Preparation of Activated Carbon from Durian Shells

Using Fixed Bed Activation Unit

for Dye Removal Application

by

Zahidah binti Ahmad Zulfa

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

MAY 2013

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

Preparation of Activated Carbon from Durian Shells

Using Fixed Bed Activation Unit

for Dye Removal Application

by

Zahidah binti Ahmad Zulfa

A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

_____
(Dr Suriati Sufian)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

May 2013

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

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.

_____

ZAHIDAH BINTI AHMAD ZULFA

ABSTRACT

This report discusses about the preliminary research done and basic understanding of the chosen topic, which is **Preparation of Activated Carbon from Durian Shells using Fixed Bed Activation Unit for Dye Removal Application.** The objective of this project is to produce low cost activated carbon from durian's biomass waste that can be used as an alternative for dye removal treatment especially for textile industry. This study presents the preparation of activated carbon from durian shells through chemical activation process in Fixed Bed Activation Unit (FBAU) with potassium hydroxide (KOH) as dehydrating agent and steam oxidizing agent under the nitrogen flow. In order to find the optimum parameters condition, six different design based on variation in impregnation ratio of precursor to KOH, activation temperature and activation time were employed. Maximum yield was 37% for durian shells impregnated with 1:4 ratio, at 400 ^{o}C for 2 hours, named DSAC5. The FESEM images showed a smooth surface of durian shells became wrinkle porous structure of activated carbon that were favored for adsorption and BET result of 410 m^2/g for durian precursors. The removal of methylene blue dye from the solution was found to be feasible with the developed lab scale process. Maximum adsorption percentage was 98.35% with maximum adsorption capacity of 24.59 mg/g for DSAC5.

ACKNOWLEDGEMENT

I would like to take this opportunity to acknowledge and extend my heartfelt gratitude to the following persons who have made the completion of this Final Year Project possible. First and foremost, I would like to extend my gratitude to my respected supervisor, Dr Suriati Sufian, who gave me the most thorough support and guidance towards completing this project.

Special thanks to the examiners for Proposal Defence and Poster Presentation, who were being very supportive, and guiding me through my mistakes to make the project even better. Not to forget, the coordinator for her/his continuous monitoring and guidance and the lab technicians for their instruction and assistances. Last but not least, to my friends, and to those who assisted me directly or indirectly in helping me to complete my FYP. Thank you very much, may Allah repays your kindness.

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Textile industry as one of the fastest growing industries was the 10th largest export earner in 2011, contributing approximately 2.3% to Malaysia's total exports of manufactured goods. Exports of textiles and textile products for the year 2011 were RM10.8 billion while imports amounted to RM6.6 billion [1]. Despite the returns gain, textile industry ranks first in usage of dyes for coloration of fiber. The release of dyes into the environment during textile fiber dyeing and finishing processes is a main source of water pollution. This industry also results in high water consumption and produces high discharge rate of wastewater with high load of contaminants. However, individual wastewater treatment methods are often very expensive and may results in large amount of sludge.

Currently, there are more than 100,000 commercially available dye exist and more than $7x10^5$ tons are produced annually [2]. Dyes contented in wastewaters are very challenging to treat, since the dyes are obstinate organic molecules, are firm to light, and resistant to aerobic digestion. A synthetic dye in wastewater cannot be efficiently decolorized by traditional methods. This is because of the high cost and disposal problems for treating dye wastewater at large scale in the textile and paper industries [3].

Technologies for dyes removal from wastewater can be divided into three categories: biological, chemical and physical [4]. Biology or biodegradation methods such as fungal decolorization, microbial degradation, adsorption by microbial biomass and bioremediation systems are commonly applied to the treatment of industrial

effluents [5]. This is because many microorganisms such as bacteria, yeasts, algae's and fungi are able to store and vitiate different waste product.

Chemical treatment of dye wastewater with a coagulating/flocculating agent is one of the robust ways to remove color [7]. The process involves adding agents, such as aluminum (Al3þ), calcium (Ca2þ) or ferric (Fe3þ) ions, to the dye effluent and induces flocculation. Different physical methods are also widely used, such as membrane – filtration processes (nano - filtration, reverse osmosis, electro dialysis) and adsorption techniques. Compared with membrane separation, adsorption is a well-known equilibrium separation process and an effective method for water decontamination applications [8].

Growing demand for adsorption processes in the wastewater treatment had encourages research in the production of activated carbon from alternate precursors including industrial wastes and agricultural by-products. This is because the production of activated carbons from solid wastes is one of the most environment-friendly solutions by transforming negative–valued wastes to valuable materials. Malaysia as the largest durian exporter results in load of durian's biomass waste that has potential to produce the low cost of activated carbon. The production is estimated to increase further since Malaysia's targeted sectorial outcomes of durian's yield will increased from 3.1 mt/ha to 8.0 mt/ha (Industry Strategic S&T Plan) [6].

1.2 Problem Statement

According to the 2007 report from the Department of Environment of Malaysia, total amount of waste generated by textile industry was 743.99 metric tons per year (Environmental Quality Report, 2007). Based on this number, proper treatment for the removal of color from wastewater/effluents are vital. Although several physical and chemical processes have been used for treatment, these processes are highly cost and not efficient for the wide range of dye wastewater.

In this study, the author will used durian shells and seeds to produce activated carbon. Fixed bed activation unit is used to optimize physic-chemical activation

process of durian's shell activated carbon. Characteristics of the activated carbon produced will be compared to commercial activated carbon and the potential of dye removal using durian's activated carbon will be investigated.

1.3 Objective and Scope of Study

The objectives of this project are:

- To develop activated carbon from durian's shells using Fixed Bed Activation Unit.
- To characterize the produced activated carbon with suitable test methods.
- To study the effect of various process parameters on activated carbons produced.
- To investigate the efficiency of durian's shell adsorption on dye removal applications.

The scopes of study for this project are:

- Chemical activation of durian shells activated carbon using KOH as dehydrating agent and Fixed Bed Activation Unit (FBAU) as the activation medium.
- Characterization of activated carbon using SEM and BET.
- Optimizing the effect of impregnation of precursor to dehydrating agent ratio, activation temperature, and activation time.
- Determination of dye removal efficiency of durian shell's activated carbon using UV-VIS.

CHAPTER 2

LITERATURE REVIEW

2.1 Activated Carbon

Activated carbon is the oldest adsorbent known and is usually prepared from coal, coconut shells, lignite, wood etc., using one of the two basic activation methods: physical and chemical [12].Commercial activated carbons have surface areas greater than 800 m^2/g and many have areas over 1000 m^2/g (Merchant and Petrich, 1993). Activated carbons are versatile adsorbents and unique materials. Its absorptivity properties are due to their high surface area, a microporous structure and a high degree of surface reactivity.

There are three types of activated carbon available in the current markets which are powder, granular and pellet. The activated carbon is classified according to its particle sizes and shape, and each type has its specific application.

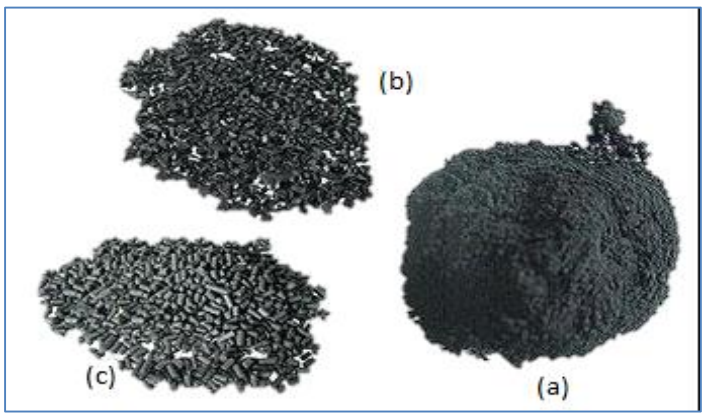

Figure 1 : PAC (a), GAC (b) and EAC (c) [12]

The powdered activated carbons (PAC) are derived from the chemical activation of carbon has a particle size of 1 – 150 μm. These carbons are commonly used for the

treatment of wastewater. While granular (GAC) and extruded activated carbons (EAC), has particle size of 0.5 – 4 mm and 0.8 – 4 mm. Both of GAC and EAC are produced through the gas or physical activation and commonly used for the purification of gases.

2.1.1 Properties

Investigation on adsorption properties of activated carbons are essentially due to their high surface area, universal adsorption effect, highly microporous structure, and a high degree of surface reactivity[12]. Generally, the total number of pores, their shape and size determine the adsorption capacity and even the dynamic adsorption rate of the activated carbon. IUPAC classifies pores as follows:

- macropores: $d_0 > 50nm$
- mesopores: $2 \leq d_0 \leq 50nm$
- micropores: $d_0 < 2nm$

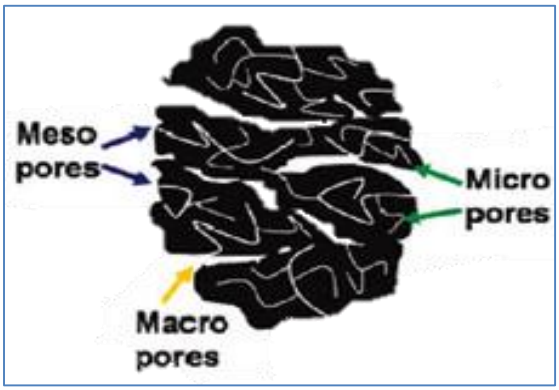

Figure 2 : Classification of pores [12]

where d_0 is the pore width for slit type pores or the pore diameter for cylindrical pores. The most widely used activated carbons have a specific surface area of 800 – 1500 m^2/g. This surface area contained predominantly within micropores. Macropore however does not contribute significantly toward surface areas. Instead, it acts as conduits for passage of adsorbate into mesopore interior and micropore surface for adsorption to take place.

In addition, adsorption capacity also is strongly influenced by chemical structure of the activated carbon surface which is the order of the crystalline structures. Besides

that, the active site of carbon surface such as form of edges, dislocations, and discontinuities will determine the chemical reactions and the catalytic properties of it.

2.1.2 Applications

There are two major applications of activated carbon which is liquid phase and gas phase. In liquid phase, activated carbons are used to remove undesirable odors, colors, and unwanted components in the solution. Examples of liquid phase applications are, preparation of alcoholic beverages, decolorization of oils and fat, and decolorization of sugar solution of white sugar manufacturing. For gas phase application, the major concerns are regarding the removal of hazardous substances from industrial exhaust gases, separation of gas mixtures, purification of process gases and recovery of solvents.

Besides that, there is several numbers of other commercial adsorbents available beside activated carbon. For example, silica gel is used to dehydrate gases and liquids to fractionate hydrocarbons, activated alumina is used to dry gases and liquids, and molecular sieve zeolites is used for drying and hydrocarbons separation.

2.2 Activation Methods

Previously, there are two methods available for carbon activations which are physical and chemical activations. Physical activation is a conventional method for manufacturing process of activated carbon. In physical activation, carbonization of precursor occurs in priori followed by their activation in the presence of activating agents [13]. On the other hand, carbonization and activation take place simultaneously within chemical activation.

For physical activation method, carbonization step is carry out at temperature ranged from 500 – 600 ^{0}C followed by activation using mild oxidizing agent at temperature range from 800 – 1000 ^{0}C[14].Mild oxidizing agent such as steam, nitrogen or carbon dioxide is used in physical activation[16].Meanwhile, precursor has

to be impregnated with dehydrating agent in chemical activation[15].Activation temperature is in range of 200 – 800 ^{0}C.Dehydrating agent such as H_2SO_4, H_3PO_4, $ZnCl_2$, and KOH is used in chemical activation.

Currently, another method known as physicochemical activation is used for carbon activation. This method combines the impregnation step with dehydrating agent in chemical activation method together with the activation step with oxidizing agent in physical activation method. This method had been proved to improve the properties of activated carbon produced.

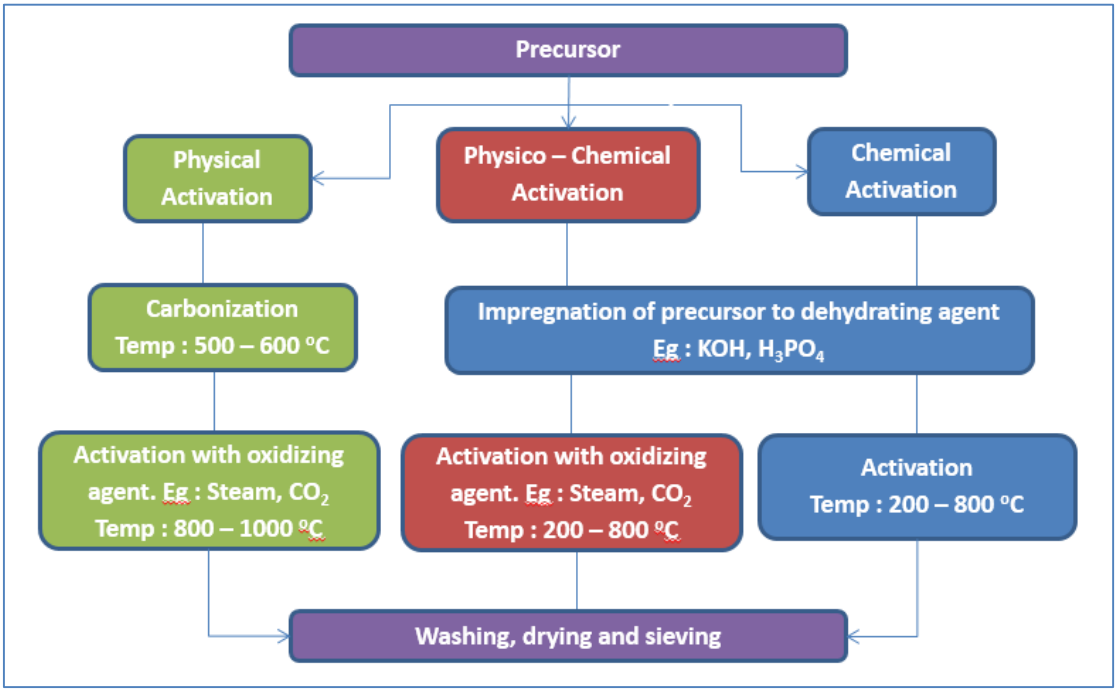

Figure 3 : General block diagram for activation methods [35]

2.3 Effect of operating parameters

Three experimental parameters that will affect the characteristics of durian shells activated carbon produced will be studied in this project are impregnation ratio, activation temperature and activation time. These parameters are important as they will determine the yield of activated carbon and the characteristics of activated

carbons produced especially the pore size, BET surface area, pore volume and adsorption capacity.

Percentage of yield obtained is different based on the activation temperature and heating time. Range of 51.78% and 57.27% of yield is obtained from activated carbon prepared at 400^0C [19]. If temperature exceeds 400^0C, the yield will decrease as the heating duration increases.

Previous study reported that durian's activated carbon have a BET values of 519 – 992 m^2/g are comparable to the commercial available activated carbon [20]. Highest surface area can be achieved because of concentration of acid incorporated into the pore of raw durian's shells and seeds will subsequently led to pore enlargement during carbonization stage [21]. However longer heating duration caused some of the pores become larger or even collapse and thus contributed to the reduction of surface area [22].In term of impregnation of precursor to acid ratios, this parameters will increased the total pore and mesopore volume but decreased the micropore volume with the increase in impregnation ratio[13].

2.4 Activated Carbon Adsorption

Adsorption process involved one or more components of a gas or liquid stream being adsorbed on the surface of a solid adsorbent [17]. The adsorbing solid is referred to as an adsorbent, and the substance to be adsorbed from the liquid or gas phase as an adsorbate. Overall adsorption process consists of several of steps in series. Molecules from gas or liquid phase will be attached in a physical way to a surface; in this case the surface is from the active carbon. The adsorption process takes place in three steps [18]:

1. Macro transport: The movement of organic material through the macro-pore system of the active carbon (macro-pore >50nm).
2. Micro transport: The movement of organic material through the mesopore and micropore system of the active carbon (micropore<2nm; mesopore 2-50nm).

3. Sorption: The physical attachment of organic material on the surface of active carbon in the mesopores and micropores of the active carbon.

2.5 Dyes

A dye can generally be described as a colored substance that has an affinity to the substrate to which it is being applied [28]. The dye is usually used as an aqueous solution, and may require a mordant to improve the fastness of the dye on the fiber. In contrast, a pigment generally has no affinity for the substrate, and is insoluble.

Basic dyes are water – soluble cationic dyes that are mainly applied to acrylic fibers, but find some use for wool and silk [29]. Usually acetic acid is added to the dye bath to help the uptake of the dye onto the fiber. Basic dyes are also used in the coloration of paper.

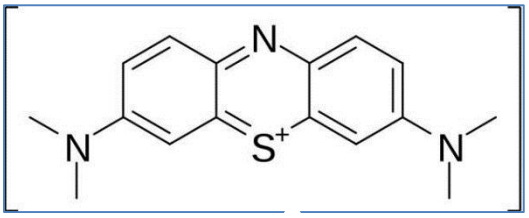

Figure 4 : Chemical structure of basic dyes – Methylene blue [30]

Acid dyes are water-soluble anionic dyes that are applied to fibers such as silk, wool, nylon and modified acrylic fibers using neutral to acid dyebaths [29]. Attachment to the fiber is attributed, at least partly, to salt formation between anionic groups in the dyes and cations groups in the fiber. Acid dyes are not substantive to cellulosic fibers.

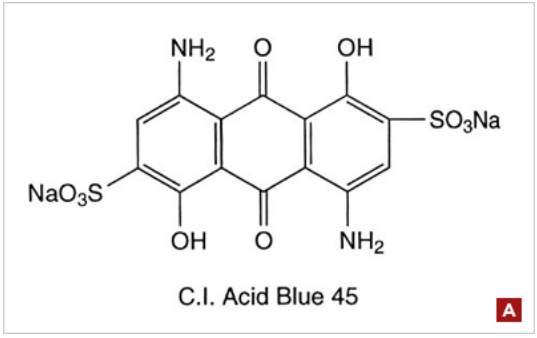

Figure 5 : Sample of acid dyes structure – Blue [31]

2.5.1 Why dye must be separated from wastewater?

Industrial wastewater contains high concentration of colored toxic compound. This can bring risk of harm to the health in the population. Dye in wastewater:

a) Obstruct light penetration
b) Highly visible and unacceptable
c) Stable to light irradiation and heat
d) Become as a toxic to microorganisms
e) Hard to remove due to their complex structure and synthetic origins

It is important to reduce the dye concentration so it can't bring any harm to the important source of life, water.

2.5.2 Methylene Blue

Methylene blue is a heterocyclic aromatic chemical compound. It has many uses in a range of different fields, such as biology or chemistry and also in textile industries[36]. At room temperature it appears as a solid, odorless, dark green powder, which yields a blue solution when dissolved in water.

Methylene blue is highly stable in the human body, and if ingested, it resists the acidic environment of the stomach as well as the many hydrolytic enzymes present. It is not significantly metabolized by the liver, and is instead quickly filtered out by the

kidneys. Therefore, it is necessary to make sure the effluent contained methylene blue was treated first before released it to environment.

2.6 Durian's as activated carbon

Durian is chosen as raw material for adsorbents because of massive generation of durian residues, chiefly in the form of durian shells, seeds, peels and rinks, which constitutes 70% of the entire fruits [32]. Durian's forecasted a total world's harvest of 1.4 Mt, dominated by its major producers, Thailand (781 kt), Malaysia (376 kt), Indonesia (265 kt), following by Philippines (Davao Region), Cambodia, Laos, Vietnam, Myanmar, India, Sri Lanka, Florida, Hawaii, Papua New Guinea, Madagascar, and northern Australia [33].

In common practice, durian residues are burned or sent to the landfills, without taking care of the surrounding environment, nor consider any precautions to prohibit the percolation of contaminants into the underlying water channels [34]. Lately, environmental rules and regulations concerning the pollution from agricultural waste streams by regulatory agencies are more stringent and restrictive; inevitably affect the design, planning, and operation of the durian processing industry.

Predictions for the next 20 years indicate an ascending impact in the textile waste production, and subsequently increase in durian residues generation [34]. This growing incongruity has raised anxieties over the use of durian residues as a measure to environmental pollution control.

2.6.1 Durian shell activated carbon properties

In one study, electron micrographs scanning of the durian shell activated carbons obtained show a well-developed porous structure after 30% of acid treatment followed by 500^0C heat treatment [19].Comparison of surface morphology between raw durian shells and activated carbon produced show that the smooth surface become

more porous structure. The cavities are form on the activated carbon external surface and this is resulted from the evaporation of activating agent.

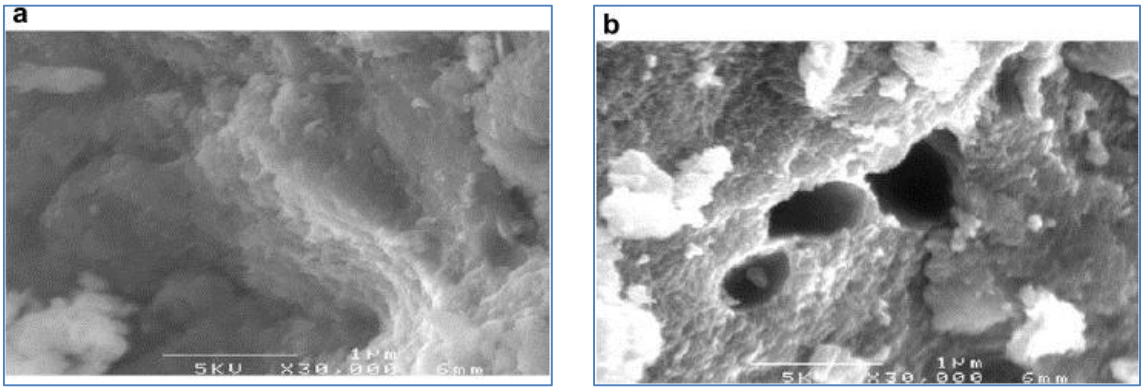

Figure 6 : SEM images of the durian shell (a) its developed activated carbon (b) [15]

Chandra, et. Al reported the SEM results comparison for pristine durian shell and its developed activated carbon as shown in Figure 6 above. From the scanned images, the pores of durian shells activated carbon are being developed after activation method. In Figure 7, the pore size distribution graph shows that micropores structured produced is much higher followed by mesopores and smaller number of macropores.

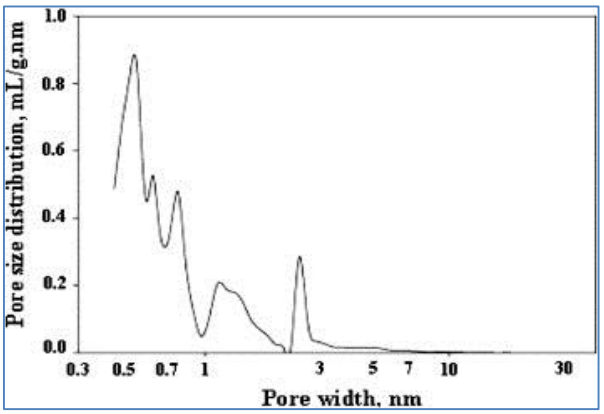

Figure 7 : size distribution of the durian shell prepared activated carbon [15]

2.6.2 Adsorption study for dye removal

Y.C. Sharma, in his study compared the adsorption capacities that have been used previously such as coconut husk, banana peel, risk husk, and etc on removal of Malachite Green dye [23]. The adsorption capacities are calculated using following equation:

Adsorption capacity, q_m $= (C_i - C_t)/W \times V$

where: C_i = Initial dye concentration

C_t = Dye concentration at time t

W = Dry weight of adsorbent used

V = Volume of solution

Table 1 : Comparison of adsorption capacities of different adsorbents for dye removal [23]

Adsorbent	qm (mg/g)
Coconut husk	99.00
Banana peel	21.0
Date pits	17.3
Rice husk	63.85
Orange peel	14.30
Sugarcane dust	4.88

From table shown above, the activated carbon produced from bio-mass waste have such as coconut husk and rice husk have potential on dye removal. However, no such data is found using durian shells adsorbent. Hence, in this study the author chose to use durian shells as the raw material to produce activated carbon adsorbents.

Table 2 below is the summaries of literature review from journals that have been studied:

Table 2 : Summary of Literatures

Title/Author	Methodology & Experimental Parameters	Activation Method	Characterization & Conclusion
Textural porosity, surface chemistry and adsorptive properties of durian shell derived activated carbon prepared by microwave assisted NaOH activation by **K.Y.Foo,** (2012)	- Durian shell (DS) is collect from local market - Collected sample is wash with distilled water - DS is cut, ground and screen to desired size of 1 – 2mm - Carbonization is perform by loading 500g of dried precursor into vertical furnace, at temperature of 700^0C under purified N_2flow ($150cm^3$/min) - Impregnation ratios (IR) is defined = Dry weight of NaOH pellet (g) / Weight of char (g)	Physical activation	- BET surface area 1475.46 m^2/g - Total pore volume $0.841cm^3/g$ - Adsorption equilibrium : Langmuir isotherm - Adsorption capacity 410.85 mg/g
Effect of activation temperature and heating duration on physical characteristics of activated carbon prepared from agriculture waste by **Tham Yee Jun** (2010)	- Durian shells are acquire from a market in Serdang, Selangor - The shells is wash and crush into 1 – 2 cm particle size before dry in an oven overnight to reduce moisture content - 10g of raw material is weigh and impregnated in 100ml 10% (v/v) concentration of H_3PO_4overnight. Ratio, Xp = 1:1.4 - After impregnation, the wet samples are dry in an oven for 12 hours at 100^0C and subsequently activated in N_2 atmosphere at 400 – 500^0C at heating rate 5^0C/min - Soaking duration at final temperature are 10, 20 and 3 min - The sample is cool down to room temperature in a stream of N_2 gas	Chemical activation	- Activation temperature and heating duration have significant influence on activated carbon characteristics - Highest surface area obtain is $1024m^2/g$ at 500^0C for 20 min - Yield of activated carbon is 63%

Title/Author	Methodology & Experimental Parameters	Activation Method	Characterization & Conclusion
	- Then the sample is batch wise at ambient temperature with distilled water until the pH reached approximately pH 6 – 7 - The sample is dry overnight at 85^0C in an oven to make sure it is moisture free		
Performances of toluene removal by activated carbon derived from durian shell by **Y. J. Tham** (2010)	- 10g of raw durian shell is immerse in 100ml of different H_3PO_4concentration solutions (5%,10%,20%,30% and 50%) for 24 hours and then dry in an oven overnight - Impregnation ratio, Xp used are 0.7, 1.4, 2.8, 4.2 and 8.4 - The sample is carbonized in tube furnace at 500^0C for 20 min - The sample is then wash with distilled water until it pH reached pH 6 -7 - Activated carbon is sieve to 2mm particle size	Chemical activation	- Highest BET surface area of is 1404 m2/g - Highest removal efficiency of toluene vapors is achieved by impregnation with 30% of H_3PO_4 heated at 500^0C for 20 min
Activated carbon from durian seed by H_3PO_4 activation: Preparation and pore structure characterization by **Amri Ismail, Hanggara Sudrajat, Desi Jumbianti** (2010)	- Durian seed is collect from local durian processing industry - The seed is dry at 100^0C in an oven for 12 hours and subsequently crushed and sieved to a particle size of 500 – 710 µm. - About 10 to 20 g of the resultant seed is impregnated with 85% $H_3PO_4$to the desired acid to durian seed ratio (Xp) - The mixture is subjected to low temperature treatment at 150^0C in muffle furnace under flowing of N_2 at atmospheric pressure for 2 hours - Final heat treatment continue at temperature of 600^0C or 900^0C for 4 hours with different heating rate - The carbon is cool to room temperature in the same N_2 flow - Excess $H_3PO_4$is wash off by hot deionized water until the pH become 6	Chemical activation	- Highest BET surface area 2123 m^2/g - Highest total surface area 2147 m^2/g - Using impregnation ratio of 2, activation temperature of 600^0C for 4 hours and heating rate of 1^0C/min

Title/Author	Methodology & Experimental Parameters	Activation Method	Characterization & Conclusion
	- After washing, the carbon is further dry at 105^0C for further analysis and characterization - Xp ratio :1,2,4 and 6 - Activation temperature : 600^0C and 900^0C - Heating rate : 1 and 5 ^{0}C/min		-
Spent tea leaves: A new non-conventional and low-cost adsorbent for removal of basic dye from aqueous solutions by **B.H. Hameed** (2009)	- Basic dye used in this study was methylene blue (MB) purchased from Sigma–Aldrich (M) Sdn Bhd, Malaysia - Spent tea bags are collected from a tea making shop located in the cafeteria of the Engineering Campus, Nibong Tebal, Penang - The spent tea leaves are removed from the bags and boil repeatedly with water until the filtered water is clear - Then it is dry in oven at 60 ◦C for 48 hours - The dried sample is ground and sieved to obtain a particle size range of 0.5–1.0mm	-	- The adsorption isotherm data were fitted well to the Langmuir isotherm and the monolayer adsorption capacity was found to be 300.052 mg/g at 30 ◦C.
Fast removal of malachite green by adsorption on rice husk activated carbon by **Y.C. Sharma** (2009)	- 0.25 g of rice husk activated carbon (RHAC) is agitated to 50 ml of dye solution of the desired dye concentrations in 250 ml conical flasks, at 150 rpm, 30^oC in a thermo stated water bath shaker to reach equilibrium. - Dye solution is separated from the adsorbent by centrifugation at 10,000 rpm for10 min. - Amount of adsorbed dye molecules per g of solid is determined as follows :qe = (Co - Ce)V/ w	Physical activation	- The monolayer adsorption capacity of rice husk activated carbon for adsorption of the dye was found to be 63.85 mg/g at room temperature.

Title/Author	Methodology & Experimental Parameters	Activation Method	Characterization & Conclusion
Adsorption of basic dye onto activated carbon prepared from durian shell: Studies of adsorption equilibrium and kinetics by **Thio Christine Chandra** (2006)	- Durian shells are collected from local fruit stores in Surabaya and repeatedly wash with distilled water to remove dirt and other impurities and then dry at 393.15K for 24 h to reduce the moisture content. - 25 g of dried durian shell was mixed with 100mL KOH solution, and then stirred at 303.15K for about 5 h - The amount of KOH in the solution was adjusted to give mass ratio of chemical activating agent to durian shell 1:2 - The resulting homogeneous slurry was dried at 383.15K for at least 24 hours - The resulting samples were placed in a horizontal tubular reactor and then heated (at heating rate (10Kmin−1) at a carbonization temperature of 673.15 K - The carbonization and activation was performed under nitrogen flow of 150 cm3 min−1 STP	Chemical activation	- BET surface area 991.82m^2/g - Micropore surface area 849.31m^2/g - Total pore volume 0.471cm^3/g - Micropore volume 0.368cm^3/g

CHAPTER 3

METHODOLOGY

3.1 Research methodology

There are three major stages for the overall methodology of this project. The first stage is preparation of raw durian shells, second stage is activation of durian shells and third stage is adsorption study on dye removal efficiency.

3.1.1 Raw Materials and Chemicals Needed

In the experiments that are going to be conducted, several raw materials and chemicals are needed. There are:

i. Durian shells
ii. Potassium hydroxide, KOH pellet
iii. Nitrogen, N_2 gas
iv. Methylene Blue dye

3.1.2 Tools required

The equipment required to analyze the properties of Durian Shells Activated Carbon (DSAC) produced and to determine adsorption efficiency is:

- Granulator and Mortar Grinder
  To crush and grind the durian shells into smaller size desired

Figure 8 : Granulator (left) and Mortar grinder (right)

- Sieve tray

  To sieve the grinded durian shells to 500 µm in size

Figure 9 : Sieve tray

- Fixed Bed Activation Unit (FBAU)

  To carbonize the impregnated durian shells at 400 and 500 ^{0}C.

Figure 10 : Fixed Bed Activation Unit

- Scanning Electron Microscope (SEM)

To examine the surface morphology of activated carbon. The magnification applied for scanning is 500X, 1000X, 1500X, 2000X, and 5000X.

- Brunauer-Emmet-Teller (BET) nitrogen adsorption technique

  To calculate specific surface area and pore distribution

- X-Ray Diffraction

  To analyze possible compound percentage

- pH Meter

  To determine the pH of the solution

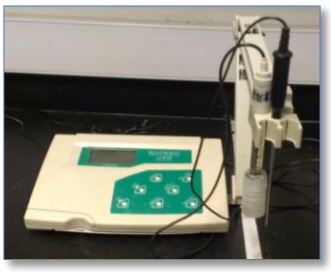

Figure 11 : pH Meter

- Rotary shaker

  To mix the adsorbent properly with the dye solution

Figure 12 : Rotary shaker

- UV – VIS

  To determine the concentration of dye before and after adsorption

Figure 13 : UV - VIS

3.2 Preparation of raw material

i. Firstly, the durian's shells were cleaned by washing with water.
ii. Then durian shells were dried under the sun for 8 hours in order to remove any dust or inorganic impurities.
iii. Drying process was continued in the oven at 100^0C for 24 hours to further reduce the moisture content.
iv. After that, the durian shells were grinded and sieved to desired geometric particle, which is 500µm in size by using granulator and mortar grinder, and sieve tray.

Figure 14 : Granulated durian shell (Left) and powdered durian shell (Right)

3.3 Activation method

i. Dried durian shells were undergoing chemical activation method.
ii. 40gof dried durian shells were impregnated with different concentration of KOH solution from 1:2 to 1:4 precursors to KOH weight ratio. The solution was stirred and left overnight.

Figure 15 : Durian shells solution mixed with KOH

iii. The impregnated precursors was filtered and dried in oven at 100^0C for 24 hours to remove excess water.

iv. Dried impregnated precursors were washed with distilled water until pH reached 6 – 7 and further dried in the oven at 100^0C for 24 hours.

Figure 16 : Dried durian shells precursor

v. The precursors were weighted in crucible and activated in Fixed Bed Activation Unit (FBAU) at temperature 400 ^{0}Cfor 2 hours and 500 ^{0}C for 1 hour durations.

vi. The flow of N_2 gas was maintained throughout the heating process.

vii. The activated carbon produced was cooled down to room temperature for storage purpose.

viii. The total yield of durian's activated carbon was calculated as:

$$Y_t = \frac{\text{Weight of durian's activated carbon}}{\text{Weight of durian's precursor}} \times 100\ \%$$

3.4 Adsorption studies on dye removal

Adsorption studies were determined according to the method proposed by Y.C Sharma et al. [23]:

i. Dye solution of 50 ppm concentration was prepared beforehand.

ii. 0.05 g of durian shells activated carbon was agitated with 25 ml of dye solution in 150 ml conical flasks.

iii. The solution was left to mix on a rotary shaker at room temperature for 1 hour, 2 hour, 4 hour, 6 hour, 12 hour, 18 hour and 24 hours.

Figure 17 : Adsorption of methylene blue using durian shells activated carbon

iv. The solutions then were filtered and the filtrates were analyzed using UV – VIS to determine the final equilibrium dye concentration.

v. The adsorption percentage and capacity were calculated by:

Percentage adsorption $= (C_i - C_t)/C_i \times 100\%$

Adsorption capacity, q_m $= (C_i - C_t)/W \times V$

where: C_i = Initial dye concentration

C_t = Dye concentration at time t

W = Dry weight of adsorbent used

V = Volume of solution

3.5 Characterization

Characterization of durian's activated carbon is necessary as it can be used as a basis to compare with commercial types of activated carbon. The main characteristics to be evaluated are:

i. Surface morphology

FESEM is used to determine the texture or topography of activated carbon surface

ii. Pore size distribution

Micromeritics Volume Analyzer is used to determine whether the pores is macropore, micropore, and mesopore

iii. Specific surface area

Micromeritics Volume Analyzer is used to measure the surface of activated carbon structures and deep texture on the particles

3.6 Gantt charts

Table 3 : FYP 1 Gantt Chart

No.	Detail /Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Selection of Project Topic															
2	Preliminary Research Work															
3	Submission of Extended Proposal															
4	Proposal Defense															
5	Perform experimental work and preparation of activated carbon															
6	Submission of Interim Draft Report															
7	Submission of Interim Report															

Table 4 : FYP 2 Gantt Chart

No.	Detail /Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Perform experimental work and ccharacterizations of activated carbon															
2	Submission of Progress Report															
3	Pre - SEDEX															
4	Submission of Dissertation Draft															
5	Submission of Technical Paper															
6	Oral Presentation															
7	Submission of Project Dissertation															

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Yield of DSAC

Six samples of Durian Shell's Activated Carbon (DSAC) had prepared from durian shells using KOH as activating agent. Range of 32 to 37% of yield is obtained from DSAC (DSAC1, DSAC3, DSAC5) activated at 400^0C. While at 500^0C, the range of yield for DSAC (DSAC2, DSAC4, DSAC6) decrease to 25 – 29%. DSAC yields are found to decrease with increasing in activation temperature because of a higher dehydration of carbonaceous structure of precursor [24]. The reduction in weight was due to the loss of the volatile matters during rapid heating of carbonization process (Rahman et al., 2004). Highest yield obtained is DSAC 5 which is impregnated by 1:4 ratio and activated at 400 ^{o}C for 2 hours.

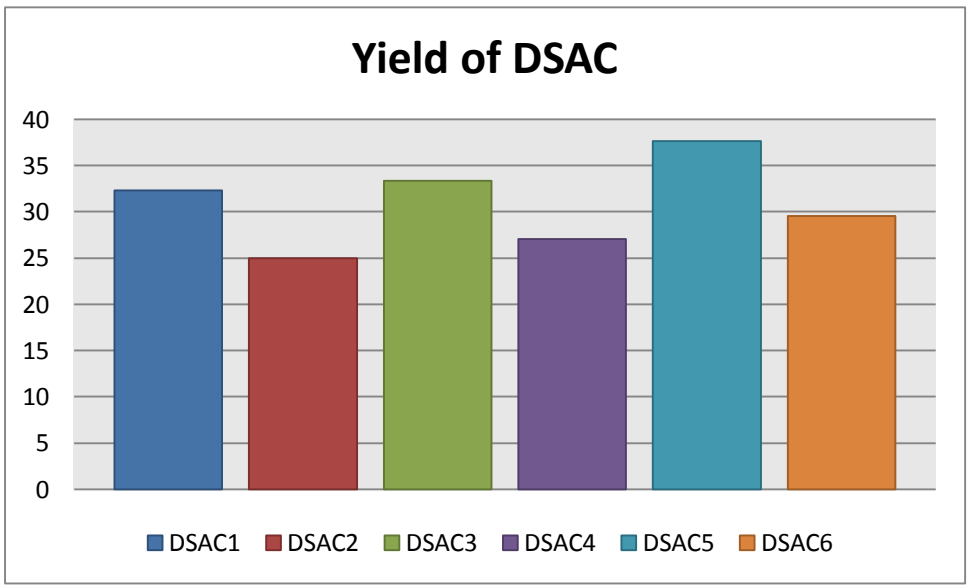

Figure 18 : Yield of DSAC

4.2 Effect of impregnation ratio

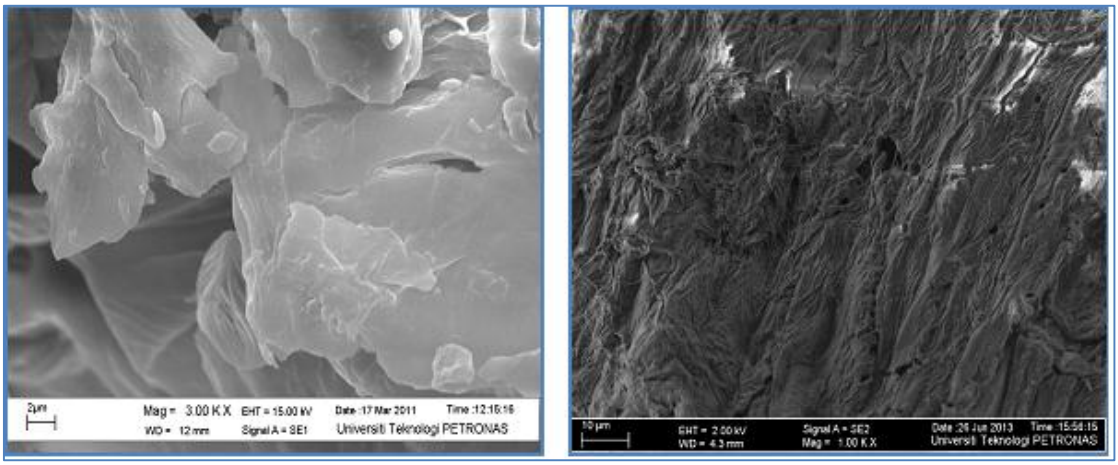

Figure 19 : (Left) SEM image of Raw Durian Shell (Right) SEM image of Durian Shell after impregnation

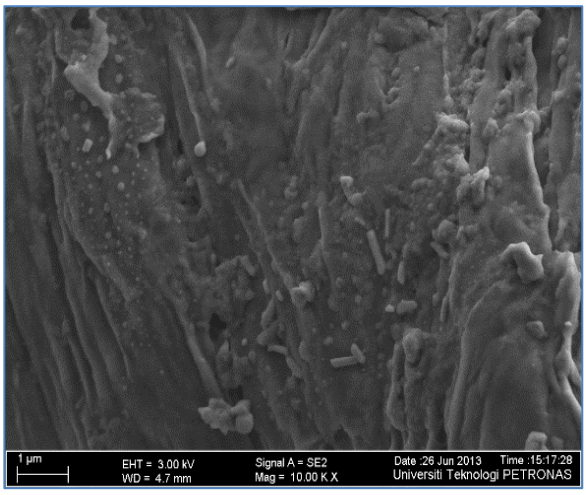

Figure 20 : SEM image DSAC11 - 400^{0}C, 2 hour

The morphological characteristics of raw durian shells, after impregnated and DSAC are observed by using Field Emission Scanning Microscope (FESEM).Impregnation of durian shells precursor with activating agent, KOH is important in order to open up the pores structure. The porosity developed is due to the formation of phosphate linkages such as phosphate and polyphosphate esters which can serve to connect and crosslink biopolymers [13]. FESEM micrograph of raw durian shell shows no presence of pores, afterwards pore formation is observed in durian shell that is treated chemically with KOH. This is consistent with theory that the chemical treatment process will produce high porous cellulose-silica material.

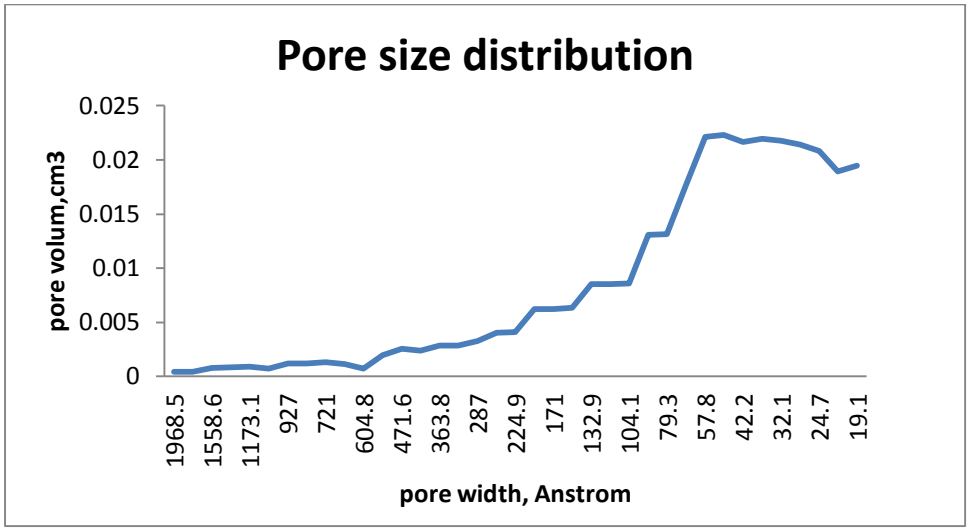

Figure 21 : Pore size distribution of Durian Shells after impregnated with 1:4 ratio

Besides that, durian shells impregnated with KOH has BET surface area of 410 m^2/g, with impregnation ratio of 1:4, precursor to KOH weight ratio. This show that the pores have been developed after treated with the activating agent. Figure 21 shows that, the pore volume for smaller pore diameter is higher indicating the presence of microporous structure.

4.3 Effect of activation temperature

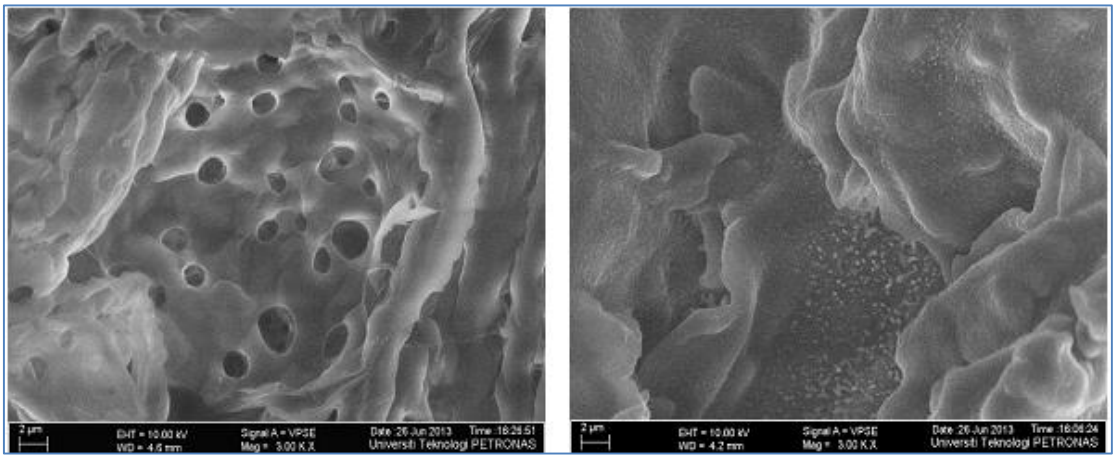

Figure 22 : (Left) DSAC5 – 400^{0}C, 2 hour (Right) DSAC6 – 500^{0}C, 1 hour

Electron micrograph scanning of the activated carbons obtained from the DSAC5, after 1:4 impregnation ratio followed by 400^{o}C for 2 hours showed a well-developed porous structure compare to the DSAC6, with the same impregnation ratio, but at 500^{o}C for 1 hour. Comparing the SEM results between both DSAC, there are clear differences of the surface morphology and porous structures.

By referring to Figure 22, carbonization process caused the formation of many fine pores in the interior structure of DSAC5 thereby increasing the surface area of the activated carbon. DSAC5 have a well-developed pores compare to DSAC6 where the pores have been collapse. Although increasing the activation temperature contributed to formation of new pores, the structure might also collapse when it reaches its temperature limits [25]. According to the micrograph, the pores were developed from the vaporization of non-carbon elements and volatile matters (such as oxygen, nitrogen and carbonate) during carbonization process with nitrogen flow.

4.4 Adsorption study

4.4.1 Adsorption percentage

The adsorption of methylene blue onto DSAC was studied by using 0.05 g of adsorbent quantity in the test solution while keeping the initial dye concentration at 50 ppm, at room temperature. The solution samples were taken at 1 to 6, 12, 18 and 24 hours. It is observed that for an initial dye concentration of 50 mg/L at 25^{o}C, the maximum amount of dye adsorbed after 24 hours was 98.35%while the minimum adsorption percentage was at 63.27%.

The contact time between adsorbate and the adsorbent is of significant importance in adsorption. In physical adsorption, most of the adsorbate species are adsorbed within a short interval of contact time. Adsorption studies in literature reveal that the uptake of adsorbate species is fast at the initial stages of the contact period, and, thereafter, it becomes slower near the equilibrium [26]. The initial rapid uptake of adsorbate species may due to large numbers of available vacant sites on the adsorbent surface at the initial stage [27].

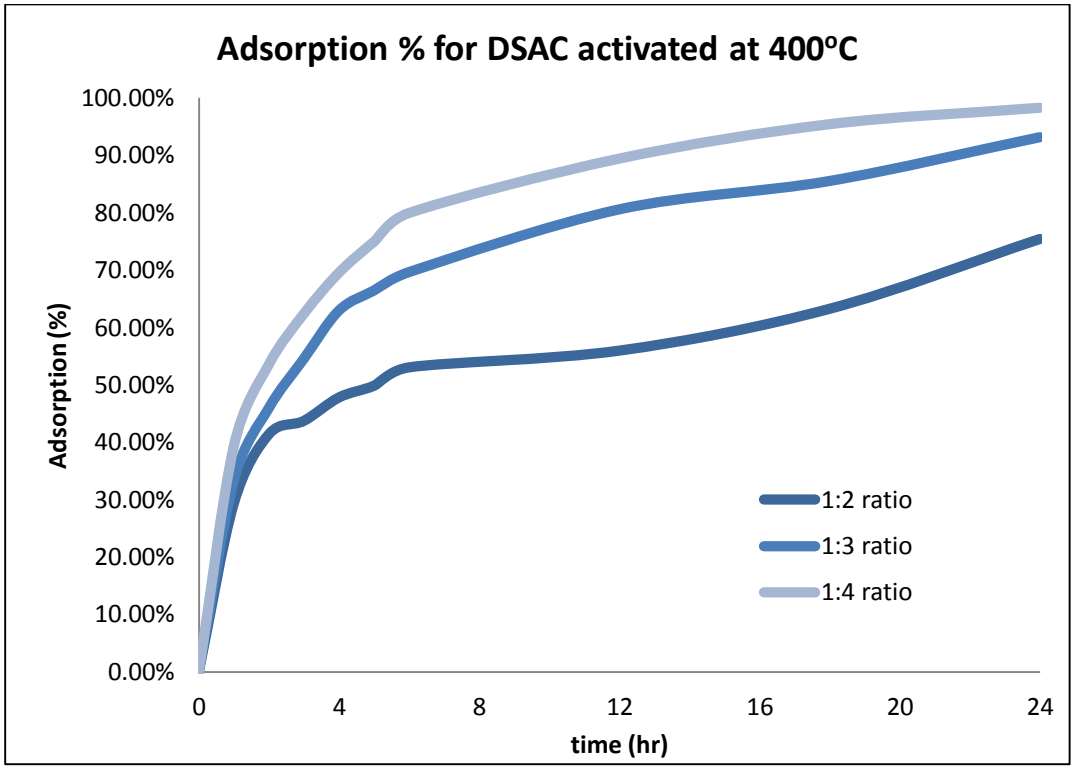

Figure 23 : Adsorption % for DSAC activated at 400 °C

From Figure 22, the adsorption capacity increased with the increase of porosity structure of DSAC. Comparing both graphs in Figure 23 and Figure 24, DSAC activated at 400 °C have higher adsorption percentage. This can be related to the properties of activated discussed previously. However, since the initial concentration of Methylene Blue dye was quite high, the adsorption was not reaching equilibrium.

It was observed that the initial adsorbate uptakes for all DSACs are quite fast. However, strong chemical binding of the adsorbate with adsorbent requires a longer contact time for the attainment of equilibrium. Increase in dye concentration will decrease the percentage of dye removal and longer time is needed to reach equilibrium.

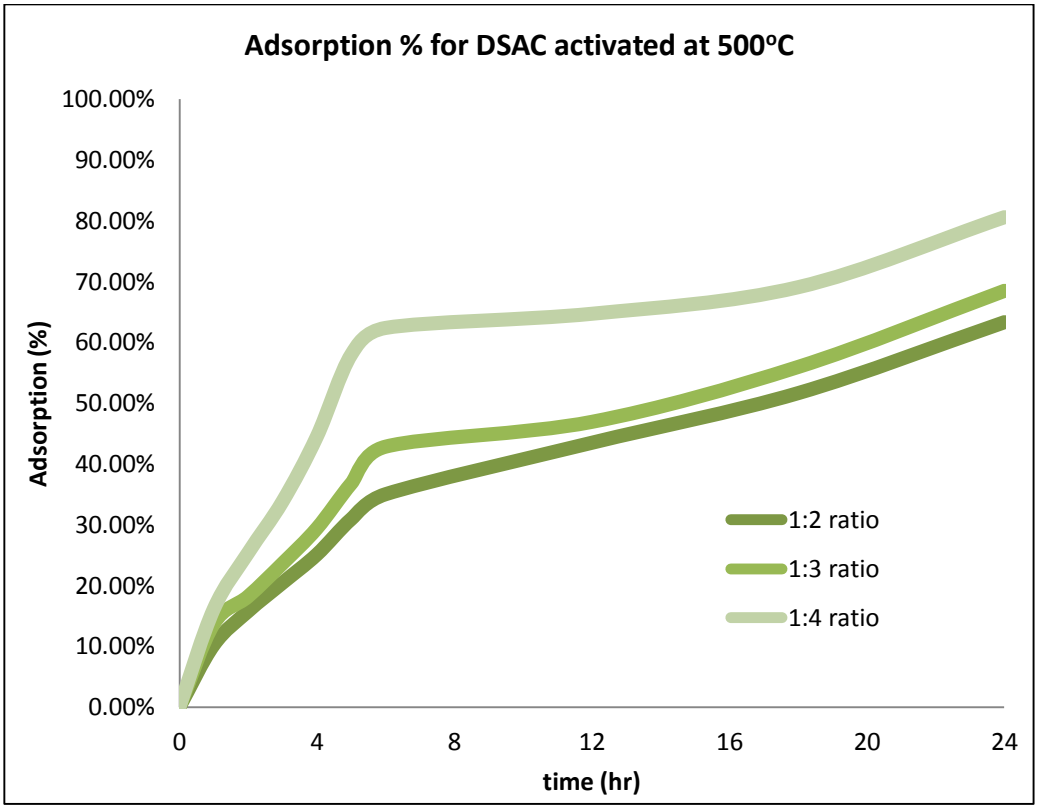

Figure 24 : Adsorption % for DSAC activated at 500 °C

4.4.2 Adsorption capacity

Measuring adsorption capacity are the rapid screening methods in determining performances of activated carbon. Batch treatment using powdered carbon, will directly correlate to the full scale plant performances.

Comparing with the adsorption percentage respectively, the highest adsorption capacity was 24.59 mg/g and the lowest was 15.82 mg/g. In this study, the adsorptive capacity is influenced by the properties of activated carbon used. Referring back to Table 1, adsorption capacity of DSAC is third after Coconut husk, 99 mg/g and Rice husk, 63.85 mg/g. Hence, DSAC produced has potential to be used as adsorbent for dye removal application. Figure 25 and Figure 26 shows the performance of activated carbon capacity for different impregnation ratio and activation time. Increase in adsorption percentage will increase the adsorption capacity as well.

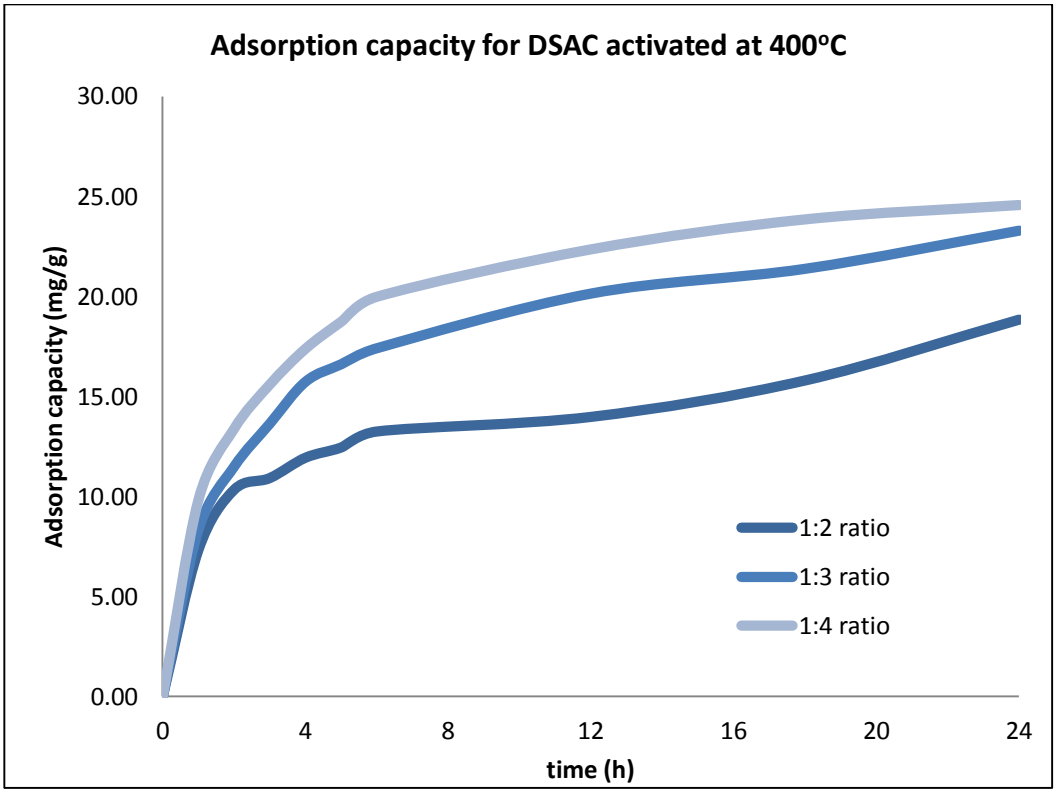

Figure 25 : Adsorption capacity for DSAC activated at 400 °C

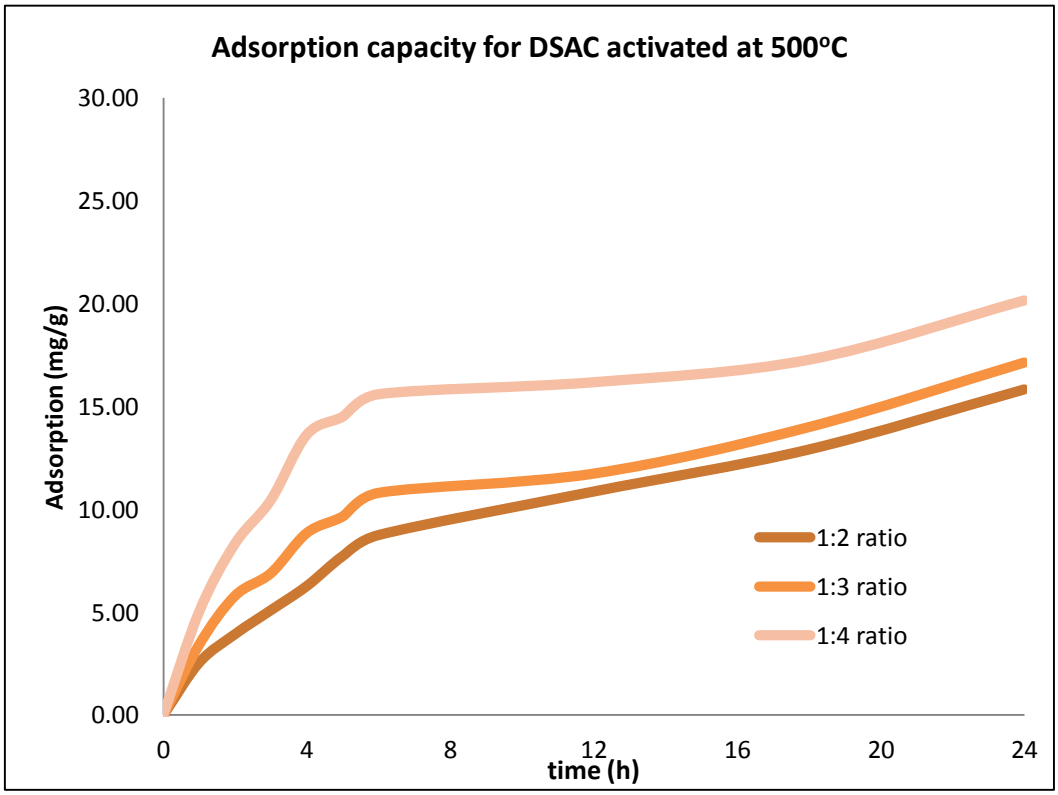

Figure 26 : Adsorption capacity for DSAC activated at 500 °C

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

In conclusion, this project helps to enhance the development of low – cost activated carbon adsorbents. Durian shell is selected as the raw material due to the high number of its biomass waste annually. Maximum yield was 37% for durian shells impregnated with 1:4 ratio, at 400 ^{o}C for 2 hours, named DSAC5. The FESEM images shown a wrinkle porous structure of activated carbon that were favored for adsorption and BET result of 410 m^2/g for durian precursors. The removal of methylene blue dye from the solution was found to be feasible with the developed lab scale process. Maximum adsorption percentage was 98.35% with maximum adsorption capacity of 24.59 mg/g for DSAC5.

5.2 Recommendation

Further testing prior to future field-scale use of the Durian Shell Activated Carbon is recommended to extend the observations and conclusions for other contaminants. In addition, testing for other available agricultural waste byproducts as a raw carbon source for activated carbon production should be investigated as durian shells will not be available throughout the year. Lastly, as polluted waters may contain multiple organic impurities, field-testing these systems with actual source waters should be conducted to characterize the level of competition for available adsorption sites on the carbon and its effect on the operating life of the material.

REFERENCE

[1] Malaysian Investment Development Authority (MIDA), 2013. Available from ((MIDA), 2013)

[2] C.I. Pearce, J.R. Lloyd, J.T. Guthrie, The removal of colour from textiles wastewater using whole bacteria cells: a review, Dye and Pigments 58 (2003) 179-196.

[3] M. Ghoreishi and R. Haghighi, Chemical catalytic reaction and biological oxidation for treatment of non-biodegradable textile effluent. Chemical Engineering Journal, 95 (2003) 163-169.

[4] G. McMullan, C. Meehan, A. Conneely, N.Kirby, T.Robinson, P.Nigam, I.M. Banat, R. Marchant, W.F.Smyth, Microbial decolourisation and degradation of textiles dyes, Application Microbial Biotechnology, 56 (2001) 81-87.

[5] T.Robinson, G. McMullan, R. Marchant, P. Nigam, Remediation of dyes in textiles effluent: a critical review on current treatment technologies with a proposed alternative, *Bioresource Technology, 77 (2001) 247-255.*

[6] DURIAN : Industry Strategic S & T Plan. http://www.pcaarrd.dost.gov.ph/home/isp/images/matrices/tropical-fruits.pdf

[7] Wang, M., Li, H., Wu, J., Huo, Y., Guo, G., Cao, F., 2006a. Flocculants for purification of printing and dyeing wastewater. Univ Shanghai Normal.

[8] A. Dabrowski, Adsorption — From theory to practice, Advances in Colloid and Interface Science, 93 (2001) 135-224.

[9] Environmental Quality Report. (2007). Malaysia: Department of Environment.

[10] Kunii D &Levenspiel O, Fluidization Engineering (Wiley, New York), 1969

[11] A.A. Merchant, M.A. Petrich, AIChE J. 39 (8) (1993) 1370–1376

[12] Bansal, R. Chand, &Goyal, M. (2005). Activated carbon adsorption. Boca Raton: Taylor & Francis.

[13] Ismail, A., Sudrajat, H., and Jumbianti, D. (2010). Activated carbon from durian seed by H_3PO_4 activation: Preparation and pore structure characterization. *Indo.J. Chem. (1), 36 - 40*

[14] Norlia, M.I., Roshazita, C.A., Nuraiti, T.I.T., Salwa, M.Z.M., Fatimah, M.S.S (2011). Preparation and characterization of activated carbon from rambutan seed (NepheliumLappaceum) by chemical activation. *UMTAS 2011.*

[15] Chandra, T. c., Mirna Maria, M., Sunarso, J., Sudaryanto, Y., & Ismadji, S. (2009). Activated Carbon from durian shell : Preparation and characterization. *Journal of taiwan institue of chemical engineering* (40), 457-462.

[16] Y. Fu and T. Viraraghavan, Fungal decolorization of dye wastewaters: a review, Bioresource Technology, 79 (2001) 251-262.

[17] Geankoplis, C. J. (2003). Transport processes and separation process principles: (includes unit operations). 4th ed. Upper Saddle River, NJ: Prentice Hall Professional.

[18] Source: Wastewater Engineering; Metcalf & Eddy; third edition; 1991; page 317.

[19] Tham, Y.J., Shamala-Devi, A., Latip, N.H.A., Abdullah, A.M., Latif, P.A (2010). Effect of activation temperature and heating duration on physical characteristics of activated carbon prepared from agriculture waste. *Environmental Asia3 (special issue), (2010) 143 – 148.*

[20] Tham, Y.J., Latip, P.A., Abdullah, A.M., Shmala-Devi, A., Taufiq-Yap, Y.H. (2011). Performances of toluene removal by activated carbon derived from durian shell. *Bioresource Technology 2011; 102: 724 - 728.*

[21] Guo, Y., Rockstraw, D.A., 2007. Physicochemical properties of carbons prepared from pecan shell by phosphoric acid activation. *Bioresource. Technol. 98, 1513–1521.*

[22] Diao Y, Walawender WP, Fan LT., 2001. Activated carbons prepared from phosphoric acid activation of grain sorghum. *Bioresource Technology; 81: 45-52.*

[23] Y.C. Sharma*, B. Singh and Uma.,2009. Fast Removal of Malachite Green by Adsorption on Rice Husk Activated Carbon. *The Open Environmental Pollution & Toxicology Journal, 1,* 74-78.

[24] Rosas J M et al, HEMP, 2000. Derived activated carbon fibres by chemical activation with phosphoric acid, *Fuel, 88, 19 – 26.*

[25] Demiral H, Demiral I., 2007. Pore structure of activated carbon prepared from hazel nut bagasse by chemical activation. Surface and Interface analysis (40): 616 – 19.

[26] Dogan, M..Ozdemir, Y. and Alkan, M. (2007). Adsorption kinetics and mechanism of cationic methyl methylene blue dyes onto sepiolite. Dyes and Pigments, 75, 701~713

[27] Kavitha, D. and Namasivayam, C. (2007) Experimental andkinetic studies on methylene blue adsorption by coir pith carbon. Bioresource Technology, 98, 14-21

[28] http://www.dyespigments.net/basic-dyes.html

[29] http://www.princeton.edu/~achaney/tmve/wiki100k/docs/Dye.html

[30] http://www.chemistry.about.com

[31] http://www.dharmatrading.com/

[32] M.A. Amiza, Y. Aziz, B.C. Ong, V.L. Wong, A.M. Pang.CHIEF: cheap high fibre flour from local fruit seed. *Expo Science, Technology and Innovation.*PWTC, Kuala Lumpur (2004 Aug 27–29)

[33] Department of Agriculture, Malaysia [Internet]. Durian [cited 2010 Aug 20]. http://www.doa.gov.my/statistik/buah03-h08.htm.

[34] K.Y. Foo, B.H. Hameed, Transformation of durian biomass into a highly valuable end commodity: Trends and opportunities. School of Chemical Engineering, Engineering Campus.

[35] V.K. Gupta, Suhas, Application of low – cost adsorbents for dye removal – A review. Journal of Environmental Management 90 (2009) 2313–2342.

[36] P.V. Shrivastava, M. Hambarde, H. Kumar. Decolorization of textile waste water using low cost adsorbent. IJGHC; 2012, Vol.1.No.1, 1-8 46-51.

APPENDIX

Appendix A : Yield calculation

DSAC1

Weight before activation = 6 g

Weight after activation = 2.87 g

Yield = (1.94/6) x 100%

= 32.33 %

Appendix B : Adsorption percentage calculation

DSAC1

Time. Hr	Concentration, ppm	Adsorption percentage, %
0	50.00	0.00%
1	35.32	29.36%
2	29.30	41.40%
3	28.13	43.74%
4	26.09	47.81%
5	25.07	49.86%
6	23.47	53.06%
12	22.01	55.98%
18	18.37	63.27%
24	12.28	75.44%

Adsorption percentage = (50-35.32)/50 x 100 % = 29.36%

Adsorption percentage = (50-29.30)/50 x 100 % = 41.40%

Adsorption percentage = (50-28.13)/50 x 100 % = 43.74%

Adsorption percentage = (50-26.09)/50 x 100 % = 47.81%

Adsorption percentage = (50-25.07)/50 x 100 % = 49.86%

Appendix C : Adsorption capacity calculation

DSAC1

Time. Hr	Concentration, ppm	Adsorption capacity, mg/g
0	50.00	0.00
1	35.32	7.34
2	29.30	10.35
3	28.13	10.94
4	26.09	11.95
5	25.07	12.46
6	23.47	13.27
12	22.01	13.99
18	18.37	15.82
24	12.28	18.86

Adsorption capacity = (50-35.32)/0.05 g x 0.025 L = 7.34

Adsorption capacity = (50-29.30)/0.05 g x 0.025 L = 10.35

Adsorption capacity = (50-28.13)/0.05 g x 0.025 L = 10.94

Adsorption capacity = (50-26.09)/0.05 g x 0.025 L = 11.95

Adsorption capacity = (50-25.07)/0.05 g x 0.025 L = 12.46