ACTIVATED CARBON FROM LONGAN SEED AND PISTACHIOS SHELL PREPARED VIA MICROWAVE IRRADIATED FOR DYE REMOVAL

SITI ZAWIYAH BINTI BAHAROM

UNIVERSITI SAINS MALAYSIA
2017

ACTIVATED CARBON FROM LONGAN SEED AND PISTACHIOS SHELL PREPARED VIA MICROWAVE IRRADIATED FOR DYE REMOVAL

by

SITI ZAWIYAH BINTI BAHAROM

Thesis submitted in fulfilment
of the requirement for the degree of
Master of Science

August 2017

ACKNOWLEDGEMENT

In the name of Allah, the Most Beneficent and the Most Merciful. All praises to Allah the Almighty for giving me the strengths, guidance and patience in completing this thesis. First and foremost, I would like to express my deepest gratitude to my beloved parents, Baharom Karim, Almarhum Nadzrah Hashim, brother and sisters for their endless love and support for me to pursue my MSc study. My deepest appreciation goes to Associate Professor Dr. Mohd Azmier Ahmad for serving as a supervisor and landing me adequate research experience and flexibility while working on this project. His understanding, wide knowledge and personal guidance have provided a good basis for the present thesis.

I would like to express my grateful thanks to all the technicians and postgraduate students of School of Chemical Engineering, especially Mohd Firdaus Yusop for their kindness assistance, professional advice and guidance in completing this project. Indeed, their willingness in sharing ideas, knowledge and skills are deeply appreciated. This study was funded by Universiti Sains Malaysia under Iconic grant scheme (Grant no. 1001/CKT/870023) for research associated with the Solid Waste Management Cluster, USM. I would like to express deepest gratitude to Ministry of Higher Education for the scholarship received under MyBrain 15. Last but not least, those who have directly and indirectly contributed to the accomplishment of this project, especially my family and friends for their motivation, encouragement and moral support. Thank you so much.

Siti Zawiyah Binti Baharom

August 2017

TABLE OF CONTENTS

CHAPTER ONE : INTRODUCTION

CHAPTER TWO : LITERATURE REVIEW

CHAPTER THREE : MATERIALS AND METHODS

CHAPTER FOUR : RESULTS AND DISCUSSIONS

CHAPTER FIVE : CONCLUSIONS AND RECOMMENDATIONS

APPENDICES

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATES

LIST OF SYMBOLS

	Symbol	**Unit**
A	Arrhenius factor	-
A_i	Measured absorbance for component i	-
A_T	Constant for Temkin isotherm	L/g
b_c	Path length of the cell	-
B_T	Constant for Temkin isotherm	mg/g h
B_t	Constant for Boyd model	-
C	Solute/outlet concentration	mg/L
C_e	Concentration of adsorbate at equilibrium	mg/L
C_i	Constant for Intraparticle diffusion model	mg/g
C_t	Concentration of adsorbate at time, t	mg/L
C_o	Initial adsorbate concentration	mg/L
$\mathrm{D_p}$	Average pore diameter	nm
E_a	Arrhenius activation energy of adsorption	kJ/mol
F	Fraction of solute adsorbed for Boyd model	-
K_F	Adsorption coefficient for Freundlich isotherm	mg/g $(\mathrm{L/mg})^{1/n}$
K_L	Rate of adsorption for Langmuir isotherm	L/mg
k_{pi}	Adsorption rate constant for intraparticle diffusion model	mg/g $\mathrm{h}^{1/2}$
k_1	Adsorption rate constant for pseudo-first-order	1/h
k_2	Adsorption rate constant for pseudo-second-order	g/mg h
N	Total number of experiments required/data point	-
n_F	Constant for Freundlich isotherm	-
Q_o	Adsorption capacity for Langmuir isotherm	mg/g
Q_m	Maximum adsorption capacity of adsorbent	mg/g
q_e	Amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium	mg/g
q_t	Amount of adsorbate adsorbed per unit mass of adsorbent at time, t	mg/g
$q_{t,\ cal}$	Calculated adsorption uptake at time, t	mg/g
$q_{t,\ exp}$	Experimental adsorption uptake at time, t	mg/g
R	Universal gas constant	8.314 J/mol K
R_L	Separation factor	-
R^2	Correlation coefficient	-

S_{BET}	BET surface area	m^2/g
V	Volume of the solution	L
V_{meso}	Mesopore volume	cm^3/g
V_T	Total pore volume	cm^3/g
W	Mass of adsorbent	g
w_c	Dry weight of prepared activated carbon	g
w_o	Dry weight of precursor	g
X	Activated carbon preparation variable	-
Y	Predicted response	-

Greek letters

ΔG^o	Changes in standard free energy	kJ/mol
ΔH^o	Changes in standard enthalpy	kJ/mol
Δq_t	Normalized standard deviation	%
ΔS^o	Changes in standard entropy	J/mol K
Λ	Wavelength	Nm
ε_λ	Molar absorptivity coefficient of solute at wavelength	-
λ	Wavelength	nm

LIST OF ABBREVIATIONS

AC	Activated Carbon
ANOVA	Analysis of Variance
BET	Brunauer–Emmett–Teller
CCD	Central Composite Design
FTIR	Fourier Transform Infrared
IR	Imprenation ratio
IUPAC	International Union of Pure and Applied Chemistry
LS	Longan seed
LSAC	Longan seed based activated carbon
MB	Methylene blue
PS	Pistachios shell
PSAC	Pistachios shell based activated carbon
RBBR	Remazol brilliant blue R
rpm	Rotation per minute
RSM	Response surface methodology
SEM	Scanning electron microscopy
STA	Simultaneous thermogravimetric analyzer

KARBON TERAKTIF TERHASIL DARIPADA BIJI LONGAN DAN KULIT PISTACHIOS MELALUI PENYINARAN GELOMBANG MIKRO UNTUK PENYINGKIRAN PENCELUP

ABSTRAK

Sisa pertanian yang berpotensi dimanfaatkan untuk penyediaan karbon teraktif untuk penyingkiran pencelup daripada larutan akuas. Untuk ujikaji ini, karbon teraktif berasaskan biji longan (KTBL) dan kulit pistachios (KTKP) telah disediakan mengunakan kaedah pengaktifan fiki-kimia yang terdiri daripada jerap isi kalium hidroksida (KOH), penggasan CO_2 dan penyinaran gelombang mikro. Prestasi KTBL dan KTKP dinilai dengan menjalankan kajian penjerapan kelompok untuk menyingkirkan pencelup metilena biru (MB) and remazol biru berkilau R (RBBR). Dengan menggunakan rekabentuk komposit pusat, keadaan optimum penyediaan bagi kuasa penyinaran, masa penyinaran dan nisbah jerap isi (NJI) telah ditentukan untuk KTBL (330 watt, 2.0 min dan 0.7) dan KTKP (440 watt, 2.07 min dan 1.0), di mana masing-masing telah menghasilkan penyingkiran MB dan RBBR sebanyak 77.0% dan 80.9% dan hasilan sebanyak 22.1% and 21.7%. KTBL dan KTKP mempunyai luas permukaan yang tinggi (>847 m^2/g), isipadu liang (> 0.49 cm^3/g) dan kandungan karbon tetap (>76%) dan mempunyai taburan saiz liang jenis heterogen dan berliang meso. Kesan kepekatan awal pencelup (25-300 mg/L), masa sentuh (0-24 jam) dan suhu larutan telah dinilai. Penjerapan pencelup oleh KTBL dan KTKP meningkat apabila kepekatan awal pencelup dan masa sentuh meningkat. Untuk data keseimbangan bagi penjerapan kedua-dua pencelup ke atas KTBL dan KTKP adalah sesuai dipadankan oleh model *Freundlich*. Manakala, data kinetik adalah terbaik

diwakili oleh model pseudo tertib pertama. Untuk kedua-dua pencelup, proses penjerapan oleh KTBL dan KTKP masing-masing adalah endotermik dan eksotermik dan semua proses penjerapan yang dikaji dikawal oleh mekanisma serapan-filem.

ACTIVATED CARBON FROM LONGAN SEED AND PISTACHIOS SHELL PREPARED VIA MICROWAVE IRRADIATED FOR DYE REMOVAL

ABSTRACT

Potential of agrowastes were harnesses for preparation of activated carbon (AC) for dyes removal from aqueous solution. In this study, longan seed based activated carbon (LSAC) and pistachios shell based activated carbon (PSAC) were prepared using physiochemical activation consisting of potassium hydroxide (KOH) impregnation, CO_2 gasification and microwave irradiation. The performance of the LSAC and PSAC were evaluated by conducting a batch adsorption study for methylene blue (MB) and remazol brilliant blue R (RBBR) removal. By using central composite design (CCD), the optimum preparation conditions of radiation power, radiation time and IR were determined for LSAC (440 watt, 2.0 min and IR 0.7) and PSAC (440 watt, 2.07 min and 1.0), which resulted MB removal of 77.0% and 80.9%, respectively; RBBR removal of 59.4% and 69.8%, respectively and yield of 22.1% and 21.7%, respectively. LSAC and PSAC have high surface area (>847 m^2/g), pore volume (> 0.49 cm^3/g) and fixed carbon content (>76%). The LSAC and PSAC have heterogeneous type pore size in mesoporous region. The effect of initial dye concentrations (25-300 mg/L), contact times (0-24 hours) and solution temperatures (30-60^oC) were evaluated. The MB and RBBR adsorption by LSAC and PSAC were increased as the initial dye concentration and contact time increased. The adsorption equilibrium data for both dyes onto LSAC and PSAC were best fitted by *Freundlich* model. Meanwhile, the kinetic data was best represented by the pseudo first-order kinetic model. For both dyes, the adsorption of LSAC and PSAC were respectively endothermic and exothermic processes. All the adsorption processes were mainly governed by the film-diffusion controlled mechanism

CHAPTER ONE

INTRODUCTION

1.1 Textile industries and environmental issue

Textile dyeing industries are facing challenges as it is one of the most chemically intensive industries in the world. This industry has been known as one of the major source of water consumption as well as water pollution (Khelifi et al., 2009) et al., 2014). The primary function of water is to rinse the excessive dyes off from the colored and printed fabric to achieve water fastness. Water is also required for cleaning the printing machine to remove loose color paste from printing blankets, screens and dye vessels (Kant and Rita, 2012). The dyeing process demands huge quantities of water for only small amount of dyed fabric. For every fabric being manufactured, the typical water to dye ratio is 15:1 (Conklin et al., 2012) et al., 2016). This excess water polluted with toxic dyes from dyeing process is often discharged into the lakes, rivers and other water resources causing water pollution and release unbearable odor.

For an average size textile mill that having 8000 kg fabric production per day, it is estimated that the daily water consumption is around 1.6 x 10^6 liters. 16 % of water usage consumed in dyeing while 8 % in printing. Depending on the types of dye used, the specific water consumption in dying process may vary from 30-50 L/kg of fabric. This represents a significant environmental problem for the textile industries.

Numerous studies have been carried out to investigate the harmful impacts of the effluent colorants to the water and ecosystem. It was found out that the dyes have (a) chronic effect towards the exposed aquatic organisms; (b) are highly visible even in small concentration and cause abnormal coloration on the water surface; (c) ability to absorb or reflect the sunlight entering the water that can upset the biological activities such as photosynthesis of aquatic flora; (d) create a toxic condition to the aquatic organisms and (e) not easily degradable by light, chemical and biological substances if not properly treated.

1.2 Industrial dye effluent treatments

Dyes are normally obtained from petroleum based intermediate, which are largely synthetic. The most common types of dye used in textile industries are basic dye and reactive dye. Basic dyes such as methylene blue (MB) and malachite green (MG) consist of amino groups or alkylamino groups as their auxochromes. Basic dye usually being applied to wool, silk, cotton and modified acrylic fibres (Dural et al., 2011). On the other hand, reactive dyes such as remazol brilliant blue reactive (RBBR) and remazol black (RB) which have been characterized by nitrogen to nitrogen double bonds (N=N) are widely used in cotton dyeing textile industry.

There are many conventional methods for dye effluent treatments such as chemical, biological and physical treatment. Although chemical treatment using coagulating agent is a robust way for dyes removal, it is not economical feasible for large scale industries operation as the accumulation of concentrated sludge can create further disposal problems such as transportation cost and environmental issue (Dash and Bibek, 2010). This process is not suitable for treating the water effluents that having large concentration of dyes.

Biological treatments such as fungal and microbial decolorization using aerobic or anaerobic condition are unsatisfactory due to its incapability of removing dyes in continuously basis and had less design and operation flexibility. Besides, biological treatment is a very time consuming process which requires larger land area.

For physical treatment, membrane filtration such as nanofiltration, reverse osmosis, electro dialysis and adsorption techniques are used in dye treatment processes. The adsorption technique so far is among the most versatile technique for dyes wastewater treatment. It has advantages such as high efficiency in removing dyes, low initial cost especially if using wastewater precursors, easy to operate and simplicity of design. Adsorbent particularly activated carbon (AC) has special characteristic such as high adsorption capacity and surface area make it suitable to be used in dyes wastewater treatment.

1.3 Longan seed and pistachios shell

In order to choose the suitable precursors for AC production, a few crucial factors must be considered such as fixed carbon content, renewable and economy friendly. The interesting area in adsorption study is to explore new waste precursor for AC production. In this study, waste of longan seed and pistachios shell waste were chosen as the precursors to be converted into AC.

Longan or scientifically known as *Dimocarpus Longan* is a tropical fruit tree that belong in Sapindaceae family together with lychee. This fruit tree can easily be found in Taiwan, China, Malaysia, Thailand and Vietnam. The edible part of this fruit ranges from 67 to 78% by weight of the whole fruit. The sugar content of this fruit is quite high and provides energy value of 1090 kcal/kg. The edible part of this fruit is juicy and sweet, making them a popular fruits among the natives. Although this fruit gets consistent demand all the year, a short harvesting season together with its highly perishable nature had caused oversupply flow to the market at certain time. The longan fruit was processed and the edible flesh part was dried and canned, left behind the accumulation of longan seed as waste.