

**JACKFRUIT SEED BASED ACTIVATED CARBON  
PREPARED BY MICROWAVE HEATING ACTIVATION  
FOR METHYLENE BLUE DYE REMOVAL**

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**by**

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the degree of Bachelor of Chemical Engineering**

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## LIST OF SYMBOLS

	Symbol	Unit
$A$	Arrhenius factor	-
$B_T$	Constant for Temkin equation	-
$C_e$	Equilibrium concentration of adsorbate	mg/L
$C_o$	Highest initial adsorbate concentration	mg/L
$C_t$	Dye concentration at time, t	mg/L
$E$	Mean free energy	J/mol
$E_a$	Arrhenius activation energy of adsorption	kJ/mol
$k_1$	Adsorption rate constant for pseudo first-order kinetic	1/hr
$k_2$	Adsorption rate constant for pseudo second-order	g/mg.hr
$K_F$	Freundlich isotherm constant	$\text{mg/g} \left(\frac{\text{L}}{\text{mg}}\right)^{1/n}$
$K_L$	Langmuir adsorption constant	L/mg
$n_f$	Constant for Freundlich isotherm	-
$q_e$	Amount of adsorbate adsorbed at equilibrium	mg/g
$q_m$	Adsorption capacity of Langmuir isotherm	mg/g

$q_t$	Amount of adsorbate adsorbed at time, t	mg/g
$R$	Universal gas constant	8.314 J/mol.K
$R^2$	Correlation coefficient	-
$R_L$	Separation factor	-
$t$	Time	min
$T$	Absolute temperature	K
$V$	Solution volume	L
$\Delta G^0$	Changes in standard Gibbs free energy	kJ/mol
$\Delta H^0$	Changes in standard enthalpy	kJ/mol
$\Delta S^0$	Changes in standard entropy	kJ/mol
$\lambda$	Wavelength	nm

## LIST OF ABBREVIATION

AC	Activated carbon
BET	Brunauer-Emmett-Teller
BN	Biji nangka
CCD	Central composite design
CO <sub>2</sub>	Carbon dioxide
FTIR	Fourier Transform Infrared
JS	Jackfruit seed
JSAC	Jackfruit seed activated carbon
KTBN	Karbon teraktif biji nangka
MB	Methylene blue
N <sub>2</sub>	Nitrogen gas
rpm	Rotation per minute
RSM	Response Surface METHodology
SEM	Scanning electron microscopy
UV	Ultraviolet

**KARBON TERAKTIF BERASASKAN BIJI NANGKA DISEDIAKAN  
MELALUI PEMANASAN GELOMBANG MIKRO UNTUK PENYINGKIRAN  
PENCELUP  
METILENA BIRU  
ABSTRAK**

Proses kelompok telah digunakan untuk menyiasat penyingkiran pencelup metilena biru (MB) dengan menggunakan karbon teraktif berasaskan biji nangka (KTBN). Bagi menyediakan KTBN, biji nangka (BN) telah menjalani proses pengaktifan fizikal yang melibatkan penyinaran gelombang mikro dan pengegasan karbon dioksida (CO<sub>2</sub>). Berdasarkan kaedah permukaan respon, penyediaan optimum telah diperolehi pada kuasa gelombang mikro dan masa pengaktifan masing-masing pada 616 W dan 6.00 minit yang menghasilkan 83.15% penyingkiran MB. Sampel optimum ini mempunyai luas permukaan (544.07 m<sup>2</sup>/g), isipadu liang (0.3034 cm<sup>3</sup>/g) dan kandungan karbon tetap (75.22%) yang tinggi. Liang KTBN adalah jenis mesoliang dengan purata diameter liang 2.23 nm. Kesan kepekatan awal pewarna (25-300 mg/L), masa sentuhan (0-24 jam) dan suhu larutan (30-60°C) turut dinilai. Data keseimbangan diperolehi bagi penyingkiran pencelup oleh KTBN MB adalah terbaik dipadankan dengan model Langmuir dengan kapasiti penjerapan maksimum sebanyak 357.14 mg/g. Sementara itu, data kinetik terbaik diwakili oleh model pseudo tertib pertama. Proses penyingkiran pencelup MB dengan KTKK adalah tindak balas serap haba yang berlaku secara spontan.

**JACKFRUIT SEED BASED ACTIVATED CARBON PREPARED BY  
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DYE REMOVAL**

**ABSTRACT**

A batch study was used to investigate the adsorption of methylene blue (MB) dye onto jackfruit seed based activated carbon (JSAC). Jackfruit seed goes through physical adsorption alongside with microwave heating and carbon dioxide (CO<sub>2</sub>) gasification. By using response surface methodology (RSM), the optimum preparation conditions were obtained with microwave power and activation time of 616W W and 6.00 minutes, respectively which resulted 83.15% MB removal. The effect of initial dye concentration (25-300 mg/L), contact time (0-24 hours) and solution temperature (30-60°C) were also evaluated throughout. This optimized sample has high surface area 544.07 m<sup>2</sup>/g, pore volume 0.3034 cm<sup>3</sup>/g and fixed carbon content of 75.22%. The pore of JSAC was mesoporous type with average pore diameter of 2.23 nm. The effect of initial dye concentration (25-300 mg/L), contact time (0-24 hours) and solution temperature (30-60°C) were also during this study. The obtained equilibrium data for MB adsorption by JSAC dye was best fitted by Langmuir model with monolayer adsorption capacity of 357.14 mg/g. Meanwhile, the kinetics data was best represented by the pseudo first-order model. The adsorption process of MB onto JSAC was endothermic which occurs spontaneous process.

# CHAPTER ONE

## INTRODUCTION

### 1.1 Dyes in textile industry

In recent years, amount of dyes being discharged by the textile, paint, pulp and paper industries have threatened the state of our environment. More than 100,000 commercially available dyes with over  $7 \times 10^5$  of dyes are produced annually throughout the world (Rangabhashiyam et al., 2013). Dyes discharge have affected the environment by posing problems to aquatic life, and our environment. Processing of 1 kg of dyed fabrics about 100 L of water are required. Dyes waste water can cause many health diseases to humans such as increased heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice, quadriplegia, and tissue necrosis(Hameed, 2009). Dyes absorb and reflect sunlight entering water which can interfere with the growth of bacteria and hinder photosynthesis in aquatic plants. Textile industry ranks first in usage of dyes for coloration of fiber.

Adsorption process has risen as one of the most effective process to treat present in the waste water effluent. Adsorption process is preferable to be utilized in industrial scale as it requires a short period of time and cost effective. Adsorption process works efficiently in dye removal process by separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another substance. There are two types of adsorption which are physical and chemical adsorption. Physical adsorption resembles the condensation of liquids which depends on Van der

Waals, force of attraction between the solid adsorbent and the adsorbate molecules whereas chemical adsorption involves activation of energy. Through adsorption process, agriculture waste can be utilized as a precursor to produce activated carbon (AC) thus providing life cycle assessment of the solid waste instead of being dumped away unnecessarily. AC can be produced in the form of powder, monolith and granular.

Companies that consume and manufacture these dyes and the government are searching for methods to treat effluent with dyes, as the year passes more information is widely available about this issue to be tackled. In this study, AC is produced from jackfruit seed waste for MB dye removal from aqueous solution. AC is highly porous that has complex structure composed of carbon atoms and carbonaceous. It has networks of pores that are channels created within rigid skeleton of disordered layers of carbon atoms, linked together by chemical bonds, stacked unevenly, creating highly porous structure of nooks, crannies, cracks, crevices and between the carbon layers (Mezohegyi et al., 2012).

## **1.2 Jackfruit (*Artocarpus heterophyllus*)**

Jackfruit is one of the potential fruits of development for domestic and international demand that have been identified under the National Agricultural Policy (1992 - 2010). It is a non-seasonal local fruit that is available throughout the year. To date, there are three registered clones which are known as NS3, NS4 and NS9 (Malaysia, 2018).

The quantity for domestic consumption and exports of reached about 29,876 MT worth RM123.8 million in revenue in 2005 whereas for the year 2010, it reached 46,183 MT with total revenue of RM228.3 million (Malaysia, 2018).

In 2008, the production value of jackfruit reached RM61,519,278 with a production of 26,748 tonnes valued at RM2.29 per kg. In 2010 the production value from jackfruit for Selangor and Sabah were RM 11,157,750 and RM10,198,350 respectively (Ismail, 2013). The price of jackfruit sold per kilogram in Malaysia during 2013 was about RM2.50 (Persekutuan, 2018).

### **1.3 Problem Statement**

Textile industry is a major contributor in Malaysia that produces large volumes of synthetic dyes waste water from different steps in the dyeing and finishing processes. Dyes are usually highly coloured effluent released into the environment. The textile industry is the largest consumer of synthetic dyes utilizing about 56% of the total world dyes production per annum of  $7 \times 10^5$  tonnes (Subramaniam, 2015). Dyes used in the textile industry are toxic to aquatic organisms and can be resistant to natural biological degradation. Among the low-cost process to treat this problem is through adsorption process. This process saves time and cost-effectiveness makes it a popular method to remove these obstructing dyes from the waste water.

Commercial coal based AC is known as the preferred adsorbent as it does not require any additional pre-treatment before its used. However, coal is non-renewable and expensive. Following this reason, an attempt was made using jackfruit (*Artocarpus heterophyllus*) seed as source of production of jackfruit seed based activated carbon (JSAC) by microwave heating along with CO<sub>2</sub> gasification. This study was conducted to explore the potential use of JS waste to remove methylene blue (MB) dye from aqueous solution.

## **1.4 Objectives**

The objectives for this research:

- i) To study the optimum parameters of microwave power and time in producing jack fruit seed based activated carbon (JSAC) using a microwave radiation.
- ii) To characterize physically JSAC in terms of surface area, surface morphology, and proximate content and surface chemistry.
- iii) To study the effects of adsorbate initial concentration, contact time, solution temperature, isotherms, kinetics and thermodynamics for MB adsorption on JSAC using batch adsorption tests.

## **1.5 Scope of Study**

In this study, JSAC was prepared via physical method that utilizes CO<sub>2</sub> as its activating agent and microwave irradiation as its heat source. The optimized operating parameters of microwave power and activation time were done using response surface methodology (RSM) method by Design Expert software. To investigate the adsorption behaviour of methylene blue (MB) dye onto JSAC, the optimized JSAC was then used in equilibrium, kinetic and thermodynamic studies. Batch adsorption study was done to carry out the analysis by analysing the effect of adsorbate on initial concentration (25-300 mg/L), contact time (0-24 hours) and solution temperature (30-60°C) for adsorption of dye onto prepared JSAC.

## **CHAPTER TWO**

### **LITERATURE REVIEW**

#### **2.1 Dyes in industry**

Dyes are colored compounds which are widely used in textiles, printing, rubber, cosmetics, plastics, pulp, paper and leather industries to color their products results in generating a large amount of coloured waste water. These kinds of dyes are classified into synthetic and natural dyes. Natural dyes are from plants, minerals or invertebrates whereas synthetic dyes are from organic molecules. Textile processing consumes and discharges large amounts of water. It is estimated that about 40 to 65 L of textile effluent is generated per kg of cloth produced (Manu, 2002).

Effluents released from industries contain a large variety of dyes. These dyes are of great environmental anxiety due to their enormous discharge, carcinogenic, mutagenic and toxic characteristics. Dyes usually have a synthetic origin and complex aromatic molecular structures, which possibly come from coal-tar based hydrocarbons such as benzene, naphthalene, anthracene, toluene and xylene (Vijayaraghavan 2013).

Dyes are released in waste water during dyeing process. Dyes can obstruct the penetration of light and dissolved oxygen into bodies of water. Depletion of dissolved oxygen distracts the growth of aquatic organisms. Along with this issue, there have been great measures to treat dye waste water especially by utilizing adsorption process.

#### **2.2 Adsorption**

Adsorption is a crucial industrial separation processes for waste water effluent. It is a mass transfer process through which the adsorbent can be selectively remove

dissolved constituents from an aqueous solution by attracting the dissolved solute toward its surface. The accumulation of concentrated matter on the surface or at the inter phase is involved in this process (Kausar, 2018). The adsorbent exists as liquid in this experiment. Adsorption can be classified into two types which are chemical or physical adsorption. Chemical adsorption occurs due to the exchange of electrons, adsorbate is chemically bounded to the surface whereas, in latter procedure waste matter is attached with adsorbent surface by physical forces as for instance, hydrogen bonding, polarity, Van der Waals forces and dipole-dipole interactions. However, the extent of adsorption depends upon adsorbent nature like molecular size, molecular structure, molecular weight, solution concentration, polarity and on adsorbent surface properties such as surface area and particle size.

### **2.3 Activated carbon as adsorbent**

Activated carbon has good capacity for sorption as it is highly porous that has complex structure composed of carbon atoms and carbonaceous. This activated carbon has many networks of pores that are channels created within rigid skeleton of disordered layers of carbon atoms, linked together by chemical bonds, stacked unevenly, creating highly porous structure of nooks, crannies, cracks, crevices and between the carbon layers (Mezohegyi et al., 2012). Carbon is being used as a potential adsorbent because of its high efficiency. Commercially available activated carbons are usually derived from coal which is considered expensive. Therefore, alternative adsorbents with an equivalent potential of activated carbon are the current thrust area of research. Alongside with that, low-cost activated carbons based on agricultural wastes are being investigated for the use of the future. Activated carbon can be utilized in this area of research by activating the

raw materials with the aid of carbon dioxide gas, CO<sub>2</sub>, so that the pores can adsorb the dyes in the effluent waste water.

#### **2.4 Jackfruit seed**

Jackfruit (*Artocarpus heterophyllus*) seed has a great potential as source of activated carbon due to its abundance in Malaysia. It is widely known for contribution to the value of agricultural production in Malaysia. In 2008, the production value of jackfruit reached RM61,519,278 with a production of 26,748 tonnes valued at RM2.29 per kg. In 2010, the states which recorded the highest production values were Selangor (RM11,157,750) and Sabah (RM10,198,350) (Ismail, 2013). There are many benefits of consuming jackfruit seed that makes it well known among those in our country. Some of the benefits are, promotes hair growth, helps in digestion, has anti-cancer nutrients, fights wrinkles and many more. Although jackfruit seed can be boiled and eaten for consumption, generally the seed is thrown away as waste. Thus, to reduce the amount of waste of jackfruit seed, it can be converted into activated carbon. By practicing this, the cost of activated carbon in market can be lowered whereas waste generation can be reduced which is beneficial to our environment.

#### **2.5 Microwave heating or irradiation**

Application of microwave heating technology for regenerating industrial waste activated carbon has been investigated with very promising results. The main difference between microwave devices and conventional heating systems is in the way of heating as show in Figure 2.1. For microwave heating, the microwaves supply energy directly to the carbon bed. Energy transfer is not by conduction or convection as in conventional heating,

but microwave energy is readily transformed heat into inside the particles by dipole rotation and ionic conduction.

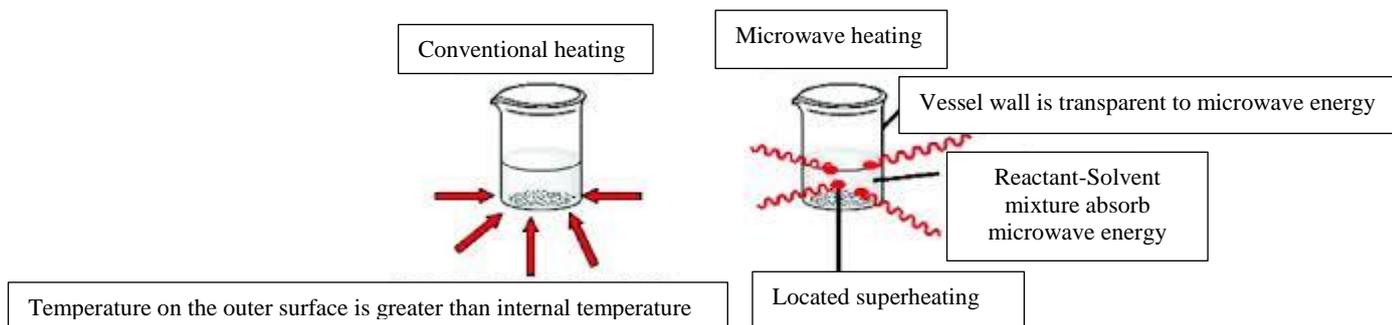


Figure 2.1: Difference between microwave and conventional heating (Nyokong, 2012)

When high frequency voltages are applied to a material, the response of the molecules with a permanent dipole moment or induced dipole to the applied potential field is to change their orientation in the direction opposite to that of the applied field. The synchronized agitation of molecules then generates heat (Makeswari, 2013). Recently, microwave energy has been widely using in several fields of applications on both research and industrial processes. Although the use of microwave energy changes the properties of carbonaceous materials very much, there are relatively few publications that describe the use of microwaves for producing activated carbons. Microwave irradiation advantages include the rapid and precise control of the carbon bed temperature, a more compact furnace, and energy saving heating method.

## 2.6 Adsorption Isotherms

Adsorption isotherm is an invaluable curve describing the phenomenon conquering the retention or movement of a substance from the aqueous porous media or aquatic environments to a solid-phase at a constant temperature and pH. The ratio

between the adsorbed amount with the remaining in the solution is established when an adsorbate containing phase has been contacted with the adsorbent for sufficient time, with its adsorbate concentration in the bulk solution is in a dynamic balance with the interface concentration. There are various adsorption isotherms but only three adsorption isotherms namely Langmuir, Freundlich and Temkin will be studied in this research. Linear regression is used to determine the best-fit isotherm and the correlation coefficient,  $R^2$  is judged to compare if the isotherm is feasible.

### 2.6.1 Langmuir Isotherm

Langmuir adsorption isotherm is to describe gas–solid-phase adsorption onto activated carbon, has traditionally been used to quantify and contrast the performance of different bio-based adsorbents. In its formulation, this empirical model assumes monolayer adsorption, with adsorption can only occur at a finite number of definite localized sites, that are identical and equivalent, with no lateral interaction and steric hindrance between the adsorbed molecules, even on adjacent sites. In its derivation, Langmuir isotherm refers to homogeneous adsorption, which each molecule possesses constant enthalpies and sorption activation energy. Theoretically, Langmuir model can be expressed as (Langmuir, 1918):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2.1)$$

which can be further rearranged to:

$$\frac{C_e}{q} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (2.2)$$

where,

$C_e$  = Equilibrium concentration of adsorbate (mg/L),

$q_e$  = Amount of adsorbate adsorbed at equilibrium (mg/g),

$q_m$  = Monolayer adsorption capacity of the adsorbent (mg/g),

$K_L$  = Langmuir adsorption constant (L/mg).

Therefore, a graph plot of  $C_e/q_e$  against  $C_e$  gives a straight line with the slope of  $1/q_m$  and intercept of  $1/K_L q_m$ . The adsorption coefficient can be determined from the slope and intercept of the straight line.

### 2.6.2 Freundlich Isotherm

Freundlich isotherm relates the non-ideal and reversible adsorption, not restricted to the formation of monolayer. This empirical model can be applied to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface. The gradient varies between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. Whereas, a value below unity implies chemisorptions process where  $1/n$  above one is an indicative of cooperative adsorption. This isotherm can be expressed as follows (Freundlich, 1906):

$$q_e = K_F C_e^{1/n_F} \quad (2.3)$$

which can be further rearranged to:

$$\ln q_e = (1/n_F) \ln C_e + \ln K_F \quad (2.4)$$

where,

$q_e$  = Amount of adsorbate adsorbed per unit mass of adsorbent (mg/g),

$1/n_F$  = Adsorption intensity,

$C_e$  = Equilibrium concentration of the adsorbate (mg/L),

$K_F$  = Freundlich isotherm constant (mg/g (L/mg)<sup>1/n</sup>).

Therefore, a graph of  $\ln q_e$  against  $\ln C_e$  gives a straight line with the slope of  $1/n_F$  and intercept of  $\ln K_F$ . From the slope of graph, the value of  $1/n_F$  measures the adsorption intensity or surface heterogeneity. Additionally, from the intercept of graph, the value of  $K_F$  can be determined. Generally,  $K_F$  is a constant related to the bonding energy of a system. It is the adsorption or distribution coefficient that represents the quantity of dye adsorbed onto adsorbents for a unit of equilibrium concentration.

### 2.6.3 Temkin Isotherm

Temkin isotherm is the early model describing the adsorption of hydrogen onto platinum electrodes within the acidic solutions. The isotherm contains a factor that explicitly taking into the account of adsorbent–adsorbate interactions. By ignoring the extremely low and large value of concentrations, the model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage. As implied in the equation, its derivation is characterized by a uniform distribution of binding energies (up to some maximum binding energy). Temkin equation is excellent for predicting the gas phase equilibrium, conversely complex adsorption systems including the liquid-phase adsorption isotherms are usually not appropriate to be represented. The theory of this isotherm is expressed as below (Temkin, 1940):

$$q_e = \left(\frac{RT}{b}\right) \ln(AtC_e) \quad (2.5)$$

which can be further rearranged to:

$$q_e = B \ln C_e + B \ln A_t \quad (2.6)$$

where,

$q_e$  = Amount of adsorbate adsorbed at equilibrium (mg/g),

$R$  = Universal gas constant (8.314 J/mol K),

$T$  = Absolute temperature (K),

$A_t$  = Equilibrium binding constant (L/mg),

$C_e$  = Equilibrium concentration of adsorbate (mg/L),

$B = RT/b$  = Constant related to the heat of adsorption (L/mg).

Therefore, a graph of  $q_e$  versus  $\ln C_e$  gives a straight line with the slope of  $B$  and intercept of  $B \ln A_t$ .

## 2.7 Adsorption kinetics

Kinetic study is crucial as it provides important information on the reaction pathways as well as the mechanism of the reaction. It is applied to examine the controlling mechanism of dye adsorption from aqueous solution (Vijayakumar 2012). In this study, two kinetic models are used which includes the pseudo-first-order and pseudo-second-order models.

### 2.7.1 Pseudo first-order model

Pseudo-first-order model is used to describe adsorption rate based on adsorption capacity and its differential equation can be expressed as:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad (2.7)$$

where,

$q_t$  = Amount of adsorbate adsorbed at time  $t$  (mg/g),

$k_1$  = Pseudo-first-order rate constant of adsorption (1/hr),

$q_e$  = Amount of adsorbate adsorbed at equilibrium (mg/g).

By integrating the above equation with boundary layer condition of  $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = q_t$ , a linear equation can be obtained as below:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2.8)$$

A graph of  $\ln (q_e - q_t)$  against  $t$  gives a straight line with the slope of  $-k_1$  and intercept of  $\ln q_e$ . This model assumes that the rate of change of solute uptake with time is directly proportional to the difference in saturation concentration and the amount of solid uptake with time.

### 2.7.2 Pseudo second-order model

Pseudo-second-order model is based on the adsorption capacity onto a solid phase, which is used to predict the behaviour over the entire observed range. It involves the valance forces through sharing or exchange of electrons during the adsorption process (Ho, 1999).

The differential equation can be expressed as:

$$\frac{dq_t}{dt} = k_2 (q_e - q)^2 \quad (2.9)$$

where,

$q_t$  = Amount of adsorbate adsorbed at time  $t$  (mg/g),

$k_2$ =Pseudo-second-order rate constant of adsorption (g/mg.h),

$q_e$  = Amount of adsorbate adsorbed at equilibrium (mg/g).

which can then be further rearranged to:

$$\frac{dq_t}{(q_e - q_t)^2} = k_2 dt \quad (2.10)$$

By integrating the above equation with boundary layer condition of  $t = 0$  to  $t = t$  and

$q_t = 0$  to  $q_t = q_t$ , a linear equation can be obtained as below:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2.11)$$

A graph of  $t/q_t$  against  $t$  gives a straight line with the slope of  $1/q_e$  and intercept of  $1/k_2 q_e^2$ .

## 2.8 Adsorption mechanism

Adsorption diffusion mechanism is made up by three stages namely film diffusion, followed by intra-particle diffusion and ended up with sorption of adsorbate molecules. Film diffusion or the first stage in adsorption mechanism starts with the transfer of bulk adsorbate across the external boundary liquid film surrounding outside the surface of adsorbent. Small amount of adsorbate molecules attaches to the exterior surface of adsorbent.

The intra-particle diffusion or referred as second stage of the adsorption process involves the adsorbate molecules to diffuse within the interior of the pores into adsorption site of adsorbent either by pore diffusion or solid surface diffusion mechanism.

Intraparticle stage is assumed to be a very rapid reaction. The final stage in adsorption process associated with the sorption mechanism of adsorbate molecules onto the active sites of adsorbent. If the external transport larger than internal transport, then the rate limiting step is intraparticle diffusion whereas if internal transport is larger than external transport, then the reaction is controlled by film diffusion. The kinetic models only consider the third stage in adsorption mechanism which is the part where sorption of adsorbate molecules is taking place on active sites of adsorbent.

Weber's intraparticle diffusion model is an empirical function that give an insight and explain the diffusion mechanism in adsorption process. As the name suggest, this model assumes that intraparticle diffusion is the rate limiting step of the adsorption process and is given as follows (Weber Jr.W.J, 1963):

$$q_t = K_p t^{0.5} + C \quad (2.12)$$

where,

$q_t$  = amount of adsorbate adsorbed at time t (mg/g)

$C$  = constant related to boundary layer thickness

$K_p$  = intraparticle diffusion rate constant (mg/g.h<sup>1/2</sup>)

A plot of  $q_t$  against  $t^{1/2}$  forms a straight line which indicates the existence of intraparticle diffusion. If the straight line passing through the origin, then the rate limiting step is confirmed to be controlled by intraparticle diffusion.

## 2.9 Adsorption thermodynamic

Thermodynamic parameters are used to indicate the energy transformation in an adsorption process. It is assumed that entropy change is the driving force in an isolated system. In this study, three thermodynamic parameters are evaluated to characterize the adsorption process due to the transfer unit mole of solute from solution onto the solid-liquid interface. They are, standard enthalpy change ( $\Delta H^\circ$ ), standard entropy change ( $\Delta S^\circ$ ), and standard free energy change ( $\Delta G^\circ$ ). These variables can be calculated as below:

$$\ln k_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (2.13)$$

where,

$k_L$  = Langmuir adsorption constant (L/g),

$\Delta S^\circ$  = Changes in standard entropy (kJ/mol K),

$R$  = Universal gas constant (8.314 J/mol K),

$\Delta H^\circ$  = Changes in standard enthalpy (kJ/mol),

$T$  = Absolute solution temperature (K).

Therefore, by plotting a graph of  $\ln k_d$  against  $1/T$ , the values of both  $\Delta H^\circ$  and  $\Delta S^\circ$  from the slope and intercept of the graph can be determined. Fundamentally, a positive  $\Delta H^\circ$  value indicates that an adsorption process is endothermic in nature while a negative value represents endothermic reaction. As for  $\Delta S^\circ$ , a positive value shows the increment in randomness at the solid/solution interface that occurs in the adsorption process besides reflecting the affinity of the adsorbent toward the adsorbate (Bello et al., 2014).

Additionally, the change in standard Gibbs energy,  $\Delta G^\circ$  can be calculated using the following relation with a negative  $\Delta G^\circ$  value indicates that an adsorption process is a spontaneous process at the study temperature and vice versa.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (2.14)$$

As the nature of adsorption is determined by the magnitude of activation energy,  $E_a$ , Arrhenius equation has been applied to determine either the process is physical or chemical. As shown in the following relationship, Arrhenius equation can be represented by:

$$\ln k_2 = \ln A - \frac{E_a}{RT} \quad (2.15)$$

where,

$k_2$  = Rate constant obtained from pseudo-second-order kinetic model (g/mg h)

A = Arrhenius factor,

$E_a$  = Arrhenius activation energy of adsorption (kJ/mol),

R = Universal gas constant (8.314 J/mol K),

T = Absolute temperature (K).

Therefore, by plotting a graph of  $\ln k_2$  against  $1/T$ , the values of  $E_a$  can be obtained from the slope of the graph. . Likewise, for thermodynamics study, the standard enthalpy,  $\Delta H^\circ$ , standard entropy,  $\Delta S^\circ$  and standard free energy,  $\Delta G^\circ$  were calculated based on the adsorption data. The value of  $\Delta H^\circ$  and  $\Delta S^\circ$  were determined by plotting Van't Hoff graph. Meanwhile, the standard Gibbs energy,  $\Delta G^\circ$  was calculated using Equation 2.16 while the Arrhenius activation energy,  $E_a$  was determined by plotting a graph of  $\ln k_2$  against  $1/T$ . With this, the effect of initial dye concentration, contact time, and solution temperature on the adsorption uptake rate were investigated.

$$\Delta G^\circ = -RT \ln K_e \quad (2.16)$$

$$K_e = \frac{qe}{c_e} \quad (2.17)$$

$$\ln K_e = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (2.18)$$

## CHAPTER THREE

### MATERIALS & METHODOLOGY

#### 3.1 Materials

Jackfruit seed (JS) was used to prepare JSAC. JS was obtained from night market in Nibong Tebal, Penang, Malaysia. MB dye as the adsorbate was supplied by Sigma-Aldrich (M) Sdn. Bhd., Malaysia. MB characteristics are summarized in Table 3.1.

Table 3.1: Properties of methylene blue (MB) dye

<b>Properties</b>	
<b>Common name</b>	Methylene blue (MB)
<b>IUPAC name</b>	3,7-bis(Dimethylamino) phenazathionium chloride
<b>Other name</b>	Basic Blue 9, Tetramethylthionine chloride
<b>Molecular formula</b>	C <sub>16</sub> H <sub>18</sub> ClN <sub>3</sub> S
<b>Molecular weight</b>	373.90 g/mol
<b>CAS number</b>	7220-79-3
<b>Maximum wavelength, λ</b>	668 nm
<b>Chemical structure</b>	

For the carbonization of JS, nitrogen gas, N<sub>2</sub> (MOX Gases Berhad, Malaysia) of 99.99% purity was allowed to pass through the pipeline to create an inert atmosphere

whereas carbon dioxide gas, CO<sub>2</sub> (MOX Gases Berhad, Malaysia) with a purity of 98.00% was used to help to activate the carbonized seed.

### 3.2 Design of Experiment

Response Surface Methodology (RSM) design also known as central composite design (CCD) was used to study the parameters prior preparing the JSAC. Parameters involved were X<sub>1</sub>, microwave power (W) and X<sub>2</sub>, activation time (min) with Y<sub>1</sub>, MB removal as the response. Table 3.2 shows the ranges and levels of the variables studied whereas Table 3.3 reflects the complete design matrix of the experiments employed. Based on Equation 3.1, 13 runs of experiment which consists of 4 factorial points, 4 axial points and 5 replicates at the centre point were applied.

$$N = 2n + 2n + n_c \quad (3.1)$$

where, N= total number of experiments required, and n is the number of factors.

Two levels which are known as low and upper limit, they were coded as -1 and +1. The center points were used to determine the experimental error and the reproducibility of the data. The response was used to develop an empirical model which correlated the response to the variables by using a second-degree polynomial equation as shown below:

$$Y = b_0 + \sum b_i x_i + (\sum b_{ij} x_i x_j) \quad (3.2)$$

where  $Y$  represents the predicted response,  $b_0$  the constant coefficient,  $b_i$  the linear coefficients,  $b_{ij}$  the quadratic coefficients and  $x_i$ ,  $x_j$  are the coded values of the activated carbon preparation variables. For all responses to be interrelated, Design Expert software version 7.1.5 (STAT-EASE Inc., Minneapolis, USA) was used to analyze the experimental condition with the highest desirability. The models were evaluated based on the correlation coefficients,  $R_2$ .

Table 3.2: Variable and coded levels of CCD

Factors	Coded variable level				
	-alpha	-1	0	+1	+alpha
Radiation power(W)	264	264	440	616	616
Activation time (min)	4	4	5	6	6

Table 3.3: Experimental design parameters according to CCD

Run	JSAC preparation operating conditions	
	Microwave power, X <sub>1</sub> (W)	Activation time, X <sub>2</sub> (min)
1	440	5
2	616	6
3	264	6
4	440	5
5	264	5
6	616	4
7	264	4
8	440	5
9	440	5
10	440	5
11	440	4
12	616	5
13	440	6

### 3.3 Experimental Methodology

#### 3.3.1 Preparation of JSAC

JS was washed and dried to remove any impurities and organic matters on its surfaces. The dried sample was cut into smaller size of 2cm. Carbonization of the sample was done by heating 500g of sample in the furnace as shown in Figure 3.1 at temperature of 350°C of heating rate 30°C/min for 30 minutes. The product which is known as char was then placed in a microwave oven as shown in Figure 3.2 at targeted radiation power

and activation time under CO<sub>2</sub> flow rate of 150 cm<sup>3</sup>/min. The sample was then cooled to room temperature under nitrogen flow and stored for characterization and adsorption study.



Figure 3.1:Furnace for carbonization process



Figure 3.2:Activation of char using microwave

### 3.3.2 Preparation of dye and stock solutions

1000 mg/L of dye solution was prepared by dissolving 1 g of methylene blue (MB) dye in 1000 ml of deionized water. A range of dilutions, ranging from 25 to 300 mg/L were then prepared by using deionized water.

### 3.3.3 Dye concentration

A double-beam UV-Visible spectrometer (Model Shimadzu UV-1800, Japan) as shown in Figure 3.3 was utilized to measure the concentration of dye solution. The wavelength of MB was set at 668 nm. For homogeneity of adsorbent readings to be obtained, calibration curve was plotted for MB dye by plotting a graph of absorbance against concentration of dye solution. It was done by diluting the concentrated dye solution into a series of known concentration and measured by using UV-Vis spectrophotometer.



Figure 3.3: UV-Visible spectrometer

### 3.3.4 Batch adsorption system

The adsorption tests were then performed in a set of Erlenmeyer flasks (250ml). 0.20 g of the prepared JSAC was added into each flask filled with 200 ml of the prepared dye solutions. Six different dye concentrations of 25, 50, 100, 200, 250 and 300 mg/L were prepared by mixing a known amount of dye with deionized water. Following that, the Erlenmeyer flasks were sealed with aluminium foil and placed in the isothermal water bath shaker as shown in Figure 3.4 at a speed of 60 rpm and 30°C for 24 hours.



Figure 3.4: Water bath shaker

By using 3 ml of disposable syringe, the sample was collected at every time interval. The respective dye concentration was determined by using UV-visible spectrometer. For MB dye, the wavelength was set at 668 nm. The linear relationship between absorbance of the dyes onto JSAC and concentration was plotted in graph of absorbance versus concentration of the dye solutions.

### 3.3.5 Batch equilibrium, kinetics and thermodynamics studies

The batch equilibrium tests were conducted for adsorption of MB on JSAC prepared. 0.20 g of JSAC was added into a series of Erlenmeyer flask filled with 200 ml of dye solutions with different initial concentrations. The Erlenmeyer flasks were then sealed and placed in the isothermal water bath shaker at 30°C with agitation speed of 60 rpm. According to every fixed time interval, the aqueous samples were then withdrawn, and the concentrations were measured using UV-Vis spectrometer based on the wavelength of maximum adsorption. These measurement steps were repeated until a steady state is reached. For equilibrium studies, the amount of adsorption at equilibrium,  $q_e$  were determined by using the following equation:

$$q_e = \frac{(C_o - C_e)V}{w} \quad (3.3)$$