PREPARATION OF ACTIVATED CARBON FROM RICE HUSK BY MICROWAVE IRRADIATION FOR ADSORPTION OF METHYLENE BLUE DYE

SITI KHAIRUNNISA BINTI ISHAK

UNIVERSITI SAINS MALAYSIA

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by

SITI KHAIRUNNISA BINTI ISHAK

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LIST OF SYMBOL

	Symbol	Unit
A	Arrhenius factor	-
B_T	Constant for Temkin equation	-
С	Boundary layer	-
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 the pseudo-first-order	1/hr
	kinetic	
k_2	Adsorption rate constant for the pseudo-second-order	g/mg.hr
K_F	Freundlich isotherm constant	$mg/g (L/mg)^{1/n}$
K_L	Langmuir adsorption constant	L/mg
W	Mass of adsorbent	g
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	-
Т	Time	Min
Т	Absolute temperature	Κ
V	Solution volume	L
$\Delta G^{ m heta}$	Changes in standard Gibbs free energy	kJ/mol
$\Delta H^{ \theta}$	Changes in standard enthalpy	kJ/mol
ΔS^{o}	Changes in standard entropy	kJ/mol
λ	Wavelength	Nm

LIST OF ABBREAVIATIONS

AC	Activated carbon
ANOVA	Analysis of variance
BET	Brunauer-Emmett-Teller
CCD	Central composite design
CO_2	Carbon dioxide
FTIR	Fourier Transform Infrared
IUPAC	International Union of Pure and Applied Chemistry
MB	Methylene blue
N_2	Nitrogen gas
RH	Rice husk
RHAC	Rice husk activated carbon
rpm	Rotation per minute
SEM	Scanning electron microscopy
STA	Simultaneous thermal analyzer
UV	Ultraviolet

PENYEDIAAN KARBON TERAKTIF DARIPADA HAMPAS PADI MELALUI PENGAKTIFAN SINARAN GELOMBANG MIKRO BAGI PENJERAPAN PEWARNA METILENA BIRU

ABSTRAK

Di dalam kajian ini, karbon teraktif berasaskan hampas padi (KTHP) dibuat untuk menyingkirkan pewarna metilena biru (MB). Hampas padi telah digunakan untuk membuat KTHP melalui kaedah pengaktifan fizikal yang melibatkan sinaran gelombang mikro dan penggasan karbon dioksida (CO₂). Kesan kepekatan awal pewarna (25-500 mg/L), masa (1-24 jam) dan suhu larutan (30-60°C) telah dikaji. Keadaan penyediaan optimum didapati pada kuasa sinaran 440 W dan masa pengaktifan 4.28 minit yang menghasilkan penyingkiran MB sebanyak 83.93% dan hasilan KTHP sebanyak 32.55%. Sampel KTHP yang optimum mempunyai luas permukaan 668.30 m²/g, isipadu liang 0.348 cm³/g dan kandungan karbon tetap 70.34%. Liang KTHP tergolong dalam kategori mesoliang dengan purata diameter liang 4.42 nm. Data keseimbangan penjerapan dipadankan kepada tiga model garis sesuhu iaitu Langmuir, Freundlich and Temkin. Penjerapan pewarna MB pada KTHP adalah terbaik dipadankan oleh garis model sesuhu Freundlich dan juga adalah terbaik dihuraikan oleh model kinetic pseudo tertib kedua. Berdasarkan kajian termodinamik, penjerapan MB ke atas KTHP adalah secara endotermik dan proses spontan.

PREPARATION OF ACTIVATED CARBON FROM RICE HUSK BY MICROWAVE IRRADIATION FOR ADSORPTION OF METHYLENE BLUE DYE

ABSTRACT

In this study, rice husk based activated carbon (RHAC) was prepared for the removal of methylene blue (MB) dye. Rice husk was used to prepare RHAC through physical activation process which involved microwave irradiation and carbon dioxide (CO₂) gasification. The effect of initial dye concentration (25-500 mg/L), contact time (1-24 h) and solution temperature (30-60°C) were evaluated. The optimum preparation conditions were obtained from response surface methodology (RSM) at radiation power of 440 W and activation time of 4.28 minutes which have resulted in 83.93% MB removal and 32.55% RHAC yield. Optimized RHAC sample has surface area of 668.30 m²/g, pore volume of 0.348 cm³/g and fixed carbon content of 70.34. The pore of RHAC was mesoporous type with average pore diameter of 4.42 nm. The adsorption equilibrium data is to be fitted into three isotherm models which are Langmuir, Freundlich and Temkin. Adsorption equilibrium and kinetic of MB on RHAC were best fitted by Freundlich isotherm and pseudo-second order kinetic models. From thermodynamic study, the adsorption process of MB onto RHAC was endothermic in nature and spontaneous process.

CHAPTER ONE

INTRODUCTION

1.1 Research background

The textile is one of the largest water consuming industries and releases larger amount of effluent (Hai et al., 2006). The textile effluent contains carcinogenic dyes, toxic heavy metals, phenolic compounds, softeners and other chemicals used in the dyeing process (Correia et al., 1994). About 60% of total dyes produced from the textile sector in a worldwide (Daneshvar et al., 2012). The textile-dyeing industry consumes large quantities of water and produces large volumes of wastewater from different steps in the dyeing and finishing processes. The presences of even very low concentration of dyes in the effluent is highly visible and undesirable. Due to their chemical structure, dyes are resistant to fading on exposure to light, water and many chemicals. Dyes are difficult to be decolorized and decomposed biologically. Therefore, the wastewater need to be properly treated before its release into the environment (Sun et al., 2013).

Dyes can be defined as organic compounds that have a color and are used to give color to different substrates like cosmetic, paper, drugs, leather, fur, greases hair, waxes, plastics and textile materials (Ngulube et al., 2017). Dyes can be classified according to where they are derived. They can be from natural or synthetic sources. However, because of the population increase and industrial activities, people are moving away from natural dyes because they are failing to meet the industrial demand. Dyes are growing to be problematic class of pollutants to the environment. The disposal of dyes in water resources has bad aesthetic and health effects, hence the need to remove them from environment (Ngulube et al., 2017). Dyes have a synthetic origin and complex aromatic molecular structures which cause it become inert and difficult to biodegrade when discharged into waste streams. Usually industrial effluents are treated by several methods including chemical degradation, advanced oxidation processes, adsorption, precipitation, biodegradation and chemical coagulation (Pajootan et al., 2012).

1.2 Problem statement

Industrial wastewater is considered as one of the major pollutants of the environment. One of the high consuming materials in the dye industry is methylene blue (MB) which is used for cotton and silk painting. Up to now, a great number of methods have been proposed in order to remove dyes from the industrial wastewater among which adsorption is the most acceptable due to its cost effectiveness and its capability to be used in large scale, simplicity of design, ease of operation and insensitivity of toxic substances.

Activated carbon (AC) as adsorbent in adsorption is considered as one of the most effective method. However, commercially coal based AC is very expensive and might not be economical for wastewater treatment. Hence, there would be the best option if the ACs are prepared from the renewable sources. In this study, rice husk was used to produce AC using microwave heating and CO₂ gasification for MB removal from aqueous solution.

1.3 Research objectives

The main objectives of this study are:

- i. To optimize the rice husk based activated carbon (RHAC) preparation conditions (microwave power and activation time) using response surface methodology.
- ii. To characterize rice husk activated carbon (RHAC) in term of surface area, surface morphology, proximate content and surface chemistry.
- iii. To study the effects of absorbate initial concentration, contact time, solution temperature, isotherms, kinetics and thermodynamics for dye adsorption on rice husk activated carbon using batch adsorption tests.

CHAPTER TWO

LITERATURE REVIEW

2.1 Dyes classification and application

Dyes can be defined as a substances that give color to different substrates like cosmetics, paper, drugs, leather, fur, greases hair, waxes, plastics and textile material (Ngulube et al., 2017). Dyes can be from natural or synthetic sources. Natural dyes are extracted from sources including plants, animals and minerals. Synthetic dyes have replaced natural dyes almost completely particularly in the fabrics and textile industry. Several types of dyes are used in numerous industries and these include basic, acid, reactive, direct, vat and disperse dyes as shown in the Table 2.1.

Dye class	Description	Fibres typically applied
Reactive	Dye react with the fibre molecules	Cotton, silk and wool
	to form colour	
Acid	There are acidified basic dyes,	Nylon and acrylics
	intended for use on protein fibres	
Direct	These substantive dyes colour	Cotton, rayon, other cellulosic
	cellulose fibres directly in a hot	
	dyebath without a mordant	
Disperse	Originally developed for acetate	Polyester, acetate, other
	fibres	synthetics
Vat	Made soluble with alkali	Cotton, other cellulosic
Basic	The colour are very bright	Acrylic and some polyester

Table 2.1Classification of dyes

2.2 Health and environmental impact of dyes

The textile sector alone consumes about 60% of total dyes produced to paint various fabrics, however 10-15% of dyes used for this purpose comes out through the effluents (Daneshvar et al., 2012). Dyeing of textiles requires high amounts of water and some harmful chemical substances. Harmful chemicals can be acquired through the skin, bronchially or through digestion. Textile materials can cause allergic reactions and can even be carcinogenic and mutagenic (Akarslan and Demiralay, 2015). Besides, the heavy metals present in textile industry effluent are not biodegradable hence, they accumulate in primary organs in the body and over time begin to fester, leading to various symptoms of diseases. During the dyeing process, about 50% of the dye remains with the spent dye bath effluent, which loses its affinity towards the fabric that cannot be re-used in the dyeing process (Watanapokasin et al., 2009). Because these dyes give color to the receiving water bodies, it is importance that their presence in a water body be managed (Rita, 2012). The presence of color in an aquatic ecosystem reduces the penetration of sunlight to benthic organism thus limiting the process of photosynthesis. Dyes also affect the aesthetic value of an aquatic ecosystem due to coloration of water resources (Yagub et al., 2014).

2.3 Activated carbon

AC has known as its larger porous surface area and controllable structure. AC can be produced by activation of carbonaceous materials (Nguyen et al., 2012). ACs are attractive materials for industrial application due to their high surface area and well developed porosity (Elmouwahidi et al., 2017). Furthermore, AC are known as excellent adsorbents in environmental applications where pollutant, at low

concentration, can be removed. An interesting environmental and sustainable concept is to utilize waste and renewable materials into ACs (Laksaci et al., 2017).

2.4 Rice husk based activated carbon (RHAC)

According to the statistics compiled by the Malaysian Ministry of Agriculture, 408,000 metric tons of rice husk are produced as waste in Malaysia each year (Noor and Rohasliney, 2012). The husk is made of hard materials including opaline silica and lignin in order to protect the seed during the growing season. The husk is mostly indigestible to humans. The characteristic of rice husk are shown in Table 2.2.

Generally, farmers and rice processor often burn the rice husk which releases the carbon dioxide (CO_2) into atmosphere. The CO_2 gas does not only elevate global temperature, it also gives negative impact to human health because its higher concentration can affect respiratory function. Thus, in this study an attempt was made to produce rice husk activated carbon (RHAC) that will provide advantage to environmental management.

		(,)
Characteristic	Unit	Value
Bulk density	g/ml	0.73
Solid density	g/ml	1.5
Surface area	m^2/g	272.5
Surface acidity	meq/gm	0.1
Surface basicity	meq/gm	0.45

Table 2.2Characteristic of rice husk (Malik, 2003)

2.5 Microwave irradiation

Recently, microwave heating technique has been applied to produce ACs. In this technique, microwave power is the predominant factor affecting the AC yield as well as AC characteristic. Enhancing microwave power led to increase of AC porosity and adsorption uptake. The application of microwave heating technology in the industrial regeneration of spent AC has indicated promising result (Xin-hui et al., 2012). Besides, microwave irradiation has been widely investigated due to its capability of molecular level heating, which leads to homogenous and quick thermal reaction (Yuen and Hameed, 2009). Comparing with traditional heating techniques, microwave heating provides additional advantages. During microwave heating, a tremendous thermal gradient from the interior of the char particle to its cool surface allows the microwave-induced reaction to proceed quickly and effectively at a low bulk temperature, energy savings and a shortened processing time are the key advantages of microwave heating (Alslaibi et al., 2013).

2.6 Adsorption isotherm

Adsorption isotherm describes the relationship between the amount of solute adsorbed and its concentration in the fluid phase at equilibrium for a constant temperature (Din et al., 2009). The quantity adsorbed is nearly always normalized by the mass of the adsorbent to allow them to different materials. In this study, 3 types of isotherm such as Langmuir, Freundlich, and Temkin were used for MB adsorption onto RHAC.

2.6.1 Langmuir isotherm

The Langmuir isotherm model is the most widely used model for describing the process of adsorption (Ruthven, 1984). This Langmuir model assumes the surface has a fixed number of surface sites that are energetically equivalent. It is further assumed that monolayer coverage occurs on the surface. The Langmuir isotherm equation can be expressed as (Langmuir, 1918):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{2.1}$$

By rearranging the equation:

$$\frac{C_{e}}{q_{e}} = \frac{1}{q_{m}}C_{e} + \frac{1}{K_{L}q_{m}}$$
(2.2)

where,

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

qe =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).

Equation 2.2 showed the linear form of Langmuir isotherm. Straight line graph

of C_e/q_e against C_e can be plotted with slope $1/q_m$ and intercept of $1/K_Lq_m$.

2.6.2 Freundlich isotherm

Freundlich isotherm is one of the earliest isotherm used to correlate the equilibrium data for multilayer adsorption on rough surface (Mannarswamy et al., 2009). This isotherm is an empirical equation can be employed to describe heterogeneous systems and is expressed as follows (Freundlich, 1906):

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

which can then be further rearranged to:

$$\ln q_e = \frac{1}{n_F} \ln C_e + \ln K_F \tag{2.4}$$

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)^{1/n}).

By plotting the experimental data on a graph of $\ln q_e$ against $\ln C_e$, it gives a straight line graph. From the slope of the graph, the value of $1/n_F$ measures of the adsorption intensity is or surface heterogeneity. Generally, when the temperature increases, K_F decreases while *n* increases, approaching unity at high temperatures. Linear isotherm is expected when the *n* value equals to 1. Unfavorable adsorption occur if *n* less than 1 while favorable adsorption occur when *n* is greater than 1 (Seader and Henley, 2011).

Figure 2.1 illustrates the effect of the parameter n on the shape of the isotherm. The closer the value of n is to unity, which limits the use of linear regression to estimate the parameters. For the most cases, the value of n is not equal to one which results in non-linearity in the model. This non-linear model can also be fitted using the method of least squares.



Figure 2.1 Freundlich isotherms with model parameters $\beta = (K_F, n)^T$.

2.6.3 Temkin isotherm

Temkin isotherm contains a factor that explicitly takes into account the adsorbent- adsorbate interactions. The heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbent-adsorbate interaction (Hosseini et al., 2003). Temkin isotherm has been used in the form as follows (Temkin and Pyzhev, 1940):

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

which can then be further rearranged to:

$$q_e = B \ln C_e + B \ln A_t \tag{2.6}$$

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 kinetic

Adsorption kinetics are the relationship between the adsorption rate and concentration of adsorbate in the solution. It can evaluate the performance of a given adsorbent and gain insight into the underlying mechanisms. Kinetic models such as pseudo-first-order kinetic and pseudo-second-order kinetic are used in this work to determine the mechanism of adsorption process.

2.7.1 Pseudo-first-order model

Pseudo-first-order model is the earliest known equation describing the adsorption rate based on the adsorption capacity. Besides, Langergren's first order rate equation has been called pseudo-first-order to distinguish kinetic equations based on adsorption capacity from solution concentration (Ho and McKay, 1998). In recent years, it has been used to describe the adsorption of pollutants from wastewater in different fields (Hameed and El-Khaiary, 2008). Its differential equation can be presented as follows:

$$\frac{\mathrm{d}q_{\mathrm{t}}}{\mathrm{d}\mathrm{t}} = \mathrm{k}_{1} \left(\mathrm{q}_{\mathrm{e}} - \mathrm{q}_{\mathrm{t}} \right) \tag{2.7}$$

where,

By integrating Equation 2.7 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:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{2.8}$$

2.7.2 Pseudo-second-order model

Pseudo-second-order is to distinguish kinetic equations based on adsorption capacity from concentration of solution (Ho, 2006). The differential equation can be expressed as:

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

$$\frac{\mathrm{d}q_{\mathrm{t}}}{(q_{\mathrm{e}}-q_{\mathrm{t}})^2} = \mathrm{k}_2 \mathrm{d}\mathrm{t} \tag{2.10}$$

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:

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

A graph of t/q_t against t gives a straight line with the slope of $1/q_e$ and intercept of $1/k_2q_e^2$.

2.8 Adsorption thermodynamic

Thermodynamic equations are developed for adsorption of multicomponent gas mixtures in micro porous adsorbents based on the principles of solution thermodynamics. Three thermodynamic parameters which is Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) are evaluated in order to characterize the adsorption process due to the transfer unit mole of solute from solution onto the solid liquid interface (Bello et al., 2012). The value of ΔH° and ΔS° is calculated by using the following equation:

$$\ln k_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$
(2.12)

where,

- $k_{\rm L}$ = Langmuir adsorption constant (L/g), ΔS° = Changes in standard entropy (kJ/mol K), R = Universal gas constant (8.314 J/mol K), ΔH° = Changes in standard enthalpy (kJ/mol),
- T = Absolute solution temperature (K).

The values of ΔH° and ΔS° are determined respectively from the slope and intercept of the graph by plotting of ln $k_{\rm L}$ versus 1/T. ΔG° are calculated using the relation below:

$$\Delta G^{\circ} = -RT \ln k_L \tag{2.13}$$

Arrhenius equation has been applied to evaluate the activation energy of adsorption representing the minimum energy reactants have for the reaction to proceed. The relationship are shown below:

$$\ln k_2 = \ln A - \frac{E_a}{RT} \tag{2.14}$$

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).

- E_{α}/R are obtained from the slope of the graph by plotting a graph of $\ln k_2$ against 1/T.

2.9 Design of experiment

Design of experiment (DoE) is a systematic, rigorous approach to engineering problem solving that applies principles and technique at the data collection stage so as to ensure the generation of valid, defensible and supportable engineering conclusion. DoE are used for the statistical design of experiments and data analysis (Alslaibi et al., 2013). Besides, to find a useful relationship are also the purpose of an experimental design. With such relationship, it can be specified a combination of variables that will achieve some practical benefit (Ahmed and Theydan, 2014).

RSM is a multivariate technique that can be used in optimization analysis. It has already been successfully utilized in diverse research areas. RSM was applied to evaluate the interaction between studied variables and determine the best conditions for the activation procedure. It allowed each independent variable to range in five levels as shown in Table 2.3.

Level	Coded values
Axial (-ve)	-1.414
Low	-1
Central	0
Superior	+1
Axial (+ve)	+1.414

Table 2.3Respective coded values for DoE for 2 variables

A total 13 experiments are performed, including 3 factorial points, 2 axial points and 8 central points. RSM can optimize the experimental parameters with a minimum number of experiments and to analyze the interactions between the parameters and the total experiment. The experimental data are analyzed using statistical software Design Expert version 7.1.5 (STAT-EASE. Inc., Minneapolis, USA).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Material

In this study, rice husk (RH) obtained from Kilang Beras Bernas Sungai Ranggam, Perak, Malaysia was used as the precursor for the production of activated carbon (AC). Methylene blue (MB) supplied by Sigma-Aldrich (M) Sdn. Bhd, Malaysia was used as adsorbate. The properties for MB is represented in Table 3.1.

Properties	
Common name	Methylene Blue (MB)
IUPAC name	3,7-bis(Dimethylamino)phenazathionium
	chloride
Other name	Basic Blue 9, Tetramethylthionine chloride
Molecular formula	$C_{16}H_{18}CIN_3S$
Molecular weight	319.85 g/mol
Maximum wavelength, λ_{max}	663 nm
Chemical structure	$H_3C_N \xrightarrow{N}_{CH_3} S \xrightarrow{N+CH_3} KH_2O$

Table 3.1Properties of MB (Aldrich, 2002)

Technical carbon dioxide (purity 99.00%) and nitrogen (purity 99.99%) gaseous were supplied by MOX Gases Berhad, Malaysia. In this study CO₂ gas are used as activating agent.

3.2 Equipment and instrumentation

3.2.1 Preparation of char

The preparation of char was carried out using the equipment shown in Figure

3.1.



Figure 3.1 Stainless steel vertical tubular furnace for char production

3.2.2 Activation of char by microwave

The activation of char was carried out by using commercial microwave as shown in Figure 3.2. Microwave has a power controller to control the heating power levels and a timer to set various time for activation process. Flow meter were used to measure CO_2 gas flow rates into microwave.



Figure 3.2 Schematic diagram of experimental setup for RHAC by microwave

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). Elemental analyzer (EA) (Model Perkin Elmer Series II 2400, USA) was used to determine the elemental composition of the samples. 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).

3.3 Experiment design of RHAC

The parameter for preparing the RHAC are determined by using a standard Response Surface Methodology (RSM) design also known as central composite design (CCD). RSM provides an estimate for the value of responses for every possible combination of the factors by varying the value of all factors. The variables used for preparing the RHAC are:

- i. x₁, Mixrowave power (Watt)
- ii. x₂, Activation time (min)

The code levels for CCD and the complete design matrix of the experiments employed are shown in Table 3.2 and Table 3.3. These experimental design represent 13 experiment for preparing the RHAC since this experiment have 2 variables. There are factorial point, axial points and replicates at the center. The experimental design given are calculated in Equation 3.1 (Azargohar and Dalai, 2005):

$$N = 2^{n} + 2n + n_{c} = 2^{2} + 2(2) + 5 = 13$$
(3.1)

Where;

- N = Total number of experiments required
- n = Number of factor

Table 3.2Independent variables and their coded levels for the CCD

Variables (factors)	Coded variables level				
	- α	-1	0	+1	$+ \alpha$
Microwave power (W)	191	264	440	616	689
Activation time (min)	3.17	4.00	6.00	8.00	8.83

To maintain rotatability, the value of α depends on the number of experimental runs in the factorial portion of the CCD:

$$\alpha = [\text{number of factorial runs}]^{1/4}$$
(3.2)

If the factorial is a full factorial, then:

$$\alpha = [2^k]^{1/4} \tag{3.3}$$

	Table 3.3Experimen	Table 3.3Experimental design matrixes			
Run	RHAC preparation variables				
_	Microwave power, x ₁	Activation time, x ₂			
	(W)	(min)			
1	440 (0)	6.00 (0)			
2	616 (0)	8.00 (+1)			
3	264 (-1)	8.00 (+1)			
4	440 (0)	8.83 (+1.414)			
5	440 (0)	6.00 (0)			
6	440 (0)	6.00 (0)			
7	616 (+1)	4.00 (-1)			
8	440 (0)	3.17 (-1.414)			
9	440 (0)	6.00 (0)			
10	689 (+1.414)	6.00 (0)			
11	191 (-1.414)	6.00 (0)			
12	264 (-1)	4.00 (-1)			
13	440 (0)	6.00 (0)			

The center points are used to determine the experimental error and the reproducibility of the data. The three variables are coded to the (-1,1) interval, where the low and high level are coded as -1 and +1 respectively. Alpha (α) is the distance of each axial point from the center in a CCD. The axial points of the variables are

located at $(\pm \alpha, 0, 0)$, $(0, \pm \alpha, 0)$ and $(0, 0, \pm \alpha)$. The alpha (α) was fixed at 1.414 and represents the distance of the axial point from center and allows the design rotatable.

MB removal (Y_1) and RHAC (Y_2) are the responses of this experiment. Each responses are used to develop an empirical model which correlated the response to the variables by using-degree polynomial equation as given by Equation 3.4:

$$Y = b_0 + \sum_{i=1}^n b_i x_i + (\sum_{i=1}^n b_{ii} x_i) + \sum_{i=1}^{n-1} \sum_{j=i+1}^n b_{ij} x_i x_j$$
(3.4)

where;

Y	= Predicted	response,
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- $b_0 = Constant coefficient,$
- $b_i = Linear coefficient,$
- $b_{ij} = Quadratic coefficient,$
- $x_i, x_i =$ Coded value of the AC.

Design Expert software version 7.1.5 (STAT- ESE Inc., Minneapolis, USA) are used to analyze the experimental condition with highest desirability. A power calculator helps establish the number of test run needed. This software determines the main effect of each factor as well as the interaction between factors by varying the values of all factors in parallel. The coefficients with one factor represent the effect of the specific factor. Meanwhile, the coefficients with two factors and those with second-order terms show the interaction between two factors and quadratic effect respectively. The models were evaluated based on the correlation coefficients, R^2 .

3.4 Experimental procedures

3.4.1 Preparation of RHAC

The dried rice husk was placed in a vertical furnace and carbonized at 330° C for 1 hour. The char produced was cooled at room temperature. After that, it was placed in a microwave oven at targeted microwave power and activation time that determined from the Design Expert software under CO₂ flow rate of 150 cm³/min. Then, the sample was stored for characterization and adsorption study.

3.4.2 Preparation of stock and dye solutions

The 1000 mg/L of stock solution was prepared by dissolving 1 g of MB dye powder with 1000 ml of deionized water. The different initial concentration of dye ranging from 25-300 mg/L was prepared by using dilution factor with deionized water.

3.4.3 Sample analysis

The sample is taken from the solution at a set time intervals by using 3 ml disposable syringe. The concentration of the MB are determined by using UV-Vis spectrometer at wavelength of 663 mm. The linear-lambert relationship between absorbance and concentration was plotted in graph of absorbance versus concentration of the dye solutions.

3.4.4 Batch equilibrium, kinetics and thermodynamics studies

The batch equilibrium test was carried out based on adsorption of MB on RHAC prepared. 0.20 g of the RHAC is added to a series of Erlenmeyer flask filled with 200 ml of dye solution with different initial concentration. The Erlenmeyer flask are then sealed and kept in an isothermal water bath shaker at temperature 30°C and speed of 60 rpm. The aqueous samples are then withdrawn for every fixed time interval. The concentrations are measured at wavelength of maximum adsorption by using UV-Vis spectrometer. The measurement steps are repeated until the reading of the concentration for each Erlenmeyer flask reach the equilibrium state. The amount of adsorbate adsorbed at equilibrium q_e (mg/g) can be calculated by using the following equation:

$$q_e = \frac{(C_o - C_e)V}{W} \tag{3.5}$$

where,

C_o = Liquid-phase dye concentrations at initial stage (mg/L),
 C_e = Liquid-phase concentrations of dye at equilibrium stage (mg/L),
 V = Volume of dye solution (L),
 W = Mass of adsorbent used (g).

And, the percent removal of adsorbate, % C can be calculated by using:

$$\% C = \frac{(C_o - C_t)}{C_o} \times 100$$
(3.6)

Where, $C_t =$ liquid-phase dye concentration at time.

The adsorption isotherm model which is Langmuir, Freundlich and Temkin are used to fit the experimental data. The best-fitted isotherm can be determined through the value of correlation coefficient; R^2 which is closest to the unity. For the kinetics studies, the amount of adsorption at time *t*, q_t (mg/g), was calculated by using:

$$q_t = \frac{(C_0 - C_t)V}{W}$$
(3.7)

where,

 C_o = Liquid-phase dye concentrations at initial stage (mg/L),

 C_t = Liquid-phase concentrations of dye at time (mg/L),

V = Volume of dye solution (L),

W = Mass of adsorbent used (g).

3.4.4 (a) Effect of initial dye concentration and contact time

To study the effect of initial dye concentration and contact time of MB on the adsorption uptake, 200 ml of respectively dye solutions are prepared in a series of 250 ml Erlenmeyer flasks with different initial concentration of 25-500 mg/L. 0.20 g of RHAC is added into each flask for the dye test. The sample solution are then sealed and kept in water bath shaker at 30°C with speed of 60 rpm until the equilibrium stage is reached. The concentration of the samples are then determined by using UV-Vis spectrometer.

3.4.4 (b) Effect of solution temperature

The experiment is conducted at 3 different solution temperatures which are 30, 45 and 60°C. 0.20 g of RHAC is added into a series of Erlenmeyer flask with constant initial dye concentration of 25 mg/L. The Erlenmeyer flask are then sealed and kept in water bath shaker at speed 60 rpm. The concentration of the samples are then determined by using UV-Vis spectrometer.