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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.

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

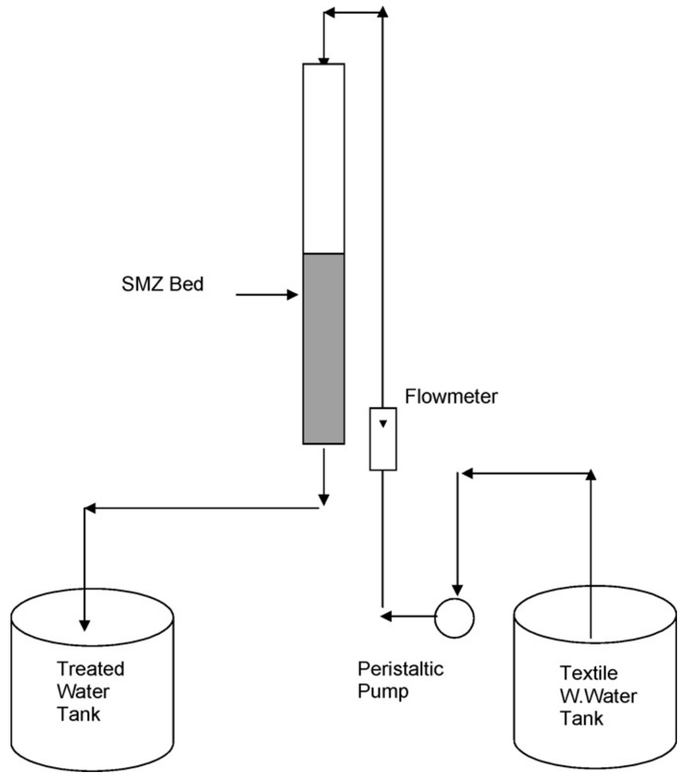

Fig. 1. Experimental set-up of fixed-bed column system.

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