SYNTHESIS OF ACTIVATED CARBON VIA MICROWAVE HEATING FOR DYES REMOVAL

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SYNTHESIS OF ACTIVATED CARBON VIA MICROWAVE HEATING FOR DYES REMOVAL

by

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LIST OF ABBREVIATIONS

AC	Activated Carbon
ANOVA	Analysis of Variance
BET	Brunauer–Emmett–Teller
CCD	Central Composite Design
DS	Durian seed
DSAC	Durian seed based activated carbon
FTIR	Fourier Transform Infrared
IR	Imprenation ratio
IUPAC	International Union of Pure and Applied Chemistry
JS	Jackfruit seed
JSAC	Jackfruit seed based activated carbon
MB	Methylene blue
MY	Metanil Yellow
rpm	Rotation per minute
RSM	Response surface methodology
SEM	Scanning electron microscopy
STA	Simultaneous thermogravimetric analyzer

LIST OF SYMBOLS

	Symbol	Unit
A	Arrhenius factor	-
A_i	Measured absorbance for component i	-
A_T	Constant for Temkin isotherm	L/mg
b_c	Path length of the cell	cm
b_T	Constant for Temkin isotherm	L/mg
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
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 or distribution coefficient for Freundlich isotherm	mg/g (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 h$^{1/2}$
k_1	Adsorption rate constant for pseudo-first-order	L/min
k_2	Adsorption rate constant for pseudo-second-order	g/mg h
M_1	Concentration of stock solution	mg/L
M_2	Concentration of desired adsorbate solution	mg/L
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_{DR}	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	mg/g

	at time, t	
$q_{t, cal}$	Calculated adsorption uptake at time, t	mg/g
$q_{t, exp}$	Experimental adsorption uptake at time, t	mg/g
R	Universal gas constant	Jol/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	-
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	kJ/mol

Greek letters

ε_λ	Molar absorptivity coefficient of solute at wavelength	-
λ	Wavelength	nm

SINTESIS KARBON TERAKTIF MENGGUNAKAN PEMANASAN GELOMBANG MIKRO UNTUK PENYINGKIRAN PENCELUP

ABSTRAK

Metilena biru (MB) sebagai pencelup bes dan metanil kuning (MY) sebagai pencelup acid larut di dalam air serta masing-masing menghasilkan ion positif dan ion negatif. Ion-ion ini tertarik kepada bahagian polar pada molekul air secara elektrostatik, lalu mengakibatkan pencelup-pencelup MB dan MY sukar untuk disingkirkan. Oleh itu, kajian ini berusaha untuk menghasilkan karbon teraktif (AC) berasaskan biji durian dan biji nangka untuk menyingkirkan MB dan MY daripada larutan akuas. Karbon teraktif ini dihasilkan melalui teknik pemanasan gelombang mikro bersama pengaktifan fizikimia menggunakan kalium hidroksida (KOH) dan penggasan karbon dioksida (CO_2). Kesan faktor-faktor penyediaan karbon teraktif (kuasa radiasi, masa radiasi dan nisbah impregnasi, (IR)), telah dioptimakan dengan menggunakan metodologi permukaan sambutan (RSM) untuk menghasilkan nilai respon yang maksimum (penyingkiran MB, penyingkiran MY dan hasilan karbon teraktif). Karbon teraktif yang di hasilkan didapati mengandungi luas permukaan Bruneaur-Emmet-Teller (BET) dan peratusan karbon tetap yang tinggi iaitu 852.30m^2/g dan 78.51% untuk karbon teraktif daripada biji durian (DSAC) manakala untuk karbon teraktif daripada biji nangka (JSAC) ialah 715.29m^2/g dan 73.94%. Kesan faktor-faktor penyediaan yang optimum ditentukan menjadi (330W, 4.49min dan 0.97 dengan 79.67% penyingkiran MB dan 23.60% hasilan), (355W, 4.15min dan 0.58 dengan 77.68% penyingkiran MB dan 24.40% hasilan), (340W, 4.44min dan 0.94 dengan 78.24% penyingkiran MY dan 23.51% hasilan) dan (370W, 4.10min dan 0.78 dengan 77.24% penyingkiran MY dan 23.67% hasilan) masing-masing untuk system-sistem MB-DSAC, MB-JSAC, MY-DSAC dan MY-JSAC. Kajian garis sesuhu mendapati semua sistem pencelup-penjerap yang dikaji mengikuti model Freundlich manakala kajian kinetik mendapati semua sistem mengikuti model kinetik pseudo-tertib kedua. Kajian mekanisme mendapati semua proses penjerapan dikawal oleh mekanisme resapan filem. Kajian termodinamik mendapati semua sistem penjerapan adalah eksotermik secara semulajadi, rawak dan dikawal oleh proses penjerapan fizikal.

SYNTHESIS OF ACTIVATED CARBON VIA MICROWAVE HEATING FOR DYES REMOVAL

ABSTRACT

Methylene blue, (MB) as basic dye and metanil yellow (MY) as acid dye dissolved in water to produce negative and positive ions respectively. These ions were electrostatically attracted to the polar side of water molecules, thus making MB and MY difficult to be removed. Therefore, an effort was made to produce activated carbon (AC) from durian seed and jackfruit seed for MB and MY dyes removal from aqueous solution. These ACs were produced by employing microwave irradiation technique as heat treatment and physicochemical activation via potassium hydroxide (KOH) chemical treatment and carbon dioxide (CO_2) gasification treatment. The preparation conditions of these ACs (radiation power, radiation time and impregnation ratio, (IR)) were optimized with the help of response surface methodology (RSM) in order to produce maximum value of responses (MB removal, MY removal, and AC's yield). Durian seed based AC (DSAC) and jackfruit based AC (JSAC) prepared were found to pose relatively high Bruneaur-Emmet-Teller (BET) surface area and fixed carbon percentage which were (852.30m^2/g and 78.51%) and (715.29m^2/g and 73.94%) respectively. Optimum preparation conditions were determined to be (330W, 4.49min and 0.97 with 79.67% of MB removal and 23.60% of yield), (355W, 4.15min and 0.58 with 77.68% of MB removal and 24.40% of yield), (340W, 4.44min and 0.94 with 78.24% of MY removal and 23.51% of yield) and (370W, 4.10min and 0.78 with 77.24% of MY removal and 23.67% of yield) for MB-DSAC, MB-JSAC, MY-DSAC and MY-JSAC systems respectively. Isotherm studies revealed that all adsorbate-adsorbent systems were best described by Freundlich model whereas kinetic studies revealed that all systems followed pseudo-second order kinetic model. Mechanism studies conducted found that the rate limiting step in adsorption process of all systems were contributed by film diffusion. Thermodynamic studies confirmed that all adsorption systems were exothermic in nature, spontaneous and governed by physisorption.

CHAPTER ONE

INTRODUCTION

This chapter highlights the characteristics of dyes and their threat to the environment together with the importance to use agrowaste as precursor for activated carbon (AC) production. Problem statements, research objectives, scopes of study and organization of thesis are also presented.

1.1 Dyes

The advancement in textile industry is driven by remarkable demand for colourful fabrics. Although this is something positive to the development of economy for the country, a concern had arisen on the extensive use of chemicals in this industry especially synthetic dye. Other industries that utilize dyes in a large scale include rubber, paper, plastics, cosmetics, leather and food (Moreira et al., 2017). Synthetic dyes can be defined as substances that are produced to have two chemical groups attached to its molecule namely, chromopore and auxochromes. Chromopore provides the colour identity to the dyes while auxochromes play a role in influencing the dyes' binding properties onto fabrics. The amount of dyes that being produced yearly is 700,000 tons with more than 10,000 of dyes' variations (Daoud et al., 2017). Out of these, 30% are estimated to escape from conventional wastewater treatment system and enter the environment during the dyeing process.

Dyes that escaped into the environment are able to exist for a very long time due to their non-biodegradable property besides being highly stable towards heat, light and oxidizing agents (Kono, 2015). Besides prohibiting the sunlight from reaching the aquatic plants and prevent photosynthesis process to take place, dyes exist in environment is also known to be very much associated with carcinogenic and toxic properties (Islam et al., 2017c). The existence of dyes even in slight amount is adverse because it can change the colour of water bodies. Dyes can easily be distinguished into two main groups of ionic dyes and non-ionic dyes. Under ionic dyes, further classification can be made in terms of cationic dyes and anionic dyes. Cationic dyes which consist of basic dye poses the property to dissolve in water to produce positive ions whereas anionic dyes which consist of acid, direct and reactive dyes pose the property to dissolve in water to produce negative ions. This characteristics increase their polar solubility in water thus making them more challenging to remove as compared to non-ionic dyes. This is the reason why most researchers are focussing on removing ionic dyes (Sangon et al., 2018, Silva et al., 2018a, Lam et al., 2017).

Methylene blue (MB) dye belongs to the basic group which is used to dye silk, wool, paper, polyacrylonitrile, modified nylon and polyesters whereas metanil yellow (MY) dye belongs in the group of acid dye and is useful to dye nylon, wool, silk, modificed acrylics, leather, paper and ink-jet printing (Ahmad et al., 2015). As basic dye, MB is popular in textile industry due to its bright colour. However, upon contact with humans and animals, MB can cause injury to the eyes and temporarily breathing difficulty. It was also reported that basic dye can cause more serious health problem including tissue necrosis, quadriplegia, methemoglobinemia and the worst of all, mental confusion (Kushwaha et al., 2014).

On the other hand, metanil yellow (MY) dye is preferred in the textile industry since it has sulfonate group (R-SO_3Na) in its molecule that enhances its binding properties with cellulose fibers. In terms of molecular structure, MY can be categorized as azo dye as well since it has stable azo bond (N=N) in its structure.

Among all dyes, azo dyes have the highest demand in textile industry which up to 60-70% of the total dyes that being consumed (Cheng et al., 2015). Upon contact with humans or living organism, acid azo dye such as MY can cause renal complications, abnormality in reproductive system and dermatological diseases (Yagub et al., 2014).

1.2 Agrowaste based activated carbon

One of the most promising dyes treatment method is adsorption process using commercial coal based activated carbon (AC) as the adsorbent. Unfortunately, high cost of raw materials, depleted sources of raw materials and non-renewable of raw materials are several factors that limit the production of AC. Therefore, researchers nowadays are making an effort to produce AC from agrowaste as an alternative to the common raw materials such as coal and petroleum coke. Some examples of agrowastes that are successfully converted into AC include date (Norouzi et al., 2018), rice straw (Sangon et al., 2018), reed (Zhou et al., 2017), corncob (Tharaneedhar et al., 2017), rattan (Islam et al., 2017a), cattail (Yu et al., 2017), karanj fruit hull (Islam et al., 2017c) and orange peel (Lam et al., 2017).

Durian seed and jackfruit seed are selected in this study to be converted into AC to treat MB and MY dyes in aqueous solution. The scientific name for durian is *Duriozibethinus L.* and is referred by the local residents as “king of fruits” (Ahmad et al., 2015). Durian is a seasonal tropical tree that belongs in the family and genus of Bombacaceae and Durio respectively. This fruit is typically ovoid in shape and famous due to its distinctive, strong and penetrating smell. The edible part of this fruit is contained inside the shell which is yellowish brown in colour and having sharply pointed pyramidal formidable thorns (Subhadrabandhu and Kesta, 2001).