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## **KINETIC STUDY OF ADSORPTION OF ACID DYEING ON COTTON WITH CETYL TRIMETHYL AMMONIUM BROMIDE**

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GAMAL, A.M, EL-SAID, A.G. AND EL-AZABAWY, R.E

*Chemistry Department, Faculty of Science, Al-Azhar University (Girls), Nasr City, Cairo, Egypt.*

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### **Abstract**

Adsorption kinetics study of two Acid dyeing C.I. Acid red 198, C.I. Acid red 99 on cotton in absence and presence of cationic surfactant cetyl trimethyl ammonium bromide "CTAB" were carried out at pH 3.0, L:R 0.5 : 50 and an initial dye concentration  $1.0 \times 10^{-4}$  mole  $\text{dm}^{-3}$ . Pseudo first and second order kinetic models were used to examine the adsorption kinetic data. It was found that the adsorption kinetic of two acid dyeing in absence and presence cationic surfactant with pH control was found to follow the pseudo second order kinetic model with an activation energy of C.I. Acid Red 198 55.80, 57.65 and 40.04 kJ/mol but on C.I. Acid Red 99 44.28, 48.40 and 16.51kJ/mol. The effect of cationic surfactant on dyeability of cotton fabric with two acid dyes have also been studied at three different temperatures (45, 60, 90°C). It was observed that the aggregation of surfactant and anionic dyes takes place at surfactant concentrations far below the critical micelle concentration of the individual surfactant

**Key words:** Acid dye, cationic surfactant, adsorption, cotton, kinetics.

### **Introduction:**

Cotton is one of the most important fibers in the textile dyes, by dyeing on printing in aqueous solution. Cotton is the most widely used of the textile fibers. Which have a combination of properties-durability, low cost, easy wash ability and comfort that have made it desirable for summer clothes, work, clothes, towels and sheets<sup>(1)</sup>.

Cotton is composed of polymer chains of cellulose. The cellulosic polymers in cotton have a high degree of polymerization. The hydroxyl (–OH) groups on the chains are responsible for many of the properties of cellulosic fibers. The attract water and dyes, making cotton absorptive and easy today. They also enable hydrogen bonding between adjacent cellulosic chains in the crystalline areas of the fiber<sup>(2)</sup>.

The negative charges on the surface of cellulose repel anionic dyes and hence the efficiency of dye fixation on cellulosic fibers is generally low<sup>(3)</sup>.

To counter this problem, a number of studies on cotton dyeing have been carried out to improve the dye uptake and fastness properties. Most research focus is on introducing cationic sites into the cotton fabrics for interactions with anionic dyes<sup>(4-7)</sup>.

In addition, cetyl trimethyl ammonium bromide "CTAB" has been used as a cationic agent in cotton dyeing with acid dye. It was found that "CTAB" increased the dye adsorbed on cotton and also decreased the desorption from the fiber<sup>(8)</sup>.

Surfactant are mainly used as wetting, dispersing and leveling agents for improving dyeing process by increasing solubility, stabilizing the dispersed state and promoting uniform distribution of the dye in the textile<sup>(9,10)</sup>.

Leveling agents act mainly by reducing the dyeing rate, increasing the rate of migration of the dye within the textile, and improving the compatibility of dyes. They can be divided into products with an affinity for dyes, and products with affinity for fibers. According to the structures of dye and substrate, surfactants used as leveling agents operate by different mechanisms depending on the ionic type of the dye. Products with an affinity for dyes form loosely bound addition compounds with the dyes whose stability is concentration dependent and usually decreases with increasing temperature. Leveling agents with an affinity for fibers are absorbed onto the fibers in competition with the dye. The competitive reaction reduces the absorption rate of the dye and promotes migration<sup>(11)</sup>.

Although, the interaction between dyes and surfactant has been studied in many papers, the studies in this area are still important and interesting for improving the dyeing process from theoretical, technological, ecological and economical points of view. The investigations into the behavior of different dyes in surfactant aqueous solutions can give useful information for understanding the thermodynamics and kinetics of the dyeing process and the finishing the textile material. UV-Vis spectroscopy.

The spectral changes of a dye observed in the presence of various amounts of surfactants are consistent with sequential equilibria involving surfactant monomers, micelles, dye aggregates, premicellar dye-surfactant complex and dye incorporated into micelle<sup>(12)</sup>.

The investigation of cationic surfactant-anionic dyes has shown that the importance of long-range electrical forces is basically to bring the dye anion and the surfactant cation close enough to enable the action of short-range noncoulombic

attractive van der Waals forces and hydrophobic interactions. So, the long-range electrical forces as well as short-range attractive forces are responsible for the dye-surfactant ion pair formation<sup>(13-15)</sup>.

The aggregation of oppositely charged dyes with surfactants is strongly dependent on noncoulombic interactions. So, the hydrophobicity increase of the surfactant or the dye, increase the binding energy.<sup>(16,17)</sup> It has been reported that the type of head group of surfactant has no large influence on the aggregation process<sup>(18,19)</sup>.

The choice of a particular surfactant for a particular purpose depends on its ability to interact with fibers and/or other components in the system.

However, the adsorption kinetics of acid dyeing on cotton with pH control has not been reported.

## Experimental

### Material:

All the chemicals were of analytical reagent grade. A stock solution of  $1.0 \times 10^{-2}$  mol dm<sup>-3</sup> of the two acid dyes C.I. Acid Red 198, C.I. Acid Red 99 was prepared by dissolving purified dyes in distilled water.

A stock solution of  $1.0 \times 10^{-2}$  mol dm<sup>-3</sup> surfactant was prepared in distilled water. The structure of two acid dyes and surfactant are shown in Fig. (1).

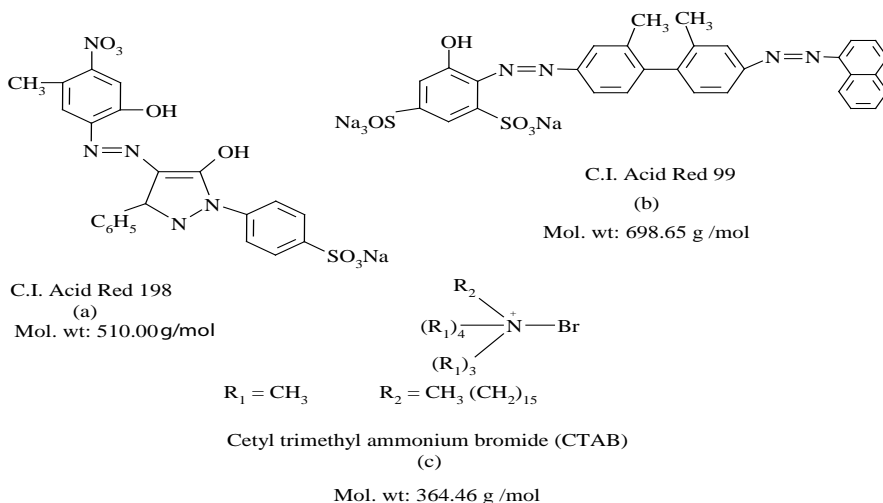


Fig. (1)

Acetic acid used in this paper obtained from Aldrich and used without further purification.

### ***Instruments and measurements:***

#### **Instruments:**

UV-Vis absorption spectra were measured using Perkin-Elmer Lambda 4B, model 201. A pH meter (Mettfer Delta 230, uk) was used to measure the pH values of the acid dye solution.

A thermostatted water bath (BTC : Biotech Company for medical and laboratory equipments) was used to study the kinetic adsorption of acid dye on cotton fabric.

### ***Measurements:***

#### **Dyeing procedure:**

Cotton samples were washed with nonionic surfactant (2g/L) at 60°C for 20 min and dried before dyeing process. The initial concentration of dyebath  $1.0 \times 10^{-4} \text{ mol dm}^{-3}$  were prepared with distilled water from the stock solution. The pH of the dye solutions was adjusted to 3.0 with glacial acetic acid.

The liquor ratio was 0.5:50 and CTAB surfactant were investigated in two different submicellar concentrations: ( $0.1 \times 10^{-3}$ ,  $2.0 \times 10^{-3} \text{ mol dm}^{-3}$ ). The effect of this surfactant was studied in three different temperatures (45, 60, 90°C) and at different times from (Zero–180 mins). The dry cotton samples were introduced into the dye baths after reaching to the specified temperature and each time taken.

The samples were then rinsed, washed and dried. Dye concentrations were determined at time zero and at subsequent times using a calibration curve based on absorbance at  $\lambda_{\text{max}}$ : 510 nm for C.I. Acid Red 198 and at  $\lambda_{\text{max}}$ : 495 nm for C.I. Acid Red 99. The amount of dye adsorbed per gram of cotton (mg/g cotton) at any time (9t) was calculated by a mass-balance relationship<sup>(20)</sup>.

### **Results and discussion:**

Dyeing of cotton fabrics with C.I. Acid Red 198, C.I. Acid Red 99 in the presence of different amounts of cationic surfactant, results show that the amounts of dye absorbed on the fabric decrease with increasing hydrophobicity of surfactant, cotton (cellulose fiber) has a negative surface charge in water, which repels the dye

anion. The affinity and substantively of an anionic azo dye such as C.I. Acid Red 99 to cotton are attributed to hydrogen bonding and van. der Waals forces.

Due to aggregation of anionic dye-cationic surfactant in aqueous solution, the dyeability of cotton samples reduces greatly. By increasing the temperature, some parts of these complexes break and the dyeability of samples improve that is a very common phenomena. Such dyeing process is a very useful method of studying the dye-surfactant aggregation in aqueous solution. Because the amounts of dye in a same condition in the presence of cationic surfactant will be investigated and insoluble precipitation and duration of sample preparation will not interfere in measurements.

The affinity of this dye to cotton is reduced by cationic surfactant mainly because of dye-surfactant aggregation and precipitation. The C.I. Acid Red 99 molecule has two azo groups, a larger linear structure and two sodium sulphonate groups which lead to higher solubility in water So, in comparing with C.I. Acid Red 198, higher electrostatic and smaller hydrophobic interactions with cationic-surfactant may occur. The C.I. Acid Red 99 samples, in contrast to C.I. Acid Red 198 solutions, do not have large and sharp bathochromic shifts in CMC region of the used cationic surfactant. Although, such bathochromic shifts happen at higher concentrations.

#### **The effect of temperature on the adsorption of acid dye on cotton:**

The effect of temperature on the adsorption of acid dye on cotton was investigated. It was found that a higher dyeing temperature resulted in higher initial dye adsorption rate ( $h_i$ ) on cotton before equilibrium in absence and presence different concentrations of "CTAB" of two acid dyes as shown in Fig. (2 and 3). The mobility of the large dye ions would be increased at higher temperature and at higher concentration of surfactant  $2.0 \times 10^{-3} \text{ mol dm}^{-3}$  and subsequently the rates of dyeing would be enhanced. A similar observation was also reported in the study on the adsorption of a basic dye on cross-linked cotton<sup>(21)</sup>. At the equilibrium time, the dye adsorbed by the cotton decrease with increasing temperature and increasing of surfactant concentrations, indicating an exothermic process. The dyeing condition of pH 3.0, initial dye concentration of  $1.0 \times 10^{-4} \text{ mol dm}^{-3}$  and L: R of 0.5: 50 was subsequently used to study the adsorption kinetics of acid dye on cotton.

***Kinetics of adsorption:***

In order to analyze the adsorption kinetics of acid dye on cotton in absence and presence of "CTAB", the pseudo first and second-order kinetic models were used to analyze the experimental data.

simple kinetic analysis of adsorption is the Lagergren equation. The Lagergren equation, a pseudo first order equation, describes the kinetics of the adsorption process as follows (22 – 24):

$$\frac{dq_1}{dt} = k_1(q_e - q_t) \quad (1)$$

where  $k_1$  is the rate constant of pseudo first -order adsorption ( $s^{-1}$ ), and  $q_e$  and  $q_t$  are the amounts of dye adsorbed per gram of cotton (mg/g cotton) at equilibrium and at time  $t$ . In many cases, the first-order equation of Lagergren does not fit well for the whole range of contact times and is generally applicable over only the initial stage of the adsorption<sup>(25)</sup>. After definite integration by applying the initial conditions  $q_t=0$  at  $t=0$  and  $q_t=q_t$  at  $t= t$ , Eq. (1) becomes.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

A straight line of  $\ln(q_e - q_t)$  versus  $t$  suggests the applicability of this kinetic model to fit the experimental data. The first-order rate constant  $k_1$  and equilibrium adsorption density  $q_e$  were calculated from the slope and intercept of this line.

The pseudo second-order kinetic model<sup>(22-25)</sup> is based on adsorption equilibrium capacity and can be expressed as follows:

$$\frac{dq_1}{dt} = k_2(q_e - q_t)^2 \quad (3)$$

where  $k_2$  (g cotton/mg min) is the rate constant for pseudo second-order adsorption. Integrating Eq.(3) and applying the initial conditions give:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \quad (4)$$

or equivalently.

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

and

$$h_i = k_2 q_e^2 \quad (6)$$

where  $h_i^{(26)}$  is the initial dye adsorption rate (mg/g cotton min). If pseudo second-order kinetics are applicable, the plot of  $(t/q_t)$  versus  $t$  would show a linear relationship. The slope and intercept of  $(t/q_t)$  versus  $t$  were used to calculate the pseudo second-order rate constant  $k_2$  and  $q_e$ . It is likely that the behaviour over the whole range of adsorption is in agreement with the chemisorption mechanism being the rate-controlling step<sup>(25)</sup>.

Kinetic data obtained from acid dye adsorption in the present study, was analyzed using the pseudo first-order kinetic model proposed by Lagergren<sup>(27)</sup>. According to Eq. (2). The results are listed in table 1. Based on the correlation coefficients obtained. The adsorption of two acid dye on cotton is not likely to be a first-order reaction.

The pseudo second-order kinetic model was also used to test the experimental data using Eq. (5) and plots of  $(t/q_t)$  against  $t$  for the adsorption of two acid dye in absence and presence surfactant dye on cotton are given in Fig. (4 and 5). The slopes and intercepts of these plots were used to calculate the adsorption capacity ( $q_{e,cal}$ ) and the rate constant ( $k_2$ ). The experimental data showed a good compliance with the pseudo second-order equation and the correlation coefficients for the linear plots were higher than 0.99 for all the experimental data. Also, the calculated  $q_{e,cal}$  values agreed very well with the experimental data. These results suggested that the experimental data for the adsorption kinetics of acid dye on cotton were fitted by the pseudo second-order kinetic model. Similar kinetics were also observed in the dyeing of wool with acid dyes<sup>(28)</sup>, in which the uptake rate of the acid dye on wool was described by a second-order rate expression based on the formation of a protein-dye complex as the rate determining step.

#### ***Activation parameters***

From the rate constant  $k_2$  (Table 1 and 2), the activation energy ( $E_a$ ) for the adsorption of acid dye on cotton was determined using the Arrhenius equation (7)<sup>(29)</sup>.

$$\ln k = \ln A - \frac{E_a}{RT} \quad (7)$$

where  $E_a$ ,  $R$  and  $A$  refer to the Arrhenius activation energy, the gas constant and the Arrhenius factor, respectively.

The Arrhenius plot of  $\ln k$  against  $1/T$  for the adsorption of acid dye on cotton is shown in Fig. (6 and 7) and the activation energy value is listed in Tables (3 and 4).

The enthalpy ( $\Delta H^*$ ), entropy ( $\Delta S^*$ ) and free energy ( $\Delta G^*$ ) of activation were also calculated using the Eyring equation (8) <sup>(29)</sup> as follows:

$$\ln \left( \frac{k}{T} \right) = \ln \left( \frac{k_b}{h} \right) + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT} \quad (8)$$

where  $k_b$  and  $h$  refer to Boltzmann's constant and Planck's constant, respectively. The enthalpy ( $\Delta H^*$ ) and entropy ( $\Delta S^*$ ) of activation were calculated from the slope and intercept of a plot of  $\ln(k/T)$  versus  $1/T$ . while the free energy of activation ( $\Delta G^*$ ) was obtained from Eq.(9).

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (9)$$

The calculated values are listed in Tables (3 and 4). The negative value of the activation entropy ( $\Delta S^*$ ) was supportive of an interaction between acid dye and cotton.

#### **Colour Assessment:**

Colour strength expressed as  $k/s$  was measured by a previously reported method by the light reflect reflectance technique and the relative colour strength was calculated by applying the kulbelka-munk equation (10)<sup>(30)</sup>.

$$\text{Colour strength (k/s)} = \frac{(1-R)^2}{2R} \quad (10)$$

The  $R$  data (reflectance of opaque dyed samples from 350–700 nm) were used for calculating the  $k/s$  values, this values of two acid dyes are listed in Tables (5 and 6).



**Table (1).** Comparison of the pseudo first-and second-order adsorption rate constant of C.I. Acid Red 198 onto cotton at an initial dye concentration  $1.0 \times 10^{-4}$  mol  $\text{dm}^{-3}$ , L:R 0.5: 50 and pH 3.0.

Dye	Temperature (°C)	$q_{e,\text{exp}}$ (mg/g cotton)	Pseudo first-order model		Pseudo second-order model			
			$k_1$ ( $\text{min}^{-1}$ )	$R^2$	$k_2$ (g cotton/ mg min)	$q_{e,\text{cal}}$ (mg/g cotton)	$h_i$ (mg/g cotton min)	$R^2$
Acid Red 198	45	63.25	$1.96 \times 10^{-2}$	0.985	$1.49 \times 10^{-4}$	63.08	0.593	0.997
	60	53.24	$1.46 \times 10^{-2}$	0.966	$6.48 \times 10^{-4}$	53.13	1.829	0.996
	90	16.57	$0.90 \times 10^{-2}$	0.954	$12.99 \times 10^{-4}$	16.23	0.340	0.990
$0.1 \times 10^{-3}$ mol $\text{dm}^{-3}$ "CTBA"	45	36.19	$2.88 \times 10^{-2}$	0.985	$4.78 \times 10^{-4}$	35.28	0.595	0.994
	60	33.22	$1.67 \times 10^{-2}$	0.969	$3.79 \times 10^{-4}$	32.94	0.411	0.992
	90	13.60	$1.25 \times 10^{-2}$	0.944	$2.01 \times 10^{-4}$	12.73	0.033	0.989
$2.0 \times 10^{-3}$ mol $\text{dm}^{-3}$ "CTBA"	45	25.13	$1.58 \times 10^{-2}$	0.968	$6.75 \times 10^{-4}$	24.88	0.418	0.993
	60	18.19	$1.37 \times 10^{-2}$	0.929	$17.29 \times 10^{-4}$	17.54	0.532	0.993
	90	11.90	$0.98 \times 10^{-2}$	0.942	$22.23 \times 10^{-4}$	11.80	0.310	0.988

**Table (2).** Comparison of the pseudo first-and second-order adsorption rate constant of C.I. Acid Red 99 onto cotton at an initial dye concentration  $1.0 \times 10^{-4}$  mol  $\text{dm}^{-3}$ , L:R 0.5: 50 and pH 3.0.

Dye	Temperature (°C)	$q_{e,\text{exp}}$ (mg/g cotton)	Pseudo first-order model		Pseudo second-order model			
			$k_1$ ( $\text{min}^{-1}$ )	$R^2$	$k_2$ (g cotton/ mg min)	$q_{e,\text{cal}}$ (mg/g cotton)	$h_i$ (mg/g cotton min)	$R^2$
Acid Red 99	45	68.19	$1.99 \times 10^{-2}$	0.985	$2.99 \times 10^{-4}$	68.11	1.387	0.998
	60	60.16	$1.52 \times 10^{-2}$	0.979	$1.01 \times 10^{-4}$	60.02	0.384	0.995
	90	19.79	$0.93 \times 10^{-2}$	0.967	$16.56 \times 10^{-4}$	19.21	0.611	0.993
$0.1 \times 10^{-3}$ mol $\text{dm}^{-3}$ "CTBA"	45	60.44	$1.49 \times 10^{-2}$	0.981	$1.36 \times 10^{-4}$	60.24	0.494	0.993
	60	39.56	$1.43 \times 10^{-2}$	0.947	$2.92 \times 10^{-4}$	39.22	0.449	0.994
	90	17.25	$1.38 \times 10^{-2}$	0.929	$12.60 \times 10^{-4}$	17.14	0.370	0.990
$2.0 \times 10^{-3}$ mol $\text{dm}^{-3}$ "CTBA"	45	34.22	$1.32 \times 10^{-2}$	0.976	$5.83 \times 10^{-4}$	34.08	0.677	0.988
	60	23.77	$1.23 \times 10^{-2}$	0.959	$9.26 \times 10^{-4}$	23.49	0.511	0.991
	90	14.39	$1.02 \times 10^{-2}$	0.950	$13.17 \times 10^{-4}$	14.14	0.263	0.981

**Table (3)** Activation parameter for the adsorption of Acid Red 198 on Cotton at initial concentration  $1.0 \times 10^{-4}$  mol  $\text{dm}^{-3}$ , L:R = 0.5:50 and pH = 3.00.

Dye	Temperature (°C)	$k_2$ (g cotton/mg min)	$E_a$ (kJ/mol)	$R^2$	$\Delta H^\ddagger$ (kJ/mol)	$\Delta S^\ddagger$ (kJ/mol)	$\Delta G^\ddagger$ (kJ/mol)	$R^2$
Acid Red 99	45	$1.49 \times 10^{-4}$	55.80	0.988	22.62	-90.38	23.43	0.999
	60	$6.48 \times 10^{-4}$						
	90	$12.99 \times 10^{-4}$						
$0.1 \times 10^{-3}$ mol $\text{dm}^{-3}$ "CTBA"	45	$4.78 \times 10^{-4}$	57.65	0.996	38.55	-84.80	42.36	0.999
	60	$3.79 \times 10^{-4}$						
	90	$2.01 \times 10^{-4}$						
$2.0 \times 10^{-3}$ mol $\text{dm}^{-3}$ "CTBA"	45	$6.75 \times 10^{-4}$	40.04	0.996	14.37	-54.68	16.83	0.999
	60	$17.29 \times 10^{-4}$						
	90	$22.23 \times 10^{-4}$						

**Table (4) Activation parameter for the adsorption of Acid Red 99 on Cotton at initial concentration  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup>/L, L:R = 0.5:50 and pH = 3.00.**

Dye	Temperature (°C)	$k_2$ (g cotton/mg min)	$E_a$ (kJ/mol)	$R^2$	$\Delta H^\ddagger$ (kJ/mol)	$\Delta S^\ddagger$ (kJ/mol)	$\Delta G^\ddagger$ (kJ/mol)	$R^2$
Acid Red 99	45	$2.99 \times 10^{-4}$	44.28	0.994	22.62	-73.54	25.93	0.999
	60	$1.01 \times 10^{-4}$					27.03	
	90	$16.56 \times 10^{-4}$					29.24	
$0.1 \times 10^{-3}$ mol dm <sup>-3</sup> "CTBA"	45	$1.36 \times 10^{-4}$	48.40	0.988	33.49	-101.03	38.04	0.995
	60	$2.92 \times 10^{-4}$					39.33	
	90	$12.60 \times 10^{-4}$					42.59	
$2.0 \times 10^{-3}$ mol dm <sup>-3</sup> "CTBA"	45	$5.83 \times 10^{-4}$	17.51	0.997	3.97	-20.83	4.91	0.992
	60	$9.26 \times 10^{-4}$					5.22	
	90	$13.17 \times 10^{-4}$					5.85	

**Table (5): Effect of cationic surfactant concentration on dyeing cotton fabric on the colour strength at different temp.**

Dye	C.I. Acid Red 198			
	Temp.	45°C	60°C	90°C
		Colour strength k/s		
Control		10.76	10.76	10.76
$0.1 \times 10^{-3}$ mol dm <sup>-3</sup> "CTAB"		11.57	12.60	13.70
$2.0 \times 10^{-3}$ mol dm <sup>-3</sup> "CTAB"		12.75	14.01	16.40

**Table (6): Effect of cationic surfactant concentration on dyeing cotton fabric on the colour strength at different temp.**

Dye	C.I. Acid Red 99			
	Temp.	45°C	60°C	90°C
		Colour strength k/s		
Control		7.26	7.26	7.26
$0.1 \times 10^{-3}$ mol dm <sup>-3</sup> "CTAB"		9.82	10.98	11.85
$2.0 \times 10^{-3}$ mol dm <sup>-3</sup> "CTAB"		11.01	12.00	14.43

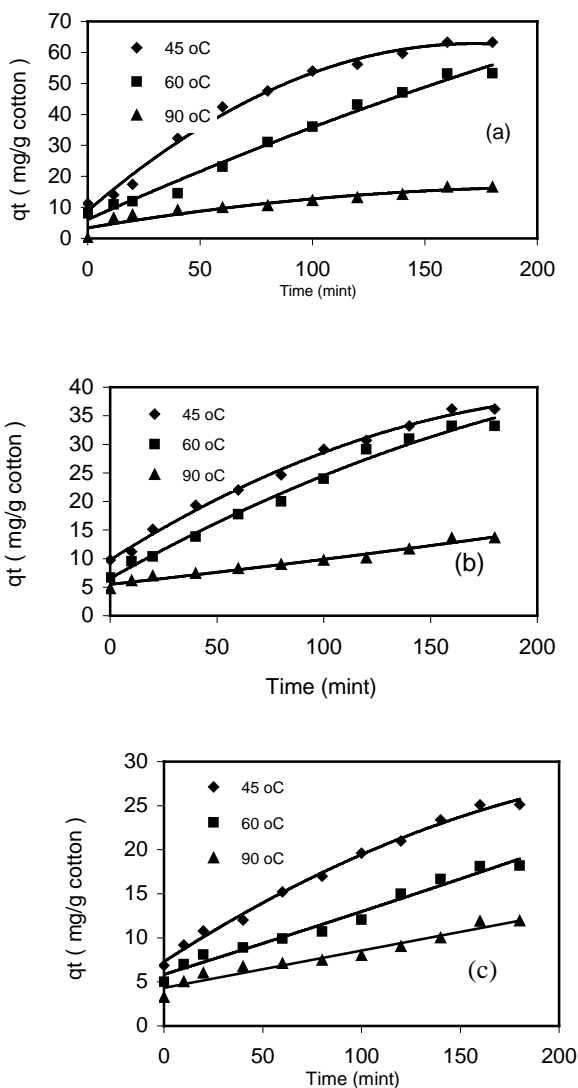


Fig. (2) the effect of contact time and temperature of Red 198 on cotton at initial dye concentration  $0.1 \times 10^{-4} \text{ mol dm}^{-3}$  L:R = 0.5:50 over 0–180 min and pH = 3.00 at (a) aqueous (b)  $0.1 \times 10^{-3} \text{ mol dm}^{-3}$  (c)  $2.0 \times 10^{-3} \text{ mol dm}^{-3}$

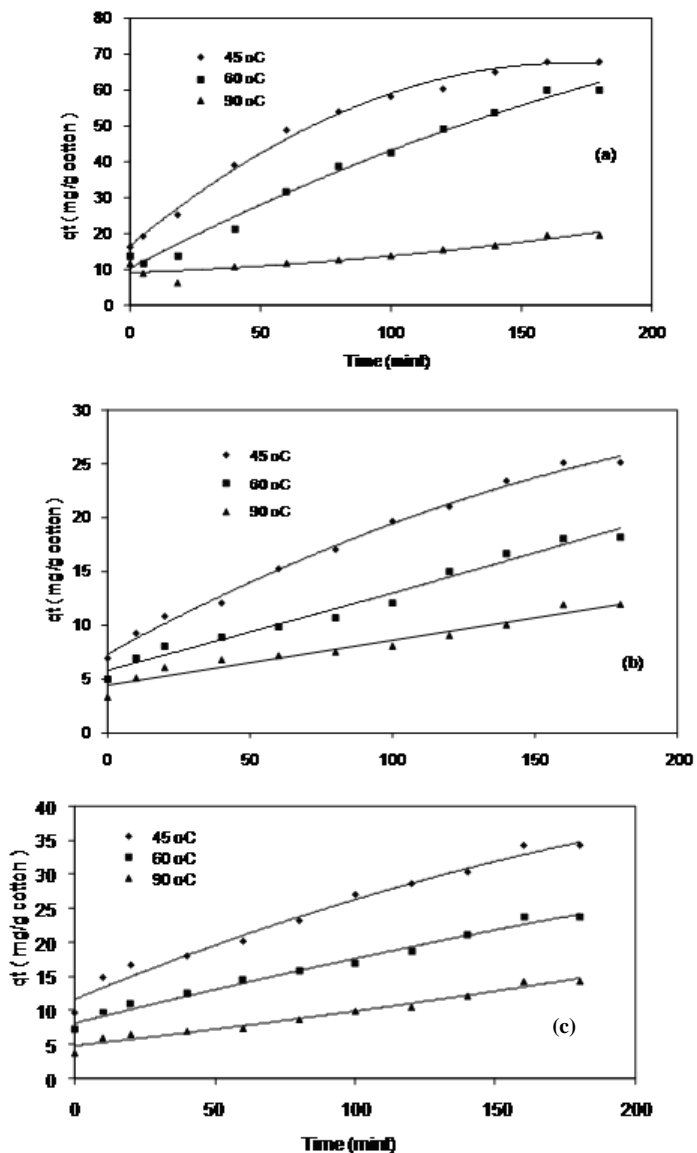


Fig. (3) the effect of contact time and temperature of Red 99 on cotton at initial dye concentration  $0.1 \times 10^{-4} \text{ mol dm}^{-3}$  L:R = 0.5:50 over 0–180 min and pH = 3.00 at (a) aqueous (b)  $0.1 \times 10^{-3} \text{ mol dm}^{-3}$  (c)  $2.0 \times 10^{-3} \text{ mol dm}^{-3}$

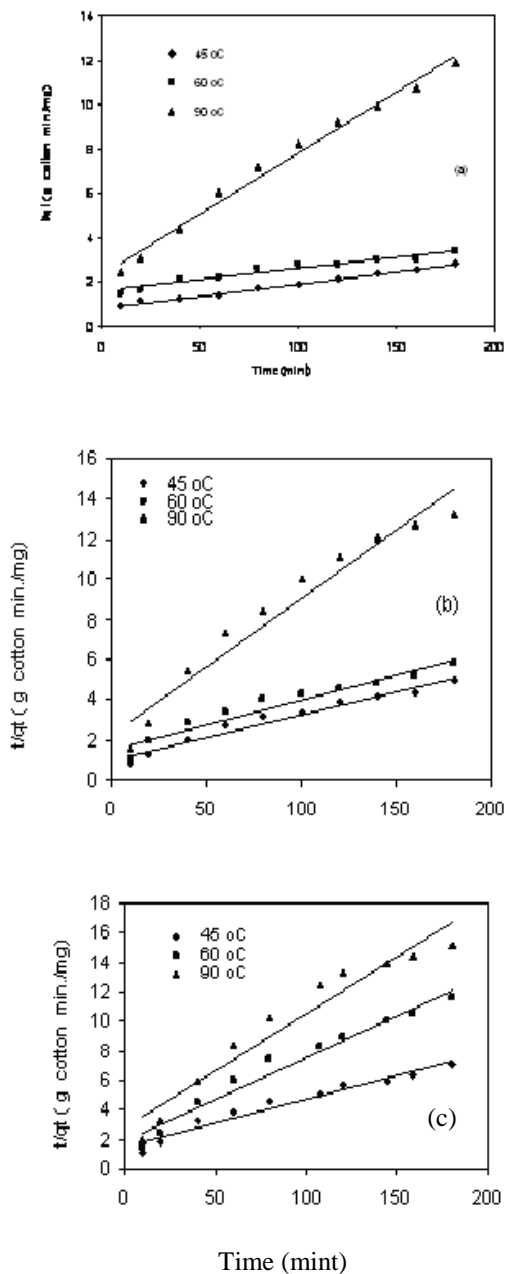


Fig. (4) Plot of pseudo second order equation at different temperature for adsorption Red 198 on cotton at (a) aqueous (b)  $0.1 \times 10^{-3} \text{ mol dm}^{-3}$  (c)  $2.0 \times 10^{-3} \text{ mol dm}^{-3}$

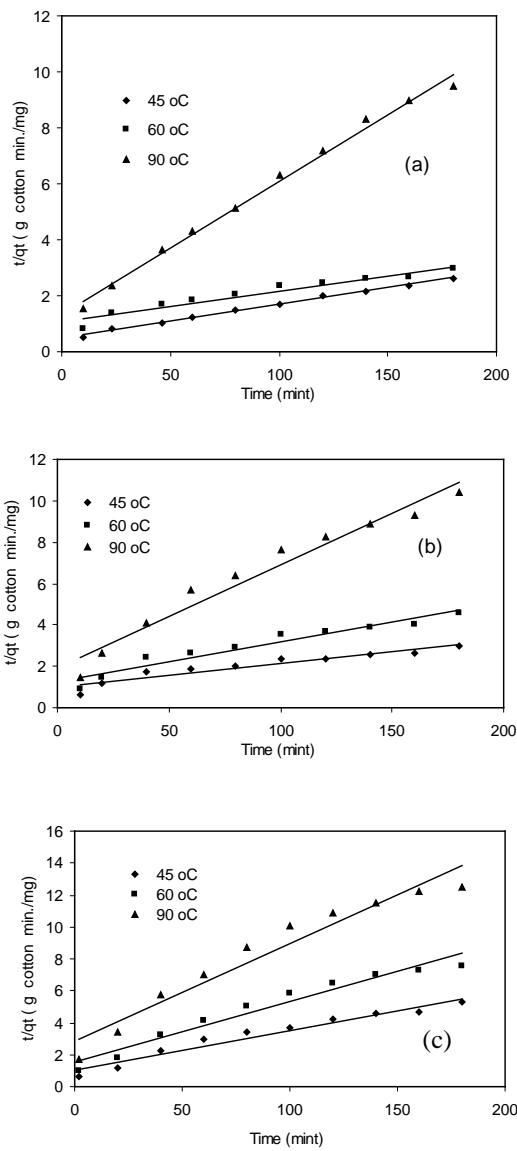


Fig. ( 5 ) Plot of pseudo second order equation at different temperatures for adsorption of Red 99 on cotton at (a) aqueous (b)  $0.1 \times 10^{-3}$  mol dm<sup>-3</sup> (c)  $2.0 \times 10^{-3}$  mol dm<sup>-3</sup>

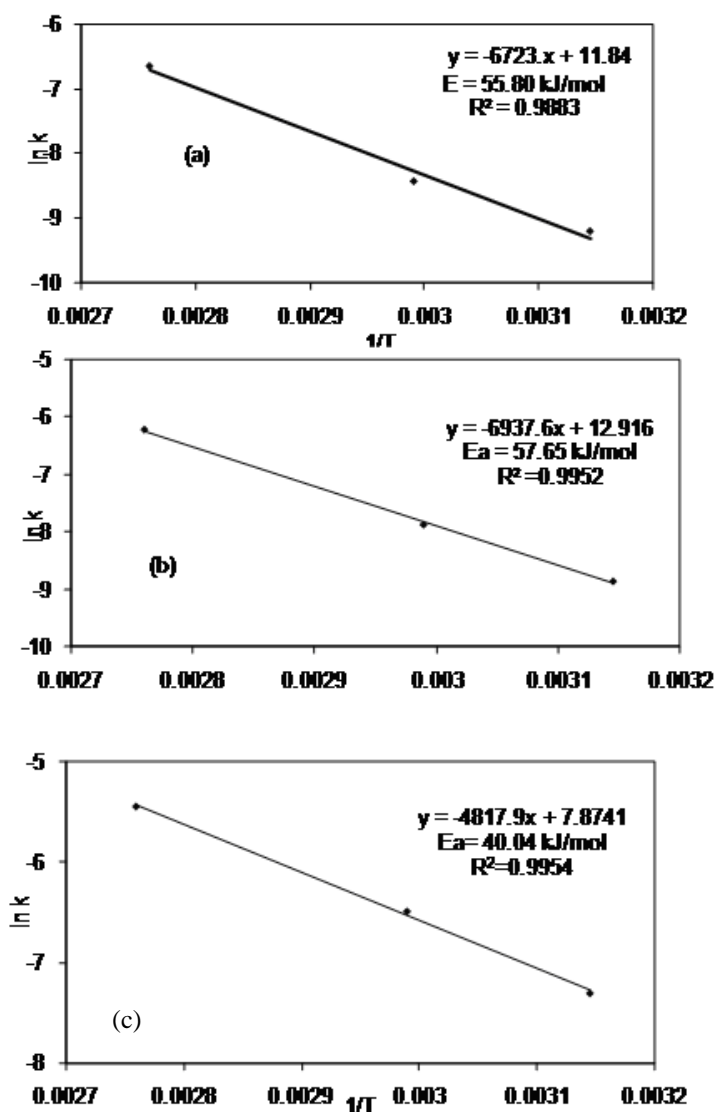


Fig. (6) Arrhenius Plot for adsorption of Red 198 on cotton at (a) aqueous (b)  $0.1 \times 10^{-3} \text{ mol dm}^{-3}$  (c)  $2.0 \times 10^{-3} \text{ mol dm}^{-3}$

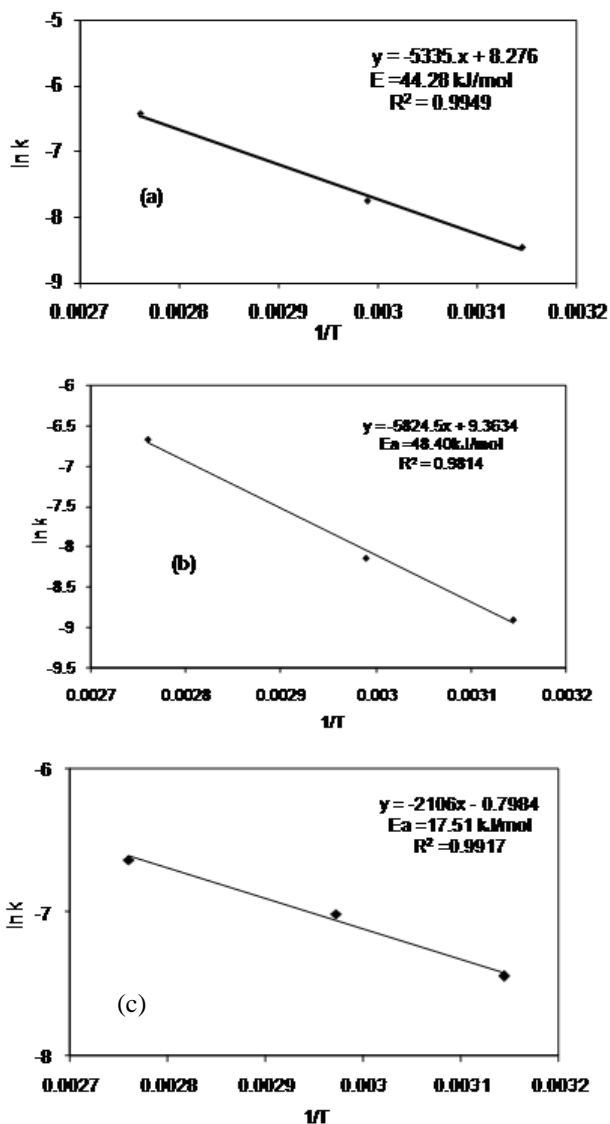


Fig. ( 7 ) Arrhenius Plot for adsorption of Red 99 on cotton at (a) aqueous (b)  $0.1 \times 10^{-3} \text{ mol dm}^{-3}$  (c)  $2.0 \times 10^{-3} \text{ mol dm}^{-3}$



**Conclusion:**

This study investigated the adsorption kinetics of acid dyes on cotton. The initial dye adsorption rates ( $h_t$ ) onto cotton in absence and presence of cationic surfactant before equilibrium time increased at higher dyeing temperatures and at higher concentrations of cationic surfactant, which indicated a kinetically controlled process. The adsorption kinetics of acid dyes on cotton in absence and presence of "CTAB" was found to follow the pseudo second-order kinetic model. The activation energy for the adsorption process on cotton in absence and presence cationic surfactant of C.I. Acid Red 198 55.80, 57.65 and 40.04 kJ/mol but on C.I. Acid Red 99 44.28, 48.40 and 17.51 kJ/mol.

The results also show the  $k/s$  values of dyed cotton samples in the presence of cationic surfactant increase with concentration of "CTAB" and temperatures increase, but on disulphonic less than monosulphonic.

**References**

1. E.R. TROTMAN, *Dyeing and Chemical Technology of Textile Fibres* 3<sup>rd</sup> Ed., Griffin, London, p. 38 (1963).
2. B.J. COLLIER AND P.G. TORTORA, *Understanding textiles*, 6<sup>th</sup> Ed., Macmillan Publishing Co., Inc. (New York), p. 72 (2001).
3. S. RATTANAPHANI, M. CHAIRAT, J.B. BREMNER AND V. RATTANAPHANI, *Dyes and pigments* 72 (2007) 88-96.
4. KAMEL MM. YOUSEF BM. SHOKRY GM. *Dyeing of cationized cotton part II: direct dyes. American Dyestuff Reporter* (1999); 88(6): 28-31.
5. CAI Y. DAVID SK, PAILTHORPE MT: *Dyeing of jute and jute/cotton blend fabrics with 2:1 pre-metallised dyes. Dyes and pigments* (2000); 45: 161-8.
6. KIN T.K. YOON S.H. SON Y.A. *Effect of reactive anionic agent on dyeing of cellulosic fibers with a berberine colorant. Dyes and pigments* (2004); 60: 121-7.
7. BURKINSHAW SM. MIGNANELLI M. FROEHLING PE, BIDE MJ. *The use of dendrimers to modify the dyeing behaviour of reactive dyes on cotton. Dyes and pigments* (2000); 47:259-67.
8. JANHOM S. GRITHS P. WATANESK R. WATANESK, S. *Enhancement of lac dye adsorption on cotton fibers by poly ethyleneimine. Dyes and pigments* (2004);63: 231-7.
9. A. R. T. BAGHA, H. BAKRAMI, B. HOVASSAGH, M. ARAMI, AND F.M. MENDER *Dyes and Pigments* 72 (2007) 331-338.

10. KARTAL C, AKBASX H. *Dyes and Pigments* (2005); 65: 191.
11. ULLAMAAN'S encyclopedia of industrial chemistry. 6<sup>th</sup> ed., vol. 36. Wiley-VCH: (2003).
12. GOKTURK S, TUNCAY M. *Spectrochimica Acta*, part A (2003); 59: 1857.
13. SIMONCIC B, KOVAC F. *Dyes and Pigments* (1999); 40: 1.
14. Forte-Tavcer Petra. *Dyes and Pigments* (2004); 63: 181.
15. HUNG J.B, ZHU B.Y., ZHAO G.X, ZHANG Z.Y. *Langmuir* (1997); 13: 5759.
16. SIMONCIC B, SPAN J. *Dyes and Pigments* (1998); 36:1.
17. ÖZLEM T., HACER T., ZÜMRIYE A. *Journal of Hazardous Materials*, 163 (2009) 187–198
18. BUWALDA RT, JONKER JM, Engberts JBFN. *Langmuir* (1999); 15: 1083.
19. BUWALDA RT, ENGBERTS JBFN. *Langmuir* (2001); 17: 1054.
20. DOGAN M. ALKAN M. Adsorption kinetics of methyl violet onto perlite. *Chemosphere* (2003); 50:517-28.
21. CHEN J.C, CHEN C.C. Crosslinking of sulfonated cotton cellulose part II: dyeing kinetics of a basic dye on crosslinking fabrics from a finite bath. *Textile Research Journal* (2000); 70(4): 311-4.
22. HO YS, MCKAY G. Sorption of dye from aqueous solution by peat. *Chemical engineering Journal* (1996); 70: 115-24.
23. SUN Q, YANG L. The adsorption of basic dyes from aqueous solution on modified peat-resin particles, *Water Research* (2003); 37: 1535-44.
24. CHIOU M.S. HO P.Y. LI H.Y. Adsorption of anionic dyes in acid solutions using chemically cross-linked chitosan beads. *Dyes and pigments* (2004); 60:69-84.
25. CHIOU M.S. Li J.Y. Equilibrium and kinetic modeling of adsorption of reactive dye on cross-linked chitosan bead. *Journal of Hazardous Materials* (2002); B93: 233-48.
26. CHIOU M.S. Li H.Y. Adsorption behaviour of reactive dye in aqueous solution on chemical cross-linked chitosan beads. *Chemosphere* (2003); 50:1095-105.
27. HO YS. CHIANG CC. Sorption studies of acid dye by mixed sorbents. *Adsorption* (2001); 7:139-47.
28. BRUCE RL. BROADWOOD NV. Kinetics of wool dyeing with acid dyes *Textile Research Journal* (2000); 70(6): 525-31.
29. Montra Chairat, Saowanee Rattanaphani, John B. Bremner, Vichitr Rattanaphani. Adsorption kinetic study of lac dyeing on cotton. *Dyes and Pigments* (2008) ,76: 435-439
30. Y. CAI, M.T. Pailthorpe and S.K. David, *Text. Res. J.*, 69(6), p. 440 (1999).