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Basic and Reactive Dye Removal Using Natural and Modified Zeolites

Dogan Karadag,*,† Eda Akgul,† Sema Tok,† Ferruh Erturk,† Mehmet Arif Kaya,‡ and Mustafa Turan§

Environmental Engineering Department, Yildiz Technical University, Besiktas, 34349, Istanbul, Turkey, Chemistry Department, Yildiz Technical University, Davutpasa, 34220, Istanbul, Turkey, and Environmental Engineering Department, Istanbul Technical University, Maslak, 34469, Istanbul, Turkey

The adsorption of the dyes Basic Red 46 (BR46) and Reactive Yellow 176 (RY176) from aqueous solution onto natural and modified zeolites has been investigated. The surfactants cetyltrimethylammonium bromide (CTAB) and hexadecyltrimethylammonium bromide (HDTMA) were used to modify the zeolite surface, and Fourier transform infrared spectroscopy (FTIR) spectral analysis was used to confirm the surface modification. The effects of initial dye concentration, contact time, pH, temperature, ionic strength, and surfactant type on adsorption were studied in a batch system. BR46 adsorption onto natural zeolite increased to minor a extent with increasing pH, whereas pH did not significantly affect RY176 adsorption. Adsorption capacities of dyes increased with contact time, initial concentration, and temperature for both BR46 and RY176. The increase in ionic strength caused a decrease in adsorption of BR46 and an increase in adsorption of RY176. Adsorption of BR46 on natural zeolite is more favorable than RY176 on the CTAB and HDTMA modified zeolites. The adsorption of basic and reactive dyes was spontaneous and endothermic as concluded from thermodynamic assays.

1. Introduction

Effluents from the textile industry contain various kinds of synthetic dyestuffs, and there has been increasing scientific interest in regard to decolorization of these effluents in the last few decades. Dyes used in the textile industry are classified into three classes: (i) anionic (direct, acid, and reactive dyes), (ii) cationic (all basic dyes), and (iii) nonionic (dispersed dyes).[1] Basic and reactive dyes are extensively used in the textile industry because of their favorable characteristics of bright color, being easily water soluble, simple application technique, and low-energy consumption.[2,3]

The adsorption process provides an attractive alternative for the decolorization of dye wastewaters, and low-cost and readily available adsorbents have been used for various applications. In the literature, aluminosilicates such as clays, zeolites, bentonite, and montmorillonite are the most commonly used low-cost adsorbents for environmental applications.[4−7]

Zeolites have negative charges that arise due to isomorphous substitution of Al^{+3} for Si^{+4}, and this negative charge is neutralized by exchangeable cations. The cation exchange properties of natural zeolites have been used for various environmental purposes such as ammonium removal[5] and heavy metal treatment.[8]

Several authors have reported that zeolites are not suitable for the treatment of anionic contaminants and reactive dyes.[9,10] To enhance the removal of anionic contaminants, zeolites modified with quaternary amine cationic surfactants have been proposed. Cetyltrimethylammonium bromide (CTAB) and hexadecyltrimethylammonium bromide (HDTMA) are most commonly used to modify natural mineral surfaces.[7,11]

In this study, the possibility of natural and surfactant modified zeolites for basic and reactive dye removal from aqueous solution was investigated in terms of initial dye concentration, pH, temperature, ionic strength, and surfactant type.

2. Materials and Methods

2.1. Materials and Chemicals. The natural zeolite sample used in this study was provided from Manisa, Turkey. It was ground, sieved through a 0.6 mm sieve, washed to remove residuals, and dried at 103 °C in an oven for 12 h. The mineralogical content of the natural zeolite is 85 % clinoptilolite, 10 % feldspar, and 5 % clay. The chemical analysis of the zeolite is given elsewhere.[5]

Cationic surfactants, namely, CTAB and HDTMA, were obtained from Merck and used for modifying the surface of zeolite. Synthetic dye solutions of Everzol Yellow 3RS/HC and Astrazon Red FBL were used for the adsorption studies. Astrazon Red FBL (C.I. Basic Red 46) (BR46) was obtained from the Dystar Company in Turkey, and it is known as a cationic dye.[12] Everzol Yellow 3RS/HC (C.I. Reactive Yellow 176) (RY176) was purchased from the Everlight Chemical Ind. Corp., Taiwan, and it contains anionic sulfonate groups.[13] Only the chemical structure of the dye BR46 was made available by the supplier and is shown in Figure 1.

NaCl and Na_2SO_4 salts were used to investigate the effect of ionic strength on the adsorption of the dyes. Concentrations of Cl^- and SO_4^{-2} ions were prepared as (1000 and 3000) mg·L^{-1} using the appropriate amount of salt chemicals, respectively.

2.2. Surface Modification. In the present study, surfactant modified zeolites were prepared using CTAB and HDTMA. Solutions of 10^{-2} M CTAB and HDTMA were prepared and mixed with 150 g of the natural zeolite. The mixture was stirred at room temperature for 4 h at 300 rpm. Zeolite was separated from the mixture by filtration, washed with distilled water, and dried at 100 °C for 15 h. These zeolites were designated as CTAB-zeolite and HDTMA-zeolite and stored for further use in the adsorption experiments. Fourier transform infrared spectroscopy (FTIR) spectra for natural, CTAB, and HDTMA

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* Corresponding author. Tel.: +90 2122597070. Fax: +90 2122619041. E-mail address: dkaradag@yildiz.edu.tr.
† Environmental Engineering Department, Yildiz Technical University.
‡ Chemistry Department, Yildiz Technical University.
§ Environmental Engineering Department, Istanbul Technical University.

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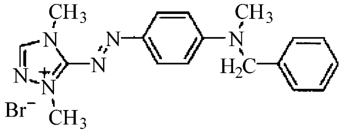

Figure 1. Chemical structure of Basic Red 46.

zeolites were obtained using a Perkin-Elmer model FTIR spectrometer to confirm surface modification.

2.3. Adsorption Studies. Adsorption experiments were carried out with a Gallenkamp orbital shaker at 200 rpm. Experiments were performed using a batch equilibrium technique by placing 0.5 g of adsorbent in a glass bottle containing 50 mL of a dye solution at various concentrations. The experiments were carried out at different pH (3, 5, 7, 9, and 11) and temperature values [(25, 30, 35, and 40) °C]. The solution pH was adjusted with NaOH or HCl solutions using a Jenway pH meter.

The equilibrium concentrations of dyes were determined at (470 and 540) nm, respectively, for BR46 and RY176 using a Jenway visible spectrophotometer. The calibration curves for each dye at the respective wavelengths were established as a function of dye concentration. After the experiments, the adsorbent is separated from the solution by gravity, and the concentration of the remaining dye solution was obtained using calibration curves. The amounts of dye adsorbed were determined by the difference between the initial and remaining concentrations of dye solution. The adsorption capacity was calculated considering the concentration of adsorbed dye ($\text{mg}\cdot\text{L}^{-1}$), solution volume (L), and adsorbent mass (g). Distilled and deionized water with a conductivity value of 0.055 $\mu\text{S}\cdot\text{cm}^{-1}$ was used in all experiments.

3. Results and Discussions

3.1. Fourier Transform Infrared Spectroscopy (FTIR) Spectra. The FTIR spectra of natural and modified zeolites in the range (450 to 3500) cm^{-1} were taken and compared with each other to confirm the surface modification. As can be seen in Figure 2, the peaks at (792 and 1635) cm^{-1} are due to symmetric stretching vibrations of SiO_4 and absorbed water in the zeolite.[14,15] The peaks observed at (2928 and 2855) cm^{-1} are indicative stretching vibrations of the $-CH_2$ and $-CH_3$ groups of CTAB and HDTMA.[16,17]

3.2. Effect of pH. Surface charge is the most important parameter for the adsorption of anionic and cationic dye molecules and is primarily affected by the solution pH. In this study, the effect of solution pH on the adsorption of dyes was investigated in the range 3 to 11, while initial concentration ($150\ \text{mg}\cdot\text{L}^{-1}$) and temperature (25 °C) were kept constant. The results in Figure 3 indicate that BR46 adsorption increases with an increase in solution pH. Basic pH increases the negative charge on the zeolite surface, and in turn this causes an increase in the adsorption capacity of BR46. This result is in good agreement with results of cationic dyes in the literature.[18,19] Generally, decreasing pH increases the positive charge on the adsorbent surface and also increases the electrostatic attraction between the negatively charged sulfonic anion and the positively charged surface.[20] In this study, we obtained different results. As shown in Figure 3, pH does not have an important effect on the adsorption of RY176 and neutral pH has slightly higher adsorption values. Similar results were obtained for the adsorption of reactive dyes by a metal hydroxide sludge.[21]

3.3. Effect of Dye Concentration and Contact Time. The effect of initial dye concentration for the two dyes was investigated in the concentration range (50 to 200) $\text{mg}\cdot\text{L}^{-1}$. The results in Figures 4 to 6 reveal that the adsorption capacity of dyes increases with the increasing concentration and contact time. It is evident from Figures 4 to 6 that removal of dye molecules was more rapid within the first 10 min of contact time. This is due to continuous decreases in the concentration driving force.[18]

The equilibrium adsorption capacity is achieved as 9.17 $\text{mg}\cdot\text{g}^{-1}$ at 50 min for adsorption of BR46 by natural zeolite. RY176 uptake reached a plateau at 40 min, and equilibrium

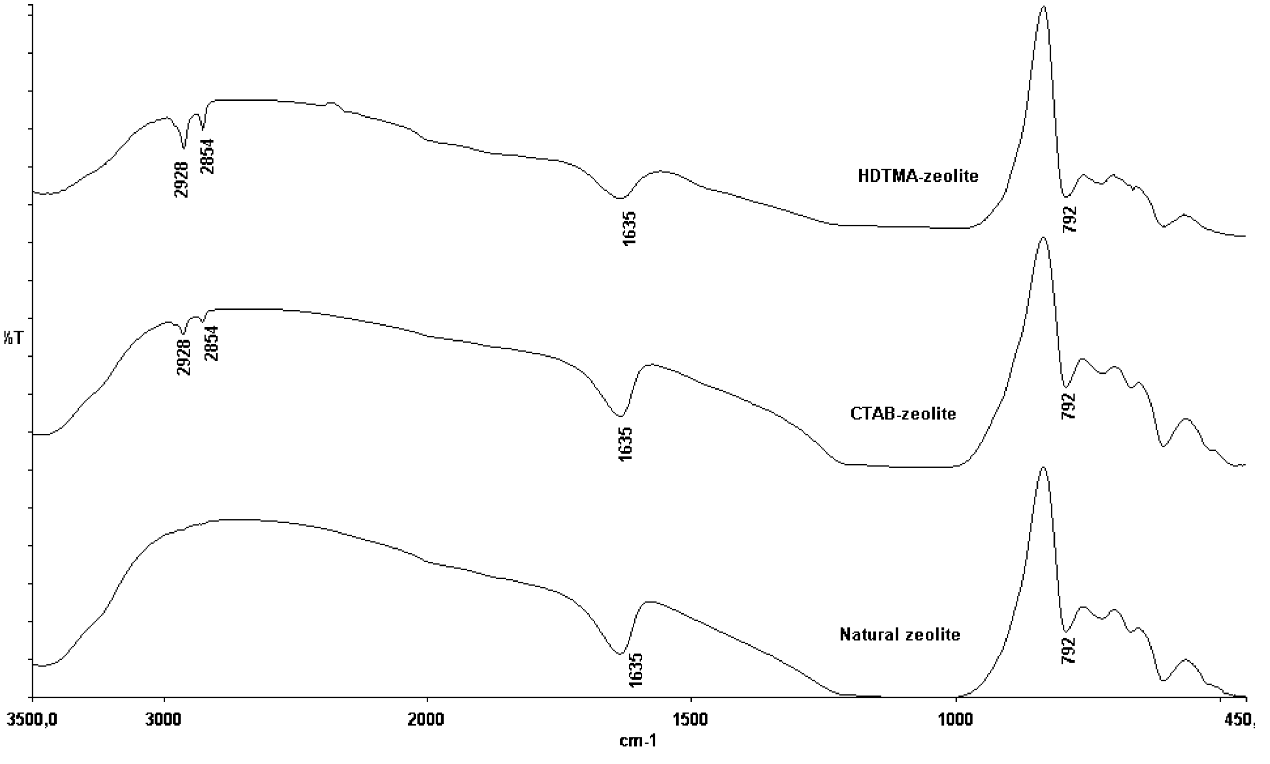

Figure 2. FTIR spectra of natural and modified zeolites.

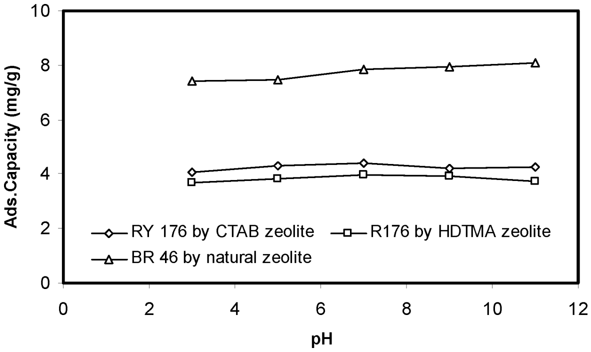

Figure 3. Effect of solution pH on the adsorption of dyes (T = 25 °C; C_o = 150 mg·L^{-1}).

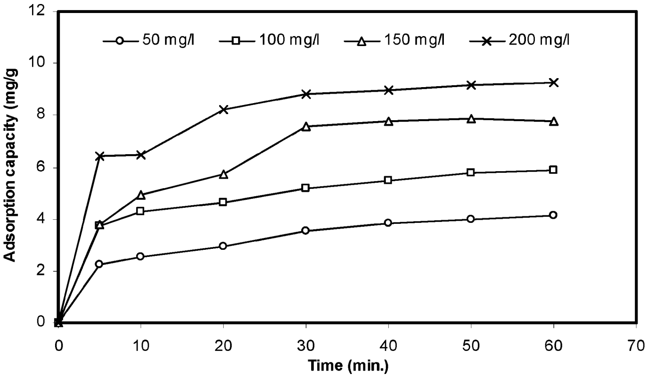

Figure 4. Kinetics of BR46 adsorption by natural zeolite (pH = 7; T = 25 °C).

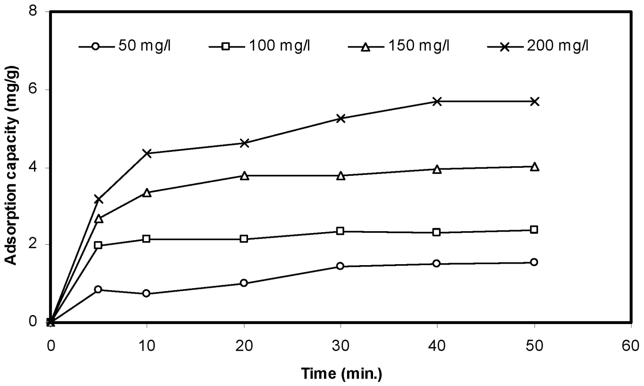

Figure 5. Kinetics of RY176 adsorption by HDTMA-zeolite (pH = 7; T = 25 °C).

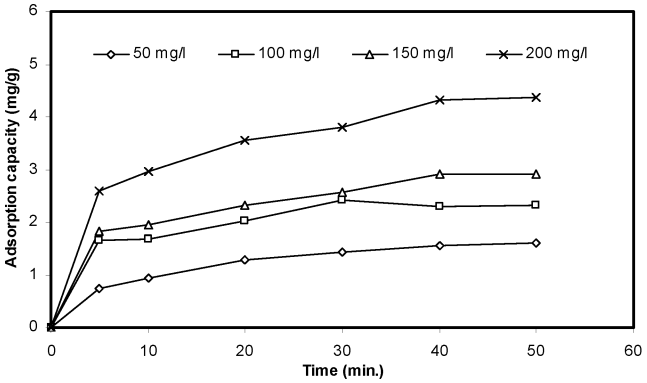

Figure 6. Kinetics of RY176 adsorption by CTAB-zeolite (pH = 7; T = 25 °C).

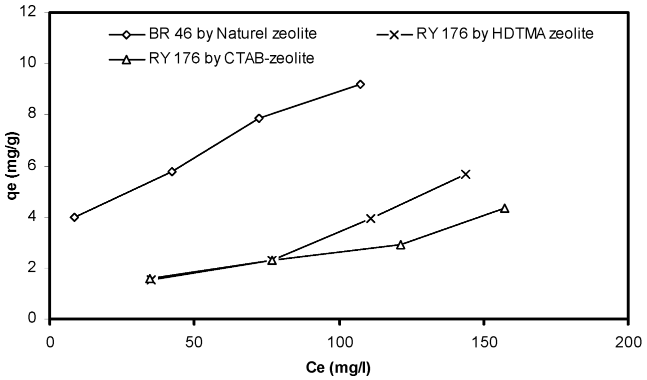

Figure 7. Comparison of equilibrium adsorption capacities of dyes (pH = 7; T = 25 °C).

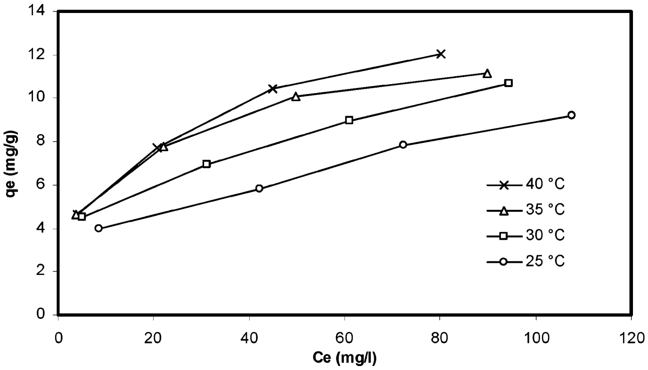

Figure 8. Effect of temperature on the adsorption of BR46 by natural zeolite (pH = 7).

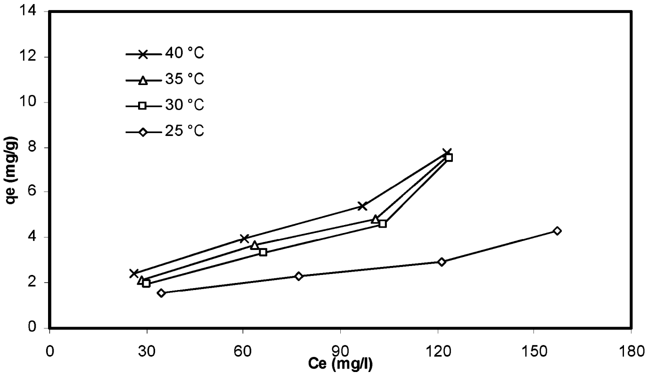

Figure 9. Effect of temperature on the adsorption of RY176 by CTAB-zeolite (pH = 7).

capacities are (5.68 and 4.33) mg·g^{-1} for HDTMA and CTAB zeolites, respectively. Comparison of equilibrium data of the two dyes in Figure 7 indicates that the adsorption capacity of BR46 by natural zeolite is higher than RY176 by modified zeolites. At lower concentrations, the two modified zeolites have the same adsorption, but at higher concentrations, HDTMA has a higher performance than CTAB. This is attributed to the structural properties of the surfactants. CTAB has a single head group molecule,[22] while HDTMA has three head groups.[23] Atkin et al. indicated that head groups of surfactants provide a greater initial driving force for adsorption of surfactants onto the surface.[24] The higher number of head groups increased the adsorption of HDTMA on the surface of the zeolite and increased the adsorption of dye molecules.

3.4. Effect of Temperature. The effect of temperature on adsorption of two dyes was studied by carrying out a series of experiments at (25, 30, 35, and 40) °C at equilibrium times of (40 and 50) min for RY176 and BR46. The equilibrium adsorption capacities as a function of the equilibrium concentration of dyes in the solution are shown in Figures 8 to 10. The results are shown in Figures 8 to 10. As can be seen from the figures, adsorption capacities of the two dyes increase with

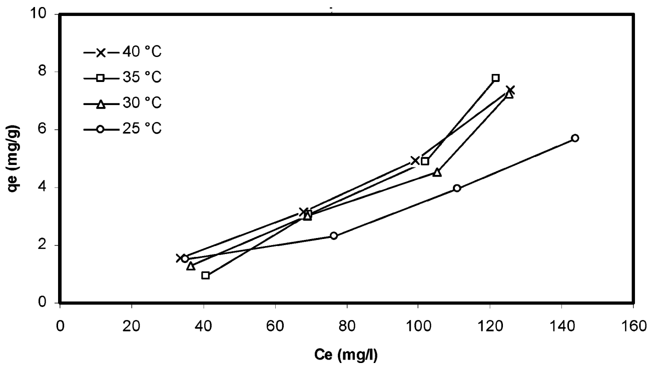

Figure 10. Effect of temperature on the adsorption of RY176 by HDTMA-zeolite (pH = 7).

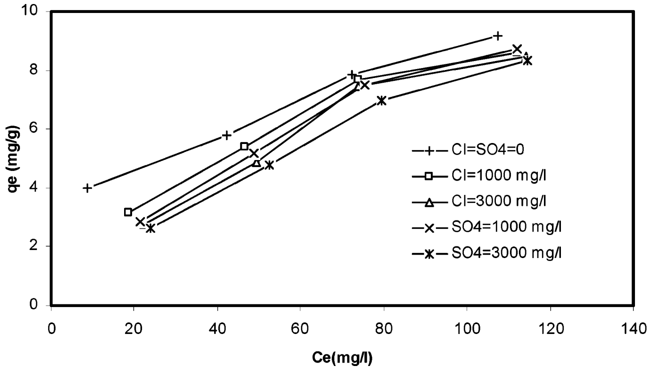

Figure 11. Effect of ionic strength on adsorption of BR46 by natural zeolite (T = 25 °C; pH = 7).

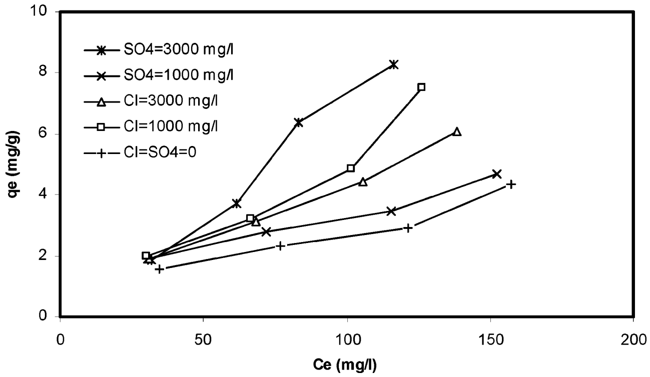

Figure 12. Effect of ionic strength on adsorption of RY176 by CTAB-zeolite (T = 25 °C; pH = 7).

temperature. Similar results have been reported for adsorption of basic dyes[25,26] and reactive dyes.[27,28] The increase of adsorption with temperature indicates that the mobility of the dye molecules increases with the rising temperature, and increasing temperature produces a swelling effect within the internal structure of the zeolite enabling large dye molecules to penetrate further.[29] The positive effect of the temperature is an indicator of a chemisorption mechanism for adsorption of the two dyes by natural and modified zeolites.[18]

Thermodynamic parameters such as change in free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$) were determined using the following equations.[30]

$$\Delta G = -RT \ln K_D \tag{1}$$

$$K_D = \frac{C_Z}{C_S} \tag{2}$$

$$\ln K_D = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{3}$$

where C_Z and C_S (mg·L^{-1}) are the equilibrium concentrations of the dye on the zeolite and in the solution, respectively; K_D is the equilibrium constant; T is the solution temperature (K); and R is the gas constant.

The free energy change is used to distinguish the spontaneity of the adsorption process, and a higher negative value suggests a more energetically favorable adsorption.[30] The $\Delta G°$ values in Table 1 indicate that BR46 adsorption by natural zeolite is spontaneous and is favorable at higher temperatures. RY176 adsorption by modified zeolites has positive $\Delta G°$ values; however, Ozer et al.[31] state that whatever the sign of $\Delta G°$ the reaction will always occur, but its rate may be very slow. The positive values of free energy indicate that at equilibrium the amount of dye adsorbed on zeolite is lower than the amount of dye in solution.

The $\Delta G°$ values in the literature for the adsorption of basic dyes indicate that adsorption of BR46 is more favorable than adsorption of crystal violet by raw bentonite,[32] but Australian zeolite[33] and Turkish sepiolite[34] are more effective for the removal of methylene blue and astrazon blue. Similarly, adsorption of RY176 has lower $\Delta G°$ values than those obtained for the adsorption of reactive dyes by CTAB modified zeolite[9] and has higher $\Delta G°$ values than adsorption of Reactive Blue 221 by raw sepiolite.[35] $\Delta H°$ and $\Delta S°$ values for all cases are positive, indicating adsorption processes are endothermic and randomness increases at the solid−solution interface during adsorption.[36]

3.5. Effect of Ionic Strength. In dye processing, NaCl and Na_2SO_4 salts are used to enhance the bath exhaustion.[37,38] Different concentrations of salts were added to the aqueous solution to investigate the effect of ionic strength on dye adsorption. As seen in Figure 11, the increase in ionic strength causes a decrease in the adsorption of BR46 by natural zeolite. In the literature, the same effect has been reported for some cationic dyes, such as methylene blue adsorption by sludge ash,[39] crystal violet by natural sepiolite,[32] and Rhodamine B by aerobic granule.[40]

Weng and Pan (2006) reported that an increase in ionic strength leads to a decrease of the thickness of the electrical double layer and finally decreases the adsorption capacity of cationic dyes. It is found that a higher salt concentration has a larger effect on the adsorption of basic dye, and the SO_4^{-2} ion further decreases the adsorption efficiency because it has a more negative charge than the Cl^- ion.[21]

Table 1. Thermodynamic Parameters

	$\Delta G°$ (kJ·mol^{-1})					
	25 °C	30 °C	35 °C	40 °C	$\Delta H°$ (kJ·mol^{-1})	$\Delta S°$ (kJ·K^{-1}·mol^{-1})
BR46 by natural zeolite	−0.17	−0.93	−1.74	−2.10	41.48	0.14
RY176 by CTAB-zeolite	3.56	1.97	1.77	1.48	40.62	0.13
RY176 by HDTMA-zeolite	2.60	2.12	1.86	1.66	19.24	0.056

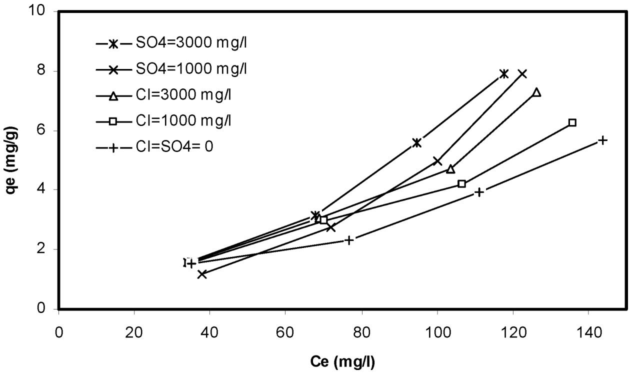

Figure 13. Effect of ionic strength on adsorption of RY176 by HDTMA-zeolite (T = 25 °C; pH = 7).

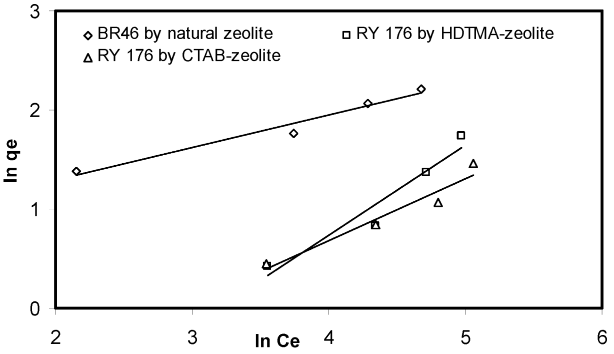

Figure 14. Linearized Freundlich plots.

Contrary to BR46, ionic strength has a positive effect on the adsorption of RY176. Salt addition increases the aggregation of dye molecules and decreases the solubility. An increase in aggregation promotes the adsorption of dye molecules.[41] The effect of ionic strength was found for higher salt concentrations due to the increase of the aggregation effect (Figures 12 and 13). Thus, increasing the ionic strength (higher salt concentration) was found to have an increase in the adsorption capacity of RY176.

3.6. Adsorption Isotherms. The equilibrium adsorption data were analyzed using the well-known Langmuir and Freundlich models. The linear form of the Langmuir and Freundlich models is given in eq 4 and eq 5

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_a q_m}\frac{1}{C_e} \tag{4}$$

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

where q_e is the amount of dye adsorbed at equilibrium and C_e is the dye concentration of the solution. K_a and K_f are constants of the Langmuir and Freundlich models, respectively, and q_m is the maximum amount of dye adsorbed in the Langmuir model. Model constants were calculated by linear plots as shown in Figures 14 and 15.

Values of correlation coefficients (R^2) and standard deviations (SD) between the measured and modeled result were used to compare the isotherm models. Standard deviation was calculated using eq 6.[42] In eq 6, the subscripts "exptl" and "calcd" show the experimental and calculated values, and N is the number of measurements.

$$\mathrm{SD}\ (\%) = 100\left\{\sum \frac{[(q_{e,\mathrm{exptl}} - q_{e,\mathrm{calcd}})/q_{e,\mathrm{exptl}}]^2}{N-1}\right\}^{1/2} \tag{6}$$

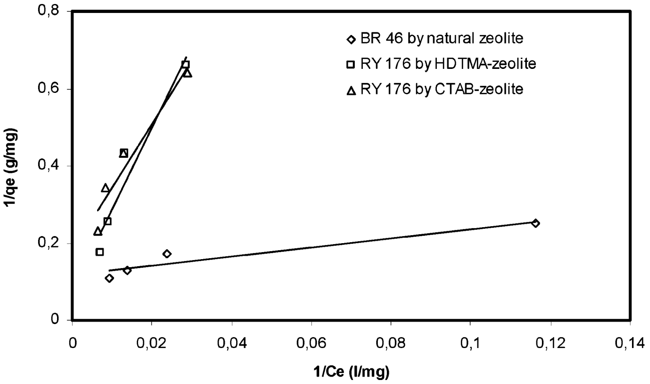

Figure 15. Linearized Langmuir plots.

Table 2. Estimated Isotherm Parameters

	BR46 by natural zeolite	RY176 by HDTMA-zeolite	RY176 by CTAB-zeolite
	Langmuir		
q_m (mg·g^{-1})	8.564	13.148	5.539
K_L (L·mg^{-1})	0.099	0.004	0.011
R^2	0.902	0.931	0.939
SD (%)	14.178	18.461	13.397
	Freundlich		
K_f (L·g^{-1})	1.918	0.054	0.163
$1/n$	0.324	0.914	0.623
R^2	0.961	0.935	0.939
SD (%)	7.4454	15.662	10.456

The parameters estimated using linear regression and values of R^2 and SD are shown in Table 2. The Freundlich model is more suitable than the Langmuir model for the representation of the adsorption data because it has higher R^2 and lower SD values in all cases.

4. Conclusions

In this study, the adsorption of the basic dye BR46 by natural zeolite and the reactive dye RY176 by surfactant modified zeolites was studied. The results indicated that higher pH is favorable for adsorption of the basic dye and neutral pH is favorable for the reactive dye. Increasing temperature, contact time, and dye concentration produced increased adsorption for both dyes. Removal of the basic dye by natural zeolite was found to have higher performance than uptake of the reactive dye by modified zeolite. HDTMA modified zeolite has higher removal capacities for RY176 than CTAB modified zeolite. The effect of ions on the adsorption of dye molecules increased with increasing negative charge. Thermodynamic results indicate that the adsorption of BR46 and RY176 dyes is spontaneous and endothermic. Isotherm modeling indicated that the Freundlich model has better performance for representation of the experimental data.

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