GREEN FUNCTIONALIZATION OF ACTIVATED CARBON FOR DYE REMOVAL APPLICATION

By

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CERTIFICATION OF APPROVAL

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Approved by,

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TRONOH, PERAK

MAY 2014

CERTIFICATION OF ORIGINALITY

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

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AHMAD ZULFADLI BIN MOHAMAD HASHIM

ABSTRACT

The objective of this study was to investigate the used of water as a medium of functionalization of commercialized activated carbon in order to be used in removal of methylene blue dyes from synthetic wastewater via adsorption. The parameters for functionalization of the commercialized activated carbon included temperature at 35°C, contact time of 5 hours and varying water bath shaker frequency (100, 150 and 200 rpm). The experiment was conducted in batch process where the commercialized activated carbon were functionalized under the stated parameters. The functionalized activated carbon were characterized using Fourier Transform Infra-Red (FTIR) Spectroscopy. The FTIR analysis indicated the increase of the amount of functional group attached to the activated carbon. The dye adsorption study was conducted by using methylene blue solution with initial concentration of 500 ppm as adsorbate and the functionalized activated carbon as adsorbent. A standard calibration curve for methylene blue solution was generated using of Ultraviolet-Visible (Uv-Vis) Spectrophotometer. The result from the adsorption study was the parameter of temperature at 35°C, contact time of 5 hours and varying water bath shaker frequency at 100 rpm yield the best adsorption rate.

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CHAPTER 1
INTRODUCTION

1.1 Background of Study

Over the past decades, the world population has increased and this has resulted in rapid industrialization and urbanization. Pollution, in general, has become a concerned issue all over the world. There are many types of pollution, however, as societies are getting more concerned about the environment that they are living in, there is an increasing awareness to protect the environment. Environmental pollution has become an alarming issue in many countries. People are becoming more concerned and sensitive about their environment. Thus, water pollution has become a great concern because water is the necessity of life and all types of organisms need water to survive. Years of modernization and rapid development in industrial activities have resulted in large amount of wastewater polluting fresh water. These wastewater consist toxic pollutants which could endanger human and animal life. To curb the presence of pollutants in the supply of fresh water, high priority is given to the pollution control and management. However, the quest to ensure that the supply of fresh water continues in our environment is a challenging task for researchers and practitioners around the world.

1.2 Dyes

Dyes or colouring is widely used in many industries such as food, plastics, textile etc. The demand by manufacturers has been growing in the past few decades as they use dye to give colour to their products. There are several categories of dyes according to their usage such as reactive, disperse, direct, vat, sulphur, cationic, acid and solvent dyes (Hunger, 2003). According to Gregory et al. (1991), most of dyes are toxic, mutagenic and carcinogenic which poses hazard to aquatic life as well as other living organisms.

Mckay and Sweeny (1980) stated that many dyes are difficult to degrade, as they are generally stable to light, oxidizing agent and are resistant to aerobic digestion. Synthetic dyes which were produced by using highly toxic, carcinogenic and even explosive materials were considered as harmful. Intense exposure to Methylene Blue (basic dye) was found to cause increase heart rate, cyanosis, Heinz body formation,

vomiting and shock. Also, Methylene Blue was also found to be mutagenic to *Micrococcus aureus*, *Salmonella typhimurium* and *Escherichia coli* as reported *by* Little (1990). The major sources for polluting the water resource are dyes and dye pigments. Barakat (2010) stated that the dyeing process is a significant consumer of water and producer of huge contaminated aqueous waste streams.

1.3 Activated Carbon

Activated carbon,which is also called activated charcoal or activated coal, is a form of carbon that has been processed to make it extremely porous and have a very large surface area available for adsorption or chemical reactions. It has been the most popular and widely used adsorbent in wastewater treatment throughout the world. The forerunner of modern activated carbon, that is charcoal, has been established as the oldest adsorbent known in wastewater treatment. It has the ability to purify water since 2000 B.C. In 1789-1790, Lowitz established the first use of charcoal for the removal of bad taste and odours from water on an experiment basis. Activated carbons are highly developed internal surface area and porosity, sometimes also known as solid sponges.

1.4 Statement of Problem

Environmental pollution control is a highly concerned issue in many countries. Wastewater is one of the major environmental pollution. Wastewater is actually the spent water used by the increasing population and industrialization such as the houses, commercial establishments, industries and public institutions for various purposes. One of the major issues in wastewater pollution is the decolourisation of wastewater. The cause of this problem is because many industries used dyes to colour their products, such as plastics, paper, textiles, rubber, leather, cosmetics, food and mineral processing industries. Wastewater has to be treated properly before they are being discharged into the rivers. If not, they may cause problems and are harmful to aquatic life in rivers. Not only that, according to Kadirvelu et al. (2003) dyes also can cause severe damage to human beings, such as dysfunction of kidney, reproductive systems, liver, brain and central nervous system.

The use of conventional physic-chemical and biological methods for removing dyes is difficult and not really efficient. One of the effective techniques for removal of

color from waste water is adsorption by activated carbon. Many researchers have in fact proven that the removal of dyes by activated carbon is more economically and technically easier. James (1991) reported that activated carbon has been found to be a versatile adsorbent which can remove diverse types of pollutants such as metal ions, dyes, phenols, and a number of other organic and inorganic compounds and bio-organisms. However, due to high cost, its usage is somewhat restricted.

1.5 Research Objectives

The objectives of the study are:

i. To prepare activated carbon with surface modification by functionalizing activate carbon using optimum conditions with distilled water.
ii. To identify the change in the amount of functional group by characterization of the functionalized activated carbon.
iii. To examine the efficiency of the functionalized activated carbon by conducting dye adsorption study.

1.6 Scope of Study

The scope of study comprises of functionalizing commercial activated carbon using water and to test the adsorption capabilities of the functionalized activated carbon. The functionalization activated carbon will be characterized and analysed using Fourier Infrared transform (FTIR) Spectroscopy. These instruments are used to indicate functional groups attached to the activated carbon.

As regard to the test of the dye adsorption capabilities, the efficiency of the functionalized activated carbon is then determined through dye adsorption study which involves the use of UV-Vis spectrophotometer.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The review of literature covers the adsorption of dyes, activated carbon for wastewater treatment, factors influencing adsorption and the summary of discussion.

2.2 Technologies for colour removal

Colour removal technologies can be divided into three categories that are: biological, chemical and physical (Robinson et al., 2001). Each of them has their own advantages and flaws.

Dyes are resistance organic molecules, resistant to aerobic digestion, and are stable to light. All these make wastewater containing dyes difficult to treat. Traditional methods cannot be used to decolorize synthetic dye in wastewater due to the high cost and also disposal problems at large scale in the textile and paper industries (Ghoreishi and Haghighi, 2003).

2.2.1 Biological methods

Compared to other physical and chemical processes, biological treatment is the often the most economical alternatives. McMullan et al.(2001), and Fu and Viraraghavan (2001) advocates that biodegradation methods such as fungal decolourization, microbial degradation, adsorption by (living or dead) microbial biomass and bioremediation systems are commonly applied to the treatment of industrial effluents because many microorganisms such as bacteria, yeasts, alges and fungi are able to accumulate and degrade different pollutants. Nonetheless, the application is often limited because of technical problems. Bhattacharyya and Sharma (2003) states that biological treatment needs a large land area and is constrained by sensitivity toward diurnal variation as well as toxicity of some chemicals, and less flexibility in design and operation. Moreover, biological treatment is incapable of obtaining satisfactory colour elimination with current conventional biodegradation processes (Robinson et al., 2001). Even though many organic molecules are degraded, many others are resistance due to their complex chemical structure and synthetic organic origin (Ravi Kumar et al., 1998).

2.2.2 Chemical methods

Chemical techniques are always expensive. Even though the dyes can be removed, the accumulation of concentrated sludge will create disposal problem. Excessive chemical use can also bring about another secondary pollution problem. Other techniques known as advanced oxidation processes have emerged in recent times. These techniques are based on the generation of very powerful oxidizing agents such as hydroxyl radicals and have been applied with success for the pollutant degradation. These methods are efficient for the treatment of waters contaminated with pollutants. However, they are very costly and commercially unappealing. There are also problems like they require high electrical energy demand and the consumption of chemical reagents.

2.2.3 Physical methods

Physical methods provides a better alternative for the treatment of contaminated waters, especially if the adsorbent is inexpensive and does not require an additional pre-treatment step before its application. According to Dabrowski, (2001), adsorption is a well-known equilibrium separation process and an effective method for water decontamination applications. Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. According to Slokar and Le Marechal (1998), decolourisation is a result of two mechanisms: adsorption and ion exchange. Kumar et al. (1998) reported that decolourisation is influenced by many physio-chemical factors, such as, dye/sorbent interaction, sorbent surface area, particle size, temperature, pH, and contact time. Adsorption also does not result in the formation of harmful substance.

2.3 Factors Influencing Adsorption

Surface Area: According to Weber (1972), adsorption is a surface phenomenon; as such, the extent of adsorption is proportional to specific surface area. Specific surface area can be defined as that portion of the total surface area that is available for adsorption. So the amount of adsorption accomplished per unit weight of a solid adsorbent is greater the more finely divided and the more porous the solid.

Nature of the Adsorbate: One fact is immediately evident; the solubility of the solute is, to a large extent, a controlling factor for adsorption equilibria (Weber, 1972).

pH: The pH of a solution from which adsorption occurs may influence the extent of adsorption. Hydrogen and hydroxide ions are adsorbed quite strongly, so the adsorption of other ions is influenced by the pH of the solution. Moreover, to the extent to which the ionization of an acidic or basic compound affects its adsorption, pH affects adsorption in that it governs the degree of ionization (Weber, 1972).

Temperature: The extent of adsorption generally increases with decreasing temperature because adsorption reactions are usually exothermic. The changes in enthalpy for adsorption are normally of the order of those for condensation or crystallization reactions. So small variations in the temperature tend not to alter the adsorption process to a significant extent (Weber, 1972).

Adsorption of Mixed Solutes: In the application of adsorption for purification of waters and wastewaters, the material to be adsorbed will be a mixture of many compounds. The compounds may act differently, it may enhance adsorption, may act relatively independently, or may also interfere with one another. Mutual inhibition of adsorption capacity can be predicted to occur provided: adsorption is confined to a single or a few molecular layers; the adsorption affinities of the solutes do not differ by several orders of magnitude; and there is not a specific interaction between solutes enhancing adsorption. Similarly, because the adsorption of one substance will tend to reduce the number of open sites, so the "concentration" of adsorbent available as a driving force to produce adsorption of the other substance, mutually depressing effects on rates of adsorption may be predicted (Weber, 1972).

Nature of the Adsorbent: The physicochemical nature of the adsorbent can have intense effects on both rate and capacity for adsorption (Weber, 1972). Every solid is a potential adsorbent with its surface characteristics.

2.4 Activated Carbon for Wastewater Treatment

Activated carbon refers to carbon materials, such as coal or wood, that are processed through dehydration, carbonization, and oxidation to produce a material that is highly adsorbent due to a large surface area and high number of internal pores per unit mass. Activated carbon, also called activated charcoal or activated coal, is a form of carbon that has been processed to make it extremely porous and have a very large surface area available for adsorption or chemical reactions. Activated carbon as an adsorbent that is often used to remove organic contaminants. It can be prepared from almost any carbonaceous material by heating it with or without addition of dehydrating chemicals in the absence of air. Activation is done to create a large surface area within the carbon which makes activated carbon ideal for adsorption. It occurs by passing mildly oxidative hot gases (carbon dioxide or steam) through the carbon at temperatures between 315°C and 925°C. This causes the formation of tiny fissures or pores (Clark and Lykins, 1989). Activated carbon can either be granular (Granular activated carbon-GAC) or powdered (Powdered activated carbon-PAC). Activated carbon has been the most popular and widely used adsorbent in wastewater treatment worldwide. Charcoal, the precursor of modern activated carbon has been recognized as the oldest adsorbent known in wastewater treatment.

2.5 Dyes

Generally, a dye can be described as a colored substance that has a closeness to the substrate to which it is being applied. The dye is usually used as a watery solution, and may require a mordant to improve the fastness of the dye on the fiber. In contrast, a pigment generally has no closeness for the substrate, and is insoluble.

Basic dyes are water-soluble - cationic dyes that are mainly applied to acrylic fibers,but there are also uses for wool and silk. Usually acetic acid is added to the dyebath to help the uptake of the dye onto the fiber. Basic dyes are also used in the coloration of paper, textile, food etc.

2.6 Theories

In this study, two main theories are applied, they are adsorption and functionalization. Adsorption is the process applied in dye removal application. Functionalization is basically a surface modification of activated carbon

2.6.1 Activated Carbon

Activated carbon, also called as activated charcoal, is a form of carbon that has been processed with oxygen to create millions tiny pores between the carbon atoms. These pores allow molecules to be adsorbed onto the surface of the carbon. Geokoplis (2003) stated activated carbon is made by thermal decomposition of wood, vegetable shells, coals and so on, and has surface areas of 300 to 1200 m^2/g with average pore diameters of 10 to 60 A.

2.6.2 Adsorption

In adsorption process one or more components of a gas or liquid stream are adsorbed on the surface of a solid adsorbent and a separation is accomplished Geokoplis (2003). Adsorption is different with absorption as the molecules are attached to surface of the adsorbents via physical or chemical bonds. According to Foo (2010), the quality of adsorption process can be influenced by various physic-chemical factors and these include properties of adsorbed material (molecular size, boiling point, molecular mass and polarity), properties of the surface of the adsorbent (polarity, pore size and spacing), effect of other ions, particle size, solution pH, temperature and contact time.

There are two types of adsorption namely chemical and physical adsorption. Chemicals adsorption refers to the process of adsorption in which adsorbate are attached to the surface of adsorbent via chemical bonds. Physical adsorption refers to the adsorbate attached to the surface of the adsorbent through Van der Waals interactions. The differences between physical adsorption and chemical adsorption are shown in Table 2.1.

Table 2.1: Differences between physical adsorption and chemical adsorption

CHARACTERISTICS	PHYSICAL ADSORPTION	CHEMICAL ADSORPTION
Energy	Exothermic	Exothermic
Effect of temperature	Occurs more readily at lower temperature Decreases with increasing temperature	Increases with increase in temperature up to a certain limit and starts decreasing after the limit
Effect of Pressure	Increasing with increase in pressure	Not affected by small change in pressure Favourable at high temperature
Specificity	Non-specific	Highly specific
Electron Transfer	No electron transfer	Electron transfer leading to bond formation

2.6.3 Functionalization

Functionalization also known as surface modification is the addition of functional group onto the surface of a material by chemical method. The addition of functional group is to increase the adsorption efficiency.

For activation carbon, surface modification can be achieved through numerous methods such as oxidation, acid treatment, thermal treatment and plasma treatment Shen (2007). Most of the literature reviewed for this study, acid based medium such as nitric acid and phosphoric acid is used as the chemical agent for functionalization of activated carbon. There is no specific research that uses water as medium for functionalization for activated carbon.

2.7 Current Works on Dye Removal Application

There are variety of works and research related to dye removal using activated carbon for adsorption process. Different method of functionalization can be seen from these researches. However, most of the functionalization medium used in acid based and only one research use water as a source for functional group.

Maofei Ran (2012) functionalize a multi-walled carbon nanotubes using water-assisted chemical vapour deposition and using an acidic medium. The results was water functionalized carbon nanotubes perform better adsorption than the acidic agent.

Mohammad Arifur Rahman (2012), A.A. Ahmad (2013) and I.A.W. Tan (2006) use acidic medium as an agent for functionalization of activated carbon. Acid such as sulphuric acid, phosphoric acid and nitric acid are common in functionalization. These authors produced their own activated carbon from their respective precursors such as rice husk, solid waste and oil palm fibre.

Some alkali medium also being used as an agent for functionalization, such as works by Solomon (2012). Some others work use zinc chloride as the functional agent Mohammad Asadullah Mohammad Asaduzzaman (2009) and acetone Jalil Ghobadi (2013). From the literature reviewed, there are no specific works that utilized water as the medium for functionalization.

Table 2.2 summarizes of all the current works on dye removal using activated carbon.

Table 2.2: Summary of all the current works on dye removal using activated carbon.

AUTHORS/ YEARS	TITLE	MATERIALS	AGENT	FUNC-TIONAL GROUP	CONDITION TO FUNTIONALIZE
Maofei Ran, Wenjing Sun, Yan Liu, Wei Chu, Chengfa Jiang (2014)	Functionalization of multi-walled carbon nanotubes using water-assisted chemical vapour deposition	Multi Walled Carbon Nanotubes (MWCNTs)	Water HNO_3	C-C C-OH C=O COOH	Water assisted CVD (Chemical Vapor Deposition)
Mohammad Arifur Rahman, S.M. Ruhul Amin, A.M. Shafiqul Alam (2012)	Removal of methylene blue from waste water using activated carbon prepared from rice husk	Activated carbon	H_2SO_4 $ZnCl_2$		• H2SO4: Soaked for 2 hours, T=100^{0}C • ZnCl2: soaked at 50^{0}C for 1 hour, and at T=100^{0}C and at 24 hours
A.A. Ahmad, A. Idris, B.H. Hameed (2013)	Organic dye adsorption on activated carbon derived from solid waste.	Activated carbon	H_3PO_4	O-H	Carried out at T=500^{0}C
Jalil Ghobadi, Mokhtar Arami, Hajir Bahrami, Niyaz Mohammad Mahmoodi (2013)	Modification of carbon nanotubes with cationic surfactant and its application for removal of direct dyes	MWCNT	Acetone	O-H N-H C=C C=N	Ultrasonic irradiation was carried out using a sonifier operated at 24 kHz
Moonis Ali Khan, B.H. Hameed, Jenny Lawler, Mahendra Kumar, Byoun Hun Jeon (2014)	Developments in activated functionalized carbons and their applications in water decontamination: a review	Activated carbon	H_3PO_4 (for methylene blue)		

I.A.W. Tan, B.H. Hameed, A.L. Ahmad (2006)	Equilibrium and kinetic studies on basic adsorption by oil palm fibre activated carbon	Activated Carbon	KOH	O-H C=C C-OH C-H	• Soaked in KOH solution • Dehydrated in oven overnight at 105^0C • Carbonization at $T_{final}=850^0$C • Washed with hot deionized water and 0.1 M HCl
Olugbenga Solomon, Mohd Azmier Ahmad (2012)	Coconut (Cocos nucifera) shell based activated carbon for the removal of malachite green dye from aqueous solutions.	Activated carbon	KOH	-OH -NH C-H C=H	Dehydrated in an oven overnight at 105^0C
Mohammad Asadullah Mohammad Asaduzzaman, Mohammad Shajahan Kabir, Mohammad Golam Mostofa, Tomohisa Miyazawa (2009)	Chemical and structural evaluation of activated carbon prepared from jute ticks for Brilliant Green dye removal from aqueous solution.	Activated carbon	$ZnCl_2$	C=O C=C C-C C-H	Mixed with $ZnCl_2$ for 12 hr

CHAPTER 3

MATERIALS AND METHODOLOGY

3.1 Introduction

The research methodology consists of project planning and experimental design. Project planning includes the preparation of plan in tabular form such as Gaant chart. Experimental design is to produce experimental procedure in order to conduct experiment.

3.1.1 Research Flowchart

This study emphasis more on results obtained from the functionalized activated carbon. The adsorption of dye will be analysed and any findings will be recorded. Thus, the study will more toward the analysis of results obtained.

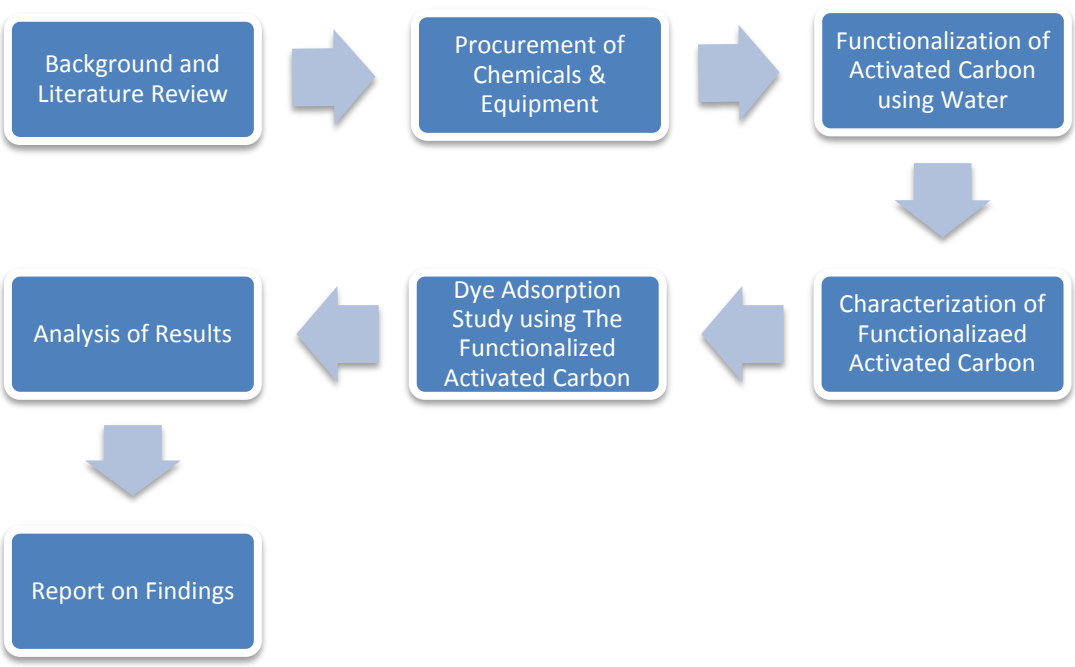

Figure 3.1: Research Flowchart

3.1.2 Project Activities

The project activities includes the planning of the project and the execution of experiment. The detailed of the plan for this project can be seen in **APPENDIX 1**.

3.2 List of Chemicals, Apparatus and Equipment

Listed below are the chemicals and apparatus required in order to conduct the study. Besides that, the equipment used is listed in Table 3.3 below.

Table 3.1 List of chemicals, apparatus and equipment

CHEMICALS	APPARATUS	EQUIPMENT
• Commercialized Activated Carbon • Methylene Blue • Distilled Water	• Magnetic Stirrer • Stirrer • Stopwatch • Microwave Oven • Ultrasonic Bath • Glassware	• Fourier Transform Infra-Red Spectroscopy • Ultraviolet Visible Spectrophotometer

3.2.1 Adsorbent (Activated Carbon)

Activated carbon is used in this study is commercialized activated carbon. The activated carbon will undergone surface modification (functionalization) to form functional group on the surface of the carbon. These functional group will aid the adsorption process.

3.2.2 Adsorbate (Methylene Blue)

Methylene blue dye was chosen in this study because of its known strong adsorption onto solids and is often serves as a model compound for removing colored bodies from aqueous solutions.

3.3 Experimental Procedures

Three experiment procedure was produced in or der to conduct the experiment. The procedures were for the functionalization of activated carbon using distilled water, characterization of the functionalization and dye adsorption study.

3.3.1 Functionalization of Activated Carbon Using Distilled Water

i. Approximately 10 gram of activated carbon is used for functionalization.
ii. For experiment purpose, an amount of commercialised activated carbon is taken as sample as a control for this experiment. The sample is labelled as Sample 1.
iii. For samples that will be functionalized, 10 gram of activated carbon is placed inside an Erlenmeyer flask
iv. Distilled water is added inside the Erlenmeyer Flask until 100 ml mark
v. The flask is then placed inside a water bath shaker where it is subjected to the following parameter as shown in Table 3.2.

Table 3.2: Table of parameters in functionalization

TYPE OF MEDIUM	**DISTILLED WATER**			
PARAMETERS	**SAMPLE**			
	1	**2**	**3**	**4**
Time Of Contact (hours)	-	5	5	5
Water Bath Temperature (^{0}C)	-	35	35	35
Stirring Frequency (rpm)	-	100	150	200

vi. After being subjected by the following parameters, the activated carbon is extracted using filtration method.
vii. The wet activated carbon is then dried in oven at temperature of 80^{0}C until the activated carbon is completely dried.
viii. The process can be summarized in the following flowchart in Figure 3.2.

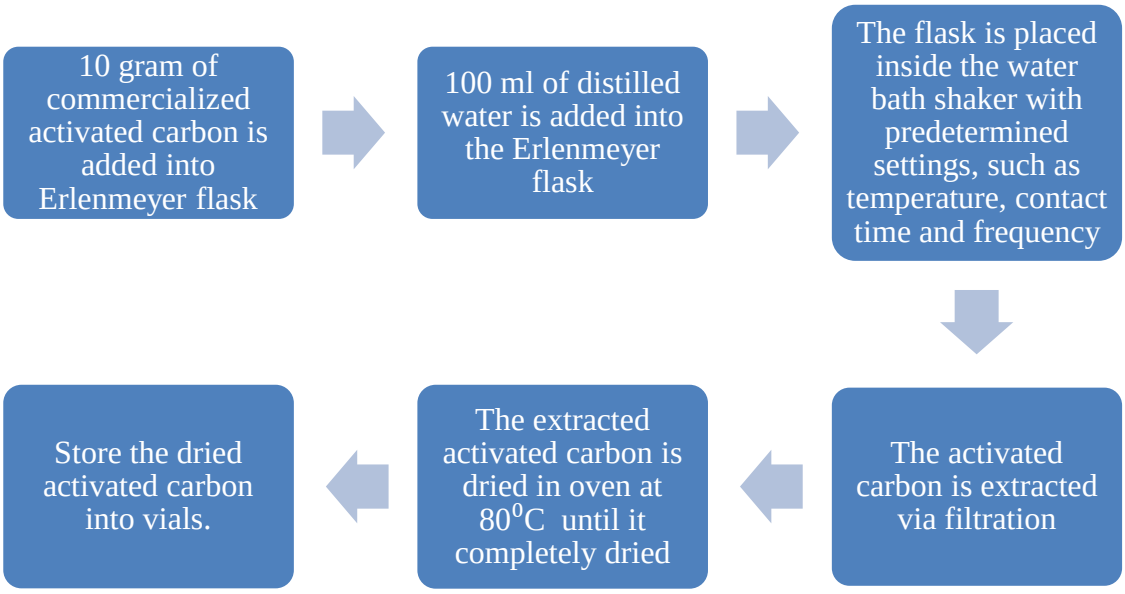

Figure 3.2: Flowchart for functionalization of activated carbon procedure.

The functionalization of activated carbon is done by using apparatus such as Erlenmeyer flask, and ultrasonificator water bath shaker as shown n figure below.

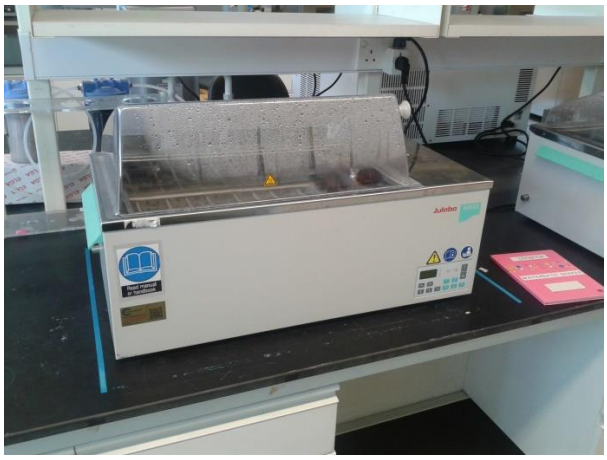

Figure 3.3: Ultrasonificator Water Bath Shaker

An amount of 10 gram of activated carbon was functionalized with distilled water with the determined parameters. Erlenmeyer flask was used and it is placed into the water bath shaker.

After the functionalization procedure was done, the activated carbon is filtered and dried inside oven at the temperature of 80^{0}C until the activated carbon is

completely dried. Figure 3 shows the oven used in drying of the filtered activated carbon. The dried activated carbon is the placed inside a vial and labelled accordingly.

Figure 3.4: Oven used for drying of filtered Activated Carbon

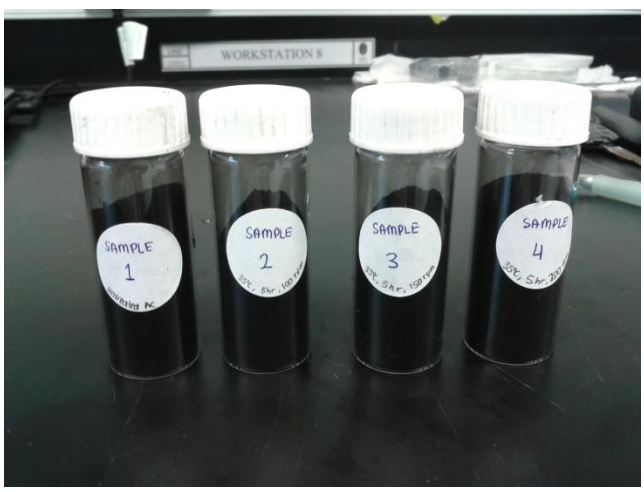

Figure 3.5: Functionalized Activated Carbon in vials

3.3.2 Characterization of Functionalization of Activated Carbon

Each set is to be analysed for detection of functional group on the activated carbon surface. Fourier Transform Infrared (FTIR) Spectroscopy is used to identify the functional group. The analysis is done by third party where the result will be obtained after the analysis done.

3.3.3 Dye Adsorption Study

Methylene Blue solution is prepared specifically for calibration purposes. The solutions were prepared by dilution method where a stock solution of 1000 ppm of Methylene Blue is prepared and the stock solution is diluted with distilled water to obtain solution with concentration of 500 ppm, 300 ppm, 100 ppm, 50 ppm and 10 ppm. A clear distilled water also to be included and to be set as 0 ppm. The procedure for dye adsorption study is as the following.

i. A standard calibration is to be made using methylene blue solution of different concentration. The concentrations of the solution are as shown in the following table.

Table 3.3: Concentrations of methylene blue solution for calibration purposes

CONCENTRATION OF METHYLENE BLUE (ppm)
500
300
200
100
50
10
0

ii. Each solution is quantified using Ultraviolet-Visible Spectrophotometer (UV-Vis).

iii. A solution of 500 ppm is used as a fixed concentration for all adsorption studies for each sample.

iv. Magnetic stirrer will be used for all adsorption studies.

v. 1 gram of functionalized activated carbon will be placed in the methylene blue solution and the time recording is started.

vi. A time interval of 10 minutes is set. Every 10 minutes, a small amount of the solution is taken using filtered syringe.

vii. The experiment is continued until the adsorption reach equilibrium.

viii. The procedure is repeated for the next sample.

CHAPTER 4
RESULTS AND DISCUSSIONS

4.1 Introduction

The project is consist of three main parts, functionalization of activated carbon, and characterization of activated carbon and dye adsorption study. In functionalization of activated carbon, the process of functionalization and the preparation will be explain and discussed. As for the characterization, the results of characterization using Fourier Transform Infrared (FTIR) Spectroscopy will be discussed. Lastly in dye adsorption study, the findings from the study and from the experiment conducted will be discussed in this chapter.

4.2 Functionalization of Activated Carbon

Functionalization is basically a process of surface modification of activated carbon to increase the number of functional group attached to the surface of the activated carbon. The additional functional group will aid as well as improve adsorption of dye onto the activated carbon. The functionalized activated carbon is labelled and kept in vials. The label of the samples are shown in Table 4.1.

Table 4.1: Sample label and its descriptions

SAMPLE	DESCRIPTIONS
1	Commercialized Activated Carbon. Untreated, to be used as control
2	Functionalized Activated Carbon, at 35^0C, 5 hour of contact time and shaken at frequency of 100 rpm.
3	Functionalized Activated Carbon, at 35^0C, 5 hour of contact time and shaken at frequency of 150 rpm.
4	Functionalized Activated Carbon, at 35^0C, 5 hour of contact time and shaken at frequency of 200 rpm.

4.3 Characterization of Functionalized Activated Carbon

The characterization of the functionalized activated carbon is analysed using Fourier Transform Infrared (FTIR) Spectroscopy to identify any presence or addition of new significant peaks that would indicates the attachment of functional groups on the surface of the activated carbon. The interpretation of the results is based from the tables of characteristic Infra-Red Absorptions in **APPENDIX 2.**

4.3.1 Fourier Transform Infrared (FTIR) Spectroscopy Results

All four samples are characterized with FTIR Spectroscopy. The results obtained can be seen from Figure 4.1 until Figure 4.4.

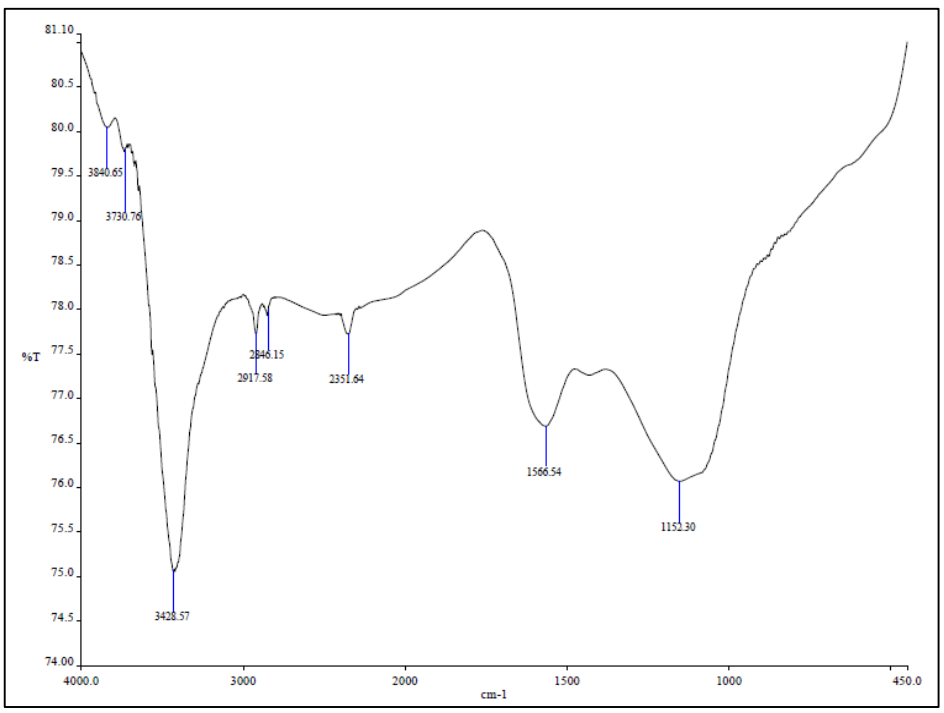

Figure 4.1: FTIR Analysis for Sample 1

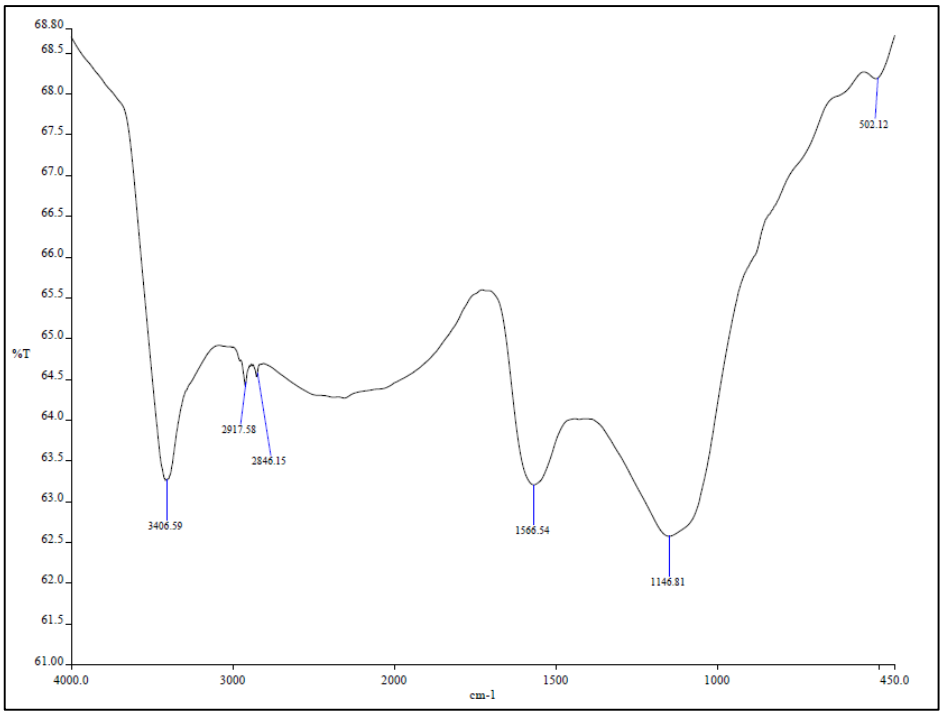

Figure 4.2: FTIR Analysis for Sample 2

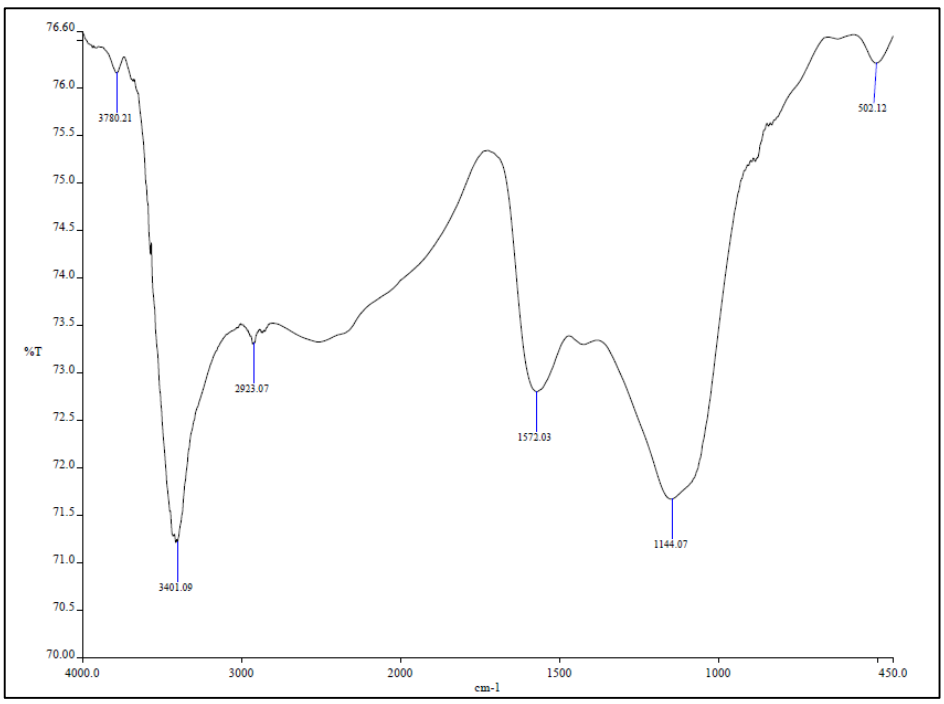

Figure 4.3: FTIR Analysis for Sample 3

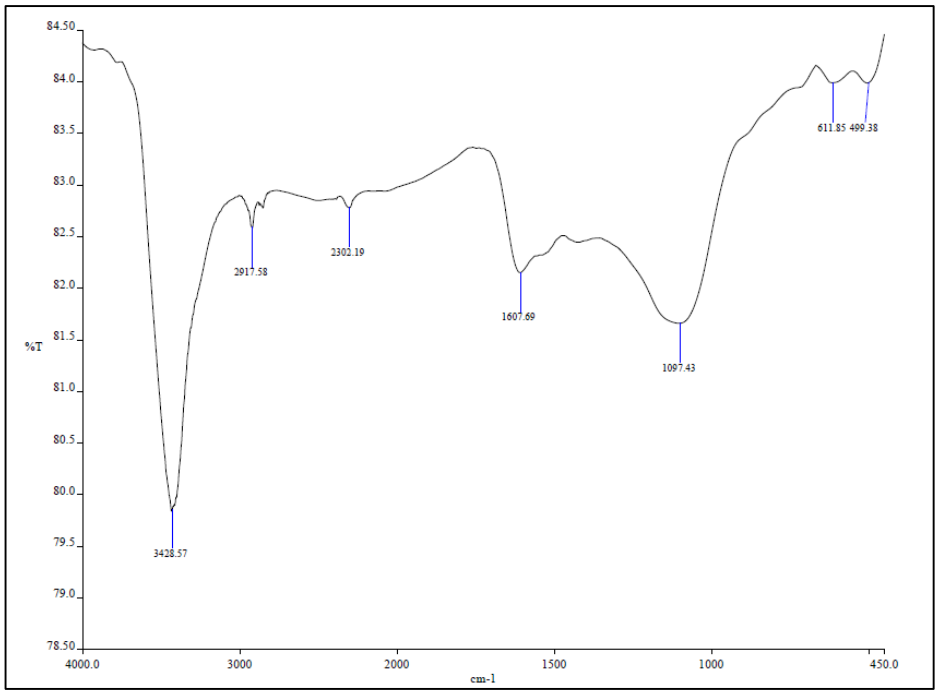

Figure 4.4: FTIR Analysis for Sample 4

Based from all the figures, it is indicates that by manipulating the Water bath shaker frequencies, the FTIR analysis indicates the presence of functional group such as –OH, C-H, C-C and C-O based on the IR Frequencies table in **APPENDIX 2**.

The functional group –OH can be identified by the indication of peaks at the wave number in the range of 3200 cm^{-1} – 3500 cm^{-1}, C-H at 2850 cm^{-1} – 3000 cm^{-1}, C-C at 1400 cm^{-1} – 1500 cm^{-1} and C-O at 1000 cm^{-1}– 1320 cm^{-1}. However, there are no indication of the presence of new functional group as all the functionalized activated carbon have the same identical peaks as the control which is the Sample 1 in Figure 4.1. The functional groups presences in all the sample can be tabulated on the following tables.

Table 4.2: Functional groups and their respective peaks' wave number for each samples

Samples	**Functional Group Wave Number (cm^{-1})**			
	-OH	**C-H**	**C-C**	**C-O**
1	3434.50	2917.50	1566.54	1103.62
2	3429.91	2917.50	1566.54	1155.03
3	3412.94	2923.07	1572.03	1148.00
4	3417.22	2917.58	1607.69	1148.40

However, the significant difference that can be observed are the difference is the percentage of transmittance in this case the vertical axis on the FTIR graph. The difference can be observed by compiling all the result in the same graph as shown Figures 4.5.

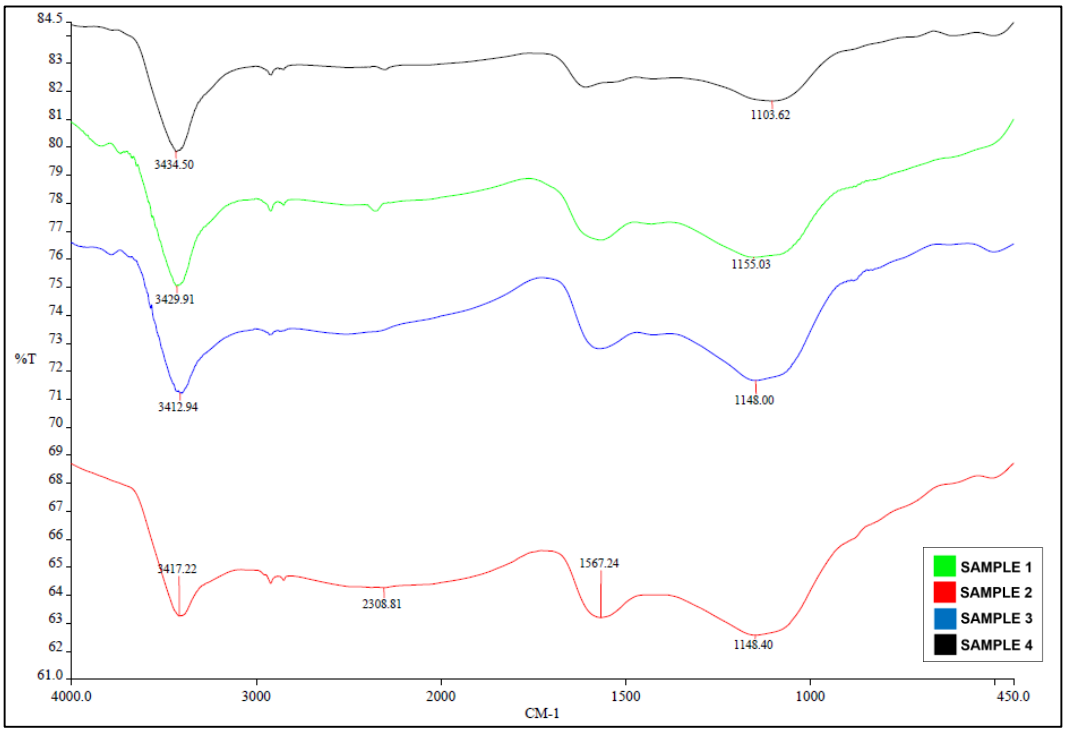

Figure 4.5: FTIR Analysis for all samples

From Figure 4.5, the samples has different ranges of transmittance percentage from one another. Sample 1 is used as the baseline as it is the untreated activated carbon and it has the percentage transmittance range of 71% - 77%. On the other hand, Sample 2, 3 and 4 has different ranges of percent transmittance, where the range of Sample 2 and 3 is below the baseline and Sample 4 is above the baseline.

Thus, the relationship of percent transmittance, absorbance can be summarized into Table 4.3 until Table 4.6.

Table 4.3: Percent transmittance and absorbance value for -OH functional group

Functional Group	Sample	Wave number (cm^{-1})	Percent Transmittance, %T	Absorbance, A
-OH	1	3434.50	75.06	0.124591
	2	3429.91	63.33	0.198391
	3	3412.94	71.22	0.147398
	4	3417.22	79.89	0.097508

Table 4.4: Percent transmittance and absorbance value for C-H functional group

Functional Group	Sample	Wave number (cm^{-1})	Percent Transmittance, %T	Absorbance, A
C-H	1	2917.50	77.5	0.110698
	2	2917.50	64.47	0.190642
	3	2923.07	73.32	0.134778
	4	2917.58	82.59	0.083073

Table 4.5: Percent transmittance and absorbance value for C-C functional group

Functional Group	Sample	Wave number (cm^{-1})	Percent Transmittance, %T	Absorbance, A
C-C	1	1566.54	76.69	0.115261
	2	1566.54	63.21	0.199214
	3	1572.03	72.81	0.137809
	4	1607.69	82.15	0.085392

Table 4.6: Percent transmittance and absorbance value for C-O functional group

Functional Group	Sample	Wave number (cm^{-1})	Percent Transmittance, %T	Absorbance, A
C-O	1	1103.62	76.14	0.118387
	2	1155.03	62.58	0.203564
	3	1148.00	71.67	0.144663
	4	1148.40	81.71	0.087725

4.4 Dye Adsorption Study

Dye adsorption consist of two part, the preparation of standard calibration curve and dye adsorption test. For standard calibration, different concentration of methylene blue solution were prepared and were analysed using UV-Vis Spectrophotometer. For dye adsorption test, the functionalized activated carbon were used to adsorb the dye from the methylene blue solution.

4.4.1 Methylene Blue Solution Preparation for Standard Calibration Curve

The calibration can be shown in the following figure. As the concentration of methylene blue increase, the value of absorbance increase. The calibration curve is to be used as the standard for analysis of concentration of dye in dye adsorption test. The calibration plot for methylene blue at 670nm was obtained as shown in Table 4.7.

Table 4.7: Concentration of methylene blue and its absorbance

CONCENTRATION (ppm)	ABSORBANCE
0	0
10	0.201
50	0.504
100	1.051
300	2.611
500	4.452

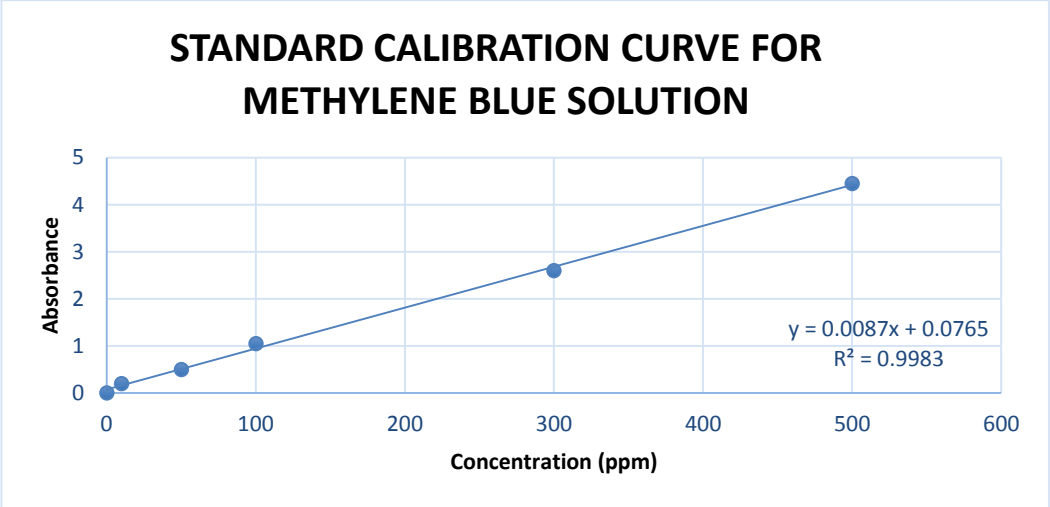

Figure 4.6: Standard Calibration Curve for Methylene Blue Solution

The data obtained in Table 4.7 were fitted by a straight line with high determination coefficient of $R^2 = 0.9983$. The high value of the determination coefficient of the calibration line observed in the study allows the concentration of dye in dye adsorption study to be determined based from this calibration curve.

4.4.2 Dye Adsorption Study Findings

All activated carbon are subjected to dye adsorption test, where the results of the test can be seen in the following figures. The sample description is described in Table 4.8.

Table 4.8: Results of adsorption of methylene blue by functionalized activated carbon

Samples	**1**	**2**	**3**	**4**
Time	**Concentration (ppm)**			
0	500	500	500	500
10	411.56	325.12	385.65	433.25
20	260.52	140.84	210.47	320.14
30	105.42	24.5	80.54	167.54
40	50.24	5.23	30.59	75.41
50	15.87	1.23	8.54	30.21
60	7.21	0.53	6.23	10.25
70	4.98	0.43	4.02	5.64
80	1.53	0.33	0.51	2.21
90	0.32	0.11	0.23	1.02

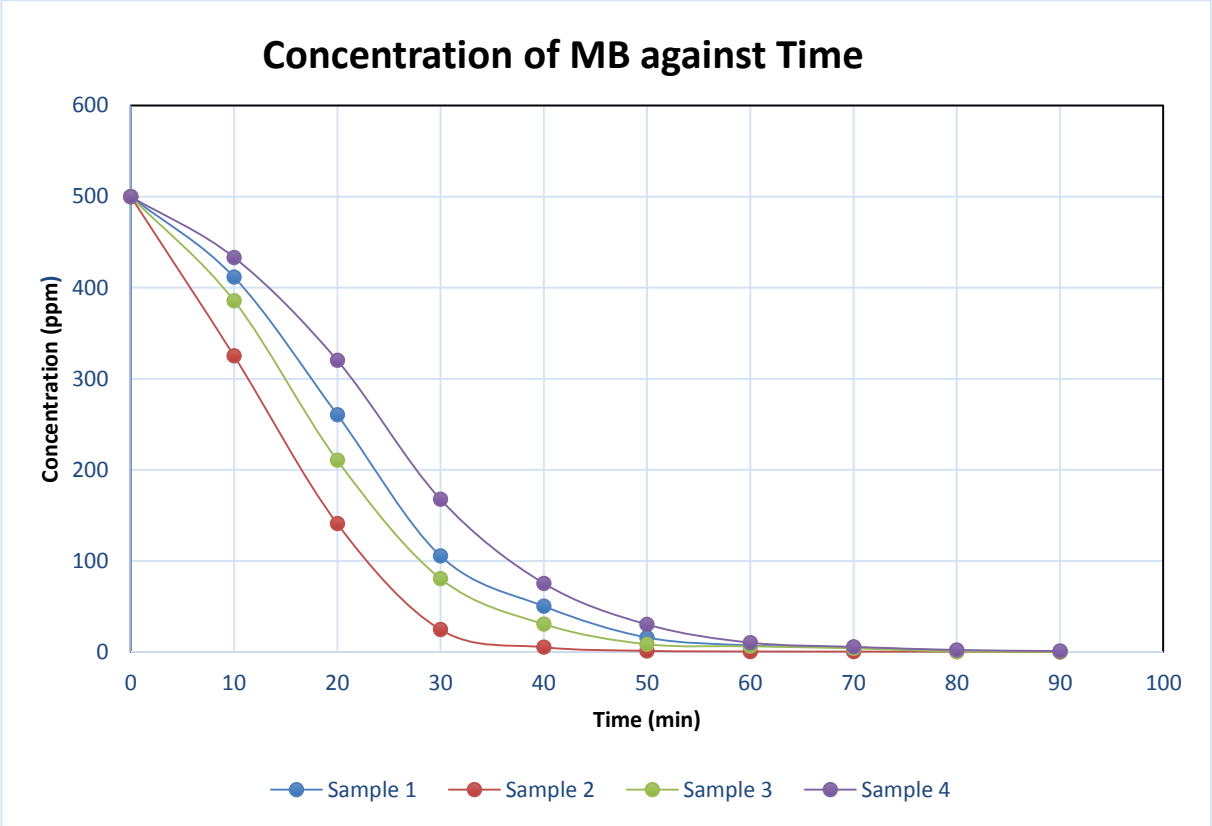

Figure 4.7: Graph of concentration of methylene blue solution against time

From Figure 4.7, all the test produce positive results in a way that the dyes were removed after a period of time. Sample 1 is the untreated activated carbon, thus is it a baseline for the other three samples. From the graph, Sample 2 reached equilibrium at the fastest time at approximately 40 minutes mark. Next is Sample 3 which reached equilibrium at 60 minutes mark which is significantly faster than the baseline. Lastly, Sample 4 reach equilibrium at approximately 80 minutes mark to remove the dye.

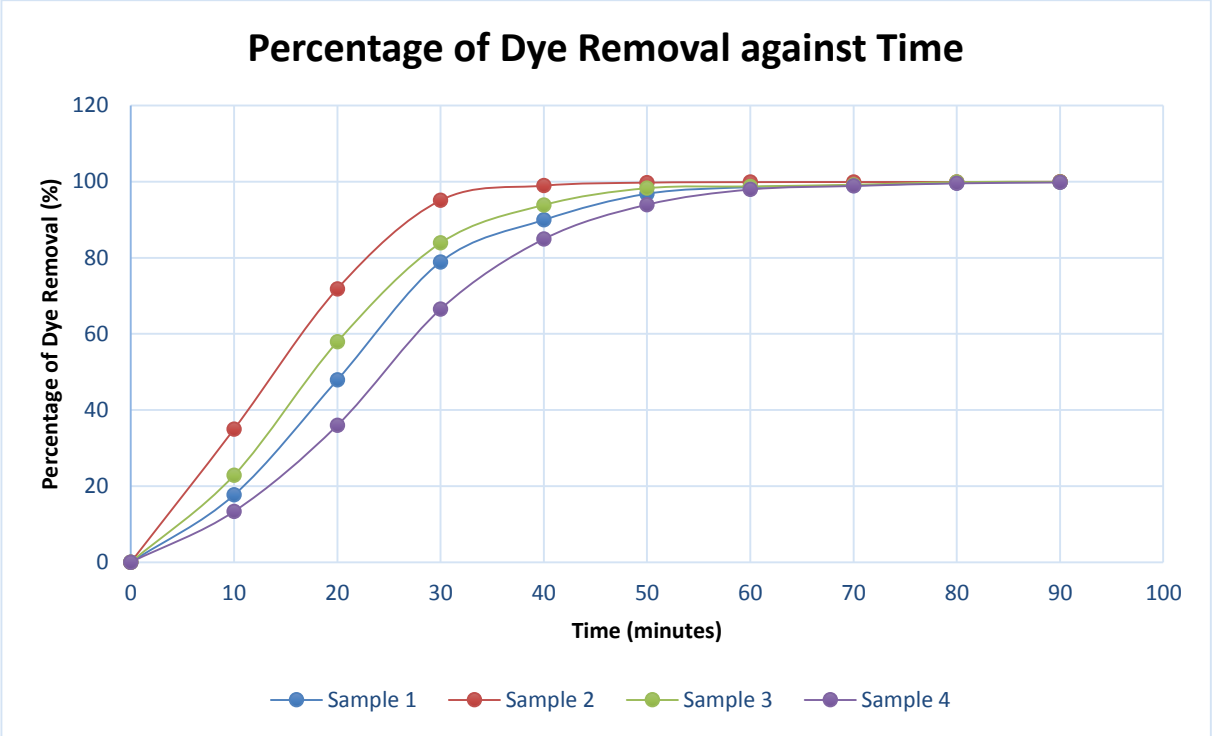

Figure 4.8: Graph of percentage of dye removal against time

Based on the Figure 4.8, the entire batch of activated carbon managed to remove dye from the dye solution at a percentage of removal between 98% - 99%. The significant observation that can be made is the time for the dye to reduce to the minimum level is difference from each sample tested. Sample 2 has the fastest time to remove dye up until 98% at around 30 to 40 minutes mark. Next is followed Sample 3, which the percentage of dye removal reach 98% at 40 to 50 minutes mark, followed by the control, Sample 1, which reach 98% percent removal of dye at around 50-60 minutes. Lastly, sample 4 which reach 98% percent removal of dye at approximately 70 minutes mark.

From Figure 4.7 and Figure 4.8, it can be concluded that Sample 2 (frequency = 100 rpm) has the best adsorption rate and the best performing adsorbent. Sample 2 has the fastest time to adsorp dye and fastest time to remove dye up until 99%.

4.5 Discussions

4.5.1 FTIR Analysis

Since there is no indication of new functional groups in all samples, thus, the amount of functional group attached is to be analysed in order to determine if there is any increase or decrease in the quantity of the functional group. The amount or concentration of functional group can be estimated according to Beer's Law, where the percent transmittance can be determined by the following equation.

$$Percent\ Transmittance, \%T = 100 \times \frac{I}{I_0}$$

Where I_0 is the incident radiation I is the transmitted radiation. To relate the transmittance percentage with the absorbance. Absorbance can be determine with the following relation.

$$Absorbance, A = -log\left(\frac{\%T}{100}\right)$$

To relate the absorbance with the concentration, the relation can be made with Beer-Lambert Law as followed.

$$A = \varepsilon bc$$

Where, ε is the molar absorptivity, b is the path length of the sample an c is the concentration of the compound, in this case the concentration of the functional group. For this study, ε and b is kept constant. Thus, as the absorbance increase, the concentration of functional group increase.

From the Table 4.3 to Table 4.6, as the percent transmittance increase, the absorbance value increase. According to Beer-Lambert Law, as the absorbance increase the concentration increase. Hence, Sample 2 have the highest value of absorbance, thus indicating Sample 2 (frequency = 100 rpm) have the highest amount of functional group attached compared to other samples. An increase amount of functional group attached would increase the dye adsorption capabilities. The addition of functional group can attract more dye molecules to be attached to the activated carbon, thus increasing the adsorption efficiency.

By varying increasing the frequency value of water bath shaker by 100 rpm, more functional group from the distilled water is attached to the activated carbon.

However as the frequency increase, the amount attached started to decrease. This can be seen in Figure 4.5, where Sample 3 (frequency = 150 rpm) has higher transmittance value and Sample 4 (frequency = 200rpm) has the highest percent transmittance value. The high value of percent transmittance indicating low amount of the concentration of functional group attached.

4.5.2 Dye Adsorption Test

Based on Figure 4.7, Sample 2 (frequency = 100 rpm) has the fastest time to reach concentration below 1 ppm. This is due to the increase of the functional group attached to the activated carbon attract more dye molecule to attach to the surface. Functional groups that have polarity such as –OH and C-O attract the methylene blue molecules due to the ionic characteristic presence on its molecular structure as seen in Figure 4.9.

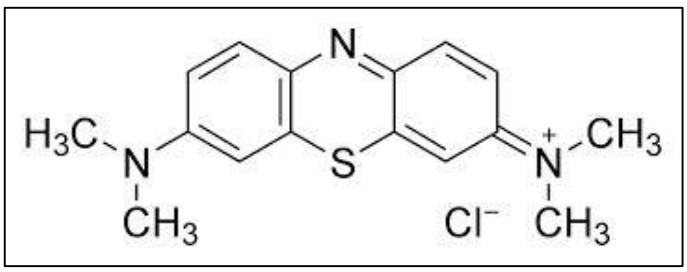

Figure 4.9: Molecular structure of methylene blue

More functional group such as –OH and C-O can attract more dye molecules to be attached, thus increasing it efficiencies. It can be concluded that Sample 2 of functional activated carbon provide the most effective adsorption of dyes as it only requires the least amount of to adsorp and remove the dye in the solution.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Introduction

The scope of study comprises of functionalizing commercial activated carbon using distilled water and to test the adsorption capabilities of the functionalized activated carbon. The purpose of the study is to examine the viability of using water as a medium to functionalize activated carbon. The objectives of the study are:

i. To prepare activated carbon with surface modification by functionalizing activate carbon using optimum conditions with distilled water.
ii. To identify the change in the amount of functional group by characterization the functionalized activated carbon.
iii. To examine the efficiency of the functionalized activated carbon by performing dye adsorption study.

5.2 Conclusion

As conclusion, water is a good medium to be used as functionalization medium. It can provide sufficient amount of functional group to be attached to the surface of the activated carbon. The functional group attached will assist in the adsorption of dye. The optimum condition of functionalization parameter is at the temperature 35 °C, 5 hours of contact time and at shaking frequency of 100 rpm. The parameters of functionalization will produce activated carbon that can remove dye at a faster rate compared to untreated activated carbon. Besides that, based on the characterization, the amount of functional group increase as the activated carbon undergone the functionalization procedure.

Water can be proposed as the substitute for other medium such as acidic and basic medium. The other medium have the potential to harm the environment due to their acidic and basic nature. However, water is environmentally friendly and in term of cost, it is the most cost effective. Thus, using water as medium for functionalization for activated carbon is highly recommended.

5.3 Future Work and Recommendations

Due to time constraint, the project have some limitations. Some recommendation for future works can be done to further improve the project. Firstly, it is suggested to use deionized water as replacement to distilled water, this is due to distilled water might still contain minerals that could alter the results obtained, whereas deionized water contain no minerals. Secondly, the use of real waste water that is contaminated with dye is highly suggested in order to test the adsorption capabilities. Thirdly, a study should be made on the potential of regeneration of the adsorbent after being used for removal of dye

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APPENDICES

APPENDIX 1: GAANT CHART

Gaant Chart for FYP I

Detail/week	1	2	3	4	5	6	7	MID SEM BREAK	8	9	10	11	12	13	14
Selection of project topic and FYP briefing															
Literature review															
Preparation of Extended proposal															
Submission of Extended Proposal															
Proposal Defence															
Preparation of Interim Report															
Project work continues															
Submission of Interim Draft Report															
Submission of Interim Report															

Gaant Chart for FYP II

Detail/week	1	2	3	4	5	6	7	MID SEM BREAK	8	9	10	11	12	13	14	15
Project Work continues and preparation of Progress Report																
Submission of Progress Report																
Project work continues																
Preparing Dissertation Report																
Pre-SEDEX																
Submission of Dissertation Report																
Submission of technical Paper																
Oral Presentation																
Submission of Dissertation report (Hard Bound)																

Project Activities	
Key Milestone	

APPENDIX 2: TABLE OF CHARACTERISTIC INFRA-RED ABSORPTIONS

Table of Characteristic IR Absorptions

frequency, cm^{-1}	*bond*	*functional group*
3640–3610 (s, sh)	O–H stretch, free hydroxyl	alcohols, phenols
3500–3200 (s,b)	O–H stretch, H–bonded	alcohols, phenols
3400–3250 (m)	N–H stretch	1°, 2° amines, amides
3300–2500 (m)	O–H stretch	carboxylic acids
3330–3270 (n, s)	–C≡C–H: C–H stretch	alkynes (terminal)
3100–3000 (s)	C–H stretch	aromatics
3100–3000 (m)	=C–H stretch	alkenes
3000–2850 (m)	C–H stretch	alkanes
2830–2695 (m)	H–C=O: C–H stretch	aldehydes
2260–2210 (v)	C≡N stretch	nitriles
2260–2100 (w)	–C≡C– stretch	alkynes
1760–1665 (s)	C=O stretch	carbonyls (general)
1760–1690 (s)	C=O stretch	carboxylic acids
1750–1735 (s)	C=O stretch	esters, saturated aliphatic
1740–1720 (s)	C=O stretch	aldehydes, saturated aliphatic
1730–1715 (s)	C=O stretch	α, β–unsaturated esters
1715 (s)	C=O stretch	ketones, saturated aliphatic
1710–1665 (s)	C=O stretch	α, β–unsaturated aldehydes, ketones
1680–1640 (m)	–C=C– stretch	alkenes
1650–1580 (m)	N–H bend	1° amines
1600–1585 (m)	C–C stretch (in–ring)	aromatics
1550–1475 (s)	N–O asymmetric stretch	nitro compounds
1500–1400 (m)	C–C stretch (in–ring)	aromatics
1470–1450 (m)	C–H bend	alkanes
1370–1350 (m)	C–H rock	alkanes
1360–1290 (m)	N–O symmetric stretch	nitro compounds
1335–1250 (s)	C–N stretch	aromatic amines
1320–1000 (s)	C–O stretch	alcohols, carboxylic acids, esters, ethers
1300–1150 (m)	C–H wag (–CH_2X)	alkyl halides
1250–1020 (m)	C–N stretch	aliphatic amines
1000–650 (s)	=C–H bend	alkenes
950–910 (m)	O–H bend	carboxylic acids
910–665 (s, b)	N–H wag	1°, 2° amines
900–675 (s)	C–H "oop"	aromatics
850–550 (m)	C–Cl stretch	alkyl halides
725–720 (m)	C–H rock	alkanes
700–610 (b, s)	–C≡C–H: C–H bend	alkynes
690–515 (m)	C–Br stretch	alkyl halides

m=medium, w=weak, s=strong, n=narrow, b=broad, sh=sharp