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Adsorption Equilibrium and Kinetics of Reactive Black 5 and Reactive Red 239 in Aqueous Solution onto Surfactant-Modified Zeolite

Dogan Karadag,[†] Mustafa Turan,^{*,‡} Eda Akgul,[†] Sema Tok,[†] and Ayşegül Faki[‡]

Department of Environmental Engineering, Yildiz Technical University, 34669, Istanbul, Turkey, and Department of Environmental Engineering, Istanbul Technical University, 34469, Istanbul, Turkey

The adsorption of Reactive Black 5 and Reactive Red 239 in aqueous solution on cetyltrimethylammonium bromide (CTAB)–zeolite was studied in a batch system. The natural zeolite and CTAB-modified zeolite were characterized by FT-IR and SEM analysis. Experiments were performed at different conditions such as initial dye concentration, contact time, temperature, and pH. CTAB modification covered the zeolite surface with positive charges, and the adsorption capacity of zeolite increased. The adsorption capacity of Reactive Red 239 was found to be two times higher than Reactive Blue 5 due to the hydrophilicity of the dye molecules. The Langmuir and Freundlich adsorption models were applied to describe the equilibrium isotherms at different temperatures, and the Freundlich agrees very well with the experimental data. The pseudo-second-order model provided a very good fitting ($R^2 > 0.992$) for the two anionic dyes. The calculated maximum adsorption capacity ($q_{e,calcd}$) increased with increasing initial dye concentration, but there is no linear relationship with pH and temperature. Thermodynamic parameters such as change in free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0) were also determined.

Introduction

The effluents of textile dyeing processes contain various kinds of synthetic dyestuffs. The dyes are released into the environment in the form of colored wastewater. This can lead to acute effects on exposed organisms due to the toxicity of the dyes, abnormal coloration, and reduction in photosynthesis because of the absorbance of light that enters the water. Therefore, color removal from textile effluents becomes environmentally important.^{1–2} Reactive dyes which are extensively used in dyeing processes contain negatively charged sulfonate azo groups. Because these dyes are highly soluble in water, their removal from wastewater is difficult by conventional coagulation and activated sludge processes.

Adsorption is an efficient and economically feasible process for separation and purification. It plays an important role to remove dyes from wastewater.^{3,4} Activated carbon is the most common adsorbent for the adsorption process because it has a high surface area and a high adsorption capacity, but it is expensive and necessitates regeneration.^{5,6} The need for an alternative low-cost easily available adsorbent has encouraged the search for new adsorbents. Many studies have been performed to find suitable adsorbents to lower dye concentrations in aqueous solutions. They have included peat,⁷ chitin,⁸ chitosan,⁹ fly ash,¹⁰ natural (raw) or modified minerals such as zeolite,¹¹ sepiolite,¹² and the other low-cost adsorbents.^{13,14}

The zeolite framework consists of symmetrically stacked alumina and silica tetrahedra which result in an open and stable three-dimensional honeycomb structure with a negative charge.¹⁵ Adsorption of reactive dyes using raw zeolite is very limited because both the zeolite surface and the dye molecules have negative charges; therefore, cationic surfactants are used to

neutralize the negative charges and increase the electrostatic attraction of anionic dye molecules to the zeolite surface.^{16,17}

In this paper, a cationic surfactant cetyltrimethylammonium bromide (CTAB) was used for the surface modification of natural (raw) zeolite, and the adsorption equilibrium and adsorption kinetics of two anionic dyes, named Reactive Black 5 and Reactive Red 239 from aqueous solutions onto CTAB–zeolite, were studied.

Experimental Section

Mineral and Chemicals. The zeolite mineral used in the experiments was received from the Incal Company in Manisa, Turkey. It was crushed, ground, and sieved to (0.6 to 1.0) mm. The zeolite has the following properties: cation exchange capacity of (1.9 to 2.2) meq·g⁻¹, pore diameter of 4 Å, purity of 92 %, bed porosity of 40 %, density of 2.15 g·cm⁻³. The surface area of zeolite was measured as 11.8 m² by the BET method using nitrogen gas.¹⁷

The anionic dyes, Reactive Black 5 (Everzol Black B) and Reactive Red 239 (Everzol Red 3BS), were supplied by the Everlight Chem. Ind. Corp. of Taipei. The chemical structures of the dyes are illustrated in Figure 1. They are all known to contain anionic sulfonate groups to various degrees.

Preparation of CTAB–Zeolite. A cationic surfactant cetyltrimethylammonium bromide (CTAB, CH₃(CH₂)₁₅N⁺(CH₃)Br⁻) was used for the surface modification of the zeolite. CTAB was from purchased Merck and specified to be of 99 % purity with a molecular weight of 346.46 g. A 2·10⁻² M CTAB solution was prepared by dissolution of an appropriate amount of CTAB in distilled water and contacted with 70 g of the raw zeolite. The mixture was stirred at room temperature for 3 h at 350 rpm. The CTAB–zeolite was separated from the mixture by filtration, washed with distilled water, and dried at 100 °C for 3 h. Raw and CTAB–zeolite were examined using FT-IR and SEM analysis. FT-IR spectra and SEM were obtained using a Perkin-Elmer Model FT-IR spectrometer and JIM (5410 LV) scanning electron microscopy, respectively.

* Corresponding author. Email: mturan@ins.itu.edu.tr. Tel.: +90-212-2856568. Fax: +90-212-2856587.

[†] Yildiz Technical University.

[‡] Istanbul Technical University.

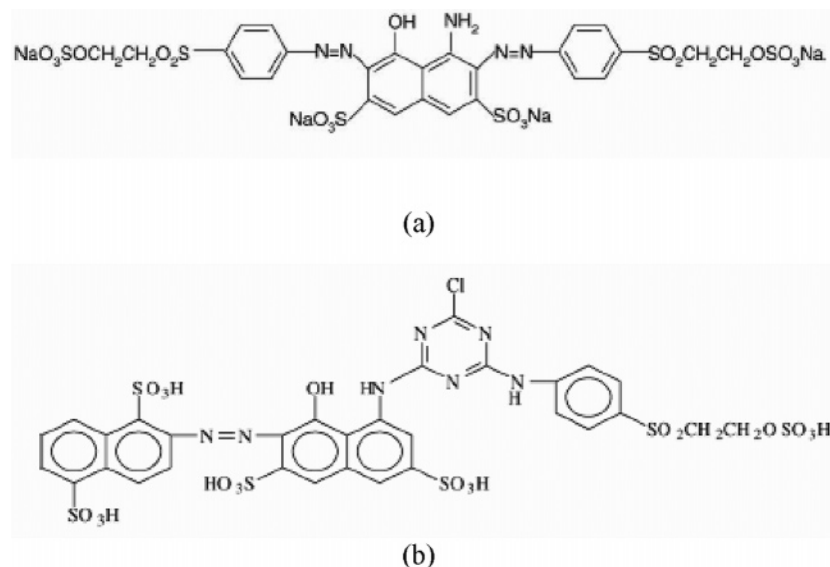


Figure 1. Chemical structure of anionic dyes: (a) Reactive Black 5; (b) Reactive Red 239.

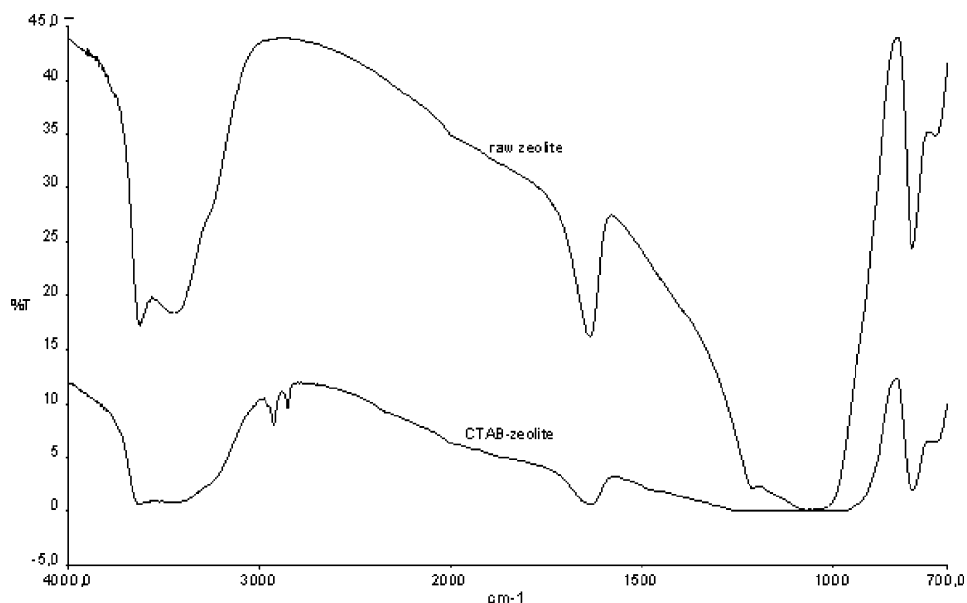


Figure 2. FT-IR spectra of raw and CTAB-zeolite.

Adsorption Experiments. The adsorption of the reactive dyes onto zeolite was carried out using a batch method. The batch tests were conducted by combining 50 mL of dye solution with 0.4 g of raw zeolite and CTAB-zeolite. The bottles were placed on a Gallenkamp orbital shaker and agitated at a constant speed of 180 rpm. The pH was adjusted by adding a small amount of dilute HCl or NaOH solution using a Jenway pH meter. All adsorption experiments were conducted at various time intervals, pH's (3, 7, and 10), and temperatures (30, 35, and 40 °C). The equilibrium concentrations of dyes were determined at (592 and 540) nm for Reactive Black 5 (RB5) and Reactive Red 239 (RR239), respectively, using a Jenway UV/visible spectrophotometer. The calibration curves for each dye at the respective wavelengths were established as a function of dye concentration. The reproducibility of the data varied in the range of $\pm 1.5\%$.

The adsorption capacity or amount of dye adsorbed by zeolite (q_e , $\text{mg}\cdot\text{g}^{-1}$) was calculated by the following formula

$$q_e = (C_i - C_e)V/m \quad (1)$$

where C_i is the initial dye concentration ($\text{mg}\cdot\text{L}^{-1}$); C_e is the

equilibrium or residual dye concentration ($\text{mg}\cdot\text{L}^{-1}$); V is the volume of the solution (L); and m is the mass of adsorbent (g). Distilled and deionized water with a conductivity value of $2\cdot 10^{-6} \text{ S}\cdot\text{cm}^{-1}$ was used in all experiments.

Results and Discussion

FT-IR Spectra. FT-IR spectra of raw and CTAB-zeolite are shown in Figure 2. FT-IR spectra of raw zeolite have four peaks at (795, 1634, 3447, and 3626) cm^{-1} . The peak at 795 is due to Si—O—Si bonds.¹⁸ The band at 3626 cm^{-1} is connected to acidic hydroxyls Si—O(H)—Al. Although the band at 3447 cm^{-1} is characteristic of hydrogen-bonding hydroxyl groups, the band at 1634 cm^{-1} is connected to deformation vibration of absorbed water.¹⁹ Modification with CTAB shifted the peaks at (3626 and 1634) cm^{-1} to (3629 and 1637) cm^{-1} and decreased the intensity of all bands. Modified zeolite shows peaks at (2850 and 2926) cm^{-1} which are characteristic symmetric and asymmetric CH_2 vibrations of CTAB, respectively.²⁰

Adsorption Yields. (a) Effect of Modification. As seen from Figure 3, the adsorption capacities of the two anionic dyes by natural (raw) zeolite were found to be negative. This is attributed

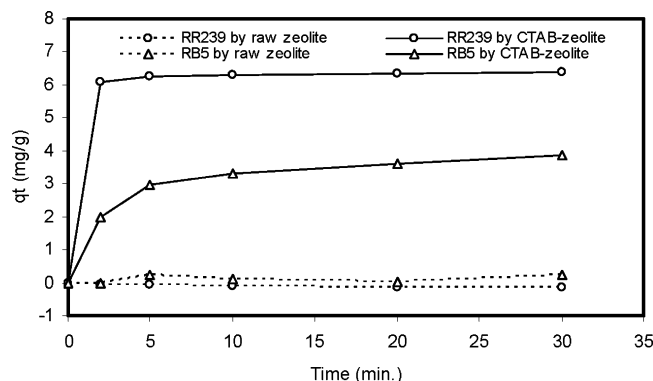


Figure 3. Comparison of anionic dye adsorption by raw and CTAB-zeolite (temperature, 25 °C; pH, 5; C_o , 60 mg·L⁻¹).

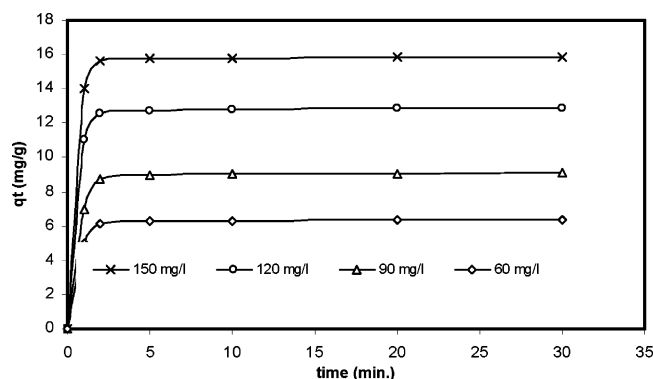


Figure 4. Adsorption kinetics of RR239 on CTAB-zeolite at different initial dye concentrations (pH, 5; temperature, 25 °C).

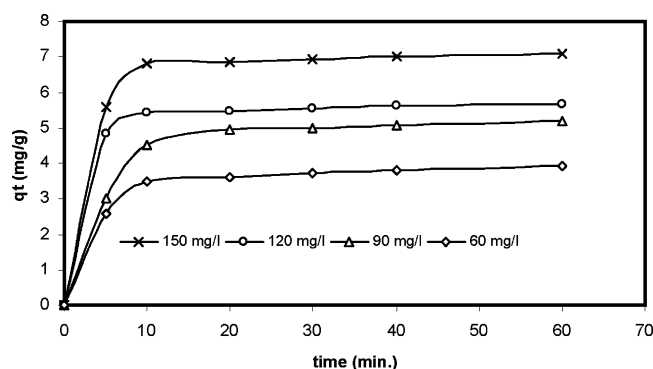


Figure 5. Adsorption kinetics of RB5 on CTAB-zeolite at different initial dye concentrations (pH, 5; temperature, 25 °C).

to the increase in the apparent concentration of dye in the solution because of adsorption of water molecules. Small water molecules are adsorbed easily by zeolite micropores, but large dye molecules are excluded.³ Jimenez et al.²¹ found that the diameter of RB5 (7.87 Å) is larger than the pore size of zeolite (4 Å). CTAB modification covered the zeolite surface with positive charges and increased electrochemical interaction between dye molecules and the zeolite surfaces; therefore, adsorption capacities increased from (0 to 6.36) mg·g⁻¹ for RR239 and from (0.22 to 3.84) mg·g⁻¹ for RB5 after 30 min.

(b) Effect of Initial Concentration and Contact Time. The increase of initial concentration from (60 to 150) mg·L⁻¹ increased adsorption capacities for the two anionic dyes by CTAB-zeolite. RR239 and RB5 reached equilibrium after (2 and 10) min of contact time, respectively (Figures 4 and 5). After the equilibrium time, the increasing rate of adsorption of both anionic dyes decreased, and the amount of dyes adsorbed remained almost the same. These results agree well with the

Table 1. Adsorption Capacities at Equilibrium (q_e) for Anionic Dyes

	RB5	RR239
	mg·g ⁻¹	mg·g ⁻¹
initial dye concentration (T , 25 °C; pH, 5)		
60 mg·L ⁻¹	3.296	6.093
90 mg·L ⁻¹	3.776	8.743
120 mg·L ⁻¹	5.333	12.551
150 mg·L ⁻¹	6.666	15.663
temperature (C_o , 60 mg·L ⁻¹ ; pH, 5)		
30 °C	2.975	6.720
35 °C	2.666	6.510
40 °C	2.332	6.175
pH (T , 25 °C; C_o , 60 mg·L ⁻¹)		
3	3.033	6.018
7	4.099	6.048
10	3.142	6.055

Table 2. Langmuir and Freundlich Isotherm Constants at Different Temperatures and pH for the Adsorption of RB5

	Langmuir				Freundlich		
	R^2	q_{max}	K_L	R_L	R^2	K_F	n
temperature (pH, 5; C_o , (0 to 150) mg·L ⁻¹)							
30 °C	0.934	12.929	0.264	0.059	0.958	2.959	2.181
35 °C	0.987	12.362	0.281	0.056	0.994	2.954	2.307
40 °C	0.933	12.177	0.261	0.060	0.943	2.621	2.033
pH (T , 25 °C; C_o , (0 to 150) mg·L ⁻¹)							
3	0.947	9.635	3.283	0.005	0.964	4.802	3.509
7	0.953	9.941	1.565	0.011	0.973	4.201	2.968
10	0.964	9.891	1.827	0.009	0.977	4.659	3.345

findings of Gucek et al.²² for anionic dye adsorption. Although the adsorption capacity of RB5 for the contact time of 30 min and concentration of 150 mg·L⁻¹ is 6.67 mg·g⁻¹, the capacity of RR239 for the same conditions is 15.66 mg·g⁻¹. This indicates that the adsorption capacity of RR239 is two times higher than that of RB5.

Netpradit et al.²³ stated that two structural factors have important effects on the adsorption efficiency of anionic dyes: (i) a lower amount of sulfonic groups (SO₃⁻) decreases the amount of negative charge and attractive force with positive charges; (ii) positioning SO₃⁻ and NH₂ groups in the same benzenic chain decreases the electrostatic interaction between anionic dyes and positive charges. As can be seen from chemical structures of anionic dyes in Figure 1, RB5 has a lower number of SO₃⁻ groups and has a benzenic chain having NH₂ and SO₃⁻ groups. These two factors lead to lower adsorption capacities of RB5 compared to RR239.

(c) Effect of Temperature and pH. Table 1 shows the equilibrium adsorption capacities of anionic dyes for different experimental conditions. Although an increase in dye concentration has a positive effect on the adsorption of anionic dyes, temperature has a negative effect. The equilibrium adsorption capacities of both RR239 and RB5 decreased from (2.975 and 6.720) mg·g⁻¹ to (2.332 and 6.175) mg·g⁻¹ with an increase in temperature from (30 to 40) °C. Decreasing adsorption capacity with increasing temperature indicates that the adsorption of anionic dyes is controlled by an exothermic reaction. Although the equilibrium adsorption capacity of RB5 showed a maximum at pH 7, the adsorption capacity of RB5 at equilibrium was not influenced from the pH variations.

Equilibrium Isotherms. In this study, the Langmuir and the Freundlich isotherm models were used to describe the equilibrium sorption data. To optimize the design of a sorption system,

Table 3. Langmuir and Freundlich Isotherm Constants at Different Temperatures and pH for the Adsorption of RR239

	Langmuir				Freundlich		
	R^2	q_{\max}	K_L	R_L	R^2	K_F	n
temperature							
(pH, 5; C_o , (60 to 150) $\text{mg}\cdot\text{L}^{-1}$)							
30 °C	0.997	15.942	0.007	0.724	0.991	0.191	1.297
35 °C	0.995	14.875	0.007	0.716	0.992	0.156	1.247
40 °C	0.972	11.020	0.008	0.708	0.967	0.154	1.289
pH							
(T , 25 °C; C_o , (60 to 150) $\text{mg}\cdot\text{L}^{-1}$)							
3	0.988	11.908	0.012	0.602	0.994	0.246	1.360
7	0.990	9.098	0.038	0.303	0.996	0.722	1.869
10	0.966	9.37	0.021	0.447	0.980	0.349	1.508

it is important to establish the most appropriate correlation for the equilibrium curves.

The Langmuir equation is widely used for adsorption equilibria because of its thermodynamical basis. The Langmuir isotherm model assumes monolayer coverage of adsorbate over a homogeneous adsorbent surface, and at equilibrium, a saturation point is reached where no further adsorption can occur.²⁴ The Langmuir isotherm model is expressed as²⁵

$$q_e = q_{\max} K_L C_e / (1 + K_L C_e) \quad (2)$$

The above equation can be rearranged as follows

$$1/q_e = 1/q_{\max} + (1/q_{\max} K_L)(1/C_e) \quad (3)$$

where C_e is the equilibrium concentration ($\text{mg}\cdot\text{L}^{-1}$); q_e is the quantity of dye adsorbed onto zeolite ($\text{mg}\cdot\text{g}^{-1}$); q_{\max} is q_e for a complete monolayer ($\text{mg}\cdot\text{g}^{-1}$), a constant related to sorption capacity; and K_L is the Langmuir constant related to the affinity of the binding sites and energy of adsorption ($\text{L}\cdot\text{mg}^{-1}$).

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems and is expressed by the following equation²⁶

$$q_e = K_F C_e^{1/n} \quad (4)$$

A logarithmic form of the Freundlich equation is given as

$$\log q_e = \log K_F + 1/n \log C_e \quad (5)$$

where K_F ($\text{L}\cdot\text{g}^{-1}$) and n are the Freundlich constants reflecting the adsorption capacity and intensity. K_F and n were calculated from the intercept and slope of the plots.

The type of isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter (R_L) which is defined as²⁷

$$R_L = 1/(1 + K_L C_i) \quad (6)$$

where C_i is the highest initial dye concentration ($\text{mg}\cdot\text{L}^{-1}$). There are four probabilities for the R_L value: (i) for favorable adsorption, $0 < R_L < 1$; (ii) for unfavorable adsorption, $R_L > 1$; (iii) for linear adsorption, $R_L = 1$; (iv) for irreversible adsorption, $R_L = 0$. As seen from Tables 2 and 3, the adsorption of these two anionic dyes on CTAB-zeolite is favorable.^{28,29}

The Langmuir and Freundlich isotherm constants at different temperatures and pH values for the adsorption of RB5 and RR239 are presented in Table 2 and Table 3, respectively. Although both of the adsorption models fit the equilibrium sorption data of RB5 and RR239 (see Figures S1, S2, S3, and S4 in Supporting Information) well, the Freundlich model exhibited a slightly better fit than the Langmuir model. The parameters K_F and q_{\max} are related to adsorption capacity, and

Table 4. Pseudo-Second-Order Adsorption Rate Constants and Calculated q_e and Experimental q_e Values of RR239 for Different Initial Dye Concentrations, Temperatures, and pH

	q_e $\text{mg}\cdot\text{g}^{-1}$	R^2	$q_{e,\text{calcd}}$ $\text{mg}\cdot\text{g}^{-1}$	k $\text{kg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$
initial dye concentration				
(T , 25 °C; pH, 5)				
60 $\text{mg}\cdot\text{L}^{-1}$	6.093	1.000	6.388	1.288
90 $\text{mg}\cdot\text{L}^{-1}$	8.743	1.000	9.132	1.073
120 $\text{mg}\cdot\text{L}^{-1}$	12.551	1.000	12.930	1.048
150 $\text{mg}\cdot\text{L}^{-1}$	15.663	1.000	15.860	2.096
temperature				
(pH, 5; C_o , 150 $\text{mg}\cdot\text{L}^{-1}$)				
30 °C	6.720	1.000	15.526	1.198
35 °C	6.510	1.000	15.394	2.016
40 °C	6.175	1.000	15.649	1.203
pH				
(T , 25 °C; C_o , 150 $\text{mg}\cdot\text{L}^{-1}$)				
3	6.018	1.000	15.853	1.216
7	6.048	1.000	15.887	1.179
10	6.055	1.000	15.532	1.555

Table 5. Pseudo-Second-Order Adsorption Rate Constants and Calculated q_e and Experimental q_e Values of RB5 for Different Initial Dye Concentrations, Temperatures, and pH

	q_e $\text{mg}\cdot\text{g}^{-1}$	R^2	$q_{e,\text{calcd}}$ $\text{mg}\cdot\text{g}^{-1}$	k $\text{kg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$
initial dye concentration				
(T , 25 °C; pH, 5)				
60 $\text{mg}\cdot\text{L}^{-1}$	3.296	0.992	4.827	0.040
90 $\text{mg}\cdot\text{L}^{-1}$	3.776	1.000	4.294	0.134
120 $\text{mg}\cdot\text{L}^{-1}$	5.333	1.000	5.749	0.195
150 $\text{mg}\cdot\text{L}^{-1}$	6.666	1.000	7.538	0.108
temperature				
(pH, 5; C_o , 150 $\text{mg}\cdot\text{L}^{-1}$)				
30 °C	2.975	1.000	7.227	0.122
35 °C	2.666	1.000	6.468	0.193
40 °C	2.332	0.999	7.530	0.042
pH				
(T , 25 °C; C_o , 150 $\text{mg}\cdot\text{L}^{-1}$)				
3	3.033	1.000	7.781	0.127
7	4.099	0.999	8.887	0.060
10	3.142	1.000	8.439	0.050

they can be used to distinguish adsorption performance.³⁰ Comparing the K_F and q_{\max} values indicates that increasing temperature decreased the adsorption capacities of the anionic dyes. For example, when increasing temperature from 30 to 40 °C, the value of q_{\max} decreased from (12.929 to 12.177) $\text{mg}\cdot\text{g}^{-1}$ for RR239 and from (15.942 to 11.020) $\text{mg}\cdot\text{g}^{-1}$ for RB5. On the other hand, q_{\max} values indicate that the optimum pH for RR 239 is 7 and for RB5 is 3 (Tables 2 and 3).

Kinetics and Thermodynamics. Researchers found that if the rate of a reaction is chemically controlled a pseudo-second-order model is the most appropriate. Thus, the kinetic data were further analyzed using a pseudo-second-order relation^{31,32} which is represented by

$$dq_t/dt = k(q_e - q_t)^2 \quad (7)$$

where k is the rate constant of the second-order model ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$) and q_e ($\text{mg}\cdot\text{g}^{-1}$) is the amount of ammonium uptake at equilibrium. For boundary conditions ($t = 0 - t$ and $q_t = 0 - q_e$), eq 7 becomes

$$t/q_t = 1/(kq_e^2) + t/q_e \quad (8)$$

where k ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$) is the rate constant. The second-order constants (k and q_e) were calculated from the slopes and intercepts of Figures S5 and S6 (see Supporting Information).

Table 6. Thermodynamic Parameters for the Adsorption of Anionic Dyes on CTAB–Zeolite (pH, 5; C_0 , (6 to 150) $\text{mg}\cdot\text{L}^{-1}$)

	RR239			RB5		
	ΔG°	ΔH°	ΔS°	ΔG°	ΔH°	ΔS°
	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
$T = 30\text{ }^\circ\text{C}$	−7.579	−11.964	−14.029	−0.116	−6.891	−23.207
$T = 35\text{ }^\circ\text{C}$	−7.704			0.263		
$T = 40\text{ }^\circ\text{C}$	−7.581			0.434		

The coefficients of determination (R^2) and estimated parameters of the pseudo-second-order model are given in Tables 4 and 5. Although the coefficients of determination for RR239 were found to be 1.000, the values ranged from 0.992 to 1.000 for RB5 adsorption. The pseudo-second-order kinetic model agrees very well with the dynamic behavior for the adsorption of dyes RR239 and RB5 onto CTAB–zeolite under several different initial dye concentrations, temperatures, and pH values.

The surface charge on the adsorbent and the solution pH play a significant role in influencing the capacity of an adsorbent toward dye ions. The calculated maximum adsorption capacity ($q_{e,\text{calcd}}$) increased with an increase of the initial dye concentration, but there is no linear relationship with pH and temperature. Under the same conditions, the adsorption capacity of RR239 was found to be two times higher than RB5 due to the hydrophilicity of the dye molecules (Tables 4 and 5). The rate constants k of both anionic dyes vary over a wide range and are independent of the experimental conditions.

The thermodynamic parameters such as change in free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) were calculated using the following equations^{4–12}

$$K_c = C_{Ae}/C_e \quad (9)$$

$$\Delta G = -RT \ln K_c \quad (10)$$

$$\ln K_c = \Delta S/R - \Delta H/RT \quad (11)$$

where R ($8.314\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) is the gas constant; T (K) is temperature; K_c is the equilibrium constant; C_{Ae} ($\text{mg}\cdot\text{L}^{-1}$) is the amount of dye adsorbed on the adsorbent at equilibrium; and C_e ($\text{mg}\cdot\text{L}^{-1}$) is the equilibrium concentration of the dye in the solution. The $q_{e,\text{calcd}}$ values of the pseudo-second-order model in Tables 4 and 5 were used to obtain C_{Ae} and C_e .

Generally, the absolute magnitude of the change in energy for physisorption is between (-20 and 0) $\text{kJ}\cdot\text{mol}^{-1}$; chemisorption has a range of (-400 to -80) $\text{kJ}\cdot\text{mol}^{-1}$. The negative value of ΔG° shows that adsorption is spontaneous and thermodynamically favorable.¹² Negative values of ΔG° in Table 6 indicate that adsorption of RR239 by CTAB–zeolite is spontaneous and can be considered as physisorption. The free energy change for RB5 has a negative sign at $30\text{ }^\circ\text{C}$ ($\Delta G^\circ = -0.12\text{ kJ}\cdot\text{mol}^{-1}$) and positive signs at (35 and 40) $^\circ\text{C}$. This indicates the presence of an energy barrier at higher temperature in the adsorption, and therefore adsorption was not spontaneous.

Although the temperature decreases from (40 to 30) $^\circ\text{C}$, the values of the free energy change of RR239 found were nearly constant (at about $-7.6\text{ kJ}\cdot\text{mol}^{-1}$) and therefore were not affected by the variations of temperatures. On the other hand, the values of the free energy change of RB5 showed very little increase (from -0.116 to 0.434) $\text{kJ}\cdot\text{mol}^{-1}$ for these temperatures.

Enthalpy (ΔH°) and entropy (ΔS°) changes were estimated from the slope and the intercept of plots in Figure S7 (see Supporting Information). ΔH° values in Table 6 (-11.96 and -6.89) $\text{kJ}\cdot\text{mol}^{-1}$ indicate that the adsorption of anionic dyes

is exothermic. The negative values of ΔS° for anionic dyes suggest that randomness decreases during adsorption.⁶

Conclusions

The adsorption of two anionic dyes from aqueous solution onto raw and surfactant modified zeolite was studied in this study. The following results were obtained.

The raw zeolite has a limited adsorption capacity for reactive dyes but is substantially improved upon modifying its surfaces with a cationic surfactant (CTAB). The adsorption capacities of RR239 and RB5 increase up to (6.36 and 3.84) $\text{mg}\cdot\text{g}^{-1}$ in the adsorption time of 30 min, respectively. Decreasing of adsorption capacity with increasing temperature indicates that adsorption of anionic dyes is controlled by an exothermic reaction. The equilibrium adsorption capacity of RB5 showed a maximum at pH 7 , but the adsorption capacity of RB5 at equilibrium was not influenced by the pH variations.

The Freundlich model fits the experimental data very well. The q_{max} values are nearly constant for RR239 (12.93 to 12.18) $\text{mg}\cdot\text{g}^{-1}$ and decrease from (15.94 to 11.02) $\text{mg}\cdot\text{g}^{-1}$ for RB5 with an increase of temperature from (30 to 40) $^\circ\text{C}$. On the other hand, pH slightly affects the maximum adsorption capacities of RB5 and RR239.

The coefficients of determination (R^2) are found to be 1.000 and 0.992 to 1.000 for RR239 and RB5 adsorption, respectively, and the pseudo-second-order model fits with the kinetic data very well. Negative values of the change in free energy, ΔG° , indicate that adsorption of RR239 by CTAB–zeolite is spontaneous. ΔG° for RB5 has a negative sign at $30\text{ }^\circ\text{C}$ ($\Delta G^\circ = -0.12\text{ kJ}\cdot\text{mol}^{-1}$) and positive signs at (35 and 40) $^\circ\text{C}$. Changes in enthalpy (ΔH°) and entropy (ΔS°) also indicate negative values, and therefore, the adsorption mechanism is found to be exothermic.

Supporting Information Available:

Figures related to adsorption isotherms and kinetics for Reactive Black 5 and Reactive Red 239 dyes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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