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# Feasibility analysis of color removal from textile dyeing wastewater in a fixed-bed column system by surfactant-modified zeolite (SMZ)

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ABSTRACT

In this study, the ability of surfactant-modified zeolite (SMZ) to remove color from real textile wastewater was investigated. Tests were performed in a fixed-bed column reactor and the surface of natural zeolite was modified with a quaternary amine surfactant hexadecyltrimethylammonium bromide (HTAB). The zeolite bed that was modified at 1 g $L^{-1}$ HTAB concentration and HTAB flow rate of 0.015 L $min^{-1}$ showed good performance in removing color. Effects of wastewater color intensity, flow rates and bed heights were also studied. Wastewater was diluted several times in the ratios of 25%, 50% and 75% in order to assess the influence of wastewater strength. The breakthrough curves of the original and diluted wastewaters are dispersed due to the fact that breakthrough came late at lower color intensities and saturation of the bed appeared faster at higher color intensities. The column had a 3-cm diameter and four different bed heights of 12.5, 25, 37.5 and 50 cm, which treated 5.25, 19.50, 35.25 and 51 L original textile wastewater, respectively, at the breakthrough time at a flow rate of 0.025 L $min^{-1}$. The theoretical service times evaluated from bed depth service time (BDST) approach for different column variables. The calculated and theoretical values of the exchange zone height were found with a difference of 27%. The various design parameters obtained from fixed-bed experimental studies showed good correlation with corresponding theoretical values, under different bed heights. The regeneration of the SMZ was also evaluated using a solution consisting of 30 g $L^{-1}$ NaCl and 1.5 g $L^{-1}$ NaOH at pH 12 and temperature 30 °C. Twice-regenerated SMZ showed the best performance compared with the others while first- and thrice-regenerated perform lower than the original SMZ.

## 1. Introduction

The textile industry wastewaters contain colorants originating from dyeing and finishing processes. Important pollutants in the textile effluent are mainly recalcitrant organics, color, toxicants and inhibitory compounds, surfactants, chlorinated compounds (AOX), pH and salts. Dye is the most difficult constituent of the textile wastewater to treat [1]. Azo-reactive dyes are presently the most important compounds, constituting about 60–70% of the total dyes used industrially for coloring [2]. Besides, azo-reactive dyes hydrolyze easily, resulting in a high portion of unfixed (or hydrolyzed) dyes, which have to be washed off during the dyeing and approximately 50% of the initial dye load is present in the dyeing wastewater [3,4].

Physico-chemical methods are applied for the treatment of this kind of wastewaters, achieving high dye removal efficiencies [5]. In the biological treatment systems, the recalcitrant nature of azo dyes, together with their toxicity to microorganisms, makes aerobic treatment difficult whereas, a wide range of azo dyes is decolorized anaerobically [6,7]. On the other hand, adsorption [8–10], oxidation [11,12] and membrane [13] processes are major technologies that are used for wastewater treatment in the textile industry.

Adsorption is advantageous to other techniques in respect of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants [14]. In addition, adsorption is one of the most important unit processes in a wastewater treatment plant and the design of the adsorption column usually requires information from pilot-plant experiments [15,16]. Most commercial systems currently use activated carbons and organic resins as adsorbents to remove the dye in wastewater because of their excellent adsorption abilities [15,17]. Several investigators reported studies on cost-effective adsorbents including sepiolite [18,19], zeolites [9,20,21], waste materials [22,23] and biomass [24] etc.

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Natural zeolite (clinoptilolite) has a three-dimensional crystal structure and its typical cell formula is given as $Na_6[(AlO_2)_6(SiO_2)_{30}]\cdot 24H_2O$ [25]. The three-dimensional crystal structure of zeolite contains two-dimensional channels [26] which embody some ion exchangeable cations such as $Na^+$, $K^+$, $Ca^{2+}$ and $Mg^{2+}$. These cations can be exchanged with organic and inorganic cations [27]. 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 [28,29] and heavy metal treatment [30,31]. Several authors have reported that zeolites are not suitable for the treatment of anionic contaminants and reactive dyes. To enhance the adsorption capacity of zeolite, the surface of natural mineral was modified using some cationic surfactants in the literature [9,20,32,33].

This paper investigates color removal from real textile wastewater in a fixed-bed reactor using zeolite modified with hexadecyltrimethylammonium bromide (HTAB). The effects of bed modification and operation conditions on color removal were studied. The dynamics of color removal using bed depth service time (BDST) and design parameters of the fixed-bed system was modeled.

## 2. Materials and methods

### 2.1. Adsorbent specifications

The zeolite (clinoptilolite) sample, hereafter referred as zeolite, used in the experiments was received from Incal Mining company in the Gördes region of Turkey with a sieve size of 0.5–1 mm (35–18 mesh). Chemical and physical properties of the sample were supplied by the producer. Gördes zeolite has the following properties: 1.9–2.2 meq $g^{-1}$ of cation exchange capacity, 0.4 nm of pore diameter, 92–96% of purity, 40% of bed porosity, 2.15 g $cm^{-3}$ of density, 1.30 g $cm^{-3}$ of apparent density. The surface area of zeolite was found 11.8 $m^2\,g^{-1}$ as measured by the BET method using nitrogen gas [20]. The chemical analysis of the clinoptilolite zeolite was given elsewhere [34].

### 2.2. Modification of natural zeolite

A quaternary amine, hexadecyltrimethylammonium bromide (HTAB, C19H42BrN) purchased from SIGMA and specified to be of 99% purity with a molecular weight of 346.46 g was used for modifying the surface of the zeolite. The chemical structure of HTAB and the procedure for preparing the modified zeolite in the batch system were given elsewhere [20]. In this study, surfactant-modified zeolite (SMZ) was prepared in a fixed-bed column using HTAB solution at different HTAB concentrations of 1–7.5 g $L^{-1}$ and flow rates of 0.015–0.075 L $min^{-1}$, respectively.

### 2.3. Column studies

The laboratory-scale experimental set-up consists of zeolite fixed-bed column, HTAB solution and real textile wastewater tanks, peristaltic pump, flowmeter, valves and treated water tank (Fig. 1). The cylindrical plexiglas column has a diameter of 3 cm and height of 100 cm. Zeolite bed heights were chosen as 12.5, 25, 37.5 and 50 cm. Column studies were performed preparing SMZ using HTAB solution and subsequent color removal from real textile wastewater. The column was fed to have a down-flow stream with a particular flow rate and the samples were collected at every 30 min and were analyzed for residual concentration in the effluents.

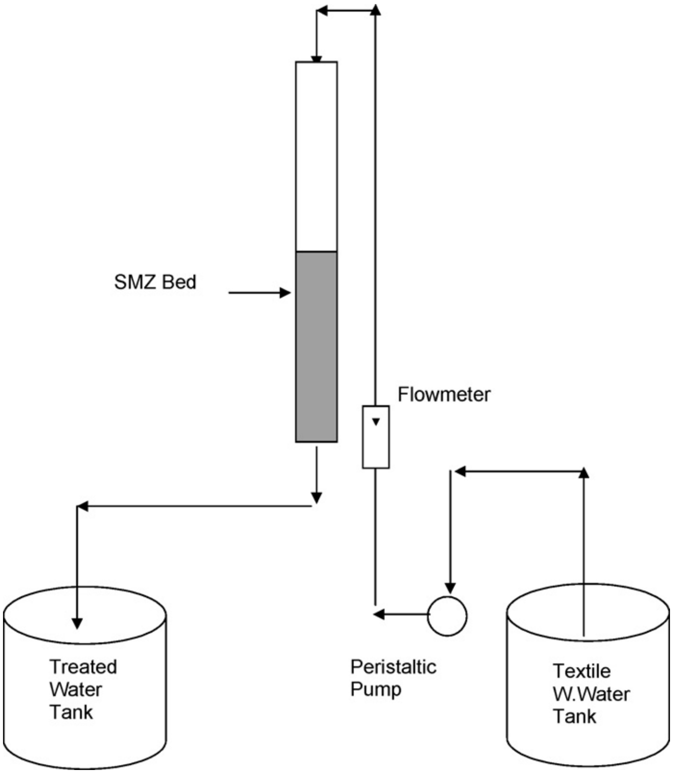

**Fig. 1.** Experimental set-up of fixed-bed column system.

In the experiments, the column was fed with real textile wastewater obtained from the dye bath effluent of a textile industry located in Kayseri, Turkey. In the dye house, different reactive dyes namely everzol, remazol, procion and evercion types of dyes and different auxiliary chemicals (Table 1) were used in five different containers. Adsorption performance of the zeolite bed can be evaluated

**Table 1**
Reactive dyes and auxiliary chemicals used in dyeing process that produce textile wastewater.

| Chemicals | Amount (kg) |
|---|---|
| Dyes | |
| Everzol orange 3R | 11 |
| Everzol red F2B | 15 |
| Everzol black GR | 166 |
| Everzol black HC | 77 |
| Remazol gelb 3R5 | 8 |
| Remazol rot 3B5 | 8 |
| Remazol black N150 | 82 |
| Procion yellow HEXL | 3 |
| Procion yellow HEGG | 3 |
| Procion red HEGXL | 1 |
| Procion crimson HEXL | 1 |
| Procion blue HERD | 2 |
| Procion navy HEXL | 3 |
| Evercion yellow HE4R | 15 |
| Evercion red HE7B | 22 |
| Evercion blau HEGN | 6 |
| Evercion navy HER | 26 |
| Evercion navy ESL | 32 |
| Auxiliary chemicals | |
| $Na_2SO_4$ | 650 |
| NaCl | 850 |
| $Na_2CO_3$ | 1500 |
| NaOH | 250 |
| $CH_3\cdot COOH$ | 350 |
| $H_2O_2$ | 220 |
| $Na_2\cdot S_2O_4$ | 45 |
| Ion holder | 90 |
| Detergent | 80 |
| Wetting | 125 |

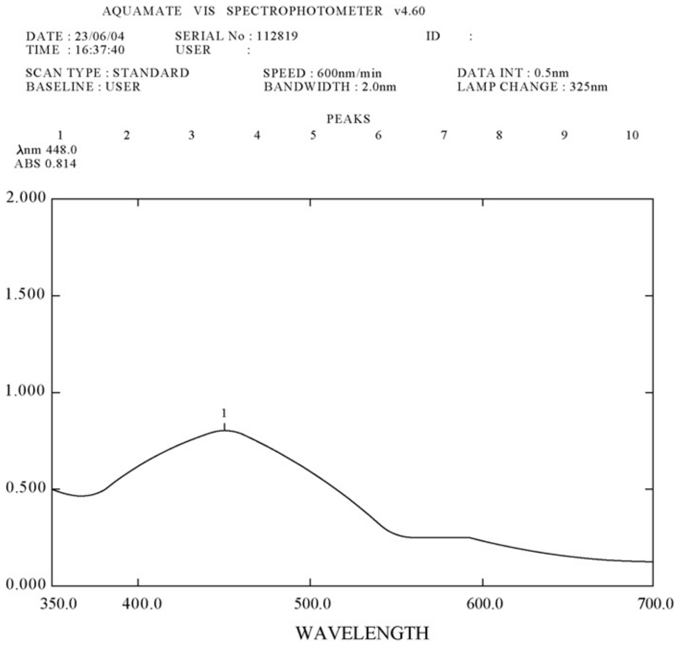

**Fig. 2.** UV–vis absorbance spectrum of textile wastewater sample used in the experiments.

while bed volumes (BV) at breakthrough point (corresponding to $C_{\mathrm{eff}}/C_{\mathrm{inf}} = 0.1$) are maximum. The breakthrough curves were constructed by plotting the normalized color intensity ($C_{\mathrm{eff}}/C_{\mathrm{inf}}$) versus service time ($t$) and/or bed volumes which is defined as follows [21]:

$$\mathrm{BV} = \frac{V_{\mathrm{F}}}{V_{\mathrm{R}}} = \frac{Q_{\mathrm{F}} t}{V_{\mathrm{R}}} \tag{1}$$

where $V_{\mathrm{F}}$ is the total water volume passing column during the adsorption process (L), $V_{\mathrm{R}}$ is the fixed-bed volume of zeolite (L), $C_{\mathrm{inf}}$ is the influent color intensity (absorbance, $\mathrm{m}^{-1}$), $C_{\mathrm{eff}}$ is the effluent color intensity (absorbance, $\mathrm{m}^{-1}$), $Q_{\mathrm{F}}$ is the feed flow rate in the fixed-bed ($\mathrm{L\,min}^{-1}$) and $t$ is the service time (min).

The column regeneration was carried out for SMZ bed using a solution consisting of $30\,\mathrm{g\,L}^{-1}$ of NaCl and $1.5\,\mathrm{g\,L}^{-1}$ of NaOH, at pH 12 and at temperature 30 °C for the exhausted 25 cm height dye adsorbed zeolite medium. The regeneration solution with a flow rate of $0.025\,\mathrm{L\,min}^{-1}$ was fed to the top of bed.

### 2.4. Analytical methods

The analysis for the cationic surfactant (HTAB) was performed by a two-phase titration technique [35,36]. A detailed information of this technique was given elsewhere [21]. Color removal was measured using a UV–vis spectrophotometer (Aquamate) at peak absorption wavelength of real textile wastewater (448 nm). Absorbance spectrum gave a peak at 448 nm between 350 and 700 nm wavelength as shown in Fig. 2. Before analysis, samples were filtered through 0.45 mm filters to remove suspended matters [37]. The color intensity of the sample was expressed as a function of absorption coefficient as follows [38]:

$$\begin{aligned}&\text{Color (absorbance, m}^{-1}\text{)}\\&\quad = \text{absorbance} \times \text{dilution factor/path-length}\,(m)\end{aligned} \tag{2}$$

Influent color intensity of the sample ($C_{\mathrm{inf}}$) was measured as absorption coefficient in the range of 0.802–0.888 (Fig. 2).

### 2.5. Theoretical background

#### 2.5.1. Bed depth service time (BDST) model

Data collected during lab- and pilot-scale tests serve as the basis for the design of full-scale adsorption columns. A number of mathematical models have been developed for the use in design. The bed depth service time model was proposed by Bohart and Adams [39] and defined as a relationship between bed height, $Z$, and the time taken for breakthrough to occur. Later, Hutchins [40] proposed modification of the Bohart–Adams equation with a linear relationship as follows:

$$t = \frac{N_0 Z}{C_{\mathrm{inf}} V} - \left(\frac{1}{k_{\mathrm{ad}} C_{\mathrm{inf}}}\right) \ln\left(\frac{C_{\mathrm{inf}}}{C_{\mathrm{b}} - 1}\right) \tag{3}$$

where $t$ is the service time (min), i.e. the time required for the effluent to reach the specific breakthrough concentration $C_{\mathrm{b}}$ ($\mathrm{mg\,L}^{-1}$), $K_{\mathrm{ad}}$ is the adsorption rate constant ($\mathrm{L\,mg}^{-1}\,\mathrm{min}^{-1}$), $Z$ is the height of adsorbent (cm), $V$ is the hydraulic loading rate (or) linear flow velocity of wastewater passing through the adsorbent ($\mathrm{cm\,min}^{-1}$), $C_{\mathrm{inf}}$ is the influent concentration of adsorbate in wastewater, $N$ is the residual adsorbing capacity per unit volume of bed ($\mathrm{mg\,L}^{-1}$). At $t = 0$, $N = N_0$ and at $Z = 0$, $C = C_{\mathrm{inf}}$ (influent dye concentration or color intensity). Eq. (3) can be expressed as

$$t = mZ + n \tag{4}$$

where $m$ is the slope of BDST graph given by $m = N_0/C_{\mathrm{inf}}V$, $Z$ is the bed depth (cm) and $n$ is the ordinate intercept.

$$n = -\left(\frac{1}{k_{\mathrm{ad}} C_{\mathrm{inf}}}\right) \ln\left(\frac{C_{\mathrm{inf}}}{C_{\mathrm{b}} - 1}\right) \tag{5}$$

#### 2.5.2. Evaluation of adsorption column design parameters

The time required for the adsorption zone to move the length of its own height up/down the column ($t_{\mathrm{z}}$) once it has become established and the time required for the adsorption zone to become established and move completely out of the bed ($t_{\mathrm{e}}$) are given as follows, respectively [16,41]:

$$t_{\mathrm{z}} = \frac{V_{\mathrm{s}}}{Q} \tag{6a}$$

$$t_{\mathrm{e}} = \frac{V_{\mathrm{e}}}{Q} \tag{6b}$$

where $V_{\mathrm{s}}$ is the total volume of textile wastewater treated between breakthrough and exhaustion (L), $V_{\mathrm{e}}$ is the total volume of textile wastewater treated to the point of exhaustion (L) and $Q$ is influent flow rate ($\mathrm{L\,min}^{-1}$). The rate at which the adsorption zone is moving up/down through the bed ($U_{\mathrm{z}}$) is

$$U_{\mathrm{z}} = \frac{h_{\mathrm{z}}}{t_{\mathrm{z}}} = \frac{h}{t_{\mathrm{e}} - t_{\mathrm{f}}} \tag{7}$$

The height of the adsorption (or exchange) zone ($h_{\mathrm{z}}$) is obtained with rearranging Eq. (7) as follows:

$$h_{\mathrm{z}} = \frac{h\, t_{\mathrm{z}}}{t_{\mathrm{e}} - t_{\mathrm{f}}} \tag{8}$$

where $h$ is the total bed height (cm), and $t_{\mathrm{f}} = (1 - F)t_{\mathrm{z}}$ is the time required for the adsorption zone to initially form (min). At breakthrough, the fraction of SMZ ($F$) present in the adsorption zone still possessing ability to treat the textile wastewater is given as

$$F = \frac{S_{\mathrm{z}}}{S_{\mathrm{max}}} = \int_{V_{\mathrm{b}}}^{V_{\mathrm{e}}} \frac{(C_{\mathrm{inf}} - C)\mathrm{d}V}{C_{\mathrm{inf}}(V_{\mathrm{e}} - V_{\mathrm{b}})} \tag{9}$$

where $V_{\mathrm{b}}$ is the total volume of wastewater treated to the breakthrough point (L), $S_{\mathrm{z}}$ is the amount of solute that has been removed by the adsorption zone from breakthrough to exhaustion; and $S_{\mathrm{max}}$

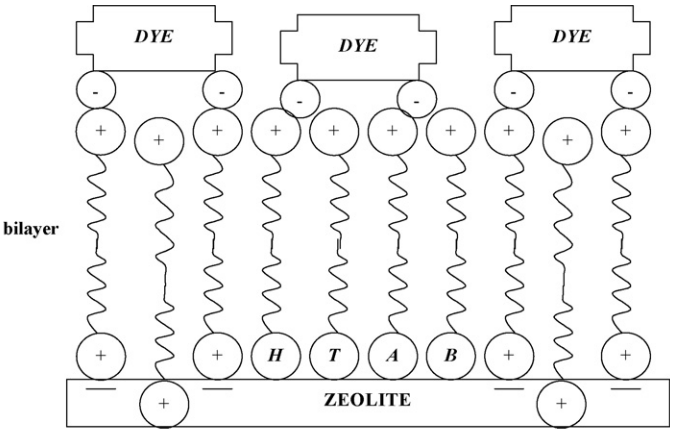

**Fig. 3.** A schematic illustration of interaction of anionic dye molecule with quaternary amines onto zeolite surface.

is the amount of solute removed by the adsorption zone if completely exhausted. Saturation of the SMZ column can be defined as follows:

$$\%\,\text{saturation} = \frac{h + (F-1)h_z}{h} \times 100 \qquad (10)$$

## 3. Results and discussion

### 3.1. Influence of modification conditions of SMZ bed for color removal

Batch adsorption tests were carried out using natural and surfactant-modified zeolite in our previous study [20]. The adsorption results indicate that the natural zeolite has a limited adsorption capacity for reactive azo dyes due to the exclusion of reactive dye anions from the pores with a corresponding increase in water adsorption within the pores. In order to increase the adsorption capacity, the surface of natural zeolite was modified with a cationic surfactant (HTAB) which not only makes the zeolite surface more hydrophobic but also neutralizes the negative charges [20].

The mechanism of anionic dye adsorption onto modified zeolite is schematically illustrated in Fig. 3. From the cross-sectional area calculations, the surface of zeolite under the modification conditions reveals coverage of about a bilayer; this indicates that the degree of hydrophobicity plays an important role in the interaction of oppositely charged groups. In addition, surface coverage as a bilayer rather than a monolayer has a strongly favorable influence on the dye adsorption [20].

The effectiveness of the modification of zeolite's surface was tested by the ability of color removing of the SMZ bed using textile wastewater. The color removal capacities of the SMZ bed which was modified with different HTAB concentrations between 1 and 7.5 g L$^{-1}$ were given in Fig. 4a. As seen in Fig. 4a, the breakthrough times (corresponding to $C_b/C_{inf} = 0.1$) for HTAB concentrations in the range of 1–7.5 g L$^{-1}$ exhibited a decrease from 780 to 330 min and the exhausting times (corresponding to $C_{eff}/C_{inf} = 0.9$) also decreased from 1380 to 600 min. Thus, the zeolite which was modified at lower HTAB concentration (1 g L$^{-1}$) showed better performance.

On the other hand, the color removal in the SMZ bed that were modified with HTAB flow rates between 0.015 and 0.075 L min$^{-1}$ were shown in Fig. 4b. The breakthrough times for HTAB flow rates in the range of 0.015–0.075 L min$^{-1}$ showed a decreasing trend from 1020 to 240 min and the exhausting times also decreased from 1440 to 660 min. The SMZ which was modified at HTAB flow rate of 0.015 L min$^{-1}$ showed better color removal than the SMZ modified at higher flow rates. Consequently, The SMZ bed that was modified at 1 g L$^{-1}$ HTAB concentration and HTAB flow rate of 0.015 L min$^{-1}$ showed good performance in removing color.

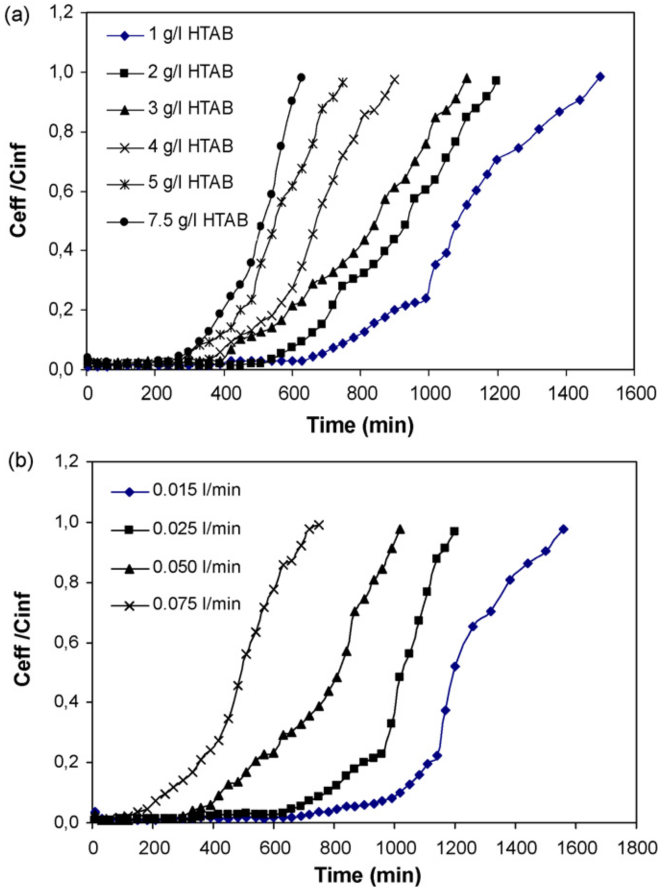

**Fig. 4.** Breakthrough curves of color removal from textile wastewater on surfactant-modified zeolite (SMZ) bed for (a) HTAB concentrations 1–7.5 g/L and (b) HTAB flow rates 15–75 mL/min at wastewater flow rate of 25 mL min$^{-1}$ and bed height of 25 cm.

### 3.2. Influence of operation conditions on color removal in SMZ bed

#### 3.2.1. Effect of wastewater color intensity

To assess the influence of wastewater strength, the textile wastewater was diluted several times in the ratios of 25%, 50% and 75%, thus, lower color intensities were obtained. The SMZ that was modified at the optimum conditions of 1 g L$^{-1}$ HTAB concentration and HTAB flow rate of 0.015 L min$^{-1}$ was fed using original and diluted textile wastewaters at flow rate of 0.025 L min$^{-1}$. The effect of dilution on color removal from the textile wastewater was shown in Fig. 5.

The breakthrough points for original wastewater and diluted wastewaters in the ratios of 25%, 50% and 75% were obtained at 780, 840, 1020 and 1320 min, respectively and the exhausting times also were 1380, 1620, 1800 and 2140 min, respectively. From Eq. (1), treated water volumes and bed volumes were found 19.43 L (111 BV), 21 L (120 BV), 25.55 L (146 BV), and 32.90 L (188 BV) at breakthrough points and 34.48 L (197 BV), 40.43 L (231 BV), 44.98 L (257 BV) and 53.50 L (306 BV) at exhausting points for original wastewater and diluted wastewaters in the ratios of 25%, 50% and 75%, respectively. A decrease at breakthrough point as well as exhaustion time at higher color intensity may be due to the rapid exhaustion of the sorption sites. Although, the breakthrough curve is dispersed

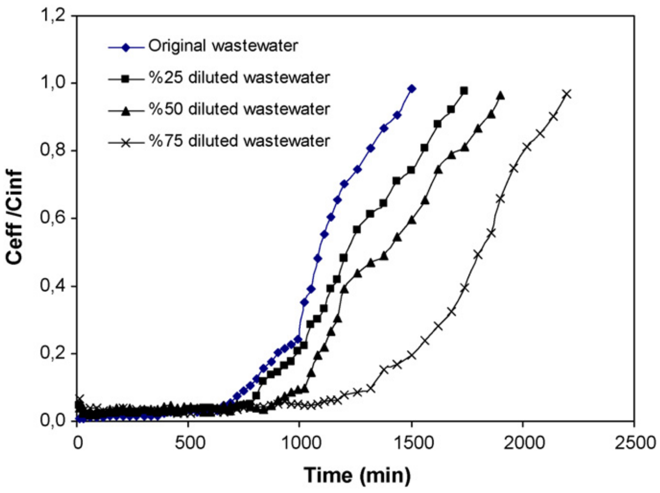

**Fig. 5.** Effect of color intensity on breakthrough curves of color removal from textile wastewater on SMZ bed at flow rate of 25 mL min$^{-1}$ and bed height of 25 cm.

and breakthrough point came late at lower color intensities, saturation of the bed appeared faster at higher color intensities. Thus, higher color intensities resulted in quick exhaustion of sorption sites, making the uptake less effective. Similar results were found for ammonia removal from landfill leachate by zeolite fixed-bed column [42] and As(III) removal in a fixed-bed system by modified calcined bauxite (MCB) [43].

### 3.2.2. *Effect of feed flow rate*

The effect of flow rate was studied at 0.025, 0.050 and 0.075 L min$^{-1}$ using the original textile wastewater in the SMZ reactor with a bed depth of 25 cm. The breakthrough curve of the lower flow rate of 0.025 L min$^{-1}$ tended to be more gradual, meaning that the column was difficult to be completely exhausted. Besides, at relatively higher flow rates (0.050 and 0.075 L min$^{-1}$), the breakthrough curves became steeper (Fig. 6a). The breakthrough times and the exhausting times for the flow rates of 0.025, 0.050 and 0.075 L min$^{-1}$ were obtained as 750, 210, and 90 min and 1440, 900 and 570 min, respectively. Treated water volumes ($V_b$) and bed volumes ($BV_b$) at breakthrough time were found as 18.73 L (107 BV), 10.50 L (60 BV) and 6.83 L (39 BV) for the flow rates of 0.025, 0.050 and 0.075 L min$^{-1}$, respectively. Besides, treated water volumes ($V_e$) and bed volumes ($BV_e$) at the exhausting time were 36.05 L (206 BV), 44.98 L (257 BV), and 42.70 L (244 BV) for the flow rates of 0.025, 0.050 and 0.075 L min$^{-1}$, respectively. Increasing the flow rate in the SMZ bed resulted with a decrease in color removal efficiency. This is attributed to the fact that low contact time between the adsorbate and adsorbent reduces the adsorption efficiency in the SMZ bed. In addition, at higher flow rates, the movement of adsorption zone along the bed is faster reducing the time for adsorption of dye on the SMZ bed [43].

### 3.2.3. *Effect of bed height*

Fig. 6b shows the breakthrough curves of different bed heights of 12.5, 25, 37.5 and 50 cm at a constant flow rate of 0.025 L min$^{-1}$.

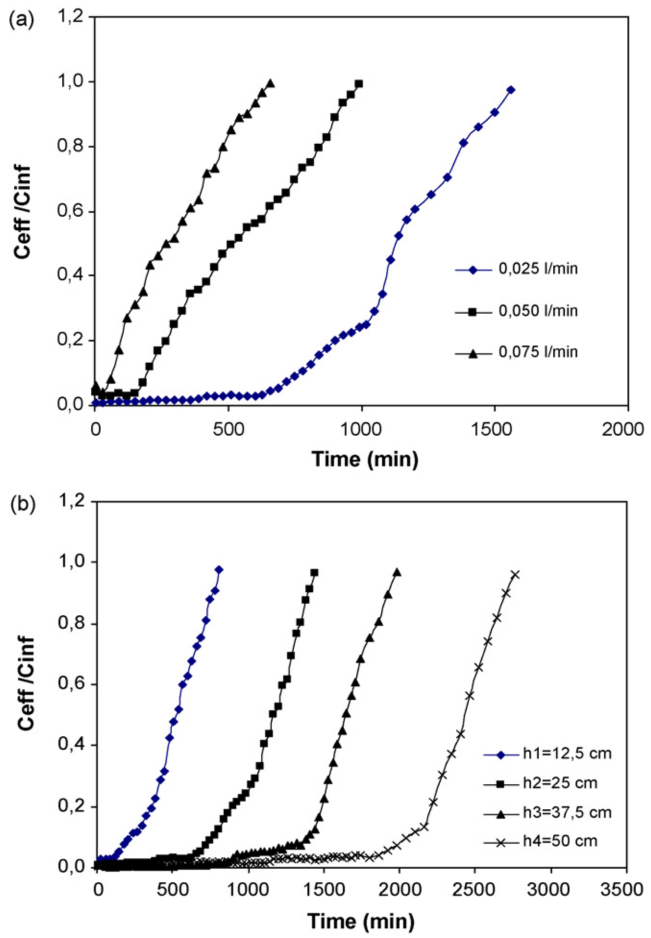

**Fig. 6.** Effect of (a) feed flow rates and (b) bed heights on breakthrough curves of color removal from textile wastewater on SMZ bed.

As expected, the treated water volumes at the breakthrough times and exhausting times increased with increasing bed height while the shape and the gradient of the breakthrough curves were slightly different for various bed heights. Decreasing the bed height caused the breakthrough curves become steeper showing faster saturation, which results in the early exhaustion of the bed (Fig. 6b). The quantity of the water treated at breakthrough point and exhaust point was given in Table 2. An increase in treated water volume per unit zeolite bed height at breakthrough time ($V_b/H$) was observed with the increase of bed heights, whereas, this value at the exhaust time ($V_e/H$) became nearly constant. Although an increase in bed depth increased the breakthrough time and the treated water volume, a very high bed depth is not practical for a single column; instead multiple-beds should be designed [44]. On the other hand, the volumes of water treated corresponding to different HTAB concentrations and flow rates, color intensities (as to dilution ratio), feed flow rates and regeneration cycles were also shown in Table 3.

**Table 2**
The quantity of water treated corresponding to different bed heights for an original textile wastewater and at flow rate of 0.025 L min$^{-1}$.

| Bed height, $H$ (cm) | Breakthrough time $t_b$, (min) | Exhaust time $t_e$, (min) | Treated water volume before breakthrough $V_b$, (L) | Treated water volume before exhaust $V_e$, (L) | $V_b/H$, (L cm$^{-1}$) | $V_e/H$, (L cm$^{-1}$) |
|---|---|---|---|---|---|---|
| 12.5 | 210 | 780 | 5.25 | 19.50 | 0.42 | 1.56 |
| 25 | 780 | 1380 | 19.50 | 34.50 | 0.78 | 1.38 |
| 37.5 | 1410 | 2040 | 35.25 | 51.00 | 0.94 | 1.36 |
| 50 | 2040 | 2700 | 51.00 | 67.50 | 1.02 | 1.35 |

**Table 3**
The volumes of water treated for different HTAB concentrations and flow rates, color intensities (as to dilution ratio), feed flow rates and regeneration cycles.

| Parameters | Breakthrough time $t_b$, (min) | Exhaust time $t_e$, (min) | Treated water volume before breakthrough $V_b$, (L) | Treated water volume before exhaust $V_e$, (L) |
|---|---|---|---|---|
| HTAB concentration (g $L^{-1}$) ($Q_{feed}$ = 0.025 L $min^{-1}$, $H$ = 25 cm) | | | | |
| 1 | 780 | 1440 | 19.50 | 36.00 |
| 2 | 630 | 1140 | 15.75 | 28.50 |
| 3 | 450 | 1050 | 11.25 | 26.25 |
| 4 | 420 | 870 | 10.50 | 21.75 |
| 5 | 360 | 720 | 9.00 | 18.00 |
| 7.5 | 330 | 600 | 8.25 | 15.00 |
| HTAB flow rate (L $min^{-1}$) ($Q_{feed}$ = 0.025 L $min^{-1}$, $H$ = 25 cm) | | | | |
| 0.015 | 1020 | 1500 | 25.50 | 37.50 |
| 0.025 | 780 | 1170 | 19.50 | 29.25 |
| 0.050 | 420 | 990 | 10.50 | 24.75 |
| 0.075 | 240 | 690 | 6.00 | 17.25 |
| Dilution ratio ($Q_{feed}$ = 0.025 L $min^{-1}$, $H$ = 25 cm) | | | | |
| Original | 780 | 1440 | 19.50 | 36.00 |
| 0.25 | 840 | 1620 | 21.00 | 40.50 |
| 0.50 | 1020 | 1860 | 25.50 | 46.50 |
| 0.75 | 1320 | 2140 | 33.00 | 53.50 |
| Feed flow rate (L $min^{-1}$) ($H$ = 25 cm) | | | | |
| 0.025 | 780 | 1500 | 19.50 | 37.50 |
| 0.050 | 210 | 900 | 5.25 | 22.50 |
| 0.075 | 90 | 570 | 2.25 | 14.25 |
| Regeneration cycles ($Q_{feed}$ = 0.025 L $min^{-1}$, $H$ = 25 cm) | | | | |
| Original | 780 | 1500 | 19.50 | 37.50 |
| 1 | 600 | 1380 | 15.00 | 34.50 |
| 2 | 900 | 1680 | 22.50 | 42.00 |
| 3 | 720 | 1260 | 18.00 | 31.50 |

### 3.3. Bed depth service time (BDST) analysis

The fixed-bed operations aim to reduce the concentration in the effluent so that a specific breakthrough concentration ($C_b$) will not be exceeded. In this study, the dynamics of adsorption process was also modeled using BDST and design parameters of the fixed-bed column. A technique has been presented by Hutchins [40] which requires only three column tests to collect the necessary data [42]. As seen in Table 2, the corresponding breakthrough times were found to be 210, 780, 1410 and 2040 min for 12.5, 25, 37.5 and 50 bed heights, respectively, and the corresponding exhaust times were 780, 1380, 2040 and 2700 min, respectively. Fig. 7 shows bed height versus service time for 10% and 90% saturation of the SMZ column, where the relation can be expressed as follows:

$$t = 48.96Z - 420 \quad \text{for 10\% saturation} \tag{11}$$

$$t = 51.36Z + 120 \quad \text{for 90\% saturation} \tag{12}$$

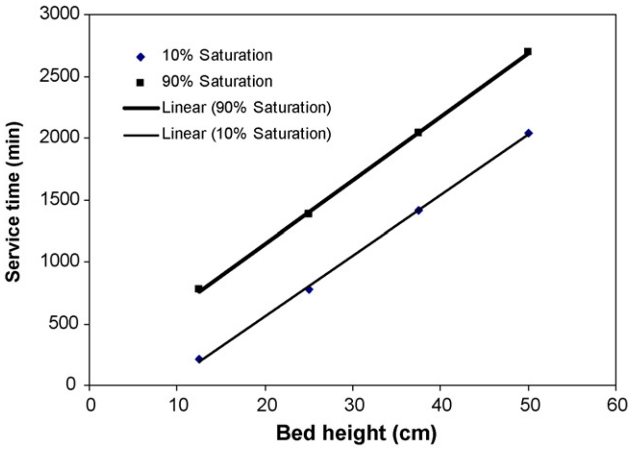

**Fig. 7.** Bed height versus service time at 10% and 90% saturation of SMZ bed.

From the slopes of Eqs. (11) and (12), the lines in Fig. 7 were nearly parallel and the horizontal distance between the lines that is referred as "height of exchange zone" [16] was found 10.92 cm.

### 3.4. Design of SMZ adsorption column

Fixed-bed column studies were conducted using columns packed with modified zeolite at different heights of 12.5, 25, 37.5 and 50 cm. Color removal from the textile wastewater in the SMZ bed can be evaluated when the treated wastewater volume at breakthrough point is maximum. Different parameters for column such as, time required for the exchange zone to move its own height ($t_Z$), height of exchange zone ($h_Z$), rate at which the exchange zone is moving up ($U_Z$), and % bed saturation were calculated using Eqs. (6)–(10) and shown in Table 4.

The height of exchange zone of 10.92 cm (Fig. 7) was found less than the lowest column height of 12.5 cm. However, its theoretical value of 13.91 cm was calculated with a difference of 27% compared to the literature [16,45], and approximate to the lowest column height (Tables 2 and 4), thus, the breakthrough time for 12.5 cm bed height would be zero. According to Maji et al. [45] this can be due to fluctuation in flow rate and canalization in bed, therefore, a lower breakthrough time was found as 210 min for 12.5 cm bed height.

**Table 4**
Design parameters for surfactant-modified zeolite (SMZ) column.

| Parameter | Bed height | | | | Average value |
|---|---|---|---|---|---|
| | 12.5 cm | 25 cm | 37.5 cm | 50 cm | |
| $t_z$ (min) | 570 | 600 | 630 | 664 | 616 |
| $h_z$ (cm) | 11.48 | 14.45 | 14.55 | 15.17 | 13.91 |
| $U_z \times 10^3$ (cm $min^{-1}$) | 20.1 | 24 | 23.1 | 22.8 | 22.5 |
| Bed saturation (%) | 74.28 | 67.05 | 74.40 | 76.64 | |

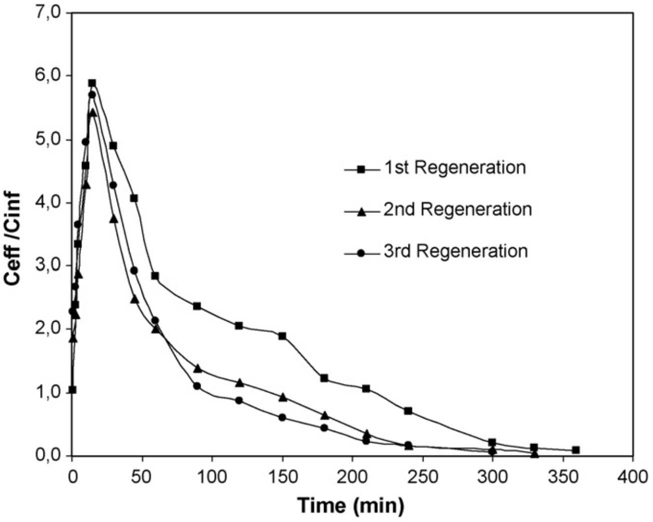

**Fig. 8.** Desorption of textile dye by different regeneration cycles as a function of time at feed flow rate of 0.025 L $\text{min}^{-1}$.

### 3.5. Effect of regeneration of SMZ on column performance

For the sorption process to be viable, efficient regeneration and reuse of the SMZ bed is necessary. When the normalized color intensity ($C_{\text{eff}}/C_{\text{inf}}$) reached the value of 0.9 at about the exhaust time, the SMZ bed was regenerated using a solution consisting of 30 g $\text{L}^{-1}$ of NaCl and 1.5 g $\text{L}^{-1}$ of NaOH at the feed flow rate of 0.025 L $\text{min}^{-1}$. Fig. 8 shows the results of the desorption of textile dye as a function of the $C_{\text{eff}}/C_{\text{inf}}$ for multiple regeneration cycles. The regeneration of the exhausted SMZ bed was found to have achieved a significant unload of the $C_{\text{eff}}/C_{\text{inf}}$ in the first 30 min at about $C_{\text{eff}}/C_{\text{inf}}$ value of 5 and then showed a decrease. The point of 0.1 $C_{\text{eff}}/C_{\text{inf}}$ for 1st, 2nd and 3rd regeneration cycles obtained at 360, 330 and 300 (or 51, 46.7 and 42.5 BV), respectively.

Fig. 9 also shows the breakthrough curves of SMZ and regenerated SMZ. The breakthrough point obtained at about 780 min (110.5 BV) for SMZ and 720 (102), 900 (127.5) and 720 min (102 BV) for regenerated SMZ in 1st, 2nd and 3rd cycles, respectively. Thus, twice-regenerated SMZ showed the best performance compared with the others while once- and thrice-regenerated perform lower than the original SMZ at about 8%. The result is fitted to the finding of zeolite/ammonia removal by Turan and Celik [28]. The regeneration of SMZ is expected to activate the SMZ by expanding the size of micropores and thus enabling the penetration of dye ions into pores. While 2nd regeneration may cause amenability of dye ions to micropores with a concomitant increase in the surface area, the 3rd regeneration causes a decrease in the specific surface area and adsorption capacity due to the appearance of macropores [28].

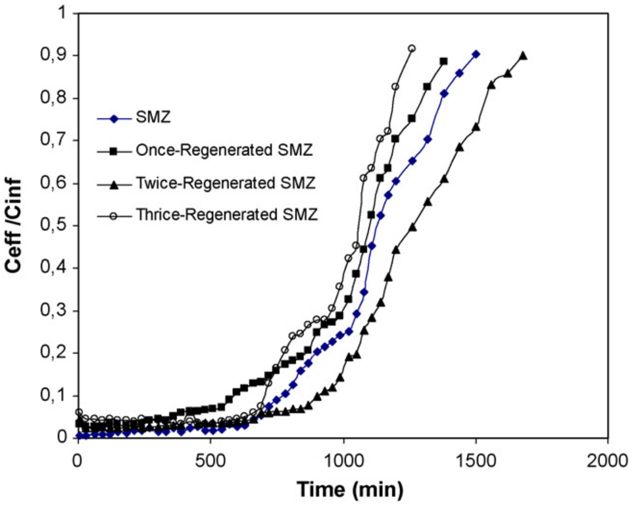

**Fig. 9.** Color removal from textile wastewater by SMZ and regenerated SMZ.

## 4. Conclusions

Fixed-bed column study was conducted to find out the effectiveness of SMZ bed for color removal from real textile wastewater. Optimum modification conditions of natural zeolite were found as lower values of surfactant concentration (1 g $\text{L}^{-1}$) and flow rate (0.015 L $\text{min}^{-1}$) for higher color removal. In the breakthrough curve, the breakthrough came late at lower color intensity (as to diluted wastewater in between 25% and 75%), saturation of the bed appeared faster at higher color intensity (original wastewater). Increasing the wastewater flow rate in the range of 0.025–0.075 L $\text{min}^{-1}$ resulted in a decrease of color removal. Decreasing the bed height made the breakthrough curves become steeper showing faster saturation, which resulted in early exhaustion of the bed. An increase in treated water volume per unit zeolite bed height at breakthrough time ($V_b/H$) was observed with increased bed heights. BDST model was used to evaluate the column design parameters, which showed good agreement with the experimental data. Design parameters for the SMZ column, like time required for adsorption (or exchange) zone to move ($t_z$), height of exchange zone ($h_z$), and rate at which the adsorption zone moves ($U_z$), were calculated as 616 min, 13.91 cm and $22.5 \times 10^{-3}$ cm $\text{min}^{-1}$, respectively. Bed saturation also varied between 67.5% and 76.64%. The SMZ was successfully regenerated twice, and after third regeneration the adsorption capacity decreased about 8%.

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## References

[1] S. Sen, G.N. Demirer, Anaerobic treatment of real textile wastewater with a fluidized bed reactor, Water Res. 37 (2003) 1868–1878.
[2] S.W. Fitzgerald, P.L. Bishop, Two-stage anaerobic/aerobic treatment of sulfonated azo dyes, J. Environ. Sci. Health A 30 (1995) 1251–1276.
[3] H. Zollinger, Color Chemistry, 2nd ed., VCH Publishers, NY, 1991.
[4] J. Shore, Dyeing with reactive dyes, in: Cellulosics Dyeing, The Alden Press, Manchester, 1995.
[5] P.C. Vandevivere, R. Bianchi, W. Verstraete, Treatment and reuse of wastewater from the textile wet-processing industry: review of emerging technologies, J. Chem. Technol. Biotechnol. 72 (1998) 289–302.
[6] I.M. Banat, P. Nigam, D. Singh, R. Marchant, Microbial decolorization of textile-dye-containing effluents: a review, Biores. Technol. 58 (1996) 217–227.
[7] S. Chinwekitvanich, M. Tuntoolvest, T. Panswad, Anaerobic decolorization of reactive dyebath effluents by a two stage UASB system with tapioca as a co-substrate, Water Res. 34 (2000) 2223–2232.
[8] M. Sankar, G. Sekaran, S. Sadulla, T. Ramasami, Removal of diazo and triphenylmethane dyes from aqueous solutions through an adsorption process, J. Chem. Technol. Biotechnol. 74 (1999) 337–344.
[9] J. Torres-Perez, M. Solache-Rios, M.T. Olguin, Sorption of azo dyes onto a Mexican surfactant-modified clinoptilolite-rich tuff, Sep. Sci. Technol. 42 (2007) 299–318.
[10] D. Karadag, E. Akgul, S. Tok, F. Erturk, M.A. Kaya, M. Turan, Basic and reactive dye removal using natural and modified zeolites, J. Chem. Eng. Data 52 (2007) 2436–2441.
[11] I. Arslan-Alaton, I.A. Balcioglu, D.W. Bahnemann, Advanced oxidation of a reactive dyebath effluent: comparison of $O_3$,$H_2O_2$/UV-C and $TiO_2$/UV-A processes, Water Res. 36 (2002) 1143–1154.

[12] I. Gultekin, N.H. Ince, Degradation of reactive azo dyes by UV/$H_2O_2$: impact of radical scavengers, J. Environ. Sci. Health A 39 (2004) 1069–1081.

[13] I. Koyuncu, D. Topacik, E. Yuksel, Comparative evaluation of the results for the synthetic and actual reactive dye bath effluent treatment by nanofiltration membranes, J. Environ. Sci. Health, Part A 38 (2003) 2209–2218.

[14] G. Crini, Kinetic and equilibrium studies on the removal of cationic dyes from aqueous solution by adsorption onto a cyclodextrin polymer, Dyes Pigments 77 (2008) 415–426.

[15] V.K. Gupta, S.K. Srivastava, D. Mohan, Equilibrium uptake, sorption dynamics, process optimization, and column operations for the removal and recovery of Malachite Green from wastewater using activated carbon and activated slag, Ind. Eng. Chem. Res. 36 (1997) 2207–2218.

[16] S. Kundu, A.K. Gupta, Analysis and modeling of fixed bed column operations on As(V) removal by adsorption onto iron oxide-coated cement (IOCC), J. Colloid Interface Sci. 290 (2005) 52–60.

[17] A.A. Attia, W.E. Rashwan, S.A. Khedr, Capacity of activated carbon in the removal of acid dyes subsequent to its thermal treatment, Dyes Pigments 69 (2006) 128–136.

[18] O. Ozdemir, B. Armagan, M. Turan, M.S. Celik, Comparison of the adsorption characteristics of azo-reactive dyes on mezoporous minerals, Dyes Pigments 62 (2004) 51–62.

[19] M. Alkan, O. Demirbas, M. Dogan, Adsorption kinetics and thermodynamics of an anionic dye onto sepiolite, Micropor. Mesopor. Mater. 101 (2007) 388–396.

[20] B. Armagan, O. Ozdemir, M. Turan, M.S. Celik, The removal of reactive azo dyes by natural and modified zeolites, J. Chem. Technol. Biotechnol. 78 (2003) 725–732.

[21] Y.E. Benkli, M.F. Can, M. Turan, M.S. Celik, Modification of organo-zeolite surface for the removal of reactive azo dyes in fixed bed reactors, Water Res. 39 (2005) 487–493.

[22] K.P. Singh, D. Mohan, S. Sinha, G.S. Tondon, D. Gosh, Color removal from wastewater using low-cost activated carbon derived from agricultural waste material, Ind. Eng. Chem. Res. 42 (2003) 1965–1976.

[23] N. Atar, A. Olgun, Removal of acid blue 062 on aqueous solution using calcinated colemanite ore waste, J. Hazard. Mater. 146 (2007) 171–179.

[24] K. Vijayaraghavan, Y.S. Yun, Utilization of fermentation waste (*Corynebacterium glutamicum*) for biosorption of reactive black 5 from aqueous solution, J. Hazard. Mater. 141 (2007) 45–52.

[25] D.W. Breck, Zeolite Molecular Sieves, John Wiley, NY, 1974.

[26] W.J. Mortier, J.R. Pearce, Thermal stability of the heulandite type framework: crystal structure of the calcium/ammonium form dehydrate at 483 K, Am. Miner. 66 (1981) 309–314.

[27] G. Blanchard, M. Maunaye, G. Martin, Removal of heavy metals from waters by means of natural zeolites, Water Res. 18 (1984) 1501–1507.

[28] M. Turan, M.S. Celik, Regenerability of Turkish clinoptilolite for use in ammonia removal from drinking water, J. Water Supply Res. Technol.-Aqua 52 (2003) 59–66.

[29] D. Karadag, Y. Koc, M. Turan, B. Armagan, Removal of ammonium ion from aqueous solution using Turkish clinoptilolite, J. Hazard. Mater. 36 (2006) 604–609.

[30] M. Turan, U. Mart, B. Yuksel, M.S. Celik, Lead removal in fixed-bed columns by zeolite and sepiolite, Chemosphere 60 (2005) 1487–1492.

[31] N.V. Medvidovic, J. Peric, M. Trgo, M.N. Muzek, Removal of lead ions by fixed bed of clinoptilolite—the effect of flow rate, Micropor. Mesopor. Mater. 105 (2007) 298–304.

[32] S. Wang, W. Gong, X. Liu, B. Gao, Q. Yue, Removal of fulvic acids using the surfactant modified zeolite in a fixed-bed reactor, Sep. Purif. Technol. 51 (2006) 367–373.

[33] D. Karadag, M. Turan, E. Akgul, S. Tok, A. Faki, Adsorption equilibrium and kinetics of reactive black 5 and reactive red 239 in aqueous solution onto surfactant-modified zeolite, J. Chem. Eng. Data 52 (2007) 1615–1620.

[34] A.B. Engin, O. Ozdemir, M. Turan, A.Z. Turan, Color removal fromtextile dyebath effluents in a zeolite fixed bed reactor: determination of optimum process conditions using Taguchi method, J. Hazard. Mater. 159 (2008) 348–353.

[35] V.W. Reid, G.F. Longman, E. Heinerth, Determination of anionic active detergents by two-phase titration, Tenside 4 (1967) 292.

[36] G.W. Powers, The Volumetric Determination of Organic Sulfates or Sulfonates by The Double Indicator Method. Communication C-225, Amoco Production Co., Tulsa, OK, 1970, pp. 1–4.

[37] O. Ozdemir, Investigation of Color Removal from Textile Industry Dyehouse Wastewater in Modified Zeolite Fixed-Bed Reactor. Ph.D. Thesis, Istanbul Technical University, Istanbul, Turkey, 2007.

[38] K. Santhy, P. Selvapathy, Removal of reactive dyes from wastewater by adsorption on coir pith activated carbon, Biores. Technol. 97 (2006) 1329–1336.

[39] G.S. Bohart, E.Q. Adams, Adsorption in columns, J. Am. Chem. Soc. 42 (1920) 523.

[40] R.A. Hutchins, New method simplifies design of activated carbon systems, Chem. Eng. 80 (1973) 133–138.

[41] L.D. Benefield, J.F. Judkins Jr., B.L. Weand, Process Chemistry for Water and Wastewater Treatment, Prentice Hall Inc., Englewood Cliffs, NJ, 1982.

[42] M. Turan, H. Gulsen, M.S. Celik, Treatment of landfill leachate by a combined anaerobic fluidized bed and zeolite column system, J. Environ. Eng. 131 (2005) 815–819.

[43] P.B. Bhakat, A.K. Gupta, S. Ayoob, Feasibility analysis of As(III) removal in a continuous flow fixed bed system by modified calcined bauxite (MCB), J. Hazard. Mater. 139 (2007) 286–292.

[44] S. Netpradit, P. Thiravetyan, S. Towprayoon, Evaluation of metal hydroxide sludge for reactive dye adsorption in a fixed-bed column system, Water Res. 38 (2004) 71–78.

[45] S.K. Maji, A. Pal, T. Pal, A. Adak, Modeling and fixed bed column adsorption of As(III) on laterite soil, Sep. Purif. Technol. 56 (2007) 284–290.