UNIVERSITI PUTRA MALAYSIA

ISOTHERM AND KINETICS OF REACTIVE DYE ADSORPTION ON PALM KERNEL SHELL-BASED ACTIVATED CARBON

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By

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DECEMBER 2007

Chairman: **Chuah Teong Guan, PhD**

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The adsorptions of two reactive dyes, Reactive Black 5 and Reactive Red E onto Palm Kernel Shell-based activated carbon (granule form) and commercial grade coal-based activated carbons (powder form) were studied. The experiment was carried out to investigate the effect of the presence of more than one type dye in solution on equilibrium and kinetic of adsorption. Equilibrium isotherm models were applied to describe the adsorption capacities of both single and binary systems. All batch experiments were carried out at a constant temperature of 28°C (±2°C) using an incubator shaker that was operated at 150 rpm.

The results showed that adsorption of reactive dyes onto commercial coal-AC from single system can be successfully described by Langmuir model. The adsorptions onto Palm Kernel Shell-AC in single and binary systems can be successfully described by Freundlich and the Redlich-Peterson models and by Modified Extended Freundlich model, respectively. Experimental data showed that competitive

adsorption for active sites on the carbon surface reduces overall uptake capacity of the reactive dyes.

The rate of adsorptions of two reactive dyes, Reactive Black 5 and Reactive Red E onto Palm Kernel Shell-AC were studied. The sorption kinetics was well described by pseudo-second-order kinetic model in single system. In addition, the experiment was carried out to investigate three models: film resistance model, film-surface and film-pore diffusion models. The results showed that the external coefficients of mass transfer, K_f, decreased with increasing of initial adsorbate concentration. Variations of K_f values, indicated that adsorption was controlled by both external and intraparticle diffusion. Furthermore, simulation results showed that the rate of the kinetic process was controlled by two resistance models. It was found that the adsorption process was better described by film-surface diffusion model.

Finally, the Chemical Oxygen Demand (COD) of the treated reactive dyes solutions from single and binary systems showed that a minimum of 4g/L dosage of PKS was needed to reduce the COD to acceptable level according to the United State Water Quality Guidelines and Pollutant Fact Sheets guidelines.

From the work, it was clearly shown that PKS-AC had good adsorption capacity on reactive dye. This study provides information on adsorption mechanism of binary reactive dye system which is useful in adsorption column design.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains.

KAJIAN ISOTERMA DAN KINETIK TERHADAP PENJERAPAN PEWARNA REAKTIF MENGGUNAKAN CENGKERANG ISIRUNG KELAPA SAWIT BERASASKAN KARBON AKTIF.

Oleh

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Penjerapan oleh dua pewarna reaktif iaitu Reaktif Hitam 5 dan Reaktif Merah E menggunakan cengkerang isirung kelapa sawit berasaskan karbon aktif dalam bentuk granul dan arang batu tahap komersial berasaskan karbon aktif dalam bentuk serbuk, telah dikaji. Ujikaji telah dijalankan untuk menentukan kesan kewujudan lebih daripada dua pewarna di dalam larutan terhadap keseimbangan dan kinetik penjerapan. Model keseimbangan isoterma telah digunakan untuk menggambarkan kapasiti penjerapan dalam sistem tunggal dan sistem dedua. Kesemua ujikaji kelompok ini dijalankan pada suhu tetap iaitu 28°C (±2°C) dengan menggunakan penggoncang eraman yang beroperasi pada 150 rpm.

Keputusan ujikaji menunjukkan bahawa penjerapan pewarna reaktif ke atas arang batu komersial-AC untuk sistem tunggal boleh dijelaskan dengan menggunakan model Langmuir. Penjerapan ke atas cengkerang isirung kelapa sawit dalam sistem tunggal dan sistem dedua boleh dijelaskan dengan menggunakan model Freundlich dan Redlich-Peterson dan juga model Freundlich yang dipanjangkan dan teruhah suai. Data ujikaji

menunjukkan bahawa penjerapan persaingan untuk tapak aktif pada permukaan karbon mengakibatkan penurunan keseluruhan kapasiti pewarna reaktif yang dijerap.

Kadar penjerapan oleh dua pewarna reaktif iaitu Reaktif Hitam 5 dan Reaktif Merah E di atas cengkerang isirung kelapa sawit-AC dikaji. Kadar penjerapan dalam sistem tunggal adalah berpadanan dengan kinetik pseudo tertib kedua. Selain itu, ujikaji ini juga dijalankan untuk mengkaji 3 jenis model iaitu model rintangan lapisan, permukaan lapisan dan resapan liang lapisan. Keputusan menunjukkan bahawa pekali luaran untuk pemindahan jisim K_f menurun dengan meningkatnya kepekatan awal zat terjerap. Nilai K_f yang berbeza-beza menunjukkan bahawa kadar penjerapan dipengaruhi oleh faktor resapan luaran dan intrazarah. Selain itu, simulasi menunjukkan bahawa proses kinetik di pengaruhi oleh model ketahanan kedua. Proses penjerapan boleh ditafsirkan dengan lebih baik dengan menggunakan model resapan permukaan lapisan.

Pada akhir ujikaji, Keperluan Oksigen Kimia(COD) untuk larutan yang dirawat dari sistem tunggal dan sistem dedua menunjukkan bahawa sekurang-kurangnya 4 g/L dos PKS diperlukan untuk menurunkan bacaan COD kepada tahap yang dibenarkan oleh Piawaian Kualiti Air dan Piawaian Fakta Pencemaran, Amerika Syarikat.

Daripada keputusan yang diperolehi, jelas menunjukkan bahawa PKS-AC mempunyai kapasiti penjerapan yang baik ke atas pewarna reaktif. Ujikaji ini memberi maklumat tentang mekanisma penjerapan untuk sistem dedua pewarna reaktif yang berguna untuk rekabentuk turus penjerapan.

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I certify that an Examination Committee has met on 17 December 2007 to conduct the final examination of Mohsen Nourouzi Mobarekeh on his Master of Science thesis entitled "Isotherm and Kinetics of Reactive Dye Adsorption on Palm Kernel Shell-Based Activated Carbon" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the student be awarded the degree Master of Science.

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This thesis submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee are as follows:

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DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously and is not concurrently submitted for any other degree at Universiti Putra Malaysia or at any other institution.

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MOHSEN NOUROUZI

MOBAREKEH

Date: 20 April 2008

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Notations / symbols

Å	Angstrom/Unit of length	10^{-10} m
α_L	Langmuir constant	$L.mg^{-1}$
a_p	Adsorbent Pellet Radius	mm
α_R	Redlich-Peterson Constant	$(L/.mg)^{b_R}$
ρ_p	Pellet Density	$mg.mm^{-3}$
λ_{max}	Max Wave Length of Adsorption	nm
ε_p	Porosity of Pellet	
b_{ij}	Correlation Constant in Empirical Freundlich Isotherm for Binary system	
b_R	Redlich-Peterson isotherm exponent	
c_{bo}	Initial Value of c_b	$mg.L^{-1}$
c_b	Adsorbate Concentration in the Bulk of Fluid	$mg.L^{-1}$
C_s	Adsorbate Concentration in the Fluid-Pellet Interface	$mg.L^{-1}$
C_e	Bulk Phase Concentration	$mg.L^{-1}$
C_t	Concentration of the Solution at Time t	$mg.L^{-1}$
D_{meso}	Average Mesopore Diameter	Å
D_{micro}	Average Micropore Diameter	Å
D_p	Pore Diffusivity	$cm^2.sec^{-2}$
D_s	surface diffusivity	$cm^2.sec^{-2}$
K	Constant of Henry's Law	$L.g^{-1}$
K_F	Freundlich adsorption capacity	$mg.g^{-1}$
k_f	Mass Transfer Coefficient	$cm.sec^{-1}$
K_L	Langmuir constant	$L.g^{-1}$
K_R	Redlich-Peterson isotherm constant	$L.g^{-1}$

M	Adsorbent mass	g
n	Surface heterogenity	
N_t	Adsorption Rate at Time	s^{-1}
r	Radial distance measured from the center of a pellet	mm
R_L	Separation factor	
t	Time	minute
p	Partial Pressure of Adsorbate in Gas Phase	
p_o	Vapor Pressure of Adsorbate	
$\bar{q}$	Average Adsorbed-Phased Concentration	$mg.g^{-1}$
q_e	Solid phase concentration at equilibrium	$mg.g^{-1}$
q_s	Adsorbed-Phase Concentration in the Solution-Pellet Interface	$mg.g^{-1}$
q_t	Solid Phase Concentration at TimeT	$mg.g^{-1}$
S_A	Specific Surface of Activated Carbon	$m^2.g^{-1}$
V	Volume of Solution	mL
V_{meso}	Mesopore Volume	$cm^3.g^{-1}$
V_{micro}	Micropore Volume	$cm^3.g^{-1}$

AC	Activated carbon
COD	Chemical Oxygen Demand
ELE	Extended Langmuir Equation
EL-FE	Extended Langmuir-Freundlich Equation
FPCDSD	Film-Pore- Concentration Dependent Surface Diffusion
GAC	Granular Activated Carbon
MEFE	Modified Extended Freundlich Equation
MW	Molecular Weight
PAC	Powdered Activated Carbon
PKS	Palm Kernel Shell
PSD	Particle Size Distribution
RB 5	Reactive Black 5
RR E	Reactive Red E
SSE	Sum of the Square of Errors

CHAPTER 1

INTRODUCTION

1.1 Water Pollution as an Environmental Pollutions Problem

The environment and everything connected with the environment, are important for the public because most of our ecological systems such as air, water and soil are continuously contaminated by domestic and industrial pollutants. Pollution has been defined in various ways. It is considered as the release of unwanted substances to the environment by man in quantities that damage either the health or the resources itself. Water pollution involves the release of small amounts of substances directly through point sources or indirectly through non point sources. Industrial effluents from various industries like textile, dyestuffs, paper and pulp, distillery, olive oil mill and metal industries etc. are the major contributors to water pollution as they create more subtle effects on behavior, reproduction or even survival of biotic communities.

1.2 Textile Dyes Effluent

Industries such as textile, ceramic, paper, printing and plastic, use dye as their raw material. Thus they consume a considerable volume of water. Robinson et al. (2001) reported, approximately two percent of total reactive dyes manufactured in the world are discharged directly into aqueous effluent and ten percent of total dye manufactured are discharged during the textile dyeing process. As a matter of fact, more than 7×10^5 tons dyestuff, are being produced annually and being used extensively in textile, dyeing and printing industries (Meyer, 1981).

The presence of dyes in water is undesirable. Even a very small amount of these coloring agents is highly visible and may be toxic to aquatic environment. Reactive dyes are the only dyes which bond covalently with the textile fabrics. These dyes contain chromophoric groups such as azo, anthraquinone, triarylmethane, *etc*. and reactive groups (*e.g*. vinyl sulfone, chlorotriazine, trichloropyrimidine, *etc*). that form covalent bonds with the fiber (Sumathi and Manju, 2000). Azo reactive dyes, being most water-soluble synthetic dyes with the widest variety of colors and structure are generally resistant to aerobic biodegradation. Conventional biological wastewater treatment is not able to degrade them. It may be due to the lack of necessary enzymes in the conventional biological treatment plants (Akhtar et al., 2005).

In Malaysia, one of the main pollution source of textile wastewater is generated from batik industry that comes from the dyeing processes. Remazol reactive dyes are, commercially a very important class of textiles dyes. Unadsorbed dyes, which enter the wastewater through processing, are significant and difficult to treat. Many physical and chemical treatment methods including adsorption, coagulation, precipitation, filtration, electrodialysis, membrane separation and oxidation have been used for the treatment of dye containing effluents. The adsorption process is one of the most efficient methods of removing pollutants from wastewater. Further, the adsorption process provides an attractive alternative treatment, especially if the adsorbent is inexpensive and readily available (Tan et al., 2000).

1.3 Problem Statement and Objectives of the Study

Activated carbon is the most widely used adsorbent for the removal of color from textile effluents because it has a high capacity for organic matter. It is produced from organic based materials such as in this case, palm kernel shells. The raw material is carbonized to obtain the char or carbonaceous material, which is activated to yield the highly porous final product. Although adsorption process using activated carbon is promising in decolorizing textile effluents, this application is limited by the high cost of adsorbents (Robinson et al., 2001). Bailey et al. (1999) reported that, in general, a sorbent can be assumed as "low cost" if it requires little processing, is abundant in nature, or is a by-product or waste material from another industry. Thus, the activated carbon derived from agricultural wastes becomes important due to the fact that it is inexpensive, easy to access and adequate to remove organic and inorganic contaminants from wastewater (Mohan and Pittman, 2007). Some of the materials used for activated carbon are listed in Table 1.1.

Table 1.1: Some materials used as activated carbon.

Material	Reference
saw dust, rice husk	Malik, 2003
peanut shells, cotton seed shell	Kim et al., 2003
myrobalan, rubber seed coat, cashew nut sheath, palm seed coat, palm tree flower, pongam seed coat	Rengaraj et al., 1999
cornelian cherry, apricot stone, almond shell	Demirbas et al., 2004
oak wood waste, corn hulls, corn stover (corn stover consists of the leaves and stalks of maize plants left in a field after harvest)	Zhang et al., 2004
cotton stalk	Attia et al., 2004

Several studies were initiated to utilize palm kernel shell as the crude material for activated carbon and it is reported that a good quality product can be obtained, such as its granular structure, insolubility in water, chemical stability, high mechanical strength (Ma, 2002; Mak, 2003; Jumasiah et al., 2005; Choong et al., 2006).

Jumasiah et al. (2005) reported adsorption of basic dye using palm kernel shell-AC. The sorption kinetics and equilibrium of basic dye onto palm kernel shell activated carbon were studied. The study showed that the isotherm data were well described by the Redlich–Peterson isotherm model, where the sorption kinetics was fitted well by the pseudo-second-order kinetic model.

Choong et al. (2006) also reported the rate of dye adsorption from aqueous effluents onto palm kernel shell-AC. The adsorption rates of methylene blue on PKS-AC for systems of different initial dye concentrations were modeled using a film-pore-concentration dependent surface diffusion (FPCDSD) model. The FPCDSD model was used to study the methylene blue/PKS system for different initial concentrations.

However, no study has been reported on the removal of reactive dyes using PKS-AC. There are also no works has been reported on study of binary reactive dyes adsorption on PKS-AC. Therefore, it is important to study the mechanism of this adsorption process in order to provide engineering information, such as uptake capacity and equilibrium time, for adsorbent design.

In this study, palm kernel shell was evaluated for its ability to remove reactive dyes, *i.e.* Reactive Black 5 and Reactive Black E, from aqueous solution by sorption. The objectives of this work are:

1. To investigate the adsorption isotherm of single and binary reactive dyes, Remazol black and Remazol red, on palm kernel shell-based activated carbon.
2. To evaluate the adsorption kinetics of single and binary reactive dyes, Remazol black (Reactive Black 5) and Remazol red (Reactive Black E), on palm kernel shell-based activated carbon.
3. To model the adsorption of reactive dyes on PKS-AC using film resistance model, film-surface and film-pore diffusion models to study their diffusion mechanism.