

**SYNTHESIS OF MICROWAVE-ASSISTED COCONUT SHELL BASED
ACTIVATED CARBON FOR REMOVAL OF METHYLENE BLUE DYE
FROM AQUEOUS SOLUTION**

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UNIVERSITI SAINS MALAYSIA

2018

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By

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**Thesis submitted in partial fulfilment of the requirement for the degree of
Bachelor of Chemical Engineering**

JUNE 2018

ACKNOWLEDGEMENT

Alhamdulillah, all praises to Allah, the Almighty God for the wisdom bestowed upon me, the strength, peace of mind and good health in completing this research. First of all, I would like to express my deepest appreciation to my mother, Rokiah binti Said and my other family members for their love and support.

My special gratitude I would like to deliver to my supervisor, Assoc Prof Dr Mohd Azmier Ahmad for sharing his precious knowledge and guidance throughout my final year as a student. His support and advices are really helping me in completing my Final Year Project with success. A big thank goes to School of Chemical Engineering for providing good facilities for me to complete my Final Year Project. Besides that, a special thank I would like to address to Dr Firdaus Yusop and Mrs Azduwin for helping and assisting me with my experimental work.

I would like to thank all the staffs and technicians especially En Syamsul for helping me with the equipment. A special thanks goes to my colleagues for supporting me and sharing their knowledge with me. Thank you for always be there whenever I needed motivation and support. Once again, I would like to thank all the people for always be there for me. Without their support I would not be able to complete my thesis successfully. Thank you very much.

Nazatul Shima Binti Nordin

June 2018

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LIST OF SYMBOLS

	Symbols	Unit
A	Arrhenius factor	-
B	Constant related to the heat of adsorption	J/mol
b_i	Linear coefficients	-
b_{ii}	Quadratic coefficient	-
b_T	Temkin isotherm constant	-
C	Boundary layer	-
C_o	Liquid-phase dye concentrations at initial stage	mg/L
C_e	Equilibrium concentration of dye in solution	mg/L
C_t	Liquid-phase concentration of dye at any given time	mg/L
E_a	Arrhenius activation energy of adsorption	kJ/mol
K_e	Langmuir adsorption constant	L/g
K_L	Langmuir adsorption constant	L/mg
K_F	Freundlich isotherm constant related to capacity	-
k_1	Rate constant of first-order sorption	h^{-1}
k_2	Pseudo-second order rate constant sorption	-
k_{dif}	Intra-particle diffusion	$mg/g(L/mg)^{1/2}$
N	The total number of experiments required	-
n	Number of factors	-
n_F	Constant for Freundlich	-
n_c	Number of replicates at the center point	-
q_t	Mass of solute absorbed per mass of adsorbent at any time	mg/g
q_e	Amount of dye adsorbed at equilibrium	mg/g
q_m	Maximum adsorption capacity	mg/g
R	Universal gas constant	8.314J/mol K
R^2	Coefficient of determination	-
t	Time	hr
T	Absolute solution temperature	K
X_1	Radiation power	W
X_2	Activation time	min

x_i	Coded value of the activated carbon experimental variables	-
x_j	Coded value of the activated carbon experimental variables	-
V	Volume of dye solution	L
W	Mass of adsorbent used	g
Y	Predicted response (Methylene blue removal)	%
ΔG°	Gibbs free energy	kJ/mol
ΔH°	Changes in standard enthalpy	kJ/mol
ΔS°	Changes in standard entropy	kJ/mol K

LIST OF ABBREVIATIONS

AC	Activated carbon
ANOVA	Analysis of variance
APCC	Asian and Pacific Coconut Community
BET	Brunauer-Emmet-Teller
CCD	Central composite design
CI	Color index
CS	Coconut shell
CSAC	Coconut shell based activated carbon
DOE	Design of experiment
EA	Elemental analyzer
FTIR	Fourier transform infrared
IUPAC	International Union of Pure and Applied Chemistry
MB	Methylene blue
RSM	Response surface method
SEM	Scanning electron morphology
TGA	Thermogravimetric analysis
UV	Ultraviolet

**PENGHASILAN KARBON TERAKTIF TEMPURUNG KELAPA DENGAN
KAEDAH GELOMBANG MIKRO UNTUK PENYINGKIRAN PEWARNA
METILENA BIRU**

ABSTRAK

Efluen pewarna yang berbahaya daripada kilang tekstil, kertas, kosmetik dan pemproses makanan telah menjadi kebimbangan utama kerana ia toksik kepada alam sekitar. Kajian ini bertujuan untuk menghasilkan karbon teraktif (KT) daripada tempurung kelapa (TK) untuk menyingkirkan metelina biru (MB) daripada larutan akuas. Karbon teraktif berasaskan tempurung kelapa (KTTK) telah disediakan melalui proses pengaktifan fizikal dengan menggunakan penyinaran gelombang mikro di bawah pengegasan karbon dioksida (CO₂). Kesan masa hubungan (0-24 jam), kepekatan awal (25mg/L-300mg/L) dan suhu (30°C, 45°C dan 60°C) terhadap prestasi penjerapan KTTK telai dinilai. Keadaan optimum untuk penyediaan KTTK diperoleh masing masing pada kuasa 440W dan masa 6 minit dengan menggunakan kaedah permukaan respon. KTTK yang dioptimumkan mempunyai luas permukaan BET yang tinggi, luas permukaan liang-meso, jumlah isipadu liang dan karbon tetap masing masing sebanyak 658.44m²/g, 502.31m²/g, 0.4898cm³/g and 82.13%. Liang KTTK adalah sejenis liang-meso dengan diameter liang sebanyak 5.72nm. Model Langmuir dan model pseudo-kedua telah didapati sebagai model terbaik untuk data keseimbangan dan data kinetik. Kapasiti penyerapan lapisan-mono MB keatas KTTK ialah 217.39 mg/g. Sistem penjerapan adalah bersifat endotermik dan ia ditadbir oleh penjerapan fizikal. Kajian mekanisme memdedahkan bahawa proses penjerapan MB keatas KTTK adalah dikawal oleh mekanisme difusi filem.

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ABSTRACT

The hazardous dye effluent from the textile, paper, cosmetic and food processing plant have become a major concern because of the toxicity to the environment. This study aims to synthesis activated carbon (AC) derived from coconut shell (CS) in order to remove methylene blue (MB) dye from aqueous solution. The coconut shell based activated carbon (CSAC) was prepared via physical activation process by using microwave irradiation under the flow of carbon dioxide (CO₂) gasification. The effect of contact time (0-24 hours), initial concentration (25mg/L-300mg/L) and temperature (30°C, 45°C and 60°C) on the adsorption performance of CSAC were evaluated. Optimum condition for the CSAC preparation was obtained at power and time of 440W and 6 minutes, respectively by using response surface methodology (RSM). The optimized CSAC has high BET surface area, mesopore surface area, total pore volume and fixed carbon of 658.44m²/g, 502.31m²/g, 0.4898cm³/g and 82.13%, respectively. The pore for CSAC was the mesoporous type with pore diameter of 5.72nm. Langmuir isotherm and pseudo-second-order was found as the best fitted model for MB adsorption equilibrium and kinetic onto CSAC. The monolayer adsorption capacity of MB onto CSAC was 217.3 mg/g. The adsorption system was endothermic in nature and it was governed by physisorption. The mechanism studies revealed that the adsorption process of MB onto CSAC were controlled by film diffusion mechanism.

CHAPTER ONE

INTRODUCTION

1.1 Dyes in industry

Dyes are complex aromatic molecular structure which intended to be stable and causing them difficult to be degraded. The use of synthetic dyes have become significant especially in fabric and textile industry. Textile industry involves a wet processing stage which require large volume of water and chemicals to be consumed and releases major amount of colorants as effluent (Arora, 2014). The inappropriate uptake of dyes can cause the industry effluent to have high concentration of dye pollutant and consequently increase wastewater pollution. The textile industry keeps up to search for an economical solution to decolorize the approximately 200 billion litres of coloured effluent produced annually. Textile dyeing industry is one of the most chemical intensive industries that caused a massive amount of environmental degradation problem, harm aquatic organism and human illness (Kant, 2012). According to Arora (2014), about 2% of dye used are discharged directly in aqueous effluent and about 10% of dyes is lost during process of coloration.

There are many types of physical treatment can be applied to treat dyes wastewater such as adsorption, ion-exchange, ultrasound and membrane filtration. Among them, activated carbon adsorption is the most common method to remove dyes from wastewater. However the commercial coal-based activated carbon is very expensive, thus leads to the research of using low cost and renewable precursors. Agricultural waste materials such as bamboo, coconut shell, corncob and peanut shell have been used as activated carbon (Bafana et al., 2011).

1.2 Coconut shell

Coconut (*Cocos nucifera*) is grown in more than 90 countries in the world (Anem, 2011). According to Asian Pacific Coconut Community (2005) it was estimated that the global coconut area was about 12 million hectares and the total production of coconut was estimated about 11.9 million metric tons (MT) (Anem, 2011). In 2014, the total of global production of coconut has increased to approximately 69.84 million metric tons (APCC Statistical Year Book, 2014). In Malaysia, coconut is one of the oldest agro-based industries and in term of planted area it is the fourth important crop after oil palm, rubber and paddy (Sivapragasam, 2008).

Coconut is commonly known as ‘tree of life’ since it has a wide range of applications (Statista, 2014). It consists of coir, meat, water, husk and shell. Coconut can be extracted to produce coconut milk and oil. It husk and shell can be used as fuel and charcoal sources while the coir, a natural elastic fiber extracted from coconut husk can be used to make brushes, roped and caulking for boats and fishing nets (Mercola, 2018). In Malaysia, coconut water is known as one of the best refreshing drink. Coconut production is used for domestic consumption and also for export and industrial processing. The domestic is demanding for fresh coconut, tender coconut, coconut oil and processed cream powder. Coconut milk is very important product for food industry.

1.3 Problem Statement

There are over 1 million tons of dyes are produced yearly (Boyter, 2007). The quality of effluent from the textile, paper, cosmetic and food processing plant have become a major concern as it created a serious pollution problem. Thus, this problem need to be treated properly.

An effective way to treat the dyes effluent is by adsorption. Coal based activated carbon has become significant adsorbent for removing dyes from industrial effluent. Even though the commercial coal based activated carbon is a preferred adsorbent, the precursor price is relatively high which led to the researches on using low cost precursor and renewable materials as AC's precursor (Rafatullah et al., 2010). In this study, activated carbon prepared from coconut shell waste was studied for dye removal.

In Malaysia, coconut shell is not used in food industry but they are being thrown away as wastes. Only small portion is used as solid fuel. In order to reduce landfill volume and pollution, this material can be converted to more valuable products that can beneficial to others such as activated carbon (Shankar, 2012). Generally, conventional furnace is used for activation process. However due to its long activation time and high energy consumption, researcher has shifted their interest towards microwave irradiation. Therefore, this research focus on the converting coconut shell to activated carbon via microwave irradiation process.

1.4 Research Objectives

The objectives of this research are as follow:

- 1) To determine the optimum preparation conditions (microwave power and time) in producing the coconut shell based activated carbon (CSAC) via microwave radiation.
- 2) To characterize CSAC in terms of surface area, surface morphology, and proximate content and surface chemistry.
- 3) To investigate the adsorption isotherm, kinetics and thermodynamics studies on adsorption of methylene blue (MB) onto CSAC.

1.5 Scope of Study

In this study, activated carbon was prepared from coconut shell for the removal of MB via single step physical activation. The preparation of CSAC was done by microwave irradiation process. The parameters that were being manipulated during activation process were microwave power and time. The effect of power and time on the percent removal of MB was analysed by using response surface methodology (RSM) in order to establish the optimum preparation conditions of CSAC for MB adsorption.

Batch studies were carried out by using the optimum sample of CSAC. Study the effect of temperature and contact time were done on the adsorption of MB dye at six different concentrations of 25, 50, 100, 200, 250 and 300 mg/L. The adsorption isotherm, kinetic, thermodynamic and diffusion mechanism were studied. The optimal CSAC was characterized by using BET, SEM, FTIR and TGA in order to analyse the surface area, surface morphology, pore volume and element content, respectively.

1.6 Thesis Organization

This thesis was organized into five chapters. In the first chapter, the introduction, problem statement, objective of the project and scope of study were described. In chapter two, the literature review were performed and discussed such as classification of dyes, method of dye removal, preparation of activated carbon, microwave irradiation and adsorption isotherm as well as adsorption kinetic, thermodynamic and diffusion mechanism. In chapter three, the materials and chemicals used were listed and the method for AC preparation, optimization and batch studies were discussed. Chapter four reported on the results and discussion of the work. In chapter five, the conclusions on this study together with the recommendation were deduced.

CHAPTER TWO

LITERATURE REVIEW

2.1 Dyes

Dye by definition is the chemical substance that being applied to impart colour on the surfaces. It is also known as the complex organic molecule and is required to be resistant to many things such as the action of detergent (Yagub et al., 2014). Dyes are the main attraction of any fabrics, foods and cosmetics. The colour of dyes depends on their ability to absorb light in the visible range of electromagnetic radiation between 400 nm to 700 nm (Bafana et al., 2011). Basically, a coloured dye has chromophores and auxochrome group. Chromophores give colour to dye since they are able to absorb light in visible region while auxochrome can deepen the colour of dyes (Bafana et al., 2011).

Generally, natural dyes are found to be extracted from vegetables, fruits and flowers. These dye provide limited and dull colour range and low colour fastness. Due to the limitation of natural dye, synthetic dyes have been used since it provides wider colour range. Its commonly contain sulphur, naphtol, vat dyes, nitrates, acetic acid, soaps, enzymes chromium compounds and heavy metals like copper, arsenic, lead, cadmium, mercury, nickel, cobalt and certain auxiliary chemicals which made it very toxic (Kant, 2012).

2.1.1 Classification of dyes

Dyes can be classified in term of its application and chemical structure. This classification is the principle system adopted by Colour Index (C.I). Classification by application characteristic is based on C.I Generic Name (i.e. acid, basic, direct, disperse, mordant, reactive, sulphur dye, pigment, vat, azo insoluble) while the classification of dye by its chemical structure is based on C.I Constitution Number (i.e. nitro, azo, anthraquinone, inorganic pigment, indamine and sulphur) (Carmen and Daniela, 2012). It is more favourable to classify dye according to its application before considering its chemical structure because of the complexities of the dye nomenclature (Gupta and Suhas, 2009). Table 2.1 below shows the classification of dye according to its application characteristics.

2.1.2 Method of dye removal

Dyes application has become essential in various industry especially textile industry. However, the presence of dye in the textile plant effluents has become a major problem due to its negative effect towards environment and human health. Thus, it is important to remove dye from the effluent wastewater. There are several ways that can be used to remove dye which are biological, physical and chemical methods. Table 2.2 summarize the advantages and disadvantages of the dye removal method.

Biological treatment is the most economical and environmental friendly method when compared to the physical and chemical processes (McMullan et al., 2001). Even so, the application of this method has disadvantages as it requires large land area and is constrained by sensitivity towards diurnal variation as well as toxicity of some chemicals and the flexibility in design (Bhattacharyya and Sarma, 2003).

Table 2 1: Dye classification based on application (Hunger, 2007)

Class	Principle substrates	Method of application	Chemical types
Acid	Nylon, wool, silk, paper, inks and leather	Usually from neutral to acidic dyebath	Azo (including premetallized), anthraquinone, triphenylmethane, azine, xanthene, nitro and nitroso azo
Basic	Paper, polyacrylonitrile, ,modified nylon, polyester and inks	Applied from acidic dyebaths	Cyanine, hemicyanine, diazahemicyanine, diphenylmethane, triarylmethane, azo, azine, xanthene, acridine, oxazine, and anthraquinone
Direct	Cotton, rayon, paper, leather and nylon	Applied from neutral or a little alkaline bath containing additional electrolyte	Azo, phtalocyanine, stilbene, and oxazine
Disperse	Polyester, polyamide, acetate, acrylic acid and plastics	Fine aqueous dispersion often applied by high temperature/pressure or lower temperature carrier methods ; dye may be padded on cloth and thermo fixed	Azo, anthraquinone, styryl, nitro, and benzodifuranone
Mordant	Wool, leather, and anodized aluminium	Applied in conjunction with Cr salts	Azo and anthraquinone
Reactive	Wool, cotton, silk and nylon	Reactive site on dye reacts with functional group on fibre to bind dye covalently under influence of heat and pH	Azo, anthraquinone, phtalocyanine, formazan, oxazine, and basic
Sulphur	Cotton and rayon	Aromatic substrate vetted with sodium sulphide and reoxidized to insoluble sulphur-containing products on fibre	Intermediate structures
Vat	Cotton rayon and wool	Water-insoluble dyes solubilized by reducing with sodium hydrogensulfide, then exhausted on fibre and reoxidized	Anthraquinone (including polycyclic quinones) and indigoids

Table 2 2: Advantages and limitations of the dye removal methods from industry effluent (Robinson et al., 2001)

Methods	Advantages	Disadvantages
<i>Chemical methods</i>		
Fentons reagent	Effective decolourisation of both soluble and insoluble dyes	Sludge generation
Ozonation	Applied in gaseous state; no alteration of volume	Short half-life (20 min)
Photochemical	No production of sludge	There is formation of by-products
Electrochemical destruction	Breakdown compound are non-hazardous	High cost of electricity
<i>Biological method</i>		
Decolourisation by white-rot fungi	White-rot fungi are able to degrade dyes using enzymes	Enzyme production has been shown to be unreliable
Other microbial cultures (mixed bacterial)	Decolourisation in 24-30 h	Azo dyes are not readily metabolized under aerobic condition
Adsorption by living/dead microbial biomass	Certain dyes have a particular affinity for binding with microbial species	Not effective for all dyes
<i>Physical method</i>		
Adsorption by activated carbon	Good removal of wide variety of dyes	Very expensive
Membrane filtration	Removes all type of dyes	Side reaction prevent commercial application
Ion exchange	Regeneration: no adsorbent loss	Not effective for all dyes
Electrokinetic coagulation	Economically feasible	High sludge production

Chemical methods involve several processes such as coagulation, flocculation, and irradiation. This method is very helpful in removing dye, however it is expensive and often creates a disposal problem due to the accumulation of concentrated sludge (Demirbas, 2009). Physical methods includes membrane-filtration processes and various adsorption techniques are used. The process that involve membrane filtration method has some limitation where the life time is limited and has a membrane fouling problem (Kharub, 2012).

2.2 Adsorption

Adsorption is known as one of the separation method. It is defined as accretion of a substance at the interface between two phases (liquid-solid interface or gas-solid interface) (Yagub et al., 2014). The substance that accumulates at the interface is called as adsorbate while the solid is referred as adsorbent (Dąbrowski, 2001). There are two classes of adsorption which are physical (physisorption) and chemical (chemisorption) adsorption.

The forces between adsorbate and adsorbent in physical adsorption is governed by weak van der Waals, hydrogen and dipole-dipole bond (Allen and Koumanova, 2005). Seader et al. (2011) stated that physisorption occurs rapidly and it can be mono molecular (unimolecular) layer or two or more layers thick (multimolecular). In their study, when physical adsorption is unimolecular it is easily reversible. Chemical adsorption involves the formation of chemical bonds or strong interparticle bonds (covalent and ionic bonds) between adsorbate and adsorbent due to exchange of electron (Seader et al., 2011, Allen and Koumanova, 2005).

Adsorption is one of the most efficient method of removing pollutants from wastewater (Noroozi et al., 2007). This technique has been found to be superior to other technique for water treatment in term of initial cost, flexibility and simplicity of design, ease of operation, insensitivity to toxic pollutants and does not result in the formation of harmful products (Crini, 2006). According to Noroozi et al. (2007), adsorption of dyes depends on the properties and structure of dyes and also surface chemistry of the adsorbent. Adsorbent can be from various materials, but among all activated carbon is the most common for the removal of pollutant from wastewater.

2.3 Activated carbon

Activated carbon is a substance that has large porosity and large specific surface area (Das et al., 2015). It is widely used in industry as an adsorbent for adsorption process from liquid and gas phases and the characteristic of the activated carbon must have high sorption capacity and selectivity (Kazmierczak-Razna et al., 2015). Other than that, it can be used to treat low concentration of wastewater streams and it is very cost effective (Das et al., 2015). According to Dejang et al. (2015), activated carbon was normally used for removal of toxic in waste water and gas. They also mentioned that the structure of activated carbon depends on the natural texture of each raw material and the activation process. Activated carbons are produced from carbonaceous material such as woods, nutshells, coconut shells and other materials that contained amorphous carbon.

Commercially, activated carbon are produced from coal, pitch and petroleum. Coal is commonly used for the production of activated carbon due to its availability and cheapness. However, the used of coal has some limitations because it is not pure material and it has variety surface properties which make it exhibit in different sorption properties (Rafatullah et al., 2010). Aside from that, the production and regeneration of

commercial activated carbon is relatively high cost and thus led to the production of activated carbon from non-conventional and low cost adsorbent.

2.3.1 Type of activated carbon precursors

The precursor has two origin of nature which are organic and inorganic. The selection of the precursor is depends on this nature. Plant and animal are the examples of organic precursor. Other materials that have high carbon contain are also considered as organic precursor. The inorganic precursors include soil, clay, mud, zeolites, ore materials, metal oxides and hydroxide (Ali et al., 2012).

For the production of low cost activated carbon, the precursor from waste materials can be used. Waste materials have little or no economic value and often cause a disposal problem (Demirbas, 2009). Thus, these wastes can be converted into activated carbon which is more beneficial to others. This can reduce the cost of disposal and also reduce the landfill volume. Table 2.3 shows the type of waste product that can be converted into activated carbon.

Table 2.3: Waste products used for activated carbon production (Pollard et al., 1992)

Waste products	Examples
Household wastes	Fruit waste, coconut shell, scrap tyres
Agricultural products	Bark and other tannin-rich materials, saw dust and other wood type materials, rice husk, other agricultural waste
Industrial waste	Petroleum wastes, fertilizer wastes, fly ash, sugar industry wastes
Sea materials	Chitosan and seafood processing waste, seaweed and algae, peat moss, miscellaneous waste
Soil and ore materials	Clays. Red mud, zeolites, ore minerals, sediment and soil

2.4 Preparation of activated carbon

Activated carbon can be produce from carbonaceous materials. Basically, there are two steps involve in the preparation of activated carbon which are carbonization and also activation. Carbonization process takes place at temperature below than 800°C (Ioannidou and Zabaniotou, 2007). Activation process involves either physical or chemical method. For physical activation, the carbonization and activation processes occur separately (two stage process) while for the chemical activation, activation and carbonization steps occur simultaneously (one stage process).

Commonly, the preparation of activated carbon involves conventional thermal heating process that performs in the tubular furnace reactor. However this method required a long preparation time for activation process (Ioannidou and Zabaniotou, 2007, Ismail et al., 2015). The thermal heating method also cause a high temperature gradient between the surface and the interior of materials and high energy consumption

is required for the process (Zhang and Hayward, 2006). Recently, researchers have shifted their attention towards microwave irradiation method which shorten the processing time and cost.

2.5 Microwave irradiation

Generally, the heating process in microwave is based on the conversion of electromagnetic energy into heat. The microwave radiation lies in the range of electromagnetic spectrum between infra-red and radio frequency and corresponds to wavelength of 1 cm to 1 m (frequencies of 30 GHz to 300 GHz) (Zhang and Hayward, 2006). Microwave has been used as a platform for activation process to take place and this has been reported by number of studies. In comparison to conventional heating, microwave irradiation has many advantages as it can reduce the activation time and eventually reduce the energy and gas consumption (Yang et al., 2017, Yuen and Hameed, 2009).

Basically, for the conventional heating, the energy is produced by the convective or conductive heating system (Foo and Hameed, 2011). In this process, heat is supplied from the surface to the centre of the sample which make the temperature at the surface higher compared to the inner sample (Zhang and Hayward, 2006). In contrast, microwave irradiation involves the heating from internal to the surface of the sample. Figure 2.1 illustrates the comparison of temperature gradient between the two heating methods.

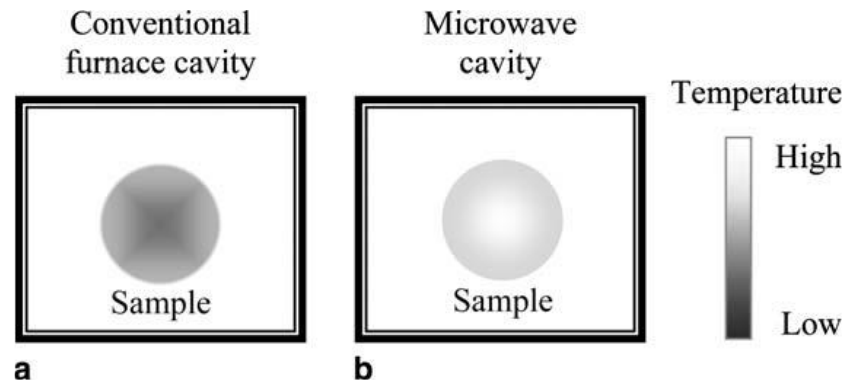


Figure 2. 1: Comparison of the temperature gradient for (a) conventional surface heating and (b) microwave heating (Zhang and Hayward, 2006)

2.6 Adsorption isotherm

Generally, adsorption isotherm describes the relation between concentration or partial pressure of adsorbate in fluid and the solute loading on the adsorbent which express as mass, moles, or volume of adsorbent per unit mass. This isotherm is an invaluable curve for the theoretical evaluation and interpretation of thermodynamic studies (Allen et al., 2004) but it is important to demonstrate the correlation for experimental equilibrium data in order to optimize the design of specific sorbate/sorbent system (Ncibi, 2008). Number of studies have been done regarding the conventional isotherm models. In this research, Langmuir, Freundlich and Temkin isotherm models have been studied. The best-fitting isotherm is determined by linear regression method and the regression coefficient, R^2 is analyzed in order to compare the suitability of isotherm equations. Based on previous study reported by Sartape et al. (2012) in the study of removal of Bi (III) by using CSAC, it showed that the equilibrium isotherm of CSAC is more fitted to Langmuir than Freundlich model. Karri et al. (2017) also reported that the adsorption isotherm of CSAC followed Langmuir isotherm.

2.6.1 Langmuir isotherm

Langmuir isotherm is corresponded to the unimolecular adsorption and it is known as the simplest isotherm model. This model describes the adsorption process that take place at definite homogenous active sites on the adsorbent used in the process. It is derived from mass-action kinetics with the assumption that chemisorption is the reaction. The linearized form of Langmuir isotherm is shown below (Langmuir, 1918) :

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

where,

q_e = Amount of dye adsorbed at equilibrium (mg/g)

C_e = Equilibrium concentration of dye in solution (mg/L)

q_m = Maximum adsorption capacity (mg/g)

K_L = Langmuir adsorption constant (L/mg)

Upon linearization, Langmuir isotherm model becomes:

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

Based on the linearized form of Langmuir equation, a graph of C_e/q_e against C_e is usually plotted and the best straight line is drawn. From the graph, K_L and q_m can be determined from the slope and y-intercept. Langmuir isotherm predicts an asymptotic limit for q_e at high pressure (Seader et al., 2011).

2.6.2 Freundlich isotherm

Freundlich isotherm is applicable for the multilayer adsorption and non-ideal adsorption on heterogeneous surfaces (Karri et al., 2017). Presently, this isotherm is workable in heterogeneous systems specifically for organic compounds or highly interactive species on activated carbon and molecular sieve. This empirical model shows can be used for low concentrations. The equation for Freundlich model is expressed as below (Freundlich, 1906):

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

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (2.4)$$

where,

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

C_e = Equilibrium concentration of adsorbate (mg/L)

n = Freundlich isotherm constant related to adsorption intensity

K_F = Freundlich isotherm constant related to capacity

For particular component and adsorbent, K_F and n is a temperature-dependent constants. Generally, K_F decreases while n increases with the increasing temperature, approaching 1 at high temperature (Seader et al., 2011). The linearize equation shown in Equation 2.4 is used to plot the graph of $\log q_e$ versus $\log C_e$. The two constant parameters are determined from the slope and y-intercept.

2.6.3 Temkin isotherm

In general, Temkin isotherm is the model that portrays the adsorption of hydrogen onto platinum electrode within the acidic solutions. This isotherm is used to evaluate the interaction of adsorption substance and adsorption interaction in heterogeneous system on the adsorption performance. An assumption has been made in this model which the heat of adsorption (function of temperature) of all the adsorbate molecules decrease linearly with the surface coverage (Karri et al., 2017). The general Temkin model equation are shown below:

$$q_e = \frac{RT}{b_T} \ln(T_T C_e) \quad (2.5)$$

Upon linearization, the isotherm is expressed as:

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

where

$$B = \frac{RT}{b_T} \quad (2.7)$$

T = Temperature at 298K

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

b_T = Temkin isotherm constant

T_T = Equilibrium binding constant (L/g)

B = Constant related to the heat of adsorption (J/mol)

2.7 Adsorption kinetics

Based on the literature, kinetic studies are carried out to measure the reaction rates at various experimental condition; to determine the effect of temperature and concentration on the reaction rates; and to determine the time required to achieve equilibrium adsorption (Mittal et al., 2007). Apart from that, kinetic study can also be used to determine the transient behaviour of the adsorption process (Bulut and Aydın, 2006) and it deals with the chemical changes properties in time (Azizian, 2004). Other than that, kinetic study also depicts the rate of solute uptake which in turn control the residence time of sorbate uptake at the solid-solution interface (Ho and McKay, 1999). Various models can be used to describe the adsorption kinetic process. According to the study done by Aljeboree et al. (2017), it described that the adsorption kinetic of CSAC followed the pseudo-second order model. Sartape et al. (2012) also reported that the adsorption kinetic of CSAC is more fitted to pseudo-second order than pseudo-first order.

2.7.1 Pseudo-first order

Lagergren (1898), suggested the linear form of pseudo first order and it has been widely applied (Ho and McKay, 1999). This model has been widely used to predict the adsorption kinetic of dye (Bulut and Aydın, 2006). The equation of pseudo-first order are expressed as:

$$\frac{dq}{dt} = k_1(q_e - q) \quad (2.8)$$

Upon the integration, by using boundary layer conditions of $t = 0$ to $t = 1$ and $q = 0$ to $q = q$ the linearized pseudo first-order model becomes:

$$\ln(q_e - q) = \ln q_e - k_1 t \quad (2.9)$$

where,

q = mass of solute absorbed per mass of adsorbent at any time (mg/g)

q_e = mass of solute absorbed per mass of adsorbent at equilibrium (mg/g)

k_1 = rate constant of first-order sorption (h^{-1})

2.7.2 Pseudo second-order

According to Ho (2006), the pseudo second-order describes the chemisorption that involves the valency forces through the sharing or exchange of electron between adsorbent and adsorbate as covalent force and ion exchange. This model has an advantageous where the equilibrium capacity from the experiment can be ignored as it can be calculated from the model (Ho, 2006). The general equation of this model can be expressed as:

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

Upon the integration by using the boundary condition of $t = 0$ to $t = 1$ and $q = 0$ to $q = q$, gives

$$\frac{1}{(q_e - q)} = \frac{1}{q_e} + k_2 t \quad (2.11)$$

where k_2 is the pseudo-second order rate constant sorption and by rearranging the equation, the linearized form of pseudo second-order are expressed as

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2.12)$$

2.8 Adsorption thermodynamic

In adsorption process, thermodynamic data provides the information about the final state of a system. Ho (2003) stated the concept of thermodynamic assumption which in an isolation system, where energy cannot be gained or lost, and the entropy change is the driving force. The thermodynamic parameters which are the standard enthalpy, ΔH° , standard entropy, ΔS° and standard free energy, ΔG° can be determined based on the adsorption data.

ΔH° is an important thermodynamic parameter which it indicates whether the system release or absorb heat. The negative value of the ΔH° represents the exothermic process while the positive value indicates the endothermic system. ΔS° is also an important parameter as it is used to identify the spontaneity in the sorption process (Kumar and Kumaran, 2005). ΔG° represents the fundamental criterion of spontaneity and if the value is negative, the reaction occur spontaneously at a given temperature. The study that was done by Sartape et al. (2012) showed the adsorption thermodynamic of CSAC was feasible, spontaneous and endoithermic. The thermodynamic parameters can be determine by the expression below:

$$\Delta G^\circ = -RT \ln Ke \quad (2.13)$$

$$Ke = \frac{qe}{ce} \quad (2.14)$$

The value of ΔH° and ΔS° can be determined by using Van't Hoff Equation as follow (Aljeboree et al., 2017):

$$\ln Ke = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (2.15)$$

By rearranging Equation 2.15, the Gibbs free energy can be represented as shown:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (2.16)$$

where,

K_e = Langmuir adsorption constant (L/g)

q_e = equilibrium concentration of dye ions on adsorbent (mg/g)

C_e = Equilibrium concentrations of dye ions in solution (mg/L)

ΔS° = Changes in standard entropy (kJ/mol K)

ΔH° = Changes in standard enthalpy (kJ/mol)

ΔG° = Gibbs free energy (kJ/mol)

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

T = Absolute solution temperature

The nature of the adsorption system whether it is governed by physisorption or chemisorption can be verified by using Arrhenius equation as shown in Equation 2.17:

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

where,

k_2 = rate constant from Freundlich model

A = Arrhenius factor

2.9 Adsorption diffusion mechanism

2.9.1 Intra-particle model

The intra-particle diffusion model is used to investigate the diffusion mechanism. The theory of this model was introduced by Weber and Morris (Weber and Morris, 1963). The equation for this model are expressed in Equation 2.18

$$q_t = k_{dif}t^{1/2} + C \quad (2.18)$$

where

C = y-intercept

k_{dif} = intra-particle diffusion rate constant

q_t = amount of solute adsorb per unit weight of adsorbent per time (mg/g)

Based on the theory, the intercept represents the boundary layer effect. The larger the intercept, the greater the contribution on the surface adsorption in the rate limiting step (Ahmad et al., 2015). When the plot of q_t versus $t^{1/2}$ is straight line and passing through the origin, then the rate limiting step is controlled by intra-particle diffusion.

CHAPTER THREE

MATERIALS AND METHOD

3.1 Overall experimental works

This chapter focuses on the overall experimental procedures and Figure 3.1 illustrated the schematic flow diagram of the experimental procedures which include preparation of precursor, carbonization of precursor, optimization study, sample characterization and lastly isotherm, kinetic, mechanism and thermodynamic study of adsorption.

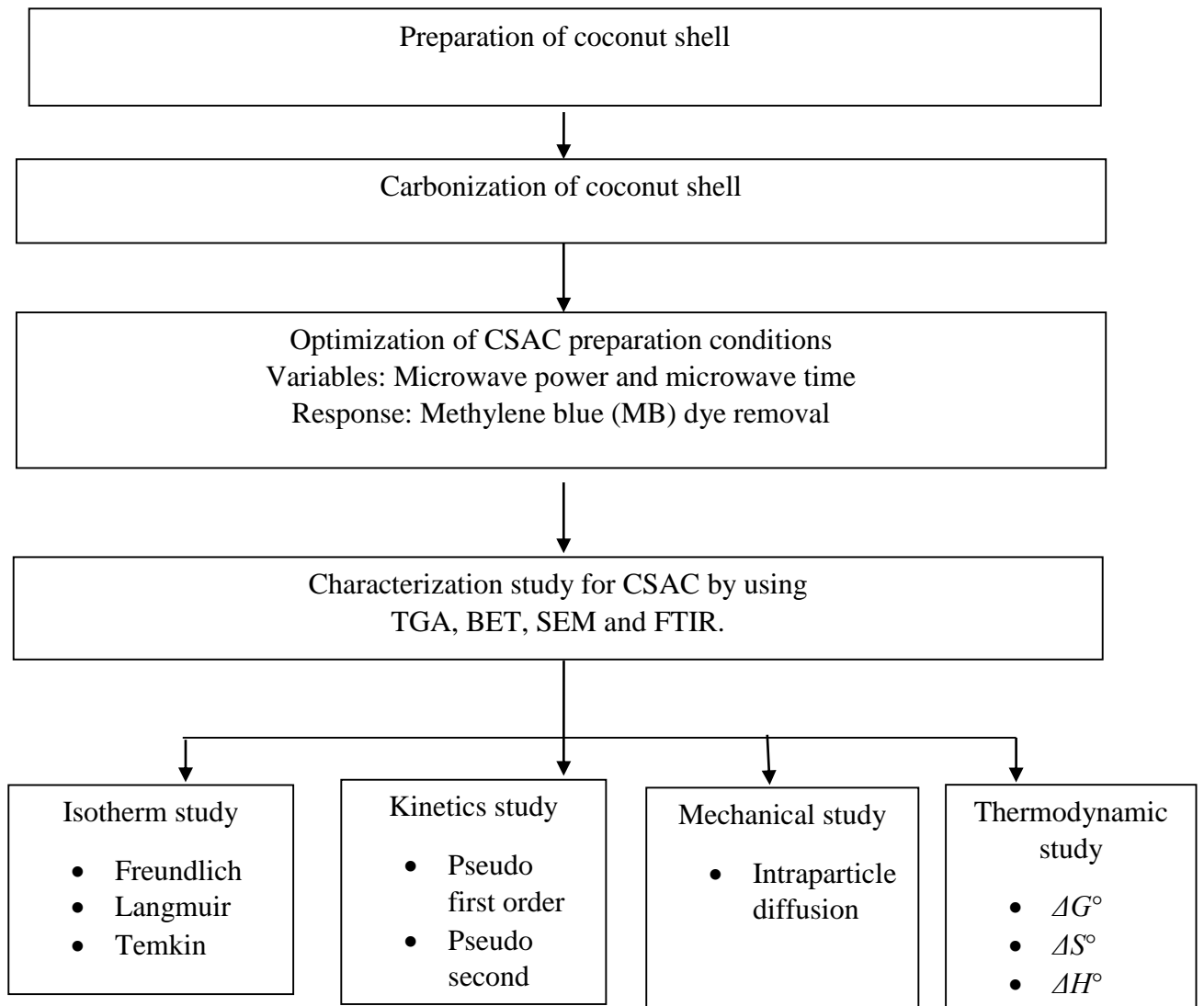


Figure 3.1: Schematic flow diagram of experimental procedures