

Removal of congo red using activated carbon and its regeneration

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Abstract

Activated carbon is used for the removal of colored toxic congo red dye. The effects of different operating conditions like, initial dye concentration, contact time, pH and temperature are studied for adsorption of congo red by a known amount of activated carbon (1.0 g/L) under stirred batch condition. The zero point of charge of the activated carbon is found about 6.6. About 90% dye is removed for initial concentration of 50 and 100 mg/L, it is about 80% at pH 7.0. Maximum adsorption (about 100%) of dye is observed at pH 2.0 for the concentration range studied here. Freundlich isotherm is found to fit the equilibrium data more adequately. Pseudo second order kinetic model explain successfully the kinetic data. The surfactant enhanced carbon regeneration (SECR) technique using both cationic and anionic surfactants is adopted for the regeneration of spent carbon by desorbing the dye. A kinetic model for dye desorption from the commercial activated carbon (CAC) is also proposed. Anionic surfactants show better performance than the cationic ones. Efficiency of dye desorption using surfactants is also compared with the desorption using pH change.

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1. 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 requirement faced by the textile finishing, dye manufacturing, pulp and paper industries. These industries are major water consumer 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 to the river stream without proper treatment causes irreparable damage to the crops and living beings, both aquatic and terrestrial. Dyes are classified in three broad categories: (a) anionic: direct, acid and reactive dyes; (b) cationic: all basic dyes and (c) nonionic: dispersed dyes [1]. Congo red is an example of diazo dyes and is prepared by coupling tetrazotised benzidine with two molecules of naphthionic acid. This is red in the pH range of 5–10, and its sodium salt dyes cotton full red. Congo red is the first synthetic dye produced that is capable of dyeing cotton directly. It is very sensitive to acids and the color changes from red to blue in the

presence of inorganic acids (below pH 5). This blue color may be attributed to resonance among charged canonical structures [2]. Congo red containing effluents are generated from textiles, printing and dyeing, paper, rubber, plastics industries, etc. Due to its structural stability, it is difficult to biodegrade. Physico-chemical or chemical treatment of such wastewaters is, however, possible. Adsorption is considered an attractive option in treating such wastewater [3]. Many investigators have studied different techniques for removal of colored dye from wastewater, e.g., chemical coagulation/flocculation [4], different advance oxidation processes [5], ozonations [6], nanofiltration [7], micellar enhanced ultrafiltration [8] and adsorption on to: (i) sludge of wastewater treatment plant [9], (ii) different bentonites [10], (iii) different types of activated carbon [11], etc.

The water purification industry is currently one of the largest market for commercial activated carbon (CAC). In fact CAC filters are used today in many drinking water and wastewater treatment plants to remove organic micro-pollutants and some metals by adsorption. The economics of the adsorption process greatly depends on the reuse of CAC. Two approaches have been considered by researchers to overcome the problems associated with the use of activated carbon adsorbents. One approach that

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has been investigated by many workers is the development of low cost adsorbents based on carbonaceous waste products that can be used on a once through basis, hence eliminating the need for regeneration [12–14]. However, this merely transfers the pollutant from the liquid to the solid phase. The second approach has been to investigate different regeneration processes to eliminate some of the complexities and reduce the processing costs.

There are several well-established methods for the regeneration of spent CAC that can be classified in three broad groups: thermal, chemical and biological regeneration [15]. In spite of being the most widely used regeneration technology, thermal regeneration has an important energy demand since temperature must be kept above 1100 K. Also, considerable amount of carbon (5–15%) is usually lost by attrition, burn-off and washout [16]. Chemical regeneration can be carried out by desorption of adsorbates using specific solvents or by decomposition of adsorbed species using oxidizing chemical agents. Extraction with solvents requires further purification of the solvent and it is only recommended when a valuable product is recovered [17]. Oxidative chemical regeneration is usually accomplished by wet oxidation (WO) under either sub-critical or supercritical conditions. Although these techniques have been successfully applied to a number of adsorbates, regeneration efficiency depends on the solubility of the sorbed substances and the effect of pressure on the chemical structure of carbon. Also, such a large investment in high-pressure equipment makes the method rather expensive [18]. Biological regeneration is usually slow and requires adsorbed species being totally biodegradable, which is not the case in many water pollutants [19]. Because of these drawbacks, a number of other alternative CAC regeneration methods are subject of current investigation. Among them, steam regeneration [20], catalytic oxidation [21], microwave regeneration [22], electrochemical methods [23] or extraction with supercritical fluids [24] can be highlighted.

Adsorption beds containing activated carbon are widely used in industry to remove organics from water and air. One of the major disadvantages of this method is the difficulty of regeneration of the saturated carbon. When the organic is highly volatile, in situ thermal regeneration (e.g., hot steam) can be used. However, often the carbon must be removed from the bed and the organic burned off in regeneration furnaces. A universal in situ regeneration process would be valuable. One such method is surfactant enhanced carbon regeneration (SECR) [25].

In the present study, experiments have been performed for the removal of congo red using adsorption techniques. Activated carbon has been selected as adsorbent and added to the solution containing dye. The effects of temperature, pH of dye solution and initial dye concentration with time have been studied under stirred condition. Surfactant based carbon regeneration technique has been adopted in the present work to make the adsorption process more economical. Regeneration study by changing pH and using both cationic and anionic surfactants has been attempted. A kinetic model for the desorption of dye is also presented.

2. Surfactant enhanced carbon regeneration (SECR)

2.1. Micelle formation and solubilization

Surfactant molecules are amphiphilic in nature having a hydrophilic (head) and hydrophobic (tail) part. The hydrophobic part is generally a long chain hydrocarbon or aromatic ring. The head part of the surfactant is hydrophilic due to the presence of some electrophilic or nucleophilic groups. Above critical micellar concentration (CMC), surfactant molecules form aggregates (micelles). Depending on the nature of the surfactant and solvent, the aggregates may form micelles, reverse micelles, micro-emulsion, vesicles, monolayers and bilayers. This configuration allows the removal of the hydrocarbon chains from the aqueous environment while the hydrophilic groups are still exposed to the polar solvent. Organic solutes tend to be solubilized in the hydrophobic core of the micelles. Any ionic pollutants having opposite charge to that of the micellar surface are bound on its outer periphery. Multivalent counter ions will bind in higher proportion compared to the monovalent counter ions. The higher is the valence state, greater is the binding [26].

In SECR, a concentrated surfactant solution is passed through the saturated carbon bed. The adsorbed solute desorbs and is solubilized in the micelles. After the organic is removed from the carbon, water is used to rinse residual surfactant from the carbon. A schematic for this process is shown in Appendix A (Fig. A.1). An advantage of SECR over solvent regeneration is the relatively innocuous nature of surfactants from an environmental point of view. Micellar enhanced ultrafiltration followed by chemical treatment [8] may be useful for further treatment of dye loaded surfactant. The product of the rinse step can be directed to the normal sewage treatment system, since it contains only surfactant. The regenerated carbon would then be ready for reuse.

2.2. Selection of surfactant

For the selection of a surfactant for use in SECR, some important desirable characteristics are: (1) high solubilization capacity for the solute; (2) formation of large micelles; (3) low monomer concentration, so that a small amount of surfactant is to be used; and (4) minimal phase-separation problems (macroemulsion formation, precipitation, gelling, etc.). Anionic, cationic and nonionic surfactants may be considered for application in SECR. Nonionic surfactants are not suitable for SECR, since they may get adsorbed on the carbon surface themselves. Cationic and anionic surfactants with larger micellar size, high solubilization capacities, and low CMC values can be used in SECR.

3. Experimental

3.1. Material

Congo red dye (C.I.: 22120, FW: 696.67, λ_{\max} : 499 nm, dye content: 97%, supplied by Aldrich Chemical Company, USA) is

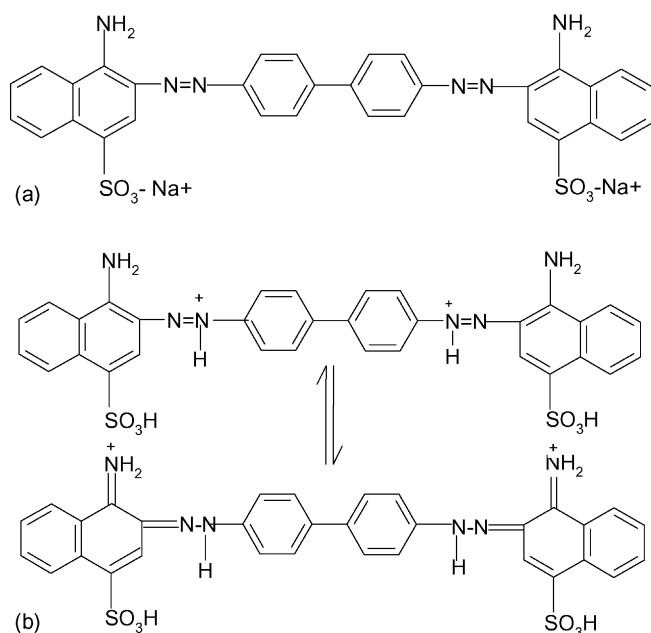


Fig. 1. Structure of congo red at: (a) $\text{pH} > 5.5$ and (b) $\text{pH} < 5.5$.

used as an adsorbate. Structure of the dye molecule is shown in Fig. 1 (a and b) at different pH. pH of the solution is maintained by using 0.1N hydrochloric acid and 0.1N sodium hydroxide. Commercial activated carbon (CAC), supplied by S.D. Fine Chem. Ltd., India, and is used as the adsorbent without further activation. The particle size distribution of CAC is evaluated using a particle size analyzer (Malvern Instruments Ltd., particle sizer 3601, UK, Worcestershire). Specific surface area and the average pore volume are obtained from the physical adsorption of nitrogen gas at 77 K (Micromeritics Instruments Corporation, Norcross, GS 30093-1877, USA). The characteristics of CAC are presented in Table 1. Prior to each experiment, the activated carbon is repeatedly washed with distilled water to remove the fine particles. For surfactant based regeneration of spent carbon, hexadecyl(cetyl) pyridinium chloride (CPC) (Mol. wt. 358.01, purity >98%) is used as cationic surfactant. Sodium dodecyl sulphate (SDS) (Mol. wt.: 288.38, purity: >90%) and di-octyl sodium sulphosuccinate (AOT) (Mol. wt.: 444.57, purity: >98%) have been used as anionic surfactants. Structures of these three surfactants are shown in Appendix B (Fig. B.1). All surfactants are procured from SISCO Research Lab. Pvt., India.

Table 1
Characterization of commercial activated carbon (CAC)

Property	CAC
Particle size	0.2–40 μm (with a peak at 25 μm)
Methylene blue adsorption	270
Moisture (at 105 °C for 2 h)	5.0%
Ash	2.5%
Acid soluble	2.5%
Water soluble	1.5%
Surface area (m^2/g)	492
pHZPC	6.6
Pore volume (mL/g)	0.231

3.2. Method

For adsorption experiments, 50, 100, 200, 380 and 545 mg/L of dye solutions are prepared by dissolving accurately weighed amount of dye in distilled water. To observe the effect of pH on dye adsorption, the pH of the solution is adjusted to 2, 5, 7, 9 and 12. Hydrochloric acid and sodium hydroxide have been used to adjust pH and is measured by pH meter supplied by Toshniwal Instruments Ltd. (India). Each experiment is conducted by adding fixed amount of activated carbon (1.0 g) to 1.0 L of dye solution. The solution is placed in a constant temperature bath (Testing Instruments Manufacturing Company Ltd., India) and stirred with the help of a stirrer (Type-RQ-123, Remi Motors Ltd., India) at 450 rpm. All the experiments are conducted at different temperatures (30, 40 and 50 °C). The concentration of dye is determined by a spectrophotometer (make: Thermo Spectronic, USA; Model: GENESYS 2). The measurement is done at a wave length of 499 nm for pH range of 5–12 [27] and at 560 nm at pH 2. pH-specific standard calibration curves are generated at these wavelengths and used in this regard.

The effects of pH and concentrations of different surfactants (both anionic and cationic) on the percentage desorption of congo red are studied in detail. The amount of congo red adsorbed to a known amount (1.0 g) of activated carbon is measured before each desorption study. This is done by keeping 1.0 g of activated carbon and 250 mL of a solution of congo red with a concentration of 5 g/L in a stoppered glass bottle and agitated by a shaker for 12 h at room temperature. The amount of dye adsorbed per gram of activated carbon is calculated by measuring the concentration of dye solution before and after adsorption. After filtration, the carbon is dried in an oven. For the desorption study, 1.0 g of carbon with adsorbed dye is mixed with 250 mL of the desorbing medium. Distilled water at different pH and both the anionic and cationic surfactant at various concentrations are used as the desorbing medium.

The zero point of charge of activated carbon is determined by batch equilibrium technique with 1:1000 and 1:80 of solid liquid ratio in 0.1 (M) KNO_3 solution. Potassium nitrate is selected as an inert electrolyte. Initial pH value of KNO_3 solution is adjusted to cover range from 2 to 12 by adding 0.1 (M) HNO_3 or KOH . The solutions are allowed to equilibrate for 24 h in an isothermal shaker at 25 ± 1 °C. Then the suspensions are filtered through filter paper and pH values are measured again using ion pH meter [28].

4. Results and discussion

4.1. Adsorption studies

4.1.1. Effect of agitation time and initial dye concentration

Fig. 2 represents the effects of agitation time and initial congo red concentration on the percentage adsorption of congo red by CAC. It may be seen that the percentage adsorption increases with an increase in the agitation time and attains equilibrium after some time. Up to an initial concentration of 50 mg/L, more than 85% adsorption has been observed within 5 min. For an initial concentration of 100 mg/L, the percentage adsorption

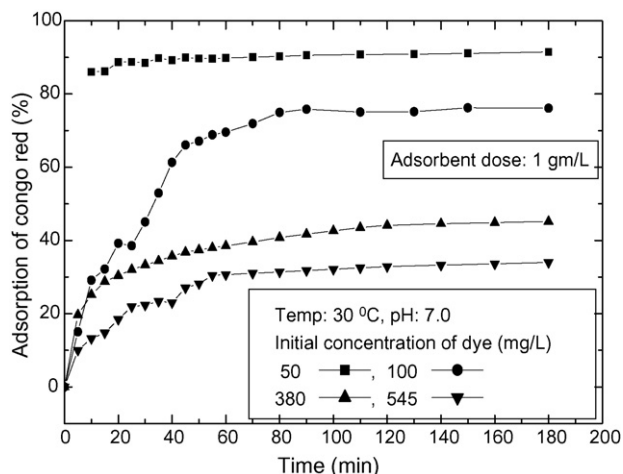


Fig. 2. Effect of agitation time and concentration of congo red on the extent of adsorption.

increases with time till 90 min and becomes constant thereafter. For a feed concentration of 545 mg/L, the percentage adsorption increases rapidly for about 90 min and the increase becomes gradual thereafter. From the above observation, it is evident that for lower initial concentration of the dye, the adsorption is very fast. For 180 min operation, the dye adsorption is 76% for an initial dye concentration of 100 mg/L but only 34% for 545 mg/L. With agitation, the external mass transfer coefficient increases resulting in quicker adsorption of the dye molecules. However, increase in initial dye concentration results in the fast attainment of saturation of activated carbon and higher residual dye in the equilibrium solution.

4.1.2. Effect of pH

The percentage of dye adsorption at different pH is shown in Fig. 3 for the initial dye concentrations of 50, 100 and 200 mg/L. The initial pH of dye solution plays an important role particularly on the adsorption capacity by influencing the chemistry of both dye molecule and activated carbon in aqueous solution. Congo red is a dipolar molecular. It exists as anionic form at basic pH (shown in Fig. 1a) and as cationic form at acidic pH (shown in

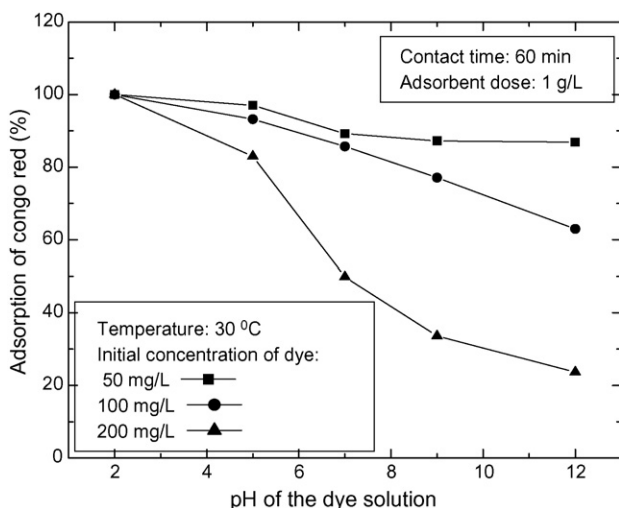


Fig. 3. Effect of pH on the percentage adsorption of congo red.

Fig. 1b). The sodium and potassium salt of anionic congo red in aqueous medium is red in color in basic pH of up to 10. It has also been found that as the pH decreases, the color of congo red solution changes from red to dark blue. These variations of color with pH suggest that the extent and nature of ionic character of congo red molecule depends on the pH of the medium. Most of the activated carbon contains some oxygen complexes on the surface, i.e. (a) strongly carboxylic groups, (b) carbonyl groups and (c) phenolic groups [29]. The pHZPC of CAC used for the adsorption experiment is about 6.6 as observed from the figure shown in Appendix C (Fig. C.1). It is already mentioned that the activity of CAC is due to the presence of different functional groups like; carboxylic ($-\text{COOH}$), phenolic ($\text{Ph}-\text{OH}$), etc. At higher pH (basic pH), these groups become anionic in nature (carboxylate ($-\text{COO}^-$) and phenoxide ($\text{Ph}-\text{O}^-$) ion) and not suitable for the adsorption of negatively charged dye (as shown in Fig. 1a) due to inter ionic repulsion between similar charged particle. Hence, extent of dye adsorption on the surface of CAC is low at basic pH. At acidic pH, the dye molecule exists as cations (as shown in Fig. 1b). At this pH, active site of CAC remains carboxylic ($-\text{COOH}$) and phenolic ($\text{Ph}-\text{OH}$). Cationic dye molecules get attached on the surface of CAC by replacing H^+ ion of carboxylic and phenolic ion. Therefore, adsorption of congo red on the CAC surface is much higher at acidic pH [30]. It is found from the figure that at pH 2, adsorption is $\sim 100\%$ for the feed dye concentrations of 50–200 mg/L. On the other hand, the percentage adsorption decreases with increase in pH of the dye solution. For the feed dye concentrations of 50, 100 and 200 mg/L, the percentage adsorption decreases to 87, 63 and 25%, respectively, at the end of the experiment when the pH is 12.

4.1.3. Effect of temperature

To observe the effect of temperature on the adsorption capacity, experiments are carried out for 100 mg/L congo red at three different temperatures (30, 40 and 50 °C) using 1.0 g of CAC per liter of the solution. It has been observed that with increase in temperature, adsorption capacity increases as shown in Fig. 4. The thermodynamic parameters ΔG^0 , ΔS^0 and ΔH^0 for the adsorption of congo red have been determined by using the

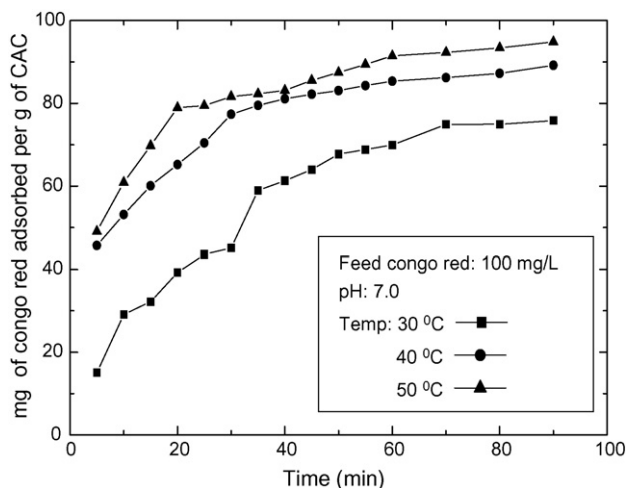


Fig. 4. Effect of temperature on adsorption capacity of activated carbon.

Table 2
Thermodynamic parameters for the adsorption of congo red in activated carbon at different temperatures

Dye concentration (mg/L)	ΔH^0 (kJ mol ⁻¹)	ΔS^0 (J mol ⁻¹ K ⁻¹)	$-\Delta G^0$ (kJ mol ⁻¹)		
			T = 303 K	T = 313 K	T = 323 K
100	51.09	178.1	2.86	4.64	6.42

following equations [31],

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

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

where q_e is the amount of dye adsorbed per unit mass of activated charcoal (mg/g), C_e the equilibrium concentration (mg/L) and T is the temperature in Kelvin. q_e/C_e is called the adsorption affinity. The values of Gibbs free energy (ΔG^0) have been calculated by knowing the enthalpy of adsorption (ΔH^0) and the entropy of adsorption (ΔS^0). ΔS^0 and ΔH^0 are obtained from a plot of $\log(q_e/C_e)$ versus $1/T$, from Eq. (2). Once these two parameters are obtained, ΔG^0 is determined from Eq. (1).

The values of ΔH^0 , ΔS^0 and ΔG^0 for the initial dye concentration of 100 mg/L are shown in Table 2. The adsorption is endothermic in nature since the value of ΔH^0 is positive. The endothermic nature is also indicated by the increase in the amount of adsorption with temperature (Fig. 4). The adsorption is associated with an increase in entropy of 178.1 J mol⁻¹ K⁻¹, which shows that the adsorbed dye molecules on the activated carbon surface are organized in more random fashion compared to those in the aqueous phase. Similar observations have been reported in the literature [32,33]. The higher heat of adsorption obtained in this work indicates that chemisorption rather than the physical adsorption is prevalent in this case [34]. It was reported in ref. [34] that a value of ΔH^0 around 51.09 kJ mol⁻¹ signifies chemisorption rather than physical adsorption. The negative values of ΔG^0 indicate that the adsorption process is spontaneous.

4.1.4. Adsorption isotherms

To determine the adsorption capacity of activated carbon, equilibrium study has been performed to analyze the experimental data using well-known Langmuir and Freundlich isotherm models at a temperature of 30 °C and at pH 7.0. 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 and after that no further adsorption takes place [35]. Freundlich model is an indicative of the extent of heterogeneity of the surface of adsorbent. The constants for both the models (Q and b for Langmuir isotherm and K_F and n for Freundlich isotherm model) are experimentally determined as in case of chrysoidine dye [31].

Both the isotherms of congo red on activated carbon at 30 °C and neutral pH have been shown in Fig. 5. The coefficients of these two isotherm models have been shown in Table 3. These data provide some information on the amount of activated carbon required to adsorb a particular mass of congo red under the specified system conditions. Correlation coefficients are calculated

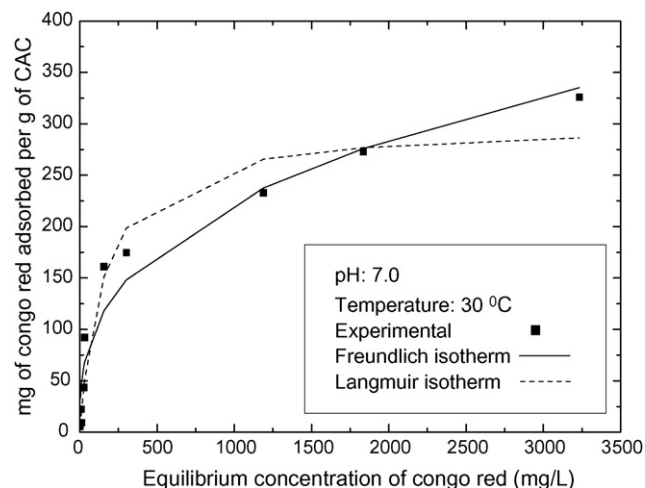


Fig. 5. Langmuir and Freundlich adsorption isotherms for congo red on activated carbon.

by fitting the experimental adsorption equilibrium data for congo red-activated carbon system using both Langmuir and Freundlich adsorption isotherm and is shown in Table 3. It is found from the correlation coefficients (r^2) that adsorption isotherm for the present congo red-activated carbon system is explained better by Freundlich isotherm model. This shows that surface heterogeneity of CAC exists and it is due to presence of widely different sized pores in the CAC matrix. The curve fitted parameters for adsorption isotherms can be compared with the adsorption of the same dye on activated carbon prepared from coir pith [3]. The feed concentration range of dye was 20–80 mg/L for their study and in the present case this range is from 50 to 545 mg/L. The value of adsorption capacity is higher in this study (300 mg/g, Table 3) compared to that in ref. [3] (6.72 mg/g).

4.1.5. Adsorption kinetics

The kinetics of adsorption of congo red dye on activated carbon is described by using first order and pseudo second order model. The Lagergren's equation for first-order kinetics is given as follows

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (3)$$

The expression for pseudo second order rate equation is given as [36].

Table 3
Langmuir and Freundlich isotherm constants for adsorption of congo red on activated carbon at 30 °C

Langmuir constant			Freundlich constant		
Q (mg/g)	b (L/mg)	r^2	K_F [mg/g(L/g) ^{1/n}]	n	r^2
300.00	6.49×10^{-3}	0.94	20.77	2.90	0.97

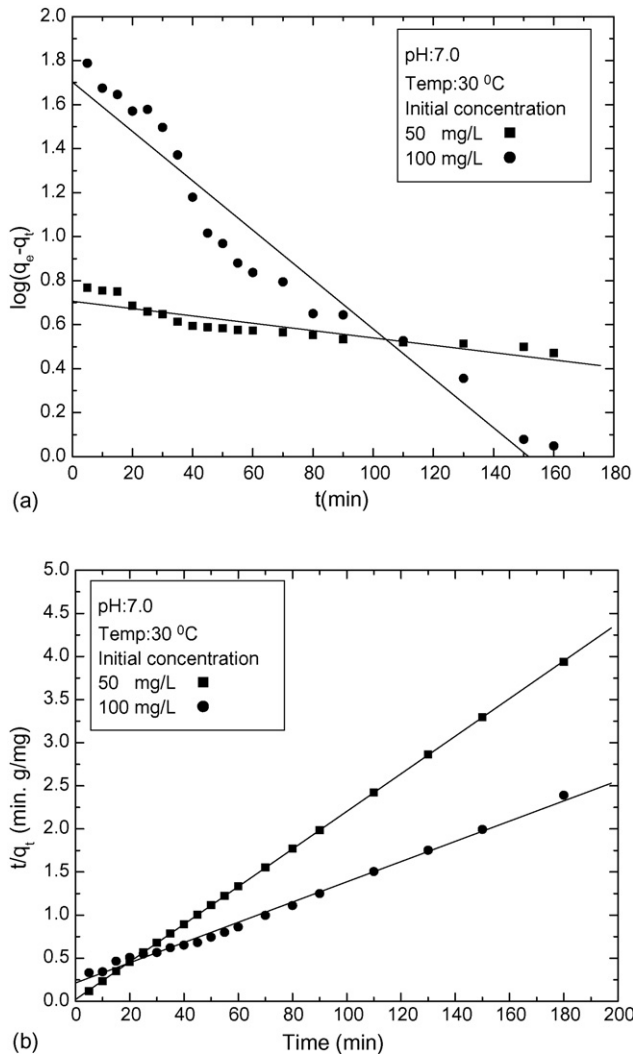


Fig. 6. (a) First-order kinetic model for the adsorption of congo red on activated carbon. (b) Pseudo second-order kinetic model for the adsorption of congo red on activated carbon.

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

where q_e and q_t are the amount of congo red adsorbed (mg/g) at equilibrium and at any time t ; k_1 is the rate constant (min^{-1}). Plot of $\log(q_e - q_t)$ versus t gives a straight line for first order adsorption kinetics and is shown in Fig. 6a for the initial dye concentrations of 50 and 100 mg/L. The value of first order rate constant k_1 is obtained from the slope of the curve. Fig. 6b shows the (t/q_t) versus t plot of the second order kinetics for the initial dye concentration of 50 and 100 mg/L. In Eq. (4), k_2 (g/mg min) is the rate constant for the pseudo second order

adsorption kinetics. The slope of the plot (t/q_t) versus t gives the value of q_e and from intercept k_2 can be calculated. The values of rate constants for these kinetic models are shown in Table 4. It is clear from the nature of fit and correlation coefficients tabulated in Table 4 that the adsorption of congo red on activated carbon is better represented by pseudo second order kinetics. Similar results of adsorption kinetics for congo red is observed by Namasivayam and Kavitha [3].

4.2. Desorption kinetics

The basic assumption of the desorption rate at any time would be proportional to the difference between the initial (at $t=0$) amount of the adsorbed dye and the dye concentration in the solution, at any time t . Again, the dye concentration in the solution, would be related to the amount of the dye still remaining adsorbed, through a mass balance. This is mathematically represented by the following equation.

$$\frac{dq}{dt} = \alpha(q_0 - kq) \quad (5)$$

where α and k are the constants ($k \neq 1$). q_0 and q are the amount of adsorbed dye present per gram of CAC at time $t=0$ and at any time $t=t$, respectively. Integrating Eq. (5) between $t=0$ to any time t , the following expression of the percentage desorption is obtained,

$$D = 100 \times \left(\frac{k-1}{k} \right) [1 - e^{-k\alpha t}] \quad (6)$$

where D is defined as, $D = (1 - q/q_0) \times 100$. The values of k and α can be determined from the experimental data under various operating conditions.

4.2.1. Effect of pH

Fig. 7 represents the variation of percent desorption of dye with pH in absence of surfactant. In Section 4.1 it is already explained that at higher pH, molecules of congo red become anionic in nature and chemisorption is restricted with active site of CAC. Thus with the increase of pH, desorption increases. From Fig. 7, it has been found that after 50 min of operation desorption of dye increases from ~ 0 to 32.5% when pH increases from 2 to 12. As discussed earlier, congo red changes its original red color beyond a pH of 10. Therefore, although the desorption of dye from activated carbon is maximum at a pH 12, it is appropriate to desorb congo red by setting a pH around 8–9 (in order to maintain its color). For each operating pH, the constants k and α are estimated by fitting the corresponding experimental data at various time using Eq. (6). The values of k vary within 1.4–1.9 for a pH range of 2–12, whereas in the same pH range, α varies from 6.72×10^{-2} to 8.85×10^{-2} (min^{-1}).

Table 4
Comparison of the different kinetic model parameters at 30 °C

Feed concentration (c_0) (mg/L)	$q_{e, \text{exp } t}$ (mg/g)	k_1 (1/min)	$q_{e, \text{cal}}$ (mg/g)	r^2	k_2 (g/mg min)	$q_{e, \text{cal}}$ (mg/g)	r^2
50	48.70	1.22×10^{-3}	44.23	0.91	3.40×10^{-4}	47.23	0.99
100	76.23	4.10×10^{-2}	64.98	0.88	5.30×10^{-2}	78.54	0.99
380	171.10	2.92×10^{-2}	119.00	0.96	4.55×10^{-2}	181.82	0.99
545	183.10	3.06×10^{-2}	144.75	0.97	2.54×10^{-2}	187.46	0.99

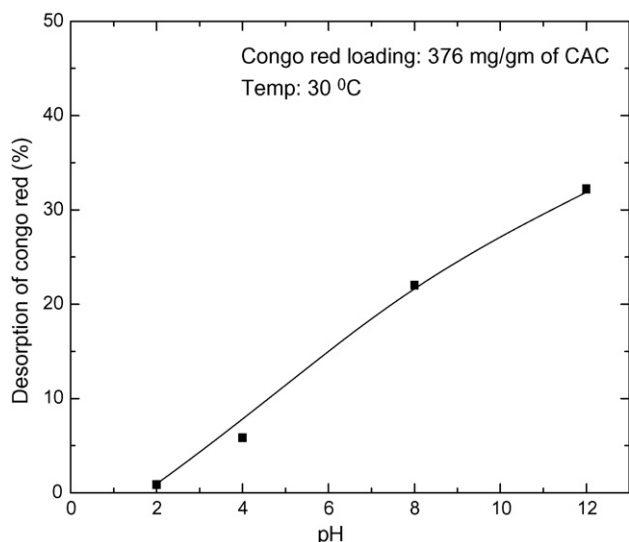


Fig. 7. Effect of pH on the desorption of congo red from spent CAC at the end of experiment (with surface loading 376 mg dye/g CAC).

4.2.2. Effect of surfactant concentration

Fig. 8 shows the variations of the percentage desorption of congo red using CPC, SDS and AOT at 2500 mg/L (higher than the corresponding critical micellar concentrations (CMC)). CMC of CPC, SDS and AOT are 350, 2307 and 1182 mg/L at 25 °C temperature in aqueous medium [26], respectively. In case of CPC (cationic surfactant), desorption is only about 2% whereas for SDS and AOT (anionic surfactant) the desorption increases up to 40 and 65%, respectively, for a feed surfactant concentration of 2500 mg/L.

Better performance of anionic surfactants (SDS and AOT) compared to cationic one (CPC) needs discussion. During adsorption, anionic congo red (at pH 7.0) gets adsorbed on the surface or may be trapped inside the pores of activated carbon. During desorption, CPC micelles are positively charged and get adsorbed on the negatively charged surface of activated carbon (pHZPC \approx 6.6), although some dye molecules may still get solu-

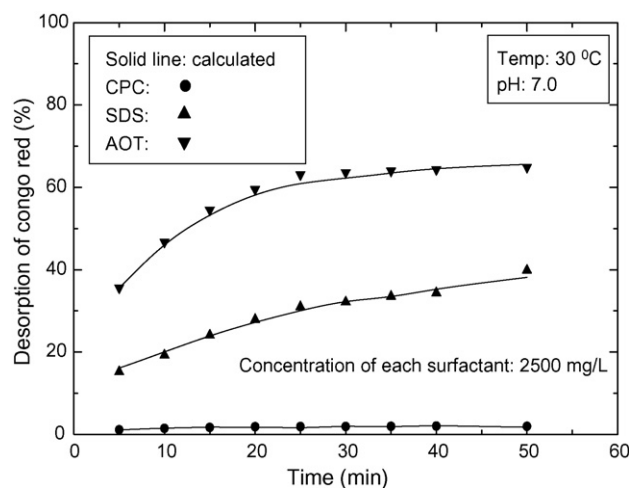


Fig. 8. Comparison of the performance of various surfactants for the desorption of congo red. Concentration of each surfactant is 2500 mg/L (with surface loading 376 mg dye/g CAC).

bilized inside the hydrophobic core of CPC micelles. Therefore, solubilization of dye in the CPC micelle is less. On the other hand, micelles of the anionic surfactants (SDS and AOT) are negatively charged and are unlikely to get adsorbed on the activated carbon. Due to strong hydrophobic attraction between micellar core and dye molecules, the adsorbed dye get solubilized in the micelle. This results in better dye desorption characteristics using anionic surfactants. From Fig. 8, it is observed that performance of AOT is better than SDS.

The extent of dye solubilization in the micelles depends on the concentration of the micelles which depends on the CMC of surfactant. As stated earlier, AOT has a much lower CMC than SDS. Therefore, it is expected that the micellar concentration is more in case of AOT at a feed surfactant concentration of 2500 mg/L. Therefore, dye solubilization capacity of AOT micelles is more than those of SDS at same surfactant feed concentration. The desorption study is carried out using a number of surfactant concentrations in the range of 500–000 mg/L. The kinetic data are then fitted to Eq. (6) and the parameters k and α , of these three surfactants are estimated separately. The average value of α is found to be 4.34×10^{-2} (min^{-1}) for CPC, 5.23×10^{-2} (min^{-1}) for SDS and 8.23×10^{-2} (min^{-1}) for AOT. The values for k vary from 1.35 to 1.66 for CPC, 2.36 to 3.44 for SDS and 2.66 to 4.12 for AOT corresponding to various feed surfactant concentrations. The continuous curves in Fig. 8 represent the fit obtained from Eq. (6) and the symbols are the experimental data. The r^2 values in all the cases are more than 0.99.

5. Conclusion

The dye congo red is adsorbed on CAC in batch mode. The effects of various operating conditions, like, pH, initial dye concentration, temperature, etc., are investigated. More than 85% adsorption is observed to take place within 5 min for the initial concentration of 50 mg/L. It is found that adsorption is \sim 100% for the initial dye concentrations of 50–200 mg/L at pH 2. The percentage adsorption decreases to 87, 63 and 25% for the initial dye concentrations of 50, 100 and 200 mg/L, respectively, at the end of the experiment when the pH is 12. Adsorption capacity increases with temperature. The thermodynamic parameters ΔG^0 , ΔS^0 and ΔH^0 for the adsorption of congo red on CAC are determined. Both equilibrium and kinetic studies are undertaken in detail. Freundlich isotherm is found to be better for congo red adsorption on activated carbon. A pseudo second order kinetic model successfully explains the kinetic data.

The desorption of dye from CAC is also investigated using SECR technique. Change of pH and use of cationic and anionic surfactants are explored for the desorption of dye from spent activated carbon. It is observed that a highly basic pH leads to better dye desorption (about 32.5% desorption at a pH of 11). Use of cationic surfactant (CPC) results in only about 2% desorption but significantly higher desorptions, (about 40 and 65%, respectively) are obtained using anionic surfactants, such as SDS and AOT with 2500 mg/L of surfactant concentration after 50 min of operation. Higher concentration of SDS and AOT may lead to better dye desorption.

Appendix A

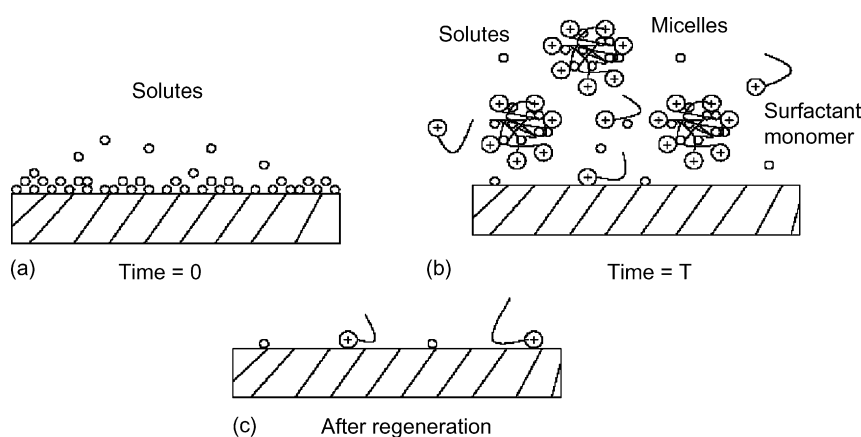


Fig. A.1. Schematic for the surfactant enhanced carbon regeneration technique.

Appendix B

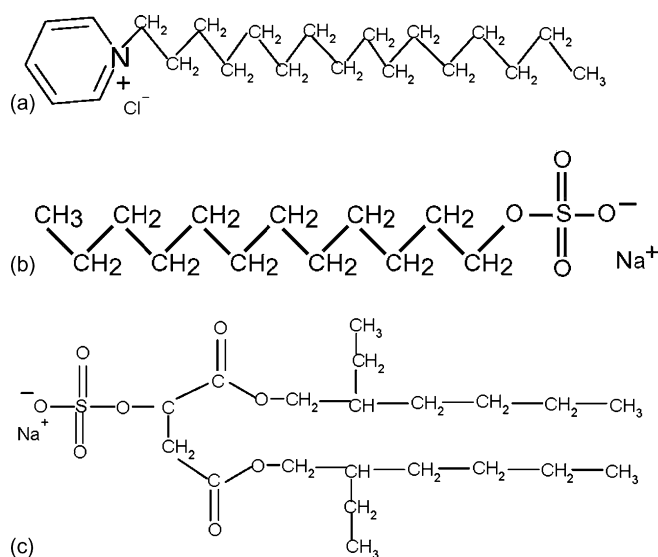


Fig. B.1. Structures of three different surfactants: (a) cetyl (hexadecyl) pyridinium chloride (CPC), (b) sodium dodecyl sulphate (SDS) and (c) sodium bis(2-ethylhexyl) sulphosuccinate (AOT).

Appendix C

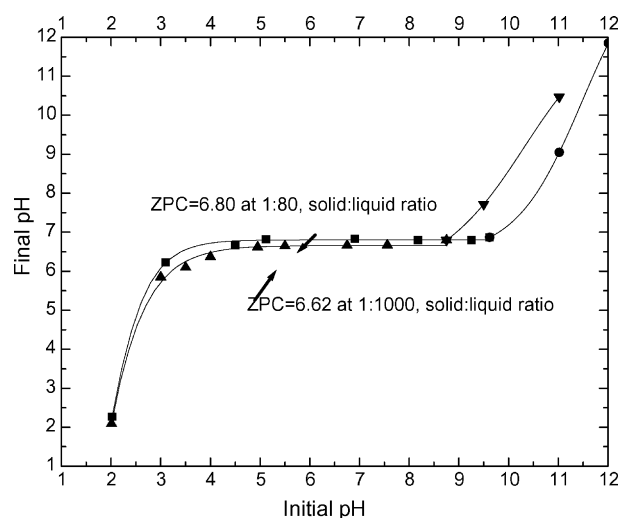


Fig. C.1. Zero point of charge of commercial activated carbon used for the adsorption experiments.

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