DYES ADSORPTION BY DRAGON FRUIT PEEL AND POMEGRANATE FRUIT PEEL WASTES BASED MICROWAVE-ASSISTED ACTIVATED CARBON

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by

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LIST OF ABBREVIATIONS

AC	Activated Carbon
AP	Adequate Precision
ANOVA	Analysis of variance
BET	Brunauer-Emmett-Teller
CCD	Central Composite Design
CO_2	Carbon Dioxide
DFP	Dragon Fruit Peel
DFPAC	Dragon Fruit Peel based Activated Carbon
FTIR	Fourier Transform Infrared
IUPAC	International Union of Pure and Applied Chemistry
IR	Impregnation Ratio
MB	Methylene Blue
N_2	Nitrogen gas
PP	Pomegranate Peel
PPAC	Pomegranate Peel based Activated Carbon
RBBR	Remazol Brilliant Blue R
rpm	Rotation per minute
RSM	Response Surface Methodology
SEM	Scanning Electron Microscopy
STA	Simultaneous Thermal Analyzer
UV	Ultraviolet

LIST OF SYMBOLS

	Symbol	Unit
$\pm\alpha$	Distance from central point	-
A	Arrhenius factor	-
A_T	Temkin equilibrium binding constant	L/mg
B_T	Temkin constant related to free energy	L/mg
C	Boundary layer	-
C_e	Equilibrium concentration of adsorbate	mg/L
C_o	Highest initial adsorbate concentration	mg/L
C_t	Dye concentration at time, t	mg/L
E_a	Arrhenius activation energy of adsorption	kJ/mol
k_1	Pseudo-first-order rate constant	1/min
k_2	Pseudo-second-order rate constant	g/mg.hr
K_F	Freundlich isotherm constant	mg/g $(L/mg)^{1/n}$
K_L	Langmuir adsorption constant	L/mg
M	Mass of adsorbent	g
M_1	Concentration of stock solution	mg/L
M_2	Concentration of diluted adsorbate solution	mg/L
N	Total number of experiments	-
n_f	Freundlich constant	-
Q_m	Langmuir monolayer adsorption capacity	mg/g
q_e	Amount of adsorbate adsorbed at equilibrium	mg/g
q_t	Amount of adsorbate adsorbed at time, t	mg/g
R	Universal gas constant	8.314 J/mol K
R^2	Coefficient of determination	-
R_L	Langmuir dimensionless separation constant	-
T	Time	Min
T	Absolute temperature	K
V	Volume of solution	L
V_1	Volume of stock solution	mL
V_2	Volume of diluted adsorbate solution	mL

V_{meso}	Mesopore volume	cm^3/g
V_T	Total pore volume	cm^3/g
W_C	Dry weight of AC	g
W_{char}	Dry weight of char	g
W_{KOH}	Dry weight of KOH pellet	g
W_o	Dry weight of precursor	g
X_1	Radiation power	Watt
X_2	Radiation time	min
X_3	Impregnation ration (IR)	-
x_i	Coded value of variables	-
x_j	Coded value of variables	-

Greek letters

ΔG^o	Changes in standard Gibbs free energy	kJ/mol
ΔH^o	Changes in standard enthalpy	kJ/mol
ΔS^o	Changes in standard entropy	kJ/mol
Δq_t	Normalized standard deviation	%
λ	Wavelength	Nm

KAJIAN PENJERAPAN PEWARNA OLEH KARBON TERAKTIF BERBANTU GELOMBANG MIKRO BERASASKAN SISA KULIT BUAH NAGA DAN KULIT BUAH DELIMA

ABSTRAK

Pewarna ionik yang terdiri daripada pewarna asas dan reaktif amat sukar untuk disingkirkan daripada sisa air menggunakan kaedah konvensional kerana sifatnya yang sangat larut. Kajian ini adalah untuk menghasilkan karbon teraktif (AC) daripada kulit buah naga (DFP) dan kulit buah delima (PP) untuk menyingkirkan metilena biru (MB) dan remazol biru berkilau R (RBBR) daripada larutan akuas. Semua AC ini dihasilkan melalui kaedah pengaktifan fizikimia menggunakan rawatan kimia kalium hidroksida (KOH), penggasan karbon dioksida (CO_2) dan dipanaskan oleh gelombang mikro. Kesan faktor-faktor penyediaan seperti kuasa radiasi, masa radiasi dan nisbah impregnasi (IR) ke atas kecekapan penyingkiran pencelup dan hasilan AC telah dioptimakan melalui metodologi permukaan sambutan. Luas permukaan Bruneaur-Emmet-Teller (BET) dan jumlah isipadu liang yang tinggi diperolehi untuk sampel DFPAC (725.80m^2/g dan 0.388cm^3/g) dan PPAC (845.96m^2/g dan 0.442cm^3/g). Keadaan penyediaan optima telah ditentukan untuk MB-DFPAC (375W, 4.50min dan 0.90) dengan 83.12% penyingkiran MB dan hasilan AC 30.5% dan RBBR-DFPAC (350W, 4.50min dan 0.90) dengan 77.85% penyingkiran RBBR dan 30.1% hasilan. Keadaan penyediaan optima bagi MB-PPAC (370W, 4.50min dan 0.90) dengan 83.4% penyingkiran MB dan 30.8% hasilan dan RBBR-PPAC (350W, 4.50min dan 0.90) dengan 78.51% penyingkiran RBBR dan 30.6% hasilan. Penjerapan MB dan RBBR ke atas semua AC mengikuti garis sesuhu Freundlich. Kapasiti jerapan 232.56mg/g, 250.00mg/g, 230.48mg/g, dan 238.09mg/g masing-masing telah diperolehi untuk MB-DFPAC, MB-PPAC, RBBR-DFPAC dan RBBR-PPAC. Kajian kinetik mendapati semua sistem penjerapan pencelup ke atas DFPAC dan PPAC mengikuti model kinetik pseudo tertib pertama manakala kajian termodinamik mendapati semua sistem adalah eksotermik secara semulajadi.

DYES ADSORPTION BY DRAGON FRUIT PEEL AND POMEGRANATE FRUIT PEEL WASTES BASED MICROWAVE-ASSISTED ACTIVATED CARBON

ABSTRACT

Ionic dyes comprised of basic and reactive dyes pose a great difficulty to be eliminated in wastewater by conventional methods due to their high soluble properties. This study aims to synthesis activated carbon (AC) derived from dragon fruit peel (DFP) and pomegranate peel (PP) to adsorb methylene blue (MB) and remazol brilliant blue R dyes (RBBR) from aqueous solution. These ACs were produced via physiochemical activation method which involves potassium hydroxide (KOH) chemical treatment, carbon dioxide (CO_2) gasification and heated with microwave. Effects of preparation conditions of microwave radiation power, radiation time and impregnation ratio (IR) on dyes removal and ACs yield were optimized by using response surface methodology (RSM). Bruneaur-Emmet-Teller (BET) surface area and total pore volume were found on prepared DFPAC (725.80m^2/g and 0.388cm^3/g) and PPAC (845.96m^2/g and 0.442cm^3/g).Optimum preparation conditions for ACs prepared were determined for MB-DFPAC (375W, 4.50min and 0.90) with 83.12% of MB removal and 30.50% of yield, RBBR-DFPAC (350W, 4.50min and 0.90) with 77.85% of RBBR removal and 30.1% of yield. Optimum preparation conditions for MB-PPAC (370W, 4.50min and 0.90) with 83.40% of MB removal and 30.80% of yield and RBBR-PPAC (350W, 4.50min and 0.90) with 78.51% of RBBR removal and 30.60% of yield. Adsorption of MB and RBBR on ACs followed Freundlich isotherm. The adsorption capacities were 232.56mg/g, 230.48mg/g, 250.00mg/g and

238.09mg/g for MB-DFPAC, RBBR-PPAC, MB-PPAC and RBBR-PPAC, respectively. Kinetic studies revealed that adsorption of dyes onto DFPAC and PPAC followed pseudo-second order kinetic model while thermodynamic studies confirmed that all systems were exothermic in nature.

CHAPTER ONE

INTRODUCTION

1.1 Dye effluent in textile industries

Textile industries produce huge volumes of contaminated wastewater, which causes significant issues for the aquatic environment. In Malaysia, textile industry is one the major contributors to the country's economic development. The industry became the country's eleventh largest export earner in 2017, making up approximately RM15.3 billion (1.6%) to Malaysia's total exports of manufactured goods (MIDA, 2018).

Due to their superior dyeing properties, especially in terms of fastness, dyes are used extensively in the textile industry. In fact, dyes have the favourable characteristics of bright colour, simple application techniques and low energy consumption as well. Basic dye and reactive dye types are the most being produced in order to meet up with the growing demands in textile industries (Bello et al., 2011). However, the industrial textile effluent contains a mixture of dyes molecules leading to a toxic effect (Bello et al., 2014). In addition, most dyes are carcinogenic, toxic and mutagenic. Therefore, removal of dyes from wastewater is very important to the environment. The dyes treatment method can be classified as physical, chemical and biological treatment. Adsorption has been proven to be an effective process for dye removal due to its low cost, high adsorption capacity and environmental friendliness (Liao et al., 2012). The excellent performances of activated carbon (AC) is well known to be closely related to the well-developed porous structures, large surface area and pore volume suitable for dyes adsorption (Ge et al., 2015).

1.2 Agrowaste as precursor for adsorbent

Actual industrial application requires an adsorbent that acquires high adsorption capacity and vastly available due to huge amount of adsorbates (heavy metals and toxic wastewaters) to be removed. Thus, adsorbent originating from agrowaste such as gram husks, waste tea leaves, dragon fruit peels and pomegranate peels possess high potential to be the most suitable adsorbent for certain adsorption processes.

The total pomegranate production in the world is about 1 million tonnes (Suat et al., 2009). Turkey is the one of the largest producers of the pomegranate. The annual production of pomegranate in Turkey is about 60,000 tons (Suat et al., 2009). According to FAMA (2015), 5,474 mt of dragon fruit and 28,773 mt of pomegranate fruit are produced in 2015 in Malaysia.

1.3 Problem statement

Textile industry is rated as one of the most polluting and chemically intensive industrial sectors (Uzal., 2015). Due to the increasing number of dyes wastewater discharged into the environment, an attempt was made in this study to produce microwave assisted AC for cationic and anionic dyes removal. Solution containing these dyes are hard to treat due to their highly soluble property in water. Without effective treatment, these dyes enter the environment leading to a toxic effect (Bello et al., 2014).

Activated carbon (AC) adsorbent is one of the best candidates as it did not require any additional pre-treatment before its application. However, AC is expensive due to the use of non-renewable and relatively expensive starting material (Demirbas, 2009). In this study, dragon fruit peel (DFP) and pomegranate peels (PP) were utilized as AC for dyes removal from aqueous solution as there has been reported about the AC prepared from pomegranate peel, via microwave assisted but using different types of dye. The conversion of agrowaste into value added adsorbent as an alternative to commercial AC can reduced the cost for waste disposal and also potentially to solve the problem of dyes removal in wastewater treatments. A growing interest in exploiting KOH for chemical activation was observed in recent years (Zhang et al., 2017) due to the fact that the reaction between carbonaceous materials with alkali especially KOH is effective in producing materials having large surface area and total pore volume.

Conventional furnace used during activation process heat the sample via conduction process. It required longer time for the heat to be transferred from the heating elements of the furnace to the sample and the energy usage increased as well (Alslaibi et al., 2013). Therefore, microwave heating technique is employed in this study to activate the samples. Microwave irradiation technique provides uniform heating along the bed, low treatment time, and low energy consumption (Ahmed & Theydan, 2013).

AC with high adsorption performance and yield are desirable but optimum preparation conditions are difficult to achieve due to the conflicted interest region between AC's performance and yield. Therefore, response surface methodology (RSM) was used in this study to determine the optimum preparation conditions.

1.4 Research objectives

The main objectives of this study are:

i. To optimize the operating parameters, i.e., radiation power and activation time in the preparation of DFPAC and PPAC adsorbents using response surface methodology.

ii. To characterize the adsorbents prepared in terms of pore size, surface morphology, surface area, pore volume, surface chemistry, proximate content and elemental composition.

iii. To study the effects of adsorbate contact time, initial concentration and solution temperature of optimized ACs on dyes removal.

iv. To investigate the behaviour of ionic dyes adsorption onto optimized ACs by studying the adsorption isotherm, kinetics and thermodynamics.

1.5 Scope of study

In this work, the dragon fruit peel (DFP) and pomegranate peel (PP) were utilized to prepare ACs for MB and RBBR dyes removal. The preparation of DFPAC and PPAC were done via physical method which applies CO_2 and microwave irradiation to improvise the adsorptive performance of the DFPAC and PPAC. The optimization of the operating parameters, i.e., radiation power and activation time were done using response surface methodology (RSM) method.

The optimized DFPAC and PPAC were characterized in terms of surface area, surface morphology, proximate content, elemental content and surface chemistry. The precursor and char samples were also included for comparison purposes.

The optimized DFPAC and PPAC were then used in equilibrium, kinetic and thermodynamic studies to investigate the adsorption behaviour of MB and RBBR dyes onto DFPAC and PPAC. In order to carry out the analysis, batch adsorption study was done by examined the effect of adsorbate initial concentration (25-300 mg/L), contact time (0-24 hours), solution temperature (30-60^{o}C) for adsorption of dye on DFPAC and PPAC prepared.

1.6 Organization of thesis

This thesis consists of five main chapters and each chapter contributes to the sequence of this study. The following are the contents for each chapter in this study:

Chapter 1 introduces the dyes effluent in textile industries, problem statement, research objectives and organization of thesis.

Chapter 2 covers the literature review of this study. An insight into dyes, discussion on adsorption process, activated carbon and raw material used in preparing activated carbon are elaborated. Moreover, the isotherm models, kinetic models and thermodynamic parameters determination are included as well.

Chapter 3 discusses the experiment materials and the details of methodology. It discusses on the description of equipment and materials used, batch adsorption experiment, experimental procedure and description of factors affecting the adsorption process.

Chapter 4 refers to the experimental results and discussions of the data obtained. Further elaboration on the effect of different factors on batch system adsorption, the results on equilibrium, kinetic and thermodynamic properties are provided in this chapter.

Chapter 5 concludes all the findings obtained in this study. Recommendations are also included as well.

CHAPTER TWO

LITERATURE REVIEW

2.1 Dyes

Dye is a coloured aromatic organic compound that has an affinity towards substrate to which it is being applied. Dyes are used in different various industries such as textiles, paint, paper, leather, plastics, rubber pharmaceuticals, food processing and also in wet process industries such as bleaching, printing, dyeing and final finishing in coloration of products (Ghasemi et al., 2016). The categorization of dye are summarized in Table 2.1.

Table 2.1 Categorization of dye based on their chemical nature (Hunger, 2007).

Category	Substrate	Application technique
Acid	Silk, nylon, wool, inks, leather and paper.	Neutral to acidic medium
Basic	Paper, polyacrylonitrile and treated nylon.	Acidic dye medium
Direct	Rayon, nylon, leather and cotton.	Little alkaline medium consists of extra electrolyte
Disperse	Acrylic, polyamide, polyester, acetate and plastics.	Fine aqueous dispersions regularly used by high temperature/pressure
Reactive	Silk, cotton, wool and nylon	Functional group on fibre reacts with reactive sites of dye
Sulphur	Cotton and rayon	Aromatic substrate wetted with sodium sulphide and reoxidised to insoluble sulphur consisting goods on fibre.
Vat	Cotton and wool	Solubilised water-insoluble dyes by mixing in sodium hydrogen sulphide.