation process, so the pores open. In this process, H3PO4 has two important functions. It promotes the pyrolytic decomposition of the initial material and promotes the formation of the cross-linked structure (Astuti W. et al., 2017).

CHAPTER 3

METHODOLOGY

3.1 Methodology overview

Materials and methods of this study is described in this chapter. It was divided into a few section consist of the preliminary study, sampling, testing for data collection, batch experiment study, data analysis and conclusion in Figure 3.1.

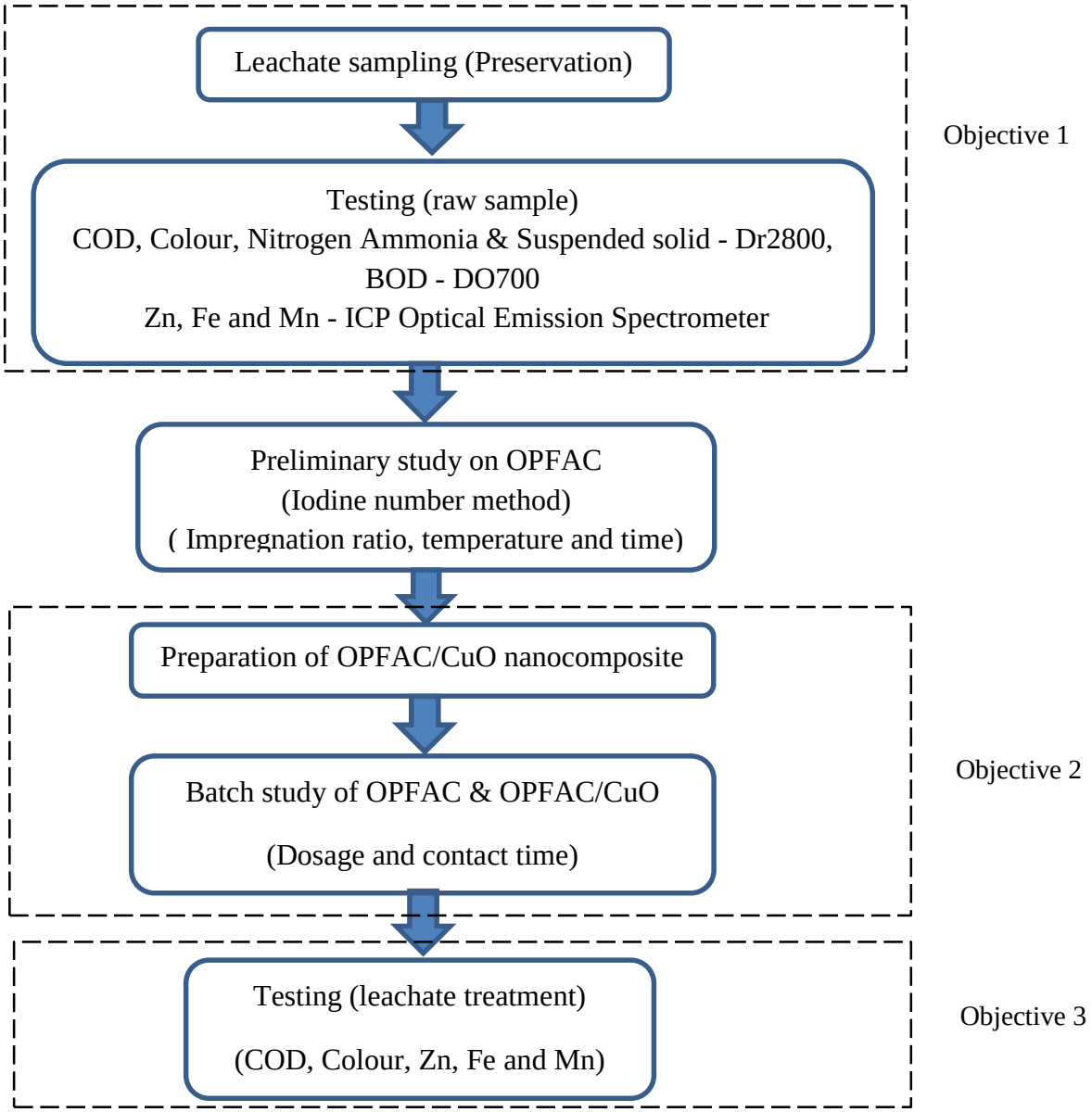

Figure 3.1 : The methodology flow chart

3.2 Sample collection and preparation

The raw oil palm frond as shown in Figure 3.2 used for the preparation of AC was obtained from the personal owned oil palm field in Sungai Kechil, Nibong Tebal, Pulau Pinang. OPF has been proposed to convert into adsorbent material to treat pollutant present in the leachate.

The OPF was firstly cut into smaller pieces, washed with water to remove the dirt and impurities from its surface and subsequently dried overnight at 105^{o}C. The dried frond was then grinded into 1-3mm.

Figure 3.2 : Grinded Oil Palm Frond

3.3 Materials and chemicals

The chemical used in this study are Phosphoric acid HNO_3, Potassium Hydroxide KOH and ionic copper (Cu[H2O]6) for preparation of AC and ACn. For iodine number test, iodine prills, Potassium thiosulfate $K_2S_2O_3$, Potassium iodate KIO_3, Potassium Iodide KI and starch.

3.4 Activated Carbon preparation

The AC sample was produced from the OPF through the method of chemical activation and carbonisation. The AC was prepared by mixing powdered OPF with the acid or base as an activation agent. In this study, Phosphoric acid was used as the chemical activation. The mixture was then soaked with a different impregnation ratios (OPF:H_3PO_4) of 1:1, 1:2, 1:3, 1:3, 1:4 and 1:5. For ratio 1:1, a 10ml of Phosphoric acid was added with distilled water until reached 100ml and mixed into 10 g of OPF powder while stirring for 1 hour. Thus, the impregnation of chemical substances into the OPF was enable. The impregnated materials were then dried at 105^{o}C for 24 hour. The carbonisation of the impregnated samples was carried out in a furnace at different temperature of 300^{o}C, 350^{o}C, 400^{o}C, 450^{o}C and 500^{o}C. Same goes to different carbonization time of 1 to 1.15 hour with 15 minutes interval. Later, the carbonized OPFAC was washed several times with hot distilled water and finally cold distilled water until it reached pH6-7. The washed sample was put into oven for drying purpose at 105^{o}C for overnight. These preparation was then repeated for the remaining impregnation ratios.

3.5 Activated carbon nanocomposite

After drying, the AC was directly embedded with ionic copper solution. 1 g of AC was embedded to ionic copper solution with ratio of 1:2 at temperature of 400^{o}C in furnace for 1 hour. Then followed by washing with distilled water until it reached pH6 to pH7 to remove residual of ionic copper solution. After the washing step, the AC (ACn) were dried for 5 hours at 105^{o}C.

3.6 Preliminary study on AC

3.6.1 Iodine number test

The amount of iodine absorbed (in milligrams) by 1 g of carbon using test conditions listed herein is called the iodine number. A standard iodine solution is treated with three different weights of activated carbon under specified conditions. The carbon treated solutions are filtered to separate the carbon from the treated iodine solution (filtrate). Then, iodine remaining in the filtrate is measured by titration. The amount of iodine removed per gram of carbon was determined for each three carbon dosage in range of 0.2g, 0.4g, 0.6g, 0.8g, 1.0g until 1.2g (depending on the available AC prepared). Next, the resulting data were used to plot an adsorption isotherm by using logarithmic paper, plot X/M (as the ordinate) versus C (as the abscissa) for each of the three carbon dosages. The amount of iodine adsorbed (in milligrams) per gram of carbon at a residual iodine concentration of 0.02 N as reported as the iodine number.

Iodine concentration in the standard solution affects the capacity of an activated carbon for iodine adsorption. Therefore, the normality of the standard iodine solution must be maintained at a constant value (0.100 6 0.001 *N*) for all iodine number measurements.

3.7 Leachate characterization

Leachate characterization was carried out by diluting to 1:10 ratio of the initial concentration to ensure that the contaminant of the leachate was highly concentrated or toxic for the COD treatment, which can be lethal to aquatic plants. Leachate was characterized for BOD, COD, colour, ammonia nitrogen, suspended solid, iron, manganese and zinc. The analytical procedures of standard method for examination of water and wastewater (APHA 2005) and HACH standard methods (modification of APHA standard method as approved by United State Environmental Protection Agency [US EPA]) were followed. The obtained parameters values were compared with the data published by previous researchers and the Environmental Quality Act of Malaysia 1974 (MDC Sdn. Bhd., 1997).

3.7.1 BOD

A Measurements of oxygen consumed in a 5-d test period (5-d BOD or BOD5, Section 5210B in Standard Method for Testing Water and Wastewater). Many other variations of oxygen demand measurements exist, including using shorter and longer incubation periods and tests to determine rates of oxygen uptake.

First, seeded dilution water is prepared by adding 1 ml of the following per litre of distilled water and then the mixture is aerated to oxygen saturation (approximately 2 h) at room temperature. (Note: Nitrification inhibitor is added to avoid nitrification during the incubation period.). There were 1 mL phosphate buffer, 1 mL magnesium sulphate solution, 1 mL calcium chloride solution and 1 mL ferric chloride solution into 1L distilled water. Then, the wastewater samples were diluted with seeded dilution water in 1 litre volumetric flasks by put in 500mL wastewater samples and the rest full filled with the dilution until 1L. After that, the volumetric flask was shaking.

The diluted samples are transferred to 2 BOD bottles. The zero day (initial) DO is determined on one bottle and the rest for 5 days ± 1 hour is incubated at 20 °C. The reading of DO was taken by using the YSI instrument. Lastly, the BOD was calculated by using this formula below:

$$BOD, mg/l = \frac{\text{D1} - \text{D2}\ (3.1)}{\text{P}} \qquad \text{Equation 3.1}$$

Where:

D1 = DO of diluted sample immediately after preparation, mg/l

D2 = DO of diluted sample after 5-day incubation, mg/l

P = fraction of wastewater sample volume to total combined volume

3.7.2 COD

(USEPA Reactor Digestion Method ~ Method 8000)

The Chemical Oxygen Demand (COD) method determines the quantity of oxygen required to oxidize the organic matter in a waste sample, under specific conditions of oxidizing agent, temperature, and time. Organic and other oxidizable materials are oxidized by digestion with an acid-dichromate solution in the presence of silver sulphate catalyst. The COD concentration is determined by spectrophotometer.

First, reagents for COD, potassium dichromate-mercuric sulphate digestion solution and silver sulphate solution should be prepared. Potassium dichromate-mercuric sulphate digestion solution prepared by 10.216g K and 33.0g HgSO added to approx. 700ml demineralized water. The solution with constant stirring and slowly 167ml concentrated H42SO added. The solution mix until dissolved. The solution is waited cools and diluted to 1 litre with demineralized water. Silver sulphate solution prepared by 22g Ag4 dissolved in a 9 pound bottle of concentrated H2SO4. The calorimetric

determination for 0 to 1500 mg/L was chosen. The programmes code of 435 is entered. COD vial adapter with the blank adapter cover place into the cell holder after spectrophotometer DR2800 show the zero sample, mh/L COD HR. Zero button is pressed for zeroing process. The sample vial is cleaned with tissue paper and place in the adapter with the same procedure as before. Then, the button of read pressed. The result in mg/L COD will be displayed. The sample should be diluted before added into the COD vial for heating if the COD value is very high.

3.7.3 Colour removal

(APHA Method: Platinum Cobalt Method ~ Method 8025)

By using DR2800, the program number for colour, the wavelength is 455nm which are for water and wastewater sample. The zero sample instruction will be shown. In this study, apparent colour is tested. A sample cell (the blank) filled with 10ml unfiltered deionized water. A second sample cell filled with 10ml of unfiltered sample. Then the blank placed into the cell holder and the light shield was closed. Zero button was pressed for zeroing process. After that, prepared sample placed into the cell holder and light shield closed, read button was pressed and then result in PtCo colour will be displayed. If the colour reading shows over range, the sample should be dilute.

3.7.4 Ammonia

(USEPA Nessler Method ~ Method 8038)

The program number for Ammonia Nitrogen 380 was entered as in CR2800 and wavelength is 455nm. The zero sample instruction will be shown. A sample cell (the blank) filled with 100ml unfiltered deionized water. A second sample cell filled with 25ml of unfiltered sample. Before that, 1ml of Nessler Reagent, 3 drops of Mineral

Stabilizer and 3 drops of Polyvinyl Alcohol Dispersing Agent were added in both sample cells. Then the blank placed into the cell holder and the light shield was closed. Zero button was pressed for zeroing process. After that, prepared sample placed into the cell holder and light shield closed, read button pressed and then result in PtCo colour will be displayed. If the Ammonia nitrogen reading shows over range, the sample should be dilute.

3.7.5 Suspended solid

(Photometric method ~ Method 8006)

Considerable information can be gained on a wastewater sample by determining its various solid contents. Various types of solids in wastewater samples can be determined gravimetrically.

3.8 Leachate treatment

3.8.1 Activated carbon

The prepared AC from the chemical activation of the HNO_3 with impregnated ratio of 1:3 at 400^{o}C in 1 hour was selected from preliminary studies based on the analysis obtained. The leachate treatment were performed to analyse the performance of the AC and ACn in COD, colour and heavy metal (Zn, Mn and Fe). The treatment carried out with different dosage and contact time in batch study.

3.8.2 Batch study

The batch of adsorption tests were performed in order to assess the removal of COD, colour and heavy metal by using AC. This batch study will include the effect of

dosage and contact time via constant shaking speed that is 200 rpm, isotherm and kinetics adsorption studies. The Orbital Shaker was used in batch study.

The test were carried out in 250 mL Erlenmeyer flasks, by containing a fixed volume of 50 mL sample leachate which varied in the range different weight of 0.2 g, 0.4 g, 0.6 g, 0.8 g and 1.0 g of AC in each flask. These were placed on an orbital shaker at 200 rpm for 15 minutes until 75 minutes with 15 minutes interval in order to achieve the optimum dosage and treatment time. All samples were then filtered by membrane filter paper (0.45μm) prior to minimize the interference of carbon fines present in the solutions for further parameter treatment check.

3.8.3 Significant parameter

The data obtained from the laboratory test were analysed to determine the percentage of colour, heavy metal and chemical oxygen demand (COD) removal by adsorption using the AC. The heavy metal tested including Zn, Fe and Mn removal from the leachate sample. The factor that affecting the adsorption in this test is adsorbent dosages and contact time are discussed with supporting previous researches.

3.8.4 Activated carbon copper-oxide nanocomposite

In this study, the AC was directly embedded with ionic copper solution. 1 g of AC was embedded to ionic copper solution with ratio of 1:2 at temperature of 400^{o}C in furnace for 1 hour. Then followed by washing with distilled water until it reached pH6-7 to remove residual of ionic copper. After the washing step, the AC (ACn) were dried for 5 hours at 105^{o}C.

In order to determine the performance of the ACn, the COD, colour and heavy metal were tested based on the optimum dosage from the AC experiments (Silva et al., 2017).

3.9 Adsorption Isotherm

The process of Adsorption is usually studied through graphs know as adsorption isotherm. It is the graph between the amounts of adsorbate (x) adsorbed on the surface of adsorbent (m) and pressure at constant temperature. Different adsorption isotherms have been used which are Freundlich, and Langmuir. Both isotherm are most widely used adsorption isotherms to represent the equilibrium state of activated carbon.

3.9.1 Langmuir and Freundlich Isotherm

In order to obtain numerical values for graphical analysis, the experimental data must first be collected and manipulated from the result obtained from treatment parameters. Using the initial and final treatment results from COD, colour, Zn, Mn and Fe, the concentration of the solution can be determined. This is called as the equilibrium concentration, Ce.

For Langmuir isotherm, a graph of Qe is plotted against Ce based on the Equation 3.2. Meanwhile in freundlich isotherm, a graph of log Qe is plotted against log Ce according to Equation 3.5. Both isotherm will be a straight line as in the Figure 3.3. Once the graph is constructed, any point can be chosen and the slope was taken as a reference. From the slope and intercept in Equation 3.3 and 3.4, the value for the Q_m and K_L were obtained for Langmuir isotherm. As for Freundlich isotherm, Equation 3.6 and 3.7 were used to determine the value of n_F and K_F. When the correlation coefficient is more than