# CHARACTERIZATION OF OIL PALM FROND AND BAMBOO AS ADSORBENT FOR METHYLENE BLUE DYE

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**SCHOOL OF CIVIL ENGINEERING**
**UNIVERSITI SAINS MALAYSIA**
**2022**

CHARACTERIZATION OF OIL PALM FROND AND BAMBOO AS ADSORBENT FOR METHYLENE BLUE DYE

By

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This dissertation is submitted to

**UNIVERSITI SAINS MALAYSIA**

As partial fulfilment of requirement for the degree of

**BACHELOR OF ENGINEERING (HONS.)**
**(CIVIL ENGINEERING)**

School of Civil Engineering
Universiti Sains Malaysia

July 2022

**Appendix A8**

**SCHOOL OF CIVIL ENGINEERING**
**ACADEMIC SESSION 2021/2022**

**FINAL YEAR PROJECT EAA492/6**
**DISSERTATION ENDORSEMENT FORM**

Title: **Characterization of Oil Palm Frond and Bamboo as Adsorbent for Methylene Blue**

Name of Student: **Mifzal Thaqif Bin Md Tajudin**

I hereby declare that all corrections and comments made by the supervisor(s) and examiner have been taken into consideration and rectified accordingly.

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(Important Note: This form can only be forwarded to examiners for his/her approval after endorsement has been obtained from supervisor)

# ACKNOWLEDGEMENT

The completion of this thesis would not have been possible without the assistance of many people who gave their support in different ways and played a crucial key or role on giving intellectual, material and moral supports.

In particular, I would like to indicate my keen and sincere gratitude to my supervisor, Dr. Nik Azimatolakma Awang for the generous advice, guidance and encouragement. Thanks for supervising and guiding me through the year to finish this project. Thanks a lot for being such a good and dedicated supervisor. In every part of the project, she has been showing great patience at the same time giving immense motivation, guidance and advice, where have been pivotal in completing this project.

In addition, my sincere appreciation is towards to both my parent, Md Tajudin Bin Morad, and Nazliza Binti Abu Seman for their fully support and love that inspired me to finish this report. Their encouragement was always faithful for me in order to complete the project.

Moreover, I also would like to thank all my friends for their support and encouragement during my study year. Last but not least, I would like to acknowledge each and every person who had contributed to the success of this report, thanks a lot for everything. May Allah bless all of you.

# ABSTRAK

Pewarna ialah cecair yang membekalkan banyak bahan pencemar dan menyebabkan pencemaran apabila ia menyusup ke dalam persekitaran semula jadi. Walau bagaimanapun, ia mesti dirawat dengan betul untuk mengelakkan sebarang kesan yang tidak menyenangkan. Dalam penyelidikan ini, kaedah penyerapan digunakan untuk merawat pewarna. Pelepah kelapa sawit (OPF) dan karbon teraktif berasaskan buluh telah dihasilkan dan digunakan sebagai penyerap untuk menjalankan rawatan pewarna iaitu metilena biru. Penyelidikan ini telah memberi tumpuan kepada ujian yang dijalankan untuk menghasilkan karbon teraktif daripada pelepah kelapa sawit dan buluh dan untuk menentukan keberkesanannya untuk merawat larutan pewarna. Keputusan ujian makmal tertumpu terutamanya pada penentuan penyingkiran warna karbon teraktif yang dihasilkan dengan dos penyerap yang berbeza, analisis mikroskop elektron imbasan (SEM) untuk mengenal pasti struktur mikro karbon teraktif yang dihasilkan dan keberkesanan karbon teraktif dalam metilena. rawatan biru dari segi warna, kekeruhan dan kapasiti penyerapan. Keputusan ujian makmal menunjukkan bahawa karbon teraktif berasaskan buluh yang dihasilkan dalam suhu pengkarbonan 500°C telah dikenal pasti sebagai sampel yang mempunyai keberkesanan tertinggi pada kapasiti penyerapan. Bagi ciri-ciri penyerap untuk buluh, cas permukaan dan saiz zarah metilena biru dan pelarasan pH buluh karbon teraktif 5 dengan menggunakan zetasizer ialah -10.1 mV dan 513.7 d.nm. Selain itu, untuk pelarasan Nilai pH 9 ialah -14.1 mV dan 824.8 d.mm. Selain itu, untuk analisis SEM imej liang karbon teraktif berasaskan buluh menunjukkan saiz liang dengan saiz pembesaran ×8000 untuk nilai pH 5 pada dos 0.4g malar dan kepekatan 93.33 mg/L metilena biru adalah liang saiz tidak sekata boleh dilihat dalam imej SEM. Sebilangan besar liang ditemui pada permukaan sampel buluh. Pembangunan liang di dalam struktur karbon teraktif adalah penting kerana ia akan meningkatkan kapasiti

penyerapan. Kemudian, bagi analisis pembelauan X-Ray (XRD), berdasarkan penyerap dalam nilai pH 5 sampel didapati kandungan bagi kristal dan amorf ialah 39.3% dan 60.7%. Puncak bagi sampel nilai pH penyerap 5 adalah lebih tinggi berbanding sampel penyerap mentah dan sampel pH penyerap pada 2. Bagi rawatan pewarna, penyingkiran warna tertinggi iaitu 97.48% berlaku apabila dos karbon teraktif berasaskan buluh ialah 0.5g dan masa goncangan adalah 30 minit pada nilai pH 5 bagi kepekatan metilena biru pada 93.33 mg/L. Walau bagaimanapun, bagi pelepah kelapa sawit sebagai penyerap, penyingkiran warna tertinggi iaitu 93.10% berlaku apabila dos karbon aktif berasaskan pelepah kelapa sawit adalah 1.0g dan masa goncangan adalah 30 minit pada nilai pH 5 di mana kepekatan metilena biru. adalah 8.67 mg/L telah digunakan

# ABSTRACT

Dye is a liquid that providing a plenty of pollutants and causing contamination when it is infiltrated into the natural environment. However, it must be treated correctly in order to avoid any unpleasant effects. In this research, adsorption method was used to treat the dye. Oil palm frond (OPF) and bamboo based activated carbon was produced and used as an adsorbent to conduct the dye treatment which is methylene blue. This research has drawn its focus on the tests conducted to produce an activated carbon from oil palm frond and bamboo and to determine its effectiveness to treat the dye solution. The results of the laboratory test mainly focused on the determination of colour removal of the activated carbon produced with different dosage of adsorbent, scanning electron microscopy (SEM) analysis to identify the microstructure of the produced activated carbon and the effectiveness of the activated carbon in methylene blue treatment in terms colour, turbidity and adsorption capacity. The laboratory test results shown that the bamboo based activated carbon that is produced in carbonization temperature of 500°C has been identified as the sample that has the highest effectiveness on adsorption capacity. For the characteristic of adsorbent for bamboo, the surface charge and particle size of methylene blue and activated carbon bamboo pH adjustment of 5 by using zetasizer was −10.1 mV and 513.7 d.nm. In addition, for the adjustment pH Value of 9 was -14.1 mV and 824.8 d.mm. Moreover, for the SEM analysis the image of the bamboo based activated carbon pore indicating the pore size with ×8000 magnification size for pH value 5 at constant 0.4g dosage and 93.33 mg/L concentration methylene blue were pores of irregular sizes can be seen in the SEM image. Large number of pores are found on the surface of bamboo sample. Pore development inside the activated carbon structure is important since it will increase the adsorption capacity. Then, for the X-Ray diffraction analysis (XRD), based on the adsorbent in the pH value of 5 sample were found that the

contain for crystalline and amorphous was 39.3% and 60.7%. The peak for the sample of adsorbent pH value of 5 were higher compare to the raw adsorbent sample and sample of adsorbent pH at 2. For the dye treatment, the highest colour removal which was 97.48% occurred when the bamboo based activated carbon dosage was 0.5g and the shaking time was 30 minutes at the pH value of 5 for the concentration of methylene blue at 93.33 mg/L. However, for the oil palm frond as adsorbent, the highest colour removal which was 93.10% occurred when the oil palm frond based activated carbon dosage was 1.0g and the shaking time was 30 minutes at the pH value of 5 where the concentration of methylene blue was 8.67 mg/L were used.

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| **Abbreviations** | **Caption** |
|---|---|
| OPF | Oil Palm Frond |
| FT-IR | Fourier Transform Infra-Red Spectroscopy |
| MB | Methylene Blue |
| rpm | Rotation per Minute |
| SEM | Scanning Electron Microscopy |
| HCL | Hydrochloric acid |
| XRD | X-Ray Diffraction Analysis |
| EDX | Energy-Dispersive X-ray |
| UV-VIS | UV-Visible spectrometer |
| IEP | Iso-electric point |
| TEM | Transmission Electron Microscopy |

# CHAPTER 1

# INTRODUCTION

## 1.1 Background of Study

Manufacture of fabric/textile were enormously use the dye in industry, where it became one of the large industries were use dye in Malaysia nowadays. Moreover, dyes are also used in carpet, food industry, paper, pharmaceutical industry, and leather industry. The existence of dye in wastewater can lead to environmental pollution because of the dyes contain toxic and colouring. In addition, dye contain of aromatic molecular structure hence exacting to degrade. Commonly dyes were categories into anionic, cationic, and non-ionic dyes. Moreover, textile industries were most industries in Malaysia that are using of dyes for coloration of fiber. The dye indicates aromatic molecular structure originating from hydrocarbon, where it toluene, anthracene, xylene, naphthalene and benzene.

The quantity of dyes was generated where estimated roughly around 10,000 tons per years and amount of dyes released in the environment were estimated 1 to 2% loss in manufacture and 1 to 10% loss in use (Forgacs et al., 2004). Dye can provide pollution on environment and bring out highly bright colour in water together with acidic properties. The colour is the contaminant of water where can be seen by naked eyes which is the water quality is highly effect by the water colour.

Methylene blue is harmful into human body. In addition, it resists the acidic environment on the stomach. Hence, it not significant metabolized by liver and will swiftly flow into kidney directly. This study focused on the adsorption treatment method by using oil palm frond (OPF) and bamboo based activated carbon as an adsorbent. Activated carbon was discovering as effective adsorbents where is manage and provide has high porosity level and large surface area for adsorption (Erabee et al., 2018). This study analyses three characteristics of the wastewater (methylene blue) which is colour, pH value concentration before and after the treatment.

## 1.2 Problem Statement

One of the major environment pollution problems in Malaysia comes from textile, leather, paper and plastic industries (Pang and Abdullah, 2013). Which is an industries of textile are crucial impact for environmental problem pollution, due to the freeing dye flow into the water. An untreated dye-containing pollutant into water bodies was harmful of aquatic ecosystem which is creates mutagenic and teratogenic on aquatic organisms. Dyes in wastewater are not only toxic to aquatic life but are also detrimental to aesthetic features of the environment. Adsorption can be specify being concentration of materials on the surface of solid bodies. The adsorption process was low cost, high efficiency, fast, and useful decontamination process. This process method was commonly used to decontamination of a plenty of pollutant in wastewater, for instance arsenic, dyes and heavy metals. Depolarization of wastewater from textile and manufacturing industries, were trouble on environment where dyes was water soluble.

Thus, this research aim to rehabilitation and clean-up of dye wastewater using adsorption process. Adsorption method including the movement solid from liquid into the surface of absorbent. Adsorbents are can be produce by the sources such as zeolites, charcoal, clays, ores, and other waste resources. In addition, adsorbents also can employ by waste resources used such as coconut shell, fertilizer wastes, rice husk, petroleum wastes, sugar industry wastes, sawdust, fly ash, and seafood processing wastes, seaweed and fruit wastes. The test was focussing on the implementation of adsorbent by using the of oil palm frond (OPF) and bamboo based on activated carbon to remove methylene blue. OPF was one of the lowest cost adsorbent, it can help to reduce cost of the disposal and reduce the environment pollution.

## 1.3 Objectives

The objectives of the research are listed below:

1. To determine the characteristic of oil palm frond (OPF) and bamboo based on Iso-electric point (IEP), X-Ray Diffraction (XRD), and Scanning Electron Microscope (SEM).
2. To study on the optimum usage for dosage of oil palm frond and bamboo based activated carbon, concentration dye for colour and pH in removing methylene blue.
3. To investigate the adsorption capacity of bamboo and oil palm frond OPF in removing methylene blue from aqueous solution.

## 1.4 Scope of Work

In this project, applying oil palm frond (OPF) and bamboo as an adsorbent to remove the methylene blue. This research focused on the adsorption capacity of the both oil palm frond and bamboo based on activated carbon form. At the same time, the study also focused to identify the potential of OPF and bamboo to removal dye efficiency by use OPF and bamboo as natural absorbent in wastewater treatment where it can help to narrow the disposal cost and reduce the environment pollution. Moreover, to obtain optimum dosage and contact time to improve efficiency adsorption.

## 1.5 Dissertation Outline

For the dissertation of this project contain together with 5 chapters, which is introduction, literature review, methodology, results and discussion, and last the one were conclusion and recommendation. For the first chapter come up with the background of study, problem statements, objectives, scope of work and dissertation outline.

Next, for the chapter 2 is the literature review where study the related review and articles research by researchers. Then, chapter 3 was methodology for this study, which discuss the research flow approach and set about to conduct the test for the project. The study aimed on the preparation of the oil palm frond and bamboo based activated carbon and laboratory testing procedures where are used to evaluate the wastewater characteristics such as pH, colour removal percentage after the dye is treated using the oil palm frond and bamboo based activated carbon. In addition, chapter 4 refers to the results and discussion of this study which the results that obtained from the analyses. The characteristics of absorbent are identified where also the characteristics of raw wastewater are identified and are then compared with the characteristics such as pH, and colour removal after the dye is treated with the oil palm frond and bamboo based activated carbon.

Lastly, chapter 5 come to the conclusion of this project based on the objectives of the project. This chapter also come out with suggestions or recommendations to improve for the next study.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Types of Dyes

Dye can be classified as natural and synthetic dye. Natural dyes are colour acquire based on sources of natural. Natural dyes were applying in textile and print dyeing. The implement of natural dyes was lessening because of the development of synthetic dyes. Natural dyes are produce from three main sources which is plants, animals and minerals. Natural dye is environment friendly type of dye that derived from natural sources. Moreover, the natural dye is considered as less efficient than other types of dyes. Organic ingredient can be used to produce the natural dyes for cotton, silk, linen and other. The shade and saturation level of dye will vary based on the plant, fruit, and the flower. These dyes are easily decomposed in nature after using and they do not pollute the environment while destroying them after end use. Clothing dyed with natural dyes lay out magnificent feel that cannot be acquired just using synthetic dyes. Due to their excellent nontoxic and non-allergenic characteristics. These dyes do not do any harm to the baby skin (Alam et al., 2020). They have wonderful capabilities to protect humane from ultra-violate radiation and extreme sun burning.

A synthetic dye may be described as a benzene derivative, to which a chromophore and an auxochrome have been added. Synthetic dye is produced by chemically, which is direct dye, reactive, basic, acid mordant or chrome, disperse, vat, sulphur, azoic or napthol, pigment and optical brighter dye. Synthetic dyes earn recognition and take place of natural dyes because of the low-cost production, easy availability, easy application, more colour stability, resistance to light, pH changes, and oxygen. Thus, synthetic dye was not environmentally friendly since synthesis consist of high pH, high temperature, strong acids, and heavy metal catalysts.

### 2.1.1 Natural Dyes

Natural dyes are divided into three part based on the sources which is vegetable, animal and mineral dye. Vegetable dye were attaining by separate part on the plants, for instance leaves, flowers, fruits, etc. Next, animal dyes were pull out from the insects and invertebrates. The colour of red and purple were acquired from animal. Then, mineral dyes it extracted from mineral sources, where bring out yellowish brown, chrome yellow, Prussian blue and manganese brown. The dyes produce by mineral sources usually toxic and harm toward human and animal hence, it is not used commercially on public. Some natural dyes have required a mordant to tie the dye to the fiber to avert it from drained or vanish. The use for the mordant were rely on the dye materials, fiber, and the duration it takes for the dye to set.

Moreover, mordants are solutions that carry dissolved metal oxides and are toxic. A mordant was commonly a polyvalent metal ion. The resulting coordination complex of dye and ion is colloidal and can be either acidic or alkaline. Also some mordants that are obtain from plant sources likes oak galls and acorns can good enough on fibers. Alum, one of the favoured mordants applied for the natural dyeing process. The mordants include tannic acid, alum, urine, chrome alum, sodium chloride, and certain salt of aluminium, chromium, copper, iron, iodine, potassium, sodium and tin. Plant-based textiles such as cotton and linens might need a fixative to help set the dye. Regular fixatives are natural materials, consist of salt, tannins, vinegar, and baking soda.

### 2.1.2 Synthetic Dyes

Direct dyes are dissolved in water. It not difficult to create hence easy apply, also low cost on production and application. Then, reactive dyes where dyes that mix with fibres and form covalent bonds where dissolved in water. Moreover, basic dyes were dyes that mix with the acidic groups. Basic dyes are dissolved in alcohol but hard into water. Next, acid dyes were dye that dissolve in water where require acid such as sulphuric, formic acid etc. for dye of silk or wool.

Synthetic dyes are produce by chemical compounds for instance mercury, lead, toluene, chromium, sodium chloride, copper, or benzene. Where can be conclude that harmful to humans, mostly toward people work in production sector. Dye could also ruinous on the environment, where untreated dye that is dispose directly into waterways bring to water pollution. Also it would pollute water that contain toxic chemicals where lead to health problems, and kill aquatic organisms.

### 2.1.3 Dye classification

Dye can be classified in plenty of ways based on the application, colour and structure. The classification based on application is commonly chosen because of the complexities of colour nomenclature from the chemical structure system (Yagub et al., 2014).

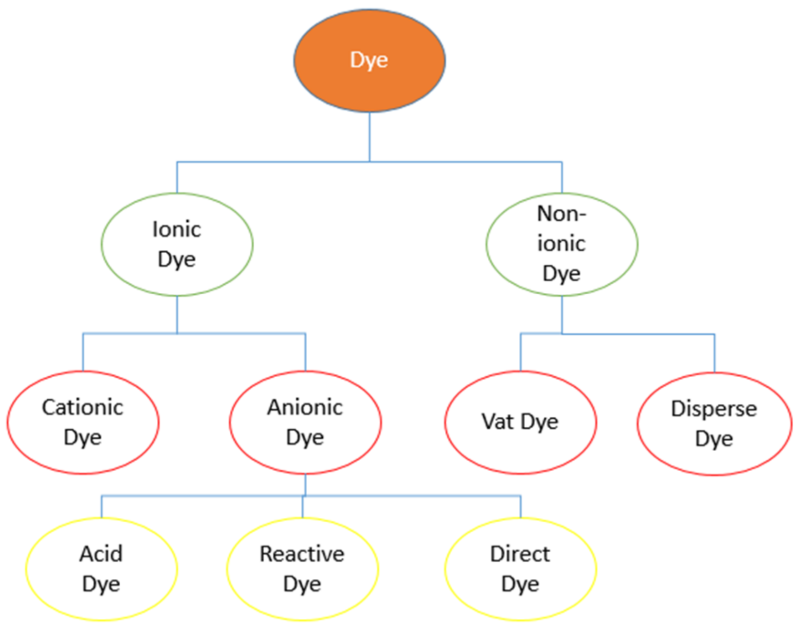


Figure 2.1: Categorization of dye based on ionic charge (Tan et al., 2015)

Based on the Figure 2.1, it indicates that the dyes are divided into two categorize which is ionic and non-ionic dyes. Ionic dyes were separate into cationic dyes and anionic dyes. Cationic dyes are cationic salts of organic coloured bases involving of imino and amino groups, formed between sulphuric or hydrochloric acid. It used on producing paper, modified polyester, nylons and also towards medicine. Then, anionic dyes were carry anionic charge and categorized into three where it acid dyes, reactive dyes and direct dyes.

Acid dye is a salt of a carboxylic, sulfonic or phenol organic acid. Commonly produce based on the large aromatic molecules contain a lot of linked rings. Hence it used on nylon, wool, leather, paper, food, ink and cosmetic. Direct dyes were soluble in water and produce aqueous solutions during the appearance of electrolytes. It usually dyeing toward cotton, paper, leather, rayon, and nylon. Reactive dyes contain chromophoric groups and own chemical structures. Non-ionic dyes were categorized into vat dyes and disperse dyes. Vat dyes are insoluble in the water. It typically for cotton, rayon and wool. Disperse dyes are insoluble non-ionic dyes containing styryl, azo, nitro, anthraquinone and benzodifuranone groups.

## 2.2 Methylene Blue

Methylene blue were a bright greenish blue organic dye that included in phenothiazine family. Mostly applied on bast for instance soft vegetable fibres. The, methylene blue is salt that used for dye, it actually cationic dye and it is usually on dyeing wood, cotton and silk (Robati et al., 2016). Presently, physical, chemical, and biological treatment methods have been widely used to remove dye wastewater. Besides, all those methods possess disadvantages of high energy (Cheng et al., 2020). Methylene blue is one such organic dye, discharged from textile industries. The methylene blue was synthesized commercially by oxidation of N,N-dimethyl-phenylenediamine with sodium dichromate ($Na_2Cr_2O_7$) in the presence of sodium thiosulfate ($Na_2S_2O_3$). Also present of antioxidant, antimalarial, antidepressant and cardioprotective properties. It has a role as an EC 1.4.3.4 (monoamine oxidase) inhibitor, an acid-base indicator, a fluorochrome, an antidepressant, a cardioprotective agent, an EC 3.1.1.8 (cholinesterase) inhibitor, a histological dye, an EC 4.6.1.2 (guanylate cyclase) inhibitor, an antioxidant, an antimicrobial agent, a neuroprotective agent, a physical tracer and an antimalarial. It contains a 3,7-bis(dimethylamino)phenothiazin-5-ium (Lee et al., 2008).

## 2.3 Methods to remove dye

The method to removal dye from wastewater can be divided into three types, biological, physical and chemical. Dyes also might react with other chemical reactants in the wastewater. Adsorption was straightforward and low-cost methods to remove the dyes from wastewater (Tehrani-Bagha et al., 2011). Physical methods include adsorption, ion exchange, and filtration or coagulation methods. However, chemical methods include ozonisation, Fenton reagent, photo catalytic reactions and biological methods include aerobic degradation, anaerobic degradation, biosorption. Adsorption discover effectual and low cost method between the all available dye removal methods. Dyes from the industrial waste water outflow are functionally detached by using adsorbent such as activated carbon but cost limited the use in large scale applications.

### 2.3.1 Physical

In physical method, it involving natural adsorbent, agricultural and industrial adsorbent. Also it was the commercial technique in the dye removal in adsorption technique. The use of adsorbent is depended on the type of pollutants. Physical method was preferred over other methods because of to the low costs and can be reuse of adsorbent without added required materials (Altmann et al., 2014). The materials from industrial waste such as fly ash, coal ash, etc. shown that able to decolourised the dye and come to be as low cost adsorbent. Next, peat also was used in post or pre-treatment in the industry and because of the cellular structure and no required activation. In spite of that, the surface area is lower than activated carbon (Yerramilli et al., 2005). The common application for dye removal is adsorption technique or method. This physico-chemical technique was discovering as manageable and economical for the removal of dyes from textile effluents. An amount of low cost materials such as agricultural waste material, naturally found material and industrial waste material have been carried out for the removal of dyes. Despite, the adsorption capacity for these adsorbents were not found much large but still they are widely needed as they are found to be cost effective, eco-friendly and somewhat effective.

### 2.3.2 Biological

Biological method used microorganisms to biochemically disintegrate the dye in wastewater. Some microbial culture for instance white-rot fungi can be used to remove dye colour in aerobic and anaerobic process. Besides, white-rot fungi are the most practical microorganism to disintegrate the dyes due to capable of generate non-specific extracellular lignin-degrading enzymes (Daâssi et al., 2013). Hence, the fungi have shown that it effective to remove dye. Next, algae were also capable to decolorize and remove dye (Tarlan et al., 2002).

The green algae- Spirogya has ability to separate synthetic azo dye from wastewater. However, the effecting of colour removal is rely on the concentration of dye and algal biomass (Venkata Mohan et al., 2002). In this biological method, there were divide by two type where aerobic and anaerobic process. Aerobic process focussing treatment on distillery, brewery, pulp and paper. And for anaerobic process for wide variation of dyes and the bio gas produced from the treatment used for steam generation (Yerramilli et al., 2005).

### 2.3.3 Chemical

In chemical methods, dye turn to oxidised undergo of hydrogen peroxide ($H_2O_2$) or ozone ($O_3$). Dye degrading by photochemical reaction under UV treatment in the appearance of hydrogen peroxide ($H_2O_2$) (Ai et al., 2014). The mixture of hydrogen peroxide and ferrous ion ($Fe^{2+}$) referring as Fenton's reagent ($H_2O_2$-$Fe^{2+}$), which is generally to remove the dyes where are not biodegradable or are poisonous to live biomass. Besides, this technique simply to perform and thoroughly react with organic compound. Ozonation is strong oxidant and capable for azodye removal (Xu et al., 1999) but it unsuitable for dispersed dyes and will releases aromatic amines which is cancerogenic (Yerramilli et al., 2005). Advanced oxidation method is one of the traditional methods that have been applied for de-colorization process. It is based on the mechanism involving generation of hydroxyl radicals (as oxidising agents), that when attack upon chromo-genic groups, leads to produce organic peroxide radicals and ultimately transform them into $CO_2$, H20 and inorganic salts. It consists of a variety of methods such as ozonisation, use of hydrogen peroxide and Fenton's process. Ozone, known as the most powerful oxidant than other oxidising agents like $Cl_2$, $H_2O_2$. Ozone is found to be quite capable in oxidising chlorinated hydrocarbons, phenols and some other hydro carbons.

## 2.4 Adsorption

Adsorption is a physicochemical process. Adsorption can be either physical or chemical, depending on the forces/interactions of adsorbate and adsorbent. The molecules or atoms get adsorbed at the surface refers as adsorbate meanwhile adsorbent was the component lay out the solid surface for adsorbate. Dye adsorption involved of four continuous steps. First step is the spreading of dye molecules along the bulk of solution. Second step during dye molecules dispersal all over a boundary layer. Third step when the molecule dye dispersal from the surface into internal of adsorbent materials. Final step is the appendage of dye molecule toward surface of materials via molecular interaction. Adsorption process stratify in two type which are physisorption and chemisorption. Physisorption are adsorption which adsorbate adhere to the absorbent surface by the forces of van der Waals between molecules and atoms on the adsorbent surface. Chemisorption are adsorption which adsorbate adhere to the absorbent surface by the chemical bond.

Adsorption was operating as main treatment procedures for the removal of dissolved organic pollutants like dyes from industrial waste water. Adsorption is defined as concentration of materials on the surface of solid bodies. Adsorption is a surface phenomenon which deals primarily with the utilization of surface forces. When a solution having absorbable solute, also called as adsorbate, comes into contact with a solid, called as adsorbent, with highly porous surface structure liquid-solid intermolecular forces of attraction causes the solute to be concentrated at the solid surface. Adsorption is one of the unit operations in the chemical engineering processes used for the separation of industrial wastewater pollutants.

## 2.5 Activated carbon as adsorbent for dye removal

Adsorbents were generated from agricultural waste, natural material, or modified biopolymers, were low cost adsorbent. Activated Carbon is assign as an adsorbent where consist sizeable surface area which allow the process of pull out heavy metals from wastewater effectively (Erabee et al., 2018). The result of adsorbent dosage, contact time and solution pH on the adsorption performance were studied in a batch mode study. A study shown that by usage biomass of oil palm tree on the removal of environment pollutants (Faridah et al., 2018). It shown to be a good solution on encourage and supporting sustainable development. Those study are focus to analysis improving in the preparation of adsorbent based on plenty parts of oil palm biomass for the removal of heavy metal and organic environmental pollutants from water. It has proved that every part of the oil palm biomass can provide suitable as biosorbents for most environmental pollutants. The high applicability of Activated Carbon is because of consist high porosity, rapid adsorption, and thermal stability (Hesas et al., 2013). The activation process and the nature of the source materials affect the properties of activated carbon. The advantageous by using agricultural waste as raw materials are renewable sources and likely low-priced to prepare (Pandey et al., 2016).

### 2.5.1 Oil Palm Frond (OPF)

The implementation of biomass waste adsorbent in removing colour and heavy metal ion from water flow as a replacement for the commercial available adsorbent had been widely used. Oil palm frond which is one of the waste from oil palm plantation are abundantly available as there is high agricultural activities at the plantation. The oil palm frond was used to remove chromium ion ($Cr^{6+}$) and lead ion ($Pb^{2+}$) from aqueous solution that acts as synthetic wastewater. This study is conducted to measure the adsorption capacity of oil palm frond by varying the adsorbent dosage and initial concentration of methylene blue solution. The findings show that removal of methylene blue colour increase as the adsorbent dosage increase. This can be seen that the amount of colour removal percentage for activated carbon dosage of 1.0g, it has reached the highest colour removal, which is 93.1%. Hence, the optimum dosage usage was selected of 1.0g for the test. In this test, the value of pH was use at value 5 and the constant concentration of methylene blue at 8.67 mg/L. The adsorbent dosage varied from 0.2g, 0.4g, 0.6g, 0.8g and 1.0g. The result showed that the adsorption capacity of the adsorbent was the highest at 1.0 g of the dosage. In can be concluded that increase amount of adsorbent can be reduce more colour removal. In overall, the findings provide that oil palm frond can be used as adsorbent to methylene blue as dye from wastewater and aqueous solution.

### 2.5.2 Bamboo

Bamboo is a grass, the most diverse group of plants in the grass family. It belongs to the sub-family Bambusoidae of the family Poaceae (Graminae). The bamboo is a very abundant and inexpensive material. Bamboo-based activated carbon is synthesized by a simple heat treatment with or without KOH activation, and characterized for possible energy storage applications. The KOH activation introduces a very large surface area of more than 3000 m2 g−1 to the bamboo-based activated carbon, resulting in high specific capacitance, energy density, and power density in an aqueous electrolyte. Through the carbonaceous materials, bamboo charcoal provides a wonderful porous microstructure and high absorptive capacity. The porous structure of bamboo was ideal for both adsorption and desorption of electrolyte ions without chemical reactions, and high conductive properties enable to complete the rapid charging. Moreover, bamboo charcoal has been used to filter and clean air and water in long time because of the porous structure, easy availability, and relatively low cost. X-ray diffraction (XRD) analysis was used to investigate the crystal structure. Morphologies of the samples were investigated using scanning electron microscopy (SEM) analysis.

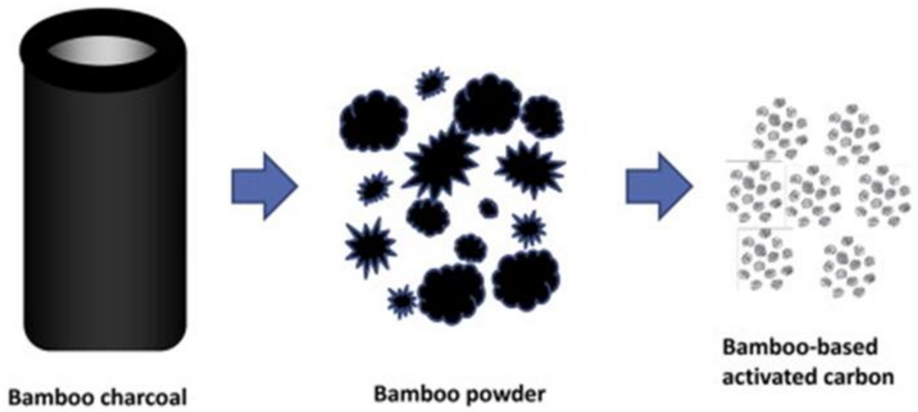


Figure 2.2 Process of bamboo based on activated carbon (Yang et al., 2014)

## 2.6 Kinetic analyses

Pseudo-first and second-order models and intraparticle diffusion model are usually used to narrate the sorption of dyes using solid adsorbent (Yao et al., 2010). Generally used of adsorption rate equations is the Lagergren rate equations which is shown below: Pseudo-first-order kinetic model of Lagergren (Yao et al., 2010):

$$\frac{dqt}{dt} = k_1(q_e - q_t)$$

Pseudo-second-order equation corresponding to adsorption equilibrium capacity (Yao et al., 2010)

$$\frac{dq}{dt} = k_2(q_e - q_t)^2$$

qe (mg/g) is the amount of methylene blue adsorbed at equilibrium. Next, qt (mg/g) is the amount of methylene blue adsorbed at time. Then, k1 (min-1) is the rate constant of pseudo-first-order adsorption. Hence, k2 (g/mg.min) is rate constant of pseudo-second-order adsorption. Intraparticle diffusion model:

$$q_t = k_i t^{1/2} + \text{C}$$

Where,

- C is intercept,

- t (min) is time

- ki is intraparticle diffusion rate constant (mg/g $min^{1/2}$).

# CHAPTER 3

# METHODOLOGY

## 3.1 Adsorbate

Regarding chapter 3, this chapter represent the approach that used to produce the oil palm frond and bamboo based activated carbon and test procedures of laboratory that were used to analyse the wastewater characteristics such as colour and pH value solution removal percentage after the dye were remove by using the oil palm frond and bamboo based activated carbon. The adsorbate were used in this study which is methylene blue. The adsorbate can be refer as material or substance that get adsorbed at the surface. For instance, particle of colour. The methylene blue was provided in the laboratory environmental 1. Moreover, after the dye were remove by using the oil palm frond and bamboo based activated carbon, the process in this study was illustrated in Figure 3.1 that showed below.

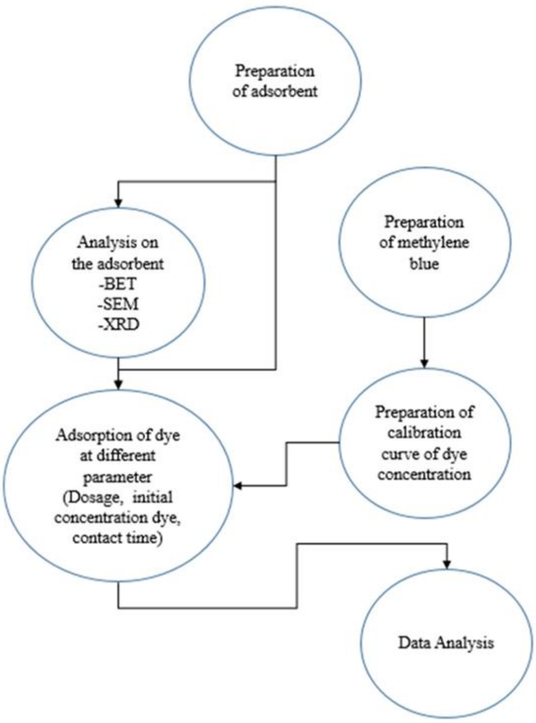


Figure 3.1: Layout of research flow diagram

The form of the methylene blue provided were in powder. For the test of oil palm frond based activated carbon as adsorbent, the powder of 0.0015 g methylene blue was poured into 150 ml of distilled water to dilute the powder and produce constant dye concentration of 8.67 mg/L in the conical flask. After 30 minutes, the present of concentration of methylene blue dye in the samples will examine by using UV-Visible spectrometer. Meanwhile for the bamboo based activated carbon as adsorbent, the powder of 0.0140 g methylene blue was poured into 150 ml of distilled water to dilute the powder and produce dye concentration of 93.33mg/L in the conical flask. After 30 minutes, the present of concentration of methylene blue dye in the samples will examine by using UV-Visible spectrometer. The experiment was repeat with vary concentration of methylene blue which is 133.33 mg/L, 200 mg/L, 266.67 mg/L, and 333.33 mg/L to obtain optimum value concentration.

### 3.2 Adsorbent

In this research, there were two of adsorbent were use which is oil palm frond and bamboo based activated carbon. For first adsorbent which is the oil palm based activated carbon were taken from the oil palm tree inside the USM Campus. Next, for the second adsorbent was bamboo based activated carbon, the bamboo was taken from the nearby of my village hometown.

#### 3.2.1 Preparation of oil palm frond based activated carbon

The oil palm frond was cut into small piece by using circular saw. 500 gram of oil palm frond was prepared to crush into crusher machine. The OPF powder were burn at 500°C into oven and leave for 3 hours to produce activated carbon. After let it to cool down, the powder was sieved to achieve preferred size (45-150 ɥm). The adsorbent powder was store in polyethylene bag until to be use. The set right process of oil palm based activated carbon preparation were key to obtain precise result because it will affect test results. Hence, the adsorbent preparation need to be unchanging and in the right technique to secure the good quality data.

### 3.2.2 Preparation bamboo based activated carbon

The raw material (bamboo) were washed, dried, crushed to desired mesh size (1–1 mm) by using the crusher machine. The raw material was then heating carbonized at 500 °C under for 1 h. A certain amount of produced char then was soaked with potassium hydroxide (KOH). The mixture was dehydrated in an oven overnight at 105 °C, then pyrolysed in a stainless steel vertical tubular reactor placed in a tube furnace. The activated product was then cooled to room temperature and washed with deionized water to remove remaining chemical. Later, the sample was transferred to a beaker containing a 250 ml solution of hydrochloric acid (about 0.1 mol $l^{-1}$), stirred for 1 h, and then washed with hot deionized water until the pH of the washing solution reached 6 to 7 (Hameed et al., 2007).

### 3.2.3 Characterization of adsorbent

In this experiment, there were two of adsorbent were used which is oil palm frond and bamboo based activated carbon, thus to determine the characteristic of the adsorbent, the large number of analysis were conducted, such as scanning electron microscopy (SEM) analysis where to identify the microstructure of the produced activated carbon. Next, Energy-Dispersive x-ray (EDX) analysis, the analysis to identify the elemental composition of materials. Then, run zetasizer (Particle Size Analyser) analysis, where to measure the characteristic of particles of the adsorbent. In addition, the next analysis was used X-Ray diffraction analysis (XRD), this analysis used to examine the detailed information about the crystallographic structure, chemical composition, and physical properties of a material. Lastly, Fourier Transform-infrared (FTIR) analysis, which is to investigate the structure oil palm frond and bamboo as adsorbent and analysis of their functional groups.

### 3.2.3.1 Energy-Dispersive x-ray (EDX) Analysis

Energy Dispersive X-Ray Analysis (EDX), referred to as EDS or EDAX, is an x-ray technique used to identify the elemental composition of materials. Applications include materials and product research, troubleshooting, deformulation, and more.EDX systems are attachments to Electron Microscopy instruments (Scanning Electron Microscopy (SEM) or Transmission Electron Microscopy (TEM)) instruments where the imaging capability of the microscope identifies the specimen of interest. The data generated by EDX analysis consist of spectra showing peaks corresponding to the elements making up the true composition of the sample being analysed. Elemental mapping of a sample and image analysis are also possible. In a multi-technique approach EDX becomes very powerful, particularly in contamination analysis and industrial forensic science investigations. The technique can be qualitative, semi-quantitative, quantitative and also provide spatial distribution of elements through mapping. The EDX technique is non-destructive and specimens of interest can be examined in situ with little or no sample preparation.

### 3.2.3.2 Scanning Electron Microscope (SEM) Analysis

Scanning electron microscopy (SEM) analysis to identify the microstructure of the produced activated carbon and the effectiveness of the activated carbon in methylene blue treatment in terms colour, turbidity and adsorption capacity. Colour measurement is carried out to discover the sample that provide the high colour value where the adsorption capacity will be the low. When the sample that contain the high colour value is discover, it can be conclude that need large amount of adsorbent to be used to treat the dye. The activated carbon with the high colour value is selected to go through scanning electron microscopy (SEM) analysis to identify its microstructure. The activated carbon bamboo sample was prepared by using filter paper to filter the sample. Approximately 14 mg of the sample adsorbent powder and 93.33 mg/L of methylene blue were stirred and mixed well for 30 min of the shaking time. The mixture was transferred to and place to sample stub. Next, the specimen was mounted on metal stub using sticky carbon disc which increases conductivity. Later, to prevent charge buildup on specimen surface, it coated with conductive material. Then, the specimen was measure by collecting the image

**3.2.3.3 Zetasizer (Particle Size Analyser)**

The Zetasizer Nano range of instruments provides the ability to measure three characteristic of particles or molecules in a liquid medium. These three fundamental parameters are Particle size, Zeta potential and Molecular weight. By using the technique technology within the Zetasizer system, the parameters can be measured over a wide range of concentrations. The Zetasizer system also has the ability to perform autotitration measurements and trend measurements, including the determination of the protein melting point. Next, molecular weight with using static light scattering (SLS) and the classical Debye plot, the molecular weight of random coiled polymers up to 5 x 105 Da as well as globular polymers and proteins up to 2 x 107 Da can be determined without the necessity for multi-angle measurements. Last, autotitrator were provided fully automated titration and sample preparation. The procedure was start by take the amount of 3 ml solution from the sample by using syringe. Then, put into clear disposable zeta cell (DTS1060C) without presence of bubble inside. Next, put the clear disposable zeta cell into the Malvern Instruments Zetasizer Nano-S to run analysis. The comprehensive analysis software calculates particle size distributions based on scattering intensity, volume, and number density as well as polydispersity. The instrument may be used to characterize sample purity, aggregations, large conformational changes, and screening for crystallization.

### 3.2.3.4 X-ray Diffraction (XRD) Analysis

X-Ray diffraction analysis (XRD) is a non-destructive technique that give detailed information about the crystallographic structure, chemical composition, and physical properties of a material. It is based on the constructive interference of monochromatic X-rays and a crystalline sample. X-rays are shorter wavelength electromagnetic radiation that are generated when electrically charged particles with sufficient energy are decelerated. In XRD, the generated X-rays are collimated and directed to a nanomaterial sample, where the interaction of the incident rays with the sample produces a diffracted ray, which is then detected, processed, and counted. The intensity of the diffracted rays scattered at different angles of material are plotted to display a diffraction pattern. Each phase of the material produces a unique diffraction pattern due to the material's specific chemistry and atomic arrangement. The diffraction pattern is a simple sum of diffraction patterns of each phase. The peaks of the XRD pattern play an essential role in the spotting of the phases as well as the properties of the nanoparticles. Moreover, the width of the peak would reveal the average crystalline size of a nanoparticle where sharp peaks indicate a large size of crystallites, whereas broad peaks indicate smaller crystallites. In the XRD graph (Intensity vs 2 theta) is used to find the nature of the material. To scan the nature of the materials using XRD patterns, we must to examination the nature of Bragg's peaks appearing in the XRD pattern.

### 3.2.3.5 Fourier Transform-infrared (FTIR) Analysis

Fourier Transform-infrared (FTIR) Analysis was used to investigate the structure of methylene blue as adsorbate and bamboo as adsorbent and analysis of their functional groups. In adsorbent case, the powder form was used since liquid solution form will only result in water. The activated carbon bamboo sample was prepared by using filter paper to filter the sample. Approximately 14 mg of the sample adsorbent powder and 93.33 mg/L of methylene blue were stirred and mixed well for 30 min of the shaking time. The mixture was transferred to the IR sampling device and then compacted using IR hydraulic press for 60 sec. The sample was placed into FTIR window and then scanned by taking blank spectrum. After completion of the blank spectrum, sample was taken off from the window and thinly coated with test sample was placed again in the FTIR window to measure the spectrum of the sample.

### 3.3 Adsorption Experiment

Adsorption of methylene blue (MB) on activated carbon was carried out using a bamboo and oil palm frond based activated carbon in shaker at 150 rpm. The effect of contact time, solution pH and adsorbent dosage were analyse. The adsorption process was conducted with five different concentrations at 93.33mg/L, 133.33 mg/L, 200 mg/L, 266.67 mg/L, and 333.33 mg/L of methylene blue. The effect of contact time was used to discover equilibrium time for the adsorption. For the effect of contact time study, the concentration 93.33mg/L of methylene blue solution was added into a conical flask containing of 0.4 g activated carbon bamboo and shaken constantly at 150 rpm. Samples solutions were withdrawn at predetermined time intervals for the colour removal analysis. In the pH study, the pH of methylene solution was adjusted in the range of 2 till 12 by adding 1 M hydrochloric acid and 0.5 M sodium hydroxide. About 0.4 g adsorbent was then added to the solution and shaken at predetermined time. In the experiment to study the effect of adsorbent dosage on methylene blue adsorption, various amounts of adsorbent in the range of 0.2 g to 0.6 g were added to concentration 93.33 mg/L of methylene blue without rearrangement of pH and shaken until equilibrium. After shaking the flasks for predetermined time intervals, all samples were withdrawn from the conical flasks and the methylene blue solutions were separated from the adsorbent by filtration. Dye concentrations in the solutions were evaluated by measuring UV-visible spectrophotometer. The isotherms study was conducted by different the dosage of the adsorbent with the same concentration of methylene blue solution. Each solution concentration where 93.33 mg/L was treated with 0.2 to 0.6 gram of adsorbent.

The oil palm based activated carbon were used in different dosages to treat the same amount concentration of methylene blue which is 8.67 mg/L in 250 ml conical flask through batch treatment at constant pH value of 5. A graph was plotted to obtain the optimum dosage of oil palm frond based activated carbon to treat the dye. The mixture was shake at 100 rpm for 30 minutes. The test was repeat with different initial dye concentration 8.67 mg/L with the different dosage use which are 0.2g, 0.4g, 0.6 g, 0.8g and 1.0 g. After completed the batch treatment, the treated samples will be tested to determine colour, pH value and amount of dye adsorbed. To determine the absorbance of dye solution, the UV Vis-spectrophotometer were used at wavelength 650 nm with dye concentration of 1.0 mg/L, 2.0 mg/L, 3.0 mg/L, and 4.0 mg/L. Repeated 3 times measurement to obtain the average reading. Calibration curve was plotted, by plotting a graph of absorbance against concentration of dye solution.

### 3.3.1 Effect of solution pH value

In the pH study for the bamboo based activated carbon, the pH of methylene blue solution was adjusted in the range of 2, 3, 5, 6, 9, 12 by adding 1 M hydrochloric acid and 0.5 M sodium hydroxide. When the usage for pH value were low or acid, the higher percentage colour removal for dye treatment on adsorption process. It is because the higher the acid in dye solution, the higher the large adsorption capacity for adsorbent to adsorb. Because the adsorbent was alkaline. Next, for the oil palm frond based activated