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## Adsorption Behavior of Chrysoidine Dye on Activated Charcoal and Its Regeneration Characteristics by Using Different Surfactants

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### ABSTRACT

Experimental investigations were carried out to adsorb red colored chrysoidine dye from an aqueous medium by using activated charcoal (AC) as an adsorbent. The effects of adsorbent dose, initial dye concentration, contact time, pH, and temperature were studied for the adsorption of chrysoidine under stirred conditions and batch wise. Standard adsorption isotherms were considered to fit the experimental equilibrium data. It was found that the adsorption of chrysoidine on AC follows the Freundlich adsorption isotherm. The rate of adsorption was described by both first- and pseudosecond-order kinetic models. Experimental investigations also were carried out for the regeneration of spent carbon by

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applying surfactant enhanced carbon regeneration (SECR) technique by using both cationic and anionic surfactant. An empirical kinetic model for regeneration of adsorbent was presented.

**Key Words:** Chrysoidine; Activated charcoal; Adsorption isotherm; Carbon regeneration; Cationic surfactant; Anionic surfactant.

## INTRODUCTION

Various types of dyes are manufactured for printing and dyeing industries from coal-tar-based hydrocarbons. Color removal from effluent is one of the most difficult requirements faced by the textile finishing, dye manufacturing, and pulp and paper industries. These industries are major water consumers and, therefore, cause water pollution. Most of these dyes are harmful when in contact with living tissues for a long time. The discharge of these into the river stream without proper treatment causes irreparable damage to the crops and living beings, both aquatic and terrestrial. Dyes are classified into three broad categories: (a) anionic—direct, acid, and reactive dyes; (b) cationic—all basic dyes; and (c) nonionic—dispersed dyes.<sup>[1]</sup> Chrysoidine is an example of a basic azo dye<sup>[2]</sup> and is built-up from a group of atoms called a chromophore, which is largely responsible for its color. Chromophores contain unsaturated groups such as C=O and —N=N—, which are often a part of an extended delocalized electron system involving arene rings.

The effluents containing such types of dyes are highly colored and result in major environmental problems. So, these colored wastes need to be treated before disposal. Many investigators have studied different techniques for removal of colored dye from wastewater, e.g., chemical coagulation/flocculation;<sup>[3]</sup> different advance oxidation processes;<sup>[4–6]</sup> ozonations;<sup>[7–9]</sup> nanofiltration (NF);<sup>[10]</sup> and adsorption on to (i) sludge of wastewater treatment plant,<sup>[11]</sup> (ii) different bentonites,<sup>[12,13]</sup> (iii) different types of activated carbon,<sup>[14,15]</sup> (iv) fly ash,<sup>[16]</sup> etc. Ultrafiltration and NF can be used for complete removal of all classes of dye, but care is needed to avoid membrane clogging, that decreases the flux. Due to low biodegradability of dyes, a conventional biological wastewater treatment process is not very efficient in treating a dye wastewater.<sup>[17]</sup> Physical or chemical treatment processes generally are used to treat it.<sup>[18]</sup> Previous investigators have studied the adsorption of dyestuffs by using a variety of natural adsorbents, but, as yet, these adsorbents are impractical for the effluent of modern textile industries. Activated charcoal (AC) can effectively be used to remove color, although it is ineffective against dispersed and vat dye.<sup>[19]</sup> In the present study, experiments were performed for the removal of chrysoidine

by using adsorption techniques. AC was selected as an adsorbent and was added to the solution containing dye. The effect of adsorbent dose, temperature, pH of dye solution, and initial dye concentration with time of adsorption was studied under stirred conditions. To make the AC more economical, it is necessary to regenerate the spent charcoal for further use. Surfactant-based charcoal regeneration technique was adopted in the present work. Regeneration of AC was done by changing pH and by using both cationic and anionic surfactants. An empirical kinetic model for desorption of dyes also is presented.

## EXPERIMENTAL

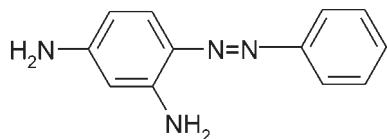
### Material

The dye used in this study is chrysoidine R (purity: 98.5%, FW: 262.74,  $\lambda_{\text{max}}$ : 457 nm), supplied by Loba Chemie Pvt Ltd, Mumbai, Maharashtra, India. The structure of the dye is shown in Fig. 1.<sup>[20]</sup> Hydrochloric acid and sodium hydroxide solutions were used to adjust the pH of dye solution. Adsorbent used is commercial activated charcoal (CAC) supplied by S.D. Fine Chem. Ltd, Mumbai, Maharashtra, India. The characterization of the AC used is presented in Table 1. Before each experiment, the AC is repeatedly washed with distilled water to remove the fine particles. For surfactant-based regeneration of AC, sodium dodecyl sulphate (SDS) was used as anionic surfactants and hexadecyl (cetyl) pyridinium chloride (CPC), and tetradecyl trimethyl ammonium bromide (TTAB) was taken as a cationic surfactant. All surfactants were supplied by SISCO Research Lab. Pvt., Ltd., Mumbai, Maharashtra, India.

### Methods

#### Adsorption Study

In the adsorption experiments, dye solution was prepared by dissolving an accurately weighed amount of dye in distilled water at a concentration of 100,



**Figure 1.** Structure of chrysoidine.

**Table 1.** Characterization of CAC.

Sl. no.	Property	CAC
1	Particle size (mesh)	300
2	Methylene blue adsorption (0.15% solution) (mL/0.1 g)	18
3	pH	6.0–7.5
4	Moisture (at 105°C for 2 hr)	5.0%
5	Ash	2.5%
6	Acid soluble	2.5%
7	Water soluble	1.5%
8	Surface area (m <sup>2</sup> /g)	345

200, 250 300, 400, and 700 mg/L. The pH of the solution was adjusted to 2.6, 4.4, 8, and 11.1 to observe the effect of pH on dye adsorption. Hydrochloric acid and sodium hydroxide were used to adjust pH and were measured by a pH meter supplied by Toshniwal Instruments Ltd. (Ajmer, Rajasthan, India). Each experiment was conducted at a constant temperature by placing the batch absorber in a constant temperature bath (supplied by Testing Instruments Manufacturing Company Ltd, Kolkata, West Bengal, India) and stirred with the help of a stirrer (Type-RQ-123, Remi Motors Ltd., Rochester, New York, India) at 450 rpm. All the experiments were conducted at different temperatures (30°C, 50°C, and 70°C). The concentration of dye was determined by a spectrophotometer (Thermo Spectronic, USA; model: GENESYS 2). Dye solution initially was calibrated for different concentrations in terms of absorbance units, which were recorded at the wavelength ( $\lambda_{\text{max}}$ : 457 nm) at which maximum absorption takes place.

#### Desorption Study

To observe the amount of desorption of dye from AC, the effects of pH and the concentrations of SDS, TTAB, and CPC were used. Before each desorption study, a known amount (mg) of chrysoidine was adsorbed on to a known amount (1.0 g) of AC. This was done by keeping 1.0 g of AC and 250 mL of 3500 mg/L chrysoidine dye in a stoppered glass bottle and agitating by a shaker for 18 days at room temperature. By measuring the concentration of dye solution before and after adsorption, the amount of dye adsorbed per gram of AC was calculated by mass balance. After filtration with Whatman filter paper, the charcoal was washed gently with distilled water to remove the unabsorbed dye and was collected. Several such samples were prepared for the desorption study. The spent charcoal (1.0 g)

was mixed with 250 mL of distilled water, was adjusted with different surfactant concentrations and pH, and was stirred, as in the case of the adsorption study. The amount of desorbed dye was estimated from the mass balance, as in the case of the adsorption study.

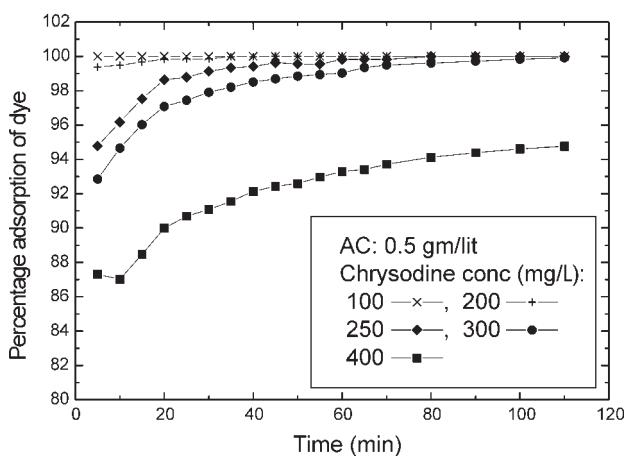
## RESULTS AND DISCUSSION

This section is divided into two parts. In the first part, the effects of various operating conditions on the extent of adsorption, different isotherms, and the kinetics of adsorption are discussed. The effect of pH and the performance of different surfactants on desorption of chrysoidine are addressed in the second part.

### Adsorption Studies

#### Effect of Agitation Time and Initial Dye Concentration

The effects of agitation time and initial dye concentration on the percentage adsorption of dye by AC at room temperature are shown in Fig. 2. The percentage adsorption increased with agitation time for the different initial dye concentrations and attained equilibrium after some time. For all the



**Figure 2.** Effect of agitation time and concentration of chrysoidine on percentage of adsorption.

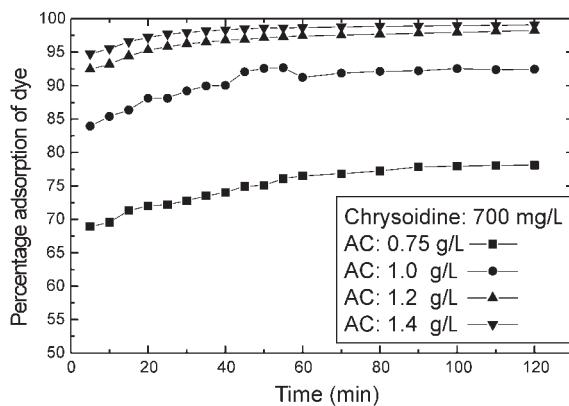
initial dye concentration, the percentage adsorption was found to be constant beyond 80 min. This indicates that the equilibrium was attained at about 80 min for the initial dye concentrations in the range of 100–400 mg/L. It also is clear that the extent of adsorption depends on the initial dye concentration. For dye solution of a lower initial concentration (up to 100 mg/L), the adsorption is very fast, and 100% of adsorption is achieved quickly. The percentage dye adsorption at equilibrium decreased from 100% to about 94% as the dye concentration increased from 100 to 400 mg/L.

#### Effect of Agitation Time and Adsorbent Dose on Percentage Adsorption

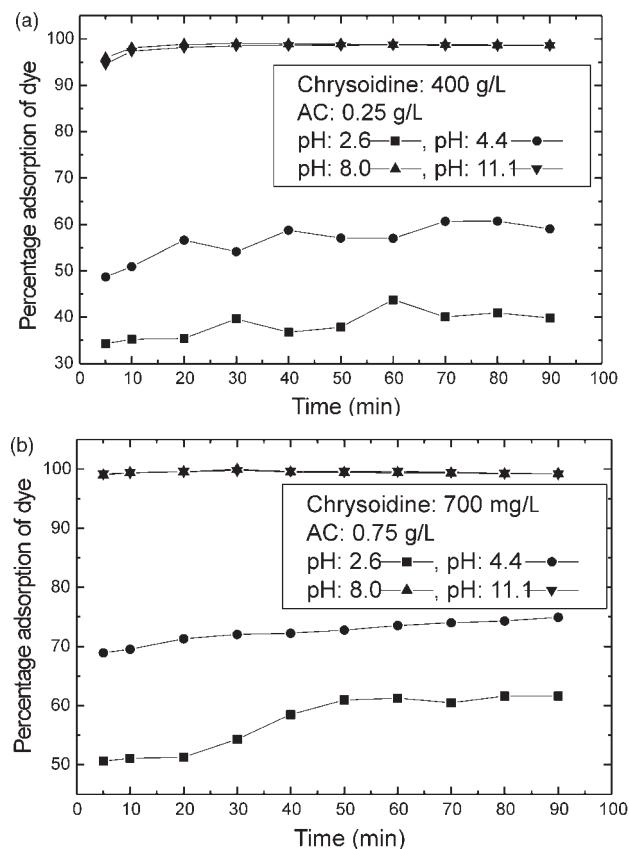
The effect of adsorbent dose on dye adsorption is shown in Fig. 3 for the initial dye concentrations of 700 mg/L. It is clear from the figure that the percentage adsorption increased with time up to 80 min and also with adsorbent dose. Percentage adsorption increased from about 77% to 99% when adsorbent dose increased from 0.75 to 1.40 g/L. This increase in percentage adsorption may be due to the fact that the number of available sites for adsorption increases with adsorbent dose.

#### Effect of pH

The percentage of dye adsorption at different pH is shown in Fig. 4(a) and (b) for the initial dye concentrations of 400 and 700 mg/L, respectively. The color of chrysoidine dye in aqueous medium is red ( $\lambda_{\text{max}}$ : 457 nm) in acidic pH but changes its color from red to yellow ( $\lambda_{\text{max}}$ : 442 nm) in basic pH. This is due to the presence of a chromophore in the structure of chrysoidine.



**Figure 3.** Effect of agitation time and adsorbent dose on percentage adsorption.



**Figure 4.** Effect of initial pH on percentage of adsorption for (a) 400 mg/L of feed dye and (b) 700 mg/L of feed dye.

A chromophore is any structural feature (in this case,  $-\text{N}=\text{N}-$ ) that produces light absorption in the ultraviolet region or color in the visible region. An auxochrome is any group (in this case  $-\text{NH}_2$ ), which, although not a chromophore, brings about a red shift when attached to a chromophore. Thus, the combination of chromophore and auxochrome behaves as a new chromophore. A bathochromic effect (red shift) and hypsochromic effect (blue shift) are the shifting of the absorption band to the longer and shorter wavelengths, respectively.<sup>[21]</sup> Therefore, due to a blue shift, chrysoidine changes its color in basic pH. On the other hand, most of the AC contains some oxygen complexes on the surface, i.e., (a) strongly carboxylic groups; (b) carbonyl groups; and (c) phenolic groups.<sup>[22]</sup> These groups are nucleophilic

in nature and potential adsorbing sites. In acidic pH, these active sites get blocked by a hydrogen ion, leading to reduction in adsorption. Hence, adsorption of chrysoidine on AC is less in acidic pH. It was found [Fig. 4(a) and (b)] that at pH 2.6, adsorption was nearly 62% and 40% for the feed dye concentrations of 400 and 700 mg/L, respectively, at the end of the experiment. The percentage adsorption decreased from about 98% to 40% for the feed dye concentration of 400 mg/L and about 99% to 62% for the feed dye concentration of 700 mg/L, when pH decreased from 11.1 to 2.6. From Fig. 4(a) and (b), it may be observed that the adsorption of this dye is more at the basic pH.

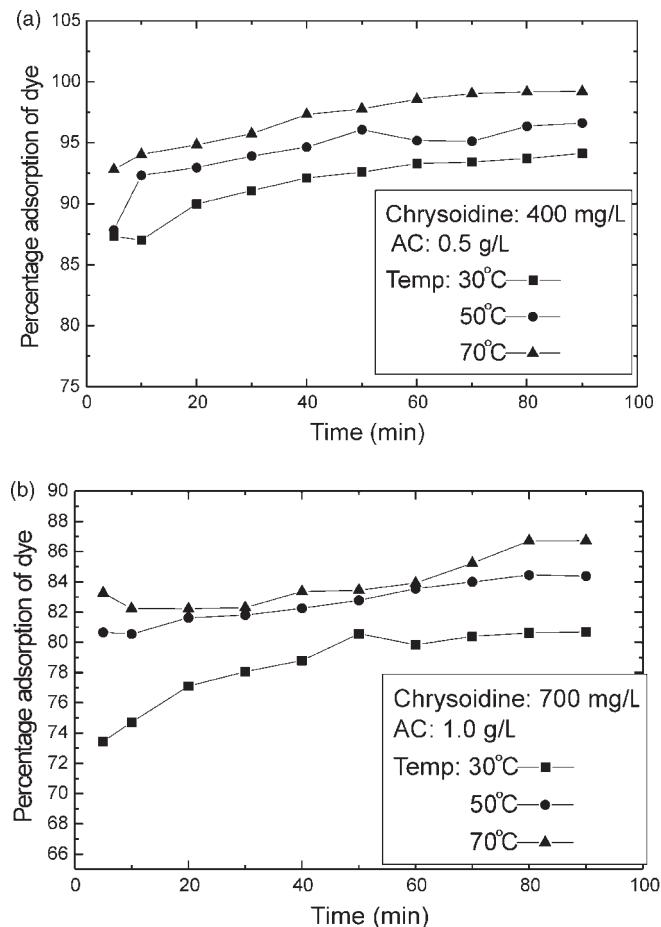
#### Effect of Temperature

Adsorption experiments were carried out for an aqueous solution of dye for two different concentrations (400 and 700 mg/L) and at three different temperatures (30°C, 50°C, and 70°C) and at a pH of 4.4. It was observed [Fig. 5(a) and (b)] that the adsorption capacity increased significantly with temperature. The percentage adsorption increased from about 94% to 99% for the feed dye concentration of 400 mg/L and about 80% to 87% for the feed dye concentration of 700 mg/L, at the end of experiment, when temperature was raised from 30°C to 70°C. The thermodynamic parameters  $\Delta G^0$ ,  $\Delta S^0$ , and  $\Delta H^0$  for this adsorption process was determined by using the following equations:<sup>[23]</sup>

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (1)$$

$$\log\left(\frac{q_e}{C_e}\right) = \frac{\Delta S^0}{2.303R} + \frac{-\Delta H^0}{2.303RT} \quad (2)$$

where  $q_e$  is the amount of dye adsorbed per unit mass of AC (mg/g),  $C_e$  is equilibrium concentration (mg/L), and  $T$  is temperature (K),  $q_e/C_e$  is called the adsorption affinity. Here, it may be noted that the experimental data considered for the calculation of the thermodynamic parameters, namely,  $\Delta G^0$ ,  $\Delta H^0$ , and  $\Delta S^0$  are in the linear range ( $q_e$  varies from 2.5 to 3.0 mmol/g and  $C_e$  varies from 0.012 to 0.2 mmol/L, as shown in Table 2; refer to Fig. 6). The values of Gibbs free energy ( $\Delta G^0$ ) were calculated by knowing the enthalpy of adsorption ( $\Delta H^0$ ) and the entropy of adsorption ( $\Delta S^0$ ).  $\Delta S^0$  and  $\Delta H^0$  are obtained from a plot of  $\log(q_e/C_e)$  vs.  $1/T$ , from Eq. (2). Once these two parameters are obtained,  $\Delta G^0$  was determined from Eq. (1). The values of  $\Delta G^0$ ,  $\Delta H^0$ , and  $\Delta S^0$  for different dye concentrations are listed in Table 3. The positive values of  $\Delta H^0$  show that the adsorption is endothermic in nature. The endothermic nature also is indicated by the increase in the amount of adsorption with temperature [Fig. 5(a) and (b)]. The adsorption is associated with an increase in entropy of 176.18 J/mol K (mean value),



**Figure 5.** Effect of temperature on adsorption capacity for (a) 400 mg/L of feed dye and (b) 700 mg/L of feed dye.

which shows that the adsorbed dye molecules on the AC surface are organized in a more random fashion compared with those in the aqueous phase. Similar observations are reported in the literature.<sup>[24,25]</sup> The higher heat of adsorption obtained in this work indicates that chemisorption rather than the physical adsorption is prevalent in this case.<sup>[26]</sup> It is reported in Ref.<sup>[26]</sup> that a value of  $\Delta H^0$  about 40 kJ/mol signifies chemisorption rather than physical adsorption. The negative values of  $\Delta G^0$  indicate that the adsorption process is spontaneous.

**Table 2.** Equilibrium data used for the calculation of thermodynamic parameters.

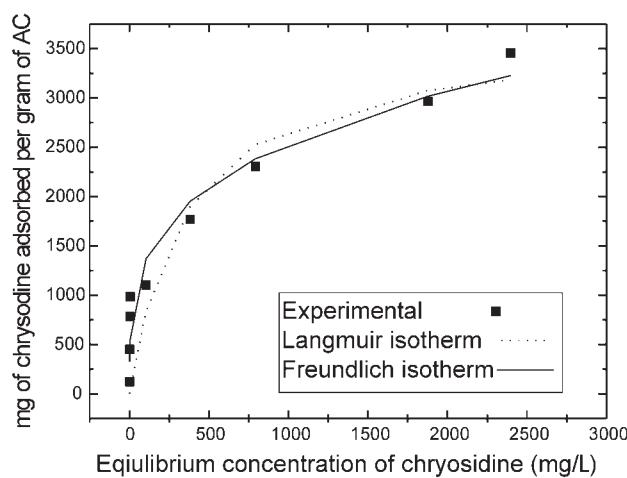
Adsorbent dose (g/L)	Feed dye (mg/L)	Temperature (°C)	$q_e$ (mg/g)	$C_e$ (mg/L)
0.5	400	30	753.0	23.5
		50	773.0	13.5
		70	793.5	3.2
1.0	700	30	645.9	54.4
		50	675.2	24.9
		70	693.9	6.2

### Adsorption Isotherms

To determine the adsorption capacity of AC, an equilibrium study was performed to analyze the experimental data by using two well-known models (viz. Langmuir and Freundlich) at a temperature of 30°C and at a pH of 4.4.

#### Langmuir Isotherm

Langmuir adsorption isotherm is applicable to explain the equilibrium data for many adsorption processes. The basic assumption of this process is the formation of monolayer of adsorbate on the outer surface of adsorbent,

**Figure 6.** Adsorption isotherms of chrysoidine on AC.

**Table 3.** Thermodynamic parameters for adsorption of chrysoidine in AC at different temperatures and dye concentrations.

Adsorbent (g/L)	Dye (mg/L)	$\Delta H^0$ (kJ/mol)	$\Delta S^0$ (J/mol K)	$-\Delta G^0$ (kJ/mol) at temperature (K)		
				303	323	343
0.5	400	43.61	171.42	8.32	11.76	15.19
1.0	700	48.88	180.93	5.94	9.56	13.18
Mean		46.25	176.18	7.13	10.66	14.19

and after that no further adsorption takes place. The expression of the Langmuir model is given as follows:<sup>[27]</sup>

$$q_e = \frac{QbC_e}{1 + bC_e} \quad (3)$$

A linear form of this expression is

$$\frac{1}{q_e} = \frac{1}{Q} + \frac{1}{Qb} \cdot \frac{1}{C_e} \quad (4)$$

where  $q_e$  is the amount of adsorbate adsorbed per unit weight of adsorbent (mg/g),  $C_e$  is the equilibrium concentration of adsorbate (mg/L). The constant  $Q$  and  $b$  are the Langmuir constants and are the significance of adsorption capacity (mg/g) and energy of adsorption (l/mg), respectively. Values of  $Q$  and  $b$  are calculated from the intercept and slope of the plot  $1/q_e$  vs.  $1/C_e$ .

#### Freundlich Isotherm

This model is an indicative of the extent of heterogeneity of the surface of adsorbent and is given as follows:

$$q_e = K_F C_e^{1/n} \quad (5)$$

where  $K_F$  and  $n$  are Freundlich constants. A linear form of the Freundlich expression is as follows:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (6)$$

where  $q_e$  is the amount of adsorbate adsorbed per unit weight of adsorbent (mg/g),  $C_e$  is the equilibrium concentration of adsorbate (mg/L). The constants  $K_F$  and  $n$  are the Freundlich constants and are the significance of adsorption capacity and intensity of adsorption, respectively. Values of  $K_F$  and  $n$  are

calculated from the intercept and slope of the plot  $\log q_e$  vs.  $\log C_e$ . Adsorption isotherms of chrysoidine on AC at 30°C and at a pH of 4.4 are shown in Fig. 6. The coefficients of these two isotherm models are shown in Table 4. These data provide information on the amount of AC required to adsorb a particular mass of chrysoidine under the specified system conditions. Correlation coefficients are calculated by fitting the experimental adsorption equilibrium data for a chrysoidine–AC system by using both Langmuir and Freundlich adsorption isotherm and are shown in Table 4. It was found from the correlation coefficients ( $r^2$ ) that adsorption isotherm for the present chrysoidine–AC system is explained better by the Freundlich equation.

#### Adsorption Kinetics

The kinetics of adsorption of chrysoidine dye on AC is described by using both first- and pseudosecond-order models. The Lagergren's equation for first-order kinetics is given as follows:

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

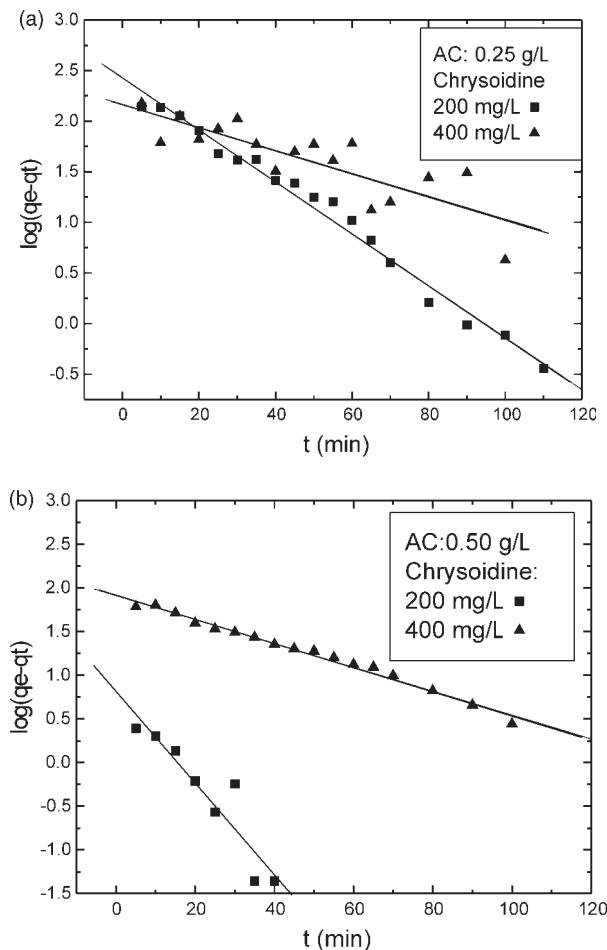
The expression for pseudosecond-order rate equation is given as<sup>[28]</sup>

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

where  $q_e$  and  $q_t$  are the amount of chrysoidine adsorbed (mg/g) at equilibrium and at any time  $t$ ;  $k_1$  is the rate constant ( $\text{sec}^{-1}$ ). The plot of  $\log(q_e - q_t)$  vs.  $t$  gives a straight line for first-order adsorption kinetics and is shown in Fig. 7(a) and (b) for the initial dye concentrations of 200 and 400 mg/L by using 0.25 and 0.5 g/L of AC, respectively. The value of first-order rate constants for the above cases,  $k_1$ , is obtained from the slope of the curve. Figure 8(a) and (b) shows  $(t/q_t)$  vs.  $t$  plot of the pseudosecond-order kinetics for the initial dye concentrations of 200 and 400 mg/L by using 0.25 and 0.5 g/L of AC, respectively. In Eq. (8),  $k_2$  (g/mg min) is the rate constant for the pseudosecond-order

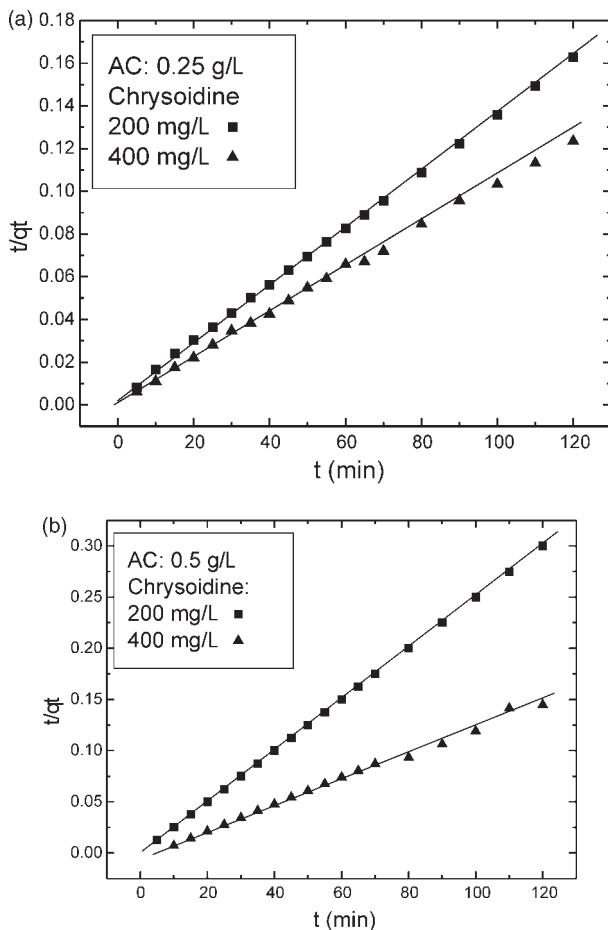
**Table 4.** Langmuir and Freundlich isotherm constants for adsorption of chrysoidine on AC.

Langmuir constant			Freundlich constant		
$Q$ (mg/g)	$b$ (L/mg)	$r^2$	$K_F$ [mg/g (L/mg) $^{1/n}$ ]	$n$	$r^2$
3652.0	$2.84 \times 10^{-3}$	0.941	384.24	3.657	0.968



**Figure 7.** Plot of the first-order kinetic model for adsorption of chrysoidine on AC (a) (0.25 g/L) and (b) 0.5 g/L. Feed chrysoidine: 200 and 400 mg/L.

adsorption kinetics. The slope of the plot ( $t/q_t$ ) vs.  $t$  gives the value of  $q_e$ , and from the intercept,  $k_2$  can be calculated. The correlation coefficients for fitting the data, both in the first- and pseudosecond-order kinetics are presented in Table 5. It may be observed from the table that the adsorption of chrysoidine on AC fits pseudosecond-order kinetics better than the first order, as can be seen from the better fit of  $q_e$  values by using pseudosecond-order kinetics. The correlation coefficients in the fitting of the second-order kinetics are more than 0.99.



**Figure 8.** Plot of the pseudosecond-order kinetic model for adsorption of chrysoidine on AC (a) 0.25 g/L and (b) 0.5 g/L. Feed chrysoidine: 200 and 400 mg/L.

### Desorption Studies

A desorption study was performed to regenerate the activity of AC. More desorption of adsorbate signifies better regeneration. In this work, surfactant enhanced carbon regeneration (SECR) technique was used to dislodge the adsorbed dye from AC to regenerate it for effective reuse. In SECR, surfactant solution was added to the spent carbon.<sup>[29]</sup> The adsorbed dye desorbs and is solubilized into micelles of surfactant present in solution.

**Table 5.** Comparison of the first- and second-order adsorption rate constants, calculated and experimental  $q_e$  value for chrysoidine on AC.

Feed concentration $c_0$ (mg/L)	$q_{e,exp}$ (mg/g)	First-order		Pseudosecond-order	
		$q_{e,fitted}$ (mg/g)	$k_1$ (1/min)	$r^2$	$k_2$ (g/mg min)
Feed AC: 0.25 g/L					
200	737.22	710.4	0.30	0.422	751.8
250	831.92	770.2	0.46	0.202	833.3
300	907.52	890.6	0.71	0.210	917.4
400	972.00	921.9	0.44	0.395	980.4
Feed AC: 0.50 g/L					
200	400.00	399.4	1.08	0.454	400.0
250	500.00	495.6	0.62	0.576	500.0
300	599.52	589.9	0.55	0.547	602.4
400	759.64	738.2	0.56	0.255	787.4

Since the surfactants, considered herein, are highly soluble in water, the amount of surfactant left on the adsorbent surface after repeated washing would be insignificant and hence, the effect of sorption of surfactants on the AC is negligible.

### Desorption Kinetics

It is proposed that the desorption rate at any instant would be proportional to the driving force, i.e., the difference between the initial (at  $t = 0$ ) amount of the adsorbed dye and the dye concentration in the solution at any time  $t$ . The dye concentration in the solution, in turn, is related to the amount of the dye still remaining adsorbed through a mass balance. This is mathematically represented by the following equation:

$$\frac{dq}{dt} = \alpha(q_0 - kq) \quad (9)$$

Where  $\alpha$  and  $k$  are the constants ( $k \neq 1.0$ ),  $q_0$  and  $q$  are the amount of adsorbed dye present per gram of AC at time  $t = 0$  and at any time  $t = t$ , respectively. The expression for the adsorbed dye remaining in the adsorbent at any time  $t$  can be obtained by integrating Eq. (9) as follows:

$$q = \frac{q_0}{k} [1 - (1 - k)e^{-k\alpha t}] \quad (10)$$

The percentage of the dye desorption can be defined as:

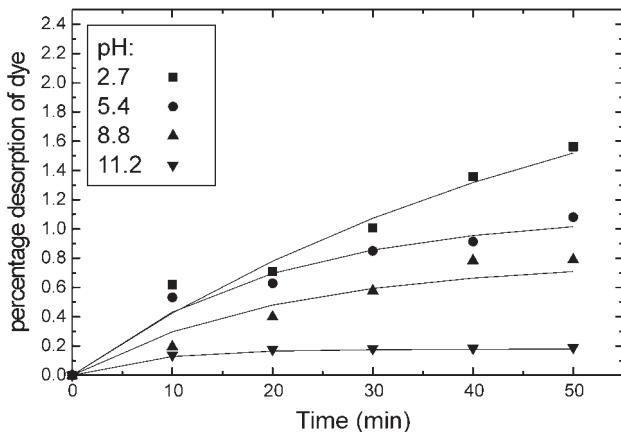
$$D = \frac{q_0 - q}{q_0} \times 100$$

By using Eq. (10), the expression of the percentage desorption at any time is expressed as:

$$D = 100 \times \left( \frac{k - 1}{k} \right) [1 - e^{-k\alpha t}] \quad (11)$$

### Effect of pH

The effect of pH, without adding any surfactants on the percent desorption of dye, also was studied and is shown in Fig. 9. At lower pH, active sites are protonated and adsorption of chrysoidine is restricted with active site of charcoal as discussed in the earlier section, "Effect of pH" (for adsorption studies). Thus, with the decrease of pH, desorption increases. From Fig. 9, it is found that after 50 min of operation, desorption of dye increases from about 0.18% to 1.6% when pH decreases from 11.2 to 2.7. As discussed earlier,

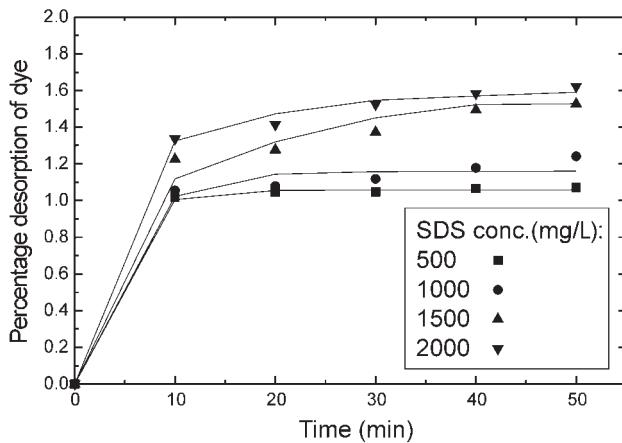


**Figure 9.** Effect of pH on desorption of chrysoidine from spent charcoal. Solid are model fitted results, and the symbols are the experimental data.

chrysoidine changes its original red color when the pH of the solution changes from acidic to basic. Therefore, it is appropriate to desorb chrysoidine by setting the acidic pH (to maintain its color). The desorption kinetic is described by Eq. (11). For each operating pH, the constants  $k$  and  $\alpha$  are estimated by using a curve fitting the corresponding experimental data. The value of  $k$  was found to be 1.02, and those for  $\alpha$  varied in a narrow range from 0.02 to 0.05 for various pH values. Here, it may be noted that the continuous curves in Fig. 9 are the fitting obtained from Eq. (11), and the symbols are the experimental data. The  $r^2$ -values of all the fits in Fig. 9 are more than 0.99.

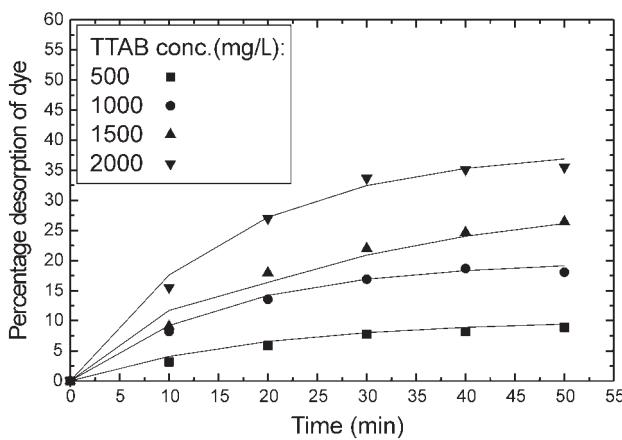
#### Effect of Surfactant Concentration

Figures 10–12 show the variations of percent desorption of dyes when using SDS, TTAB, and CPC, respectively, at various concentrations higher than the corresponding critical micellar concentrations (CMC). The CMC of SDS, CPC, and TTAB are 2.33, 0.322, and 1.345 g/L,<sup>[30]</sup> respectively. Desorption increases with an increase in surfactant concentration and also with operating time for all the cases. In the case of SDS (anionic surfactant), desorption is only about 1.7%, whereas, for TTAB and CPC, desorption increases up to about 35% and 24%, respectively, for the feed surfactant concentration of 2000 mg/L within 50 min of operation. It also may be observed from Figs. 10–12 that desorption is more for TTAB (cationic surfactant) and less for SDS (anionic surfactant). Therefore, a suitable cationic surfactant may be a better agent for desorption of chrysoidine dye from AC.

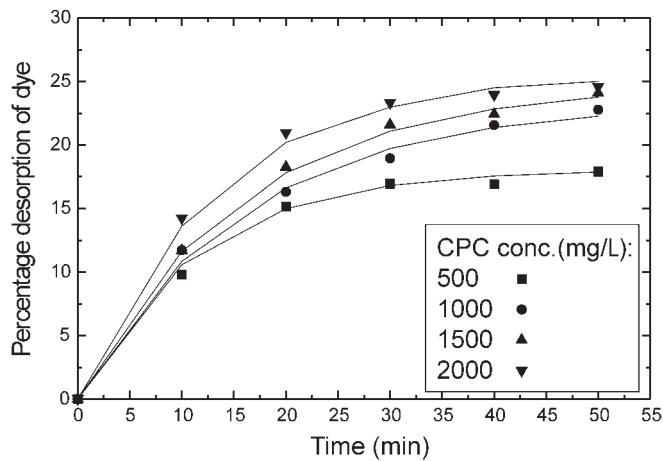


**Figure 10.** Effect of SDS on desorption of chrysoidine from spent charcoal. Solid are model fitted results, and the symbols are the experimental data.

The better performance of cationic surfactants (TTAB and CPC) compared with an anionic one (SDS) may be explained as follows. During adsorption, chrysoidine dye gets adsorbed onto the surface or may be inside the pores of AC. AC itself is negatively charged, as discussed in the earlier section, “Effect of pH” (for adsorption studies). The cationic surfactant, TTAB and CPC, micelles are positively charged, and there is a high possibility of the



**Figure 11.** Effect of TTAB on regeneration of chrysoidine from spent charcoal. Solid are model fitted results, and the symbols are the experimental data.



**Figure 12.** Effect of CPC on regeneration of chrysoidine from spent charcoal. Solid are model fitted results, and the symbols are the experimental data.

cationic surfactant getting adsorbed onto the surface of the negatively charged AC by replacing the adsorbed dye, although some dyes may still get solubilized inside the hydrophobic core of the aggregated surfactant molecule (micelles). On the other hand, micelles of anionic surfactant (SDS) are negatively charged, and, therefore, it is unlikely that micelles are adsorbed onto charcoal as such, due to electrostatic repulsion. Therefore, when AC adsorbed with chrysoidine dye is exposed to a SDS solution, the dye molecule remains on the surface of adsorbent. These result in very less dye-desorption characteristics while using anionic surfactants. The desorption kinetics using the surfactants are described by Eq. (11). For each surfactant feed concentration, the constants  $k$  and  $\alpha$  were estimated by using a curve fitting the corresponding experimental data. The value of  $k$  was found to be 1.015 for SDS, 1.35 for TTAB, and 1.3 for CPC. The values for  $\alpha$  varied in a narrow range from 0.13 to 0.03 for SDS, 0.03 to 0.04 for TTAB, and 0.04 to 0.07 for CPC, corresponding to various feed surfactant concentrations. The continuous curves in Figs. 10–12 are the fittings obtained from Eq. (11), and the symbols are the experimental data. The  $r^2$ -values of all the fits in Figs. 10–12 are more than 0.99.

## CONCLUSIONS

Adsorption of chrysoidine onto AC was studied. The effects of various operation conditions, namely, pH, adsorbent dose, initial dye concentration,

temperature etc., have been investigated. Both equilibrium and kinetic studies are undertaken. Freundlich isotherm is found to be suitable for chrysoidine adsorption onto AC. A pseudosecond-order kinetics explains the kinetic data well. Changes of pH and use of cationic and anionic surfactant were explored for desorption of dye from adsorbent. It was observed that a highly acidic pH (11.2) leads to about 1.6% desorption; on the other hand, anionic surfactant (SDS) results in about 1.7% desorption, but cationic surfactants TTAB and CPC lead to desorb dye of the order of 35% and 25%, respectively, during 50 min of operation. From the desorption study, it may be concluded that for dyes like chrysoidine, which is very sensitive to the pH of the solution, it is better to use cationic surfactant to desorb the adsorbed dye from the spent charcoal for its regeneration rather than using the conventional regeneration techniques (e.g., changing the pH of the solution) to maintain the color of the dye.

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