

**PREPARATION OF ACTIVATED CARBON FROM BAMBOO  
STEM USING MICROWAVE IRRADIATION FOR METHYLENE  
BLUE DYE REMOVAL FROM AQUEOUS SOLUTION**

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BLUE DYE REMOVAL FROM AQUEOUS SOLUTION**

**by**

**NAVENPRASATH A/L SANDRASEGARAN**

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## LIST OF SYMBOLS

	Symbol	Unit
<i>A</i>	Arrhenius factor	-
<i>B<sub>T</sub></i>	Constant for Temkin equation	-
<i>C</i>	Boundary layer	-
<i>C<sub>e</sub></i>	Equilibrium concentration of adsorbate	mg/L
<i>C<sub>o</sub></i>	Highest initial adsorbate concentration	mg/L
<i>C<sub>t</sub></i>	Dye concentration at time, t	mg/L
<i>E</i>	Mean free energy	J/mol
<i>E<sub>a</sub></i>	Arrhenius activation energy of adsorption	kJ/mol
<i>k<sub>1</sub></i>	Adsorption rate constant for pseudo first-order kinetic	1/hr
<i>k<sub>2</sub></i>	Adsorption rate constant for pseudo second-order	g/mg.hr
<i>K<sub>F</sub></i>	Freundlich isotherm constant	mg/g ( $\frac{L}{mg}$ ) <sup>1/n</sup>
<i>K<sub>L</sub></i>	Langmuir adsorption constant	L/mg
<i>n<sub>f</sub></i>	Constant for Freundlich isotherm	-
<i>q<sub>e</sub></i>	Amount of adsorbate adsorbed at equilibrium	mg/g
<i>q<sub>m</sub></i>	Adsorption capacity of Langmuir isotherm	mg/g
<i>q<sub>t</sub></i>	Amount of adsorbate adsorbed at time, t	mg/g
<i>R</i>	Universal gas constant	8.314 J/mol.K
<i>R<sup>2</sup></i>	Correlation coefficient	-
<i>R<sub>L</sub></i>	Separation factor	-
<i>T</i>	Time	min

$T$	Absolute temperature	K
$V$	Solution volume	L
$\Delta G^\circ$	Changes in standard Gibbs free energy	kJ/mol
$\Delta H^\circ$	Changes in standard enthalpy	kJ/mol
$\Delta S^\circ$	Changes in standard entropy	kJ/mol
$\lambda$	Wavelength	nm

## LIST OF ABBREVIATIONS

AC	Activated carbon
BET	Brunauer-Emmett-Teller
CCD	Central composite design
FTIR	Fourier Transform Infrared
BS	Bamboo stem
BSAC	Bamboo stem activated carbon
MB	Methylene blue
rpm	Rotation per minute
SEM	Scanning electron microscopy
UV	Ultraviolet

**PENYEDIAAN KARBON TERAKTIF TERHASIL DARIPADA BATANG BULUH  
YANG DIBANTU OLEH GELOMBANG MIKRO UNTUK PENJERAPAN  
PEWARNA METILENA BIRU**

**ABSTRAK**

Proses kelompok telah digunakan untuk menyiasat penjerapan pewarna metilena biru (MB) dengan karbon teraktif berasaskan batang buluh (BBKK). Bagi menyediakan BBKK, batang buluh (BB) 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 440 W dan 6.00 minit yang menghasilkan 88.27% penyingkiran MB. Sampel optimum ini mempunyai luas permukaan (636.48 m<sup>2</sup>/g), isipadu liang (0.4558 cm<sup>2</sup>/g) dan kandungan karbon tetap (75.34%) yang tinggi. Liang BBKK adalah jenis mesolintang dengan purata diameter liang 2.75nm. 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 penjerapan oleh BBKK MB adalah terbaik dipadankan dengan model Langmuir yang mempunyai kapasiti penyerapan maksimum sehingga 222.22 mg/g. Sementara itu, data kinetik terbaik diwakili oleh model pseudo tertib kedua. Proses penjerapan MB ke BBKK adalah endotermik dan berlaku secara spontan.

# **PREPARATION OF ACTIVATED CARBON FROM BAMBOO STEM USING MICROWAVE IRRADIATION FOR METHYLENE BLUE DYE REMOVAL FROM AQUEOUS SOLUTION**

## **ABSTRACT**

A batch process was used to investigate the adsorption of the methylene blue (MB) dye onto bamboo stem based activated carbon (BSAC). In order to prepare the BSAC, bamboo stem (BS) undergoes physical activation process which involves microwave irradiation and carbon dioxide (CO<sub>2</sub>) gasification. By using response surface methodology (RSM), the optimum preparation conditions were obtained at microwave power and activation time of 440 W and 6.00 minutes respectively which resulted 88.27% MB removal. The optimized sample has high surface area (636.48 m<sup>2</sup>/g), pore volume (0.4558 cm<sup>3</sup>/g) and fixed carbon content (75.34%). The pore of BSAC was mesoporous type with average pore diameter of 2.75nm. The effect of initial dye concentration (25-300 mg/L), contact time (0-24 hours) and solution temperature (30-60° C) were also evaluated through. The obtained equilibrium data for MB adsorption by BSAC dye was best fitted by Langmuir model with monolayer maximum adsorption capacity of 222.22 mg/g. Meanwhile, the kinetics data was best represented by the pseudo second-order model. The adsorption process of MB onto BSAC was endothermic and spontaneous process.

# CHAPTER ONE

## INTRODUCTION

### 1.1 Research Background

In this modern and advanced era, environmental pollution is a major problem that needs a serious attention worldwide. Environmental pollution has reached a critical stage where this problem should be seriously examined and find the solutions to overcome it. However, among the various types of pollution, water pollution has attracted the attention of most of the researchers. One of the main sources of water contamination are the effluent from textile industries. These effluents consist of dye residues which eventually pollute the water and leads to serious effects (Pathania et al., 2017).

Currently, there are about 10,000 different commercial dyes exist and over  $7 \times 10^5$  tones of synthetic dyes are produced annually worldwide. It is estimated that 10–15% of the dyes are lost in the effluent during the dyeing processes. Exposure to these dyes can cause increased heart rate, vomiting, shock, cyanosis, jaundice and tissue necrosis for humans due to its mutagenic and carcinogenic characteristics (Hameed and Ahmad, 2009).

Among the dye treatment process, the adsorption process remains the most effective process. This process is preferred because of its universal nature, inexpensiveness, ease of operation, flexibility, insensitivity to toxic pollutants, as well as high efficiency and effectiveness. Moreover, adsorption can also remove soluble and insoluble organic pollutants without the generation of hazardous by-products. Adsorption is the phenomenon of accumulation of large number of molecular species at the surface of liquid or solid phase in comparison to the bulk. There are two types of adsorption which are physical and chemical adsorption. Agriculture waste can be used as precursor for production of activated carbon



thus providing life cycle assessment of the waste instead of being dumped away unnecessarily (Yagub et al., 2014).

For this study, activated carbon is produced from bamboo stem (BS) for MB dye removal. Activated carbon has a large surface area and total pore volume where adsorption takes place.

## **1.2 Problem Statement**

The conventional methods for coloured wastewater treatment are physical, chemical and biological treatments. Each of the methods has their own advantages and disadvantages. Most of these methods are not applicable due to high cost and disposal problems. The major drawback of chemical treatment is the price of chemicals used for coagulation and flocculation is expensive. Even though biological treatment is cheaper than chemical method, it requires additional land area for the method to take place. Meanwhile, physical treatment such as membrane filtration is limited life time and high cost of membrane replacement is needed. However, adsorption technique has been found to be superior compared to other physical and chemical methods for dyes removal in terms of its applicability at very low concentration, suitability for batch and continuous processes, ease of operation, possibility of regeneration and reuse and low capital cost (Yagub et al., 2014).

Activated carbon (AC) is known as the highly preferred adsorbent especially its precursor is from cheap and renewable material such as agrowaste. Thus, an attempt was made using bamboo stem waste as precursor of activated carbon production. According to research, in 1970, the estimated total area of bamboos in Peninsular Malaysia was about 20 000 ha and in 1994 the total area has increased to about 421 722 ha (Mohamed, 1999). Bamboo stem based activated carbon (BSAC) is produced through microwave heating along

with CO<sub>2</sub> gasification. Bamboo stem commonly known widely for contribution to the value of agricultural production in Malaysia. This study was conducted to explore the potential use of BS waste to remove MB dye from aqueous solution.

### **1.3 Research Objectives**

The main objectives of this study are:

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

#### **1.4 Scope of Study**

In this study, preparation of BSAC applies CO<sub>2</sub> as activation agent and microwave irradiation as the heat source. The optimization of the operating parameters such as microwave power and activation time was done using response surface methodology (RSM) method. The BSAC was used in equilibrium, kinetic and thermodynamic adsorption studies using MB dye as adsorbate in batch system. The effect of MB initial concentration (25-300 mg/l), contact time (0-24 hour) and solution temperature (30-60°C) for MB adsorption onto BSAC were investigated. The BS and BSAC were characterized for their surface area, proximate analysis, elemental analysis and surface morphology.

## CHAPTER TWO

### LITERATURE REVIEW

#### 2.1 Dyes

Dye is considered to be a chemical substance that consists of its own colouring material. Due to its affinity towards the substrate to which it is applied, dye is widely known as an ionising and aromatic organic compound. Generally, it requires a mordant to increase the attraction of the dye on the material. It is broadly used in several industries such as plastics, paper, textiles, cosmetics, food and many more.

Dyes can be divided into two categories which is natural dye and synthetic dye. Natural dye is derived from plant sources such as roots, wood, leaves and bark. On the other hand, synthetic dye is manufactured from combination of petroleum and mineral-derived components (Tan et al., 2007). The manufacture of synthetic dye is performing commercially better than natural dyes. Different types of dyes are shown in Table 2.1.

Table 2.1 : Types of dyes

<b>Type</b>	<b>Characteristics/Properties</b>	<b>Materials</b>
Acid	Water-soluble anionic	Silk/wool/nylon
Basic	Water-soluble cationic	Acrylic fibres
Direct/substantive	Carried out in neutral/ slightly alkaline dye bath	Cotton/paper/leather/ silk/nylon
Mordant	Require a mordant	Wool
Vat	Insoluble in water	Textile fibre
Reactive	Use a chromophore	Cotton/Cellulose fibre
Disperse	Water-insoluble	Cellulose acetate
Sulfur	Inexpensive	Cotton

Dyeing industry is one of the biggest water consuming industry which effluents released still contain residues of dyes. Discharge of dyes effluent into the surroundings without proper treatment can lead to many serious problems such as high chemical oxygen demand (COD) and high toxicity. It can lower the light penetration into the water bodies and damage the aesthetic nature of the water surface. It can may cause allergic dermatitis, skin irritation, dysfunction of kidney, liver, brain, reproductive and central nervous system (Rafatullah et al., 2010). Along with this serious environmental issue, there have been great measures to treat dye effluent especially by using adsorption process.

## **2.2 Adsorption**

Adsorption is the phenomenon of accumulation of large number of molecular species at the surface of liquid or solid phase in comparison to the bulk. The process of adsorption arises due to presence of unbalanced or residual forces at the surface of liquid or solid phase. These unbalanced residual forces have tendency to attract and retain the molecular species with which it comes in contact with the surface. Adsorption is essentially a surface phenomenon. Adsorption process involves two components adsorbent and adsorbate. Adsorbent is the substance on the surface of which adsorption takes place. Adsorbate is the substance which is being adsorbed on the surface of adsorbent (Bansal and Goyal, 2005).

Adsorption can be classified into two types which are chemical and physical adsorption. When the force of attraction existing between adsorbate and adsorbent are weak Vander Waal forces of attraction, the process is called physical adsorption. Physical adsorption takes place with formation of multilayer of adsorbate on adsorbent. On the other hand, when the force of attraction existing between adsorbate and adsorbent are chemical forces of attraction or chemical bond, the process is called chemical Adsorption or

chemisorption. Chemisorption takes place with formation of uni-layer of adsorbate on adsorbent.

### **2.3 Activated carbon**

Activated carbon is a material that is produced from carbonaceous source materials, such as coal, coconuts, nutshells, peat, wood and lignite. Activated carbon has an incredibly large surface area ( $> 500 \text{ m}^2/\text{g}$ ) and a network of sub-microscopic pores where adsorption takes place. It is widely used for removal of pollutants in water. The primary raw material used for activated carbon is any organic material with high carbon content. Nonetheless, the activated carbons are different because of the preliminary material and manufacturing methods (Bansal and Goyal, 2005).

Activated carbon use physical adsorption to remove contaminants from liquid or vapour streams. Carbon's large surface area per unit weight allows contaminants to adhere to the activated carbon media. The large internal surface area of carbon has several attractive forces that work to attract other molecules. Physical adsorption occurs because all molecules exert attractive forces, especially molecules at the surface of a solid (pore walls of carbon), and these surface molecules seek to adhere to other molecules. The dissolved adsorbate migrates from the solution through the pore channels to reach the area where the strongest attractive forces are located. Contaminants adsorb because the attraction of the carbon surface for them is stronger than the attractive forces that keep them dissolved in solution. Those compounds that exhibit this preference to adsorb are able to do so when there is enough energy on the surface of the carbon to overcome the energy needed to adsorb the contaminant. Contaminants that are organic, have high molecular weights, and are neutral, or non-polar, in their chemical nature are readily adsorbed on activated carbon. For water adsorbate to become physically adsorbed onto activated carbon, they must both be dissolved

in water so that they are smaller than the size of the carbon pore openings and can pass through the carbon pores and accumulate (Bao and Zhang, 2012).

## **2.4 Bamboo stems AC**

In this study, bamboo stem waste was used as precursor of activated carbon due to its abundance in Malaysia. Malaysia is a heavily forested country and forest products including bamboo are important sources of income. Bamboo is widely, easily available and it has remained a poor man's crop compared to timber and other non-timber crops like rattan. Most of Malaysian bamboos grow gregariously and mainly on river banks, in disturbed lowland forests, and on hillsides. In 1970, the estimated total area of bamboos in Peninsular Malaysia was about 20 000 ha and in 1994 the total area has increased to about 421 722 ha (Mohamed, 1999). The potential growth of the bamboo industry is tremendous due to the wide usage of every part of the bamboo plant. Forest Research Institute Malaysia (FRIM) has given very high priority for bamboo development, both in terms of growth and the manufacturing aspects. There are 12 bamboo species commonly exploited for commercial purposes.

Bamboo stem is a lignocellulosic biomass and can be converted into a beneficial material that can directly maximize the economic potential of this industry. Converting the bamboo stem to the activated carbon is the one of the best opportunities since it is a lignocellulosic material (Tong et al., 1998). Hence, this research focus on the converting of bamboo stem as the raw material for activated carbon that prepared by using the microwave radiation. By practicing this, the cost of activated carbon in market can be reduced which is beneficial to our environment.

## 2.5 Microwave Irradiation

There are some ways to prepare the activated carbon from the raw materials which are by thermal heating method and by using a microwave radiation method. The most common and applicable method is by using the thermal heating method under a controlled atmosphere and temperature. The drawbacks of this method are it required a long preparation time and have a temperature gradient between the surface and the interior of material. Recently, the researchers are tend to use the alternative method to prepare the activated carbon which is microwave radiation method. 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 and regenerating activated carbons (Jacob et al., 1995). Microwave heating technology has been applied to produce activated carbon due to its ability to heat rapidly and uniformly. Moreover, microwave radiation method can be easily handle and control. Differences between microwave heating and thermal heating is shown in Figure 2.1.

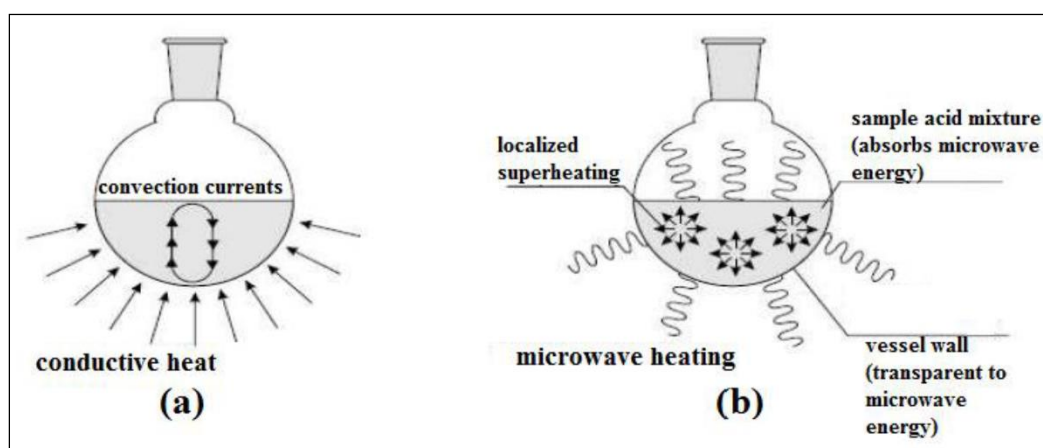


Figure 2.1: Differences between microwave heating and thermal heating

## 2.6 Adsorption Isotherms

At constant temperature, adsorption isotherm strategy is used to describe clearly about the equilibrium relationship between concentration of adsorbate in liquid phase and adsorbent



phase. This adsorption isotherm strategy is usually used to demonstrate the interactions between pollutant and adsorbents. Apart from that, it is also used to express the surface properties and capacities of the adsorbents. The data is suited into different isotherm models so that can establish the most suitable relationship for the equilibrium data in each system. So, three adsorption isotherms which are Langmuir, Freundlich and Temkin were examined. To determine the best-fitting isotherm and the correlation coefficient, the linear regression is used,  $R^2$  is determined in order to compare the appropriateness of isotherm equations.

### 2.6.1 Langmuir Isotherm

The most commonly used isotherm for the adsorption of solute from liquid solution is Langmuir isotherm. In this particular isotherm, a few assumptions have been made such as: (i) it is a monolayer adsorption; (ii) all sites on the adsorbent are identical with equivalent energy; (iii) there is zero interaction between the molecules adsorbed on neighbouring sites; (iv) no further adsorption can take place once a particular site is occupied by a molecule and (v) adsorption energy does not depend on the degree of occupation of an adsorbent's active sites (Chung et al., 2015). Theoretically, Langmuir model can be expressed as:

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

which can be further rearranged to:

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

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 of  $C_e/q_e$  against  $C_e$  is plotted and obtained 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 chemisorption process where  $1/n$  above one is an indicative of cooperative adsorption (Chung et al., 2015). This isotherm can be expressed as follows:

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

which can be further rearranged to:

$$\ln q_e = \frac{1}{n_F} \ln C_e + \ln K_F \quad (2.4)$$

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

By using Temkin isotherm, it is assumed that due to the indirect interactions between adsorbate and adsorbent, so the heat of adsorption decreases linearly rather than logarithmic. The heat of adsorption of all molecules in each layer decreases linearly with coverage. Temkin model gives even higher equilibrium constants when compared with Langmuir parameters (Tan et al., 2007). Theoretically, Temkin model can be expressed as:

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

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  $\ln C_e$  is plotted and it gives a straight line. Moreover, the slope of  $B$  and intercept of  $B \ln A_t$  are obtained from the same graph.

## 2.7 Adsorption Kinetics

Kinetic study is vital as it gives a lot of significant information on the reaction pathways and the mechanism of the reaction. Moreover, this kinetic study relates the relationship between adsorption rate and concentration of adsorbate in the solution. In addition, it also can be used to determine how the adsorption capacity and adsorbent affect the adsorption rate in terms of kinetics. Two kinetic models are used in this study which are the pseudo first-order and pseudo-second-order models (El Nemr et al., 2009).

### 2.7.1 Pseudo first-order-model

To describe adsorption rate based on adsorption capacity, Pseudo-first-order model is used 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  $t$  is plotted and gives a straight line with the slope of  $-k_1$  and intercept of  $\ln q_e$ . This particular 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

The adsorption capacity onto a solid phase depends on the pseudo-second-order model. It is used to determine the behaviour over the entire observed range. This model uses the valance forces through sharing or exchange of electrons during the adsorption process. 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. They are film diffusion, intraparticle diffusion and sorption of adsorbate molecules. Film diffusion or known as 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 outer surface of adsorbent.

Secondly, the intra-particle diffusion involves the adsorbate molecules to diffuse within the interior of the pores into adsorption site of adsorbent through pore diffusion or solid surface diffusion mechanism. This 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 intra-particle 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 (Ofomaja, 2008).

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

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

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

The energy transformation in an adsorption process is indicated by using thermodynamic parameters. For an isolated system, the entropy change is the driving force. Three thermodynamic parameters are taken into count in this study, in order to characterize the adsorption process due to the transfer unit mole of solute from solution onto the solid-liquid interface. The three thermodynamic parameters are: (i) standard enthalpy change ( $\Delta H^\circ$ ); (ii) standard entropy change ( $\Delta S^\circ$ ); and (iii) standard free energy change ( $\Delta G^\circ$ ).

The value of  $\Delta H^\circ$  and  $\Delta S^\circ$  can be calculated by using the following equation:

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

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  $\ln k_L$  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 exothermic 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. 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 (Otero et al., 2003).

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

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.

## 2.10 Design of Experiment

The relationship between the different factors affecting a process and the output of that process are determined by using a structured and organized method known as Design of experiment (DoE). This particular method (DoE) helps in designing a set of ten to twenty experiments or more and all related factors are differentiated systematically. Eventually, the



optimal conditions, the factors that most influence the results and those do not, as well as details such as the existence of interactions and collaboration between factors are able to be identified when the results of these experiments are analysed thoroughly.

DoE is an efficient procedure in conducting experiment as it helps in analyse resulted data significantly thus producing a valid objective conclusion in the experiment. Improved process yields, reduced variability and closer conformance to target requirement, reduced development time and reduced overall costs are achieved when DoE techniques are applied in process development. Based on the function and objective of statistical analysis DoE can be further divided into several groups. The most typical design used in the experiment was crossed, factorial, mixture and response surface.

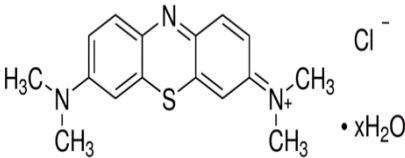
## CHAPTER 3

### MATERIALS AND METHODS

#### 3.1 Materials

Bamboo stem (BS) was used as the precursor for the preparation of BSAC. This raw material was obtained from Ladang Padang Meiha, Kuala Ketil, Kedah. The adsorbate that was used in this experiment is Methylene blue (MB) and it was supplied by Sigma-Aldrich (M) Sdn. Bhd, Malaysia. The properties of MB are shown below in Table 3.1.

Table 3.1: Properties of Methylene Blue (MB)

<b>Properties</b>	
Common name	Methylene Blue (MB)
IUPAC name	3,7-Bis(dimethylamino)phenothiazine-5-ium-chloride
Other name	<ul style="list-style-type: none"><li>• Tetramethylthionine chloride</li><li>• Basic Blue 9</li></ul>
Molecular formula	$C_{16}H_{18}ClN_3S \cdot 3H_2O$
Molecular weight	373.90 g/mol
CAS number	7220-79-3
Maximum wavelength	663 nm
Chemical structure	 <chem>CN(C)c1ccc2c(c1)nc3ccc(N(C)C)cc3s2.[Cl-].xO</chem>

During the carbonization of BS process, nitrogen gas,  $N_2$  (MOX Gases Berhad, Malaysia) of 99.99% purity was allowed to pass through the pipeline to create an inert

atmosphere. On the other hand, carbon dioxide gas, CO<sub>2</sub> (MOX Gases Berhad, Malaysia) with a purity of 98.00% was utilized to activate the carbonized BS.

## **3.2 Equipment and Instrumentations**

### **3.2.1 Preparation of BSAC (Carbonization)**

A Carbolite AAF 1100 furnace as shown in Figure 3.1 was used for BSAC preparation. BS was carbonized in the furnace at temperature of 350°C for about 1 hour. This process is carried out to remove water molecules and inorganic matters from the raw material. The maximum operating temperature of this furnace is 1100°C.



Figure 3.1: Carbolite AAF 1100 Furnace

### **3.2.2 Char activation by microwave heating**

Char was activated by using microwave heating as shown in Figure 3.2. The microwave is equipped with a timer (0-35 mins) and power controller (264-616 W) for

different range of readings. Gas flow meter was used to measure the flow rate that was supplied through the teflon tubing. Gas supplied through the tubing for activation is carbon dioxide gas, CO<sub>2</sub>.



Figure 3.2: Char activation via microwave irradiation

### 3.2.3 Characterization system

The surface area, pore volume and average pore diameter of the samples were determined by using Micromeritics ASAP 2020 volumetric adsorption analyzer. The Brunauer-Emmett-Teller (BET) surface area was measured from the adsorption isotherm using BET equation. The total pore volume was estimated to be the liquid volume of nitrogen at a relative pressure of 0.98. The surface morphology of the samples was examined using a scanning electron microscope (LEO SUPRA 55VP, Germany). The proximate analysis was carried out using simultaneous thermal analyzer (Perkin Elmer STA 6000, USA). The sample was capsulated with tin and placed inside the combustion chamber for pyrolysis process at temperature of 975°C. The surface

characteristic of the samples were characterized using a FT-IR spectrometer (IR Prestige 21 Shimadzu, Japan).

### 3.2.4 Dye concentration

A double-beam UV-Visible spectrometer as shown in Figure 3.3 was used to measure the concentration of dye solution. The wavelength of MB was set at 668 nm. In order to make sure the homogeneity of the adsorbent readings, 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: Double-beam UV-Visible spectrometer

### 3.2.5 Fourier Transform Infrared (FTIR) spectroscopy

Chemical characteristics of surface functional group of char or ACs were detected by mixing the BSAC sample in K-Br pellets were recorded with FTIR spectroscope (IR Prestige 21 Shimadzu, Japan) in 400-4000  $1/\text{cm}$  wave number range as shown in Figure 3.4. Prior to analysis, samples were ground to a fine powder and dried at  $105^{\circ}\text{C}$  for 24 hrs. Around 5 mg of carbon sample was pelletized into a thin

pellet (12.7 mm in internal diameter and 1 mm in thickness) using a manual hydraulic press at 10 tones.



Figure 3.4: FTIR spectroscope

### 3.2.6 Batch adsorption system

The adsorption tests were performed in a set of Erlenmeyer flasks (250ml). 0.20 g of the prepared BSAC 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. After that, the Erlenmeyer flasks were sealed with aluminium foil and placed in the isothermal water bath shaker as Figure 3.5 at a speed of 60 rpm and 30°C for 24 hours.



Figure 3.5: Water bath shaker

### 3.3 Optimum Operating Conditions via Design Expert

For an optimum operating condition to be obtained, Response Surface Methodology (RSM) design also known as central composite design (CCD) was used to study the parameters prior preparing the BSAC which were  $X_1$ , microwave power (W) and  $X_2$ , activation time (min).

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 for samples of BSAC were done. There were 4 factorial points, 4 axial points and 5 replicates at the centre point.

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

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

By using RSM, there two levels which are known as low and upper limit, they are coded as -1 and +1. The center points were used to determine the experimental error and the reproducibility of the data. Only one response was investigated which is percentage of MB removal, % ( $Y_1$ ). 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 in Equation 3.2 below:

$$Y = b_0 + \sum_{i=1}^n b_i x_i + (\sum_{i=1}^n b_{ii} x_i^2) + \sum_{i=1}^{n-1} \sum_{j=i+1}^n b_{ij} x_i x_j \quad (3.2)$$

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