PREPARATION OF MICROWAVE-ASSISTED PALM TRUNK BASED ACTIVATED CARBON FOR ADSORPTION OF METHYLENE BLUE DYE

MOHD SHAFIQ BIN ABD LATIF

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by

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LIST OF SYMBOL

Symbol		Unit
A	Arrhenius factor	-
B_T	Constant for Temkin equation	-
C	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 kinetic	1/hr
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	-
t	Time	hr
T	Absolute temperature	K
V	Solution volume	L
ΔG^o	Changes in standard Gibbs free energy	kJ/mol
ΔH^o	Changes in standard enthalpy	kJ/mol
ΔS^o	Changes in standard entropy	kJ/mol
λ	Wavelength	Nm

LIST OF ABBREVIATIONS

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
PTAC	Palm trunk based activated carbon
rpm	Rotation per minute
SEM	Scanning electron microscopy
STA	Simultaneous thermal analyzer
UV	Ultraviolet

PENYEDIAAN KARBON TERAKTIF BERASASKAN PELEPAH KELAPA SAWIT DENGAN BERBANTU GELOMBANG MIKRO UNTUK PENJERAPAN PEWARNA METILENA BIRU

ABSTRAK

Dalam kajian ini, proses penjerapan oleh karbon teraktif berasaskan pelepah kelapa sawit (KTPKS) untuk menyingkirkan pewarna metilena biru (MB) telah dikaji menggunakan proses kelompok pada kepekatan awal pewarna (25-300 mg / L), masa sentuhan (0-24 jam) dan suhu larutan (30-60 ºC) yang pelbagai. KTPKS telah disediakan melalui pengaktifan fizikal yang melibatkan radiasi gelombang mikro dan penggasan karbon dioksida (CO_2). Keadaan penyediaan KTPKS yang optimum untuk diperolehi daripada kaedah sambutan permukaan (RSM) adalah pada kuasa radiasi dan pengaktifan masa masing-masing 501 W dan 4.00 minit. Sampel ini menghasilkan 91.25% penyingkiran pewarna MB dan 32.37% hasilan KTPKS. Sampel ini mempunyai luas permukaan 772.35 m^2/g, isi padu liang 0.45 cm^3/g dan kandungan karbon tetap 74.3%. Liang yang dihasilkan adalah tergolong dalam jenis mesoliang yang mempunyai saiz 3.88 nm purata diameter. Model isoterma penjerapan yang yang terbaik dengan KTPKS adalah dari model Freundlich manakala data kinetik yang terbaik adalah model pseudo tertib pertama. Proses penjerapan MB ke KTPKS adalah endotermik dan spontan.

PREPARATION OF MICROWAVE-ASSISTED BASED ACTIVATED CARBON FOR ADSORPTION OF METHYLENE BLUE DYE

ABSTRACT

In this study, the adsorption process by the palm trunk based activated carbon was investigated in batch process at various initial dye concentration (25-300 mg/L), contact time (0-24 hours) and solution temperature (30-60 ºC). The PTAC was prepared by physical activation which involve microwave radiation and carbon dioxide (CO_2) gasification were applied. The optimum PTAC preparations obtained from response surface methodology (RSM) were at radiation power and activation time of 501 W and 4.00 minutes, respectively. This sample has 91.25% MB dye removal and 32.37% PTAC yield. This sample has 772.35 m^2/g BET surface area, 0.45 cm^3/g pore volume and 74.3% fixed carbon content. The pores developed were mesopores type which have 3.88 nm average pore size diameter. The adsorption isotherm was fitted with Freundlich model while the kinetics data was best represented by the pseudo first-order model. The adsorption process of MB onto PTAC was endothermic and spontaneous.

CHAPTER ONE

INTRODUCTION

1.1 Textile industries and dye effluent

Textile industry especially textile wet-processing is one of the largest consumers of water in manufacturing their product and hence produce a lot of contaminated wastewater. Since a various chemical are used in this industry, the textile wastewater may contains many toxic which if not treated properly before discharging to the environment and can cause serious problem for natural ecosystem (Hasanbeigi and Price, 2015).

Dye is used in textile industry for painting and colouring their fabric. Unfortunately, the dye used in this industry is not 100% consume and escape as the waste product due to inefficiency of the process. Dye have the ability to reduce light penetration into the water. Therefore, discharging waste water with the presence of dye compound will affect the photosynthetic activity an aquatic environment.

Considering the fact that the textile dyeing process is recognized as one of the most environmentally unfriendly industrial processes, more people were started to play much attention by developing a new technology and procedure to the dyes waste. The government also playing their role by imposing strict requirements on environmental legislation in several countries.

1.2 Problem statement

Several technologies were developed for the dyes removal from wastewater. The technologies can be divided into three main categories which are physical, chemical and biological treatments. Chemical treatment consists of number of process such as coagulation, flocculation and followed by filtration. This method required a chemical as the coagulating and flocculating agent to initiate the reaction. These

processes are helpful for removal of dyes from the wastewater but it was an expensive way. In addition, this chemical treatment will produce the concentrated sludge that can cause a problem to dispose.

On the other hand, biological treatment process is more economical operation and has flexibility in design and operation toward the toxicity treatment. However, it's required a large land area, longer times and not proven satisfactory for colour elimination (Lim, 2016). Physical treatment consists a several methods such as membrane filtration and adsorption techniques. However, membrane filtration technique is expensive. This is because periodic replacement for the membrane is must due to the membrane fouling and limited lifetime. Adsorption technique was reported as the best technique and efficient for dye removal especially if the adsorbent is inexpensive.

Activated Carbon (AC) is commonly used as adsorbent. This is because it's has a great capacity to adsorb dyes. This capacity is mainly due to their structural characteristics and their porous texture which gives them a large surface area. Moreover, their chemical nature which can be easily modified by chemical treatment to increase their properties. However, its expensive price in market due to the price of coal as precursor has limited its commercial application. For this reason, an attempt was made in using palm trunk for the production of PTAC.

Malaysia is among the largest palm oil plantation area in the world. According to the Malaysian Oil Palm Industry 2016 report, it was stated that the palm area in Malaysia was reached 5.74 million hectares and contributed to 64.58 billion to the national income (Din, 2017). From this industry, there are many waste product generated such as palm trunk, palm frond, empty fruit bunch (EFB) and palm oil mill effluent (POME). Therefore, this study will only focusing on palm trunk to explore its

potential to make an activated carbon assisted by microwave radiation that can be used as adsorbent in dye removal from wastewater since the source is abundant and just left at the field.

1.3 Scope of study

In this work, the palm trunk was utilized to prepare PTAC for MB dye removal. The preparation of PTAC was done via physical method which applies CO_2 and microwave irradiation to improvise the adsorptive performance of the PTAC. The optimization of the operating parameters radiation power and activation time were done using response surface methodology (RSM) method.

The optimized PTAC was characterized in terms of surface area, surface morphology, proximate content, elemental content and surface chemistry.

The optimized PTAC was then used in equilibrium, kinetic and thermodynamic studies to investigate the adsorption behaviour of MB dye onto PTAC. In order to carry out the analysis, batch adsorption study was done by examined the effect of adsorbate initial concentration (25-300 mg/L), contact time (0-24 hour), solution temperature (30-60 ^{o}C) for adsorption of dye onto PTAC prepared.

1.4 Research objectives

The main objectives of this study are:

i. To study the optimum parameters (radiation power and activation time) in producing PTAC using response surface methodology.
ii. To study the effects of adsorbate initial concentration, contact time, solution temperature, isotherms, kinetics and thermodynamics for dye adsorption of basic dye on the PTAC using batch adsorption tests.

iii. To characterize PTAC in terms of surface area, pore volume, pore size distribution, surface morphology, proximate content, elemental composition and surface chemistry.

1.5 Organization of thesis

This thesis is written in five main chapter and each chapter will brief to the sequence of this study. The contents for each chapter in this study as following below:

Chapter 1 includes a brief introduction of textile industry, problem statement, research objectives and organization of thesis.

Chapter 2 discusses the isotherm models, kinetic models and thermodynamic parameters.

Chapter 3 covers the experiment materials and the details of methodology. It will give the general description of equipment and materials used in this study. It continues with the explanation on the methods and experimental procedure and batch adsorption experiment.

Chapter 4 present the result obtained from the experiment. Each of the results will be followed by the discussion according to the PTAC performance. Further elaboration on the effect of different factors on batch system adsorption, the results on equilibrium, kinetic and thermodynamic properties are provided in this chapter.

Chapter 5 gives the conclusion of the result obtained in this study. Some recommendations for this study are also included in this chapter.

CHAPTER TWO

LITERATURE REVIEW

2.1 Dyes

Dye is a substance used to add colour or to change the colour of material. Basically, it was a natural or synthetic, organic compounds that have an ability to connect themselves to surface of material to provide a colour. It was used in various industries like textile, leather, rubber, paper, cosmetics, plastics, pharmaceuticals and food industries. Most of them are designed with complex organic molecules and resistant to many things especially to detergent to prevent the colour faded when it was applied to the product.

The dye can be classified in many way such as structure, colour or application method. However, the classification based on application method is more favourable due to the complexities of the colour nomenclature from the chemical structure system. The classification of dye based on application method is presented in Table 2.1.

Until now, there are more than 100,000 commercial dyes are known with over $7\times^{105}$ tonnes of dyes produced annually. From this number, it was estimated that 2% of the dyes are discharged in effluent from manufacturing operation, while 10% was discharged from textile and associated industries (Allen et al., 2004). The dyes can cause can cause allergy, dermatitis, skin irritation, cancer and mutations in humans. So discharging of these dyes into the water streams will affects the people who may use these effluents for living purposes such as washing, bathing and drinking (Lim, 2016). Furthermore, dyes can reduce light penetration through water and cause problematic to aquatic life. Therefore, the removal of dye waste in effluent is important even a small amount of dye in water is visible and toxic.

Table 2.1 Classification of dyes based on applications

Dye class	Description
Acid	Water-soluble anionic compounds
Basic	Water-soluble, applied in weakly acidic dyebaths; very bright dyes
Direct	Water-soluble, anionic compounds; can be applied directly to cellulosic without mordant (or metals like chromium and copper)
Disperse	Water-insoluble
Reactive	Water-soluble, anionic compounds; largest dye class
Sulfur	Organic compounds containing sulfur or sodium sulphide
Vat	Water-insoluble; oldest dyes; more chemically complex

There are many methods was developed by many researcher for dye removal in waste water. These include adsorption, precipitation, flocculation, electro-kinetic coagulation, electro-flotation, ion exchange, membrane filtration, electro-chemical destruction, irradiation and ozonation (Lim, 2016). However, from the previous study it was stated that adsorption is the best method to applied because of its cheapness, simple design, easy operation, less energy intensiveness, no effect by toxic substances and high quality of the treated effluents particularly for well-designed sorption processes (Sulaymon and Abood, 2013).

2.2 Adsorption

Adsorption is the process where are the multi-components (gas or liquid) are attached on the surface of solid adsorbent to attachment via physical or chemical bond. The term of adsorbent is referred to the solid that provide a surface for attachment while the material that attached to surface is known as adsorbate. This process was commonly used in waste water treatment process due its capability to remove the unwanted material efficiently and economically

Adsorption can be classified into two types which are physical adsorption and chemical adsorption (Sulaymon and Abood, 2013). Physical adsorption is also known as physiorption. It was occurred when weak interparticle bond exist between the adsorbate and adsorbent. Example such bonds are van der Waals bond, hydrogen bond and dipole-dipole bond (Lajide., 2013). Most of the physiorption is reversible reaction (M.Ruthven, 1984). On the other hand, chemical adsorption is a process of exchange particle between the particles. This bond is stronger compare to the physical adsorption. Example of the bonds are ionic bond and covalent bond. For chemical adsorption, most of the case is irreversible reaction (Lajide., 2013).

In adsorption process, separation occurs because of difference in molecular mass, shape or polarity causing some molecules attached to the surface than the others because the pores are too small to admit the larger molecule. Therefore, most of the adsorbent was designed have high porous structure. As the pores is high, the internal surface area is greater than external area.

Comparing industrial dye removal techniques like coagulation, flocculation, membrane filtration and enzymatic treatment, adsorption is much favoured to be utilized due to its simplicity of design and flexibility of process. Other advantage in

this technique is the flexibility of using wide range of adsorbent based on the structure of dye treated.

2.3 Activated carbon

Activated carbon is define as the porosity space that enclosed by carbon atoms (Harry Marsh, 2006). Activated carbons are excellent adsorbent for adsorption process. It is already widely used for removal of pollutants in water and air. The advantages of the activated carbons are high in surface area, well-developed internal structure and presence of various surface functional groups. (Liu et al., 2010). The types of organic used as a raw material and experimental condition for preparing the activated carbon are also contributes to the performance of the activated carbon itself (Thue et al., 2016b). Basically, the pore structure of AC is classified into three major groups by International Union of Pure and Applied Chemistry (IUPAC) which were micropores (pore size < 2 nm), mesopores (pore size 2 – 50 nm) and macropores (pore size > 50 nm).

There are several ways to prepare the activated carbon 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. However, this method has some disadvantages which are required a long preparation time and have a temperature gradient between the surface and the interior of material. Nowadays, the researchers are tend to use the alternative method to prepare the activated carbon which is microwave radiation method. By using this method, a temperature gradient problem of the material while heating process can be overcome (Hoseinzadeh Hesas et al., 2013).

Recently, the production of activated carbon from agricultural by-products of waste material has been noticed by many researcher. The production can be done

through the pyrolysis with under control preparing condition. By using that material, it is relatively cheap and also a renewable raw material for activated carbon production. Moreover, it also can turn the waste material to something wealth (Yahya et al., 2015). Activated carbon also can be in a different structure or format such as monolith, powder and granular (Laginhas et al., 2016).

Basically, the activation step in the preparation of activated carbons can be done in two ways which are physical and thermal activation and also by chemical activation. In physical and thermal activation, the carbonization of the raw materials is done at high temperature without presence of oxygen while activation chemical activation is by using a chemical agent such as KOH, H_3PO_4 and NaOH. However, physical and thermal activation required a high temperature (600°C -1000°C) compared to chemical activation (400°C -900°C). Moreover, by using the chemical activation also will produce high yield of carbon compared to physical and thermal activation (Lu et al., 2016).

2.4 Microwave irradiation

Microwave irradiation is an electromagnetic irradiation in the frequency range of 0.3 -300 GHz (wavelengths of 1 mm to 1 m). Within this range, the electromagnetic spectrum lies between infrared and radio frequencies (Figure 2.1). Usually, microwave irradiation is used for transmission data and transmission of energy (Mirzaei and Neri, 2016). By internal agreement, all domestic microwave ovens and commercial microwave reactors for chemical synthesis operate at a frequency of 2.45 GHz (with a maximum output power of 1 kW), in order to avoid interference with telecommunication, wireless networks and cellular phone frequencies (Mirzaei and Neri, 2016).

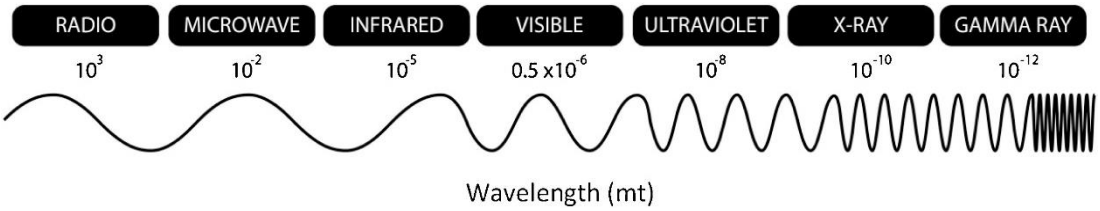

Figure 2.1: Electromagnetic spectrum

Microwave heating technology is developed rapidly since 1940 when the thermal effect of the microwave irradiation was discovered (Osepchuk, 1984). Microwave heating technology has been used in various field including: food processing, activated carbon regeneration, sintering of metals and ceramics, plasma processing, solution treatment, polymer processing, preparation of functional materials, pollution control, pyrolysis reactions and many other physical and chemical fields (Sun et al., 2016) .

The microwave heating gives the number of advantages the conventional heating methods such as (i) non-contact heating; (ii) selective material heating; (iii) rapid heating; (iv); volumetric heating; (v) quick start-up and stopping; (vi) improved product yield; (vii) reduction in processing time; and (viii) unique material microstructure and properties (Sun et al., 2016).

By using conventional heating technique, a temperature gradient from outside to inside of the feedstock particle is formed due to the poor thermal conductivity of the feedstock material and make the heating process becomes slow. However, by using microwave heating method, the microwave irradiation is penetrated and accumulate inside the material and then released from the inside core to the outside surface through a lower temperature region (Figure 2.2) (Zhang et al., 2017)).

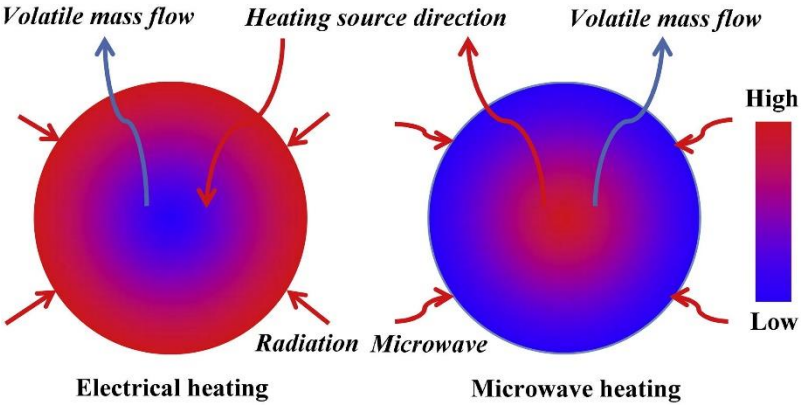

Figure 2.2: Schematic diagram of temperature distribution, heat transfer, and mass transfer in the conventional electrical heating and microwave-assisted heating

2.5 Adsorption isotherm

Adsorption isotherm is a method to describe a phenomena governing the mobility of a substances from the porous media or aquatic environment to a solid-phase at a constant temperature and pH (Foo and Hameed, 2010). This phenomenon is described by making a relationship between the concentration of the adsorbate in fluid phase and adsorbent phase at constant temperature. Adsorption equilibrium is reached when an adsorbate 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 (Foo and Hameed, 2010).

There are various models that has been developed such as Langmuir, Freundlich, Brunauer–Emmett–Teller, Redlich–Peterson, Dubinin–Radushkevich, Temkin, Toth, Koble–Corrigan, Sips, Khan, Hill, Flory–Huggins and Radke–Prausnitz isotherms in order to get the most appropriate correlation of an adsorption equilibrium (Foo and Hameed, 2010). In this study, Langmuir, Freundlich and Temkin isotherms were used. Linear regression also will be applied to determine the most suitable isotherm by judging the correlation coefficient, R^2.

2.5.1 Langmuir isotherm

Langmuir isotherm theory is a simplest isotherm model. This theory assumes monolayer coverage of adsorbate over the adsorbent surface (Allen et al., 2004). Another study was reported that another assumption in Langmuir isotherm is only identical and equivalent sites with equal sorption activation energy of each molecule resulting in homogeneous adsorption and no transmigration or interaction between the adsorbed species in the plane of the surface (Ghosal and Gupta, 2017).

Theoretically, Langmuir model can be expressed as:

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

which can then be further rearranged to:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_L q_m} \tag{2.2}$$

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).

Hence by plotting 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 obtained from the slope and intercept of the straight line.

2.5.2 Freundlich isotherm

Freundlich isotherm is the earliest model to describe the reversible and non-ideal adsorption (Foo and Hameed, 2010). This means that this model can be applied to multilayer adsorption with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface.

The Freundlich expression is an exponential equation and therefore assumes that as the adsorbate concentration increases so too does the concentration of adsorbate on the adsorbent surface (Allen et al., 2004). The Freundlich isotherm model can be written as (Chung et al., 2015):

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

which can then be further rearranged to get the linear form equation 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) $^{1/n}$).

Similar to the Langmuir adsorption isotherm, the above equation can be used to identify the adsorption constant by plotting a graph of of ln q_e against ln C_e. The graph plotted then gives a straight line with the slope of $1/n_F$ and intercept of ln K_F.

2.5.3 Temkin isotherm

Temkin isotherm considered the effects of some indirect adsorbate interactions on adsorption isotherm. It is also assumes that the heat of adsorption of all the molecules in the layer would decrease linearly with coverage (Allen et al., 2004). Comparing with Langmuir parameters, Temkin model gives higher equilibrium constants (Arshadi, 2003). The Temkin isotherm is given as the equation below (Chung et al., 2015):

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

which can then 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.

2.6 Adsorption kinetic

The kinetic study has the important practical task to determine the degree of utilization of the adsorption capacity as a function of the time of contact between the liquid and the solid (Hristova, 2011). Therefore, different models are used to fit the obtained kinetic curves in order to define the rate parameters and explain the mechanism of mass transfer. The determination of the models adsorption parameters permits to optimize the adsorption mechanism pathways, to express the dependence of the surface properties of the adsorbent to the sorption results, to determine the adsorbent capacities and design effectively the adsorption systems. Over the years, a variety of kinetics models (Langmuir, Pseudo order 1, Pseudo order 2, Pseudo order *n*, Elovich, Crank, Boyd, Bangham, Weber and Morris, pore volume and surface diffusion) have been developed (Largitte and Pasquier, 2016). In this study, two kinetic models are used which includes the pseudo-first-order and pseudo-second-order models.

2.6.1 Pseudo-first-order model

Pseudo-first-order model was presented by the Lagergren in 1898. It is used to describe the kinetics of liquid-solid phase adsorption of oxalic acid and malonic acid onto charcoal, pertaining to the adsorption rate, based on the adsorption capacity (Kadu; and Muthreja, 2015). The equation presented as follows:

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

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 equation with boundary conditions of $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, a linear equation can be obtained as below:

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

By plotting a graph of ln $(q_e - q_t)$ against t, it will gives a straight line with the slope of $-k_1$ and intercept of ln q_e.

2.6.2 Pseudo-second-order model

Pseudo-second-order was found to explain the sorption kinetics of the most of systems very well for the entire range of period. And it was found that it exhibits a better fit towards the sorption of heavy metals (Tripathi, 2015). 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:

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

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:

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

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

2.7 Adsorption thermodynamics

Thermodynamic study is important to determine whether the process is spontaneous or not (Arshadi, 2003). The parameters that considered for thermodynamics study are free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°). During adsorption process, these parameters are changes (Sivanesan, 2010). The value of ΔH° and ΔS° can be calculated by using the following equation:

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

where,

k_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)

Therefore, by plotting a graph of ln k_d against 1/T, the values of both $\Delta H°$ and $\Delta S°$ from the slope and intercept of the graph can be determined. Fundamentally, a positive $\Delta H°$ value indicates that an adsorption process is endothermic in nature while a negative value represents exothermic process. As for $\Delta S°$, 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., 2015). Additionally, the change in standard Gibbs energy, $\Delta G°$ can be calculated using the following relation with a negative $\Delta G°$ value indicates that an adsorption process is a spontaneous process at the study temperature and vice versa.

$$\Delta G° = \Delta H° - T\Delta S° \tag{2.13}$$

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 adsorption. Normally, physisorption process has activation energy ranging from 5 to 40 kJ/mol. On the other hand, for chemisorption process, the activation energy is in range from 40 to 800 kJ/mol (Nollet et al., 2003). Arrhenius equation can be represented by following equation:

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

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).

Therefore, by plotting a graph of lnk_2 against 1/T, we are able to determine the values of E_a from the slope of the graph, - E_a/R.

2.8 Design of experiment

Design of Experiments (DoE) as a methodology for systematically applying statistics to experimentation. Its lets experimenters develop a mathematical model that predicts how input variables interact to create output variables or responses in a process or system (Lye, 2005). DoE can be used in various field of study such as engineering studies, science studies and even in marketing studies. It consists of a series of tests in which purposeful changes are made to the input variables (factors) of a product or process so that one may observe and identify the reasons for these changes in the output response (Álvarez, 2007).

DoE is a most efficient and cost-effective method to understand and optimize products and processes. It is able to maximise the information obtained from each experiment and minimise the number of analyses (Lye, 2005). Therefore, the using of DoE in early process of experiment can reduced the experiment time requirement, reduced the cost with good result of data.

2.8.1 Response surface methodology

Response surface methodology (RSM) is a collection of mathematical and statistical techniques based on the fit of a polynomial equation to the experimental data, which must describe the behaviour of a data set with the objective of making statistical previsions. It is applied to the system when a response or set of responses influenced by several variables. The objective is to optimize simultaneously the variables to attain the best system performance (Bezerra et al., 2008).

To apply the RSM methodology in the experiment, it is necessary to choose an experimental design. First order model experimental design can be used for the data set that not present a curvature. It is mean that the data set can be described by linear function. There are other experimental designs for quadratic response surface such as

three-level factorial, Box–Behnken, central composite, and Doehlert designs. This study used central composite design for the experimental design.

2.8.2 Central composite design

Central composite design (CCD) able to evaluate the interaction of the variables toward the response (Garba et al., 2016). This design contains an imbedded factorial or fractional factorial design with centre points that is augmented with a group of 'star points' that allow estimation of curvature. If the distance from the centre of the design space to a factorial point is ±1 unit for each factor, the distance from the centre of the design space to a star point is$|\alpha| > 1$. The precise value of α depends on certain properties desired for the design and on the number of factors involved. Generally, the CCD consists of a 2^n factorial runs with $2n$ axial runs and n_c centre runs (Salman, 2013).

CCD types are summarized in Figure 2.5 and Table 2.2. The α symbol is represent the distance of each axial point (also called star point) from the centre in a central composite design.

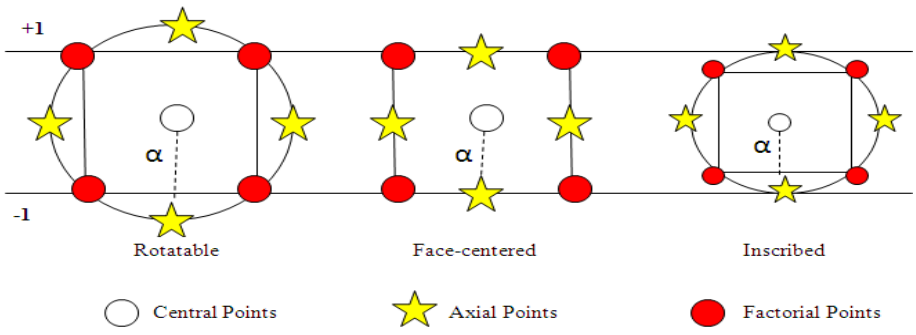

Figure 2.3: Three type of CCD

Table 2.2 Central composite designs

Central Composite Design Type	Comments
Circumscribed	• The original form of the CCD • The star is at some distance α from the centre based on the properties desired for the design and the number of factors in the design. • The star establishes new extremes for the low and high settings for all factors. • The designs have circular, spherical or hyperspherical symmetry. • Require 5 levels for each factor. • Augmenting an existing fractional factorial design with star can produces this design.
Inscribed	• This design is scaled down rotatable design with each factor level for the rotatable design divided by α.
Face centred	• Require 5 levels for each factor • The star is at the centre of each face of the factorial space at $\alpha = \pm 1$. • Require 3 levels for each factor. • Augmenting an existing factorial design with appropriate star can also produce this design.

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2.8.3 Analysis of data

A response surface model represents the functional form of a response surface based on either theoretical or empirical considerations. When a theoretical model cannot be specified in an experimental investigation (the usual case), polynomial models can be used to approximate the response surface. A quadratic model can provide a useful approximation for a broad range of applications. In addition, a quadratic (second-order) model is the most widely used for design fitting in the CCD. A complete second-order model is of the form:

$$Y = b_0 + \sum_{i=1}^{3} b_i x_i + \sum_{i=1}^{3} b_{ii} x_i^2 + \sum_{i=1}^{2} \sum_{j=i+1}^{3} b_{ij} x_i x_j + \varepsilon \qquad (2.15)$$

Where Y is the response (dependent variable), b_0 is the constant coefficient, b_i is the coefficient for the linear effect, b_{ii} is the coefficient for the quadratic effect, b_{ij} is the coefficient for the interaction effect, x_i and x_j are the independent variables (factors).

The analysis of the data is started by fitting a response surface model using provided software inside DoE program. The stepwise regression procedure allowed the selection of probabilities (*p*-values) for adding or deleting model terms. Stepwise will generate a screen with recommended model terms checked and *p*-values shown (these are called "Prob>F" in the output). Sometimes, based on *p*-values, some term might be chosen to reduce or uncheck. However, hierarchy principle should be followed and keep all main effects that are part of significant higher-order terms or interactions, even if the main effect *p*-value is higher than 0.05 which is common statistical significance level chosen.

A next step was proceeding with the analysis of variance (ANOVA). The ANOVA statistics consists of value for R^2, adjusted R^2, predicted R^2, lack of fit test, standard deviation, etc. in order to confirm the adequacy of the regression model. Generally, the R^2 value must be in the range of $0<R^2<1$. However, a large value of R^2

does not imply that the regression model is good. Then, the subsequent work was done with diagnostic of the statistical properties of the regression model. Inspection of various diagnostic plots was carried out to statistically validate the model. The most important diagnostic will be the normal probability plot of the standardized residuals (normal probability distribution). The data points should be approximately linear. A non-linear pattern indicates non-normality in the error term, which may be corrected by a transformation. Generation of model graphs such as contours and 3D graphs for interpretation is the last step before optimization of the overall data. All of these plots and statistics were used to determine whether the model fit is satisfactory. After each response get analysed and the model fitting was satisfied, optimization can be done either by inspection of the interpretation plots or with the graphical and numerical tools provided in the software packages.

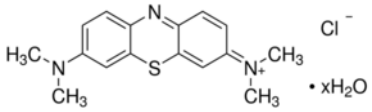
CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

In this study, palm trunk used as precursor for the preparation of PTAC. The raw material was collected at oil palm plantation at Nibong Tebal, Penang. Methylene blue (MB) supplied by Sigma-Aldrich (M) Sdn. Bhd was used as adsorbate and it properties were summarized in Tables 3.1.

Table 3.1 Properties of MB (Aldrich, 2017)

Properties	
Common name	Methylene Blue (MB)
IUPAC name	3,7-bis(Dimethylamino)phenazathionium chloride
Other name	Basic Blue 9, Tetramethylthionine chloride
Molecular formula	$C_{16}H_{18}ClN_3S$
Molecular weight	319.85 g/mol
CAS number	122965-43-9
Maximum wavelength, λ_{max}	663 nm
Chemical structure	

During the activation process, carbon dioxide (CO_2) was used as activating agent. The CO_2 gas was supplied by MOX Gases Berhad, Malaysia with its purity 98.00%.

3.2 Equipment and instrumentations

3.2.1 Preparation of PTAC

The palm trunk was obtained from oil palm plantation at Nibong Tebal, Penang. The palm trunk was cut into approximately 5 mm in size. The sample then undergo oven drying at 100^{o}C for two night to remove the excess moisture. Carbonization of the sample was done by pyrolized the sample in the furnace at 350^{o}C for 10 minutes. Then chars produced were left to cool to room temperature.

3.2.2 Activation of char by microwave heating

Activation of char produced was carried out by using the microwave heating. In this experiment, a commercial microwave was used with some modification in order to accommodate the experiment condition. The microwave has a power controller to regulate the power levels and time for various experiment condition. The top of the microwave was modified to allow the CO_2 to enter in the microwave by connecting a tube from the gas system. The gas supplied into the microwave flew with the constant flow rates that can be adjusted and measured by the gas flow meter. In addition, outlet gas from valve was passed to back side of microwave.

3.2.3 Characterization system

The samples are to be characterized by various techniques in order to study their characteristics that affected the performance of PTAC. Characteristics of samples were analyzed by using surface area analyzer, scanning electron microscopy (SEM) and Simultaneous Thermal Analyzer (STA). The surface area, pore volume and average pore diameter of the samples were determined by using Micromeritics ASAP 2020 volumetric adsorption analyzer. The BET surface area was measured from the adsorption isotherm using Brunauer-Emmett-Teller equation. The total pore volume