

**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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UNIVERSITI SAINS MALAYSIA

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by

AZDUWIN BINTI KHASRI

**Thesis submitted in fulfilment of the requirements
for the degree of
Doctor of Philosophy**

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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 | $\text{mol}^2 / \text{kJ}^2$ |
| 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_{ii} | Intraparticle diffusion rate constant | $\text{mg}/\text{g h}^{1/2}$ |
| 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 | $(\text{m/g})(\text{L/mg})^{1/n}$ |
| 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 |
| $q_{e,\text{exp}}$ | Experimental amount of adsorbate adsorbed at equilibrium | mg/g |
| $q_{e,\text{cal}}$ | 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° | Change in free energy | kJ/mol |
| ΔH° | Change in enthalpy | kJ/mol |
| ΔS° | 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 | <i>Hevea brasiliensis</i> sawdust |
| HSAC | <i>Hevea brasiliensis</i> sawdust-based activated carbon |
| IR | Impregnation ratio |
| IS | <i>Intsia bijuga</i> sawdust |
| ISAC | <i>Intsia bijuga</i> sawdust-based activated carbon |
| IUPAC | International Union of Pure and Applied Chemistry |
| MB | Methylene blue |
| MTZ | Mass transfer zone |
| PS | <i>Pentace triptera</i> sawdust |
| PSAC | <i>Pentace triptera</i> 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 (CO₂). Keadaan penyediaan optimum untuk semua AC ditentukan menggunakan kaedah permukaan respon (RSM). ISAC telah menunjukkan luas permukaan Brunauer-Emmet-Teller (BET) dan jumlah jisim liang yang tinggi iaitu 952.23 m²/g dan 0.584 cm³/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 30°C. 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 kebolegunaan yang baik untuk penjerapan MB dan RBV terutamanya sehingga tiga kitaran menggunakan etanol sebagai pelarut.

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

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 (CO₂) gasification. Optimum preparation conditions for all ACs prepared were determined using response surface methodology (RSM). ISAC showed high Brunaur-Emmet-Teller (BET) surface area and total pore volume of 952.23 m²/g and 0.584 cm³/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 30°C. 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 ($> 400 \text{ m}^2/\text{g}$), 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 planing 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/m³, 515-1,040 kg/m³ and 560 - 640 kg/m³, 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