SYNTHESIS AND CHARACTERIZATION OF MODIFIED BIO-CHARS FROM BIOMASS WASTE USING MICROWAVE-ASSISTED PYROLYSIS FOR METHYLENE BLUE REMOVAL

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This thesis is dedicated to my beloved parents, siblings, friends and those who directly or indirectly assist me in this research for their endless love and support

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ABSTRAK

Bio-arang (BC) adalah sumber yang boleh diperbaharui, unik dan kaya dengan karbon. Dalam beberapa tahun ini, pirolisis berbantu gelombang mikro telah menjadi alternatif yang baik berbanding pirolisis konvensional kerana kosnya yang rendah, masa pemprosesan yang pendek dan kecekapan tenaganya. Bio-arang berasaskan batang pisang (BP-BC) dan bio-arang berasaskan tempurung sawit (PK-BC) dihasilkan oleh pirolisis berbantu gelombang mikro dan digunakan untuk menjerap metilena biru (MB) dalam kajian ini. Batang pisang dan tempurung sawit dikumpulkan dan dikisar ke saiz zarah yang dikehendaki (200µm). Bahan yang telah dikisar kemudian menjalani pirolisis berbantu gelombang mikro pada 800W selama 20 minit. Sifat fizik-kimia BP-BC dan PK-BC telah dicirikan dengan menggunakan spectroskopi inframerah jelmaan Fourier, analisis termal gravimetrik, Brunauer-Emmett-Teller dan mikroskop imbasan elektron. Luas permukaan BET BP-BC dan PK-BC adalah masing-masing 46.58 dan 12.54 m^2/g, di mana BP-BC memberikan luas permukaan yang lebih tinggi. Ujikaji penjerapan berkelompok MB telah dikaji dengan BP-BC dan PK-BC dan kesan kepekatan awal pencelup dan masa sentuhan telah disiasat. BP-BC mempamerkan kapasiti jerapan maksimum yang tertinggi iaitu 165.2 mg/g. Dari data kinetik, penjerapan MB ke BP-BC mencapai keseimbangan dalam 100 minit manakala penjerapan MB ke PK-BC mencapai keseimbangan dalam 270 minit. Data kinetik juga menunjukkan bahawa penjerapan MB ke BP-BC mematuhi model kinetik pseudo tertib kedua manakala penjerapan MB ke PK-BC mematuhi model kinetik pseudo tertib pertama. Ini menunjukkan penjerapan MB ke BP-BC bersifat kimia manakala penjerapan MB ke PK-BC bersifat fizikal. Menurut data isoterma, penjerapan MB ke BP-BC dan PK-BC adalah satu lapisan. Menurut kajian termodinamik, penjerapan MB ke BP-BC adalah endotermik dan spontan manakala penjerapan MB ke PK-BC adalah eksotermik dan tidak spontan. Kajian ini telah menunjukkan bahawa BP-BC mempunyai hasil yang tinggi dan kapasiti jerapan yang tinggi dalam penjerapan MB.

ABSTRACT

Bio-char (BC) is a unique renewable resource which is porous and carbon-rich. In the past years, microwave-assisted pyrolysis has arisen to be a promising alternative to conventional pyrolysis due to its low cost, short processing time and energy efficiency. Banana pseudo-stem based bio-char (BP-BC) and palm kernel shell based bio-char (PK-BC) were produced by microwave-assisted pyrolysis and used to remove methylene blue (MB) in this study. The banana pseudo-stem and palm kernel shell were collected and grinded to desired particle size (200µm). The pre-treated materials then underwent microwave-assisted pyrolysis at 800W for 20min. The physicochemical properties of the BP-BC and PK-BC were characterized using Fourier tranform infrared spectroscopy, thermo-gravimetric analysis, Brunauer-Emmett-Teller and scanning electron microscope. The BET surface area of BP-BC and PK-BC were 46.58 and 12.54 m^2/g, where the BP-BC was higher. Batch adsorption experiment of MB was studied with BP-BC and PK-BC and the effect of initial concentration of MB and contact time were investigated. The BP-BC exhibited the highest maximum adsorption capacity of 165.2 mg/g. From the kinetic data, the MB adsorption onto BP-BC reached equilibrium within 100 min of contact time whereas the MB adsorption onto PK-BC reached equilibrium within 270 min. The kinetic data have also shown that the MB adsorption onto BP-BC followed pseudo second order kinetic model whereas MB adsorption onto PK-BC followed pseudo first order. This indicated that the adsorption of MB onto BP-BC was chemical whereas the adsorption of MB onto PK-BC was physical. According to the isotherm data, adsorption of MB onto BP-BC and PK-BC was monolayer. Last but not least, the thermodynamic studies showed that the adsorption of MB onto BP-BC was endothermic and spontaneous whereas the adsorption of MB onto PK-BC was exothermic and non-spontaneous. This study revealed that the BP-BC had high yield and high performance in the MB adsorption.

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LIST OF SYMBOLS AND ABBREVIATIONS

°C	-	Degree Celsius
ppm	-	Parts Per Million
R^2	-	Regression Coefficient
T	-	Temperature
K	-	Kelvin
q_e	-	Equilibrium Adsorption Capacity
q_m	-	Maximum Adsorption Capacity
M	-	Mass of Adsorbent
m^2	-	Meter Square
g	-	Gram
mg	-	Miligram
L	-	Liter
%	-	Percent
h	-	Hour
kg	-	Kilogram
W	-	Watt
min	-	Minute
nm	-	Nanometer
cm^2	-	Centimeter square
s	-	Second
mL	-	MiliLiter
J	-	Joules
kJ	-	KiloJoules
C_o	-	Initial Dye Concentration
C_e	-	Equilibrium Dye Concentration
K_L	-	Langmuir Isotherm Constant
K_F	-	Freundlich Isotherm Constant
n	-	Adsorption Intensity
ε	-	Dubinin-Radushkevich Isotherm Constant
E_A	-	Mean Free Energy

R	-	Universal Gas Constant
β	-	Temkin Isotherm Constant
K_T	-	Temkin Isotherm Equilibrium Binding Constant
q_t	-	Amount of Dye adsorbed at Time, t
K_1	-	Rate Constant of Pseudo First Order Model
K_2	-	Rate Constant of Pseudo Second Order Model
$\Delta G°$	-	Gibbs Energy
$\Delta H°$	-	Enthalpy
$\Delta S°$	-	Entropy
BOD	-	Biochemical Oxygen Demand
BET	-	Brunauer-Emmett-Teller
BP	-	Banana Pseudo Stem
BP-BC	-	Banana Pseudo Stem Based bio-char
COD	-	Chemical Oxygen Demand
FTIR	-	Fourier transform infrared
MB	-	Methylene Blue
PK	-	Palm kernel shell
PK-BC	-	Palm kernel shell based bio-char
SEM	-	Scanning electron microscopy
TGA	-	Thermal gravity analysis
UV-Vis	-	Ultraviolet-Visible Spectroscopy

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Dyes are commonly used in industry for colouring the products. Dyes are very stable and hard to biodegrade because of its complex aromatic molecular structure. There are several types of dyes that used commonly in industry like acid dyes, basic dyes, direct dyes and reactive dyes (Pearce, 2003). There are above 100,000 types of different commercial dyes that used in industry and the main concern dyes in this study is methylene blue.

Methylene blue is the first dyes in the world that synthesized by Heinrich Caro in 1876. Methylene blue has chemical formula of $C_{16}H_{18}ClN_3S$. Methylene blue is dark green colour in powder form and deep blue colour in aqueous form. Methylene blue is usually used in textile, food, paper and cosmetic industry for the purpose of colouring the products. Because of these few industrial activities, methylene blue is used extensively and contain in the effluent and finally discharge to the environment (Shahinyan *et al.*, 2019). The average American Dye Manufactures Institute (ADMI) value of methylene blue contain in the river in Malaysia is 3000 which is exceed the limit of the standard value of 200 set by Ministry of Natural Resources and Environment in Malaysia.

The pollution of water by methylene blue is bring a lot of impacts to the both human body and environment. Firstly, this pollution can cause destructive effect to the aquatic life which live in the receiving environment. The water contain methylene blue show high level of biochemical oxygen demand (BOD) and chemical oxygen demand (COD). High level of BOD implies that the water is highly polluted and high level of COD means that there are great amount of organic pollutants contain in the water (Li *et al.*, 2016). Methylene blue contain in the polluted water can cause the penetration of sunlight is block into the water and hence influence the photosynthesis of the aquatic plant. This cause is disrupting the ecosystem of the aquatic life and also the food chain. Meanwhile, methylene blue can cause hyperpyrexia, eyes burn, vomiting, and permanent injury to the nervous system of human body (Hasanzadeh *et al.*, 2020).

Methylene blue has a long lifetime in the environment due to its high stability and resistant to biodegradation. So that, there are a few method that used to treat the methylene blue from the polluted water for instant, membrane filtration, flocculation, oxidation and adsorption. One of the feasible removal methods is adsorption because it is the easiest, safest and most economical physicochemical treatment process.

Adsorbents are playing an important role in adsorption process where the adsorption process is occur on the surface of the adsorbents. There are few types of adsorbents used in industry which are silica gel, zeolites, polymers, clay and carbonaceous adsorbents. Carbonaceous adsorbents provide higher adsorption capacity compare to other adsorbents. For instance, natural activated carbon, carbon nanotube and bio-chars are carbonaceous adsorbents. Compare to other carbonaceous adsorbents, bio-chars is lower cost and easier to access. Bio-chars is a type of charcoal that made from biomass wastes by pyrolysis process. Bio-chars is refer to those porous carbonaceous material generated by thermal decomposition under low oxygen or no oxygen environment from different biomass feedstock (Benis et al., 2020). Biomass feedstock is refer to those organic waste that comes from animals and plants such as woods, forest residue, food crops, manures, sewage plants and municipal solid waste.

There are several methods for thermal decomposition to produce biochar which are slow pyrolysis, fast pyrolysis, microwave-assisted pyrolysis, torrefaction and hydrothermal carbonization. There are many advantages or benefits of biochar which lead to an increasing in research on biochar over past ten years. For instant, biochar is high energy efficient, low cost and environmental friendly as an adsorbent that used in wastewater treatment due to its large surface area and high adsorption capacity (Pandey et al., 2020).

Malaysia is a famous tropical rainforest climate country in world. Therefore, Malaysia is suitable for agricultural industry. Activities of agricultural industry such as terrace farming, slash and burn, sharecropping, ranching and urban farming can produce a large amount of biomass wastes annually which is total 1.2 million tonnes (Agamuthu, 2009). Currently, all the biomass wastes are abandoned during the harvest season, naturally left to putrid in the field or even burnt out. To reduce the biomass wastes in Malaysia, an alternative solutions are pursued. Incineration is an option to overcome this problem because it can reduce the volume of biomass wastes and also can converted the thermal energy into useful energy such as electrical energy. But, it is very costly to incinerate and it can bring impacts to both human health and environment. There are a lot of researchers that utilize and converted biomass wastes biomass into bio-chars due to biomasswastes biomass are abundantly available, low cost and renewable. biomass wastes biomass such as tea branches (Wang *et al.*, 2019), corn stalk (Chang *et al.*, 2019), banana peel (Zhang *et al.*, 2019) and peanut shell (Wu *et al.*, 2019) have been studied as precursors of bio-chars.

There are two pyrolysis processes that used to produce bio-chars which are conventional pyrolysis and microwave-assisted pyrolysis. Conventional pyrolysis is a process that the heat is transferred from the surface of the particles to inside of the particles by conventional oven. The temperature gradient is from the outside of the particle to the inside whereas the released volatiles diffuse from the inside of the particle to the surface of the particles. Microwave-assisted pyrolysis is totally different compare to conventional pyrolysis which the heating process is from internal of the particles to outside of the particles. This distinct heating phenomenon of microwave-assisted pyrolysis has become an alternative way in preparation of bio-chars from biomass wastes. Microwave-assisted pyrolysis can produce high product quality with low cost, less impact to both human body and environment and the processing time is short (Haeldermans *et al.*, 2019).

1.2 Problem Statement

In Malaysia, agricultural industry is one of the sources of economic growth. But, agricultural industry produce a huge amount of biomass waste such as trunks, leaves, husks, manures and plant stalks. This waste brings severe effects to the environment if managed poorly. Therefore, this waste can be employed as the precursor for bio-chars synthesis to minimize the effect to the environment. Also, biomass waste is abundantly available at low cost.

Many studies reported about the preparation of bio-chars from biomass wastes by conventional pyrolysis. However, less information was found regarding the bio-chars by microwave-assisted pyrolysis. Conventional pyrolysis has long processing time, low energy efficiency and high cost. Whereas, microwave-assisted pyrolysis can solve these problems. The processing time of microwave-assisted pyrolysis is short which is 20 - 30 minutes. The heating process of microwave-assisted pyrolysis is start from the internal part to the surface and this can reduce the energy lost. Thus, the energy efficiency of microwave-assisted pyrolysis is high. Information on bio-chars synthesis by microwave-assisted pyrolysis could offer some insights to achieve reproducible high quality bio-chars. The production of bio-chars from biomass wastes is important to reduce the environmental issues. This is because there is no any chemicals involve in the production of bio-chars. These conditions have not been given full attention in previous studies.

Methylene blue (MB) is a deep blue colour dye which commonly used in industry as coloring agent. It is very soluble in water and difficult to remove from effluent through conventional chemical and biological treatment. Since the characteristic of high solubility in water, MB can easily remove from wastewater through adsorption by using solid adsorbents. Thus, more research and studies should be focused on the removal of MB from wastewater to maintain the quality of water, environment and even human health.

There are some removal technique to remove MB from wastewater such as membrane filtration, flocculation, chemical treatment method, adsorption and gravity separation. However, some of these methods are high cost, non environmental friendly and need supplementary treatments. Among the existing MB removal technique, adsorption process has the highest popularity due to it is low cost and easiest physicochemical methods. Activated carbon has been widely used to remove MB. Activated carbon has high adsorption capacity but their main disadvantages are non environmental friendly and high cost. As a result, new research directions are being focused on developing low-cost and environmental friendly adsorbent such as bio-chars.

In this study, banana pseudo stem (BP) and palm kernel shell (PK) were selected as precursors. BP was chosen due to its hollow structure whereas PK was chosen due to its high abundance to environment. Thus, the synthesis and characterization of bio-chars in this study provide knowledge on the microwave-assisted pyrolysis.

1.3 Objectives

There are two objectives in this study:

1. To synthesis and characterize bio-chars from biomass waste by microwave assisted pyrolysis.

2. To evaluate adsorption capacity of the synthesized bio-chars for methylene blue removal process.

3. To analyse kinetics, isotherms and thermodynamics from the adsorption data.

1.4 Scopes of Research

There are few scopes in this study which are:

1. biomass wastes biomass i.e. banana pseudo stem (BP) and palm kernel shell (PK) were selected as precursors of bio-chars which were banana pseudo-stem based bio-char (BP-BC) and palm kernel shell based bio-char (PK-BC). The power of the microwave was set as 800 W whereas the time for the pyrolysis is 20 min. The physicochemical properties of synthesized bio-chars such as functional groups, weight loss of raw material, specific surface area, and surface morphology were determined by using FTIR, TGA, BET and SEM.

2. The bio-chars synthesized by microwave-assisted pyrolysis were used to undergo adsorption process. Methylene blue (MB) dye was used as an absorbate and the batch adsorption was performed to evaluate the adsorption performance of bio-chars. The effect of initial concentration of MB, contact time and temperature were studied at equilibrium.

3. The kinetic was studied at three concentration and at varying time intervals. The adsorption data obtained was analysed by using the kinetic models namely, pseudo first order (PFO), pseudo second order (PSO) and Elovich to study the interaction on the surface active sites. The isotherm of the adsorption process was studied via the concentration dependent adsorption experiments. The experiment was conducted at different initial concentration ranged from 25-400 ppm with contact time of 72h. The obtain data was further analysed by the most widely used isotherm models which are Freundlich, Langmuir, Temkin, Dubinin-Radushkevich and Redlich-Peterson to obtain the best fitted model that described the adsorption process. Thermodynamic study was carried out at temperature between 25 and

55°C. The thermodynamics model was used to evaluate the parameters of Gibbs free energy ($\Delta G°$), enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$).

1.5 Significance of Study

This study is to produce the high quality of bio-chars by microwave-assisted pyrolysis which will be significant by compare the different raw materials. The bio-chars produce is then used as adsorbent to determine the adsorption capacity on removal of methylene blue. It will help the industry to minimize the problem of dyes pollution and reduce cost by employing bio-chars in adsorptive treatment. In addition, this project is intended to be the beginning of an ongoing research into the topic of dyes pollution.

1.6 Thesis Outline

This proposal consists of five chapter. Chapter 1 presents the research background, problem statement, objectives, scope of study and significance of study. Chapter 2 presents the critically reviews of the dyes, methylene blue, dyes removal technologies, technical aspect of dyes adsorption, potential carbonaceous adsorbents for dyes removal and microwave-assisted pyrolysis. The discussion about the research materials and methods (i.e. materials, synthesis of bio-chars, bio-chars characterizations and adsorption of dyes) were presented in Chapter 3. Chapter 4 presents the result and discussion about characterization and evaluation of equilibrium and kinetics performance of the bio-chars in the methylene blue adsorption process. Last but not least, the conclusion of research findings and the recommendation for future research were presented in Chapter 5.

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