DYES ADSORPTION ON SALAK PEEL BASED ACTIVATED CARBON: OPTIMIZATION, EQUILIBRIUM, KINETIC AND THERMODYNAMIC STUDIES

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by

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	Symbol	Unit
A	Arrhenius factor	-
B_T	Constant for Temkin equation	-
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	Mean free energy	J/mol
E_a	Arrhenius activation energy of adsorption	kJ/mol
k_1	Adsorption rate constant for the pseudo-first-order kinetic	1/min
k_2	Adsorption rate constant for the pseudo-second-order	g/mg.min
k_{diff}	Intraparticle diffusion rate constant	$\mathrm{mg/g.min}^{1/2}$
K_F	Freundlich isotherm constant	$\mathrm{mg/g\ (L/mg)}^{1/n}$
K_L	Rate of adsorption for Langmuir isotherm	L/mg
M	Mass of adsorbent	G
n_F	Constant for Freundlich isotherm	-
q_e	Amount of adsorbate adsorbed at equilibrium	mg/g
q_m	Adsorption capacity of Langmuir isotherm	mg/g
q_t	Amount of adsorbate adsorbed at time, t	mg/g
R	Universal gas constant	8.314 J/mol K
R^2	Correlation coefficient	-
R_L	Separation factor	-
T	Time	Min
T	Absolute temperature	K
V	Solution volume	L
ΔH°	Changes in standard enthalpy	kJ/mol
ΔS°	Changes in standard entropy	kJ/mol
ΔG°	Changes in standard Gibbs free energy	kJ/mol
Λ	Wavelength	Nm

LIST OF ABBREVIATIONS

AC	Activated carbon
ANOVA	Analysis of variance
BET	Brunauer-Emmett-Teller
CCD	Central composite design
CO_2	Carbon dioxide
FTIR	Fourier Transform Infrared
IUPAC	International Union of Pure and Applied Chemistry
MG	Malachite green
N_2	Nitrogen gas
RBBR	Remazol Brilliant Blue R
SEM	Surface morphology
STA	Simultaneous thermal analyzer
SP	Salak peel
SPAC	Salak peel based activated carbon
rpm	Rotation per minute
SEM	Scanning electron microscopy
UV	Ultraviolet

PENJERAPAN PENCELUP OLEH KARBON TERAKTIF BERASASKAN KULIT BUAH SALAK: KAJIAN PENGOPTIMUMAN, KESEIMBANGAN, KINETIK DAN TERMODINAMIK

ABSTRAK

Penjerapan pewarna malacit hijau (MH) dan remazol berkilau biru R (RBBR) telah diuji secara kelompok dengan menggunakan karbon teraktif berasaskan kulit buah salak (KTKBS). Kulit buah salak telah melalui proses pengaktifan fizikimia yang melibatkan enap jerap kalium hidroksida (KOH) dan penggasan karbon dioksida (CO_2). Semasa proses penyediaan KTKBS, keadaan optimum telah diperoleh daripada kaedah sambutan permukaan (KSP). Keadaan optimum tersebut adalah suhu pengaktifan, masa pengaktifan dan nisbah KOH:arang, masing-masing pada 792°C, 1 jam dan 3:1 yang menghasilkan penyingkiran MH 81.74%, penyingkiran RBBR 63.97% dan hasilan KTKBS sebanyak 32.45%. KTKBS yang optimum mempunyai luas permukaan (968.32 m^2/g), isi padu liang (0.503 cm^3/g) dan karbon tetap (79.3%) yang tinggi. Liang KTKBS tergolong dalam kategori mesoliang dengan purata diameter liang 4.41 nm. Kesan kepekatan awal pewarna (100-500 mg/L), masa sentuhan (0–24 jam) dan suhu larutan (30-60^{o}C) turut telah dinilai. Didapati bahawa model Langmuir adalah paling berpadanan untuk kedua-dua data garis sesuhu MH dan RBBR. Manakala, untuk analisa kinetik, didapati bahawa model pseudo-tertib-kedua dan pseudo-tertib-pertama adalah masing-masing paling sesuai digunakan untuk menentukan mekanisma penjerapan MH dan RBBR. Penjerapan MH dan RBBR yang diuji ke atas KTKBS adalah secara endotermik.

DYES ADSORPTION ON SALAK PEEL BASED ACTIVATED CARBON: OPTIMIZATION, EQUILIBRIUM, KINETIC AND THERMODYNAMIC STUDIES

ABSTRACT

The adsorption of malachite green (MG) and remazol brilliant blue R (RBBR) dyes onto salak peel activated carbon (SPAC) were investigated in a batch process. Salak peel undergoes physiochemical activation process which involves potassium hydroxide (KOH) impregnation and carbon dioxide (CO_2) gasification. During the preparation of SPAC, the optimum preparation conditions were obtained from response surface methodology (RSM). The optimum conditions are activation temperature, activation time and KOH:char impregnation ratio (IR) with 792°C and 1 hours and 3:1 respectively, which has resulted in 81.74% MG removal, 63.97% RBBR removal and 32.45% SPAC yield. Optimized SPAC has high of surface area ($968.32 m^2/g$), pore volume ($0.503\ cm^3/g$) and fixed carbon content (79.3%). The pore of SPAC was mesoporous type with average pore diameter of 4.41 nm. The effect of initial dye concentration (100-500 mg/L), contact time (0–24 hours) and solution temperature (30-60^oC) were also evaluated through. The obtained equilibrium data for both dyes were best fitted by Langmuir model. Meanwhile, the kinetics data were best represented by the pseudo second-order model for MG and pseudo-first-order model for RBBR. The adsorption process of MG and RBBR onto SPAC were endothermic in nature.

CHAPTER ONE

INTRODUCTION

1.1 Textile industries and dye effluent

There are 10,000 different dyes available in the market and the production of these dyestuffs has reach up to 700,000 tonnes per year worldwide (Ahmad and Rahman, 2010). In Malaysia, textiles industry is one of the contributors to the country's economic development. Basic dye and reactive dye types are the most being produced in order to meet up with the growing demands textile industries (Bello *et al.*, 2011). However, due to their highly complicated structures and difficulties in bio-degradable, their elimination from wastewater is undesirable. Yet, a very small amount of these dyes are highly visible and toxic to aquatic environment. These dyes reflect sunlight from entering the water which then interfere with the growth of bacteria and hinder photosynthesis in aquatic plant. Also, the degradation products from the textile dyes are also often carcinogenic and harmful to flora and fauna (Bouasla *et al.*, 2010).

1.2 Treatment of industrial dye effluent

The removal of dyes from industrial effluent via an economical way is still remains as an important issue for many countries. Generally, the dyes removal treatments can be categorized into: (i) physical (coagulation and flocculation, membrane filtration and adsorption), (ii) chemical (chlorination, ozonation and electrochemical), and (iii) biological (fungal decolonization) methods. Although the chemical and biological methods are effective in removing dyes, their requirements in specialized equipment, high energy intensive and formation of large amount of by-products causing them unfavorable to be utilized in long term application (Yahya *et al*., 2008).

Adsorption process as an alternative way is still one of the best wastewater treatment method in term of its efficiency and the possibility of using adsorbents for wide range of different type of dyes. In addition, its potential in regeneration, recovery and recycling of the adsorbent, made it recognized as one of the effective and well-established techniques (Onal, 2006). Activated carbon (AC) is porous carbon materials, possesses high surface area (>500m^2/g), adsorption capacity and adsorption capability for gas to liquid phase application. It has been widely used for dyes wastewater treatment as it did not require any additional pre-treatment before its application (Bangash and Manaf, 2005). However, its expensive price in market due to the price of coal as precursor has limited its commercial application. For this reason, growing interest in searching low cost, renewable and readily available materials as precursor has been carried out particularly from agriculture wastes such as palm kernels, cassava peel, bagasse, jute fiber, palm-tree cobs, olive stones, date pits and fruit stones (Kumar *et al*., 2010). In this work, an attempt was made in using salak peel for the production of AC.

1.3 Problem statement

The discharge of colored dyes in wastewater from various industries such as textile and dyeing, pulp and paper and food processing industries have currently gained attention from different parties especially in industrialized countries. Direct discharge of them has cause pollution to the water bodies. Dyes are easily detectable as they are inherently highly visible with low concentration of 0.005 mg/l (Ofomaja, 2008). This has captured the attention of the public and the authorities. Moreover, most of the dyes present in the textile wastewater are difficult to be removed as they are stable towards light, oxidizing agents and resistance towards aerobic digestion. Most of them are mutagenic, carcinogenic and possess great threat to human kidneys, liver, brain, central nervous system and reproductive system. Consequently, it is crucial to ensure that the quality of the wastewater discharged is able to meet the requirements enforced in the environment legislation.

Meanwhile, adsorption has been recognized as an excellent dyes removal technique especially in terms of efficiency and simplicity of design. Unfortunately, owing to the expensive price of commercial coal based AC, its applications in dyes removal from wastewater is limited. Therefore, this studied was conducted to find out other alternatives precursor from agricultural waste which is cheap for preparing AC. Concerning to this, an attempt was made to use salak peel waste as precursor. The salak peel based AC (SPAC) prepared was then tested it performance for adsorption of malachite green (MG) and remazol brilliant blue R (RBBR) from aqueous solution.

1.4 Scope of Study

In this work, the salak peel was utilized to prepare AC for MG and RBBR dyes removal. The preparation of SPAC was done via physiochemical method which applies impregnation of KOH to improvise the adsorptive characteristic of the AC. The optimizations of the operating parameters of activation temperature, activation time and impregnation ratio (IR) were done using response surface methodology (RSM) method. RSM generates the design of experiment and the responses for every experimental run were analyzed to obtain optimum operating conditions for preparation of SPAC for dyes removal as well as SPAC yield.

The optimized SPAC was latter characterized in terms of surface area, surface morphology, proximate content and surface chemistry by using surface area analyzer, SEM, STA and FTIR respectively. The precursor and char samples were also included for comparison purposes.

The optimized SPAC were then used in equilibrium, kinetic and thermodynamic studies to investigate the adsorption behavior of each dye (MG and RBBR) onto SPAC. In order to carry out the analysis, batch adsorption study were done by examined the effect of adsorbate initial concentration (25-300 mg/L), contact time (0-24 hour), solution temperature (30-60°C) and solution pH (2-12) for adsorption of dyes onto SPAC prepared.

1.5 Research objectives

The main objectives of this study are:

(i) To optimize the SPAC preparation conditions (activation temperature, activation time and impregnation ratio) by using response surface methodology.

(ii) To study the effect of malachite green (MG) and remazol brilliant blue R (RBBR) adsorption onto SPAC in batch process under different initial dye concentrations, contact time and solution temperature.

(iii) To evaluate the adsorption isotherms, kinetics and thermodynamic properties of MG and RBBR adsorption onto SPAC.

1.6 Organization of thesis

This thesis consists of five main chapters and each chapter contributes to the sequence of this study. The content of the chapters are summarized as follows:

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

Chapter 2 discusses 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 covers the experiment materials and the details of methodology. It discuss 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 colored, ionizing and aromatic organic compound that shows affinity towards substrate to which it is being applied. It is extensively used to give color to textiles, paper and leather. Usually, dyes applied in an aqueous solution and mordant is required to act as an agent in order to have better affinity on the substrate (Bouasla *et al*., 2010). Most of the natural dyes are derived from plant such as roots, berries, bark, leaves and woods. Synthetic dyes are replacing natural dyes in textile industry as they offered a vast range of new colors and better properties to the substrate. Synthetic dyes that are commonly used in textile industry can be categorized as basic dyes and reactive dyes. The classification of dyes based on applications are summarized in Table 2.1.

Table 2.1 Classification of dyes based on applications (Karim *et al*., 2015)

Dye class	Method of application	Types of fibres
Basic	Applied from acidic dye baths	Paper, polyester and inks
Reactive	Dye reacts with fibre to bind dye covalently under influence of heat	Cotton, wool, silk and nylon

A large volume of wastewater is produced from different steps in the dyeing and finishing processes. This wastewater is often rich in color and contains residues of dyes and chemicals, such as complex components, aerosols, high COD and BOD concentrations, and hard-degradation materials. For example in a cotton mill, there are various steps involved in the processing textile in which each step discharge of some amount of pollutants as shown in Table 2.2.

Table 2.2 Pollutants from dyeing processing operations (Babu *et al*., 2007).

Process	Compounds
Desizing	Sizes, enzymes, starch, waxes, ammonia
Scouring	Disinfectants and insecticides residues, NaOH, surfactants, soaps, fats, waxes, pectin, oils, sizes, anti-static agents, spent solvents, enzymes
Bleaching	H_2O_2, AOX, sodium silicate or organic stabiliser, high pH
Mercerizing	High pH, NaOH
Dyeing	Metals, salts, surfactants, organic processing assistants, sulphide, acidity/alkalinity, formaldehyde
Printing	Urea, solvents, metals
Finishing	Resins, waxes, acetate, stearate, spent solvents, softeners

In addition, the effluents produced from the textile industry contain ammonia, alkali salts, toxic solids, heavy metals and large amounts of pigments. Due to the complex aromatic molecular structures of dyes, it makes them inert and difficult to be degradable when discharged into the waste stream (Bello *et al*., 2011). Yet, the accumulation of dyes may lead to the formation of toxic by-products which caused harmful to both the environment and human. Therefore, in recent years, there have been great concerns to treat dye wastewater particularly by using adsorption technique.

2.2 Adsorption

In the past few decades, many techniques have been developed to find an economic and efficient way to treat textile industrial effluent. These technologies usually consist of physical, chemical and biological treatment. Table 2.3 simplified the advantages and limitations of dyes removal practiced in industry.

Table 2.3 Advantages and limitations of dyes removal methods (Crini, 2006)

Methods	Advantages	Limitations
	Physical treatment	
Adsorption	Effective in removing a wide variety of dyes	High capital costs
Membrane Filtration	Good permeate qualities	High pressure and limited lifetime of membrane before fouling occurs
Ion exchange	No adsorbent loss due to the capability of regeneration	Not applicable for wide range of dyes and high operating costs
	Chemical treatment	
Coagulation/ precipitation	Simple and economically feasible	High sludge production leading to waste disposal problems
Oxidation	Rapid and efficient	High operating cost and require the use of chemical
Ozonation	Able to produce biodegradable products	Short half-life (20 minutes)
Photocatalysis	Mild operating condition	Effective for small capacity operation
Sodium Hypochloride	Effective in attacking amino group of dye with Cl^+ ion	Require the use of chlorine (Cl) and formation of aromatic amine
	Biological treatment	
Anaerobic	Produce biogas that can be reused in power generation	Formation of hydrogen sulphite
Biomass	Low operating cost, non-toxic effect on microorganisms	Slow process and performance depends on pH
Biosorbent	Economically attractive, high selectivity	Require chemical modification

Adsorption is a process that occurs when liquid accumulates on the surface of an adsorbent, forming a molecular or atomic film (adsorbate). More precisely, it occurs at the interfacial layers, the surface of the adsorbent and the adsorption space (whereby enrichment of adsorptive occurs). Adsorption can be classified into