

EQUILIBRIUM AND KINETICS OF DISPERSE DYE ADSORPTION ON ACTIVATED CARBON PREPARED FROM RATTAN SAWDUST BY CHEMICAL ACTIVATION

A.A. AHMAD, B.H. HAMEED*, A.L. AHMAD

School of Chemical Engineering, Engineering Campus,
Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia

* Corresponding author. Fax: +604-5941013

E-mail address: chbassim@eng.usm.my

ABSTRACT

The liquid-phase adsorption of C.I. Disperse Orange 30 (DO30) onto activated carbon prepared from rattan sawdust by chemical activation with H_3PO_4 . The rattan sawdust was carbonized at $500^\circ C$, 2h and impregnated ratio weight with H_3PO_4 at 1:4.5. The effects of various parameters such as contact time, initial DO30 concentration and pH were investigated at temperature $30 \pm 1^\circ C$. Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm models were used to illustrate the experimental isotherms and isotherms constants. The equilibrium data were best represented by Langmuir isotherm model, showing maximum monolayer adsorption capacity of 89.29 mg/g. The rates of adsorption were found to obey the rules of pseudo-second order model with good correlations. Rattan sawdust-based activated carbon (RSAC) was shown to be a promising material for adsorption of DO30 from aqueous solutions.

Keywords: rattan sawdust; activated carbon; disperse orange 30; adsorption isotherms; kinetics

INTRODUCTION

Disperse dyes are widely used in variety of industries, such as textiles, paper and leather. Disperse dyes are non-ionic aromatic compounds, scarcely soluble in water but soluble in organic solvent. The majority of them are azo and anthraquinone dyes. These dyes can be applied to synthetic fibers such as polyester, nylon, acetate, cellulose and acrylic [1]. Textile industries effluent contains many dyes which are containing carcinogen and mutagen chemicals such as benzidine, metals, etc. and causes serious environmental problems. Dyes are visible even at low concentrations and are difficult to biodegrade in the environment due to their resistance to light, heat, chemical and water [2]. In this manner, these kinds of pollutants must be treated prior to their discharge into the receiving water bodies. The conventional treatments of dyed wastewater include chemical coagulation, biological and electrochemical processes, ozonation and adsorption [3]. Adsorption onto activated carbon has been proven to be an effective process for dye removal, but it is an expensive process. This has largely been associated with the cost of producing activated carbon, and the lack of suitable and inexpensive regeneration procedures for these adsorbents. The activation method to be proposed is important for the cost of producing activated carbons. In this respect, these have led many researchers to use low-cost plant and wood-based materials for activated carbon production. Numerous low-cost plants, agricultural and/or wood-based materials such as pistachio shells [4], palm kernel shell [5], coconut husk [6], bamboo waste [7], coir pith [8], rice husk [9] and oil palm shell activated carbon [10], have been used for the production of activated carbon for the removal of the textile dye effluents. Rattan (*Palmae/Arecaceae* family) is spiny climbing plant belonging to the palm family. It is considered

to be the most important non-wood forest product in Peninsular Malaysia. There are about 600 species in the world, of which 106 species are found in Peninsular Malaysia [11]. The aim of this study was to evaluate the ability of using activated carbon prepared from rattan sawdust by phosphoric acid activation for the adsorption of disperse dye from aqueous solutions.

MATERIALS AND METHODS

Adsorbate. C.I. Disperse Orange 30 dye (DO30), 4-((2,6-Dichloro-4-nitrophenyl)azo)-N-(cyanoethyl)-N-(acetoxylethyl) supplied by Sigma–Aldrich (M) Sdn Bhd, Malaysia was used as an adsorbate and was not purified prior to use. Distilled water was used to prepare all the solutions and reagents. DO30 has a chemical formula of $C_{19}H_{17}Cl_2N_5O_4$, with molecular weight of 450.27g/mol. The chemical structure of DO30 dye is illustrated in Fig. 1.

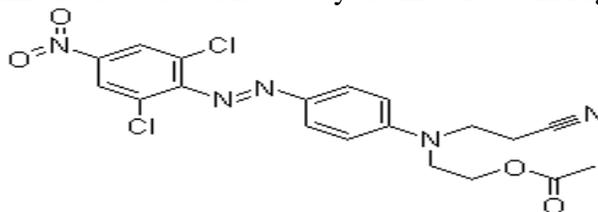


Figure1: The chemical structure of DO30

Preparation of activated carbon. Rattan sawdust was used in this study as a source of activated carbon, collected from a local furniture factory, Penang, Malaysia. It was washed with hot distilled water to remove dust like impurities, dried at 105°C and activation (1:4.5) with 40% phosphoric acid (purity 85% Merck, Germany) as a chemical reagent added during the chemical activation process helps produce more effective adsorbent. The activation was completed by heating rate of 10°C/min to the final temperature of 500°C for 2 hours. After cooling, the activated carbon was repeatedly washed with hot distilled water until the pH of the washing solution reached 6-6.5 and then dried at 105°C.

Adsorption studies. Batch equilibrium studies were carried out by adding a fixed amount of RSAC 0.30g into 250-mL Erlenmeyer flasks containing 100mL of different initial concentrations (50–500 mg/L) of dye solution. The flasks were agitated in an isothermal water-bath shaker at 120rpm and 30°C for 24 h until equilibrium was reached. The pH was adjusted by adding a few drops of diluted 0.1N NaOH or 0.1N HCl and was measured by using a pH meter (Ecoscan, EUTECH Instruments, Singapore). The dye concentrations were measured by a double beam UV/vis spectrophotometer (Shimadzu, Model UV 1601, Japan) at 425 nm. The amount of equilibrium adsorption, q_e (mg/g), was calculated by:

$$q_e = \frac{(C_o - C_e)V}{W} \quad (1)$$

where C_0 and C_e (mg/L) are the liquid-phase concentrations of dye at initial and equilibrium, respectively. V (L) is the volume of the solution and W (g) is the mass of dry adsorbent used. The procedures of kinetic experiments were basically identical to those of equilibrium tests. The

aqueous samples were taken at preset time intervals and the concentrations of dye were similarly measured.

$$q_t = \frac{(C_o - C_t)V}{W} \quad (2)$$

RESULTS AND DISCUSSION

Effect of contact time and initial dye concentration. Fig. 2(a) illustrates the adsorption of DO30 for different initial concentrations of DO30 between 50 and 500mg/L at 30°C as a function of contact time. It is evident from Fig. 2(a) that the amount adsorbed increased with the increase in the concentration of solution. When the initial DO30 concentration was increased from 50 to 500 mg/L, the adsorption uptake of RSAC increased from 12.99 to 70.96 mg/g. A higher initial concentration provides an important driving force to overcome all resistances of the dye between the aqueous and solid phases, thus increasing the uptake. The effect of contact time on the removal of DO30 by the RSAC at initial concentrations 50–500mg/L and 30°C showed rapid adsorption of dye in the first 8 hours. The adsorption rate decreased gradually and the adsorption reached equilibrium in about 10 hours for initial concentrations of 50–100 mg/L. The time required to attain this state of equilibrium was termed the equilibrium time and the amount of dye adsorbed at the equilibrium time reflected the maximum dye adsorption capacity of the adsorbent under these particular conditions.

Effect of pH. The pH of the solution was an important controlling parameter in the adsorption process. Fig. 2(b) indicates the effect of pH on the removal of the DO30 onto RSAC by H₃PO₄ activation from aqueous solution. It was observed that the adsorption of DO30 is unaffected by changing solution pH and remained nearly constant over the initial pH ranges of 4–12. The percentage adsorption of DO30 was not significantly changed when the initial pH was increased from 4 to 12. Thus pH 7 was selected as the optimum pH value for all further experiments due to the advantage of neutral pH value. As the solubility of disperse dyes in aqueous solution is low, they have a tendency to accumulate at the surface of adsorbents [12]. It was found that the adsorption of DO30 onto RSAC remained approximately constant in the pH range of 4–12. When the adsorbing species is not ionized, no such electrical repulsion exists, and thus the packing density on the surface can be higher. Isa et al. [13] also reported a similar trend for the adsorption of disperse blue and disperse red onto palm ash surface and the percent removal of disperse dyes remained approximately constant in the pH range of 5–10. Ramakrishna and Viraraghavan [12] also reported a similar observation for the adsorption of disperse red 1 dye onto slag in pH range of 5–11.

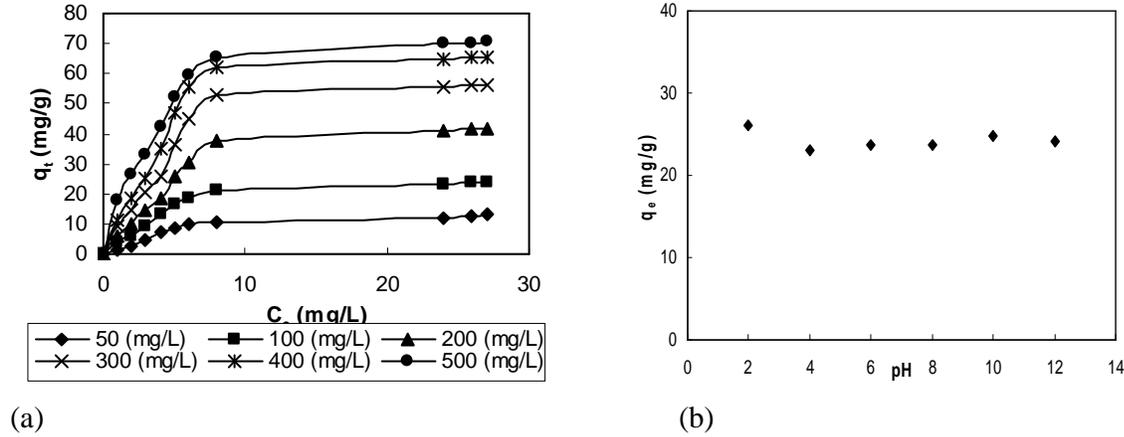


Figure 2: Effect of (a) initial dye concentrations (b) pH for adsorption of DO30 on RSAC at 30°C

Adsorption isotherms. The equilibrium adsorption isotherm is one of the most important data to understand the mechanism of the adsorption systems. In this manner, the Langmuir [14], the Freundlich [15] Temkin [16] and the D–R [17], isotherm equations were used to interpret the experimental data. Langmuir isotherm theory is based on the assumption that adsorption on a homogeneous surface, i.e., the surface consists of identical sites, equally available for adsorption and with equal energies of adsorption and that the adsorbent is saturated after one layer of adsorbate molecules forms onto surface [18]. The linearized form of the Langmuir adsorption isotherm equation is

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad (3)$$

The Langmuir constants, which are q_m and K_L values, can be calculated from the plot C_e/q_e versus C_e . Fig. 3(a) shows the Langmuir adsorption isotherm of the DO30 onto RSAC. The maximum adsorption capacity was determined as 89.29 mg/g at 30°C. All of the isotherm model parameters for the DO30 onto RSAC listed in Table 1.

The linearized Freundlich isotherm equation that corresponds to the adsorption on heterogeneous surface is given as

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

where C_e is the equilibrium concentration of the solute (mg/L) and q_e is the equilibrium adsorption capacity (mg/g). The Freundlich isotherm constants K_F and $1/n$ can be calculated from the plot of $\ln q_e$ versus $\ln C_e$ (Fig. 3(b)). The slope ($1/n$) measures the surface heterogeneity. Heterogeneity becomes more prevalent as $1/n$ gets closer to zero [19].

The Temkin isotherm equation assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent–adsorbate interactions, and that the

adsorption is characterized by a uniform distribution of the binding energies, up to some maximum binding energy. Eq. (5) can be linearized as:

$$q_e = B \ln K_T + B \ln C_e \quad (5)$$

where $RT/b = B$. b and K_T are the constants. K_T is the equilibrium binding constant (L/mg) corresponding to the maximum binding energy and constant B is related to the heat of adsorption. A plot of q_e versus $\ln C_e$ (Fig.2(c)) enables the determination of the isotherm constants K_T and B . Values of K_T and B as obtained are shown in Table 1 along with the value of the correlation coefficients.

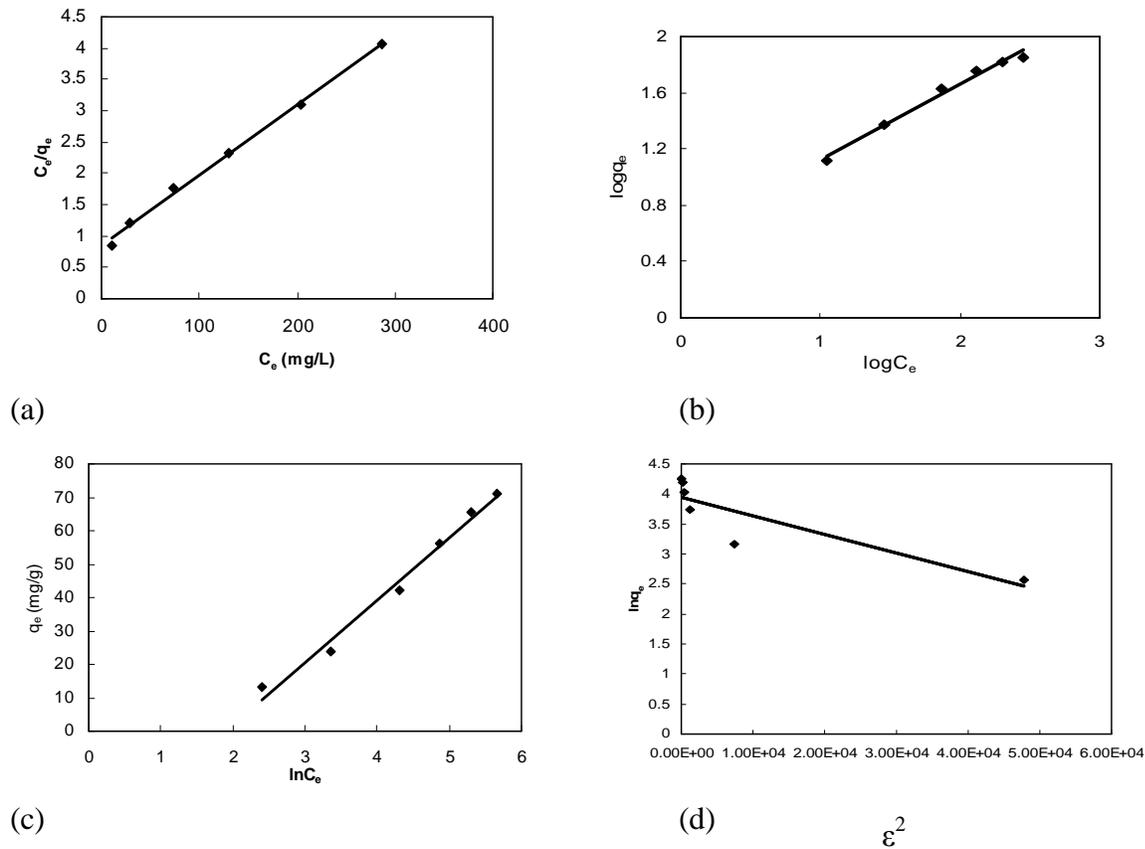


Figure 3: (a) Langmuir (b) Freundlich (c) Temkin (d) D–R isotherms for DO30 adsorption by RSAC at 30°C.

The D–R isotherm equation is more general than the Langmuir isotherm because it does not assume a homogeneous surface or constant adsorption potential. It was applied to distinguish between the physical and chemical adsorption of dye. The linear form of D–R isotherm equation is

$$\ln q_e = \ln q_m - \beta \epsilon^2 \quad (6)$$

where is a constant related to the mean free energy of adsorption per mole of the adsorbate (mol/J); q_m , the theoretical saturation capacity, and ε is the Polanyi potential, which is equal to $RT \ln(1 + (1/C_e))$, where R (J/mol K) is the gas constant; and T (K), the absolute temperature. Hence by plotting $\ln q_e$ against ε^2 it is possible to generate the value of q_m (mol/g) from the intercept, and the value of from the slope (Table1). The D–R adsorption isotherm for DO30 onto RSAC at 30°C was not presented as figures due to the lower correlation coefficients than Langmuir isotherm model. The correlation coefficients showed that the Langmuir model fitted better than the other isotherm models.

Kinetics of adsorption. The kinetics of adsorption data was processed to understand the dynamics of adsorption process in terms of the order of rate constant. In order to investigate the mechanism of adsorption, the rate constants of chemical adsorption for DO30 were determined using the equations of a pseudo-first-order [20] and pseudo-second-order [21]. The pseudo-first-order kinetic model equation is

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (7)$$

where q_{e1} and q_t are the amounts of the dye adsorbed at equilibrium and at time t , in mg/g, and k_1 the pseudo-first-order rate constant (h^{-1}), was applied to the adsorption of DO30. Values of k_1 calculated from the slope of the plots of $\log(q_e - q_t)$ versus t (Figure 4) are given in Table 1. The pseudo-second-order kinetic model is expressed as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

where q_2 is the maximum adsorption capacity (mg/g) for the pseudo-second-order adsorption, k_2 is the equilibrium rate constant for the pseudo-second-order adsorption (g/mg h). Values of k_2 and q_2 were calculated from the plot of t/q_t against t (Fig. 4). The kinetic data for the adsorption of DO30 under various conditions were calculated from the related plots and were given in Table 1. The correlation coefficients for the pseudo-second-order kinetic model ($R^2 > 0.96$) were higher than first-order. These results imply that the adsorption system studied obeys to the pseudo-second-order kinetic model.

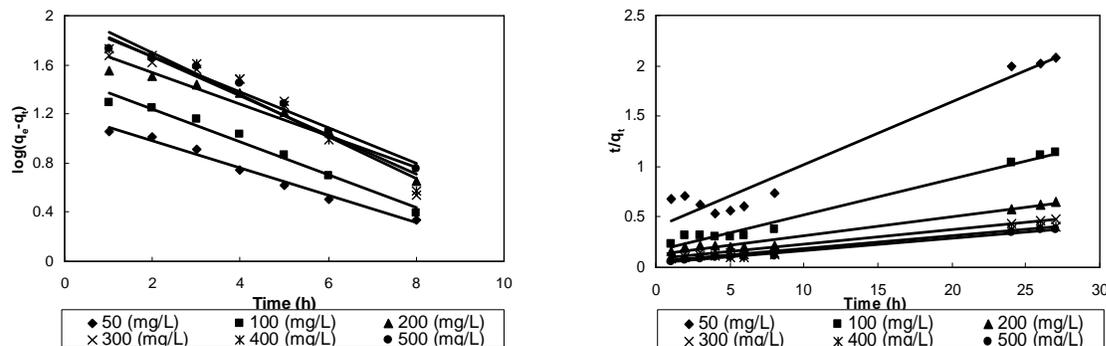


Figure 4: Pseudo-first and second order kinetics for adsorption of DO30 onto RSAC at 30°C.

Table 1: Isotherm constants and kinetic parameters for adsorption of DO30 on RSAC at 30°C

Isotherm constants												
T (°C)	Langmur			Freundlich			Temkin			D-R		
	q_m (mg/g)	K_L (L/mg)	R^2	K_F (mg/g) (mg/L) ^{-1/n}	n	R^2	K_T (L/mg)	B	R^2	q_m (mg/g)	β	R^2
30	89.29	0.209	0.99	3.41 66	1.702	0.98	18.62	71.59	0.98	51.94	0.00 3	0.77
Kinetic models												
C_o (mg/L)	q_{exp} (mg/g)	Pseudo-first-order			Pseudo-second-order							
		q_{e1} (mg/g)	k_1 (h ⁻¹)	R^2	q_{e2} (mg/g)	k_2 (g/mg min) 10 ⁻³	R^2					
50	12.99	15.896	0.256	0.95	16.03	9.88	0.96					
100	23.74	32.077	0.974	0.97	28.17	9.33	0.98					
200	41.96	61.108	0.93	0.93	52.91	2.85	0.97					
300	56.37	95.433	0.908	0.90	68.96	2.59	0.98					
400	65.61	109.37	0.944	0.94	78.12	2.78	0.98					
500	70.89	89.949	0.971	0.97	80.01	3.88	0.99					

CONCLUSION

The adsorption of DO30 from aqueous solution using activated carbon from rattan sawdust was investigated under different experimental conditions in batch process. The Langmuir adsorption isotherm was found to have the best fit to the experimental data with maximum adsorption capacity of 89.29 mg/g. The adsorption kinetics can be predicted by pseudo-second-order kinetic. The results indicate that activated carbon prepared from rattan sawdust is suitable as adsorbent material for adsorption of DO30 from aqueous solutions.

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