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Improved removal and decolorization of C.I. anionic reactive yellow 145 A dye from water in a wide pH range via active carbon adsorbent-loaded-cationic surfactant

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ABSTRACT

A fast and highly efficient method was developed for decolorization of C.I. anionic reactive yellow 145 A dye from wastewater under a wide pH range (1.0–13.0) using a loaded cationic surfactant on the surface of an active carbon adsorbent (HTAB-AC). The efficiency of dye removal by the proposed adsorbent was studied by the batch equilibrium technique under the influence of various controlling experimental factors such as adsorbent dosage, contact time, and initial dye concentration. The determined percentage removal values of reactive yellow 145 A dye by (HTAB-AC) adsorbent in the examined solutions were found 92.5–99.6, 90.7–98.1, and 88.5–96.9% for 120, 150, and 180 mg L^{-1} solutions, respectively. The equilibrium of removal (93.0–96.0%) was established at 20.0 min of shaking time. The effects of other system variables were evaluated and the adsorption behavior was investigated by the Langmuir and Freundlich models. Adsorption kinetic data were tested using pseudo-first-order, pseudo-second-order, and intraparticle diffusion models. Successful removal (90.2–97.6%) was accomplished in the presence of various pH values from real industrial wastewater samples.

Keywords: Cationic surfactant; Activated carbon; Adsorption; Reactive yellow 145 A dye; Wastewater treatment

1. Introduction

Dyes are produced from industrial activities as one of the major constituents of wastewater. Textile, paint and varnishes, ink, plastics, pulp and paper, cosmetics, tannery, and dyes productions are among the various industrial sectors responsible for water contamination with dyes. Reactive dyes are the most common types of dyestuffs owing to their unique properties such as bright colors. Direct discharge of colored effluents causes formation of toxic materials in waste receiving media. Several classes of synthetic dyes are defined as extremely toxic, carcinogenic, and poising leading to a serious threat to human/animal health in addition to their adverse impact in terms of chemical oxygen demand, biological oxygen demand, and their visual effects even at low concentration [1]. The impact of dyes toxicity is not only limited to a certain present level but it may be passed onto further generations by the way of genetic mutations, birth defects, and inherited diseases [2].

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Generally, treatment of contaminated wastewater with reactive dyes is considered a difficult task, due to their complex structures, water solubility, and synthetic nature. Therefore, this type of pollutants must be chemically or biologically treated prior to their discharge into the receiving water bodies. Several treatment approaches are well known and applied for the removal of dyes from wastewater matrices such as photodegradation [3–6], coagulation flocculation [7], chemical oxidation [8], electrochemical oxidation [9], and biological process [10]. However, these methodologies were characterized by suffering from various disadvantages such as incomplete removal of dyes, relatively high operating cost, colored effluent, high energy requirement, and generation of chemical sludge or by-products that are likely to be more toxic than the starting materials. On the other hand, adsorption has been recently found as an efficient methodology and superior technique to face the current challenges in wastewater treatment of textile effluents. The advantages of adsorption process are mainly based on the low initial cost, simplicity of design, availability of a wide range of adsorbents, ease of operation, and insensitivity to toxic substances [11]. In this regard, activated carbon adsorbents afford high adsorption capabilities due to their high surface area, microporous structure, and high degree of surface reactivity [12–16].

Surfactants molecules are characterized by the so-called amphiphilic character due to the presence of both hydrophilic and hydrophobic counterparts [17]. The hydrophilic part is called the head and the hydrophobic portion is known as the tail of molecule. The hydrophobic part may consist of a single chain or may have up to four chains. The head is either a charged or uncharged polar group. However, according to the nature of the head groups, the surfactants are classified into anionic, cationic, non-ionic, and zwitterionic (amphoteric) [18]. Surfactants are generally used as leveling agents in dyeing stuff [19]. Recently, adsorptive removal of organic contaminants using some surfactant has drawn much attention [20,21]. Therefore, combined surfactant with some adsorbents such as activated carbon was found to form micelle-like structure on the adsorbent surface with a high potential to solubilize the organic molecules within the produced structure. These micelles are called hemimicelle or admicelle and the phenomenon is called adsolubilization. This pre-treatment would increase the surface area with the aim of enhancing the percentage of dye removal [22–24].

The aim of the present study is mainly directed towards the development of an efficient adsorbent for implementation in the removal process of an anionic dye, reactive yellow 145 A, from real industrial wastewater samples. This target was accomplished using a cationic surfactant, hexadecyl-N,N-trimethyl ammonium bromide, loaded on the surface of activated carbon sorbent (HTAB-AC). The adsorptive removal properties of reactive yellow 145 by (HTAB-AC) were studied, monitored, optimized, and evaluated in the presence of various key experimental interaction parameters. The adsorption efficiency characteristics were also investigated by different isotherm and kinetic models.

2. Experimental

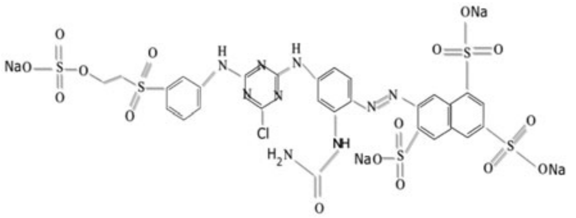
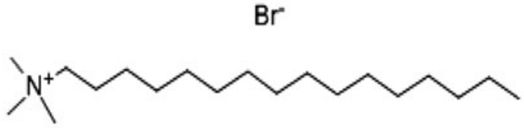
2.1. Instrumentations

JASCO V-530 UV–vis spectrophotometer was used to measure the absorption spectrum of the dye samples in the wavelength range 190–1,100 nm. The light sources used in the V-530 are a deuterium lamp (190–350 nm) and in the UV region, a halogen (WI) lamp (340–1,100 nm) for the VIS/NIR region. The apparatus is connected to water bath thermostatic unit for adjusting the desired temperature. The FT-IR spectra of free activated carbon (AC) and (HTAB-AC) adsorbents as well as (HTAB-AC)-loaded reactive yellow 145 A dye were recorded from KBr pellets using a BRUKER Tensor 37 Fourier transform infrared spectrophotometer in the range of 400–4,500 cm^{-1}. A calibrated CRISON pH-meter against standard buffer solutions, 4.01, 7.00, and 9.21, was used to measure the pH-value of the dye solutions. A scanning electron microscope (SEM) (JSM-6360LA, JEOL Ltd.), (JSM-5,300, JEOL Ltd.) and an ion sputtering coating device (JEOL-JFC-1100E) were used to image the various (AC), (HTAB-AC) and (HTAB-AC)-loaded-dye materials. The SEM specimens were coated with gold to increase the conductivity.

2.2. Materials and methods

The anionic azo-dye, C.I. reactive yellow 145 A (RY 145), was purchased from JAY chemicals, India and used without further purification. The chemical structure of reactive yellow 145 A dye is shown in Table 1. The cationic surfactant, hexadecyl-N,N-trimethyl ammonium bromide (HTAB), was supplied by Aldrich with a 99.9% purity and used as received. The chemical structure and the general specifications of reactive yellow 145 A dye and HTAB are summarized in Table 1. Sodium sulfate (Na_2SO_4), potassium chloride (KCl), sodium chloride (NaCl), and magnesium sulfate heptahydrate ($MgSO_4{\cdot}7H_2O$) were purchased from Analar BDH with 99.0% purity. Calcium chloride

Table 1
General specifications of (a) C.I. Reactive yellow 145 A and (b) Hexadecyl-N, N-trimethyl ammonium bromide (HTAB)

Compound	Specifications	
(a) 	Chemical formula	$C_{28}H_{20}ClN_9O_{16}S_5Na_4$
	Formula weight	1026.25 g mol^{-1}
	λ_{max}	417 nm
	C.I.	Yellow 145 A
(b) 	Chemical formula	$CH_3(CH_2)_{15}N(Br)(CH_3)_3$
	Formula weight	364.5 g mol^{-1}
	Critical micelle concentration (cmc) in water	0.92–1.0 mM

hexahydrate ($CaCl_2{\cdot}6H_2O$) was supplied by Gateway Co and other chemicals were all of analytical grade.

2.3. Synthesis of (HTAB-AC) adsorbent

Activated carbon, 20.0 g, was mixed with 20.0 mmol of cationic surfactant solution (HTAB) already dissolved in ethanol and the mixture was refluxed with stirring for 4 h. The produced (HTAB-AC) adsorbent was separated by filtration and washed with ethanol several times to remove superficially retained surfactant. Finally, the (HTAB-AC) adsorbent was dried in an oven at 70˚C for 3 h and stored in an airtight glass container.

2.4. Batch adsorption experiments

A study was made to explore the effect of various key experimental parameters such as pH, contact time, initial dye concentration, adsorbent dose, salt effect, and temperature on the adsorptive removal of reactive yellow 145 A dye. The batch experiments were carried out at 25 ± 1˚C. A stock solution (1,000 mg L^{-1}) was prepared by dissolving accurately the dye weight in double distilled water. Working solutions of the desired concentrations were obtained by successive dilutions of the stock solution.

The effect of contact time was studied by addition of 20.0 mL of the dye solution (initial concentrations 90 and 150 mg L^{-1}) to 50.0 ± 1.0 mg of (HTAB-AC) adsorbent. The pH of this solution was adjusted to 6.0 ± 0.1 and the shaking time was varied from 0.0 to 90.0 min. The unextracted reactive yellow 145 dye was filtered and the absorbance was measured by UV-spectrophotometer at $\lambda_{max} = 417$ nm as the selected wavelength.

The effect of pH on the removal process of reactive yellow 145 A dye by (HTAB-AC) adsorbent was accomplished using three different concentration values, viz. 120, 150, and 180 mg L^{-1}. The pH values of 20.0 mL dye solution were varied from 1.0 to 13.0 using a solution of either 1.0 M HCl or NaOH. A sample of 50.0 ± 1.0 mg of (HTAB-AC) adsorbent was then added and automatically shaken for 20.0 min. The unretained dye concentration was filtered and detected by measuring the absorbance at $\lambda_{max} = 417$ nm.

The effect of adsorbent dosage on the adsorptive removal of reactive yellow 145 A dye by (HTAB-AC) adsorbent was also studied by mixing a 20.0 mL of 120, 150, and 180 mg L^{-1} solutions of the dye as the initial concentration values. The selected dosages of (HTAB-AC) adsorbent were in the range of 5.0–50.0 mg. This mixture was adjusted to the optimum pH value 1.0 and automatically shaken for 20 min at 25˚C. The adsorption reaction was ended by filtration and measuring the absorbance of the unretained dye solution at $\lambda_{max} = 417$ nm.

The effect of initial dye concentration on the adsorption of reactive yellow 145 A dye by the (HTAB-AC) adsorbent was studied by shaking a 50.0 ± 1.0 mg sample of the adsorbent with 20.0 mL of the dye solution at different initial concentration 60, 100, 120, 150, 180, and 210 mg L^{-1} for 20.0 min at 25˚C. The pH was adjusted to 6.0 ± 0.1 and the absorbance of the unretained dye solution was measured at λ_{max}= 417 nm.

The effect of different interfering substances such as NaCl, KCl, $CaCl_2$, Na_2SO_4, $MgSO_4$, and K_2SO_4 were studied by adding a 20.0 mL solution of the dye at different initial concentration (120, 150, and 180 mg L^{-1}) to a 20.0 ± 1.0 mg of different interfering salts. The pH of the dye solution was adjusted to 6.0 ± 0.1. This mixture was added to a 50.0 ± 1.0 mg of (HTAB-AC) adsorbent and shaken for 20.0 min at 25℃. The absorbance of the unretained dye solution was measured at $\lambda_{max} = 417$ nm.

The effect of temperature was also investigated using 20.0 mL of 120 and 180 mg L^{-1} of the dye solutions adjusted to five different temperature values (10, 20, 30, 40, and 50 ± 1.0℃). The dye solution was then added to the optimum (HTAB-AC) sorbent dose (25 ± 1.0 mg) and optimum pH solution (pH 1.0) and was shaken for 20 min. The procedure was completed as described above.

The efficiency of (HTAB-AC) adsorbent for removal of reactive yellow 145 A dye was also tested using real industrial wastewater, tap water, and sea water samples. The selected sample volume was 50.0 mL and this was adjusted to the optimum pH 1.0 condition. The adsorbent dose was selected as 62.5 ± 1.0 mg and the shaking time was 20.0 min. After equilibrium, the final concentration (C_e) was measured by finding out the absorbance at $\lambda_{max} = 417$ nm. All experiments were carried out in triplicate and the mean values are calculated. The percentage removal values of dye were calculated using the Eq. (1).

$$\text{Removal efficiency}\,(\%) = \frac{C_o - C_e}{C_o} \times 100 \tag{1}$$

where C_o and C_e are the initial and equilibrium concentrations of the dye expressed in mg L^{-1}, respectively. The amount of adsorbed dye per unit mass of (HTAB-AC) adsorbent at equilibrium, q_e (mg g^{-1}) was calculated from Eq. (2).

$$q_e = \frac{C_o - C_e}{W/V} \tag{2}$$

where V is the volume of dye solution (L) and W is the mass of (HTAB-AC) sorbent (g) added to the volume V.

3. Results and discussion

3.1. Characterization of adsorbent

A SEM was used for characterizing the surface morphology of various adsorbents. Fig. 1(a)–(c) show the SEM-images of free AC as well as (HTAB-AC) and (HTAB-AC) loaded with the dye, respectively. The AC adsorbent was characterized by a large number of surface pores with different particle sizes as shown in Fig. 1(a). Fig. 1(b) shows the image of (HTAB-AC) adsorbent and it appears to have a number of homogenous layers of pores that contain the loaded surfactant into these pores. Therefore, a good possibility for the adsorption and trapping of the dye molecules into these pores will be much greater than those of the AC sorbent as represented in Fig. 1(c). In addition, the surface of (HTAB-AC) loaded with the dye was identified as smoother and brighter than that of the (HTAB-AC) adsorbent itself. This behavior was attributed to the aggregation of the dye molecules into the surfactant pores leading to the formation of a complex species with the ionic dyes through chemical interaction [25].

The FT-IR spectra of the AC, modified activated carbon (HTAB-AC), and (HTAB-AC) loaded with the dye were acquired in the range of 400–4,000 cm^{-1} as represented in Fig. 2 in order to explore the loaded surface functional groups. As shown in Fig. 2(a), the spectrum of AC displayed a number of peaks referring to the complex nature of the adsorbent. The band centered at 3,422 cm^{-1} is mainly due to the O–H stretching vibration, which is probably attributed to surface-adsorbed water molecules on AC [26,27]. The observed band at 2,914 cm^{-1} is assigned to aliphatic CH stretching. The peak at 1,630 cm^{-1} is ascribed to the formation of oxygen functional group due to a highly conjugated C=O stretching in carboxylic groups [28]. The assigned band at 1,430 cm^{-1} indicates the presence of δ(C–H) owing to the presence of methyl group. The frequency range of 611–1,000 cm^{-1} may be used to refer to the =C–H band in alkenes. The peak at 1,115 cm^{-1} indicates the presence of S=O group [29]. Most of the above-assigned peaks were also found to exist in the FT-IR spectrum of (HTAB-AC) adsorbent (Fig. 2(b)) and can be used to account for the same major functional groups. However, the simple comparison of Fig. 2(c) with (b) reveals that some of the listed peaks were either shifted or disappeared due to adsorption of the dye molecules on the surface of (HTAB-AC) adsorbent. In addition, some other peaks (2,320–2,918 cm^{-1}) were identified in Fig. 2(c) due to the contribution of the adsorbed surfactant moiety in the form of a C–C group. Thus, such observed variations in the infrared peaks assignment are mainly related to the direct involvement and participation of surface functional groups in the adsorption process of reactive yellow 145 A dye by (HTAB-AC) adsorbent.

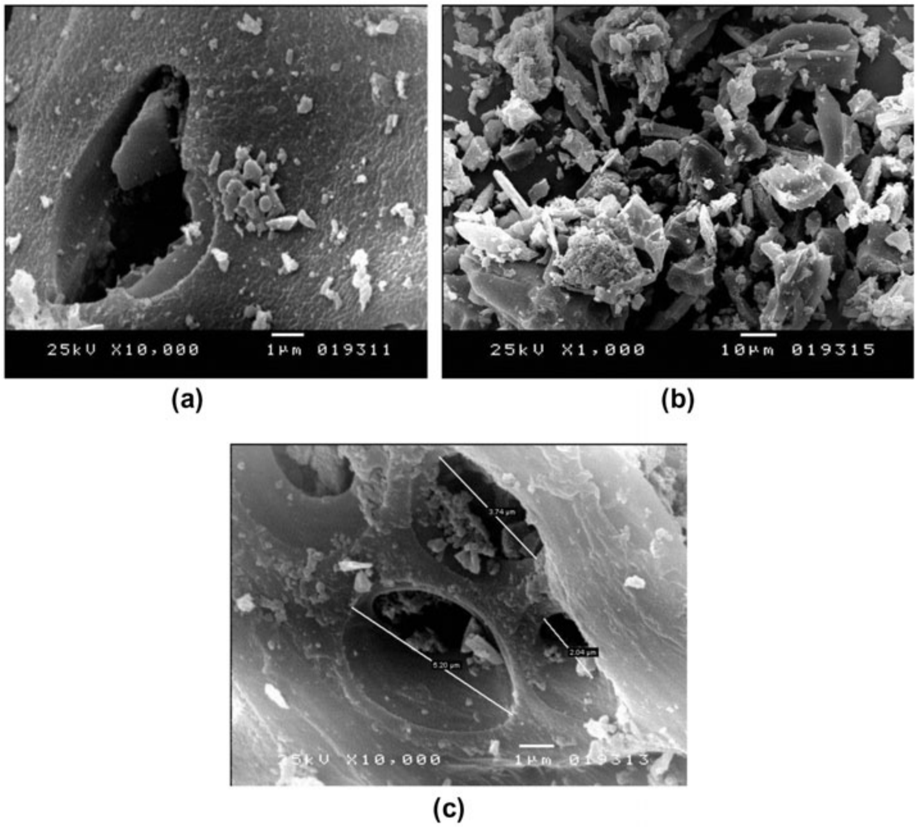


Fig. 1. SEM images of (a) AC, (b) (HTAB-AC) adsorbent and (c) (HTAB-AC) adsorbent-loaded-dye.

3.2. *Sorption of reactive yellow 145 A dye by (HTAB-AC) adsorbent*

3.2.1. *Effect of contact time*

The effect of contact time (1.0–60.0 min) on the percentage extraction values of reactive yellow 145 dye was investigated using two different initial dye concentrations, 90 and 150 mg L^{-1}, and the results of this study are shown in Fig. 3. The efficiency of dye removal by (HTAB-AC) adsorbent was found to proceed via two steps. The first is mainly related to the gradual and rapid increase in the removal values with the increase in the time of reaction due to the high availability of surface functional groups as well as the existence of a high number of active surface pores for dye adsorption. This initial step was found to require ~20.0 min for removal of ≥90.0% of the dye by (HTAB-AC) adsorbent. It is important also to report that the adsorptive interaction and removal of reactive yellow 145 dye by (HTAB-AC) adsorbent was very rapid judging from the percentage removal values (≥77%) based on only one minute of contact time. The second step was found to start at time >20 min and this step was characterized by reaching the equilibrium condition due to a complete surface saturation with dye molecules. In addition, the remaining vacant sites are difficult to occupy due to possible repulsion between the various interacting molecules [30].

3.2.2. *Effect of solution pH*

The effect of pH on the removal efficiency of dye material from aqueous or nonaqueous solutions plays an important role in determining the adsorption capacity. The effect of initial pH of dye solution on the percentage removal of dye was studied by varying the initial pH values in the range of 1.0–13.0. The selected initial dye concentrations were 120, 150, and 180 mg L^{-1} and the adsorbent dosage was taken as 50.0 ± 1.0 mg at 25˚C. The results of this study are represented in Fig. 4 and summarized in Table 2. It is clearly shown that the minimum uptake behavior of reactive yellow 145 A dye by (HTAB-AC) adsorbent was identified in pH 7.0 providing the percentage range of 88.5–92.5%. In addition, the maximum dye removal by (HTAB-AC) adsorbent was established in the presence of strongly acidic solution (pH 1.0) as

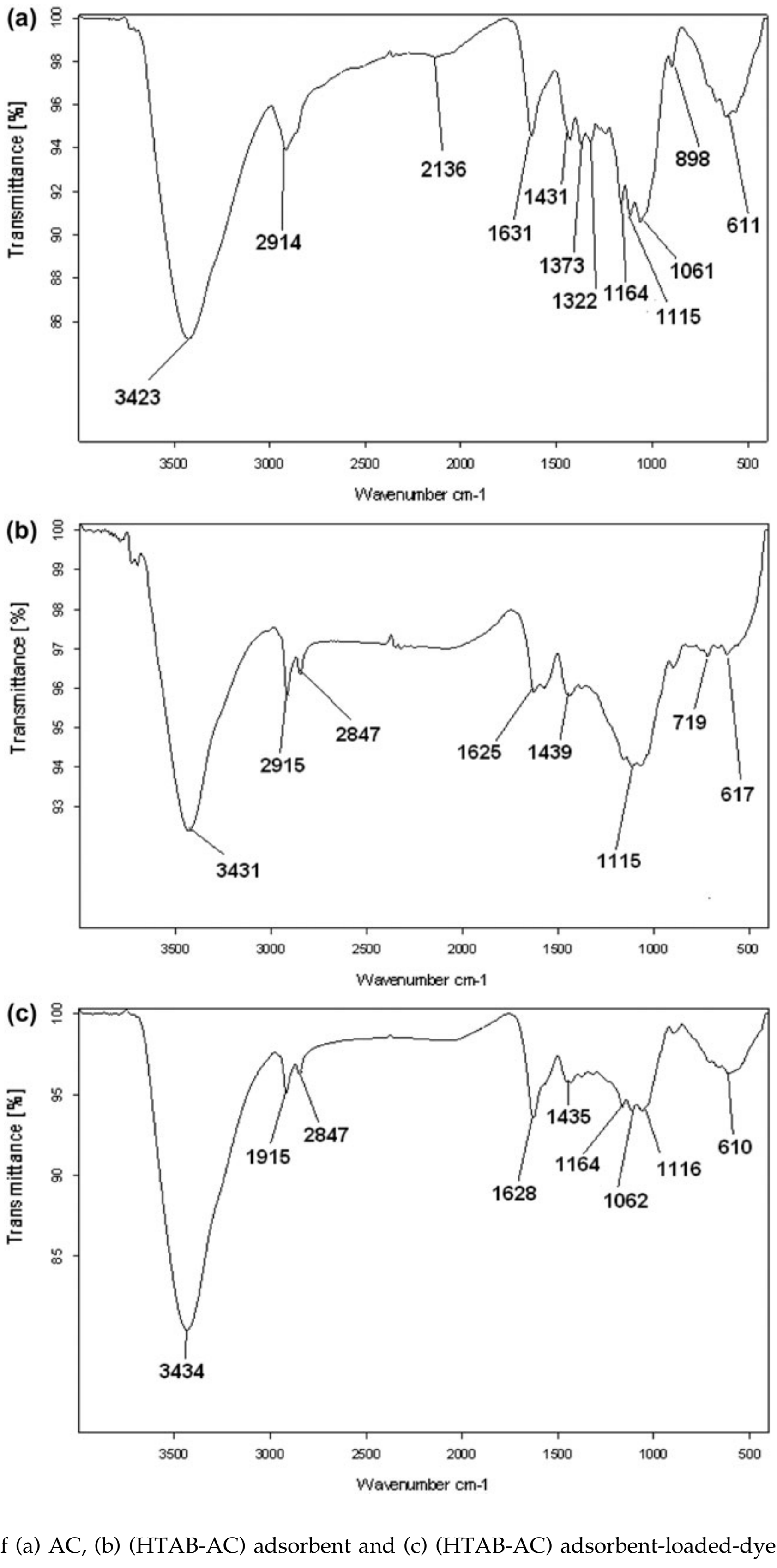


Fig. 2. FT-IR spectra of (a) AC, (b) (HTAB-AC) adsorbent and (c) (HTAB-AC) adsorbent-loaded-dye.

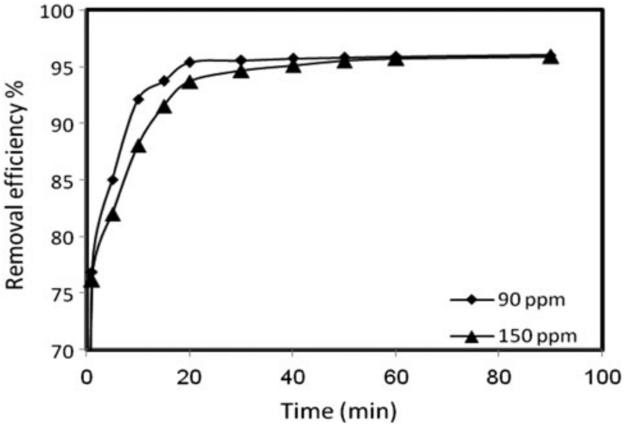


Fig. 3. Effect of reaction time on the removal efficiency (%) of reactive yellow 145 A dye by (HTAB-AC) adsorbent.

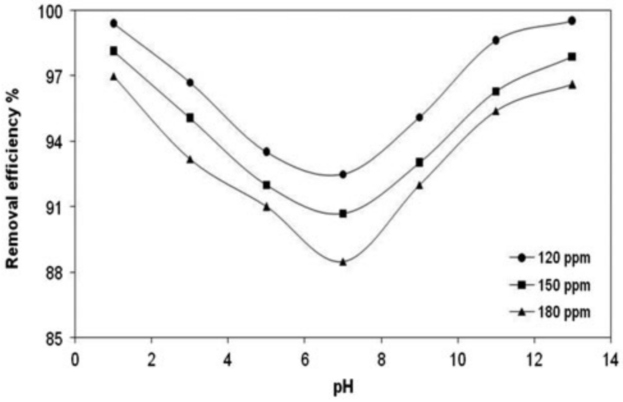


Fig. 4. Effect of solution pH on the removal of reactive yellow 145 A dye by (HTAB-AC) adsorbent.

Table 2
Effect of solution pH on the percentage removal of reactive yellow 145 A dye by (HTAB-AC) adsorbent

	Efficiency of dye removal (%)		
pH	120 (mg L^{-1})	150 (mg L^{-1})	180 (mg L^{-1})
1.0	99.4	98.1	96.9
7.0	92.5	90.7	88.5
13.0	99.5	97.9	96.6

well as strongly basic solution with percentage values corresponding to 96.9–94.6 and 96.6–99.5%, respectively. The higher uptake values in strongly acidic solutions may be explained in terms of complex formation between the adsorbed reactive yellow 145 dye and surface-loaded functional groups of the cationic surfactant through anion exchange mechanism. The surface-loaded counter bromide ion was also expected to be exchanged by the dye negatively charged sulfonate moiety. In addition, the surface of (HTAB-AC) adsorbent in such low pH condition is highly protonated or positively charged and this allows the non-bonded excessive sulfonate group to react with the positively charged (HTAB-AC) adsorbent for the formation of ion pair interaction [31]. On the other hand, the efficiency of dye removal was found to increase with the increase in pH up to a range of 11.0–13.0 and this can be attributed to the presence of basic medium that causes the surface coverage of (HTAB-AC) adsorbent with OH^- groups. In this case, anion exchange is the dominating mechanism by the reaction of surface-loaded OH^- and surface-loaded counter bromide ion by the dye sulfonic groups. However, the lower percentage values of dye removal were detected in neutral pH values in which the surface of (HTAB-AC) adsorbent is also neutral. Such lower percentage of dye removal in neutral solution may be attributed to the formation of zwitter ion of reactive yellow 145 dye in water and this may increase the aggregation of dye molecules to form a bigger dimer molecular form and become unable to enter into the pore structure of the adsorbent surface [32].

The results of this study were also confirmed by determination of the COD values of the dye solution before and after extraction by (HTAB-AC) adsorbent. The COD values of the dye solutions in the presence of pH 1, 7, and 13 were found to produce the percentage extraction values of 93.9, 89.6, and 92.4%, respectively.

3.2.3. *Effect of adsorbent dosage*

The effect of adsorbent dosage on the removal of reactive yellow 145 A dye by (HTAB-AC) was studied by varying the adsorbent dosage in the range of 5.0–50.0 mg and keeping the initial concentration of dye at 120, 150, and 180 mg L^{-1} and pH 1.0. The selected shaking time was adjusted to 20.0 min at 25˚C. The results of adsorbent dosage at optimum pH 1.0 are graphed in Fig. 5 and listed in Table 3. It is evident that the adsorption percentage values of reactive yellow 145 A dye by (HTAB-AC) adsorbent were found to increase with the increase in adsorbent dosage. This trend is mainly due to the increase in adsorbent surface area as well as the high availability of more accessible adsorption sites on the surface of (HTAB-AC) adsorbent [33]. The outlined results refer to a 25.0 mg as the optimum adsorbent dosage. However, the detected adsorbed amounts of dye per

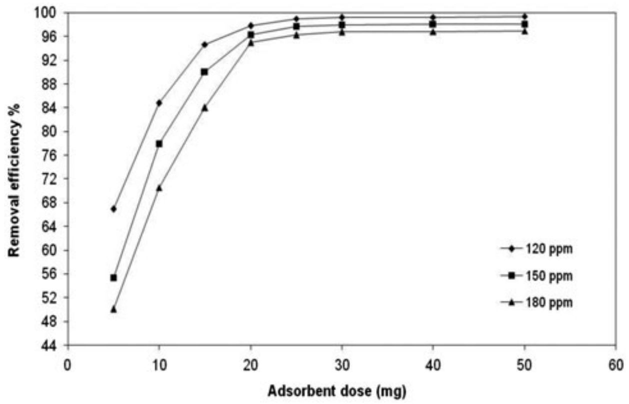


Fig. 5. Effect of adsorbent dosage on adsorption efficiency of reactive yellow 145 A dye by (HTAB-AC) adsorbent at pH 1.0.

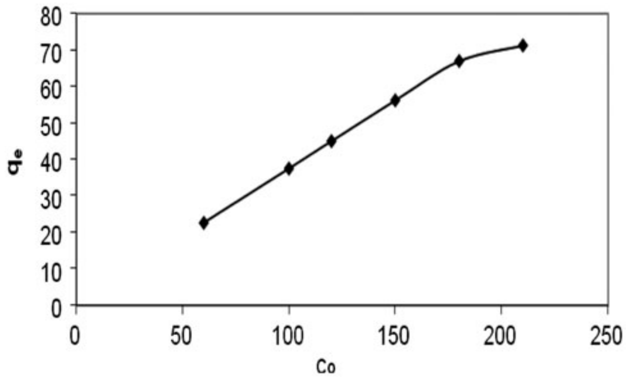


Fig. 6. Effect of initial dye concentration C_o (mg L^{-1}) on adsorption capacity q_e (mg/g) of reactive yellow 145 A dye by (HTAB-AC) adsorbent.

Table 3
Effect of adsorption dosage on the percentage removal of reactive yellow 145 A dye by (HTAB-AC) adsorbent at pH 1.0

	Efficiency of dye removal (%)		
Adsorbent dose (mg)	120 (mg L^{-1})	150 (mg L^{-1})	180 (mg L^{-1})
5	66.92	55.4	50.10
10	84.80	78.0	70.5
15	94.7	90.04	84.0
20	97.80	96.3	95.0
25	99.00	97.71	96.27
30	99.19	98.01	96.75
40	99.25	98.1	96.8
50	99.38	98.11	96.98

unit mass of adsorbent are expected to decrease with the increase in adsorbent dosage. This behavior may be due to the presence of excessive number of active surface functional groups compared to the limited number of dissolved molecules of reactive yellow 145 A dye [34].

3.2.4. Effect of initial dye concentration

The effect of initial dye concentration on the adsorption efficiency of (HTAB-AC) was investigated and evaluated using various concentration values (60, 100, 120, 150, 180, and 210 mg L^{-1}) and the results of this study are shown in Fig. 6. The identified percentage values of dye removal were found to slightly decrease by a range of ≤1.0–3.0% with the increasing in the initial dye concentration. However, the actual amount of dye adsorbed per unit mass of (HTAB-AC) adsorbent was found to increase with the increase in the initial dye concentration. This behavior is mainly due to the decrease in resistance to the uptake of dye molecules by the adsorbent. In addition, the increase in the initial dye concentration provides an important driving force to overcome the mass transfer resistance of dye between the aqueous and solid surface.

3.2.5. Effect of different interfering substances

The effect of some cations such as Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, and SO_4^{2-} on the removal process of reactive yellow 145 dye by (HTAB-AC) adsorbent was also examined under the optimum conditions and the results of this study are listed in Table 4. Generally, the adsorption of negatively charged dye molecules on positively charged modified activated carbon was found to increase by the addition of salt. Due to the formation of a precipitate with the Ca^{2+} ion, the results of this interfering ion were not listed in Table 4. The significant increase in the percentage removal of

Table 4
Effect of interfering inorganic salts on the percent extraction of reactive yellow 145 A dye by (HTAB-AC) adsorbent

	Removal efficiency (%)			
Interfering salts	90 (mg L^{-1})	120 (mg L^{-1})	150 (mg L^{-1})	180 (mg L^{-1})
NaCl	97.9	96.8	95.9	94.7
KCl	96.5	95.3	94.6	93.2
Na_2SO_4	99.5	98.5	97.2	96.8
$MgSO_4$	99.6	98.2	97.0	96.7
In absence of salt	94.4	93.6	93.2	92.9

dye after salt addition may be attributed to the increase of dimerization of reactive dyes in solution. The effect of salt on the dimerization of reactive dyes has been extensively investigated by Alberghina and coworkers [35]. A number of intermolecular forces have been suggested to explain such dimerization process and these forces include the ion dipole as well as the dipole–dipole interactions and van der Waals forces which occur between dye molecules in the solution. It was also reported that an increase in these types of forces may occur upon the addition of salt to the dye solution [35]. Accordingly, the higher adsorption capacity of reactive dyes under these conditions may be attributed to the dimerization of dye molecules induced by the action of salt ions and this behavior leads to an increasing order in the extent of dye sorption on the surface of (HTAB-AC) adsorbent. German-Heins and Flury reported a similar increase in the Brilliant Blue (a reactive dye) adsorption after addition of a salt to the solution [36].

3.3. Adsorption isotherms

The equilibrium adsorption isotherm is one of the most important expressions to understand the mechanism of adsorption systems. Equilibrium isotherm studies were carried out using different initial concentrations of reactive yellow 145 A dye (60–210 mg L^{-1}). In this study, Langmuir and Freundlich models were used to interpret the experimental data. The Langmuir isotherm theory is based on the assumption that adsorption on a homogeneous surface, i.e. the surface consists of identical sites, equally available for adsorption with equal energy of adsorption, and thus the adsorbent is saturated after surface coverage with one layer of adsorbate molecules [37]. The linearized form of Langmuir adsorption isotherm is given by Eq. (3).

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \tag{3}$$

where q_e (mg g^{-1}) and C_e (mg L^{-1}) are the amounts of adsorbed dye per unit mass of adsorbent and dye concentration in solution at equilibrium, respectively. Q_o is the maximum amount of adsorbed dye per unit mass of adsorbent to form a complete monolayer on the surface bound at high C_e (mg g^{-1}), and b (L mg^{-1}) is a constant related to the affinity of binding sites on the adsorbent surface.

The linear plot of C_e/q_e vs. C_e (Fig. 7(a)) refers to the suitability of Langmuir isotherm model in explaining the adsorption process of reactive yellow 145 A dye by (HTAB-AC) adsorbent and proves a monolayer

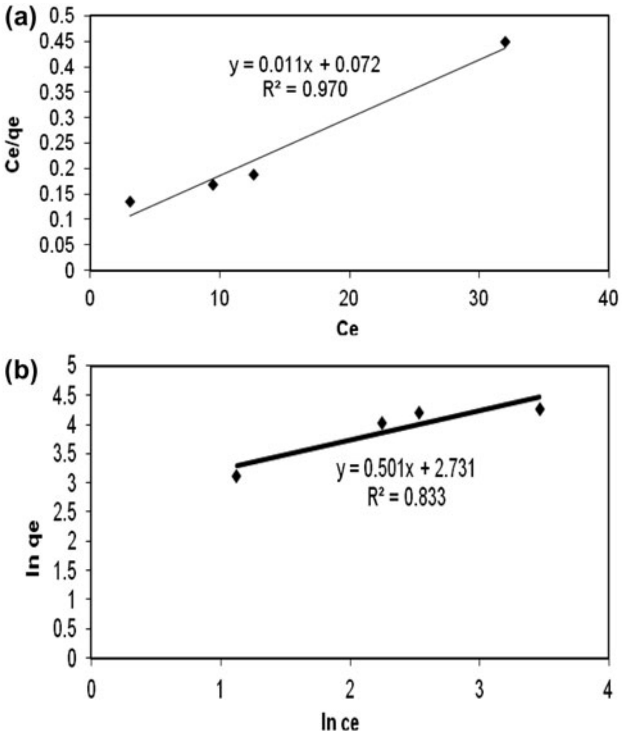


Fig. 7. (a) Langmuir isotherm and (b) Freundlich isotherm plots for adsorption of reactive yellow 145 A dye by (HTAB-AC) adsorbent.

coverage behavior. The Q_o and b values are given in Table 5 and these two values were determined from the slope and intercept, respectively, of the linearized plot of Langmuir isotherm. The correlation coefficient value, R^2, obtained from the linear plot of Fig. 7 was found very close to the unity and this represents an additional evidence for the applicability of the Langmuir isotherm model for describing the removal of reactive yellow 145 dye by (HTAB-AC) adsorbent. The essential characteristics of Langmuir isotherm can be expressed in terms of dimensionless separation factor of equilibrium parameter defined by Eq. (4) [38].

$$R_L = \frac{1}{1 + bC_o} \tag{4}$$

where C_o represents the initial concentration of dye (mg L^{-1}) and b the Langmuir constant related to adsorption energy (L mg^{-1}). The R_L value implies that the shape of the isotherm will be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$). As listed in Table 5, the R_L values at different concentrations were identified in the range of 0–1, and this indicates a favorable shape of the Langmuir isotherm model.

The Freundlich equilibrium adsorption isotherm was also implemented in this study to describe the adsorption data. The Freundlich isotherm model is derived by assuming a heterogeneous adsorption approach due to the diversity of active sites on the surface and it is generally expressed in the linear form as given by Eq. (5).

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{5}$$

where K_F (L mg^{-1}) and n are the isotherm constants which are related to the capacity and intensity of the adsorption, respectively. The linear plot of ln q_e vs ln C_e (Fig. 7 (b)) indicates that the adsorption of reactive yellow 145 A dye by (HTAB-AC) adsorbent is following the Freundlich isotherm. The Freundlich adsorption isotherm constant and correlation coefficients are listed in Table 5. The calculated value of $1/n$ from the Freundlich isotherm was found in the range 0–1 and this indicates that the reactive yellow 145 dye is favorably adsorbed by (HTAB-AC) adsorbent under all examined concentration values.

Thus, the adsorption data reveal that the Langmuir model is very suitable for describing the adsorption of reactive yellow 145 dye by (HTAB-AC) adsorbent. This conclusion is based on the R^2 (0.9709) which is higher than the corresponding R^2-value (0.8337) of the Freundlich isotherm.

3.4. Effect of temperature

Temperature is an important parameter in the adsorptive removal process of dyes from their solutions and matrices. Therefore, a study was made to evaluate the contribution of reaction temperature on the adsorption behavior of reactive yellow 145 A dye by (HTAB-AC) adsorbent at five different temperature values (10, 20, 30, 40, and 50°C). The change in adsorption reaction temperature value was found to exhibit a slight effect on the adsorption process of reactive yellow 145 A dye by (HTAB-AC) adsorbent. This trend indicates that the adsorption process is independent on the reaction temperature as well as the progress of reactive yellow 145 A dye removal by (HTAB-AC) adsorbent. This conclusion refers to the validity of using (HTAB-AC) adsorbent for adsorption of reactive yellow 145 dye under the specified temperature range (10–50°C).

3.5. Kinetics of Adsorption

The rate constants for adsorption of reactive yellow 145 A dye by (HTAB-AC) adsorbent were also determined in this study using the Lagergren first-order model which is generally expressed by Eq. (6).

$$\ln (q_e - q_t) = \ln q_e - k_1 t \tag{6}$$

where k_1 is the first-order-rate constant which is identified from the slope of the plot $\ln (q_e - q_t)$ vs. time as represented in Fig. 8. The determined correlation

Table 5
Freundlich and Langmuir parameters

	Langmuir				Freundlich		
Adsorbent	Q_o (mg g^{-1})	b (L mg^{-1})	R_L	R^2	K_F (mg g^{-1})	n	R^2
MAC	87.71	0.1583	(0.095–0.292)	0.970	15.35	1.99	0.8337

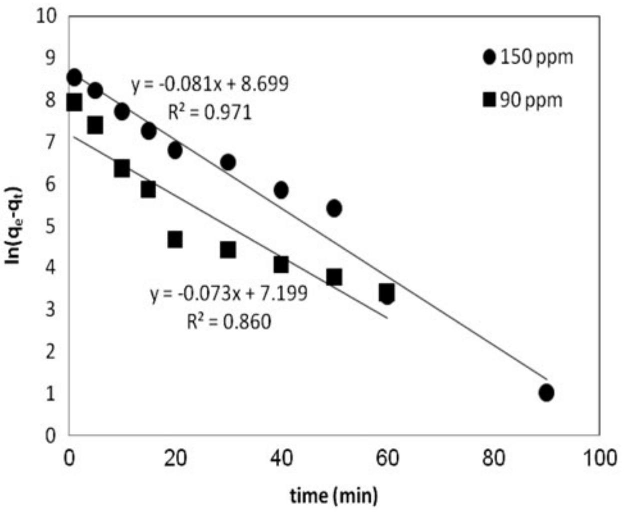


Fig. 8. Pesudo-first-order kinetics for adsorption of reactive yellow 145 A dye by (HTAB-AC) adsorbent.

coefficients by the first-order-kinetic model were of smaller values for all examined concentrations. In addition, the estimated q_e values based on the first-order model equation were greatly different from the experimental values (Table 6). These results indicate that the model is not applicable to describe the adsorption process. Therefore, the adsorption kinetics were explained by the pseudo-second-order model as given by Eq. (7) [39].

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{7}$$

where k_2 is the second-order-rate constant ($\text{g mg}^{-1}\,\text{min}^{-1}$). The values of k_2 at different initial dye concentrations were calculated from the slope of the respective linear plots of t/q_t vs. t (Fig. 9). The correlation coefficients were found in the range 0.999–1.000, suggesting a strong relationship between the various parameters as well as explaining the pseudo-second-order kinetics of the adsorptive removal of reactive yellow 145 A dye by (HTAB-AC) adsorbent.

3.6. Intraparticle diffusion model

The adsorbate species are most probably transported from the bulk of solution into the solid phase through intraparticle diffusion transport process, which is often known as the rate-limiting step in many adsorption processes, especially in a rapidly stirred batch reactor. Thus, the dye molecules are also probably transported from its aqueous solution to the surface of (HTAB-AC) adsorbent by the intraparticle diffusion. Therefore, the intraparticle diffusion is another important kinetic factor that must be evaluated to study the rate of dye adsorption onto (HTAB-AC) adsorbent. The possibility of this process was explored using the intraparticle diffusion model, which is commonly expressed by Eq. (8) [40,41].

$$q_t = k_{id}^{t^{1/2}} + C \tag{8}$$

where C (mg g^{-1}) is the intercept and k_{id} is the intraparticle diffusion rate constant expressed in $\text{mg g}^{-1}\,\text{min}^{-1/2}$. The values of q_t were found to be linearly correlated with the values of $t^{1/2}$ and the rate constant k_{id} was directly evaluated from the slope of the straight line (Fig. 10). The values of intercept C (Table 6) provide information about the thickness of the boundary layer whereas the resistance to the external mass transfer increases as the intercept increase. The constant C was found to increase with the increase in the dye concentration and this behavior may be attributed to the increase in thickness of the boundary layer. Therefore, the chance of the external mass transfer decreases and hence the chance of internal mass transfer increases. The R^2 values are close to unity as given in Table 6 and this refers to the potential applicability of this model for the adsorptive removal of reactive yellow 145 A dye by (HTAB-AC)

Table 6
Adsorption kinetic models and parameters for adsorption of reactive yellow 145 A dye by (HTAB-AC) adsorbent

		Pesudo first-order kinetic model			Pesudo second-order kinetic model			Intra-particle diffusion model		
C_o (mg L^{-1})	q_e (mg g^{-1}) (Exp.)	q_e (mg g^{-1}) (Calc.)	k_1 (min^{-1})	R^2	q_e (Calc.) (mgg^{-1})	k_2(g mg^{-1} min^{-1})	R^2	k_{id} (mg g^{-1} $\text{min}^{-1/2}$)	C	R^2
90	34.56	15.81	0.073	0.86	35.71	0.071	1	1.25	27.86	0.81
150	58.46	500	0.081	0.97	58.82	0.024	0.99	2.29	44.59	0.92

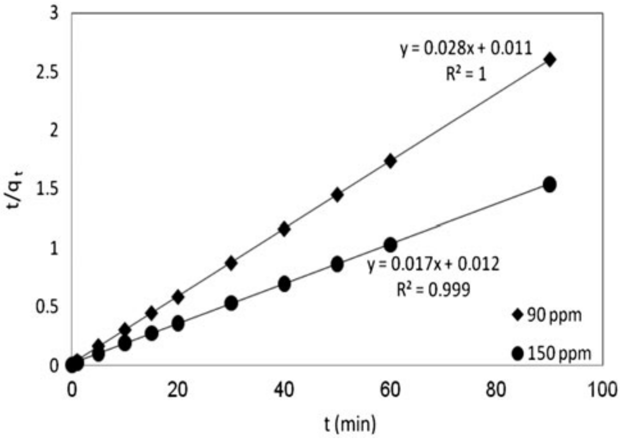


Fig. 9. Pesudo-second-order kinetics for adsorption of reactive yellow 145 A dye by (HTAB-AC) adsorbent.

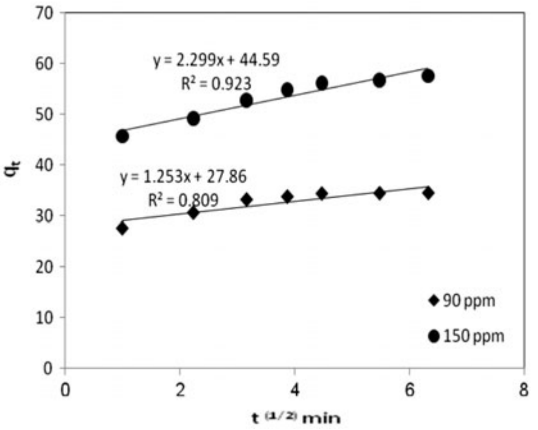


Fig. 10. Intraparticle diffusion plot for adsorption of reactive yellow 145 A dye by (HTAB-AC) adsorbent.

adsorbent. This may also confirm that the rate-limiting step is the intraparticle diffusion process and the linearity of the plots demonstrate that the intraparticle diffusion process played a significant role in the uptake of reactive yellow 145 A dye by (HTAB-AC) adsorbent.

3.7. Application to real samples

In order to examine the reliability and validity of the proposed methodology for removal of reactive yellow 145 A dye from various water samples by (HTAB-AC) adsorbent, a study was made and applied to evaluate the potential extraction process of reactive yellow A 145 from real industrial wastewater, tap water, and sea water samples. For this purpose, 50.0 mL of the selected sample was treated under optimum pH conditions, adsorbent dosage, and shaking time. The results of this study are compiled in Table 7 and clearly show the excellent efficiency of (HTAB-AC) adsorbent for adsorptive removal of reactive yellow

Table 7
Removal of reactive yellow 145 A dye from selected real water samples by (HTAB-AC) adsorbent

Sample	pH	Extraction efficiency (%)*
Real wastewater	1.0	97.4
	9.5	90.2
Spiked tap water	1.0	97.6
	7.5	91.2
Spiked sea water	1.0	96.5
	7.9	92.6

*Percentage extraction values are based on triplicate analysis with standard deviation in the range 0.5–1.0%.

Table 8
Comparison of the evaluated (HTAB-AC) adsorbent versus others

Adsorbents	AC-HTAB	Fly ash	Mycelium pellets of penicillium oxalicum	Pine needles	Bentonite	Activated carbon from waste tea
Dye	RY 145	RY 145	RY 145	RY 145	Congo red	RY 120
Optimum time	20 min	60 min	80 min	90 min	90 min	200 min
Optimum adsorbent dose	25 mg	600 mg	200 mg	800 mg	100 mg	200 mg
Working pH	1–13	2–8	2–10	2–10	5–10	2–12
Optimum pH	1 & 13	6	2	2	5	2
Adsorbed dye per adsorbent mass	58.8 mg g^{-1}	3–3.6 mg g^{-1}	137.0 mg g^{-1}	7.2 mg g^{-1}	37.1 mg g^{-1}	50.0 mg g^{-1}
Reference	This work	[42]	[43]	[44]	[45]	[46]

145 A dye from real industrial wastewater, spiked tap water, and sea water samples. The determined percentage recovery and extraction values of reactive yellow 145 A dye were found to correspond to 92.6–97.6% and 90.2–92.6% in adjusted pH 1.0 and real pH values of water samples, respectively.

The collected results from this study confirm the superiority of (HTAB-AC) adsorbent for removal of reactive yellow 145 A dye from various real water samples and the advantages of this adsorbent are compared with other previously reported adsorbents as listed in Table 8.

4. Conclusion

In this study, (HTAB-AC) was identified as a superior effective adsorbent for water treatment from reactive yellow 145 dye via adsorption process. The studied dye was optimally extracted from both strongly acidic (pH 1.0–2.0) and strongly basic (pH 13.0) aqueous solutions. The anion exchange and ion–ion interaction mechanisms were proposed in strongly acidic solution, while only anion exchange mechanism was suggested in strongly basic aqueous solutions. The adsorptive interaction processes between reactive yellow 145 A dye and (HTAB-AC) adsorbent were studied and evaluated by various isotherm models and found to better fit with the Langmuir model. Different adsorption kinetics were studied and the applied models showed that the adsorption process is based on a pseudo-second-order reaction. Excellent percentage removal values (>90.0%) of reactive yellow 145 A dye from real water samples by (HTAB-AC) adsorbent were also accomplished in this study using the optimum conditions.

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