Adsorption of Methylene Blue Dye using Functionalized Granular Activated Carbon

by

Alvin Chan Kai Yi

14761

Dissertation submitted in partial fulfilment of

the requirements for the

Final Year Project II

Bachelor of Engineering (Hons)

(Chemical)

JANUARY 2015

Universiti Teknologi PETRONAS

Bandar Seri Iskandar,

31750 Tronoh,

Perak Darul Ridzuan.

CERTIFICATION OF APPROVAL

Adsorption of Methylene Blue Dye using Functionalized Granular Activated Carbon

by

Alvin Chan Kai Yi

14761

A project dissertation submitted to the

Chemical Engineering Programme

Universiti Teknologi PETRONAS

in partial fulfillment of the requirement for the

BACHELOR OF ENGINEERING (Hons)

(CHEMICAL)

Approved by,

____

(AP DR SURIATI BT SUFIAN)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

January 2015

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 acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

____

ALVIN CHAN KAI YI

ABSTRACT

Urbanization and rapid industrial development in recent years have created a major threat to the environment especially water pollution. Pollution from wastewater not only depreciates land values; it also increases municipal costs for wastewater treatment and causes harm to biological and human health. Industries such as ceramic, printing, plastic and paper use dyes in their coloring process and these dyes are usually disposed to streams, ponds, lakes and river which then cause water pollution. Not only that the dyes can be very toxic even at low concentration, they are also generally non-biodegradable and difficult to be removed using conventional biological treatment. Many researches have been done on ways to treat wastewater effectively namely membrane separation, aerobic and anaerobic degradation using various microorganisms, chemical oxidation, coagulation and flocculation, adsorption using various kinds of adsorbents and reverse osmosis. However, most of the current wastewater treatment techniques are selective and expensive. Adsorption process has been identified as the most feasible wastewater treatment technique as it is cheap economically, simplicity in design and has the ability to adsorb a wide range of both organic and inorganic pollutants. With that, this project aims to study methylene blue dye removal using functionalized granular activated carbon.

ACKNOWLEDGEMENTS

Throughout this project, I have received a lot of assistance from various parties. Without their input and assistance, this Final Year Project (FYP) would not be successfully completed.

Firstly, I would like to express my deepest gratitude to my very supportive supervisor, AP Dr. Suriati bt. Sufian for all her assistance, guidance and advice. Throughout the entire period of this project, she had provided me with many insights of separation process and wastewater treatment. Her vast knowledge in the field of separation process had helped me to gain valuable knowledge on adsorption and dye removal. I really appreciate the effort that AP Dr. Suriati has put in my project.

I would like to express my gratitude towards my family members and friends for giving me support and words of encouragement during the period of undertaking Final Year Project. Not to forget, all the laboratory technicians that have been kind and helpful towards me.

Last but not least, I would like to thanks all individuals involved in my FYP. All your assistance and support are very much appreciated.

TABLE OF CONTENTS

Contents

LIST OF FIGURE

LIST OF TABLE

CHAPTER 1: INTRODUCTION

1.1 Background of Study

Urbanization and rapid industrial development in recent years have created a major threat to the environment especially water pollution. This is due to the fact that people tend to throw garbage literally everywhere while industrial effluents are discharged into rivers, ponds and streams without an effective treatment system. According to a paper by Nwabanne and Igbokwe (2012), pollution from wastewater depreciates land values, increases municipal costs and causes numerous adverse biological and human health effects.

A few examples of industries which use dyes in their products are textile, ceramic, paper, printing and plastic industry. As a part of the coloring process, these industries consume substantial volumes of water which consequently leads to large amount of colored wastewater to be generated (Chandra et al., 2007). Not only that the dyes can be very toxic even at low concentration, they are also generally non-biodegradable and difficult to be removed using conventional biological treatment process such as activated sludge process (Toor & Jin, 2012).

According to Chandra et al. (2007), some of the methods for dye removal from wastewater are membrane separation, aerobic and anaerobic degradation using various microorganisms, chemical oxidation, coagulation and flocculation, adsorption using various kinds of adsorbents and reverse osmosis. Chandra et al. (2007) says that adsorption is a very good removal technique which produces effluents with very low levels of dissolved organic compounds. In addition, the paper by Nwabanne and Igbokwe (2012) also shows that adsorption is superior compared to all other techniques due to its capability for adsorbing a wide range of adsorbates and simplicity in design.

With that, dye removal using adsorption with functionalized activated carbon has become the primary focus in this project. Utilizing and applying knowledge on adsorption will definitely bring positive impact to the wastewater treatment system and reduce water pollution.

1.2 Problem Statement

Environmental pollution control is a highly concerned issue in many countries with wastewater being one the major contributor to environmental pollution. Wastewater is actually the spent water used by the increasing population and industrialization for various purposes such as houses, commercial establishments, industries and many others. Wastewater has to be treated before being discharged into streams of river as pollutants such as dyes are harmful to the aquatic life. According to Mohd Salleh et al. (2011), dyes can also cause severe damage to human beings such as dysfunction to kidney, reproduction system, liver, brain and central nervous system.

The use of conventional physical-chemical and biological methods for removing dyes is difficult and not really efficient. One of the effective techniques for dye removal from wastewater 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. Rivera-Utrilla et al. (2011) 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.

For project and experimental purposes, the adsorbent and adsorbate has to be chosen based on certain parameters such as pore structure of adsorbent, porosity of adsorbent, size of adsorbent, costs, regeneration capability of adsorbent and many others. Commercialized granular activated carbon has been chosen as adsorbent while the adsorbate selected was methylene blue solution for the ease of experiment running.

1.3 Research Objective

There are several objectives identified in this project

1. To prepare activated carbon with surface modification by functionalizing activated carbon using optimum conditions with distilled water
2. To study the effects of contact time, granular activated carbon dosage, and effect of temperature in adsorption between functionalized activated carbon and dye.

1.4 Scope of Study

The scope of study comprise of few elements:

- Understanding on the principle of adsorption and its applications in the wide range of industries.
- Understanding and identifying critical parameters (i.e. concentration, dosage, temperature) that needs to be manipulated or constant for experiment purposes.
- Analyze the kinetics and isotherms of adsorption.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

A literature review is a critical and in depth evaluation of previous research done by others. It can also be defined as the summary and synopsis of a particular area of research. For this project, literature review covers the adsorption process, adsorption system, factors affecting adsorption, adsorbent, activated carbon, methylene blue and isotherms.

2.2 Adsorption

Generally, adsorption is the separation of components in particular fluid mixtures by the transfer of one or more components (the adsorbate), to the internal surface of a porous solid (the adsorbent) where they are held by intermolecular forces. When a solution containing absorbable solute comes into contact with a solid with a highly porous surface structure, liquid–solid intermolecular forces of attraction cause some of the solute molecules from the solution to be concentrated or deposited at the solid surface. This surface accumulation of adsorbate on adsorbent is called adsorption. This creation of an adsorbed phase having a composition different from that of the bulk fluid phase forms the basis of separation by adsorption technology (Nageeb, 2013).

Adsorption is operative in most natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins and water purification (Nageeb, 2013).

Similar to surface tension, adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements such as ionic, covalent or even metallic of the constituent atoms of the material are filled. But atoms on the clean surface experience a bond deficiency, because they are not wholly surrounded by other atoms. Thus it is energetically favourable for them to bond with whatever happens to be available (Nageeb, 2013).

The driving force for adsorption is the reduction in surface tension between the fluid and the solid adsorbent as a result of the adsorption of the adsorbate on the surface of the solid. The surface or interfacial tension, σ is the change in free energy, G, resulting when the area between two phases, A, is increased. The definition of σ is given by the following equation:

$$\sigma = \left(\frac{\partial G}{\partial A}\right)_{T,P,n_j}$$

The exact nature of the bonding depends on the details of the species involved, but the adsorbed material is generally classified as exhibiting physisorption or chemisorption.

2.2.1 Physisorption

Physisorption or physical adsorption is a type of adsorption in which the adsorbate adheres to the surface only through Van der Waals (weak intermolecular) interactions, which are also responsible for the non-ideal behaviour of real gases.

2.2.2 Chemisorption

Chemisorption is a type of adsorption whereby a molecule adheres to a surface through the formation of a chemical bond, as opposed to the Van der Waals forces which cause physisorption.

Table 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 it
Effect of pressure	• Increase 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

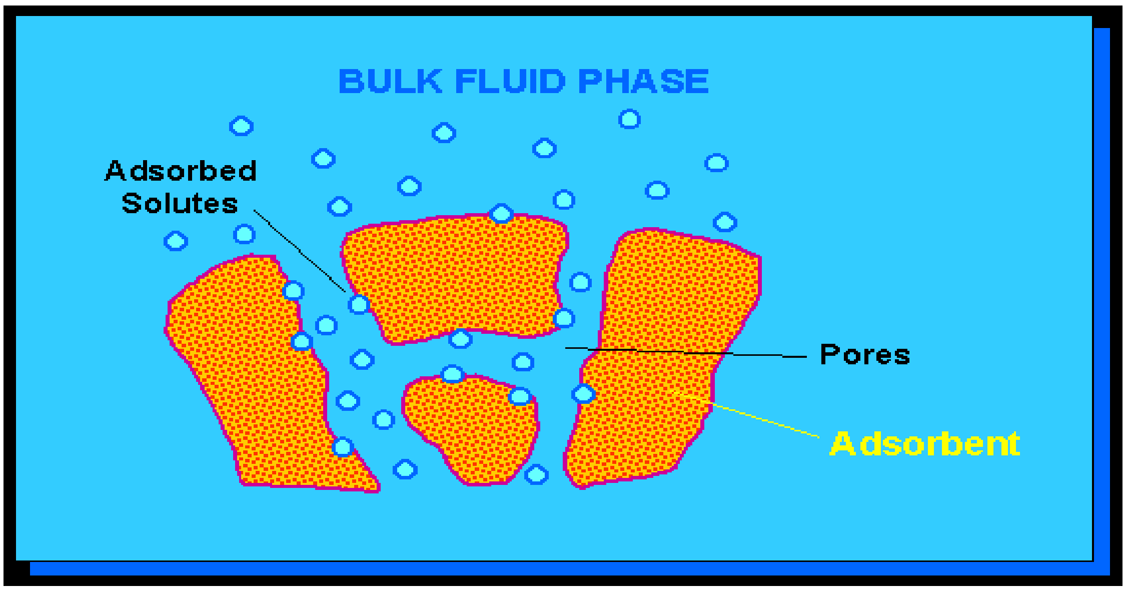

Figure 1: Differentiating Adsorbate and Adsorbent

2.3 Adsorption System

The configuration of the adsorption system can be divided into three main categories (Ridzuan, 2006):

a) Batch

According to Ridzuan (2006), batch process is the simplest possible mode of operation but have low efficiency. Batch adsorption is said to be suitable and often used when the quantities treated are small in amount. Ridzuan (2006) states that once equilibrium has been achieved, the adsorbent and solution are then separated, usually by filtration, decantation or centrifugation.

b) Fixed bed

The fixed bed operation is where adsorbent is held in a fixed position in a vessel or column. In fixed bed, adsorbate is continuously in contact with a given quantity of fresh adsorbent thus providing the required concentration gradient between adsorbent and adsorbate for adsorption (Ridzuan, 2006).

c) Moving bed

According to Ridzuan (2006), solid-liquid adsorption can be carried out in pulsed bed or moving bed in which some carbon is removed from the bottom of the column at a constant time

2.4 Factors Affecting Adsorption

There are a lot of factors that affects the adsorption process. Some of the factors are as follow:

2.4.1 Surface Area of Adsorbent

Adsorption is a surface phenomenon in a way that it is proportional to specific surface area. In addition, specific surface area can be defined as the portion of the total surface area that is available for adsorption. Larger sizes imply a greater adsorption capacity (Delle, 2000).

2.4.2 Particle Size of Adsorbent

Smaller particle sizes reduce internal diffusional and mass transfer limitation to the penetration of the adsorbate inside the adsorbent. For instance, equilibrium is more easily achieved and nearly full adsorption capability can be attained (Delle, 2000).

2.4.3 Contact time or Residence Time

The longer the contact time between adsorbate and adsorbent, the more complete the adsorption will be. This is because longer contact time allows adsorption process to take place (Delle, 2000)

2.4.4 Solubillity of Solute in Liquid

According to Delle (2000), substances that are slightly soluble in water will be more easily removed from water than those substances with high solubility. Besides that, non-polar substances will be more easily removed than polar substances due to greater affinity for water.

2.4.5 Affinity of the Solute for the Adsorbent

The surface of activated carbon is only slightly polar. Hence non-polar substances will be more easily picked up by the carbon compared to polar ones (Delle, 2000)

2.4.6 Number of Carbon Atoms

Delle (2000) states that for substances in the same homologous series, a larger number of carbon atoms is generally associated with a lower polarity and hence a greater potential for being adsorbed. For example, the degree of adsorption increases in the sequence of formic-acetic-propionic-butyric acid.

2.4.7 Size of the Molecule With Respect to Size of the Pores

Large molecules may be too large to enter small pores. This may reduce adsorption independently of other causes (Delle, 2000).

2.4.8 Degree of Ionization of the Adsorbate Molecule

More highly ionized molecules are adsorbed to a smaller degree than neutral molecules (Delle, 2000).

2.4.9 pH

The pH of a solution from which adsorption occurs may influence the extent of adsorption. Hydrogen and hydroxide ions are adsorbed quite strongly, therefore adsorption of other ions are influenced by the pH of the solution. The degree of ionization of a species is affected by the pH (Delle, 2000).

2.4.10 Temperature

In most cases, adsorption 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. With that, slight or small variations in the temperature tend not to alter the adsorption process to a significant extent (Delle, 2000).

2.5 Adsorbent

Different kinds of adsorbents can be categorized into two which are natural adsorbents and synthetic adsorbents (Nageeb, 2013). Each adsorbent has its own characteristics such as pore structure, porosity, surface area and nature of its adsorbing surfaces. In most cases, natural adsorbents are considerably cheap, abundant in supply and have high potential for surface modification which improves adsorption capabilities. Some examples of natural adsorbents are charcoal, clays, clay minerals, zeolites, and ores. On the other hand, man-made or synthetic adsorbents are usually prepared from agriculture products and waste, household wastes, sewage sludge and industrial waste (Nageeb, 2013). Some examples of waste materials are fruit wastes, scrap tires, sawdust, rice husk, petroleum wastes, clays, algae and many other examples.

The most common industrial adsorbents are activated carbon, silica gel and alumina because they have very large surface area per unit weight which is important for good adsorption. According to Nageeb (2013), activated carbon is produced by roasting organic material usually from coconut shell, wood, and bone to decompose it to granules of carbon. Silica gel is a matrix of hydrated silicon dioxide while alumina is mined or precipitated aluminum oxide and hydroxide. Although activated carbon is a magnificent material for adsorption, its natural black color persists and adds a grey tinge if even trace amounts are left after treatment. Despite that, filter materials with fine pores can remove carbon quite well.

2.6 Activated Carbon

Activated carbon can exist in two forms namely in granular and powdered forms (Nageeb, 2013). Both granular activated carbon and powdered activated carbon are common adsorbents used for the removal of any undesirable odor, color, taste and other organic and inorganic impurities usually from both domestic and industrial wastewater.

Activated carbon has been proven to be an effective adsorbent for the removal of a wide range of organic and inorganic pollutants from both aqueous and gaseous states due to its exceptionally high surface area, well-developed internal microporosity, and wide spectrum of surface functional groups (Rivera-Utrilla et al., 2011). A paper by

Nageeb (2013) states that the major constituent of a particular activated carbon is the carbon actually accounts up to 95% of the mass weight and also contains other hetero atoms such as hydrogen, nitrogen, sulfur and even oxygen.

Table 2: Properties of typical activated carbon

Bulk Density	0.35-0.54 g/cm^3
Heat capacity	1.13-1.51 kJ-kg°C
Pore volume	0.56-1.20 cm^3/g
Surface area	600-1600 m^2/g
Average pore diameter	15-25 A
Regeneration temperature	100-140°C
Maximum allowable temperature	1500 °C

Figure 2: Picture showing Granular Activated Carbon

2.7 Methylene Blue

Methylene blue is a cationic dye which is very popular for dyeing process in many industries (Mohd Salleh et al., 2011). Mohd Salleh et al., (2001) continues to add that acute exposure to methylene blue dye may cause harmful effects such as shock, vomiting, increased heart rate, Heinz body formation, cyanosis and many others. Being a common dye used by industries with harmful effects to people and environment, it is vital to remove such dye from effluents.

Figure 3: Picture showing Methylene Blue Dye

2.8 Isotherms

Adsorption is usually described through isotherms which are the amount of adsorbate on the adsorbent as a function of its pressure for gas or concentration for liquid at constant temperature. The quantity adsorbed is nearly as always normalized by the mass of the adsorbent to allow comparison of different materials. There are basically two established types of adsorption isotherm namely the Langmuir adsorption isotherm and Freundlich adsorption isotherm.

2.8.1 Langmuir Isotherm

Langmuir adsorption isotherm is based on the assumption that the molecules of the adsorbate form a monolayer on the surface of the adsorbent (Toor & Jin, 2012). Adjacent adsorbed molecules are independent and do not interact with each other. The Langmuir isotherm model assumes that the adsorption occur at homogeneous sites at adsorbent surface, and saturation happen when the dye molecule fill the site where no more adsorption can occur at that site (Mohd Salleh et al., 2011). Langmuir isotherm is widely used to describe the adsorption reaction and can be represented as equation below:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m}$$

where q_e is the amount of dye per unit mass of adsorbent at equilibrium (mg g^{-1}), qm is the maximum amount of dye adsorbed per unit mass of adsorbent for the formation of complete monolayer on the surface of adsorbent (mg g^{-1}), K_L is Langmuir constant related to energy of adsorption (L mg^{-1}). Langmuir constant can be estimated from the linear plot of C_e/q_e versus C_e.

2.8.2 Freundlich Isotherm

Unlike Langmuir isotherm which only takes into account of homogeneous adsorption, Freundlich isotherm is applicable for heterogeneous adsorption reactions and involves formation of multilayers (Toor & Jin, 2012). Freundlich isotherm can be represented as equation below:

$$q_e = k_f C_e^{\frac{1}{n}}$$

where k_f and n are the Freundlich constant. K is a measure of amount of adsorption and n indicate the degree of non-linearity. The value of k and n can be obtained from the slope and intercept of a linear plot of log q_e versus log C_e.

2.9 Functionalization of Activated Carbon

Functionalization or surface modification of an adsorbent, functions in a way that it can add functional groups onto the surface of adsorbent through chemical method. The additional functional group helps to increase the adsorption efficiency by attracting 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.

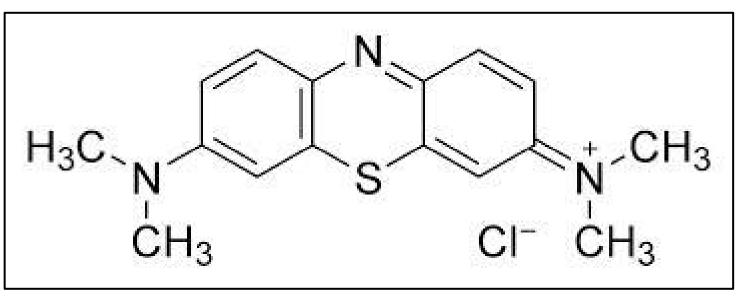

Figure 4: Molecular structure of methylene blue

There are a lot of functionalization methods for activated carbon. Some examples of surface modifications are oxidation, acid treatment, thermal treatment and plasma treatment (Rivera-Utrilla et al., 2011). 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.

CHAPTER 3: METHODOLOGY/PROJECT WORK

3.1 Introduction

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

3.1.1 Research Flowchart

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

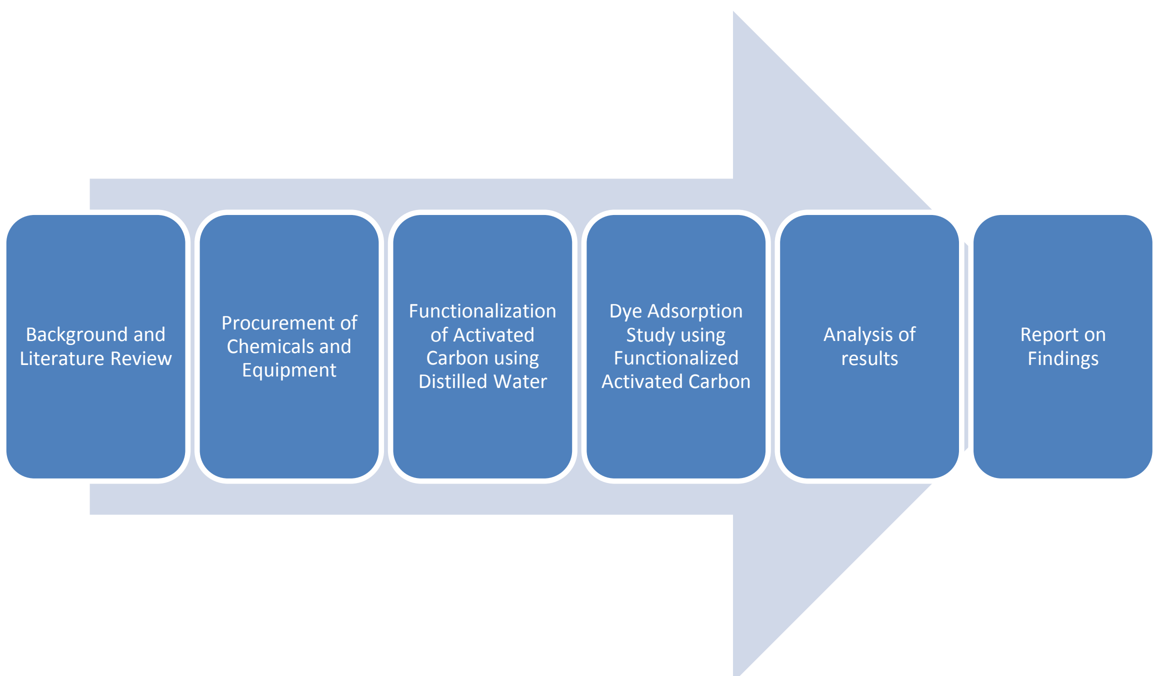

Figure 5: Research Flowchart

3.1.2 Project Activities

The project activities include the planning of the project and the execution of experiment. The details of the plan and project milestones 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 3.1, Table 3.2 and Table 3.3 below.

Table 3: List of Chemicals

No	Chemicals	Purity	Amount
1	Commercialized Granular Activated Carbon	99%	500g
2	Methylene Blue	99%	500mL
3	Distilled Water	99%	3L

Table 4: List of Apparatus

No	Apparatus	Amount
1	Magnetic Stirrer	5
2	Orbital Shaker	1
3	Glass rod	3
4	Beaker	5
5	Petri Dish	5
6	Erlenmeyer Flask	5
7	Vials	10
8	Aluminium foil	1
9	Spatula	1
10	Volumetric flask	5

Table 5: List of Equipment

No	Equipment	Amount
1	Fourier Transform Infrared Spectrometer	1
2	Ultraviolet-Visible Spectrometer	1
3	Ultrasonificator Water Bath Shaker	1
4	Drying Oven	1

3.2.1 Adsorbent (Activated Carbon)

Activated carbon is used in this study is commercialized activated carbon. The activated carbon will undergo surface modification (functionalization) to form functional group on the surface of the carbon. This 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 Procedure

Two experiment procedures were produced in order to conduct the experiment. The procedures were for the functionalization of activated carbon using distilled water and dye adsorption study. Dye adsorption study further consists of three experiments to test on the effect of granular activated carbon dosage, effect of temperature and effect of contact time between adsorbent and adsorbate.

3.3.1 Functionalization of Granular Activated Carbon Using Distilled Water

I. Approximately 10 gram of activated carbon is used for functionalization.

II. For experiment purpose, an amount of commercialized activated carbon is taken as sample as a control for this experiment.

III. For samples that will be functionalized, 10 gram of activated carbon is placed insides 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.

VI. The activated carbon is then extracted using filtration method.

VII. The wet or moist activated carbon is then dried in oven at temperature of $80^{o}C$ until the activated carbon is completely dried.

VIII. The process can be summarized in the following flowchart in Figure 3.1.

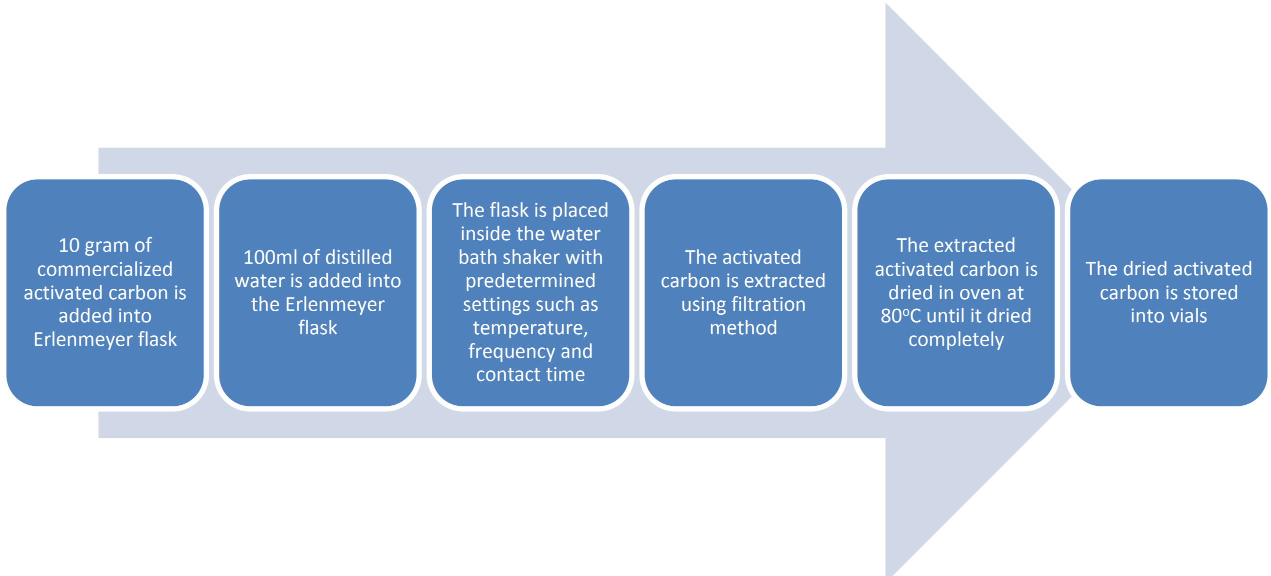

Figure 6: Functionalization of Granular Activated Carbon

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

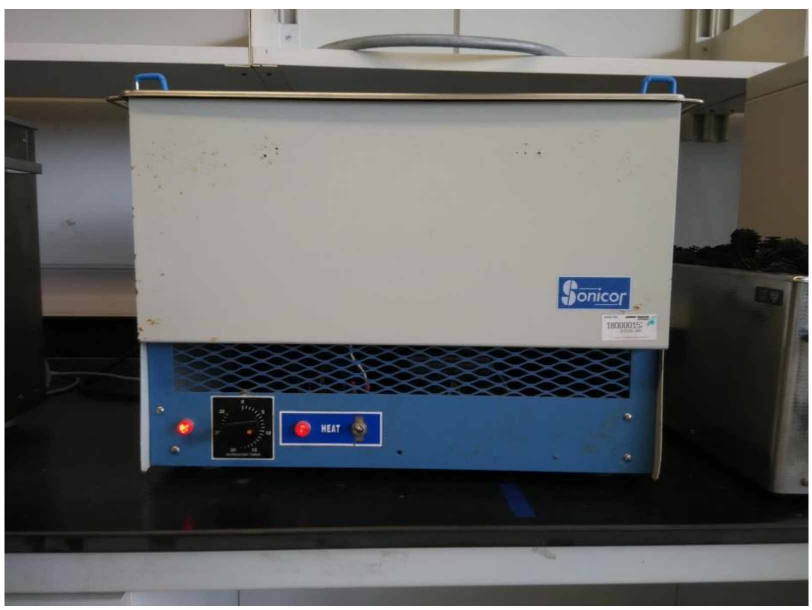

Figure 7: Ultrasonificator Water Bath Shaker

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.

Figure 8: Functionalization of Granular Activated Carbon using Ultrasonficator 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 9: Oven used for drying the filtered activated carbon

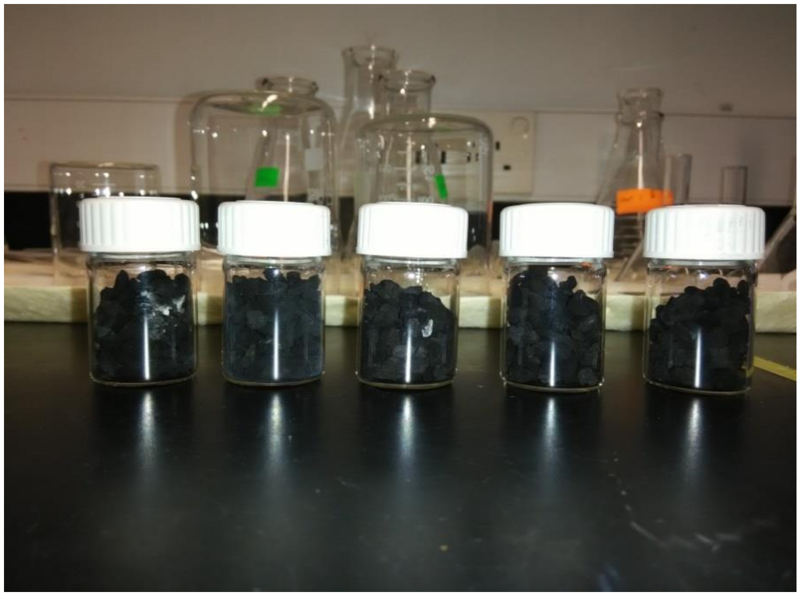

Figure 10: Functionalized Activated Carbon in vials

3.3.2 Dye Adsorption Study

Different concentrations of Methylene Blue solution were prepared specifically for calibration purposes. The solutions were prepared using dilution method where a stock solution of 1000 ppm of Methylene Blue 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.

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 6: Concentrations of Methylene Blue Solution for calibration purposes

Concentration of Methylene Blue (ppm)
500
300
200
100
50
10
0

For dye adsorption tests, three effects were tested which were effect of granular activated carbon dosage, effect of temperature, and effect of contact time. The experiment procedures can be seen as follow:

I. Effect of Granular Activated Carbon Dosage

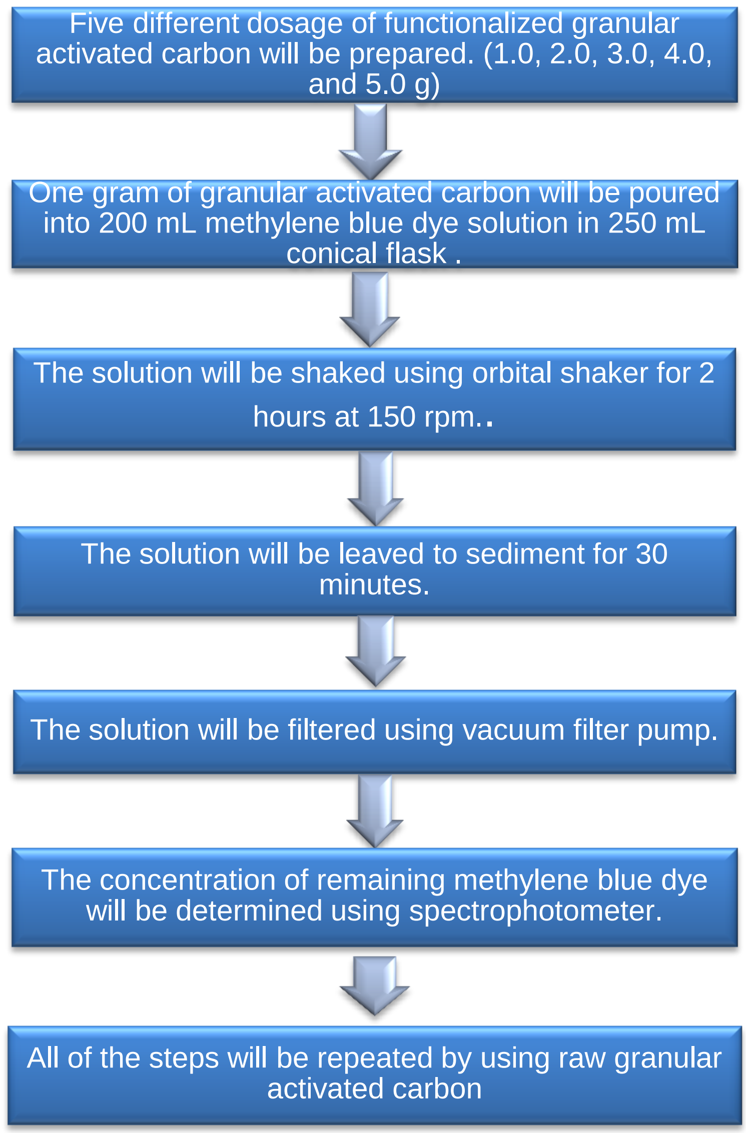

Figure 11: Procedure to study the effect of granular activated carbon dosage

II. Effect of Temperature

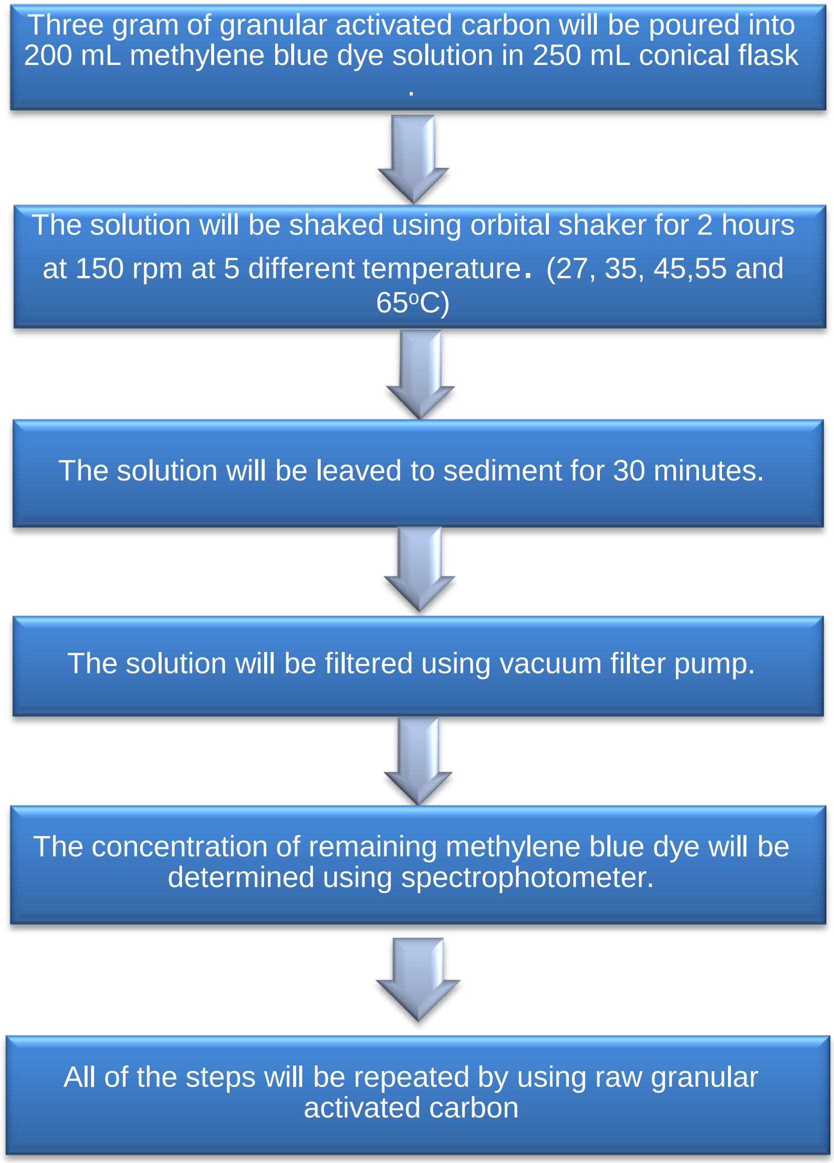

Figure 12: Procedure to study the effect of temperature

III. Effect of Contact Time

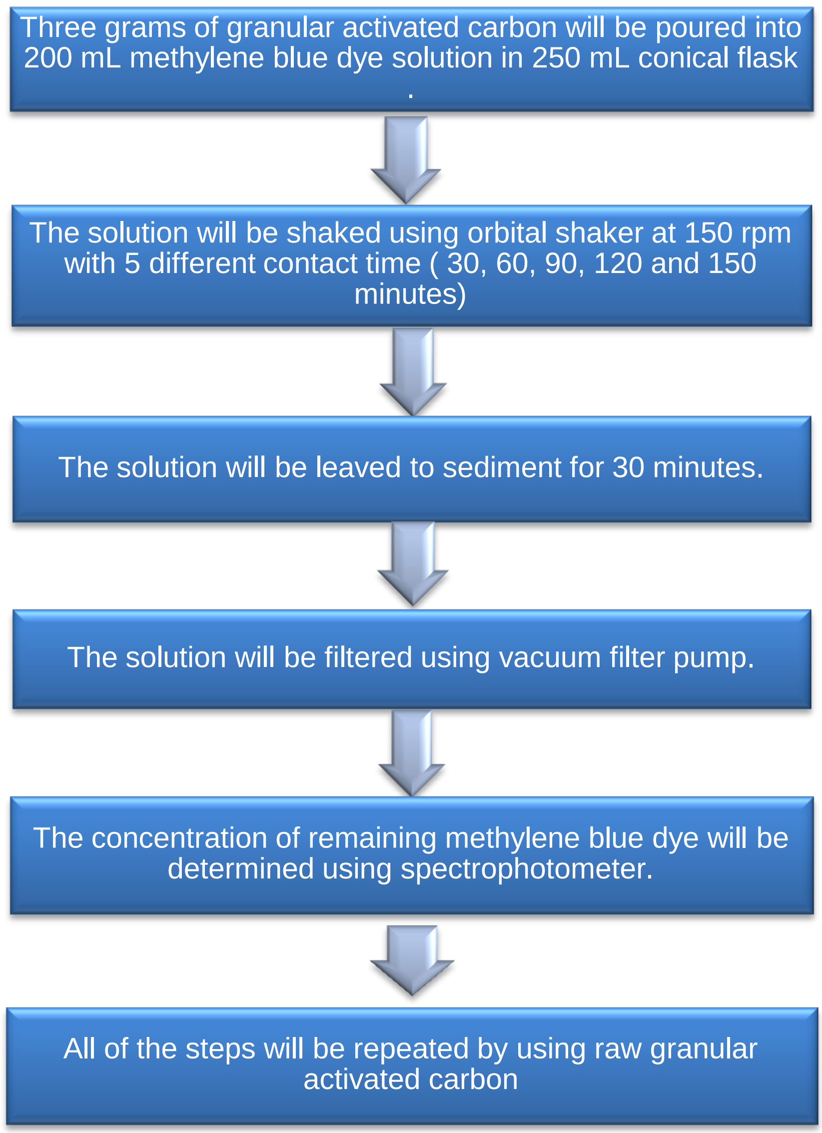

Figure 13: Procedure to study the effect of contact time

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Introduction

The project consists of two main parts which are functionalization of activated carbon and dye adsorption study. In this chapter, the preparation and process of functionalizing the activated carbon will be discussed. In addition, the results and findings in dye adsorption study were tabulated and discussed.

4.2 Formula for Calculations

The amount of adsorption at time t, q_t(mg/g), can be calculated by:

$$q_t = \frac{(C_o - C_t)V}{M}$$

The amount of adsorption at equilibrium, q_e(mg/g), can be calculated by:

$$q_e = \frac{(C_o - C_e)V}{M}$$

The percentage of dye removal can be calculated as follows:

$$\%C = \frac{(C_o - C_e)}{C_o} \text{ X } 100\%$$

Where

C_t (mg/L) is the liquid-phase concentration of dye at any time

C_o (mg/L) is the liquid-phase concentration of dye at initial

C_e (mg/L) is the liquid-phase concentration of dye at equilibrium

V (L) is the volume of solution

M (g) is the mass of dry adsorbent used.

4.3 Functionalization of Activated Carbon

The process of functionalizing the activated carbon helps to modify the surface structure of the activated carbon. This is because functionalization increases the number of functional groups attached to the surface of the activated carbon, which increases the adsorptivity or adsorption capabilities of the activated carbon. The functionalized activated carbon is then labelled and kept in vials.

4.4 Dye Adsorption Study

Dye adsorption study consists of two parts which are the preparation of standard calibration curve and dye adsorption test by conducting experiments. In order to prepare standard calibration curve prior dye adsorption test, different concentration of methylene blue solution were prepared and analyzed using UV-Vis Spectrophotometer. The performance of functionalized activated carbon was analyzed by manipulating temperature, contact time between adsorbent and adsorbate and granular activated carbon dosage for dye adsorption test.

4.4.1 Methylene Blue Solution Preparation for Standard Calibration Curve

The function of calibration curve is to act as the standard for concentration of dye analysis in dye adsorption test. The calibration plot for methylene blue at the wavelength of 396nm was obtained as shown in Table 4.1. Based on Table 4.1, the value of absorbance increases as the concentration of methylene blue increased.

Table 7: Concentration of Methylene Blue Solution and its Absorbance

Concentration (ppm)	Absorbance (A)
0	0
10	0.1332
50	0.1914
100	0.3574
200	0.4765
300	0.79
500	1.5315

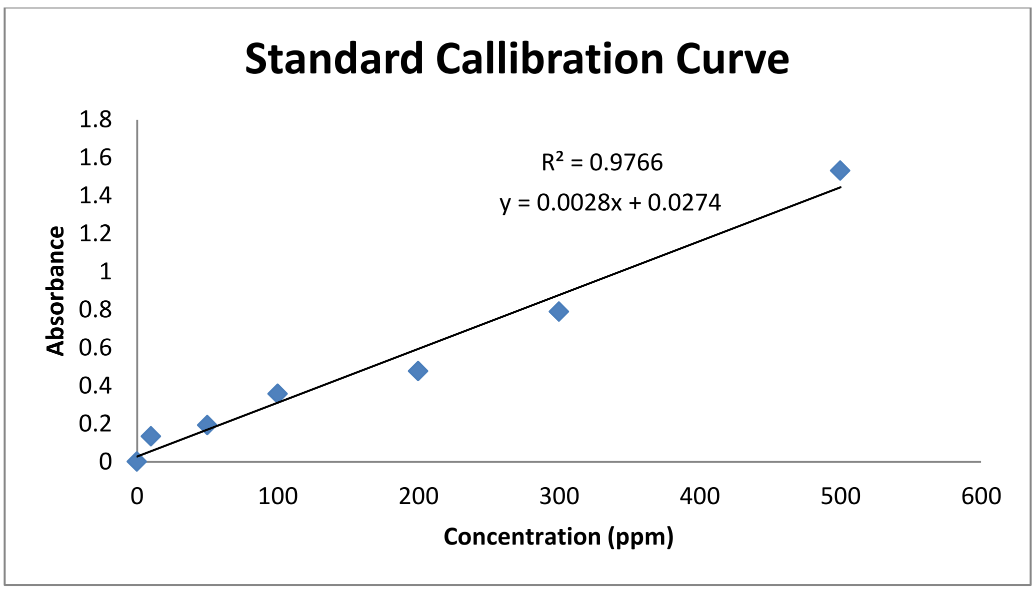

Figure 14: Standard Calibration Curve for Methylene Blue Solution

The data obtained in Table 4.1 were fitted by a straight line of best fit with high determination coefficient of $R^2 = 0.9766$. The high value of the determination coefficient calibration line indicates that the data obtained is feasible, dependable and can be used to study the concentration of dye in dye adsorption test.

4.4.2 Effect of Contact Time

The results obtained for effect of contact time study can be seen in the following table and figures:

Table 8: Effect of Contact Time

Time (min)	Absorbance (A)	Concentration (ppm)	%Removal
0	1.427	500.000	0.00
30	0.989	343.429	31.31
60	0.676	231.725	53.66
90	0.234	73.786	85.24
120	0.110	29.429	94.11
150	0.087	21.286	95.74

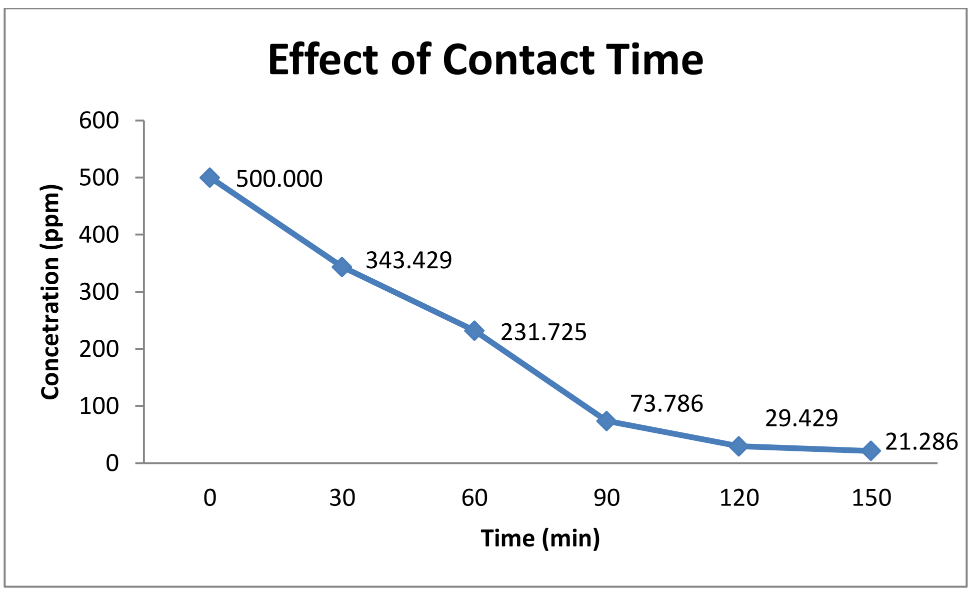

Figure 15: Graph of Concentration (ppm) against Time (min) for Effect of Contact Time

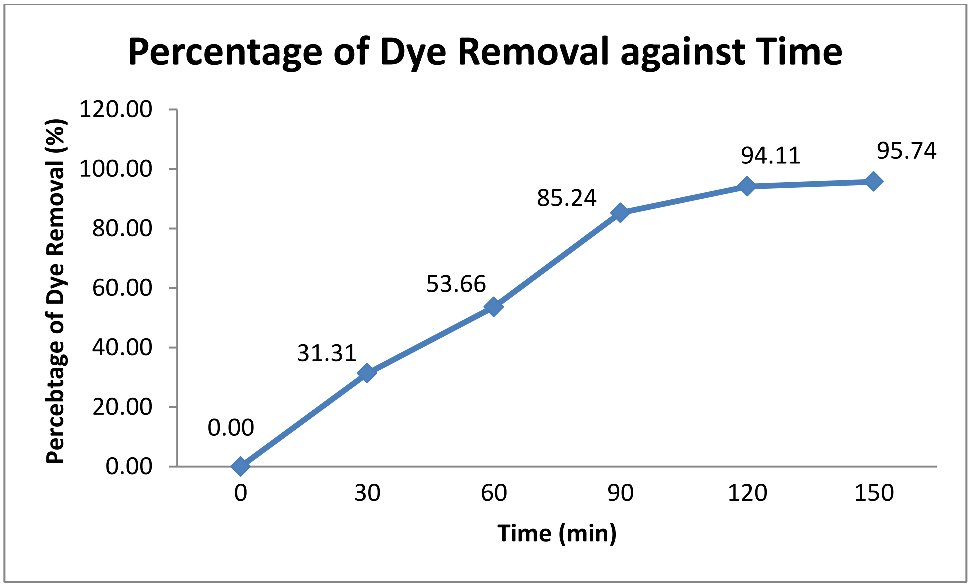

Figure 16: Graph showing Percentage of Dye Removal against Time for Effect of Contact Time

Based on Table 4.2 and Figure 4.2, it can be seen that as time increases, concentration of methylene blue dye decreases. This shows that the adsorption of methylene blue dye by functionalized granular activated carbon took place. From Figure 4.3, it can be observed that as time increases, the amount of dye removed decreases indicating that the adsorption is reaching its equilibrium which is around 120 minutes.

4.4.3 Effect of Temperature

The results obtained for the effect of temperature in dye adsorption study can be seen in the following tables and figures:

Table 9: Effect of temperature at 27°C

Temperature, °C	Time (min)	Absorbance (A)	Concentration (ppm)	Percentage removal (%)
27°C	10	1.259	439.86	12.03
	20	1.109	386.29	22.74
	30	0.979	339.86	32.03
	40	0.828	285.93	42.81
	50	0.734	252.36	49.53
	60	0.683	234.14	53.17
	70	0.539	182.71	63.46
	80	0.378	125.21	74.96
	90	0.245	77.71	84.46
	100	0.2081	64.54	87.09
	110	0.1579	46.61	90.68
	120	0.1179	32.32	93.54

Table 10: Effect of temperature at 35°C

Temperature, °C	Time (min)	Absorbance (A)	Concentration (ppm)	Percentage removal (%)
35°C	10	1.28	447.36	10.53
	20	1.14	397.36	20.53
	30	1.094	380.93	23.81
	40	0.89	308.07	38.39
	50	0.7891	272.04	45.59
	60	0.723	248.43	50.31
	70	0.6291	214.89	57.02
	80	0.517	174.86	65.03
	90	0.349	114.86	77.03
	100	0.258	82.36	83.53
	110	0.219	68.43	86.31
	120	0.171	51.29	89.74

Table 11: Effect of temperature at 45°C

Temperature, °C	Time (min)	Absorbance (A)	Concentration (ppm)	Percentage removal (%)
45°C	10	1.312	458.79	8.24
	20	1.231	429.86	14.03
	30	1.109	386.29	22.74
	40	0.934	323.79	35.24
	50	0.839	289.86	42.03
	60	0.757	260.57	47.89
	70	0.668	228.79	54.24
	80	0.578	196.64	60.67
	90	0.378	125.21	74.96
	100	0.332	108.79	78.24
	110	0.291	94.14	81.17
	120	0.278	89.50	82.10

Table 12: Effect of temperature at 55°C

Temperature, °C	Time (min)	Absorbance (A)	Concentration (ppm)	Percentage removal (%)
55°C	10	1.325	463.43	7.31
	20	1.249	436.29	12.74
	30	1.132	394.50	21.10
	40	0.969	336.29	32.74
	50	0.859	297.00	40.60
	60	0.789	272.00	45.60
	70	0.681	233.43	53.31
	80	0.586	199.50	60.10
	90	0.401	133.43	73.31
	100	0.377	124.86	75.03
	110	0.312	101.64	79.67
	120	0.289	93.43	81.31

Table 13: Effect of temperature at 65°C

Temperature, °C	Time (min)	Absorbance (A)	Concentration (ppm)	Percentage removal (%)
65°C	10	1.38	483.07	3.39
	20	1.289	450.57	9.89
	30	1.167	407.00	18.60
	40	1.083	377.00	24.60
	50	0.891	308.43	38.31
	60	0.829	286.29	42.74
	70	0.711	244.14	51.17
	80	0.613	209.14	58.17
	90	0.43	143.79	71.24
	100	0.381	126.29	74.74
	110	0.356	117.36	76.53
	120	0.321	104.86	79.03

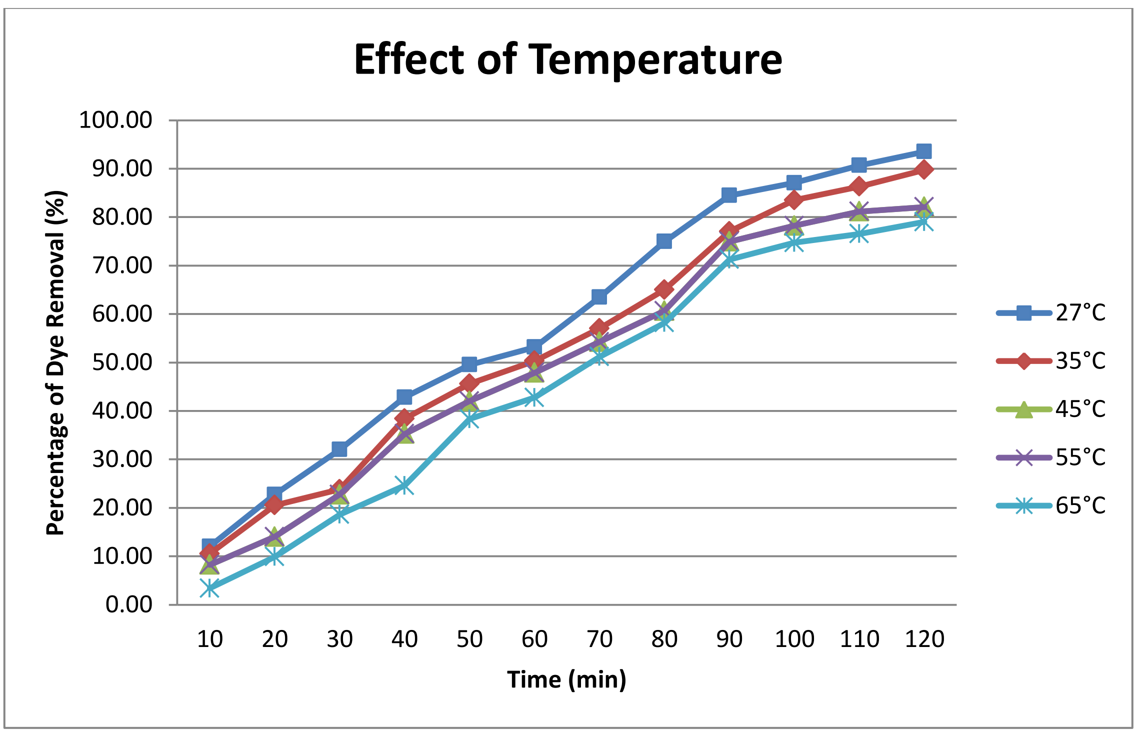

Figure 17: Graph plot for the effect of temperature

Based on the results shown in Table 4.3, 4.4, 4.5, 4.6, and 4.7 as well as Figure 4.4, 27°C has the highest the percentage of dye removal while 65°C has the lowest dye removal percentage. For the effect of temperature, it can be deduced that as temperature increases, the percentage of dye removal decreases.

4.4.4 Effect of Granular Activated Carbon Dosage

The results obtained for the effect of temperature in dye adsorption study can be seen in the following tables and figures:

Table 14: Effect of granular activated carbon dosage at 1g

Dosage, g	Time (min)	Absorbance (A)	Concentration (ppm)	Percentage removal (%)
1g	10	1.369	479.14	4.17
	20	1.269	443.43	11.31
	30	1.179	411.29	17.74
	40	1.098	382.36	23.53
	50	0.894	309.50	38.10
	60	0.7993	275.68	44.86
	70	0.7119	244.46	51.11
	80	0.628	214.50	57.10
	90	0.595	202.71	59.46
	100	0.4321	144.54	71.09
	110	0.3979	132.32	73.54
	120	0.2579	82.32	83.54

Table 15: Effect of granular activated carbon dosage at 2g

Dosage, g	Time (min)	Absorbance (A)	Concentration (ppm)	Percentage removal (%)
2g	10	1.2999	454.46	9.11
	20	1.169	407.71	18.46
	30	1.079	375.57	24.89
	40	0.898	310.93	37.81
	50	0.774	266.64	46.67
	60	0.713	244.86	51.03
	70	0.5719	194.46	61.11
	80	0.428	143.07	71.39
	90	0.295	95.57	80.89
	100	0.2321	73.11	85.38
	110	0.1979	60.89	87.82
	120	0.1579	46.61	90.68

Table 16: Effect of granular activated carbon dosage at 3g

Dosage, g	Time (min)	Absorbance (A)	Concentration (ppm)	Percentage removal (%)
3g	10	1.259	439.86	12.03
	20	1.109	386.29	22.74
	30	0.979	339.86	32.03
	40	0.828	285.93	42.81
	50	0.734	252.36	49.53
	60	0.683	234.14	53.17
	70	0.539	182.71	63.46
	80	0.378	125.21	74.96
	90	0.245	77.71	84.46
	100	0.2081	64.54	87.09
	110	0.1579	46.61	90.68
	120	0.1179	32.32	93.54

Table 17: Effect of granular activated carbon dosage at 4g

Dosage, g	Time (min)	Absorbance (A)	Concentration (ppm)	Percentage removal (%)
4g	10	1.229	429.14	14.17
	20	1.089	379.14	24.17
	30	0.949	329.14	34.17
	40	0.788	271.64	45.67
	50	0.714	245.21	50.96
	60	0.656	224.50	55.10
	70	0.509	172.00	65.60
	80	0.348	114.50	77.10
	90	0.225	70.57	85.89
	100	0.1941	59.54	88.09
	110	0.1549	45.54	90.89
	120	0.1079	28.75	94.25

Table 18: Effect of granular activated carbon dosage at 5g

Dosage, g	Time (min)	Absorbance (A)	Concentration (ppm)	Percentage removal (%)
5g	10	1.189	414.86	17.03
	20	1.049	364.86	27.03
	30	0.918	318.07	36.39
	40	0.758	260.93	47.81
	50	0.684	234.50	53.10
	60	0.606	206.64	58.67
	70	0.489	164.86	67.03
	80	0.328	107.36	78.53
	90	0.205	63.43	87.31
	100	0.1801	54.54	89.09
	110	0.1519	44.46	91.11
	120	0.0949	24.11	95.18

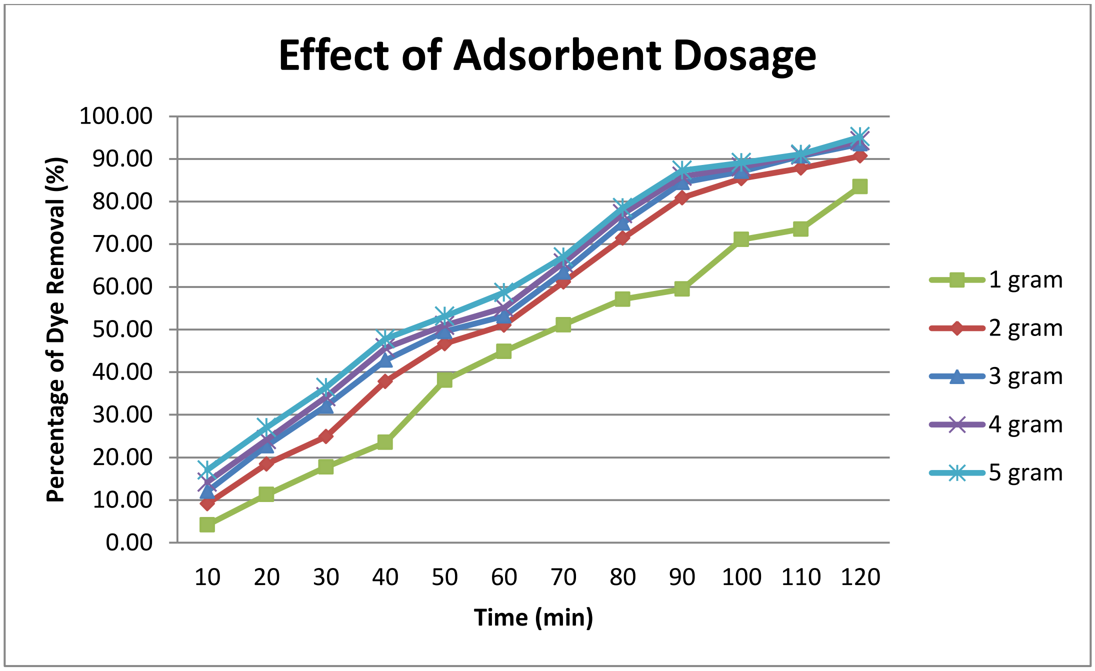

Figure 18: Graph plot for effect of granular activated carbon dosage

From Table 4.8, 4.9, 4.10, 4.11 and 4.12 as well as Figure 4.5, it can be seen that 5g of granular activated carbon has the highest percentage of dye removal compared to 4g, 3g, 2g and 1g of activated carbon. This means that the percentage of dye removal increases as granular activated carbon dosage increases.

4.5 Discussion

4.5.1 Effect of Contact Time

Based on the results obtained and graph plotted in Figure 4.3, it can be observed that as time increases, the amount of dye removed decreases indicating that the adsorption is reaching its equilibrium which is around 120 minutes. Therefore, the optimum time for the functionalized activated carbon will be 120 minutes.

4.5.2 Effect of Temperature

Knowing the optimum contact time for adsorption, the effect of temperature was then determined. Based on the results shown in Table 4.3, 4.4, 4.5, 4.6, and 4.7 as well as Figure 4.4, the lowest temperature which is 27°C has the highest the percentage of dye removal while the highest temperature, 65°C has the lowest dye removal percentage.

With that, it can be deduced that as temperature increases, the percentage of dye removal decreases. The decrease of adsorption effectiveness caused by the increase in temperature also indicates the exothermic nature of the adsorption process. One possible reason is as the temperature increases, the energy content increases and thus, the adsorbent requires more energy to remain in its state which then affects the adsorption balance.

4.5.3 Effect of Granular Activated Carbon Dosage

With optimum time of 120 minutes and optimum temperature of 27°C, the effect of adsorbent dosage was then determined. Based on the graph plotted in Figure 4.5, percentage of dye removal increases as granular activated carbon dosage increases. Having higher dosage, more activated carbon provides larger surface area for adsorption and therefore removes more dyes.

CHAPTER 5: CONCLUSION AND RECOMMENDATION

5.1 Introduction

The scope of study comprises a few elements which are understanding the principles of adsorption and its application, understanding and identifying critical parameters such as concentration, dosage and temperature which needs to be manipulated or held constant for research purposed and finally analyze the kinetics of adsorption.

The objectives of the study are as follow:

- To prepare activated carbon with surface modification by functionalizing activated carbon using optimum conditions with distilled water
- To study the effects of contact time, granular activated carbon dosage, and effect of temperature in adsorption between functionalized activated carbon and dye.

5.2 Conclusion and Recommendation

As a conclusion, water is a good medium to be used to functionalize the granular activated carbon. Water provides sufficient amount of functional group to be attached to the surface of the activated carbon which helps to increase the adsorption capabilities. The optimum condition of functionalization parameter is at the temperature of 35^{o}C, 5 hours contact time and shaking frequency of 100 rpm.

From this project, factors affecting the adsorption or dye removal can be analyzed from the experimental work done by manipulating contact time between functionalized activated carbon and methylene blue, temperature and granular activated carbon dosage.

5.3 Key Milestone

- Successfully functionalized the granular activated carbon using distilled water.
- Analyze the effects of contact time, granular activated carbon dosage, and effect of temperature in adsorption

5.4 Future Work and Recommendation

Due to time constraint, the project has some limitations which can be further improved. One recommendation is to use deionized water instead of distilled water because distilled water might contain minerals and impurities which will affect the results obtained. Another recommendation is to use real wastewater contaminated with dye rather than methylene blue solution for dye adsorption studies.

REFERENCES

Al-Degs, Y. S., Khraisheh, M. A., Allen, S. J., & Ahmad, M. N. (2009). Adsorption characteristics of reactive dyes in columns of activated carbon. *J Hazard Mater, 165*(1-3), 944-949. doi: 10.1016/j.jhazmat.2008.10.081

Chandra, T. C., Mirna, M. M., Sudaryanto, Y., & Ismadji, S. (2007). Adsorption of basic dye onto activated carbon prepared from durian shell: Studies of adsorption equilibrium and kinetics. *Chemical Engineering Journal, 127*(1-3), 121-129. doi: 10.1016/j.cej.2006.09.011

Delle, A. (2000). Factors Affecting Sorption of Organic Compounds in Natural Sorbent/Water System and Sorption Coefficients for Selected Pollutants. A Review. *J.Phys.Chem, 30*.

Foo, K. Y., & Hameed, B. H. (2012). Adsorption characteristics of industrial solid waste derived activated carbon prepared by microwave heating for methylene blue. *Fuel Processing Technology, 99*, 103-109. doi: 10.1016/j.fuproc.2012.01.031

Gobi, K., Mashitah, M. D., & Vadivelu, V. M. (2011). Adsorptive removal of Methylene Blue using novel adsorbent from palm oil mill effluent waste activated sludge: Equilibrium, thermodynamics and kinetic studies. *Chemical Engineering Journal, 171*(3), 1246-1252. doi: 10.1016/j.cej.2011.05.036

Gomes, H. T., Miranda, S. M., Sampaio, M. J., Figueiredo, J. L., Silva, A. M. T., & Faria, J. L. (2011). The role of activated carbons functionalized with thiol and sulfonic acid groups in catalytic wet peroxide oxidation. *Applied Catalysis B: Environmental, 106*(3-4), 390-397. doi: 10.1016/j.apcatb.2011.05.044

Kavitha, D., & Namasivayam, C. (2007). Experimental and kinetic studies on methylene blue adsorption by coir pith carbon. *Bioresour Technol, 98*(1), 14-21. doi: 10.1016/j.biortech.2005.12.008

Mohd Salleh, M. A., Mahmoud, D. K., & Al-Maamary, E. A. (2011). Adsorption of Basic Dye From Aqueous Solution Using Mixture of Agricultural Solid Wastes (Maw) Isotherm, Kinetic Studies and Process Design. *Journal of Advanced Science and Engineering Research, 1*, 76-97.

Nageeb, M. (2013). Adsorption Technique for the Removal of Organic Pollutants from Water and Wastewater. doi: 10.5772/54048

Nwabanne, J. T., & Igbokwe, P. K. (2012). Adsorption Performance of Packed Bed Column for the removal of Lead (ii) using oil Palm Fibre.pdf. *International Journal of Applied Science and Technology, 2*(5).

Pathania, D., Sharma, S., & Singh, P. (2013). Removal of methylene blue by adsorption onto activated carbon developed from Ficus carica bast. *Arabian Journal of Chemistry*. doi: 10.1016/j.arabjc.2013.04.021

Rashidi, N. A., Yusup, S., Ahmad, M. M., Mohamed, N. M., & Hameed, B. H. (2012). Activated Carbon from the Renewable Agricultural Residues Using Single Step Physical Activation: A Preliminary Analysis. *APCBEE Procedia, 3,* 84-92. doi: 10.1016/j.apcbee.2012.06.051

Ridzuan, S. S. (2006). Wastewater treatment using combination of stainless steel membrane and adsorption system.

Rivera-Utrilla, J., Sanchez-Polo, M., Gomez-Serrano, V., Alvarez, P. M., Alvim-Ferraz, M. C., & Dias, J. M. (2011). Activated carbon modifications to enhance its water treatment applications. An overview. *J Hazard Mater, 187*(1-3), 1-23. doi: 10.1016/j.jhazmat.2011.01.033

Sarkar, M., Banerjee, A., Pramanick, P. P., & Sarkar, A. R. (2007). Design and operation of fixed bed laterite column for the removal of fluoride from water. *Chemical Engineering Journal, 131*(1-3), 329-335. doi: 10.1016/j.cej.2006.12.016

Shahryari, Z., Goharrizi, A. S., & Azadi, M. (2010). Experimental Study of Methylene Blue Adsorption from Aqueous Solutions onto Carbon Nano Tubes. *International Journal of Water Resources and Environmental Engineering, 2*(2), 16-28.

Toor, M., & Jin, B. (2012). Adsorption characteristics, isotherm, kinetics, and diffusion of modified natural bentonite for removing diazo dye. *Chemical Engineering Journal*, *187,* 79-88. doi: 10.1016/j.cej.2012.01.089

Vocciante, M., Trofa, M., Rodríguez-Estupiñán, P., Giraldo, L., D'Auria, T., Moreno-Piraján, J. C., & Erto, A. (2014). A rigorous procedure for the design of adsorption units for the removal of cadmium and nickel from process wastewaters. *Journal of Cleaner Production*, *77,* 35-46. doi: 10.1016/j.jclepro.2013.12.001

APPENDICES

APPENDIX I: GANTT CHART

Gantt Chart for FYP I

Task / Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
First briefing by FYP coordinator														
Selection and finalization of FYP Title and supervisor														
First meeting with supervisor / FYP Title introduction														
Research on adsorption column design														
Timeline planning / Listing of chemicals and equipment needed														
Literature review														
Preparation of extended proposal draft														
Purchasing of granular activated carbon / Equipment booking														
Extended proposal submission														
Proposal defense														
Purchasing of bench scale adsorption column														
Preparation of interim draft report / Discussion with supervisor														
Submission of interim draft report														
Finalization of interim report / Discussion with supervisor														
Submission of interim report														

Gantt Chart for FYP II

Task / Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
First briefing by FYP coordinator															
First meeting with supervisor for the semester															
Booking of lab workstation															
Booking of equipment and apparatus															
FYP II Project Activities: Experimental work															
Preparation of progress report															
Progress report submission															
FYP II Project Activities: Experimental work															
Pre-EDX															
Submission of draft															
Submission of softbound															
Submission of technical paper															
Oral Presentation															
Submission of hardbound															