The removal of reactive azo dyes by natural and modified zeolites

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Abstract: The adsorption mechanism of three reactive dyes by zeolite has been examined with the aim of identifying the ability of zeolite to remove textile dyes from aqueous solutions. Towards this aim, a series of batch adsorption experiments was carried out, along with determination of the electrokinetic properties of both natural and modified zeolites. The adsorbent in this study is a clinoptilolite from the Gördes region of Turkey. The reactive dyes CI Reactive Black 5, Red 239 and Yellow 176 are typical azo dyes extensively used in textile dyeing. Adsorption tests were carried out as a function of mixing time, solids concentration, dye concentration and pH. The adsorption results indicate that the natural zeolite has a limited adsorption capacity for reactive dyes but is substantially improved upon modifying its surfaces with quaternary amines. An electrostatic adsorption mechanism involving the formation of a bilayer of amine molecules on the clinoptilolite surface onto which anionic dye molecules adsorb, depending on their polarities, is proposed. The results are also supported by electrokinetic measurements.

NOTATION

- $a_L$: Langmuir isotherm constant ($\text{dm}^3 \text{mg}^{-1}$)
- $C_e$: Equilibrium liquid-phase concentration (mg $\text{dm}^{-3}$)
- $C_i$: Initial liquid-phase concentration (mg $\text{dm}^{-3}$)
- $K_L$: Langmuir isotherm constant ($\text{dm}^3 \text{g}^{-1}$)
- $m$: Mass of adsorbent (g)
- $q_e$: Adsorption capacity or amount of dye adsorbed by adsorbent (mg $\text{g}^{-1}$)
- $q_{\text{max}}$: Adsorption capacity at the plateau region (mol $\text{g}^{-1}$)
- $V$: Volume of solution (cm$^3$)

INTRODUCTION

Wastewater from textile industries contains colorants originating from printing or dyeing processes. Azo dyes are presently the most important compounds, constituting about 20–40% of the total dyes used for coloring.1,2 These dyes are based on the azo chromogen ($\text{N} \equiv \text{N}$).3,4 The use of organic dyes has increased in these industries; for an annual world production of 30 million tonnes of textiles, 700,000 tonnes of different dyes are required.3 Such voluminous quantities pose considerable environmental problems because reactive dyes are water-soluble and cannot be easily removed by conventional methods such as chemical coagulation/flocculation and biological methods.5 For example, these dyes are hardly biodegraded in an aerobic environment.7,8

The removal of colorants and other organic pollutants from industrial wastewater is considered an important application of the adsorption process using suitable adsorbents.9 Activated carbon and polymer resins appear to be the best adsorbents for removing chemicals from relatively concentrated wastewater, but these are expensive and necessitate regeneration.10–13 In addition to this, activated carbon has a rather low capacity for some reactive dyes.14 Nevertheless, several investigators reported studies on cost-effective adsorbent systems: natural clay/basic and acid dyes,15 chitosan/vinyl sulfone and chlorotriazine reactive dyes,14 sunflower stalk/basic dyes,16 sepiolite/Rhodamine,17 shale oil ash/azo dyes,9 montmorillonite and sepiolite/Methyl Green,18 and natural zeolite/basic dye.13 The typical unit cell formula of natural zeolite mineral, clinoptilolite, is given as $\text{Na}_6[(\text{AlO}_2)_6(\text{SiO}_2)_{30}]24\text{H}_2\text{O}.19$ The three-dimensional crystal structure of zeolite contains two-dimensional channels20,21 which embody some ion exchangeable...
cations such as Na\textsuperscript{+}, K\textsuperscript{+}, Ca\textsuperscript{2+} and Mg\textsuperscript{2+}. These cations can be exchanged with organic and inorganic cations\textsuperscript{22–25} Such sorptive properties have been utilized for a variety of purposes such as adsorption of ammonia by natural clinoptilolite\textsuperscript{26–29} and removal of metal ions.\textsuperscript{30–32} However to our knowledge, there has been no study on the interaction of azo dyes with modified zeolites.

The object of this study was therefore to examine the adsorption capacities of the three anionic reactive dyes by natural and modified zeolites, elucidate the mechanism of their uptake and comment on their applicability to textile wastewaters.

**EXPERIMENTAL**

**Materials**

The clinoptilolite sample, hereafter referred as zeolite, used in the experiments was received from the Incal Company in the Gördes region of Turkey. The chemical analysis of this zeolite (<63 \(\mu\)m) was performed by inductively coupled plasma (ICP, Perkin Elmer Model 3800). Gördes zeolite has the following properties: 1.9–2.2 meq g\textsuperscript{-1} cation exchange capacity, 0.4 nm pore diameter, 92% purity, 40% bed porosity, 2.15 g cm\textsuperscript{-3} density, 1.30 g cm\textsuperscript{-3} apparent density. Table 1 presents the chemical analysis of zeolite.\textsuperscript{25} The surface area of zeolite is 11.8 m\textsuperscript{2} g\textsuperscript{-1} as measured by the BET method using nitrogen gas.

The reactive dyes marketed by Everlight Chem Ind Corp of Taipei are anionic azo dyes: Everzol Black B (CI Reactive Black 5), Everzol Brilliant Red 3BS (CI Reactive Red 239), Everzol Yellow 3RS H/C (CI Reactive Yellow 176). Only the chemical structure of the dye Everzol Black B was made available by the supplier, see Fig 1. The exact chemical structures of the other dyes are not available. However they are all known to contain anionic sulfonate groups to various degrees. Distilled and deionized water with a conductivity value of 2 \(\times\) 10\textsuperscript{-6} mhos cm\textsuperscript{-1} was used in all experiments.

A quaternary amine, hexadecyltrimethylammonium bromide (HTAB, C\textsubscript{19}H\textsubscript{42}BrN) purchased from Sigma and specified to be of 99% purity was used for modifying the surface of zeolite. The modification procedure for zeolite is shown in Fig 2. A number of studies on the removal of organic impurities by modified clays are available. These include the removal of benzene, toluene, ethylene and o-xylene using modified bentonite\textsuperscript{33} adsorption of benzene, toluene and ethylene by modified soil minerals\textsuperscript{34} removal of tetrachloromethane from liquid wastes with modified bentonite\textsuperscript{35} adsorption of 1-naphthylamine, nitrobenzene and aniline onto modified bentonite.\textsuperscript{36}

![Figure 2. Flowsheet for preparing modified sepiolite.\textsuperscript{26}](image-url)

![Figure 1. Structural formula of Everzol Black B.](image-url)
Methods
The electrokinetic properties of zeolite were determined by a Zeta Meter 3.0 equipped with a microprocessor unit. The unit automatically calculates the electrophoretic mobility of particles and then converts it to the zeta potential. A sepiolite sample of 0.5 g was conditioned in 100 cm$^3$ of distilled water for 10 min. The suspension was kept still for 5 min to allow the larger particles to settle. Each data point is an average of approximately 10 measurements. All measurements were made at ambient temperature (22.5 ± 1°C).

Adsorption tests were conducted in 20 or 40 cm$^3$ glass vials using 5% solids concentration for the natural zeolite and 0.1% and 5% for the modified zeolite. The bottles were placed on an orbital shaker at 400 rpm at room temperature for 4 h followed by centrifugation for 10 min.

The equilibrium concentrations of dyes were respectively determined at 592, 400, and 540 nm for Black, Yellow and Red dyes using a 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 ±1.5%. The adsorption capacity was calculated by the following formula:

$$q_e = \frac{(C_i - C_e) \times V}{1000 \times m}$$  \hspace{1cm} (1)

where $q_e$ = adsorption capacity or amount of dye adsorbed by adsorbent (mg g$^{-1}$), $C_i$ = initial dye concentration (mg dm$^{-3}$), $C_e$ = equilibrium or residual dye concentration (mg dm$^{-3}$), $V$ = the volume of the solution (cm$^3$), and $m$ = mass of adsorbent (g).

RESULTS AND DISCUSSION
Effect of solids concentration
A series of adsorption experiments has been carried out with different solids concentrations at 25 mg dm$^{-3}$ initial dye concentration. The results are given in Fig 3. Examination of Fig 3 reveals that adsorption density decreases with increasing solids concentrations down to a solids concentration of 50 mg cm$^{-3}$ (zeolite/dye = 0.75 g/15 cm$^3$), above which adsorption density remains practically constant. While adding more sepiolite results in the adsorption of a very small amount of reactive dye, the adsorption density gradually decreases. In this system, most of the dye molecules added to the solution are adsorbed by sepiolite. Based on the results in Fig 3, an optimum solids concentration of 50 mg cm$^{-3}$ was (5%) selected and used in the subsequent adsorption experiments with natural zeolite.

In the literature, the solids concentrations chosen for similar studies were 1.7 mg cm$^{-3}$ (0.17%) for oil ash,\textsuperscript{9} 1 mg cm$^{-3}$ (0.1%) for montmorillonites, and 10 mg cm$^{-3}$ (1%) for sepiolite,\textsuperscript{7} 0.5 g for granular activated carbon and 2.0 g for natural zeolite in 100 cm$^3$.\textsuperscript{13} It should be noted that, as per eq (1), the lower the solids concentration, the higher the apparent adsorption density.

Effect of mixing time
A series of experiments has been performed to optimize the adsorption time at an initial dye concentration of 25 mg dm$^{-3}$ and solids concentration of 5%. The effect of mixing time on adsorption density of natural zeolite is presented in Fig 4. As shown in Fig 4, the adsorption density increases with increasing the conditioning time until about 2 h and then reaches a plateau value for the Yellow and Red dyes, but adsorption of the Black dye proceeds more slowly. Because adsorption reaches equilibrium in less than 4 h, it indicates the difficulty for the access of bulky dye molecules to the zeolite surface. Considering the extreme changes like pH and concentration, the mixing period of 4 h was selected for further testing. Adsorption of Methyl Green, a divalent organic cation, on sepiolite showed that significant adsorption occurs within the first hour of the reaction.\textsuperscript{18}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure3}
\caption{Adsorption capacity of dye versus solids concentration in natural zeolite–dye systems ($C_i$ = 25 mg dm$^{-3}$, mixing time = 2 h, natural pH 6.5 ± 0.25).}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4}
\caption{Effect of mixing period on adsorption capacity of natural zeolite–dye systems (solids concentration = 5%, $C_i$ = 25 mg dm$^{-3}$, Natural pH 6.5).}
\end{figure}
Adsortion isotherms
An adsorption isotherm shows how the adsorbate molecules partition between the liquid and solid phases when the adsorption process reaches equilibrium conditions. The isotherm data are usually fitted to different models in order to find a suitable model that can be used for design purposes.\(^1\)

Adsorption isotherms have been recorded using both natural and modified zeolites. Figure 5 presents the adsorption isotherms for natural zeolite/reactive dyes systems. As seen in Fig 5, there is a negative adsorption on zeolite for all dyes, except for the Red dye above 25 ppm. Exclusion of reactive dye anions due to their large size is expected as clinoptilolite contains micropores. However, these pores are amenable to the adsorption of simple cations, anions and water; adsorption of water in particular increases the apparent concentration of dye in the bulk leading to a negative adsorption. Such negative adsorption arising from the exclusion of micelles by a porous substrate, Bio-Sil, is well documented in the literature.\(^3\)\(^8\)\(^9\) Clinoptilolites and microporous resins are reported to exclude reactive dye anions,\(^1\)\(^0\) in particular for geometric reasons.\(^4\)\(^1\)

The zeta potential profiles of natural and modified zeolites against pH are given in Fig 6. Natural zeolite has a negative charge in the entire range pH. Since the reactive dyes have negative sulfonate groups, they are repelled by the negatively charged zeolite surface. This induces a relatively low adsorption capacity, as shown in Fig 5. For this reason, in order to increase the adsorption capacity, the surface of natural zeolite was modified with a typical quaternary amine surfactant (HTAB) which not only makes the zeolite surface more hydrophobic but also neutralizes the negative charges.\(^5\)\(^2\)\(^3\)\(^4\) The zeta potential of modified zeolite shown in Fig 6 reveals that the surface acquires positive charges and consequently becomes receptive to the uptake of negatively charged dye anions through electrostatic attraction.

Figure 7 shows the adsorption isotherms of the three reactive dyes on modified zeolite at 5% solids concentration. A comparison of natural and modified zeolites at 5% solids concentration indicates that modification of zeolite with HTAB substantially improves the adsorbability of reactive dyes. The adsorption isotherms in Fig 7 are characterized by the three regions of interest. Although the rising branches of the adsorption isotherms show a linear increase in Region I up to the residual concentration of at least 10 mg dm\(^{-3}\) \((C_0 = 500 \text{ mg dm}^{-3})\), the isotherms then show a much steeper linear rise in Region II followed by a reversal towards the adsorption density axis, Region III. Such abnormal behavior is evidence of the formation of a solid phase, i.e., precipitation in Region II. Indeed, under normal conditions, the isotherms are expected to reach a plateau region with constant adsorption densities above saturation. The formation of precipitation can be ascribed to the interaction of anionic sulfonate groups with the cationic polar head of the quaternary amine molecules through electrostatic attraction. Such interactions can be initiated below the onset of precipitation \((C_e = 10 \text{ mg dm}^{-3})\) in the form of a surface precipitate on the zeolite surface and continue in the bulk solution in the form of bulk precipitates.\(^4\)\(^5\) In fact, the precipitates formed in Region II above \(C_e = 10 \text{ mg dm}^{-3}\) dye concentration were visually observed. While the precipitation in Region II is a typical behavior observed in systems where the solid phase is governed by a solubility product, e.g., dye–quaternary amine complex, that, however, observed in Region III is unusual. It appears that in Region III precipitation is not stoichiometric and is basically governed by the precipitation of the dye alone due to an increase in pH of the solution. It is shown elsewhere that in the sepiolite/azo dye system no precipitation occurs below the solids concentration of 0.1%, indicating that precipitation is also influenced by the presence of ions released from the solid.\(^4\)\(^5\) Interestingly, precipitation is largely dependent upon the combination of three factors: pH, solids concentration, and the initial dye concentration.

Figure 5. Adsorption isotherms of natural zeolite–dyes systems at 5% solids concentration.

Figure 6. Zeta potential–pH profiles of natural and modified zeolites.
Removal of reactive azo dyes by zeolites

MODIFIED CLINOPTILOLITE/ISOTHERM

Effect of pH on adsorption
Adsorption tests as a function of pH were carried out with the Black dye only to determine the extent of precipitation and also to identify the role of pH in adsorption. As seen in Fig 8, the adsorption density of Black dye on sepiolite decreases to a minimum at pH 5–8 and then increases above pH 8. Precipitate formation takes place only at these alkaline pH values, corresponding to Region III in Fig 7.

Adsorption mechanism of dyes onto zeolite
Since no precipitation is formed at and below 0.1% solids concentration for all dye concentrations, further experiments were conducted under these conditions. Adsorption isotherms with modified zeolite are presented in Fig 9 at 0.1% solids concentration. The adsorption density of modified zeolite shows a relatively good performance, increasing steadily with Ce towards a near-constant value of about 100 mg g\(^{-1}\) at equilibrium concentrations of 60 mg dm\(^{-3}\) or higher. Since the uptake of dye molecules largely depends on the packing and configuration of the HTAB molecules, it is appropriate to calculate the cross-sectional area of a HTAB molecule in nm\(^2\)/molecule by:

\[
\text{Cross-sectional Area} = \frac{10^{18}}{\Gamma_{\max} A S}\]

where \(\Gamma_{\max}\) is the adsorption capacity at the plateau region, \(A\) is the Avogadro number \((6.02 \times 10^{23})\), \(\Gamma_{\max} = 1 \times 10^{-4} \text{ mol g}^{-1}\),\(^{23}\) and \(S\): specific surface area of zeolite: 11.80 m\(^2\)/g. Using the values given above, the area occupied by HTAB is found to be 1.96 nm\(^2\)/molecule. Considering the cross-sectional area of 3.782 nm\(^2\)/molecule reported for an amine molecule,\(^{46}\) the surface coverage (\(\theta\)) is found to be 3.782/1.96 = 1.93 \(\approx\) 2.0.

In order to identify the mechanism of dye adsorption onto modified zeolite a set of zeta potential measurements against dye concentration (shown in Fig 10) was performed. The surface of modified zeolite is initially positively charged in line with the data in Fig 6. However, as the dye concentration is increased, the positive charges gradually diminish until an initial dye concentration of 25 mg dm\(^{-3}\)
followed by a sharp decrease in zeta potential. The isoelectric point (iep) for all dyes occurs at about 40 mg dm\(^{-3}\) of initial dye concentration above which the zeolite surface rapidly acquires negative charges and reaches a maximum zeta potential of \(-35\) mV at about 500 mg dm\(^{-3}\) of initial dye concentration. The fall in zeta potential decreases in the order of Red > Yellow > Black. This is also the order of adsorption data given in Fig 9. These curves dramatically illustrate the effect on reactive dye adsorption of changing from natural to modified zeolites. The mechanism of anionic dye adsorption onto modified zeolite is schematically illustrated in Fig 11. Evidently, according to the cross-sectional area calculations, the surface of zeolite under the modification conditions reveals a coverage of about a bilayer; this indicates that the degree of hydrophobicity plays an important role in the interaction of oppositely charged groups. More importantly, surface coverage as a bilayer rather than a monolayer has a strongly favorable influence on the dye uptake.

The Langmuir equation can accurately describe the equilibrium data over the concentration range used in this investigation. For that reason, the Langmuir model was fitted into the developed kinetic model.

The plots of the Langmuir isotherms illustrated in Fig 12 yield linearity over the whole concentration range. The parameters, \(K_L\) and \(a_L\), of the Langmuir equation have been calculated for various dyes and are listed in Table 2. The values of the ratios \(K_L/a_L\) represent the maximum adsorption capacity \(q_{\text{max}}\) of sepiolite for a particular dye. The capacity of modified sepiolite for the three types of reactive dyes is also analyzed according to the linear form of the Langmuir isotherm as follows:

\[
\frac{C_e}{q_e} = \frac{1}{K_L} + \left( \frac{a_L}{K_L} \right) C_e
\]

where \(a_L = \text{Langmuir constant (dm}^3 \text{g}^{-1}\) and \(K_L = \text{Langmuir constant, dm}^3 \text{g}^{-1}\). As seen from Fig 12, when \(C_e/q_e\) is plotted against \(C_e\), the Langmuir model fits the data very well. While the value of \((a_L/K_L)\) gives the slope of the line, \((1/K_L)\) yields the intersection of the line with the \(C_e/q_e\) axis.

It should be noted that Langmuir model has four limitations of which two are very significant in the context of this paper; the adsorbate and solvent molecules should be of the same size and the adsorbate and solvent molecules should be of the same size and the adsorbate...
layer is limited to a monolayer. While the cross-sectional area of the HTAB molecule is approximately 3.75 nm², that of water is 1.25 nm², this indicates the ratio of 3. These two limitations are all mutually interacting terms resulting in a good Langmuir fit.

Adsorption capacity ($q_e$) and the parameters $K_L$ and $a_1$ of modified sepiolite/reactive dye systems are listed and compared with activated carbon and maize cob in Table 2. Juang et al. reported that adsorption capacities of reactive dyes on activated carbon, natural clay and maize cob are often less than 30 mg·g⁻¹. In the same study, the adsorption capacities of CI Reactive Red 222, Reactive Yellow 145 and Reactive Blue 222 on chitosan were found to be 380, 179 and 87 mg·g⁻¹, respectively. Rytwo et al. found that the adsorption of Methyl Green (CI Basic Blue 20) and carbino1 on sepiolite were 0.09 and 0.30 mol·kg⁻¹ respectively. Meshko et al. indicated that the adsorption density of the dye Maxilon Golden Yellow GL EC 400% (MG-400) and that of the dye Maxilon Black FBL-01 300% (MS-300) on natural zeolite were 14.91 and 55.86 mg·g⁻¹, respectively. In addition to this, they found that the adsorption of MG-400 and MS-300 on granular activated carbon was 159.00 and 309.2 mg·g⁻¹, respectively. These results generally show that the properties of dyes are most important when selecting a suitable adsorbent in wastewater treatment systems.

Table 2 shows that Everzol Red 3BS has the highest adsorption capacity ($q_{max}$) with a value of 111.11 mg·g⁻¹. Under the same conditions, the adsorption capacity decreases in the following manner:

Red > Yellow > Black

This is also the order of hydrophilicity of the dye molecules.

CONCLUSIONS

The adsorption of three types of reactive dyes onto natural and modified zeolites has been investigated in this study. The salient findings are summarized below:

Natural zeolite is not a suitable adsorbent for the uptake of reactive azo dyes and even exhibits negative adsorption due to the exclusion of reactive dye anions from the pores with a corresponding increase in water adsorption within the pores.

Zeolite modified with a typical quaternary amine surfactant (HTAB) was made amenable for the adsorption of anionic dyes. The modified zeolite exhibits cationic charges that can interact with the anionic dye sulfonate groups. The adsorption isotherms with modified adsorbents indicate the three regions of interest, each corresponding to a different adsorption mechanism. The adsorption of dyes onto modified zeolite in Region I is governed initially by electrostatic attraction of anionic dye groups onto already adsorbed cationic head groups of the HTAB molecules. The zeta potential results support this mechanism. Regions II and III are ascribed to the precipitation of an anionic dye–cationic HTAB complex, and the formation of solid phase of the dye, respectively.

The maximum adsorption capacities of Everzol Red 3BS, Everzol Yellow 3RS H/C, Everzol Black B and respectively are 111.11, 88.50 and 60.61 mg·g⁻¹ under the same conditions: the adsorption capacity decreases in the order of hydrophilicity of the dye molecule in the following manner:

Reactive Red > Reactive Yellow > Reactive Black

Modified zeolite can be a good alternative to activated carbon for the removal of reactive dyes from wastewater streams due to its cheap price and abundance in nature. Studies are in progress to find out its regenerability.

REFERENCES
