

Kinetic and Equilibrium Study of Adsorption of Di-Azo Dyes on Commercial Activated Carbon

Emad Abdulilah Saleh Al-Hyali* and Ra'ed Tariq Ghanim Al-Abady
Chemistry Department, College of Education, University of Mosul, Mosul, Iraq

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Abstract. This research work is concerned with studying the adsorption of a number of di-azo dyes on commercial activated carbon (CAC). The synthesized dyes vary in their structures by the central parts, which are either ortho, meta or para phenylene diamine. This variation affects the linearity of molecules, their spatial arrangement and electron movement throughout the molecule by resonance. Factors affecting adsorption process, such as the effect of contact time, initial concentration, pH of the adsorption medium, adsorbent dose, effect of solvent and temperature were studied. The results indicated that, the adsorption process is fast in the first 10 min, then gradually decreased with time and approaches maximum within 70-80 min for all the studied dyes. The increase of initial concentration and temperature decreased the adsorption efficiency. The results also shows that, the adsorption is found to be more efficient at low pH value. The increase of the adsorbent dose increases the adsorption efficiency and decreases its capacity. The variation of solvent (ethanol-water ratio) indicates that the decrease of dielectric constant lowers the adsorption efficiency. The study included application of three adsorption isotherms; Freundlich, Langmuir and Tempkin on the experimental data of the studied systems. The results indicated that, Freundlich isotherm fits better the adsorption data. Kinetic analysis of the adsorption data was also conducted by employing 4 kinetic models; pseudo first order and pseudo second order, Elovich and intra particle diffusion equations. The results obtained conclude that, the studied systems follow the Pseudo second order model.

Keywords: kinetic study, equilibrium of adsorption, di-azo dyes, activated carbon

Introduction

Dyes are organic compounds; usually have a complex aromatic molecular structure making them stable and resistant to biodegradation (Mohorcic *et al.*, 2004).

Azo dyes represent the largest class of commercially produced dyes, in which the chromophores are the azo group (Sutherland, 2004; Wallace, 2001). Synthetically, they were produced in a huge amounts, exceeding (500,000) tons annually (Lewis, 1999), and were used in various industrial fields including the textile industry. The high stability and distinguishing colour of azo dyes, especially those with di and multiple azo groups attracted the attention of many manufactures and become valuable for such industry. The excess of dye remains in the effluent after dyeing process is commonly forms a wastewater with concentration ranging (from 10 to 200 g/L) of dyestuffs (Van der Zee, 2002).

Since some azo dyes and their degradation products are toxic and carcinogenic, their disposal into wastewater without advanced treatment creates a dramatic

source of pollution and damages the aquatic life. For this reason, a proper treatment is needed and dyes removal from wastewater became essential.

Intensive research work was carried out concerning treatment of such problems and aiming for providing a suitable technology for environmental protection. Various physiochemical and biological methods are described in the literature which can be employed for removing dyes from wastewater including; filtration (Dushankov *et al.*, 1995), chemical precipitation, flocculation (Vandevivere *et al.*, 1998; Smith *et al.*, 1993), ion exchange (Annadurai *et al.*, 2002; Slokar and Marechal, 1998), membrane separation, flotation (Dushankov *et al.*, 1995) and adsorption (Suteu and Bilba, 2005). Each of these techniques has its advantages and limitations regarding the environmental conditions. Its technical and economic feasibility is determined by different measures related to the dye type, wastewater composition, and cost. Sometimes, the use of one individual technique is not sufficient for achieving complete decolourization; therefore, the dye removal strategy may involve more than one technique (Suteu and Bilba, 2005).

*Author for correspondence; E-mail: emadabd2006@yahoo.com

Adsorption seems to be the most potential technique for dye removal from wastewater because of its simple design, initial cost, ease of operation and insensitivity to toxic substances (Eren and Acar, 2006). The use of various low cost materials as adsorbents for the removal of dyes from wastewater such as, chitin (McKay *et al.*, 1982), natural clay (El-Geundi, 1991), rice husk (Malik, 2003) etc. have been investigated. Activate carbon remains the most effective and widely used adsorbent for the dye uptake from aqueous solutions because of its large surface area, dye binding capacity and regeneration properties (Yasin *et al.*, 2007).

The rate of adsorbate uptake from solution onto the adsorbent solid surface after surmounting all the molecular forces, those trying to preclude the adsorption process is termed as adsorption kinetic. The kinetic data are valuable for determining the period required to reach equilibrium and assessing the adsorbent efficiency for adsorbate removal from effluents (Hameed, 2009; Ahmed *et al.*, 2007). Such data can also provide a clue for understanding the mechanism of adsorption, which is essential for improving the efficiency of such process and optimization of various parameters in dye recovery (Eren and Acar, 2006) for this reason, several research groups have focused their efforts on developing such studies (Hameed, 2009; AL-Hyali and Al-Jarjari, 2008; Ahmed *et al.*, 2007; Yasin *et al.*, 2007; Ho, 2006; Malik, 2003).

Kinetic models. The significance of the kinetic analysis of adsorption data lies in that, it provides a valuable insight into the adsorption pathways and mechanism of the attachment of adsorbate onto solid surfaces of adsorbents, which involve mass transfer and chemical reactions, those important for determining the efficiency of adsorption process.

The kinetic data of the adsorption of diazo dyes considered in this study onto a commercial activated carbon (CAC) were analyzed using four different kinetic models, namely; Pseudo first order and Pseudo second order, Elovich equation and intra particle diffusion model rate equation.

Pseudo first order model. It was suggested by Lagergren (Lagergren, 1898), which can be represented as in equation (1):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \dots \dots \dots (1)$$

Where, (k_1/min) is the Pseudo first order rate constant, q_e and q_t (mg/g) represent the adsorption capacities (amount of adsorbed dye on unit mass of carbon) at equilibrium and time (t), respectively. The integrating rate law by applying the initial condition of $t=0$ to $t=t$ and $q_t=0$ to $q_t=q_t$, equation (1) becomes:

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.0303} t \dots \dots \dots (2)$$

The adsorption data of the considered system fits this model, if the plot of $\log(q_e - q_t)$ versus time gave a linear relationship with correlation coefficient (R^2) close to unity, and the experimental (q_e) value was consistent with the value calculated from the intercept of the plot.

Pseudo second order model. This model is first applied by Ho *et al.* (1996), to assess the kinetic of adsorption data of heavy metal adsorption. It showed that, the rate depends on the adsorption capacity on the solid and not on the concentration of the adsorbate (Eren and Acar, 2006; Ho, 2006).

The Pseudo second order kinetic model can be represented as in equation (3); (Ho *et al.*, 1996):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \dots \dots \dots (3)$$

Where, k_2 is the rate constant of Pseudo second order adsorption (g/mg/min). The integrated linear form of equation (3) is (McKay and Ho, 1999):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_t} t \dots \dots \dots (4)$$

This model is applicable only when the value of t/q_t is linearly correlated with time and the value of calculated q_e is well fit the experimental data.

Elovich kinetic model. The Elovich as modified by Chien and Clayton (1980), is the rate equation based on the adsorption capacity commonly expressed as in equation (5); (Chien and Clayton, 1980):

$$\frac{dq_t}{dt} = \alpha \exp (- \beta q_t) \dots \dots \dots (5)$$

Where, α (mg/g/min) is the initial rate of adsorption, β (g/mg) the adsorption constant during any experiment related to extent of surface coverage and activation energy of chemisorptions.

The Elovich equation can be simplified by assuming $\alpha\beta t \gg t$ by applying the boundary conditions $q_t=0$ at $t=0$ and $q_t=q_t$ at $t=t$, equation (5) becomes:

$$q_t = \frac{1}{\beta} \ln = (\alpha\beta) + \frac{1}{\beta} \ln t \dots\dots\dots(6)$$

The plot of q_t versus $\ln(t)$ gives a linear relationship. The value of α and β can be calculated from the intercept and slope, respectively.

Intra particle diffusion model. This model was first developed by Weber and Morris (1963) and used to explore the possibility of intra-particle diffusion resistance affecting the adsorption. It can be represented by the relation between q_t and the square root of time ($t^{1/2}$), as in equation (7):

$$q_t = K_{diff} t^{1/2} + C \dots\dots\dots(7)$$

Where, K_{diff} (mg/g/min) is the diffusion rate constant and C (mg/g) is a value proportional to boundary layer thickness (Kannan and Sundaram, 2001).

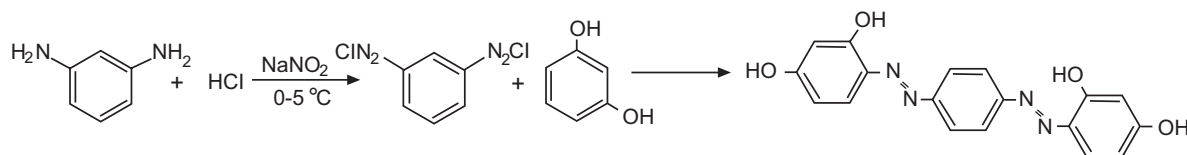
According to this model, if the plot of adsorption capacity (q_t) versus $t^{1/2}$ is linear, the Intra particle diffusion is involved and if the line passes through the origin, diffusion into the adsorbent pores is the only controlling step.

Materials and Methods

All the experiments in this study were performed as batch method.

Adsorbent. The adsorbent used in this study for removing dyes from their aqueous solutions is a commercial powdered activated carbon with particle size of 50 μ l and ash ratio less than 2%. The CAC was dried at 100 °C for 24 h before used and kept in a sealed bottle for further use.

Adsorbate. Five di-azo dyes were used as adsorbate in this study. These dyes vary in structure by their central parts, which are either ortho, meta or para phenylene diamine. They were synthesized from the reaction of phenylene diamine with the resorcinol or *m*-amino phenol with (1:2) mole ratio, via dizonium salts, respectively (AL-Abady, 2010; Volgel, 1964), as in the following equation:



The chemical compositions and other physical properties of the synthesized dyes are listed in Table 1.

The starting materials used for the preparation of these dyes and other chemicals such as *o*, *m*, and *p*-phenylene diamine, *m*-amino phenol, ethanol, NaNO₂, HCl and NaOH are of analytical grade and supplied by BDH and Fluka chemical companies.

Analytical method. The dye concentrations were monitored by measuring the absorbance of the filtrate of each dye at its λ_{max} (indicated in Table 1). By employing a single beam, UV-Vis spectrophotometer (Cecil-CE.1021) after separation of the adsorbent from dye solution by filtration. A calibration curve for each dye was constructed prior to the measurement by using various solution of known concentrations and within the detection limit of the dye according to Beers Law ($A = \epsilon b C$).

The amount of dye bound on the unit volume of adsorbent was estimated from the difference between the initial concentration of dye and free (unbound) dye concentration left in the solution.

Equilibrium study. As batch mode experiments, samples of 2 g of CAC were equilibrated with 1L of solutions containing various concentrations of each dye (35-245 mg/L) under continuous stirring.

The initial pH of the solution was adjusted by employing diluted solutions of NaOH or HCl and pH meter of the (pH 720 WTW 82362 Weilheim) type.

The study is conducted at various temperatures (20, 30, 40, 50 and 60 °C). The temperature was controlled by thermostatic water bath shaker (Julabo SW23). Constant rate of shaker (90 rpm) was used throughout the study. The samples were filtered to isolate the carbon particles. The residual dye concentration was determined spectrophotometrically at the maximum wave length corresponding to each dye.

The amount of adsorbed dye is evaluated in terms of the adsorption capacity (q_e , mg of dye per gram

of adsorbent), which can be calculated by equation (8):

$$q_e = \frac{C_i - C_e}{M} \times \frac{V}{1000} \dots\dots\dots(8)$$

And by the percent of adsorbed dye (Ads. %) as,

$$\text{Ads. \%} = \frac{C_i - C_e}{C_i} \times 100 \dots\dots\dots(9)$$

Where, C_i and C_e , are the initial and equilibrium concentrations (mg/L) of the dye solutions. M is the amount of adsorbent (g) and V is the volume of the agitated dye solution (mL).

Kinetic study. The effect of contact time was determined by carrying out series of experiments. In each of them, dye solution with initial concentration 87 mg/L was agitated with CAC (dose 2 g/L) at different time intervals. The temperature of solution was held constant

(20 °C) by using thermostatic bath shaker at constant rate of stirring (90 rpm). The samples were filtered and the residual dye concentrations were determined spectrophotometrically at the λ_{max} of the dye under study.

The effect of contact time experiments were repeated at various initial concentrations of dye (60, 87, 100 and 120 mg/L) and the data were tested to fit the kinetic models selected for achieving this study.

Results and Discussion

Effect of adsorption dose. Two dyes, 1,3DHAB and 1,4HAAB, with initial concentrations 87 and 192 mg/L, respectively were selected for this study. The investigation was carried out at different doses of adsorbent (0.8 - 6 g of CAC per liter of dye solution), 20 °C and pH=7. The results obtained are shown in Fig. 1a-b. It indicates that, the increase of adsorbent dose increases the adsorption efficiency (%Ads), but decreases the adsorption capacity (q_e , mg/g). This can be readily

Table 1. Chemical composition, physical properties and molar absorptivity (ϵ_{max}) of the synthesized dyes

Dye (Abbreviation)	Structure	Colour	M.P. (°C)	λ_{max} (nm)	ϵ_{max} L/mol/cm
1,4-di(2,4-dihydroxy phenyl azo) benzene (1,4DHAB)		Dark grey	165-167	421	29460
1,3-di(2,4-dihydroxy phenyl azo) benzene (1,3DHAB)		Black	207-208	390	25590
1,4-di(2-amino 4-hydroxy phenyl azo) benzene (1,4HAAB)		Dark red	256-258	449	19750
1,2-di(2-amino 4-hydroxy phenyl azo) benzene (1,2HAAB)		Dark grey	103-105	440	17760
1,3-di(2-amino 4-hydroxy phenyl azo) benzene (1,3HAAB)		Dark grey	101-103	455	17760

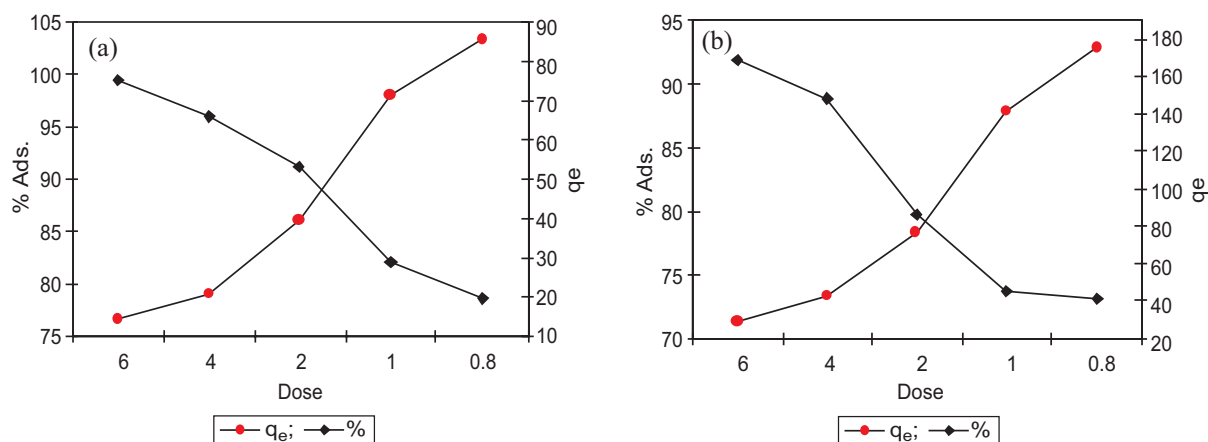


Fig. 1a-b. Relation between adsorption capacity (mg/g), adsorption efficiency and adsorbent dose (mg/g) of two azo dyes; (a) 1,3DHAB; (b) 1,4-HAAB.

illustrated; the increase of adsorbent dose increases the active sites available for adsorption on the carbon surface which in turn increases the percentage of dye adsorbed.

The decrease in adsorption capacity with the increase of adsorbent dose is apparently because of the instauration of the additional adsorption sites through adsorption process (Eren and Acar, 2006; Yu *et al.*, 2003; Shukla *et al.*, 2002).

Effect of contact time. The effect of contact time was investigated at initial concentration of 87 mg/L, neutral medium (pH=7), carbon dose 2 g/L and 20 °C. The variations of adsorption efficiency with time for the studied dyes are shown in Fig. 2.

The variation of the adsorption efficiency with time portrayed in Fig. 2 shows that the adsorption process proceeded in two stages; an initial rapid stage represented by the first 10 min being very sharp. In this stage 70-80% of the dyes were removed from solution by CAC. This stage is followed by a slower one in which the uptake rate is gradually decreased with time and reaches equilibrium with in 70-80 min. The time 80 min is used for further studies.

The curve representing the variation of adsorption ratio of the dye 1,3HAAB with time shows different adsorption pattern. This could be attributed to the non linear shape of the molecule, in addition to that, the electronic distribution through the resonance effect is restricted on two rings only in contrast to the other molecules in which the mesomeric effect is distributed over all the three rings.

Effect of initial concentration. The importance of initial concentration lies in that, it may provide an important driving force to overcome all the mass transfer resistances of the dye between the aqueous and solid phases.

The effect of varying initial concentrations of the dye on adsorption efficiency is tested in the range of 35 to 245 (mg/L), while keeping all other parameters constant. The results obtained are listed in Table 2. The adsorption capacity and efficiency are calculated as in equations (8) and (9), respectively.

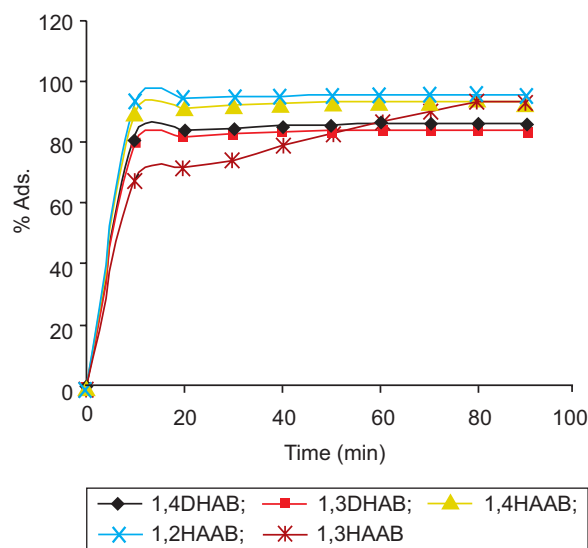


Fig. 2. Variation of adsorption efficiency with time for the considered dyes.

The results of Table 2 show that, the removal of the studied dyes showed the same trend of variation. The adsorption efficiency of dye on activated carbon is highly dependent on the initial concentration. The amount of adsorbed dye is increased with the increase of initial concentration, while the adsorption efficiency is decreased. This could be attributed to the increase of competition among dye molecules to be adsorbed on a constant number of active sites available for adsorption on a certain amount of adsorbent. This competition decreases the binding energy between the dye and the solid surface, and preclude the adsorption process as a result (Shah *et al.*, 2009; Sharma and Goyal *et al.*, 2009). This result indicates that, the adsorption of such dyes on CAC is more efficient at low concentration.

Effect of initial pH. The pH of an aqueous medium is an important factor that could affect the uptake efficiency of a dye by activated carbon, since the chemical characteristics of functional groups of both dye structures and carbon surface can be affected by the variation of pH.

Table 2. Effect of initial concentration on adsorption capacity and efficiency

Dye	C _i (mg/L)	C _e (mg/L)	q _e (mg/g)	%Ads.
1,4DHAB	35	4.131	15.435	88.20
	87	11.960	37.520	86.25
	140	21.595	59.203	84.58
	192	31.993	80.004	83.34
	245	-	-	-
1,3DHAB	35	4.128	15.436	88.21
	87	12.517	37.242	85.61
	140	23.986	58.007	82.87
	192	37.430	77.285	80.51
	245	-	-	-
1,4HAAB	35	1.057	16.972	96.98
	87	5.413	40.794	93.78
	140	12.654	63.673	90.96
	192	25.659	83.171	86.64
	245	42.847	101.077	82.51
1,2HAAB	35	0.460	17.270	98.69
	87	3.301	41.850	96.21
	140	9.728	65.136	93.05
	192	18.505	86.748	90.36
	245	30.408	107.296	87.59
1,3HAAB	35	1.402	16.799	96.00
	87	5.377	40.812	93.82
	140	14.754	62.623	89.46
	192	29.524	81.238	84.62
	245	45.901	99.550	81.26

This investigation is carried out by varying the initial pH from 4 to 11, under a constant initial dye concentration of 87 mg/L, carbon dosage of 2 g/L and constant temperature (20 °C). The dependence of the removal capacity of CAC to adsorb the dyes considered in this study on pH is presented in Table 3.

Table 3. Effect of pH medium of dye on adsorption capacity and efficiency, initial concentration of dye is 87 mg/L, CAC dose 2 g/L and 20 °C

Dye	pH	C _e (mg/L)	q _e (mg/g)	%Ads.
1,4DHAB	4	4.418	41.541	94.95
	6	9.412	41.291	89.18
	7	11.894	37.803	86.41
	9.4	14.507	36.496	83.42
	11	19.449	33.776	61.17
1,3DHAB	4	1.318	43.091	98.49
	6	9.860	38.57	88.67
	7	13.981	36.759	84.45
	9.4	22.343	32.578	74.46
	11	27.910	29.545	67.92
1,4HAAB	4	1.986	42.507	97.72
	6	4.371	41.315	95.04
	7	5.413	40.793	93.78
	9.4	11.336	37.832	86.97
	11	16.136	35.432	81.45
1,2HAAB	4	1.553	42.723	98.21
	6	2.593	42.204	97.02
	7	3.262	41.869	96.25
	9.4	4.582	41.209	94.73
	11	6.022	40.489	93.08
1,3HAAB	4	2.656	42.172	96.95
	6	4.336	41.332	95.02
	7	5.311	40.844	93.89
	9.4	11.656	37.672	86.60
	11	17.913	34.544	79.4

According to the results of Table 3, both adsorption efficiency and capacity estimated at equilibrium decreased with increasing the pH value of dye solution. The maximum removal of the tested dyes by CAC is observed at pH=4, which may due to reduce of the negative charges on the carbon surface as a result of the excess of portions present in solution (Shukla *et al.*, 2002). On the other hand, the basic medium increases the repulsion between the dye molecules and the negatively charged surface of carbon. This result is consistent with the results of other studies reported in the literature (EL-Ashtouky, 2009; Arami *et al.*, 2005).

Effect of solvent. One of the main problem encountered this study is the weak solubility of the investigated dye

in water. Ethanol was selected for this purpose because it is cheap, available and commonly used in various industries. Preliminary tests proved that, few milliliters of ethanol can dissolve the dye and dilution with water (to a certain limit) dose not affects the dye solubility in ethanol. Therefore, mixtures of ethanol-water were tested as dye solvent with varying ethanol ratio from 10-90%. The effect of solvent with different ethanol ratio was estimated. The investigation was carried out using initial concentration 87 mg/L of dye solution at neutral medium (pH=7) and 20 °C, the results of this study are listed in Table (4).

Table 4. Effect of ethanol ratio on the adsorption efficiency, $C_i=87$ mg/L, temperature = 20 °C and pH=7

Dye	% Ethanol	C_e (mg/L)	q_e (mg/g)	% Ads.
1,4 DHAB	10	9.757	38.622	88.79
	30	10.576	38.212	87.84
	50	11.960	37.520	86.25
	70	13.488	36.756	84.50
	90	14.939	36.031	82.83
1,3 DHAB	10	10.080	38.460	88.41
	30	10.945	38.028	87.42
	50	12.517	37.242	85.61
	70	14.115	36.443	83.78
	90	15.752	35.624	81.89
1,4 HAAB	10	4.482	41.259	94.85
	30	5.026	40.987	94.22
	50	5.413	40.794	93.78
	70	5.729	40.636	93.41
	90	6.415	40.293	92.63
1,2 HAAB	10	2.660	42.170	96.94
	30	2.990	42.005	96.56
	50	3.301	41.850	96.21
	70	3.748	41.626	95.69
	90	4.233	41.384	95.13
1,3 HAAB	10	3.623	41.689	95.84
	30	4.541	41.230	94.78
	50	5.377	40.812	93.82
	70	6.639	40.181	92.73
	90	8.082	39.459	90.71

The results of Table 4 showed that, the decrease of dielectric constant of the solvent (increase of ethanol ratio) decreases the adsorption efficiency and adsorption capacity. A solvent of 50% ethanol was used for achieving this study in order to ensure clear dye solution that stand for sufficient period without precipitation.

Effect of temperature. The Effect of temperature on adsorption is important for providing information regarding the nature of the studied system and the kind of forces controlling the adsorption process.

In this work, the effect of varying temperature on the adsorption of di-azo dyes on CAC is investigated in the range of 20-60 °C and at concentration of 87 mg/L. The obtained results are listed in Table 5.

Table 5. Effect of temperature on adsorption efficiency of the tested dyes $C_i=87$ mg/L, pH=7

Dye	% Adsorption				
	20 °C	30 °C	40 °C	50 °C	60 °C
1,4 DHAB	86.25	86.04	85.83	85.57	85.46
1,3 DHAB	85.61	85.40	85.08	84.82	84.60
1,4 HAAB	93.78	93.27	92.73	92.28	91.84
1,2 HAAB	96.21	85.58	95.11	94.44	93.95
3 HAAB	93.82	93.50	93.22	92.84	92.63

The results of Table 5 indicate the adsorption efficiency decreased with increasing the temperature in all of the studied dyes regardless of their straps. This observation is naturally acceptable since rising the temperature increases the desorption process.

Adsorption isotherms. Adsorption isotherms are usually used for describing the relationship between adsorbent and adsorbate at equilibrium. This relationship is expressed in terms of the ratio between the quantity of the adsorbed and remained solute in the solution at certain temperature at equilibrium.

Several models have been observed in the literature, applied to fit experimental data of adsorption in various systems.

In this work, the experimental data of the tested dyes were fitted to Freundlich, Langmuir and Tempkin isotherm equations.

Freundlich isotherm (Freundlich, 1906) is an empirical equation that can be applied to non-ideal adsorption systems involving heterogeneous adsorbent surface. It can be represented by the following linear form:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \dots\dots\dots(10)$$

Where, K_f (L/g) and n are constant related to adsorption capacity and adsorption intensity, respectively.

Their values can be calculated from the intercept and slope of the line plotted between log q_e versus log C_e , respectively. The obtained values of K_f and n are shown in Table 6.

The Langmuir isotherm (Woodard, 2001) can be expressed as in equation (El-Geundi, 1991). It suggests mono layer coverage of dye on adsorbent.

$$\frac{C_e}{q_e} = \frac{1}{K_L \cdot Q_{max}} + \frac{1}{Q_{max}} C_e \dots\dots\dots(11)$$

Where, C_e is the concentration of dye in the solution at equilibrium, Q_{max} (mg/g) and K_L (L/mg) are Langmuir constants related the maximum adsorption capacity and energy of adsorption, respectively.

The values of Q_{max} and K_L are estimated from the slope and intercept of the straight line plotted between C_e/q_e against C_e , respectively. The values obtained are given in Table 6.

A dimensionless constant termed as separation factor (R_L) can be deduced from the Langmuir isotherm data describing the essential under investigation. It can be defined by equation (12):

$$R_L = \frac{1}{1 + K_L \cdot C_o} \dots\dots\dots(12)$$

Where, C_o is the initial dye concentration, K_L is the Langmuir constant which is related to the affinity of binding sites and is calculated by equation (13) shown below (Aksu, 2003).

$$K_L = Q_{max} \times b \dots\dots\dots(13)$$

According to McKay *et al.*, (1982) R_L value refers to irreversible adsorption process when ($R_L=0$), favourable ($0 < R_L < 1$), linear ($R_L=1$) or unfavourable ($R_L > 1$). The values of K_L obtained are shown in Table 7.

The Tempkin isotherm (Thambavani and Sabitha, 2012) is presented as in equation (14):

$$q_e = B_T \ln K_T + B_T \ln C_e \dots\dots\dots(14)$$

Where,

$$B_T = RT / b_T \dots\dots\dots(15)$$

T is the absolute temperature, R is the gas constant (8.314 J/mol/K), b_T (J/mol) is a constant related to the heat of adsorption and K_T (L/mg) is the equilibrium binding constant, and representing an indication on to the maximum binding energy.

The plot of q_e against $\ln C_e$ can help for the determination of Tempkin constants, K_T and B_T . The later enables the calculation of b_T . The results obtained from the application of Tempkin isotherm on the adsorption of the tested dye on CAC are presented in Table 6.

Looking at the results of Table 6, the following conclusion can be driven; the high correlation coefficient (R) values (0.992-0.999) obtained from the application of Freundlich model show that, it fits the experimental data better than the other isotherms. Good fit is also observed from applying Langmuir equation on the adsorption data of the studied dyes on CAC indicated by the values of R which are in range (0.982-0.995).

Table 6. Isotherms constants obtained from adsorption data of dyes on CAC at 20 °C

Isotherm	1,4 DHAB	1,3 DHAB	1,4 HAAB	1,2 HAAB	1,3 HAAB
Freundlich					
n_f	1.243	1.364	2.057	2.298	2.001
K_f	4.990	5.591	17.282	24.400	15.513
R	0.999	0.998	0.997	0.999	0.992
Langmuir					
b (L/mg)	0.018	0.026	0.107	0.173	0.0940
Q_{max} (mg/g)	212 766	153 846	11 047	121 951	117 647
R	0.989	0.995	0.991	0.982	0.991
Tempkin					
B_T	30.526	27.388	22.553	20.713	23.037
K_T (L/mg)	0.354	0.379	1.574	3.555	1.257
R	0.979	0.984	0.984	0.969	0.989
b_T (J/mol)	79.800	88.944	108.012	117.607	105.743

Although weaker values of correlation coefficients are obtained from the application of Tempkin isotherm on the adsorption data, its parameters can still provide valuable information since it does not oppose the chemical intuition. Figs. 3-5 show the relations obtained from the fit of Freundlich, Langmuir and Tempkin isotherms, respectively.

The values of n_f are higher than unity ($1 < n_f < 10$), referring that, the adsorption of the investigated dyes on CAC is a favourable process (Khaled *et al.*, 2009; Crini *et al.*, 2007).

The values of maximum adsorption obtained from the fitting of Langmuir isotherm on the adsorption data lie in the range (119-212, mg/g), which are in agreement

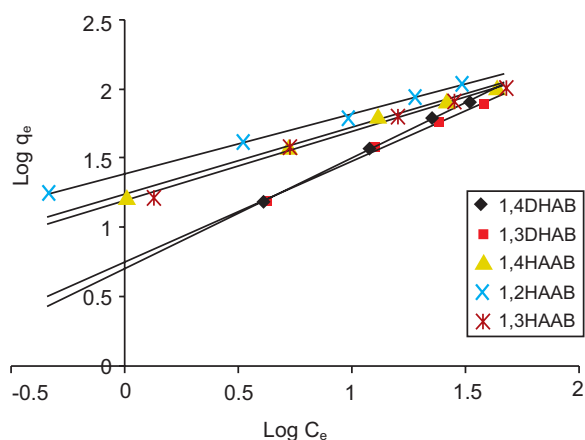


Fig. 3. Application of Freundlich isotherm on the adsorption data at 20 °C.

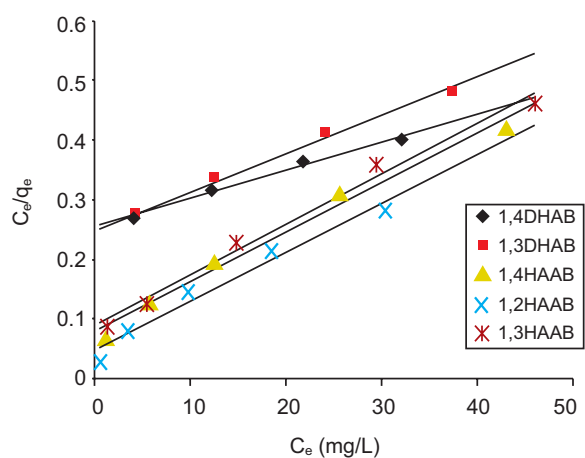


Fig. 4. Application of Langmuir isotherm on the adsorption data at 20 °C.

with the results reported in the literature for similar studies (Khaled *et al.*, 2009; Crini *et al.*, 2007; Reddy *et al.*, 2006).

The results listed in Table 7, explain that, all R_L values calculated by employing equation (12), are greater than zero and less than unity, showing favourable adsorption of dye on CAC.

According to the results of applying Tempkin isotherm on the adsorption data on CAC, the values of the heat of adsorption (b_T) decrease and the binding energies (K_T) fall with surface coverage of the adsorbent due to the increase of adsorbate-adsorbate-interactions (Khaled *et al.*, 2009).

Kinetic study. In this work, four models are employed for examining the controlling mechanism of adsorption process such as mass transfer and chemical reaction. The experimental data were analyzed by using the pseudo first order, pseudo second order, Elovich, and intraparticle diffusion kinetic models. The study is conducted at various initial dye concentrations (16-120 mg/L), adsorbent dose (2 g/L) and constant temperature (20 °C), as follow:

Pseudo first order model. According to this model (eq. 2), the value of k_1 and q_e are determined from the plot of $\log(q_e - q_t)$ versus time. Their values, the value of correlation coefficient and experimental q_e are given in Table 8.

The results of Table 8 indicated that, this model cannot be applied for the entire adsorption process. This may

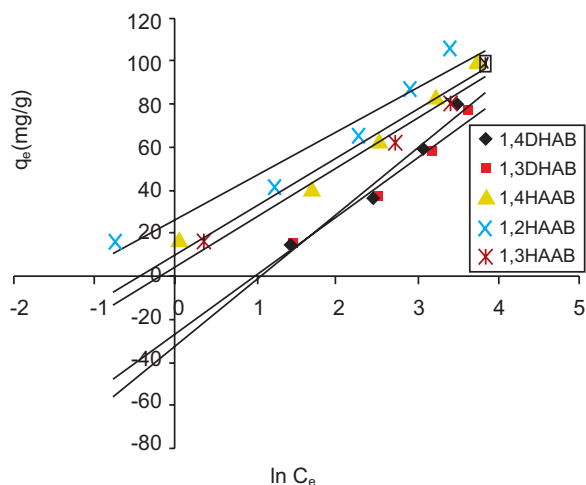


Fig. 5. Application of Tempkin isotherm on the adsorption data at 20 °C.

Table 7. Values of R_L and b obtained from the application of Langmuir isotherm at 20 °C

Dye	B (L/mg)	C_i (mg/L)	R_L
1,4 DHAB	0.0184	35	0.6083
		87	0.3845
		140	0.2796
		192	0.2206
		245	0.1816
1,3 DHAB	0.0261	35	0.5226
		87	0.3057
		140	0.2149
		192	0.1664
		245	0.1352
1,4 HAAB	0.1074	35	0.2101
		87	0.0967
		140	0.0624
		192	0.0463
		245	0.0366
1,2 HAAB	0.1734	35	0.1415
		87	0.0622
		140	0.0396
		192	0.0292
		245	0.023
1,3 HAAB	0.0944	35	0.2323
		87	0.1085
		140	0.0703
		192	0.0523
		245	0.0414

be attributed to the decrease in the adsorption rate (which is initially fast) due to pore diffusion (Eren and Acar, 2006; Ozacar and Sengil, 2003). For this reason, the calculated q_e values are quite low if compared to the experimental q_e . Furthermore, the values of R for all of the plotted lines are far less than unity denoting that, the adsorption of the studied dyes on to CAC is not first order reaction.

Pseudo second order model. The experimental data of the adsorption of the diazo dyes on activated carbon are fitted to the Pseudo second order model (eq. 4). The values of k_2 (g/mg/min) and q_e (mg/g) are calculated from the slope and intercept of the straight lines obtained by plotting t/q_e against time (Fig. 6a-e), respectively. The initial rate of adsorption (h , mg/g/min), is evaluated using equation (12):

$$h = k_2 q_e^2 \dots\dots\dots(12)$$

The results obtained from the application of this kinetic model are portrayed in Table 9.

The results of Table 9 indicated that, contrary to the first order equation, this model fit the adsorption data well for the whole range of contact time. Excellent linear relationships obtained (Fig. 7) indicated by the values of correlation coefficients which found to be in

Table 8. Results of the fitting of the pseudo first order model on adsorption data, pH=7 and T= 20 °C

Dye	C_i (mg/L)	q_e calc (mg/g)	k_1 (min)	q_e exp (mg/g)	R
1,4DHAB	60	-0.447	0.0378	25.847	0.6074
	87	-	0.0113	37.737	0.2480
	100	-0.853	0.0412	42.304	0.5116
	120	-	0.0299	50.720	0.4572
1,3DHAB	60	-0.306	0.0292	25.340	0.7549
	87	-0.560	0.0472	36.786	0.5361
	100	-0.944	0.0302	41.159	0.5208
	120	-	0.0184	49.548	0.4399
1,4HAAB	60	-0.482	0.0327	28.400	0.6181
	87	-0.377	0.0523	40.793	0.7232
	100	-1.241	0.0316	46.116	0.4641
	120	-	0.0249	54.851	0.3939
1,2HAAB	60	-	0.027636	28.835	0.4954
	87	-0.440	0.036618	41.862	0.5093
	100	-	0.025103	47.088	0.4706
	120	-	-4.6E-05	56.010	0.0008
1,3HAAB	60	0.134	0.0359	28.295	0.9654
	87	0.124	0.0355	40.828	0.9670
	100	0.120	0.0359	45.574	0.9707
	120	0.114	0.0366	53.861	0.9768

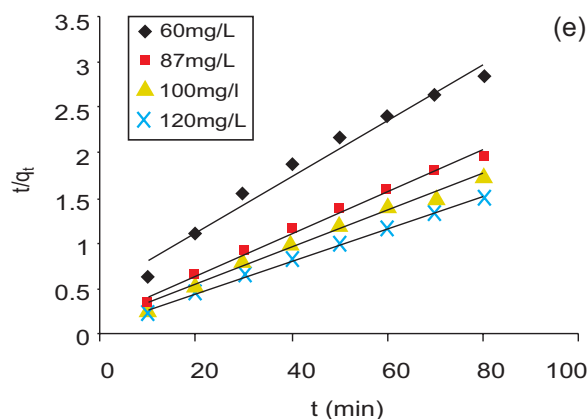
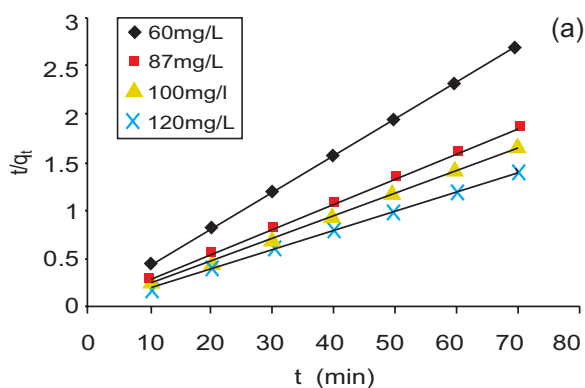
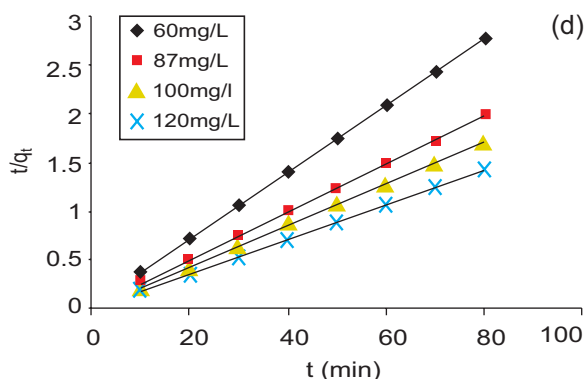
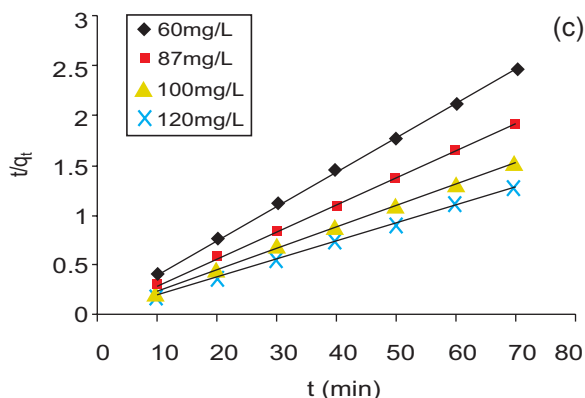
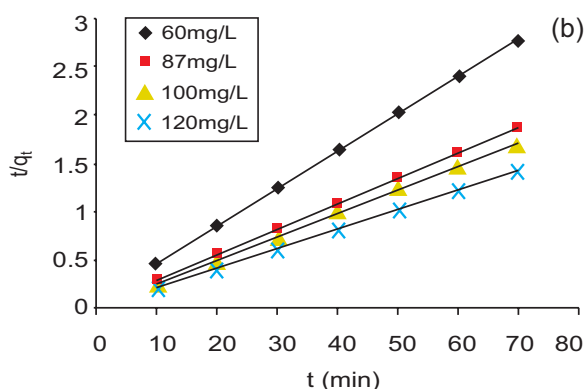


Fig. 6a-e. Relation between t/q_t versus time of the tested dye at different concentrations, (a) 1,4DHAB; (b) 1,3DHAB; (c) 1,4HAAB; (d) 1,2HAAB and (e) 1,3HAAB.



the range between (0.98-1.0) for all of the dyes and at all concentrations. In addition, the values of calculated q_e (q_e calc.) agreed very well with the experimental q_e (q_e exp) data. These results suggest that, the adsorption of the considered dyes on CAC obeys the second order kinetic model for the entire period of adsorptions based on the assumption that, the rate limiting step may involve chemisorptions. The investigation also revealed that, the increase of the initial concentration increases the initial rate of adsorption (h), since it enables the mass transfer of the adsorbate molecules from the solution to the solid surface of adsorbent. The results obtained are similar to data of other studies observed in the literature (EL-Nemr *et al.*, 2009; Khaled *et al.*, 2009).

Elovich kinetic model. This model (eq. 6) is fitted to the adsorption data of the studied dyes under similar conditions that used when applying the Pseudo first and second order models. The linear relationships between q_t and $\ln t$ shown in (Fig. 8) are used to calculate the values of Elovich constant represented by the initial rate of adsorption (α , mg/g/min) and desorption constant (β , g/mg). These constants were determined at various concentrations, from the slope and intercept of the straight lines (Fig. 8), respectively. The estimated values are listed in Table 10.

Increase in the initial rate of adsorption (α) is observed with the increase of initial concentration, accompanied by increase of desorption constant. These results can be interpreted as follow; as mentioned earlier, the increase of initial concentration facilitate the molecular

Table 9. Results of the fitting of the pseudo second order model on adsorption data, pH=7, T= 20 °C and CAC dose = 2 g/L

Dye	C _i (mg/L)	q _e calc (mg/g)	k ₂ (g/mg/min)	H (mg/g/min)	q _e exp (mg/g)	R
1,4DHAB	60	26.315	0.0278	19.251	25.847	1
	87	38.167	0.0390	56.812	37.737	1
	100	42.553	0.0472	85.468	42.304	1
	120	51.020	0.0600	156.182	50.720	1
1,3DHAB	60	25.906	0.0188	12.617	25.340	0.9998
	87	37.174	0.0387	53.480	36.786	1
	100	41.493	0.0443	76.270	41.159	1
	120	49.751	0.0546	135.144	49.548	1
1,4HAAB	60	28.818	0.0283	23.503	28.400	1
	87	41.152	0.0451	76.376	40.793	1
	100	46.296	0.0518	111.024	46.116	1
	120	54.945	0.0705	212.836	54.851	1
1,2HAAB	60	29.069	0.0595	50.278	28.835	1
	87	42.016	0.0584	103.096	41.862	1
	100	47.169	0.0671	149.292	47.088	1
	120	56.179	0.0792	249.962	56.010	1
1,3HAAB	60	32.467	0.0013	1.370	28.295	0.9864
	87	46.511	0.0009	1.947	40.828	0.9951
	100	48.309	0.0030	7.001	45.574	0.9969
	120	56.497	0.0033	10.533	53.861	0.9984

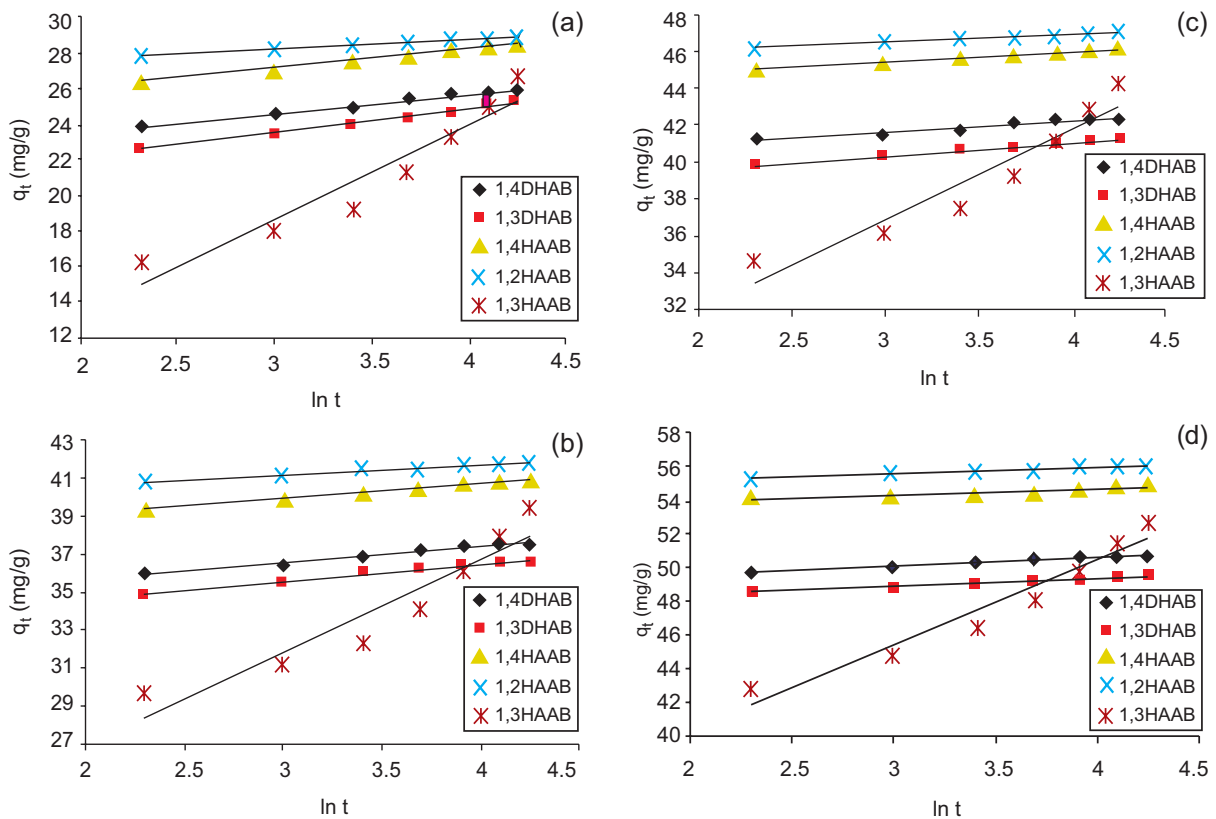


Fig. 7a-d. The relation between q_t versus ln t at different initial concentrations, (a) 60 mg/L; (b) 87 mg/L; (c) 100 mg/L and (d) 120 mg/L.

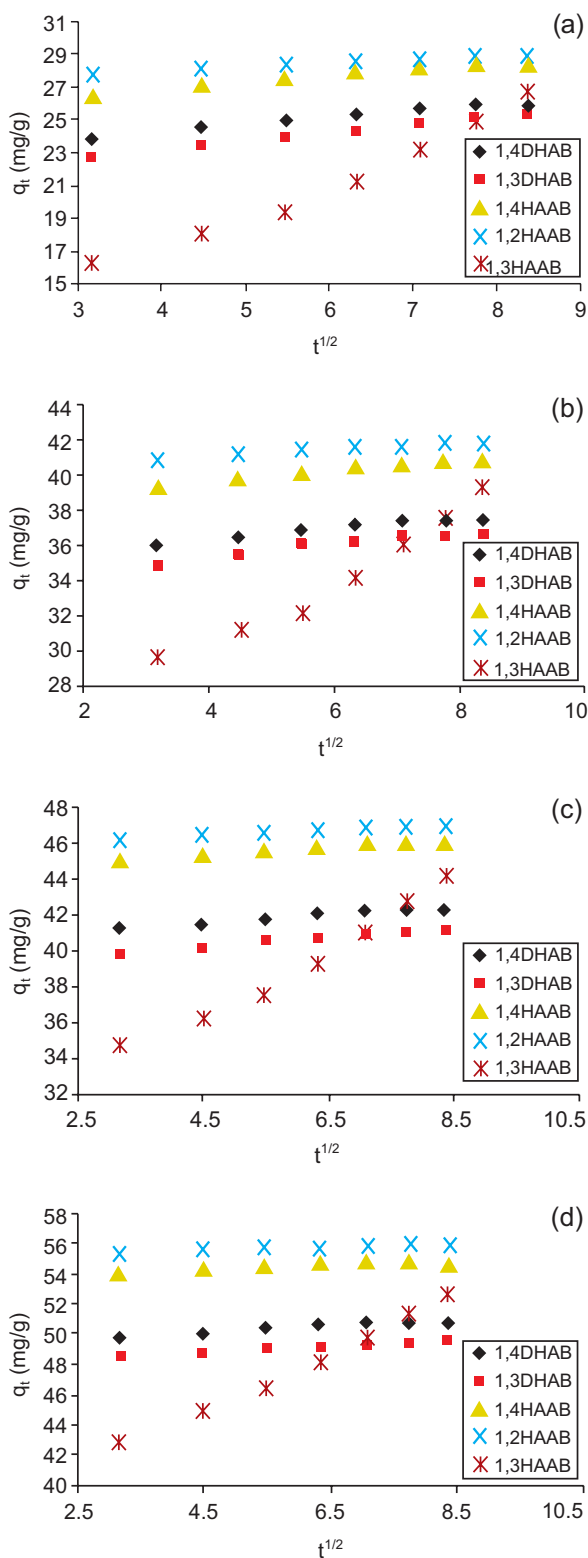


Fig. 8a-d. Relationship between q_t versus $t^{1/2}$ at different initial concentrations, (a) 60 mg/L; (b) 87 mg/L; (c) 100 mg/L and (d) 120 mg/L.

Table 10. Results of the application of Elovich equation on the adsorption data, pH = 7, CAC dose = 2 g/L and T = 20 °C

Dye	C_i (mg/L)	β (g/mg)	α (mg/g/min)	R
1,4DHAB	60	0.927	4.344E08	0.9918
	87	1.211	9.464E17	0.9903
	100	1.402	6.706E23	0.9895
	120	1.793	2.793E37	0.9936
1,3DHAB	60	0.720	1.603E06	0.9952
	87	1.090	4.145E15	0.9866
	100	1.384	6.287E22	0.9968
	120	1.926	1.914E39	0.9933
1,4HAAB	60	0.959	1.053E10	0.9956
	87	1.318	2.723E21	0.9944
	100	1.791	6.007E33	0.9930
	120	2.569	8.182E58	0.9698
1,2HAAB	60	1.857	1.407E21	0.9901
	87	1.968	4.278E33	0.9970
	100	2.318	1.400E45	0.9937
	120	2.881	5.789E67	0.9944
1,3HAAB	60	0.172	1.105E02	0.9536
	87	0.184	1.011E05	0.9497
	100	0.187	6.003E04	0.9553
	120	0.186	7.545E06	0.9722

transfer on to the solid surface which leads to increase in the initial concentration due to the availability of active sites on the carbon surface in the first few minutes. As the coverage of carbon surface increase, the competition among adsorbate molecules to be attached on the limited number of active sites remained on the carbon surface increased, creating a repulsion forces toward the adsorbent surface which weaken the bonding energy and increasing the desorption process. This observation is consistent with other results found in the literature (EL-Nemr *et al.*, 2009; Khaled *et al.*, 2009).

The intraparticle diffusion model. The possibility of applying this model on the adsorption data of the studied azo dyes on CAC is tested in terms of the graphical relationship (eq. 7) between the amount of dye adsorbed and the square root of time.

The plot between q_t against $t^{1/2}$, shown in (Fig. 8), is found to give two lines. The rate of diffusion constant (K_{diff} , mg/g/min) is directly estimated from the slope of the second regression line and the value of C is represented by the intercept.

The values of correlation coefficients, K_{diff} and C are given in Table 11.

Table 11. Results of the application of the intraparticle diffusion model on adsorption data, pH = 7, T = 20 °C and CAC dose = 2 g/L

Dye	C _i (mg/L)	K _{diff} (mg/g/min)	C (mg/g)	R
1,4DHAB	60	0.3964	22.735	0.9852
	87	0.3020	35.399	0.9785
	100	0.2601	40.296	0.9745
	120	0.2031	49.138	0.9775
1,3DHAB	60	0.5152	21.110	0.9984
	87	0.3298	34.265	0.9585
	100	0.2645	39.074	0.9863
	120	0.1932	47.954	0.9985
1,4HAAB	60	0.3840	25.347	0.9907
	87	0.2761	38.646	0.9773
	100	0.2072	44.453	0.9952
	120	0.1473	53.637	0.9912
1,2HAAB	60	0.1854	27.315	0.9632
	87	0.1774	40.383	0.9842
	100	0.1521	45.793	0.9932
	120	0.1214	55.002	0.9827
1,3HAAB	60	2.1234	8.5916	0.9878
	87	1.9919	22.359	0.9856
	100	1.9500	27.601	0.9888
	120	1.9461	36.207	0.9963

Figure 8 confirms that, the adsorption of the tested dyes on CAC vary in a similar trend. The two intersecting lines obtained in each plot indicate that, the adsorption mechanism includes two steps independent of each other. The first one is fast and representing the attachment of dye onto the external surface of carbon at the beginning of the adsorption process. The second step occurs with a slower rate in which the dye molecules diffuse into the pores exist on the carbon surface. Since the plots of q_t versus $t^{1/2}$ obtained for all of the dyes do not pass through the origin point, the intraparticle diffusion is not the rate limiting step, and the surface adsorption is operating concurrently during the dye-carbon interactions.

The values of the thickness of the boundary layer(C) were found to increase with the increase of initial concentrations, which reflect the decrease of probability of the external mass transfer and increasing the chance of internal transfer. This observation is supported by the values of the intraparticle diffusion constants (K_{diff}) which decrease with the increase of the initial dye concentrations. The main reason for such behaviour is the increase of adsorbate-adsorbate interactions that

result from the increase of initial concentration (Kannan and Sundaram, 2001).

The linear relationships between q_t and $t^{1/2}$ based on the correlation coefficient values close to unity is a good indication of the application of this model on the studied systems and may confirm that, the intraparticle diffusion process is the rate determining step.

Conclusion

In this study, a number of di-azo dyes are synthesized. These dyes were of great stability and have properties that making them suitable for industrial application specially textile industry. The results of the investigation dealing with the methodology of treating the water pollution, that may occur as a result of throwing such dyes into water sources as an industrial waste, by adsorption.

The forces controlling the adsorption process and the mechanism by which the adsorption is performed are investigated by employing equilibrium and kinetic studies which are conducted at the optimal conditions of the adsorption system.

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