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Role of activated carbon from natural adsorbent for removal of textile dyes: effect of pH, kinetic and adsorbent mass

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ABSTRACT

In the present work, we have investigated the sorption efficiency of the treated activated carbon from walnut shell (ACW) towards Direct Red 81 (DR81) and Direct Blue 71 (DB71) for the removal from aqueous solution. The sorption study of ACW at the solid-liquid interface was investigated using kinetic, sorption isotherms, pH effect and amount of adsorbent. Experimental data were analyzed by Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) isotherms. Langmuir isotherm model (R^2 =0.9664 and R^2 =0.9484) fitted the equilibrium data the best other isotherms for DR81 and DB71. According to the results maximum adsorption occurred in acidic pH. The results showed that the sorption processes of DR81 and DB71 on ACW are in good agreement with pseudo-second order kinetic. Maximum amount of adsorbent for adsorption of mentioned dyes was 1 gr.

Keywords: Walnut shell; Textile dyes; Isotherms; Kinetic; Adsorption

INTRODUCTION

The effluents from the dyestuff manufacturing and some similar industries are also generally highly colored with a large amount of suspended organic solids and hence are the important sources of water pollution [1]. Textile industry rank first in the usage of dyes for coloration of fibre [2]. Color can cause hazards to the environment due to the presence of a large number of contaminants like toxic organic residues, acids, bases and inorganic contaminant [3]. The removal of color from wast effluents has become environmentally important. Various methods including coagulation [4], chemical oxidation [5], photocatalysis [6, 7], electrochemical [8] and adsorption techniques have been examined. Azo dyes require an effective treatment technique for their complete removal. The effects of pH, initial dye concentration, kinetic and adsorbent mass on the adsorption of direct dyes onto ash were investigated. The experimental data were analyzed using the pseudo-first order and pseudo-second order adsorption kinetic models.

MATERIALS AND METHODS

Ash and dyes

The walnut shell was collected from walnut trees in north of Iran. At first, walnut shell were heated and burned. The charcoal was grinded and then filtered by mesh No.100. It was activated to a final temperature of 500 ^{0}C in the muffle furnace for 6 hours. The active product was then cooled to room temperature. DR81 and DB71 were all purchased from alvan Sabet Company in Iran and used without any further purification. An accurately weighted quantity of each dye was dissolved in distilled water to prepare the desired concentrations of dye solution. For each of dyes, the adsorbance was read in the rang of visible

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wavelengths (350-700 nm) using a UV-Vis spectrophotometer. The optimum adsorbance wavelength was found to be 510 nm and 588.5 nm for DR81 and DB71, respectively. The characteristics of the dyes are listed in tables 1 and 2.

Equilibrium and kinetic studies

Adsorption equilibrium and kinetics studies were determined by batch method. Adsorption equilibrium experiments were carried out by adding a fixed amount of adsorbent (1g) in to a number of 100 ml conical flasks of different initial concentrations (3.5×10^{-5} to $7.5\times10^{-5} mol.L^{-1}$) of DR81 and DB71 solutions. The flasks were placed in room temperature for 48 hours. The amount of adsorption at equilibrium, q_e ($mol.g^{-1}$) was calculated by:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

Where C_0 and C_e(mol.L^{-1}) are the liquid-phase concentration of dyes at initial and equilibrium, respectively. V (L) is the volume of the solution and W (g) is the mass of adsorbent. The dyes removal percentage can be calculated as follows:

$$\text{Removal percentage} = \frac{(C_0 - C_e)}{C_0}\times 100 \quad (2)$$

To study the effect of ACW does (g) on DR81 and DB71 adsorbed, different amounts of ACW (0.2, 0.4, 0.6, 0.8, 1, 1.2, 1.4, and 1.6 g) were respectively added into a number of 100 ml conical flasks of fixed initial concentration (5.5×10^{-5} mol.L^{-1}) of dyes solution. The flasks were placed in room temperature for 48 hours. To study the effect of solution pH, 100 ml of dyes solution of 5.5×10^{-5} (mol.L^{-1}) initial concentration at different pH values (1-11) was agitated with 1 g of ACW. The flasks were placed in room temperature for 48 hours. The pH was adjusted with 1 M NaOH and 1 M H_2SO_4 solutions and measured by using pH meter (PB-11). 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. The amount of sorption at time t, q_t (mol. g^{-1}), was calculated by:

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (3)$$

Where C_t (mol.L^{-1}) is the liquid-phase concentrations of dyes at any time.

RESULTS AND DISCUSSION

Effect of adsorbent dose on dye adsorption

To study the effect of ACW dose (g) on DR81 and DB71 adsorption, experiments were conducted at initial of dye of $5.5\times10^{-5} mol.L^{-1}$, while the amount of adsorbent added was varied. Fig. 1 shows the effect of adsorbent dose on the removal percentage of DR81 and DB71. It was observed that the removal percentage of DR81 and DB71 rapidly increased with the increase in adsorbent dose up to 1 g and then it remains almost constant. The increase in color removal percentage was due to the increase in the available sorption surface sites.

Table 1. Properties and characteristics of DR81

Generic name	Direct Red 81
Color index number	28160
Molecular formula	$C_{29}H_{19}N_5Na_2O_8S_2$
Abbreviation	DR81
Molecular weight (g/mol)	675.6
λ_{max} (nm)	510

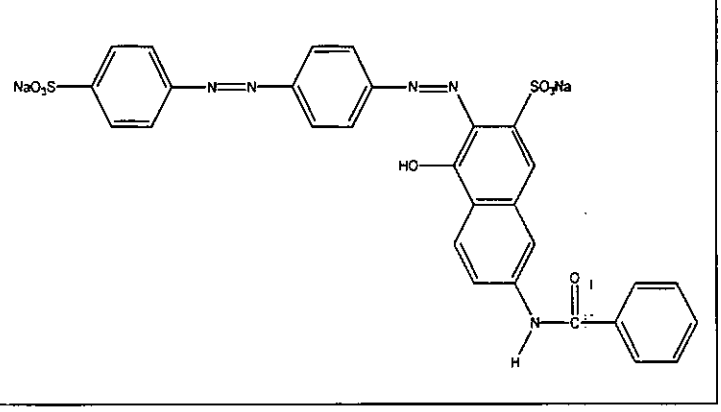
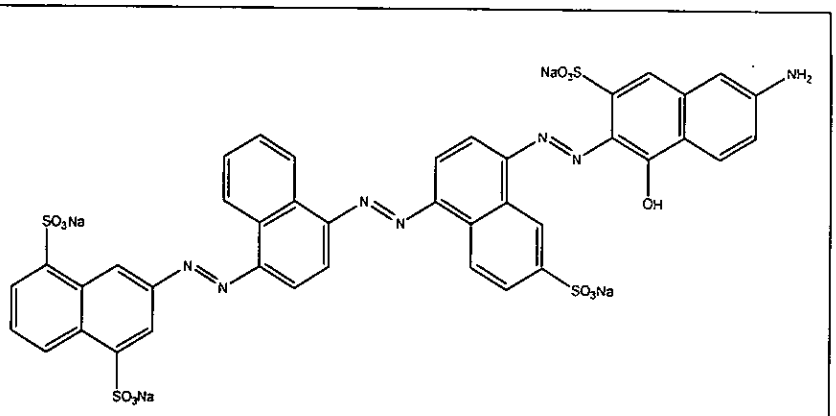


Table 2. Properties and characteristics of DB71

Generic name	Direct Blue 71
Color index number	34140
Molecular formula	$C_{40}H_{23}N_7Na_4O_{13}S_4$
Abbreviation	DB71
Molecular weight (g/mol)	1029.88
λ_{max} (nm)	588.5



Effect of pH

The pH of the aqueous solution is an important controlling parameter in the adsorption process [9, 10]. Fig. 2 shows that the sorption of DR81 and DB71 onto ACW in various pH. It was observed that the adsorption capacity increases significantly with a decrease in the pH and maximum adsorption was observed at pH 1. The acidic medium activated the adsorbent surface chemically and the adsorbent surface gains positive charge and reacts accompanying SO_3^- existing in DR81 and DB71 dyestuffs and results in the electrostatic attraction between adsorbates and adsorbent and this finally leads to more adsorption. Hence all the succeeding investigations were performed at pH 1 for both of dyes.

Adsorption kinetics

The experimental data for the adsorption of DR81 and DB71 on ACW were fitted using the pseudo- first order (Eq. (4)) [11] and pseudo-second order kinetic models (Eq. (5)) [12].

$$Log(q_e - q_t) = Log\, q_e - \frac{k_1}{2.303}t \qquad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad (5)$$

Where q_e and q_t $(mol.g^{-1})$ are the amount of adsorbate adsorbed at equilibrium and time t, respectively, $k_1(\min^{-1})$ is the rate constant of pseudo- first order adsorption, k_2 $(g.mol^{-1}\min^{-1})$ is the rate constant of pseudo-second order adsorption. The values of adsorption rate constant (k_1) were determined from the plot of log (q_e-q_t) vs. t (Figs.3 and 4).

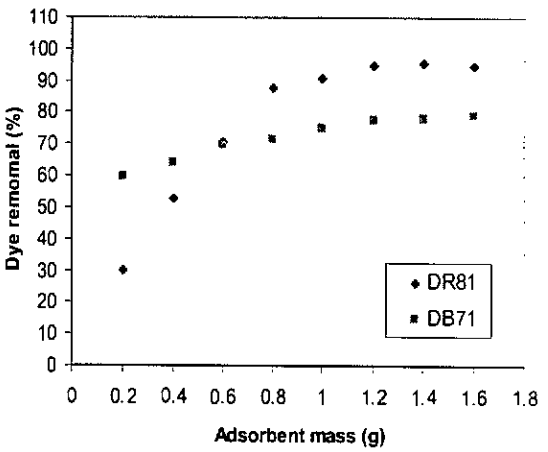


Fig. 1. Effect of adsorbent dose for the adsorption DR81 and DB71 onto ACW.

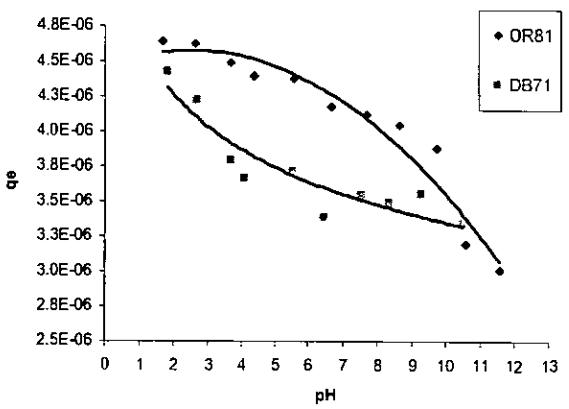


Fig. 2. Effect of pH for the adsorption of DR81 and DB71.

Plot of t/q_t versus t (Fig.5 and 6) enables one to determine q_e and k_2 from the slope and intercept, respectively. These values are given in table 3. Therefore, the adsorption reaction can be most satisfactorily by the pseudo-second order kinetic model for DR81 and DB71 adsorption onto ACW found on the hypothesis that the rate determining step may be chemisorption relating valency forces through sharing or exchange of electrons between adsorbent and adsorbate.

Adsorption isotherms

The relationship between amount of dye adsorbed at constant temperature and its concentration in the equilibrium solution is called the adsorption isotherm. The equilibrium data were analyzed by Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) isotherms. These isotherms are useful for estimating the total amount of adsorbent needed to adsorb a required amount of adsorbate from solution [13, 14, 15].

$$\text{Langmuir: } \frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{k_L q_{max}} \frac{1}{C_e} \quad (6)$$

$$\text{Freundlich: } Log q_e = Log K_F + \frac{1}{n} Log C_e \quad (7)$$

$$\text{Temkin: } q_e = \frac{RT}{b} \ln(A.C_e) \quad (8)$$

$$\text{D-R: } \ln q_e = \ln Q_m - K\varepsilon^2 \quad (9)$$

In Eq. (6), C_e is the concentration of dye solution (mol. L^{-1}) at equilibrium. The constant q_{max} signifies the adsorption capacity ($mol.g^{-1}$) and K_L is related to the energy of adsorption (L. mol^{-1}). Linear plot of $1/q_e$ versus $1/C_e$ shows that adsorption follows Langmuir isotherm (Fig.7). Values of q_{max} and K_L were calculated from the intercept and slop of the linear plot. In Eq. (7), K_F and 1/n are Freundlich constants. N is related to the adsorption energy distribution, and K_F indicates the adsorption capacity. Linear plot of log q_e versus Log C_e shows that adsorption follows Freundlich isotherm (Fig.8). Values of K_F and n were calculated from intercept and slop of plot. The Temkin isotherm (Eq. (8)), T is the absolute temperature in (K) and R is the universal gas constant, 8.314 J. mol^{-1} K^{-1}. The constant, b is related to the heat of adsorption, A is the equilibrium binding constant (L. mol^{-1}) corresponding to the maximum binding energy [16, 17]. Fig.9 shows the adsorption data according to the linear form of the Temkin isotherm. In Eq. 9, K (mol^2 . J^{-2}) is a constant related to the adsorption energy, Q_m (mol. g^{-1}) the theoretical saturation capacity, and ε is the Polanyi potential that can be calculated from Eq. (10):

$$\varepsilon = RT \ln(1 + \frac{1}{C_e}) \quad (10)$$

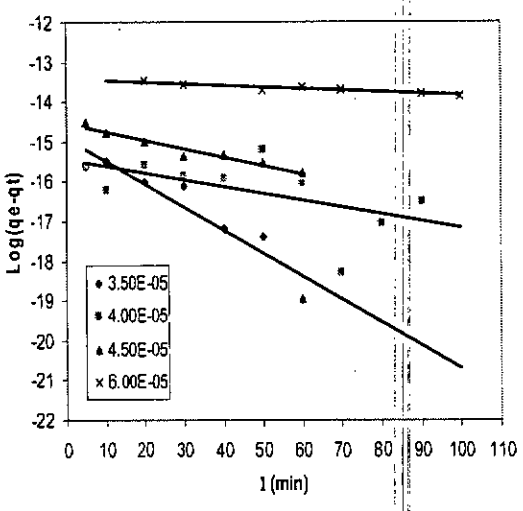


Fig. 3. Pseudo- first order kinetics for adsorption of DR81 dye onto ACW.

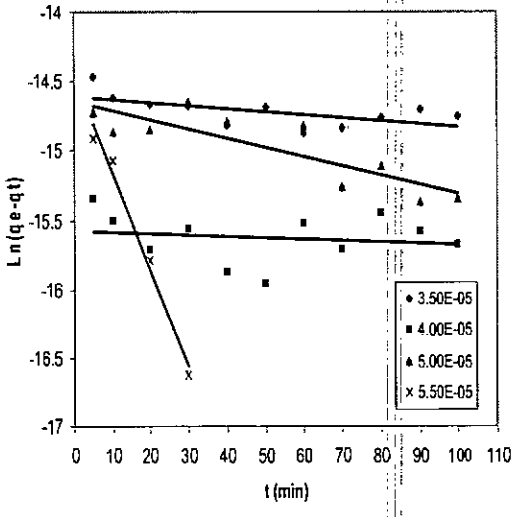


Fig. 4. Pseudo- first order kinetics for adsorption of DB71 dye onto ACW.

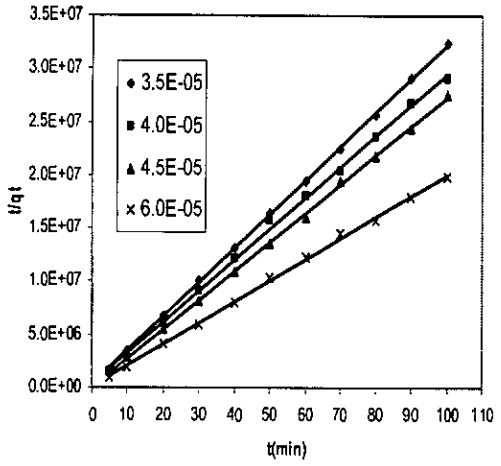


Fig. 5. Pseudo- second order kinetics for adsorption of DR81 dye onto ACW.

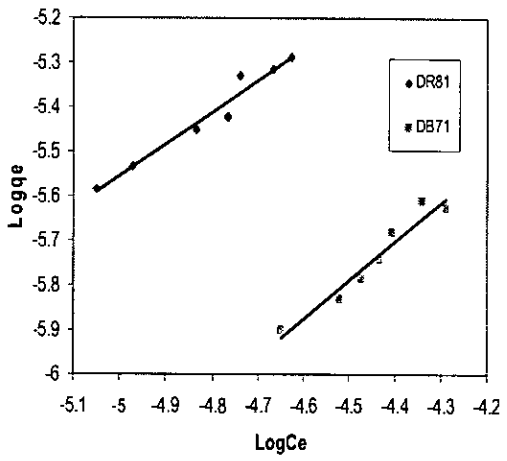


Fig. 8. Freundlich isotherm plots for adsorption of DR81 and DB71 onto ACW.

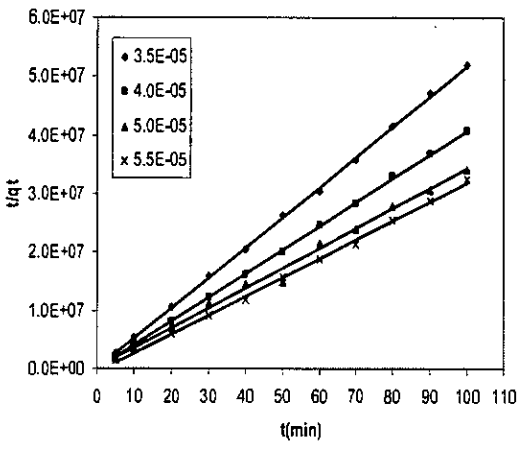


Fig. 6. Pseudo- second order kinetics for adsorption of DB71 dye onto ACW.

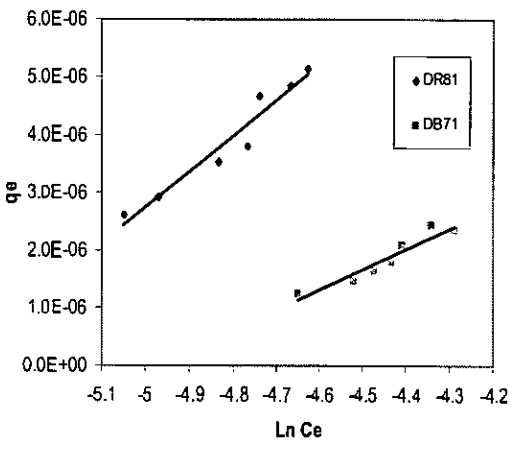


Fig. 9. Temkin isotherm plots for adsorption of DR81 and DB71 onto ACW.

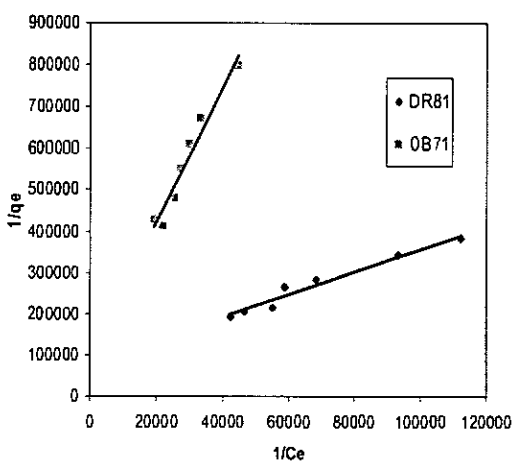


Fig. 7. Langmuir isotherm plots for adsorption of DR81 and DB71 onto ACW.

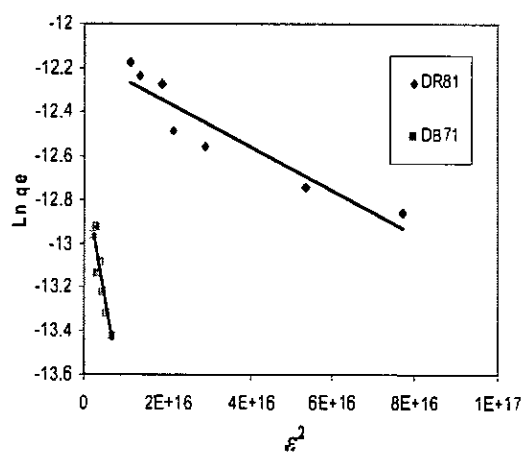


Fig.10. D-R isotherm plots for adsorption of DR81 and DB71 onto ACW.

Fig. (10) Shows the plot of Lnq_e versus ε^2 of the experimental data for the adsorption of DR81 and DB71 onto ACW. The slop gives K and the intercept yields the adsorption capacity, Q_m.

Sorption equations were obtained by experimental data with Eqs. 6, 7, 8 and 9. The isotherm constants were calculated from the least square method and presented in table 4. The Langmuir equation represents the sorption process well, the R^2 value is higher than another isotherms. This may be due to homogenous of active sites on shell surface.

Table 3. Parameter values of pseudo- second order models

Dyes	$C_0\times10^5$	$k_2\times10^{-3}$	$q_{e,cal}\times10^{+6}$	R^2 (second-order)	$q_{e,exp}\times10^{-6}$	R^2 (first-order)
DR81	3.5	319.6	2.607	0.9999	3.082	0.8905
	4.0	320.2	2.928	0.9988	3.437	0.3182
	4.5	337.8	3.070	0.9995	3.892	0.9441
	6.0	553.4	4.011	0.9985	4.799	0.9244
DB71	3.5	40.48	1.255	0.9995	2.316	0.3883
	4.0	131.7	1.090	0.9997	2.613	0.0265
	5.0	461.3	1.637	0.9939	3.143	0.7216
	5.5	644.4	1.810	0.9921	3.412	0.8719

Table 4. Langmuir, Freundlich, Temkin and D-R isotherm models constants for adsorption of DB71 and DR81 onto ACW

Dyes	Isotherms	Parameters	Values
DR81	Langmuir	q_{max} (mol. g^{-1})	1.232×10^{-3}
		K_L(Lit. mol^{-1})	2.934×10^{4}
		R^2	0.9664
	Freundlich	K_F	1.118×10^{-3}
		n	1.387
		R^2	0.9629
	Temkin	A (Lit. mol^{-1})	148.41
		b (J. mol^{-1})	4.129×10^{-3}
		R^2	0.9397
	D-R	K (mol^2. J^{-2})	1×10^{-7}
		Q_m (mol. g^{-1})	5.27×10^{-6}
		R^2	0.8828
DB71	Langmuir	q_{max}(mol. g^{-1})	1.073×10^{-3}
		K_L(Lit. mol^{-1})	5.685×10^{-3}
		R^2	0.9484
	Freundlich	K_F	1.274×10^{-2}
		n	1.155
		R^2	0.9425
	Temkin	A (Lit. mol^{-1})	148.413
		b (J. mol^{-1})	6.193×10^{-3}
		R^2	0.9130
	D-R	K (mol^2. J^{-2})	1×10^{-16}
		Q_m (mol. g^{-1})	3.035×10^{-6}
		R^2	0.8680

CONCLUSION

Equilibrium and kinetic studies were done for the adsorption of Direct Red 81 (DR81) and Direct Blue 71(DB71) from aqueous solutions onto ACW. Results of adsorption showed that ACW can be effectively used as a biosorbent for removal of direct dyes. The data indicate that the adsorption kinetics of dyes on ACW followed the pseudo-second order. The results showed that the experimental data were correlated reasonably well by the Langmuir isotherm and maximum adsorption occurred in acidic pH.

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