ACTIVATED CARBON DERIVED FROM *PENTACE TRIPTERA*, *INTSIA BIJUGA* AND *HEVEA BRASILIENSIS* SAWDUST VIA MICROWAVE-INDUCED POTASSIUM HYDROXIDE ACTIVATION FOR DYES ADSORPTION

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by

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LIST OF SYMBOLS

	Symbol	Unit
A	Arrhenius pre-exponential factor	-
A_T	Temkin isotherm constant	L/g
b_i	Linear coefficient	-
b_0	Constant coefficient	-
b_{ii}	Quadratic coefficient	-
b_{ij}	Interaction coefficient	-
B	Boyd plot slope	-
B_{DR}	Dubinin–Radushkevich model constant	mol^2 /kJ^2
B_T	Temkin constant related to the heat of adsorption	J/mol
B_t	Boyd plot constant	-
C	Intercept related to the boundary layer effect	mg/g
C_e	Adsorbate concentration at equilibrium	mg/L
C_0	Adsorbate concentration at initial	mg/L
C_t	Adsorbate concentration at time “t”	mg/L
C_{ad}	Adsorbed solute concentration	mg/L
D_i	Effective diffusion coefficient	m^2/h
e_i	Error	-
E_a	Activation energy	kJ/mol
E_{DR}	Mean energy of sorption	kJ/mol
H	The bed depth of column	cm
k_A	Adams-Bohart kinetic constant	L/min.mg
k_{TH}	Thomas rate constant	L/min mg
k_Y	Yoon Nelson rate constant	1/min
k_{AV}	Avrami constant	1/h
k_{ti}	Intraparticle diffusion rate constant	mg/g $h^{1/2}$
k_1	Pseudo-first order model rate constant	1/h
k_2	Pseudo-second order rate constant	g/mg h
Kc	The equilibrium constant	-
K_L	Langmuir model constant	L/mg

K_f	Freundlich constant related to adsorption capacity	$(m/g)(L/mg)^{1/n}$
m_s	Dry weight of the adsorbent after exhausted	g
m_{tot}	Quantity of adsorbates deposited in the column	g
M	Mass of activated carbon	g
n	Number of variables	-
n_c	Number of centre runs	-
n_F	Freundlich constant related to sorption intensity of the sorbent	-
n_{AV}	Avrami model exponent of time	-
N	Number of data points	-
N_0	Adams-Bohart saturation concentration	mg/L
q_e	Amount of adsorbate adsorbed at equilibrium	mg/g
q_{TH}	Thomas adsorption capacity of the bed	mg/g
q_t	Adsorption capacity of adsorbent at time "t"	mg/g
q_{bed}	Bed capacity	mg/g
q_{tot}	Total adsorbed quantity of adsorbate	mg
$q_{e,exp}$	Experimental amount of adsorbate adsorbed at equilibrium	mg/g
$q_{e,cal}$	Calculated amount of adsorbate adsorbed at equilibrium	mg/g
Q	Volumetric flow rate	mL/min
Q_m	Maximum Langmuir monolayer capacity	mg/g
Q_{DR}	Theoretical monolayer saturation capacity	mg/g
r	Radius of the adsorbent particle	m
R	Perfect gas constant	J/mol.K
R_L	Langmuir adsorption isotherm characteristic	-
R^2	Correlation coefficient	-
S_{BET}	BET surface area	m^2/g
t_{tot}	Total flow time until exhaustion	min
T	Absolute temperature	K
U_o	Linear velocity	cm/min
V	Volume of the solution	L
w_{char}	Dry weight of char	g
w_{KOH}	Dry weight of KOH pellets	g
W	Mass of adsorbent	g
x_1	Radiation power	Watt

x_2	Radiation time	min
x_3	Impregnation ratio	-
Y_1	Percentage of adsorbate removal	%
Y_2	Yield percentage	%

Greek letters

$\pm\alpha$	Distance of axial point from centre	-
α_E	Elovich initial adsorption rate	mg/g min
β_E	Elovich desorption constant	g/mg
ΔG^o	Change in free energy	kJ/mol
ΔH^o	Change in enthalpy	kJ/mol
ΔS^o	Change in entropy	kJ/mol
Δq	The normalised standard deviation	-
ε	Polanyi potential	kJ/mol
λ	Wavelength	nm
π	Ratio of a circle's circumference to its diameter	-
τ	Time required for 50% adsorbate breakthrough	min
χ^2	Chi-square	-

LIST OF ABBREVIATIONS

AC	Activated carbon
ANOVA	Analysis of variance
AP	Adequate Precision
BET	Brunauer-Emmett-Teller
CCD	Central composite design
DoE	Design of experiment
FC	Fixed carbon
FRIM	Forest Research Institute Malaysia
FTIR	Fourier transform infrared
HS	*Hevea brasiliensis* sawdust
HSAC	*Hevea brasiliensis* sawdust-based activated carbon
IR	Impregnation ratio
IS	*Intsia bijuga* sawdust
ISAC	*Intsia bijuga* sawdust-based activated carbon
IUPAC	International Union of Pure and Applied Chemistry
MB	Methylene blue
MTZ	Mass transfer zone
PS	*Pentace triptera* sawdust
PSAC	*Pentace triptera* sawdust-based activated carbon
RBV	Reactive Brilliant Violet 5R
rpm	Rotation per minute
RSM	Response surface methodology
SD	Standard deviation
SEM	Scanning electron microscopy
spp.	Species
TGA	Thermogravimetric analyzer
VM	Volatile matter

KARBON TERAKTIF DARIPADA HABUK KAYU *PENTACE TRIPTERA*, *INTSIA BIJUGA* DAN *HEVEA BRASILIENSIS* TERHASIL MELALUI PENGAKTIFAN GELOMBANG MIKRO TERINDUKSI KALIUM HIDROKSIDA UNTUK PENYERAPAN PEWARNA

ABSTRAK

Pewarna sintetik digunakan secara meluas dalam pelbagai industri yang mengakibatkan pencemaran air. Oleh itu, kajian ini bertujuan untuk menghasilkan karbon teraktif (AC) daripada *Pentace triptera* (PS), *Intsia bijuga* (IS) dan *Hevea brasiliensis* (HS) untuk penjerapan pewarna metilena biru (MB) dan remazol ungu berkilau 5R (RBV) melalui pengaktifan gelombang mikro-terinduksi kalium hidroksida (KOH) bersama dengan gasifikasi karbon dioksida (CO_2). Keadaan penyediaan optimum untuk semua AC ditentukan menggunakan kaedah permukaan respon (RSM). ISAC telah menunjukkan luas permukaan Bruneaur-Emmet-Teller (BET) dan jumlah jisim liang yang tinggi iaitu 952.23 m^2/g dan 0.584 cm^3/g, masing-masing berbanding PSAC dan HSAC. Semua penjerap berpadanan dengan model isoterma Langmuir dengan ISAC telah menunjukkan kapasiti penjerapan monolayer maksimum (Q_m) tertinggi sebanyak 434.78 dan 212.77 mg/g, masing-masing untuk pewarna MB dan RBV pada 30ºC. Kajian kinetik menunjukkan bahawa semua sistem mengikuti model pseudo-tertib kedua dengan resapan filem adalah langkah pengehad yang mengawal penjerapan. Kajian termodinamik mengesahkan bahawa semua sistem bersifat endotermik. Untuk kajian turus, korelasi data terobosan yang lebih baik ditunjukkan oleh model Thomas dan Yoon-Nelson. Semua AC mempunyai prestasi kebolehgunaan yang baik untuk penjerapan MB dan RBV terutamanya sehingga tiga kitaran menggunakan etanol sebagai pelarut.

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ABSTRACT

Synthetic dyes are widely applied in various industries which has resulted in the water pollution. Therefore, this study aims to synthesis activated carbon (AC) from *Pentace triptera* (PS), *Intsia bijuga* (IS) and *Hevea brasiliensis* (HS) for methylene blue (MB) and remazol brilliant violet 5R (RBV) dye adsorption via microwave-induced potassium hydroxide (KOH) activation adopted together with carbon dioxide (CO_2) gasification. Optimum preparation conditions for all ACs prepared were determined using response surface methodology (RSM). ISAC showed high Bruneaur-Emmet-Teller (BET) surface area and total pore volume of 952.23 m^2/g and 0.584 cm^3/g, respectively compared to PSAC and HSAC. All adsorbents best fitted to the Langmuir isotherm model with ISAC showed higher maximum monolayer adsorption capacity (Q_m) of 434.78 and 212.77 mg/g, respectively for MB and RBV dye at 30ºC. Kinetic studies showed that all system followed a pseudo-second order model with film diffusion was the rate-limiting step controlling adsorption. Thermodynamic studies confirmed that all systems were endothermic in nature. For the column studies, the better correlation of breakthrough data shown by Thomas and Yoon-Nelson model. The ACs had good reusability performance for MB and RBV adsorption especially up to three cycle using ethanol as solvent.

CHAPTER 1

INTRODUCTION

This chapter highlights the background of the study, problem statement, research objectives as well as scope of study.

1.1 Background of study

Dyes are common pollutants that can be found in aqueous waste streams from industrial sections including paint, textile, plastic, cosmetic and paper industries. Greater than 700,000 metric tons of dyes are produced annually, with 2-3% is reported loss to industrial wastewaters during manufacturing and dyeing (Sangon *et al.*, 2018). Many of these dyes can cause allergies, skin irritation or even cancer and human mutations (Wang *et al.*, 2018). They are also considered dangerous to the environment and result in the deterioration of water quality, thus affecting aquatic life (Heidarinejad *et al.*, 2018). It is therefore essential to remove these dyes from the waste stream prior to release into watercourses.

Various methods such as adsorption, coagulation, advanced oxidation and membrane separation are used in the removal of dyes from wastewater. Adsorption via activated carbon (AC) as adsorbent is one of the most effective wastewater treatment processes used by the textile industry to reduce pollutants present in the effluent (Yagub *et al.*, 2014). AC is a term used to express carbon-rich materials which contain well-built internal pore structure. The high surface area (> 400 m^2/g), well-organized pores and a wide range of chemical functional groups present on the surface of AC make it a versatile and popular adsorbent in wastewater treatment industries (Danish and Ahmad, 2018).

Recently, heating systems employing microwave irradiation have been widely used for the preparation of AC. The microwave energy is transferred to the interior part of the samples by dipole rotation and ionic conduction, rather than by conduction and convection (Makhado *et al.*, 2018). Consequently, microwave heating results in a significantly reduced treatment time. The removal of dyes from wastewater using AC prepared by microwave-assisted activation from various source such as date stones (Abbas and Ahmed, 2016), coconut shells (Mohammed *et al.*, 2015), pomegranate peel (Ahmad *et al.*, 2014), oil palm shells (Hesas *et al.*, 2013a), peanut shells (Georgin *et al.*, 2016), coffee shells (Li *et al.*, 2016a), palm kernel shells (Kundu *et al.*, 2015a), Jatropha (Khalil *et al.*, 2013) and rice husks (Muniandy *et al.*, 2014) have been studied by other researchers. Out of these presursors, woody materials are significant sources for AC preparation, because they contain appropriate carbon fractions (50–90%) and low ash content (< 5 %) (Kazemi *et al.*, 2016).

Malaysia produces large amount of forest and wood processing mass where logging residues were produced during various phases of logging. The secondary processing residues are produced during the process of planning mills, moulding plants, and furniture factories in the form of sawdust, plane shavings, small pieces of lumber trimming, edging, bark and fragments (Osman *et al.*, 2014). With the growing of wood activities has also increased the wood waste amount resulted from this process. *Pentace triptera* (PS), *Intsia bijuga* (IS) and *Hevea brasiliensis* (HS) are among commercially important hardwoods used in Malaysian wooden furniture manufacturing industry which has resulted in the increasing of the waste sawdust from these wood species. These three woods PS, IS and HS possess different density of 530-755 kg/m^3, 515-1,040 kg/m^3 and 560 - 640 kg/m^3, respectively. It was hypothesized that different density of wood will results in different characteristic and adsorption capability for batch and column mode of studies. Therefore, the potential of these three waste sawdust as a precursor in producing novel AC has been explored in this study.

1.2 Problem statement

Various cationic and anionic synthetic dyes such as methylene blue (MB) and Remazol Brilliant Violet 5R (RBV) are released in water bodies through the effluents of these industries. The discharge of MB basic dye into the water stream has a number of harmful effects such as allergic dermatitis, skin irritation, mutations, and even cancer (Rangabhashiyam and Balasubramanian, 2018). The reactive RBV dye is an anthracene derivative and represents an important class of toxic and recalcitrant organic pollutants (Bello and Ahmad, 2011a). Due to stable conjugation structures by the presence of an -N=N- (azo) bond in the chemical structure, RBV dye is difficult to eliminate by biodegradation process (Li *et al.*, 2017). Therefore, the strategy to eliminate the colour and to reduce its effect on the industrial effluents before they are mixed up with natural water bodies is of significant importance.

Adsorption process using AC has been considered superior method for dye treatment due its high efficiency and operational simplicity. However, this application is limited by the cost of production and vague methods (Danish and Ahmad, 2018). The heating techniques strongly affect the physical and chemical characteristics of AC. Through conventional heating, heat is transferred to the samples by conduction and convection mechanisms which leads to an inhomogeneous heating samples of dissimilar shapes and sizes. Furthermore, this thermal heating takes a longer time to achieve the preferred phase of activation. Consequently, volatile components may remain inside the particles, giving rise to carbon deposition problems. The deposited carbon leading to distortion and inhomogeneous structure, low values of total pore