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Comparison of the adsorption characteristics of azo-reactive dyes on mezoporous minerals

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Abstract

Sepiolite and zeolite, highly porous minerals, are becoming widely used as alternative materials in areas where sorptive, catalytic and rheological applications are required. High ion exchange capacity and high surface areas and more importantly their relatively cheap prices make them attractive adsorbents. In this study, the adsorption mechanism of three reactive azo dyes (Reactive Black 5, Red 239 and Yellow 176) by two natural mezoporous minerals has been examined in order to identify the ability of these minerals to remove coloured textile dyes from wastewaters. For this purpose, a series of batch adsorption tests were carried out as a function of solids concentration, time and dye concentration using natural and modified sepiolites and zeolites. The adsorption results indicate that both natural sepiolite and zeolite have limited adsorption capacities of the reactive dyes but are substantially improved upon modifying their surfaces with quaternary amines. The mechanism of adsorption process is elucidated on the basis of experimental data.

Keywords: Sepiolite; Zeolite; Mezoporous minerals; Reactive azo dyes; Adsorption

1. Introduction

Reactive dyes are extensively used in dyeing processes in textile industry but about 20–40% of these dyes remain in the effluents [1,2]. Reactive dyes exhibit a wide range of different chemical structures, primarily based on substituted aromatic and heterocyclic groups. A large number of reactive dyes are azo compounds that are linked by an azo bridge [3]. Since reactive dyes are highly soluble in water, their removal from wastewater is difficult by conventional coagulation and the activated sludge processes [4]. Therefore, oxidation and adsorption are two major technologies that are used for wastewater treatment in the textile industry. Among oxidation methods, UV/Ozone and UV/H_2O_2 treatments are technologies for decolourizing wastewater [5]. Adsorption is rapidly becoming a prominent method of treating aqueous effluents and has been extensively used in industrial processes for a variety of separation and purification purposes [6].

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Nomenclature

a_L	Langmuir isotherm constant (m^3/g)
C_i	initial liquid-phase concentration (g/m^3)
C_e	equilibrium liquid-phase concentration (g/m^3)
K_L	Langmuir isotherm constant (m^3/kg)
M	mass of adsorbent (kg)
q_e	equilibrium solid-phase concentration (g/kg)
V	volume of the solution (cm^3)
Γ	adsorption density (g/kg)

Activated carbon and polymer resins are claimed to be the best adsorbents for removing chemicals from relatively concentrated wastewater but are expensive and necessitate regeneration [6–8]. It is known that activated carbon has a rather low adsorption capacity for some reactive dyes [9]. Nevertheless, studies have been made on decolourization of wastewater using cost-effective adsorbent systems; natural clay/basic and acid dyes [10], chitosan/ reactive dyes [9], cotton/direct dye [11], sunflower stalk/basic dyes [12], sepiolite/ Rhodamine [13], montmorillonite and sepiolite/ methylgreen [14], and natural zeolite/basic dye [8].

Natural clay minerals due to their high surface area and molecular sieve structure are very effective sorbents for organic contaminants of cationic or polar in character [15,16]. Sepiolite is a fibrous hydrated magnesium silicate with a formula of $(Si_{12})(Mg_9)O_{30}(OH)_6(OH_2)4H_2O$ [17]. The fibrous structure of sepiolite induces sorptive, colloidal/ rheological, and catalytic properties which find various diverse applications (18). This is ascribed to its unique structure with interior channels ($3.6\times10.6\times10^{-10}$ m) which allows penetration of organic and inorganic ions together with solutes into the structure of sepiolite [18].

A natural zeolite mineral, clinoptilolite, has a three dimensional crystal structure and its typical unit cell formula is given either as $Na_6[(AlO_2)_6(SiO_2)_{30}].24H_2O$ or $(Na_2, K_2, Ca, Mg)_3[(AlO_2)_6(SiO_2)_{30}].24H_2O$ [19,20]. The three-dimensional crystal structure of zeolite contains channels [21] which embody some ion exchangeable cations such as Na, K, Ca and Mg. These cations have high cation exchange capability with organic and inorganic cations [22,23].

Sepiolites and zeolites have been studied in wastewater treatment in recent years. Adsorption of aromatic amines by activated sepiolite [24,25], removal of lead by zeolite [26,27], removal of ammonia [28–30] by natural clay materials (sepiolite and zeolite) are some of the examples pertinent to the use of these minerals in wastewater treatment systems.

The objective of this study is to examine the adsorption mechanism of three reactive dyes by natural and modified sepiolites and zeolites and assess their applicability to textile wastewaters.

2. Experimental

2.1. Materials

Zeolite and sepiolite samples were obtained from the Incal Zeolite (Gordes, Turkey) and Mayas Sepiolite (Sivrihisar, Turkey) companies, respectively. The chemical analysis of these zeolite (clinoptilolite) and sepiolite samples is given in Table 1. The sepiolite has an average particle size (d_{50}) of 2×10^{-6} m as determined by Zetasizer. The X-ray diffraction analysis together with the chemical analysis indicates that calcite and dolomite are the major impurities accompanying sepiolite [25]. Gordes zeolite have the following properties: cation exchange capacity of 1.9–2.2 eq/kg, pore diameter of 4×10^{-10} m, purity of 92%, bed porosity of 40%, density of 2150 kg/m^3, apparent density of 1300 kg/m^3, and suspension pH of 7.5–7.8 [23].

The dyes (Everzol Black B: C.I. Reactive Black 5, Everzol Red 3BS: C.I.. Red 239, and Everzol Yellow 3RS H/C: C.I. Yellow 176) used in adsorption experiments are azo dyes and basic in character. These dyes are known to contain anionic sulphonate groups to various degrees.

A quaternary amine, hexadecyltrimethylammonium bromide (HTAB, $C_{19}H_{42}BrN$) purchased from SIGMA and specified to be of 99%

Table 1
Chemical analyses of Gördes zeolite and Sivrihisar sepiolite

Constituent	Zeolite % by wt.	Sepiolite % by wt.
SiO_2	70.0	52.76
CaO	2.5	3.26
K_2O	2.3	0.75
SO_3	0,01	–
AI_2O_3	14.0	4.17
MgO	1.15	15.17
TiO_2	0.05	0.30
P_2O_5	0.02	–
Fe_2O_3	0.75	1.92
Na_2O	0.2	0.25
LOI	9.02	21.42

purity with a molecular weight of 346.46 gram was used for modifying the surface of the zeolite. The chemical structure of HTAB and the procedure for preparing the modified sepiolite and zeolite are given elsewhere [16,23]. The procedure briefly involves mixing of 5% solids with 2×10^{-2} kmol/m^3 HTAB followed by conditioning, solid–liquid separation and drying [31]. A number of studies on the removal of organic impurities by modified clays have been reported. These include the removal of benzene, toluene, ethylene and *o*-xylene using modified bentonite [32]; the adsorption of benzene, toluene and ethylene by modified soil minerals [33]; the removal of tetrachloramethane from liquid wastes with modified bentonite [34].

2.2. Methods

The electrokinetic properties of clay minerals (sepiolite and zeolite) were determined by a Zeta Meter 3.0 equipped with a microprocessor unit. This unit automatically calculates the electrophoretic mobility of particles and then converts it to the zeta potential. A clay 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 get 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 ml glass vials. Adsorption test were carried out with 5% solids concentration for the natural clay and with 0.1% and 5% for the modified clay. The bottles were placed on an orbital shaker (400 rpm) at room temperature for 4 h followed by centrifugation for 10 min. Distilled and deionized water with a conductivity value of 2.10^{-6} mhos/cm was used in all experiments.

The equilibrium concentrations of dyes were determined at the maximum adsorption wavelength of 592, 400, and 540 nm for Black, Yellow and Red dyes, respectively using a visible spectrophotometer. The adsorption density was calculated by the following formula:

$$qe = \frac{(Ci - Ce).V}{1000.m} \tag{1}$$

where q_e = amount of dye adsorbed per gram of adsorbent in g/kg, C_i = initial dye concentration in g/m^3, C_e = equilibrium (residual) dye concentration in g/m^3, V = the volume of the solution in cm^3 and m = mass of adsorbent (g).

3. Results and discussion

3.1. Adsorption isotherms with 5% solid concentration

A series of experiments were carried out with different% solids concentration at 25 g/m^3 initial dye concentration in order to determine the amount of solid to be used in the adsorption tests. An optimum solids concentration was selected as 50 kg/m^3 (5%), and this was used in the subsequent adsorption experiments for natural sepiolite and zeolite. In another study, a series of experiments were carried out to optimize the adsorption time at an initial dye concentration of 25 g/m^3 and solids concentration of 5%. Most of the adsorption was found to take place within the first 2 h of mixing. Taking into account the extreme changes that occur in parameters such as the pH and concentration, the mixing period of 4 h was selected for further testing [35].

Adsorption isotherms constructed for the natural sepiolite/reactive dyes system is presented in Fig. 1a. The adsorption isotherms with natural sepiolite for the three dyes exhibit a linear increase

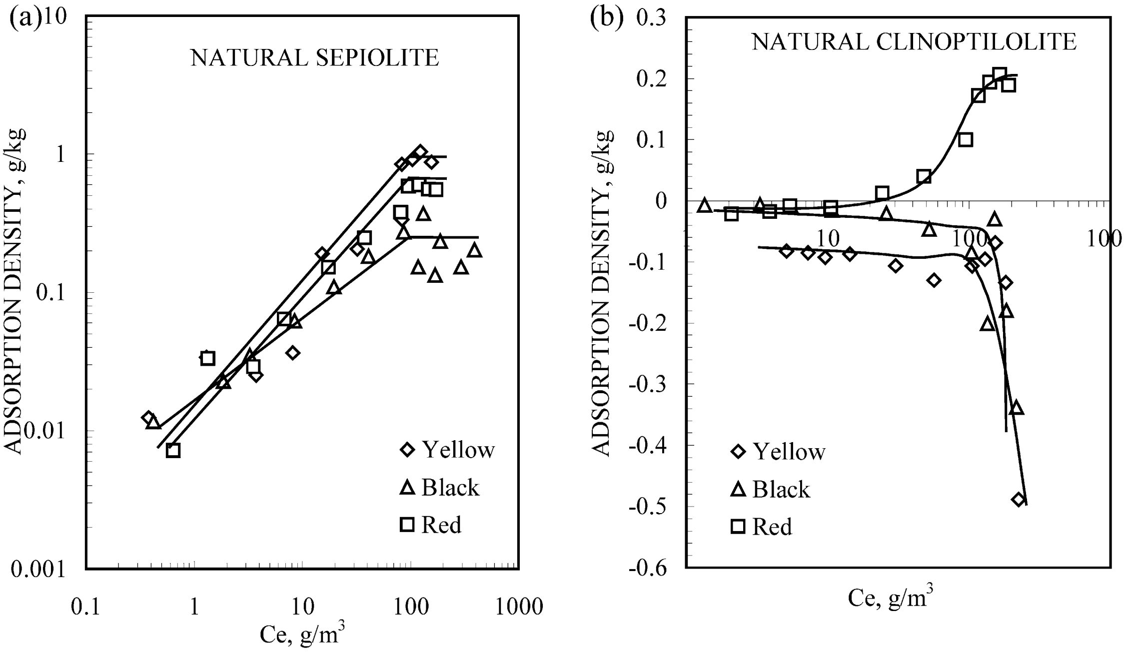

Fig. 1. Adsorption isotherms of natural (a) sepiolite/dyes system, (b) zeolite/dyes system at 5% solids concentration.

till 100 g/m^3 equilibrium concentration followed by a plateau region. As can be seen from Fig. 1a, the maximum capacity of sepiolite for the reactive dyes occurs at around 0.5–1 g/kg. The plateau region is characterized by a decrease in adsorption density. This is ascribed to the precipitation of dyes above about 100 kg/m^3 of dye concentration at natural pH. The precipitation in adsorption systems was visually determined above the plateau region. The results reveal that natural sepiolite appears to have a little affinity for reactive dyes.

Adsorption isotherms for natural zeolite/reactive dyes system is given in Fig. 1b. As seen in Fig. 1b, there is a negative adsorption on zeolite for all dyes, except for the red dye above 25 g/m^3. The exclusion of large molecules such as azo dyes is expected as the zeolite contains micropores. However, these pores are amenable to the adsorption of small molecules such as 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 miceles by a porous substrate, Bio-Sil, is well known in the literature [36,37]. Zeolites and microporous resins are reported to exclude large dye molecules [38] in particular for geometric reasons [39].

3.2. HTAB modification of sepiolite and zeolite

The zeta potential profiles of natural and modified samples versus pH are given in Fig. 2. While natural sepiolite yields an isoelectric point of about 6 with a negative charge prevailing at natural pH, natural zeolite has a negative charge over the entire pH range. These reactive dyes contain negatively charged sulphonate azo groups in equilibrium with the free acid; these are thus repelled by the negatively charged samples surfaces. This induces a relatively low adsorption capacity, as shown in Fig. 1a and b. For this reason, in order to increase the adsorption capacity, the surface of natural samples was modified with a typical quaternary amine surfactant (HTAB) which not only hydrophobises the surface of the samples but also neutralizes the negative charges [12,40]. Fig. 2 reveals that the surface acquires positive charges and consequently becomes receptive to the

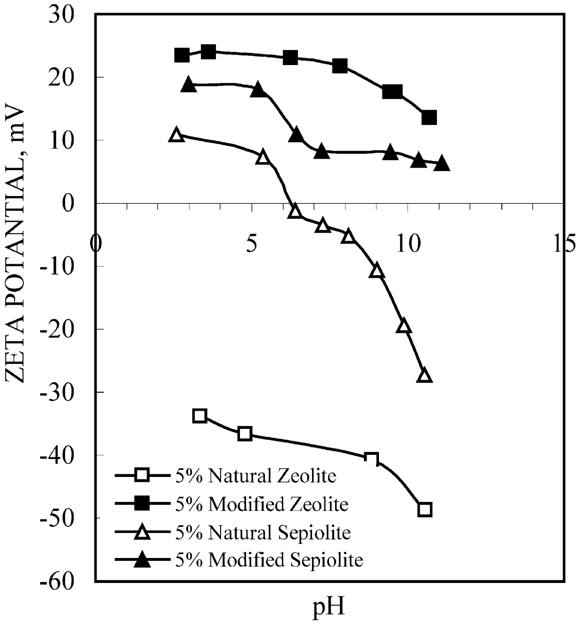

Fig. 2. The zeta potential–pH profiles of natural and modified sepiolite.

negative charges of the dye molecules by means of electrostatic attraction. It should be noted that the dissociated hydroxyl groups of the dye molecules may also weakly compete with the sulphonate groups for the positive sites. The competition is expected to favor the sulphonate groups.

Fig. 3a and b shows the adsorption isotherm of the modified samples at 5% solids concentration. A comparison of natural and modified zeolites at this concentration indicates that modification of samples with HTAB substantially improves the adsorbability of reactive dyes. The adsorption isotherms are characterized by three regions of interest. Although the rising branches of the adsorption isotherms show a linear increase (Region I) up to the residual concentration of 10 g/m^3 ($C_i = 500$ g/m^3), the isotherms then rise virtually vertical (Region II) followed by the occurrence of a reverse trend (Region III). Such abnormal behavior is an evidence for the formation of a solid phase, i.e., precipitation in Region II. Indeed, under normal conditions, the isotherms are expected to undergo a plateau region with constant adsorption density above saturation. The formation of precipitation can be ascribed to the interaction of anionic groups of the dye molecules with the cationic polar site of the quaternary amine molecule through electrostatic attraction. Such interactions can initiate below the onset of precipitation ($C_e = 10$ g/m^3) in the form of surface precipitate on sepiolite surface and continue in the bulk solution in the form of bulk precipitates. In fact, the precipitates formed in Region II above $C_e = 10$ g/m^3 dye concentration can be observed visually.

Precipitation in Region II is a typical behavior observed in systems where the solid phase is governed by a solubility product. However, that observed in Region III is unusual. It appears that in region III precipitation is not stoichometric and basically governed by the ionization of sulphonate groups against pH, which is found to increase significantly in this region. In order to ascertain the mechanism of precipitate formation in the system, a series of precipitation tests with sepiolite supernatants were conducted as a function of solids concentration. The results presented in Fig. 4 show that the residual concentration undergoes a minimum at around 1% solids concentration. It should be noted that no

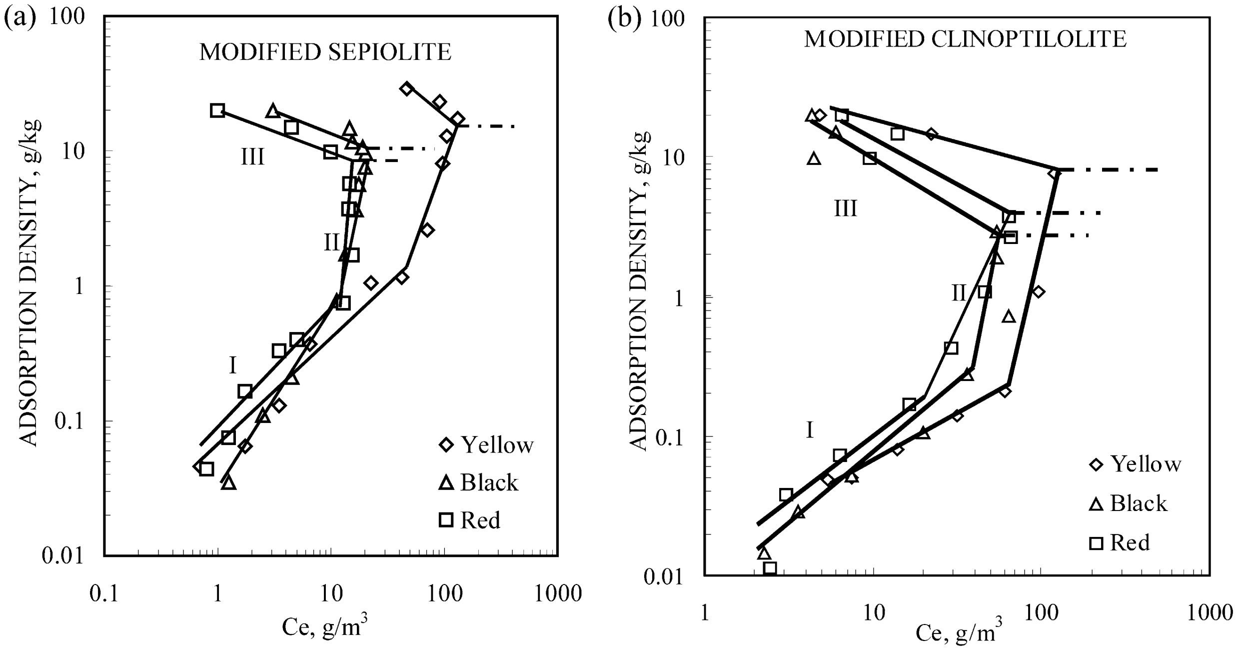

Fig. 3. Modified (a) sepiolite, and (b) zeolite-dye isotherms at 5% solids concentration.

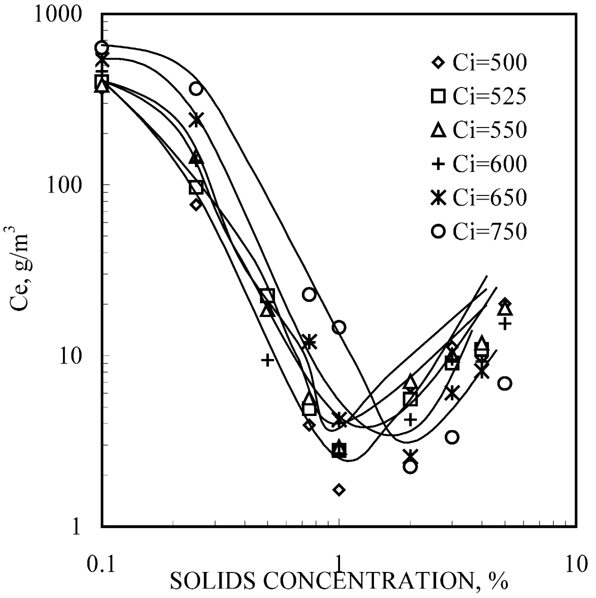

Fig. 4. Precipitation isotherms conducted in sepiolite supernatants against % solids concentration at different initial dye concentrations.

precipitation is formed at and below 0.1% solids concentration at all dye concentrations. However, above the initial concentration of 500 g/m^3 and above 0.1% solids concentration, the precipitate formation is observed. Interestingly, precipitation is largely dependent upon the combination of the three factors: pH, solids concentration, and the initial dye concentration. Similar results were also obtained for the zeolite.

Adsorption tests as a function of pH with only the Black dye were carried out to determine the extent of precipitation and also to identify the role of pH in adsorption. As seen in Fig. 5, while the adsorption density of black dye on zeolite decreases until the natural pH of 7.5 that on the sepiolite decreases marginally until the natural pH of 8.9 is attained and then increases above it. The precipitate formation is found to prevail only at and above the natural pH. The precipitate formed in this region is envisaged to correspond to that of Region III in Fig. 3a and b.

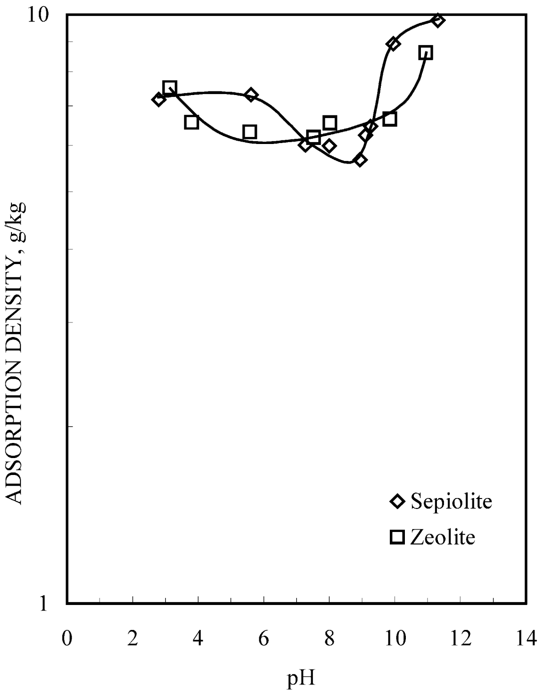

Fig. 5. The adsorption density of dye adsorbed on modified sample surfaces versus final pH (solids concentration = 0.1%, $C_i = 100$ g/m^3).

3.3. Adsorption isotherms with 0.1% solid concentration

Since adsorption tests on modified sepiolite indicated precipitation above 0.1% solids concentration, a set of experiments was conducted at 0.1% solids concentration to avoid precipitation. Adsorption isotherms with modified sepiolite are presented in Fig. 6a at 0.1% solids concentration. The adsorption density of modified sepiolite shows good performance and increases to 200 g/kg with increasing equilibrium concentration until 100 g/m^3 above which the adsorption density remains nearly constant.

Adsorption isotherms with modified zeolite are also presented in Fig. 6b at 0.1% solids concentration. The adsorption density of modified zeolite shows the same behaviour as sepiolite. The adsorption density increases to 100 g/kg with increasing equilibrium concentration until 60 g/m^3 above which the adsorption density remains nearly constant.

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 (Å/molecule) using the formula

$$\text{Cross-sectional area} = \frac{10^{20}}{\Gamma_{\max} A} S \qquad (2)$$

where $\Gamma_{\max}$ is the adsorption density at the plateau region, A is Avagadro number, and S is the specific surface area of the solid. Using the values of $\Gamma_{\max(\text{sepiolite})}$: $6.68.10^{-6}$ mol/m^2 [16], $\Gamma_{\max(\text{zeolite})}$: 1.10^{-4} kmol/kg [25], $S_{\text{sepiolite}}$: 50.5 ± 2 m^2/g, S_{zeolite}: 11.80 m^2/g (BET surface area measurement technique using nitrogen gas), A: $6.02.10^{23}$.

The packing area of HTAB on sepiolite is found to be 24.87 Å/molecule. Considering the cross sectional area of 37.82 Å/molecule reported for an amine molecule [41] the surface coverage (θ) is found to be 37.82/24.87 = 1.52. The packing area of HTAB on zeolite is found to be 19.60 Å/molecule. Considering the cross sectional area of 37.82 Å/molecule reported for trimethylammonium polar group [41], the surface coverage (θ) is found to be 37.82/19.60 = 1.93≈2.0.

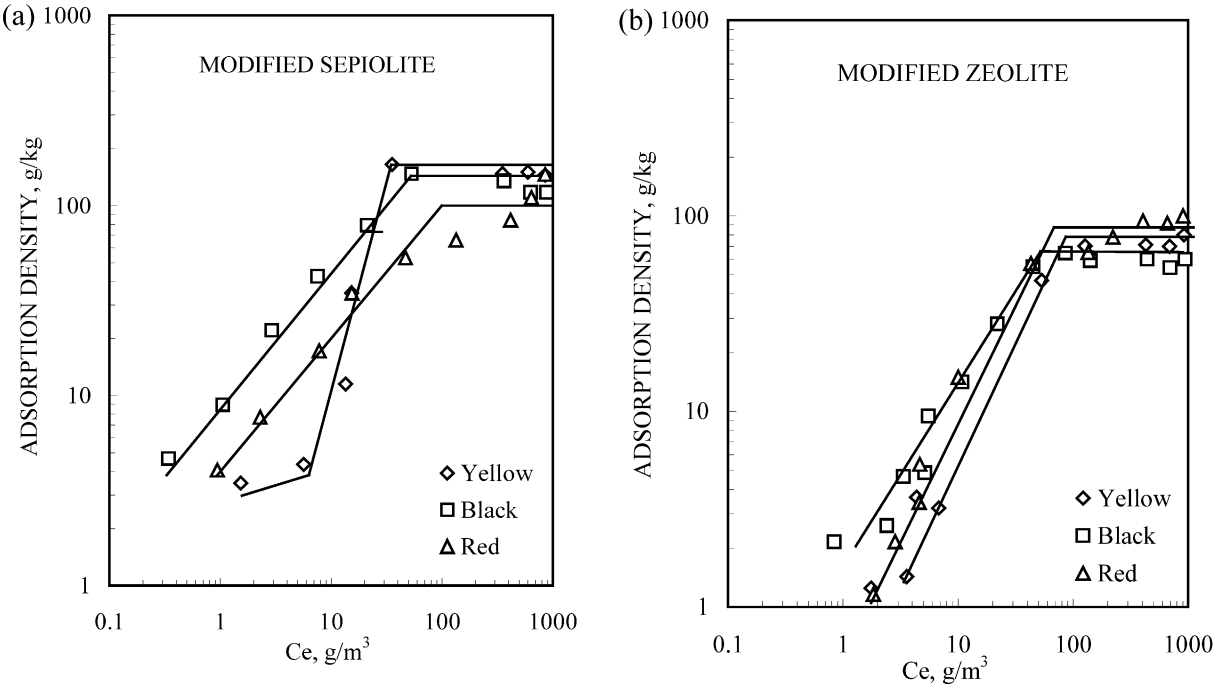

Fig. 6. Adsorption isotherms of modified (a) sepiolite/dye system, (b) zeolite/dye system for 0.1% solids concentration.

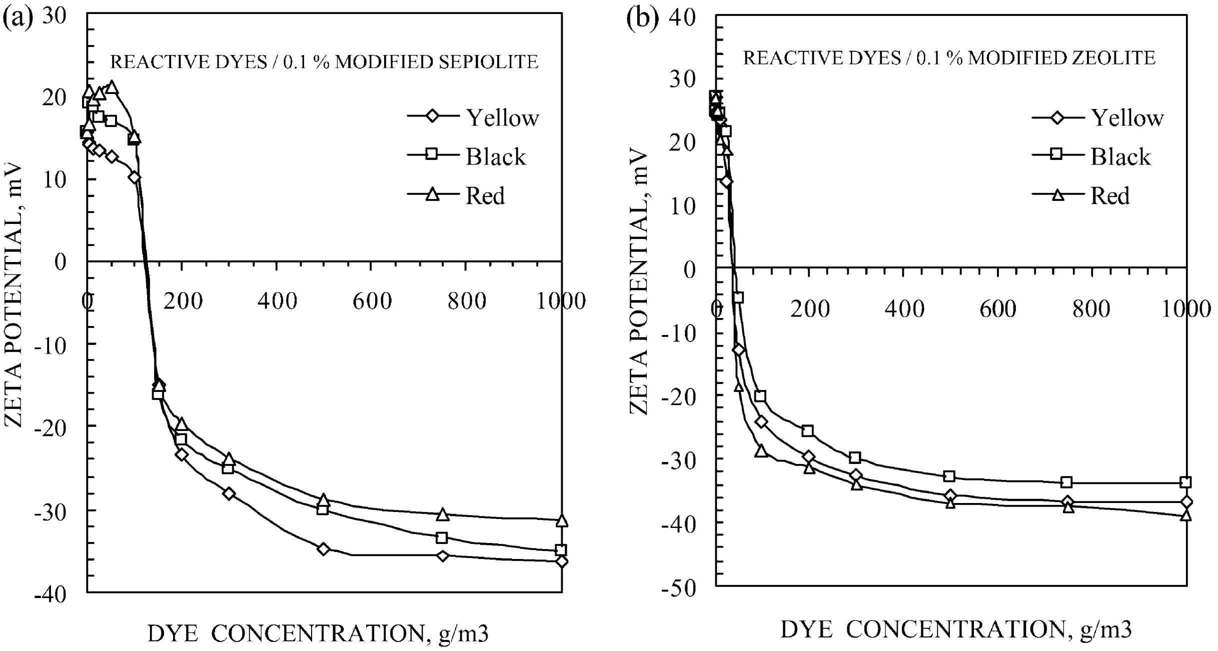

Fig. 7. Effect of dye concentration on zeta potential of (a) modified sepiolite, (b) modified zeolite at 0.1% solids concentration.

In order to identify the mechanism of dye adsorption onto modified samples, a set of zeta potential measurements against dye was performed. Fig. 7a and b show the effect of dye concentration on the zeta potential of modified samples. The surfaces of modified samples are initially positively charged in line with the data in Fig. 2. However, as the dye concentration is increased, the positive charges gradually diminish until an initial dye concentration of 100 g/m^3 for sepiolite and 25 g/m^3 for zeolite followed by a sharp decrease in zeta potential. The isoelectric point (iep) for all dyes occurs at initial dye concentration of about 125 g/m^3 for sepiolite and 40 g/m^3 for zeolite; above these concentrations the surface charge rapidly acquires negative charges and reaches a maximum at about 500 g/m^3 of initial dye concentration. The highest zeta potential reduction follows the order of Yellow > Black > Red for sepiolite and Red > Yellow > Black for zeolite. These are also the order of adsorption data given in Fig. 6a and b and vividly illustrates that the enhanced sorption of the dyes when the adsorbent is changed from natural to modified samples. The mechanism of anionic dye adsorption onto modified samples is schematically illustrated in Fig. 8a and b. Evidently, according to the packing area calculation the surface of samples under the modified conditions reveals coverage of about 1.5 layers for sepiolite and two layers for zeolite; this indicates that the degree of hydrophobicity plays an important role in the interaction of oppositely charged groups. More importantly, whether the surface covered by monolayer or bilayer becomes an important parameter in the uptake of anionic dye molecules by the modified samples.

The Langmuir equation describes the equilibrium data over the concentration range used in this investigation. The plots of the Langmuir isotherms illustrated in Fig. 9a and b 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 of sample for a particular dye. The capacity values of modified samples for the three types of reactive dyes are also analyzed according to the linear form of the Langmuir isotherm as follows:

$$C_e/q_e = \frac{1}{K_L} + \left(\frac{a_L}{K_L}\right).C_e \qquad (3)$$

where a_L = Langmuir constant (m^3/g) and K_L = Langmuir constant (m^3/kg). As seen from Fig. 9(a) and (b), when C_e/q_e is plotted against C_e, the Langmuir model fits the data very well. While

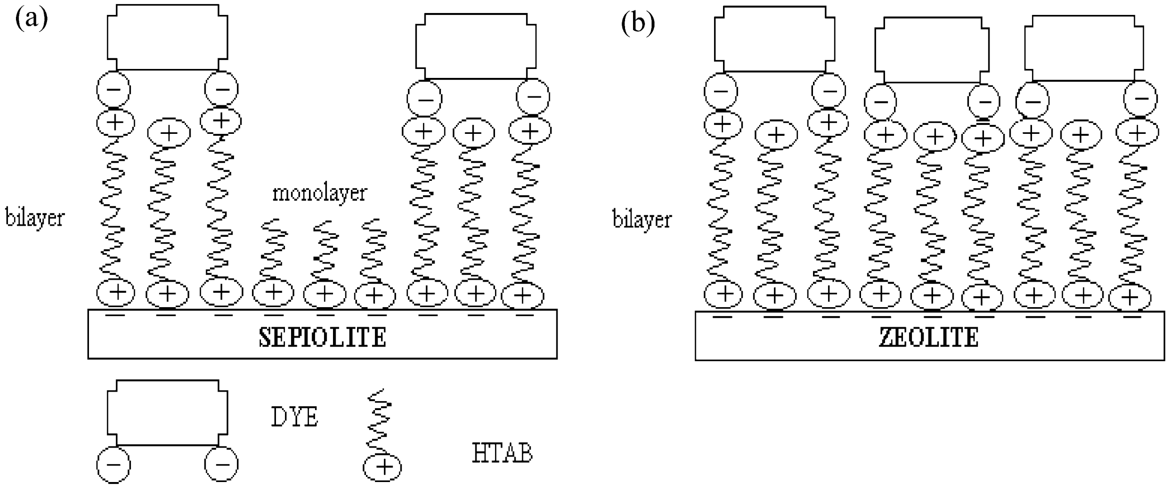

Fig. 8. A schematic illustration of the interaction of anionic dye molecule with quaternary amines adsorbed onto (a) sepiolite, (b) zeolite.

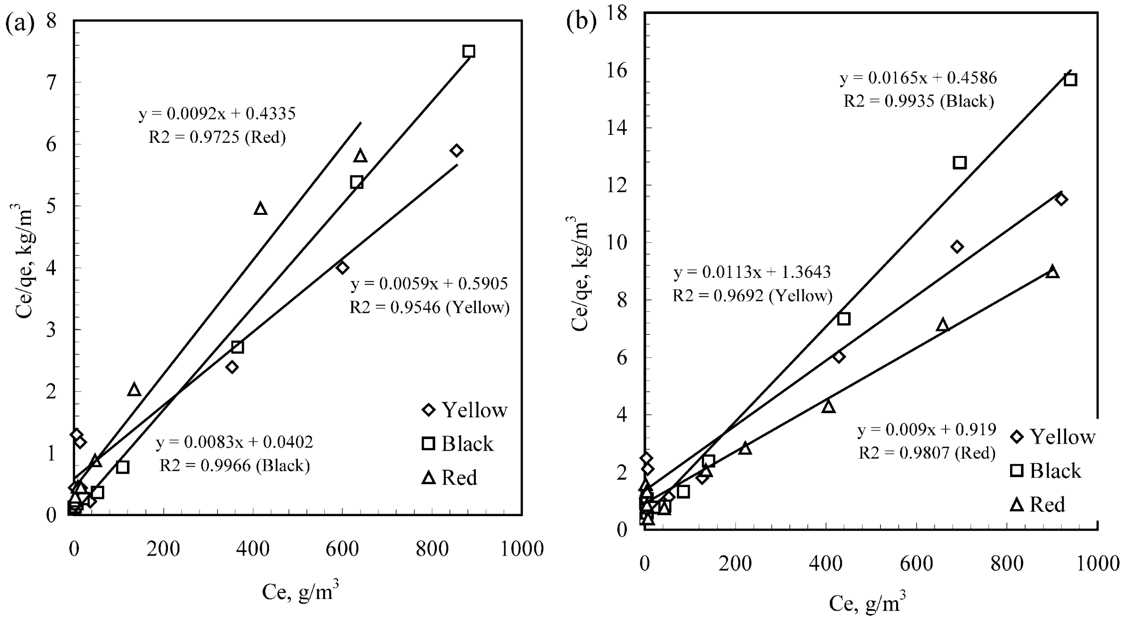

Fig. 9. Langmuir plot for adsorption of reactive dyes onto (a) modified sepiolite, (b) modified zeolite.

Table 2
Parameters of langmuir isotherm for different reactive dyes

No.	Adsorbate	Sample	Particle diameter (μm)	K_L (m^3/kg)	a_L (m^3/g)	q_{max} (g/kg)	Correlation coefficient
1	Everzol Yellow 3RS H/C	Sepiolite	−63	1.69	0.01	169.1	0.95
2	Everzol Black B	Sepiolite	−63	24.88	2.065	120.5	0.99
3	Everzol Red 3BS	Sepiolite	−63	2.31	0.021	108.8	0.97
4	Everzol Red 3BS	Zeolite	−63	0.919	0.009	111.1	0.98
5	Everzol Yellow 3RS H/C	Zeolite	−63	1.364	0.008	88.5	0.97
6	Everzol Black B	Zeolite	−63	0.458	0.036	60.6	0.99

the value of (a_L/K_L) gives the slope of the line, ($1/K_L$) yields the intersection of line with C_e/q_e axis. Adsorption density q_e and the parameters, K_L and a_L, of modified samples/ reactive dye systems are listed.

Table 2 shows that the yellow dye has the highest adsorption capacity (q_{max}) for sepiolite with a value of 169.14 g/kg. Under the same conditions, the adsorption capacity decreases in the following manner:

Yellow > Black > Red

Table 2 also shows that the red dye has the highest adsorption capacity (q_{max}) for zeolite with a value of 111.11 g/kg. Under the same conditions, the adsorption capacity decreases in the following manner:

Red > Yellow > Black

4. Conclusions

In general, sepiolite and zeolite in their natural forms are not suitable adsorbents for reactive azo dyes, however, treatment of the porous adsorbents by quaternary amines is found to modify the solid surfaces and make them amenable to the adsorption of dyes.

Adsorption isotherms with modified mezoporous adsorbents indicate that there are three regions of interest, each of which corresponds to a different adsorption mechanism. The adsorption of dyes onto modified samples is governed initially by electrostatic attraction onto already adsorbed cationic head groups of the HTAB molecules. Precipitation is found to be an important phenomenon taking place in the system. The initial dye concentration, solids concentration and pH appear to determine the magnitude of dye precipitation.

The maximum adsorption capacities of the yellow, black and red calculated using the Langmuir Equation on modified sepiolite at 0.1% solids concentration respectively are 169.1 g/kg, 120.5 g/kg and 108.8 g/kg: Under the same conditions, the adsorption capacity decreases in the order of hydrophilicity of the dye molecule in the following manner:

Yellow > Black > Red.

Under the same conditions, the maximum adsorption capacities using the Langmuir Equation on modified zeolite respectively are 111.1 g/kg, 88.5 g/kg and 60.5 g/kg. The adsorption capacity decreases in the order of hydrophilicity of the dye molecule as:

Red > Yellow > Black.

The comparison of adsorption isotherms of reactive dyes on both modified sepiolite and zeolite shows that sepiolite appears to be a better adsorbent than zeolite on the basis of mg/g. However, considering the substantial differences in the surface areas of sepiolite (50.5 m^2/g) and zeolite (11.80 m^2/g), the latter seems to be a better adsorbent. Column studies are in progress to determine the adsorption capacities of each adsorbent in a more realistic manner. It is interesting to emphasize that modified porous adsorbents are found to conveniently decolour the dye solutions.

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