Faculty of Mechanical Engineering

EFFECT OF ACTIVATION CONDITIONS ON THE PINANG FROND BASED ACTIVATED CARBON PERFORMANCE IN DYES REMOVAL

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EFFECT OF ACTIVATION CONDITIONS ON THE PINANG FROND BASED ACTIVATED CARBON PERFORMANCE IN DYES REMOVAL

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DECLARATION

I hereby declare that this thesis entitled "Effect of Activation Conditions on The Pinang Frond Based Activated Carbon Performance in Dyes Removal" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature :……..

Name : MOHD AZHAR BIN AHMAD

Date : 25th AUGUST 2014

APPROVAL

I hereby declare that I have read this thesis and in my opinion this thesis is sufficient in terms of scope and quality for the award of Master of Mechanical Engineering.

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Date : 25th AUGUST 2014

DEDICATION

To my beloved family

ABSTRACT

The production of activated carbon from agriculture waste offers both economical and environmental advantages. This study aims to prepare a novel pinang frond based activated carbon (PFAC) using a single-step physical activation method for removal of methylene blue (MB) and remazol brilliant blue R (RBBR) dyes from aqueous solution. The PFAC was produced at various activation conditions; i.e. activation temperature (600-900^{o}C), activation time (1-7 hours) and CO_2 flow rate (150-600 mL/min). All PFAC samples prepared have large surface area (<576 m^2/g) and consist of pore in mesopore region. The experimental design results obtained via face centered composite design (FCCD) revealed that activation temperature, activation time and CO_2 flow rate were important variables that influence the dyes removal performance by PFAC. The optimum conditions obtained for preparing PFAC were 867°C, 6.0 hour and 476 mL/min for activation temperature, activation time and CO_2 flow rate, respectively. This optimum sample gave high surface area of 992.0 m^2/g, pore volume of 0.551 mL/g and fixed carbon content of 80.24%. MB and RBBR removal of 96.8% and 76.4%, respectively were achieved by using this sample. Adsorption equilibrium and kinetic data of MB adsorption by PFAC were fitted well with Langmuir isotherm and pseudo-first-order kinetic model, respectively. On the other hand, the adsorption equilibrium and kinetic data of RBBR by PFAC were fitted well with Freundlich isotherm and the pseudo-second-order kinetic model, respectively.

ABSTRAK

Pengeluaran karbon teraktif daripada sisa pertanian menawarkan dua kelebihan iaitu dari segi ekonomi dan alam sekitar. Kajian terbaru ini bertujuan untuk menyediakan upih pinang berasaskan karbon teraktif (UPKT) menggunakan kaedah pengaktifan fizikal satu langkah untuk penyingkiran pewarna metilina biru (MB) dan remazol berkilau biru R (RBBR) daripada larutan akuas. UPKT ini dihasilkan pada keadaan pengaktifan yang pelbagai; suhu pengaktifan (600-900^{o}C), masa pengaktifan (1-7 jam) dan kadar aliran CO_2 (150-600 mL/min). Kesemua UPKT yang terhasil mempunyai luas permukaan yang besar (576 m^2/g) serta liang daripada kumpulan mesoporos. Keputusan daripada rekabentuk eksperimen menggunakan rekabentuk komposit berpusat muka mendapati suhu pengaktifan, masa pengaktifan dan kadar aliran CO_2 merupakan parameter yang penting dalam mempengaruhi kecekapan UPKT menyingkirkan pewarna. Keadaan optimum bagi penyediaan UPKT adalah 867^{o}C, 6.0 jam dan 476 mL/min masing-masing untuk suhu pengaktifan, masa pengaktifan dan kadar aliran CO_2. Sampel optimum ini mempunyai luas permukaan 992.0 m^2/g dan isipadu liang 0.551 mL/g. Penyingkiran MB dan RBBR masing-masing adalah 96.8% dan 76.4% telah diperolehi dengan menggunakan sampel ini. Data penjerapan keseimbangan dan kinetik untuk penjerapan MB oleh UPKT telah menepati model isoterma Langmuir dan tertib kinetik pseudo-pertama. Data keseimbangan dan kinetik untuk penjerapan RBBR oleh PFAC pula telah menepati model isoterma Freundlich dan tertib kinetik pseudo-kedua.

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Mohd Azhar Bin Ahmad
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LIST OF ABBREVIATIONS

AC	Activated carbon
BET	Brunauer-Emmett-Teller
DoE	Design of experiment
FCCD	Face centered composite design
IUPAC	International Union of Pure and Applied Chemistry
MB	Methylene blue
PF	Pinang frond
PFAC	Pinang frond based activated carbon
RBBR	Remazol brilliant blue R
RSM	Response surface methodology
SEM	Scanning electron microscopy
STA	Simultaneous thermogravimetric analyzer
UPKT	Upih pinang berasaskan karbon teraktif
UNEP	United Nations Environment Programme

LIST OF SYMBOLS

C_e	Equilibrium concentration of adsorbate	mg/L
D_p	Average pore diameter	nm
k_1	Equilibrium rate constant of pseudo-first-order sorption	1/h
K_L	Langmuir adsorption constant related to the free energy adsorption	L/mg
K_F	Freundlich isotherm constant	mg/g(L/mg)$^{1/n}$
k_2	The rate constant of pseudo-second-order sorption	g/mg h
n_F	Heterogeneity factor	-
q_e	Amount of adsorbate adsorbed at equilibrium	mg/g
q_m	Monolayer adsorption capacity of the adsorbent	mg/g
q_t	Amount of adsorbate adsorbed at any time	mg/g
Q_o	Monolayer adsorption capacity	mg/g
R^2	Correlation coefficients	-
S_{BET}	BET surface area	m^2/g
t	Time	h
V	Volume of the solution	L
V_T	Total pore volume	cm^3/g
w_0	The dry weight of precursor	g
w_c	Dry weight of final PFAC	g
W	Mass of adsorbent used	g
Y	Predicted response	-

LIST OF PUBLICATIONS

Journal publications

Ahmad, M. A., Herawan, S. G. & Yusof, A. A. (2014). Equilibrium, Kinetics, and Thermodynamics of Remazol Brilliant Blue R Dye Adsorption onto Activated Carbon Prepared from Pinang Frond. *ISRN Mechanical Engineering*, 2014.

Ahmad, M. A., Herawan, S. G. & Yusof, A. A. (2014). Effect of Activation Time on the Pinang Frond Based Activated Carbon for Remazol Brilliant Blue R Removal. *Journal of Mechanical Engineering and Sciences.*

Herawan, S. G., **Ahmad, M. A**., Putra, A. & Yusof, A. A. (2013). Effect of flow rate on the pinang frond-based activated carbon for methylene blue removal. *The Scientific World Journal*, 2013.

Conference paper

M.A. Ahmad, S.G. Herawan, A.A. Yusof (2013). Effect of Activation Time on the Pinang Frond Based Activated Carbon for Remazol Brilliant Blue R Removal, *Proceeding of Malaysian Technical Universities Conference on Engineering and Technology (MUCET 2013),* MS Garden Hotel, Kuantan, Pahang, 3-4 Dec 2013.

CHAPTER 1

INTRODUCTION

1.1 Background of study

Agrowaste pyrolysis is a method to convert biomass and organic waste into diverse products by heating in the absence of oxygen. Understanding the pyrolysis process is crucial in order to fully grasp the pyrolytic-cracking mechanism of a specific ligno-cellulosic waste (Lopez-Velazquez et al., 2013). Pyrolysis process using oxidizing gases such as carbon dioxide (CO_2) or steam (H_2O) is known as activation process and the final product is known as activated carbon (Sekirifa et al., 2013).

Activated carbon is amorphous carbonaceous material which exhibits a high degree of porosity, adsorption capacity and surface area. Activated carbon has ability to adsorb pollutant in wastewater such as dyes and heavy metal. Nearly 80% (~300,000 ton/year) of the total activated carbon is consumed for liquid-phase application in wastewater treatment. (Bansal and Goyal, 2005). The high raw material cost of those commercial coal based activated carbons has limited their application (Gupta and Suhas, 2009). Other sources of cheap activated carbon's precursor have also been investigated especially from agricultural by-products.

Activated carbons have been produced from banana stalk (Bello et al., 2011), bamboo species (González and Pliego-Cuervo, 2013), coffee husk (Ahmad and Rahman, 2011), oil palm

stone (Lua and Guo, 2000), date pits (Bouchelta et al., 2012) oil palm shell (Herawan et al., 2013, Yusof et al., 2012) and parkinsonia aculeata wood (Nunell et al., 2012). In this work, an attempt was made to produce a novel pinang frond based activated carbon (PFAC) via activation process. This study tested the hypothesis that activation conditions play a key role in the characteristic of PFAC as well as PFAC performance in dyes removal. To test this hypothesis, the activation temperature, activation time and CO_2 flow rate were used as parameters for activation conditions with dyes removal as the performance indicator.

1.2 Problem statement

The textile industry has become one of the greatest sources of liquid effluent that contaminated with various kinds of dyes due to the high quantities of water used in the dyeing processes. Around 10,000 of different dyes are produced annually which weighing approximately 0.7 million tons (Senthilkumaar et al., 2006). However 10–15% of these dyes are left as effluent during dyeing process (Murugesan et al., 2007). Dyes effluent has complex aromatic molecular structures which make it difficult to biodegrade and decolourize. This effluent contains colour and a large amount of suspended organic solids (El-Sharkawy et al., 2007). Hence, the presence of dyes into water bodies constitute a source of water pollution that cannot be neglected (Dulman and Cucu-Man, 2009).

Activated carbon adsorption has been proved to be suitable for dyes removal in terms of its simplicity of design, high efficiency and ease of operation. However, the raw material for commercial activated carbon of bituminous coal is very expensive and non-renewable source

which cause to the high price of the product. As such, there is a need to produce activated carbon from alternative material that is cheaper, renewable and readily available.

The amount of agriculture wastes generated in Malaysia is increasing enormously. Conversion of these agriculture wastes into activated carbons which can be used as adsorbents in dyes wastewater treatment would add value to these agricultural commodities, help reduce the cost of waste disposal and provide a potentially cheap alternative to existing commercial activated carbons. This study investigates the feasibility of preparing PFAC for application in removing basic dye (methylene blue) and reactive dye (remazol brilliant blue R) from aqueous solution.

1.3 Pinang (Areca catechu) frond

Pinang or *Areca catechu* in its scientific name is a tropical tree that belongs to *Arecaceae* family. It mainly grows from East Africa to the Arabian Peninsula across tropical Asia to the central Pacific and New Guinea. Traditionally, the main part used from this tree is the nut (or seed endosperm) where it is chewed as a stimulant masticatory. The practice can be found usually in India and some parts of Asia. Utilization of the frond is lacking and it is usually disposed (Staples and Bevacqua, 2006). In fact, there is no research work on the utilization of pinang frond as activated carbon adsorbent in the previous literature. Therefore, in this work pinang frond was used for activated carbon production.

Figure 1.1: Picture of (a) pinang tree and (b) pinang frond

1.4 Research objectives

i. To prepare pinang frond based activated carbon (PFAC) at various activation conditions; (i) temperature, (ii) time and (iii) CO_2 flow rate.

ii. To characterize the PFAC in terms of proximate content, surface morphology, BET surface area, total pore volume, average pore diameter and yield production.

iii. To study the adsorption isotherm and kinetic for the methylene blue (MB) and remazol brilliant blue R (RBBR) dyes adsorbed onto optimized PFAC obtained from face centered composite design.

1.5 Organization of the thesis

This thesis consists of five chapters and each chapter represents an important build for the construction of the thesis. Chapter one presents background of study, problem statements and objectives of the study. Chapter two provides the general information regarding (i) utilization of agriculture waste, (ii) pyrolysis process via activation process and (iii) activated carbon adsorption. Chapter three explains the materials, experimental equipment, characterization method and batch adsorption studies. Chapter four presents the experimental results and discussion on the characterization of the PFAC prepared at various activation temperature, time and CO_2 flow rate. Characterization performed on PFAC were proximate analysis, surface morphology, BET surface area, total pore volume, average pore diameter and carbon yield. Furthermore the results on MB and RBBR dyes removal were also included. Subsequently, the face centered composite design (FCCD) was used to obtain the optimum PFAC's preparation conditions for both dyes removal. The optimized PFAC sample was used for adsorption isotherm and kinetic studies. Chapter five finally presents the conclusions that reflect the achievements of all the objectives which were obtained throughout the study as well as the recommendations for the future research.