Sorption of acid dye by surfactant modificated natural zeolites

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ABSTRACT

The adsorption of Acid Red 18 (AR18) by a natural zeolite (NZ) and its surfactant modified form (SMNZ) was investigated. The effects of initial dye concentration, contact time and adsorbent dose on the removal of AR18 were examined. Sorption kinetic was evaluated using the pseudo-second order, Elovich and Lagergren's first-order models. The equilibrium was analyzed by Freundlich, Langmuir, and Dubinin–Radushkevich models. The pseudo-second order kinetic model was found to agree well with the experimental data. The Langmuir isotherm was found to best represent the sorption data. The capacities of SMNZ and NZ for AR18 were found 20.42 and 1.17 mg/g, respectively. SMNZ could be a useful sorbent for the removal of AR18 from aqueous solutions.

1. Introduction

Due to the toxicity of dye effluents, their discharge to the environment, especially to water system, has becomes a major concern worldwide. These dyes are usually originated from industries such as dyestuff manufacturing, textiles, printing and dyeing. They can consume the dissolved oxygen content of water bodies which is needed for aquatic life. Some of them have a direct toxicity effect on microbial populations and even can be carcinogen or toxic to the mammals [1,2].

The structural varieties of dyes can fall into either the cationic, non-ionic or anionic types. Among these types, the anionic dyes include direct, acid and reactive dyes [3]. Brightly colored water-soluble reactive and acid dyes are the most problematic dyes, which tend to pass through the conventional treatment systems unaffected easily [4]. In addition, the presence of the dyes in water bodies can decreases the rate of photosynthetic process [5].

Nowadays, several treatment processes are used in the removal of dyes from aqueous solutions including: precipitation, ultrafiltration, ion exchange, phytoextraction, electrodialysis and reverse osmosis. However, the adsorption process is preferred for the removal of these pollutants due to easy handling and high removal performance [2,6–8]. On the other hand, the efficacy of the adsorption process and its economy are limited by the physicochemical characteristics and the cost of the adsorbent [9]. In this context, several researchers have studied the removal of dyes from mono-component solutions using low-cost adsorbents with inorganic origin such as clay materials. Clay minerals, as low cost natural adsorbents, are natural scavenger of pollutants from water through adsorption mechanisms [10] and ion exchange process [11]. Natural zeolites are good adsorbent for the dyes [12,13] and they have already found many applications because of their high cation-exchange capacity and surface area. They are mainly composed of aluminosilicates with a three dimensional framework structure bearing AlO_4 and SiO_4 tetrahedra that are linked to each other by sharing all of their oxygens to form interconnected cages and channels containing mobile water molecules and alkalis and/or alkaline earths [14]. Nowadays, functionalization of zeolites is a very promising approach for designing materials with novel surface properties and making them more suitable for specific applications [15,16].The common surface functionalization of these materials is via adsorption of cationic surfactants [17]. The natural zeolites (NZ) are most common inorganic materials used for surface modification, because they possess permanent negative charges in their crystal structure, making them suitable for this kind of modification. Sorption of a cationic surfactant onto a negatively charged surface involves both cation exchange and hydrophobic bonding mechanisms [18]. Surfactant modified natural zeolite (SMNZ) can remove organic compounds and oxyanions from water. Partitioning is responsible for organic sorption by SMNZ [19]. The capacity of zeolites for the dye sorption is limited

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and in many of studies their modification have been reported by surfactants, such as hexadecyltrimethylammonium (HTAB) [20], tetramethylammonium(TMA) [21], cetylpyridiniumbromide (CPB), and octadecyldimethylbenzyl (ODMBA) [22] to improve their sorption capacities. SMNZ has been used for the removal of various pollutants from aqueous solutions, such as phosphorous [23], humic acid [24], and heavy metals [25,26]. However, SMNZ is used as a sorbent for removal of dyes from aqueous solutions. For example it has been used for the removal of Congo Red [13], reactive dyes [27], Remazol Brillant Blue R and Remazol Yellow [28] from aqueous solutions. It seems that further batch studies are needed to investigate the capacity of SMNZ for the removal of dyes from aqueous environments.

A batch equilibrium adsorption study can be carried out to assess the adsorption capacity of a given sorbent for the sorption of an adsorbate. The equilibrium of the sorption of a material at a surface can be described by adsorption isotherms which are often used as empirical models [29]. An adsorption isotherm is the relationship between the adsorbate in the liquid phase and the adsorbate adsorbed on the surface of the adsorbent at equilibrium condition and a constant temperature. The adsorption isotherm is very important to design the adsorption systems. Isotherm models are obtained from measured data by means of regression analysis. The most frequently used isotherms are the Freundlich and Langmuir models [30]. Except for adsorption capacity, kinetic performance of a given adsorbent is also of a great importance in the pilot application. From the kinetic analysis, the solute uptake rate, which determines the residence time required for completion of adsorption reaction, may be established and one can know the scale of an adsorption apparatus based on the kinetic information [31].

This study aims to examine the adsorption capacities of locally-derived sorbents, SMNZ and NZ (obtained from natural mines in the southeast Semnan, a city in north eastern Iran) for the sorption of Acid Red 18 (AR18) from aqueous solutions. The sorption of AR18 onto SMNZ was studied by performing batch kinetic and equilibrium experiments. The experimental data were analyzed using the Freundlich, Langmuir and Dubinin–Radushkevich isotherm models. The kinetic data were also analyzed to predict the constant rate of adsorption using three common kinetic models: pseudo-second order, Elovich and Lagergren first-order models. The effects of parameters such as dye concentration, pH and dosage of sorbent were analyzed for the purpose of understanding the adsorption behavior of dye onto SMNZ.

2. Experimental

2.1. Sorbent preparation

Local natural zeolitefrom the mines in the southeast of Semnan (a province in northeastern Iran) was used to prepare modified sorbent. First of all the zeolite was crushed and passed through a series of sieves (50 and 70 U.S. standard mesh sizes). In order to remove dirt and dust particles, zeolite samples were washed in tap water and then twicewith distilled water. To remove the dissolved salts and impurities, the samples were placed in contact with distilled water for 1 h and then were washed with distilled water and dried at 200 C in an oven overnight [26,32,33]. The dried samples were sieved using metal sieves and a mixture of the residuals on 50 and 70 sieves was kept in a bottle and used for further investigation. The average adsorbent particle size was 0.27 mm.

To improve the cation exchange capacity of zeolite samples, a solution of sodium chloride salt was used to saturate the exchange sites with sodium ions, before modifying the surface of zeolites with surfactant. For this purpose, a one molar solution of sodium chloride was prepared and a dosage of 100 g/L of zeolites was contacted with the solution and shaked with speed of 170 rpm for 48 h. Because the
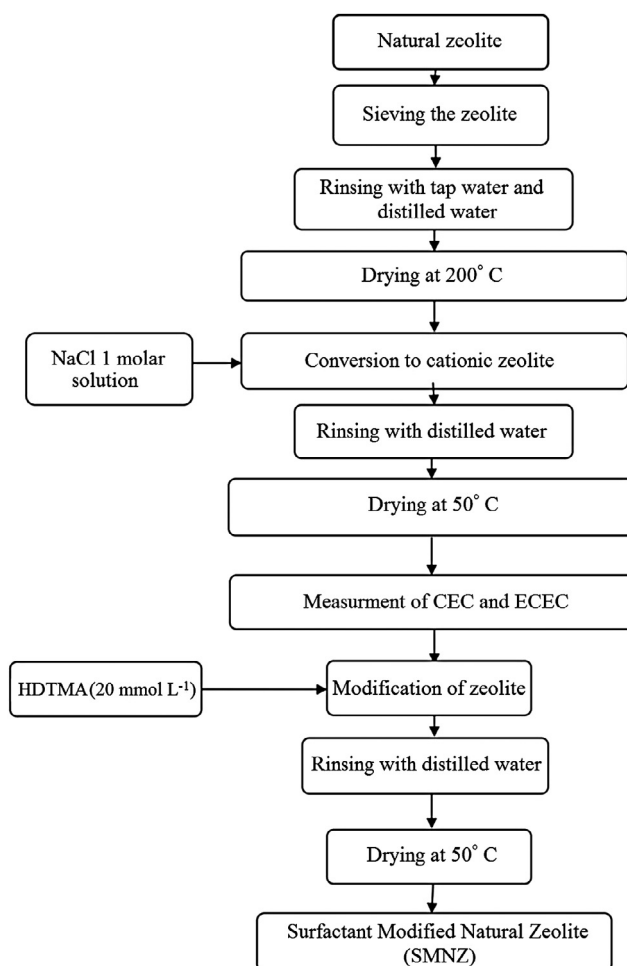

Fig. 1. Preparation of SMNZ.

chloride ions may affect the properties of modified zeolite, samples were washed with distilled water to remove residual chloride ions. The wash waste solution was analyzed for the presence of chloride ion using the argentometric titration method in order to ensure the removal of chloride ions [17,20,34].

The improved-cation-exchange-capacity samples were dried at 50 C in an oven overnight and used as natural zeolite (NZ) in the adsorption experiments.

Total cation exchange capacity (CEC) and the external CEC (ECEC) of zeolites were measured using Haggerty and Bowman [35] method.

Surfactant modified natural zeolite (SMNZ) affords a hydrophobic environment for the partitioning of organic molecules with low polarity and high molecular weight [36]. The preparation of SMNZ was carried out according to Fig. 1. Hexadecyltrimethylammonium bromide (HTAB) supplied by Merck with a concentration of 20 mmol/L was used for the preparation of SMNZ. 10 g of prepared cationic zeolite samples with 100 mL of HTAB solution were added to a 125 mL polyethylene bottle. The dispersions were shaked at room temperature by a mechanic shaker for 24 h followed by washing with distilled water. Therefore, the modified zeolite samples were dried at 50 C in an oven overnight [20]. In a study conducted by Ghadiri et al. [32], the modification of a clinoptilolite-type zeolite with a concentration of 20 mmol/L of HTAB provides the highest sorption capacity for the removal of MTBE from aqueous solutions.

The properties of zeolites were investigated by X-ray fluorescence (XRF) (PW 2404 Philips Holland) and X-ray diffractometer (X'Pert MPD Philips Holland) operated at 40 kV and 40 mA. The XRD

Table 1
XRF analysis results of NZ and SMNZ.

Sorbent	Oxides								
	Na_2O	MgO	K_2O	CaO	TiO_2	Fe_2O_3	SiO_2	Al_2O_3	L.O.I
NZ	2.24	0.41	4.028	1.28	0.19	0.66	69.32	10.47	11.27
SMNZ	2.25	0.42	4.05	1.30	0.20	0.68	69.33	10.49	11.28
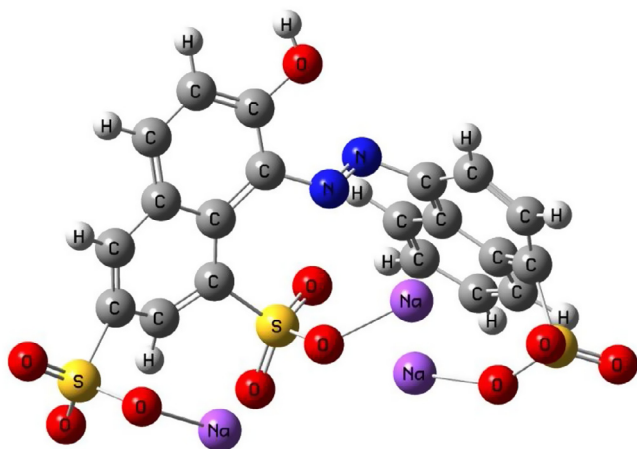
Fig. 2. Optimized-structure of the azo dye, Acid Red 18.

analysis was performed on the natural and modified zeolite samples to confirm the crystal structure and identity. The surface morphology of the zeolite samples was also investigated using scanning electron microscopy (XL30 Philips Holland).The chemical composition of natural zeolite was given in Table 1. The capacities of SMNZ and NZ for the sorption of Acid Red 18 from aqueous solutions were compared by conducting the kinetic and equilibrium adsorption studies.

2.2. Reagents

Acid Red 18 (AR18), known as C.I. 16255 and an acidic dye, was bought from Alvansabet company at Hamadan, a city in west Iran. The dye was used without any additional purification and its optimized structure (the dye's structure was optimized in Hyperchem software by PM3 method) was shown in Fig. 2. Molar mass of AR18 is 604.47 g/mol and its molecular formula is $C_{20}H_{11}N_2Na_3O_{10}S_3$.

A dye stock solution was prepared by dissolving of 500 mg of AR18 in 1000 mL deionized water. The working solutions were prepared by diluting of the stock solution.

2.3. Kinetics and equilibrium studies

The kinetic and equilibrium adsorption studies were carried out to evaluate the maximum sorption capacity of the dye by sorbents (NZ and SMNZ) from aqueous solutions using batch contact adsorption process at $25 \pm 2 °C$ and pH 6.5 ± 0.2. The initial concentration of dye solution was 50 mg/L. Adsorption experiments were conducted in 1000 mL Erlenmeyer flasks containing a suspension of 4 g of adsorbent and one liter of dye solution with different concentrations. The contents of all Erlenmeyer flasks were mixed thoroughly using magnetic stirrers with a constant speed.

A series 5 mL samples were taken at irregular intervals and one at the equilibrium time to measure the residual dye concentration for conducting kinetic and equilibrium studies, respectively. The samples were centrifuged at 3500 rpm for 20 min. The adsorption time was not included in the length of centrifugation time in this study. The dye concentration in each sample was measured spectrophotometrically

Table 2
The name and non-linear form of studied isotherm models.

Model types	Name	Non-linear form	References
Isotherm models	Langmuir	$q_e = \frac{q_m b C_e}{1 + b C_e}$	[37]
	Freundlich	$q_e = k_f C_e^{1/n}$	[38]
	Dubinin–Radushkevich	$q_e = Q_s \exp(-B_D \varepsilon^2)$	[39]
		$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right)$	
Kinetic models	Pseudo-second order	$q_t = \frac{q_e^2 k_2 t}{q_e k_2 t + 1}$	[44]
	Elovich kinetic model	$q_t = \frac{\ln \alpha \beta}{\beta} + \frac{1}{\beta} \ln t$	[46]
	Lagergren first-order model	$q_t = q_e - \exp(\ln q_e - k_1 t)$	[45]

at the maximum absorption wavelength (λ_{max}), 506 nm. The amount of dye adsorbed onto the zeolite sorbents, q_e (mg/g), was calculated as follows:

$$q_e = \frac{(C_0 - C_e)V}{W}, \tag{1}$$

where V is the liquid volume (L), C_0 is the initial concentration in the solution (mg/L), C_e is the equilibrium concentration (mg/L), and W is the amount of the adsorbent sample (g), respectively. Each experiment was carried out twice to check the reproducibility of the results and the average results are reported. Adsorbent-free blanks were used as control. The reproducibility of the experiments was acceptable and a maximum error of about 5% between the replicates of adsorption experiments was estimated.

Three adsorption isotherm models, Langmuir [37], Freundlich [38] and Dubinin–Radushkevich [39] were used to describe the equilibrium between the adsorbed dye on the adsorbent and dye in solution. The non-linear forms of isotherm models are given in Table 2.

The Langmuir equation is valid for monolayer sorption onto a surface with a finite number of identical sites. In the Langmuir equation C_e (mg/L) is the equilibrium concentration of dye in solution, q_m (mg/g) is the maximum amount of adsorbed dye per unit mass of sorbent corresponding to complete coverage of the adsorptive sites, q_e (mg/g) refers to the amount of the dye adsorbed at equilibrium time and b (L/mg) is the Langmuir constant related to the energy of adsorption. The essential characteristics of the Langmuir isotherm can be expressed in terms of the dimensionless constant separation factor or equilibrium parameter, R_L [40] which is defined by Eq. (2):

$$R_L = \frac{1}{1 + bC_0}, \tag{2}$$

where b is the Langmuir model constant and C_0 (mg/L) is the initial concentration of the dye in solution. The value of R_L indicates the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$).

The constant n in the Freundlich equation is a constant that represents the parameter characterizing quasi-Gaussian energetic heterogeneity of the adsorption surface [41]. The n constant gives an indication on the favorability of adsorption. It is generally stated that value of n in the range of 2–10 represent good, 1–2 moderately difficult, and less than 1 poor adsorption characteristics [42].

Dubinin and Radushkevich (D–R) proposed an empirical equation has been widely used to describe the case of liquid-phase adsorption. Several studies have shown that the adsorption energy can be estimated according to the D–R equation, assuming that the adsorption in micropores is limited to a monolayer [20,43]. The adsorption capacity per unit surface area of the adsorbent at equilibrium, q_e, can be written as Table 2, where Q_s is the ultimate capacity per unit area in adsorbent micropores, B_D (mol²/kJ²) is the constant related to the adsorption energy, ε is the Polenyi potential, R is the gas constant (8.314 J/mol K) and T is the absolute temperature (K). The most probable energy of adsorption, E (kJ/mol) has been defined as:

$$E = (2B_D)^{-1/2}, \tag{3}$$

For evaluating the adsorption kinetics of AR18 dye, three kinetic models, namely pseudo-second order [44], Lagergren's first-order [45] and Elovich [46] models were applied to the experimental data. The non-linear equation forms of these kinetic models are given in Table 2.

3. Results and discussion

3.1. Structural analysis of zeolite

The XRD diffractogram and SEM micrograph for NZ and its modified form (SMNZ) are shown in Figs. 3–5. The XRD spectrum of the NZ was shown in Fig. 3. It is evident that the XRD pattern of the zeolite was similar to that of reflectance spectra of clinoptilolite. Thus, clinoptilolite is the main mineral species in the zeolite's structure.

For the natural zeolite used in this study, CEC and ECEC values were 1.85 mEq/g, and 0.20 mEq/g, respectively. Generally zeolites possess a net negative charge, thus due to isomorphic substitution of the cations in the crystal lattice, they are excellent adsorbents for cationic sorbates [35]. Accordingly, this negative surface charge results in zeolites having little or no affinity for anions. The ECEC value of modified zeolite in this study is lower than the CEC value and this represents that the main negative charges, are located in the internal pore of zeolites [47].

A close resemblance was observed by comparing the diffraction pattern of SMNZ (Fig. 4) with NZ. This finding is confirmed by the results obtained by XRF analysis of the zeolite samples summarized in Table 1 and indicates the structural integrity of material before and after surfactant treatment [48]. Thus, the structure of zeolite was not changed by chemical treatment. The SEM images of NZ and SMNZ samples are illustrated in Fig. 5. SEM micrograph of NZ reveals that the natural zeolites have drusy texture with high microporosity. The aggregated particles having size 100–1000 nm and appeared as flakes like crystals. No obvious differences are observed in surface
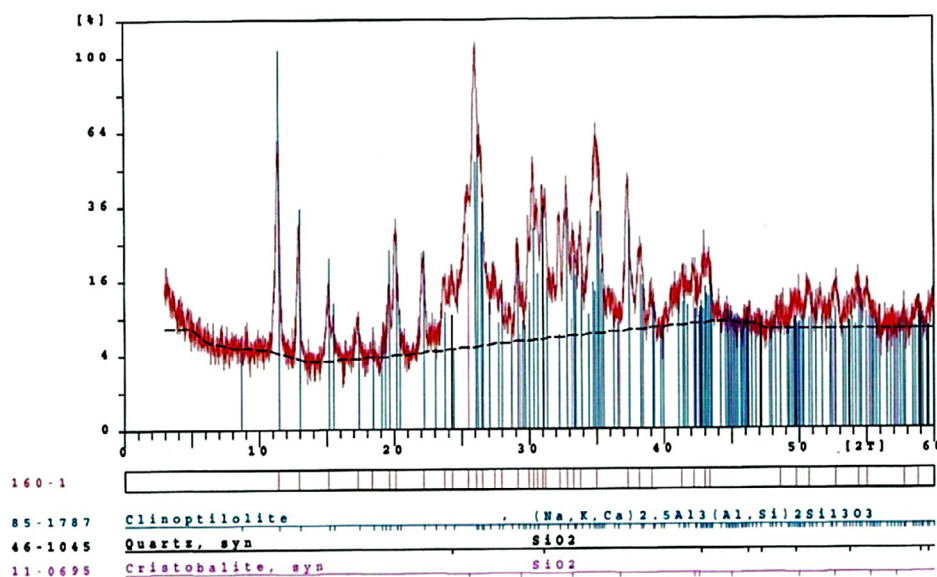

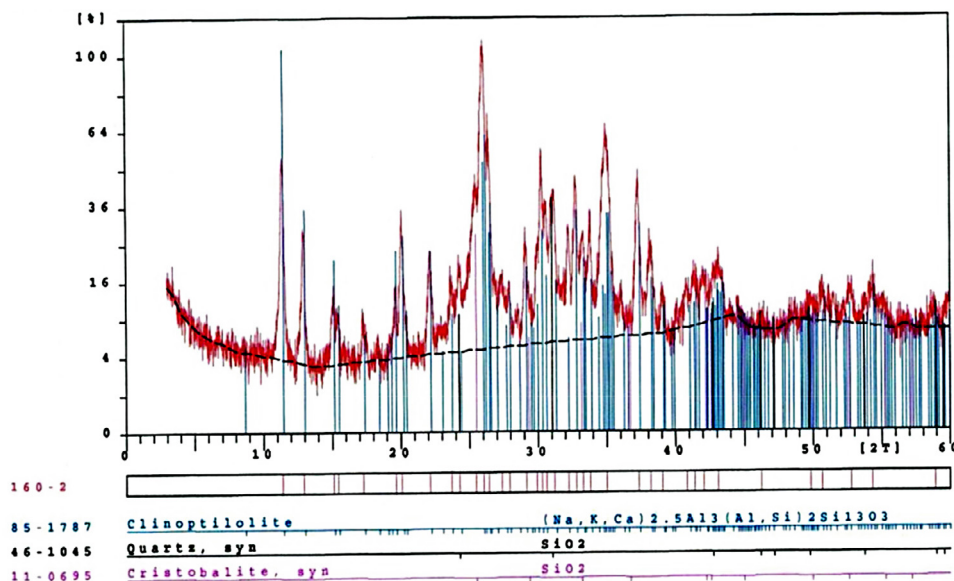
Fig. 3. XRD diffractogram of natural zeolite (NZ).

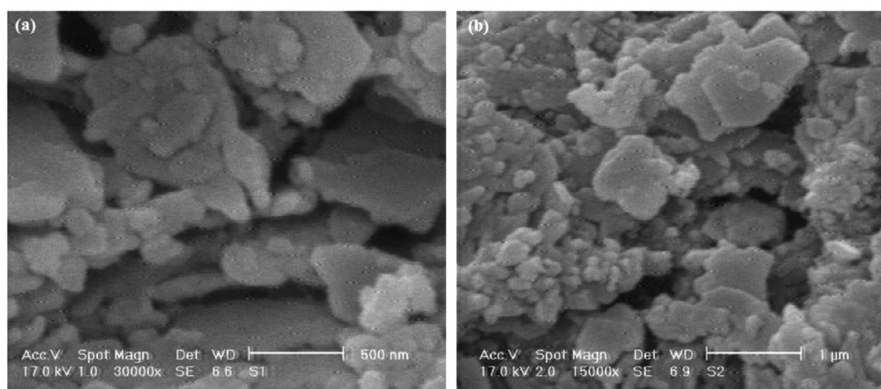Fig. 4. XRD diffractogram of surfactant modified natural zeolite (SMNZ).
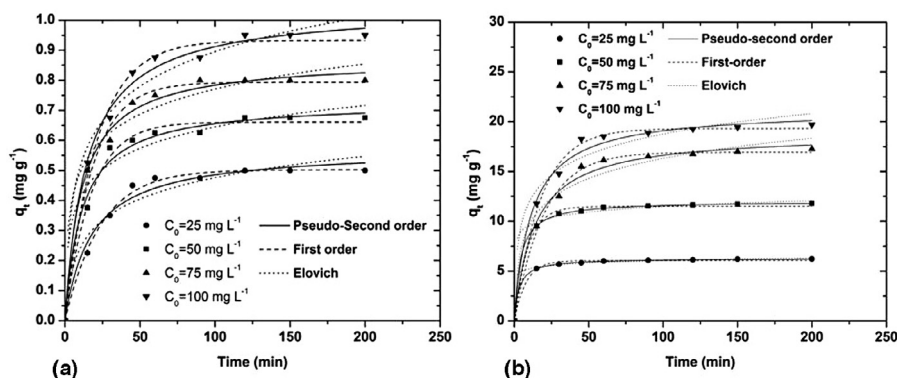
Fig. 5. SEM micrograph of NZ (a) and SMNZ (b).

Fig. 6. Kinetics of AR18 dye adsorption by (a) NZ and (b) SMNZ at several initial dye concentrations (pH 6.5 ± 0.2, temperature = 25 ± 2°C, sorbent mass = 4 g/L).

Table 3
Kinetic parameters of dye uptake by NZ and SMNZ zeolites.

Experimental		Elovich model			First-order model			Pseudo-second model		
Sorbent	C_0 (mg/L)	B (g/mg)	α (mg/g min)	R^2	K_1 (min)	q_e (mg/g)	R^2	k_2 (mg/g min)	q_e (mg/g)	R^2
SMNZ	25	2.77	74761.2	0.998	0.128	6.05	0.994	0.052	6.29	0.999
	50	1.22	10831.7	0.995	0.111	11.48	0.995	0.021	12.02	0.999
	75	0.34	8.03	0.966	0.050	16.93	0.995	0.004	18.83	0.998
	100	0.33	16.65	0.969	0.056	19.30	0.992	0.003	21.21	0.995
NZ	25	9.77	0.106	0.943	0.042	0.50	0.994	0.098	0.57	0.995
	50	9.72	0.544	0.962	0.058	0.66	0.991	0.122	0.72	0.995
	75	8.29	0.71842	0.975	0.056	0.79	0.989	0.103	0.87	0.992
	100	5.99	0.35747	0.976	0.048	0.93	0.990	0.066	1.04	0.992

morphologies between NZ and SMNZ samples. This may implies that surfactant molecules distributed homogeneously into the micropores of SMNZ samples [49].

3.2. Sorption equilibrium and kinetics

A series of experiments were performed to determine the optimum time needed to reach equilibrium in this study. Fig. 6(a) and (b) show the adsorption capacities of NZ and SMNZ for the removal of AR18 plotted against contact time at the several initial concentration (*i.e.* 25, 50, 75 and 100 mg/L), respectively. As shown in Fig. 6(a), as the contact time increases, the amount of dye adsorbed into the zeolite samples is increased significantly. The rate of removal of the dye was found to be rapid during the initial 100 min and remained nearly constant thereafter. No significant change in the removal of dye was observed after about 100 min. Therefore, the optimum contact time of 100 min was selected in the adsorption isotherm experiments. The maximum sorption capacity of AR18 was reached only up to 0.6 mg/g

for NZ, while in the case of SMNZ it was reached up to 10 mg/g for an initial concentration of 50 mg/L of the dye.

The values of the kinetic models constants obtained for the adsorption of AR18 onto NZ and SMNZ are summarized in Table 3. Good coefficients of determination (>0.99) was obtained for the pseudo-second-order kinetic model and reveals that the sorption process follows this model. A similar phenomenon was observed in sorption of Orange II dye from aqueous solution onto surfactant-coated zeolite [12] and Acid Blue 193 by surfactant modified Sepiolite [50]. The reduction in the pseudo-second-order rate constant, k_2, from 0.052 to 0.003 g/mg min, can be resulted from the prolongation of the sorption equilibrium time period due to the increase in the initial concentration of the dye [12].

The equilibrium isotherms curves of the SMNZ and NZ zeolites are shown in Fig. 7. The SMNZ has much higher sorption capacity than its non-modified form. Fig. 7 indicates that the NZ has a limited adsorption capacity for AR18 due to the exclusion of the dye anions from the pores of NZ by increasing of the water adsorption within the pores
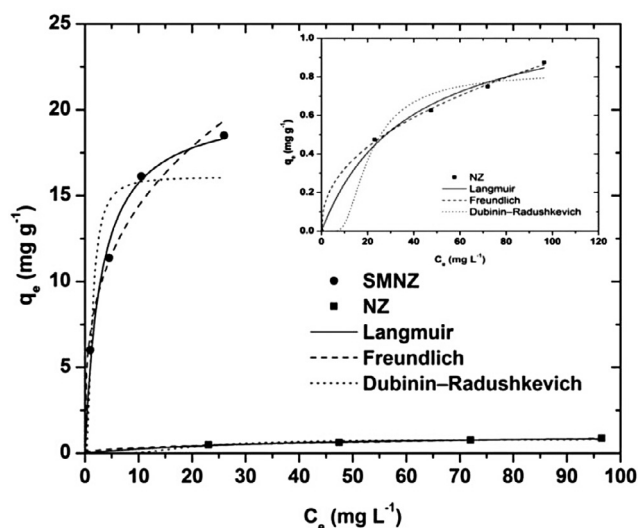
Fig. 7. Equilibrium isotherms for the removal of AR18 on SMNZ and NZ (contact time: 100 min, adsorbent dosage: 4 g/L).

Fig. 8. A schematic illustration of interaction of anionic dye molecule with quaternary amines onto zeolite surface (adapted from [51]).

[51]. At the initial concentration of 25 mg/L, the sorption capacity for the dye by SMNZ was about 6 mg/g, while it was only 0.5 mg/g for NZ for same initial concentration. From the XRF results (Table 1) the NZ is composed of clinoptilolite and quartz (SiO_2/Al_2O_3 ratio: 6.6). It can also be find that the content of quartz is high. The structure of quartz consists of corner sharing SiO_4 tetrahedra, each Si is bonded to four oxygens, and each oxygen is bonded to two silicon atoms. Therefore, it has no ion exchangeable capacity for cations [52]. This reduces the uptake of anionic compound onto it [52].

In order to increase the sorption capacity of zeolite, the HTAB not only makes the zeolite surface more hydrophobic but also neutralizes the negative charges [53]. The possible mechanism of anionic dye adsorption onto modified zeolite was reported by Armagan et al. [53]. It is schematically illustrated in Fig. 8. This indicates that the degree of hydrophobicity may 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. The diameter of HTAB cation is 0.4 nm, its length is 2.3 nm, and the diameter of its polar head is 0.694 nm, which makes it too large to penetrate the channels of clinoptilolite zeolite, which have dimensions 0.42×0.72 nm. Thus the reaction in the system of SMNZ and HTAB cations involve only external cation exchange capacity, leaving the internal cation exchange capacity unchanged [54].

The values of isotherm constants for AR18 adsorption onto SMNZ and NZ are presented in Table 4. The R^2 value for the Langmuir isotherm is higher than that for the Freundlich and D–R models. For both, NZ and SMNZ, the Langmuir model provides a slightly more
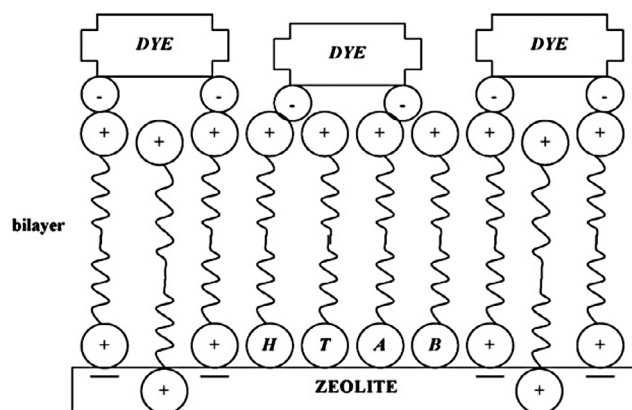
consistent fit to the data in comparison with the Freundlich and Dubinin–Radushkevich. In Langmuir equation, the capacity parameter, q_m, represents the maximum amount of dye that can be adsorbed. Furthermore, K_f in Freundlich equation is an index to the sorption capacity of sorbent. Both parameters, q_m and K_f, indicate that the SMNZ has a higher sorption capacity than that for NZ. The Freundlich exponent $1/n$ provides information on surface heterogeneity and surface affinity for the solute. This exponent was found to be 0.43 and 0.31 for NZ and SMNZ, respectively. These values indicate that the adsorption process is favorable. The degree of favorability increases as $1/n$ approaches zero. The Langmuir constant b was found to be 0.33 for SMNZ and 0.02 for NZ. These values also indicate a higher affinity of dye for SMNZ is expected in comparison with NZ. Moreover, R_L values indicate favorable adsorption of AR18 onto zeolite samples as it was found 0.057 and 0.50 and lies between 0 and 1 for SMNZ and NZ, respectively. The maximum capacities of SMNZ and NZ for AR18 were calculated to be 20.42 and 1.17 mg/g, respectively. These values were compared with those were reported in other studies (Table 5) on the sorption of AR18 by other adsorbents. The highest and lowest adsorption capacity for AR18 by other sorbents were found to be 948.5 mg/g for starches [55] and 1.0 mg/g for bone char [56], respectively. The D–R model allows estimating the adsorption energy of the system. The calculated adsorption energy for SMNZ was 1,961 J/mol. This value could be related to the structure of the sorbent and is independent from the adsorption capacity [43].

3.3. Effects of experimental conditions

The effect of SMNZ dosage on the sorption of AR18 was studied while pH and initial concentration were fixed on 3 and 50 mg/L, respectively. The results obtained are illustrated in Fig. 9(a). This figure

Table 4
Isotherm models parameters of dye uptake by NZ and SMNZ zeolites.

Sorbent	Model	Parameter symbol	Unit	Parameter value	R^2
SMNZ	Freundlich	K_f	$mg^{1-1/n}\,L^{1/n}\,g^{-1}$	7.01	0.975
		n	–	3.20	
	Langmuir	q_m	mg/g	20.42	0.990
		b	L/mg	0.33	
	Dubinin–Radushkevich	Q_s	mg/g	16.10	0.897
		B_D	mol^2/kJ^2	9.54E−4	
NZ	Freundlich	K_f	$mg^{1-1/n}\,L^{1/n}\,g^{-1}$	0.11	0.991
		n	–	2.30	
	Langmuir	q_m	mg/g	1.17	0.998
		b	L/mg	0.02	
	Dubinin–Radushkevich	Q_s	mg/g	0.82	0.956
		B_D	mol^2/kJ^2	0.13	

Table 5
Adsorption of AR18 by other sorbents in literature.

Adsorbent	Sorption capacity (mg/g)	Best descriptive isotherm	Best descriptive kinetic	Reference
Starches modified by diethylenetriamine	948.5	Langmuir	Pseudo-second-order	[55]
Chitosan, derived from deacetylated crab shell chitin	693.2	Langmuir	Lagergren	[57]
Poly(ethylenimine) grafted anaerobic granular sludge	520.5	Langmuir	Pseudo-first order	[58]
Dithiocarbamate-modified starch	245.3	Freundlich	Pseudo-first-order	[59]
Bamboo derived active carbon	196.6	Redlich–Peterson	–	[56]
Peat	13.6	Langmuir	–	[56]
Bone char	1.0	Langmuir	–	[56]
Nanochitosan emulsion	828.0	Langmuir	–	[60]
Bentonite based composite	69.8	Redlich–Peterson	–	[61]
Activated carbon from flamboyant pods	551.7	Vieth–Sladek	Pseudo-second order	[62]
Chitosan films	194.6	Redlich–Peterson	Elovich	[63]
SMNZ	20.4	Langmuir	Pseudo-second order	This study
NZ	1.1	Langmuir	Pseudo-second order	This study
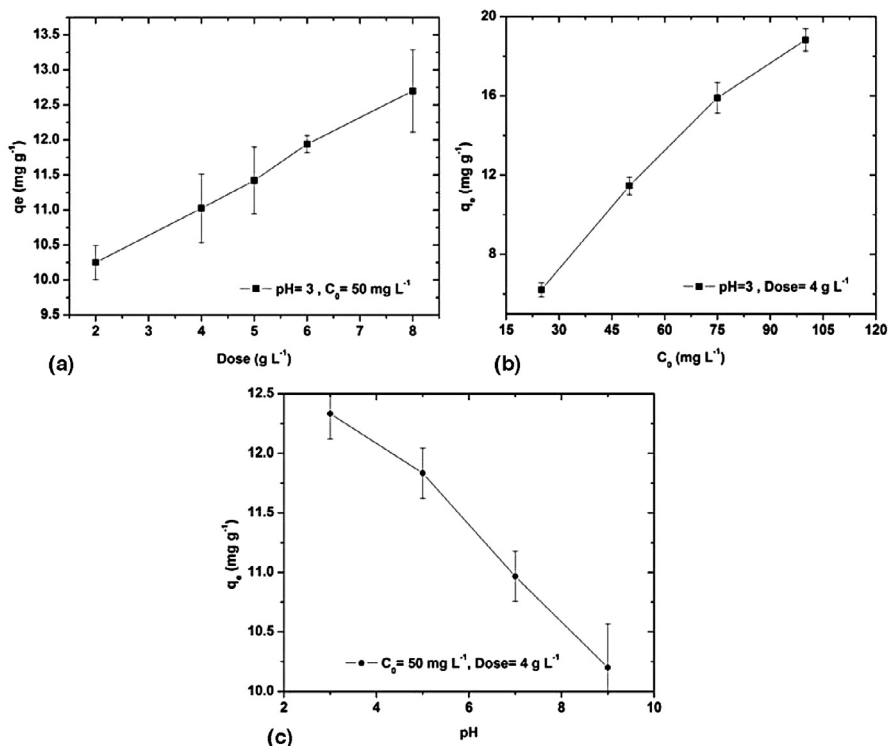
Fig. 9. The effects of experimental parameters (a) sorbent dosage, (b) dye concentration, and (c) pH on the sorption of AR18 onto SMNZ.

clearly shows that with increasing the amount of SMNZ from 2 to 8 g/L, the sorption of the dye increases from 10.2 to 12.6 mg/g. This confirms the dependence of the adsorption process on the availability of binding sites. The increase in the dye sorption with increasing the sorbent dosage can be ascribed to the greater surface area and the accessibility of more adsorption sites [64].

The results of dye sorption on SMNZ with different initial concentrations (*i.e.* 25, 50, 75 and 100 mg/L) are presented in Fig. 9(b). As shown, the adsorption of AR18 by SMNZ increases as the initial dye concentration increases. The increase of the initial concentration of the dye may increases the mass transfer driving force and therefore the rate at which the molecules of the dye pas from the solution to the particle surface [28]. This leads to higher adsorption of the dye.

The dye sorption capacity on SMNZ *versus* pH (*i.e.* 3 to 9) under a fixed initial dye concentration of 50 mg/L and a dosage of 4 g/L of sorbent, was illustrated in Fig. 9(c). It is evident that by increasing the pH from 3 to 9, the sorption capacity decreased from 12.3 to 10.2 mg/g. It can be seen that the maximum sorption of dye by SMNZ takes place in acidic condition. This effect of pH can be explained with regards to the different interaction between AR18 and sufactant in terms of

surface charge. The AR18 is an acidic dye and its sulfonate moiety contains negative sulfonic groups ($-SO_3^-$) (Fig. 2). An acidic condition with a low pH leads to increase in the concentration of H^+ ion [13]. On the other hand, a layer of HTAB on the surface of zeolite increases the positive charges on the external surface of zeolite [65]. Therefore, the strong electrostatic attraction between the positively charged sorption site and the dye molecules leads to high adsorption capacity of dye. The considerable decrease in the dye sorption capacity by increasing the pH, is in agreement with the results of a study on adsorption of Congo Red using surfactant modified natural zeolite [13]. Torabian et al. [66] reported that surfactants specially HTAB, are stable at various pH. Therefore, the possibility of the degradation of SMNZ or desorption of surfactant from the surface of the zeolite is very low.

4. Conclusion

A locally derived natural zeolite was modified with HTAB surfactant and was used as low cost adsorbent of dye (Acid Red 18) in aqueous solution. Natural zeolite (NZ) has a limited dye removal capacity

for acidic dye. Nevertheless, this study showed that the dye removal capacity of NZ can be substantially improved by modifying its surface with HTAB surfactant. According to the results obtained in this work, the modified zeolite (SMNZ) is an effective sorbent for the removal of acidic dyes from aqueous solutions. The removal efficiency of SMNZ for the sorption of AR18 was dependent to the pH of solution and adsorbent dosage. The sorption capacity of AR18 was increased with decreasing pH and increasing adsorbent dose. The conditioning (mixing) time of about 100 min was found to be sufficient for reaching the equilibrium point. The sorption kinetics of AR18 on SMNZ could be explained by a pseudo-second-order kinetic model. The maximum capacities for AR118 by SMNZ and NZ forms of zeolite were determined to be 20.42 and 1.17 mg/g, respectively, according to the Langmuir isotherm equation. The comparison the SMNZ's capacity value for the sorption of AR18 with that for other adsorbents in literature was revealed that SMNZ has higher sorption capacity for the dye in comparison with peat and bone char. Thus, SMNZ could be a good candidate for the removal of AR18 from aqueous solutions. The developed sorbent has a considerable potential for removal of acid dyes and could be considered as a promising sorbent for other dyes and other organic pollutants wherever the zeolite is abundant and cheap.

Acknowledgment

References

[1] Gupta V, Mittal A, Krishnan L, Mittal J. Adsorption treatment and recovery of the hazardous dye, Brilliant Blue FCF, over bottom ash and de-oiled soya. J Coll Interface Sci 2006;293:16–26.

[2] Hadi M, Samarghandi MR, McKay G. Simplified fixed bed design models for the adsorption of acid dyes on novel pine cone derived activated carbon. Water Air Soil Pollut 2011;218:197–212.

[3] Mishra G, Tripathy M. A critical review of the treatments for decolouration of textile effluent. Colourage 1993;40:35–8.

[4] Willmott N, Guthrie J, Nelson G. The biotechnology approach to colour removal from textile effluent. J Soc Dyes Colour 1998;114:38–41.

[5] Samarghandi MR, Hadi M, McKay G. Breakthrough curve analysis for fixed-bed adsorption of azo dyes using novel pine cone-derived active carbon. Adsorption Sci Technol 2014;32:791–806.

[6] Hadi M, Samarghandi MR, McKay G. Equilibrium two-parameter isotherms of acid dyes sorption by activated carbons: study of residual errors. J Chem Eng 2010;160:408–16.

[7] McKay G, Hadi M, Samadi MT, Rahmani AR, Aminabad MS, Nazemi F. Adsorption of reactive dye from aqueous solutions by compost. Desalin Water Treat 2011;28:164–73.

[8] McKay G, Mesdaghinia A, Nasseri S, Hadi M, Solaimany Aminabad M. Optimum isotherms of dyes sorption by activated carbon: fractional theoretical capacity & error analysis. J Chem Eng 2014;251:236–47.

[9] Hernández-Montoya V, Pérez-Cruz MA, Mendoza-Castillo DI, Moreno-Virgen M. Bonilla–Petriciolet A: competitive adsorption of dyes and heavy metals on zeolitic structures. J Environ Manag 2013;116:213–21.

[10] Matsuska OV, Paranyak RP, Gumnitskii YM. Adsorption of wastewater components by natural sorbents. J Water Chem Technol 2010;32:218–22.

[11] Carrizosa MJ, Koskinen WC, Hermosin MC, Cornejo J. Dicamba adsorption–desorption on organoclays. Appl Clay Sci 2001;18:223–31.

[12] Jin X, Yu B, Chen Z, Arocena JM, Thring RW. Adsorption of Orange II dye in aqueous solution onto surfactant-coated zeolite: characterization, kinetic and thermodynamic studies. J Coll Interface Sci 2014;435:15–20.

[13] Liu S, Ding Y, Li P, Diao K, Tan X, Lei F, et al. Adsorption of the anionic dye Congo red from aqueous solution onto natural zeolites modified with *N,N*-dimethyl dehydroabietylamine oxide. J Chem Eng 2014;248:135–44.

[14] Mortier WJ, Pearce JR. Thermal stability of the heulandite-type framework; crystal structure of the calcium/ammonium form dehydrated at 483 K. Am Miner 1981;66:309–14.

[15] Bowman RS. Applications of surfactant-modified zeolites to environmental remediation. Microporous Mesoporous Mater 2003;61:43–56.

[16] Ilinoiu EC, Pode R, Manea F, Colar LA, Jakab A, Orha C, et al. Photocatalytic activity of a nitrogen-doped TiO₂ modified zeolite in the degradation of Reactive Yellow 125 azo dye. J Taiwan Inst Chem Eng 2013;44:270–8.

[17] Ghiaci M, Abbaspur A, Kia R, Seyedeyn-Azad F. Equilibrium isotherm studies for the sorption of benzene, toluene, and phenol onto organo-zeolites and as-synthesized MCM-41. Sep Purif Technol 2004;40:217–29.

[18] Gennaro B, Catalanotti L, Bowman RS, Mercurio M. Anion exchange selectivity of surfactant modified clinoptilolite-rich tuff for environmental remediation. J Colloid Interface Sci 2014;430:178–83.

[19] Sullivan EJ, Hunter DB, Bowman RS. Fourier transform Raman spectroscopy of sorbed HTAB and the mechanism of chromate sorption to surfactant-modified clinoptilolite. Environ Sci Technol 1998;32:1948–55.

[20] Kuleyin A. Removal of phenol and 4-chlorophenol by surfactant-modified natural zeolite. J Hazard Mater 2007;144:307–15.

[21] Bouffard SC, Duff SJ. Uptake of dehydroabietic acid using organically-tailored zeolites. Water Res 2000;34:2469–76.

[22] Daković A, Tomašević-Čanović M, Rottinghaus G, Dondur V, Mašić Z. Adsorption of ochratoxin A on octadecyldimethyl benzyl ammonium exchanged-clinoptilolite-heulandite tuff. Coll Surf B 2003;30:157–65.

[23] Samadi M, Saghi M, Ghadiri K, Hadi M, Beikmohammadi M. Performance of simple nano zeolite Y and modified nano zeolite Y in phosphor removal from aqueous solutions. Iranian J Health Environ 2010;3:27–36.

[24] Zhan Y, Zhu Z, Lin J, Qiu Y, Zhao J. Removal of humic acid from aqueous solution by cetylpyridinium bromide modified zeolite. J Environ Sci 2010;22:1327–34.

[25] Leyva-Ramos R, Jacobo-Azuara A, Diaz-Flores P, Guerrero-Coronado R, Mendoza-Barron J, Berber-Mendoza M. Adsorption of chromium (VI) from an aqueous solution on a surfactant-modified zeolite. Coll Surf A 2008;330:35–41.

[26] Chutia P, Kato S, Kojima T, Satokawa S. Adsorption of As (V) on surfactant-modified natural zeolites. J Hazard Mater 2009;162:204–11.

[27] Armagan B, Turan M, Karadag D. Adsorption of different reactive dyes onto surfactant-modified zeolite: kinetic and equilibrium modeling. In: Hüseyin G, Umut T, James, WL, editors. Survival and sustainability. Springer; 2011. p. 1237–54.

[28] Kuleyin A, Aydin F. Removal of reactive textile dyes (Remazol Brillant Blue R and Remazol Yellow) by surfactant-modified natural zeolite. Environ Prog Sustainable Energy 2011;30:141–51.

[29] Atkins P. Physical chemistry. 6th ed. Oxford University Press; 1998.

[30] Sincero AP, Sincero GA. Physical-chemical treatment of water and wastewater. CRC Press; 2002.

[31] Qiu H, Lv L, Pan B-c, Zhang Q-j, Zhang W-m, Zhang Q-x. Critical review in adsorption kinetic models. J Zhejiang Univ Sci A 2009;10:716–24.

[32] Ghadiri S, Nabizadeh R, Mahvi A, Nasseri S, Kazemian H, Mesdaghinia A, et al. Methyl tert-butyl ether adsorption on surfactant modified natural zeolites. Iranian J Environ Health Sci Eng 2010;7:241–52.

[33] Yousef RI, El-Eswed B. The effect of pH on the adsorption of phenol and chlorophenols onto natural zeolite. Coll Surf A 2009;334:92–9.

[34] Díaz-Nava C, Olguín M, Solache-Ríos M, Alarcón-Herrera M, Aguilar-Elguezabal A. Phenol sorption on surfactant-modified Mexican zeolitic-rich tuff in batch and continuous systems. J Hazard Mater 2009;167:1063–9.

[35] Thirumavalavan M, Wang Y-T, Lin L-C, Lee J-F. Monitoring of the structure of mesoporous silica materials tailored using different organic templates and their effect on the adsorption of heavy metal ions. J Phys Chem C 2011;115:8165–74.

[36] Wang S, Peng Y. Natural zeolites as effective adsorbents in water and wastewater treatment. J Chem Eng 2010;156:11–24.

[37] Langmuir I. The adsorption of gases on plane surfaces of glass, mica and platinum. J Am Chem Soc 1918;40:1361–403.

[38] Freundlich H. Over the adsorption in solution. J Phys Chem 1906;57:1100–7.

[39] Dubinin MM. The potential theory of adsorption of gases and vapors for adsorbents with energetically non-uniform surface. Chem Rev 1960;60:235–66.

[40] Hall K, Eagleton L, Acrivos A, Vermeulen T. Pore-and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern conditions. Ind Eng Chem Fundam 1966;5:212–23.

[41] Bansal RC, Goyal M. Activated carbon adsorption. CRC Press; 2010.

[42] Treybal RE, Treybal Robert E. Mass-transfer operations. New York: McGraw-Hill; 1968.

[43] Caqueret V, Bostyn S, Cagnon B, Fauduet H. Purification of sugar beet vinasse—adsorption of polyphenolic and dark colored compounds on different commercial activated carbons. Bioresour Technol 2008;99:5814–21.

[44] Ho Y-S, McKay G. Sorption of dye from aqueous solution by peat. Chem Eng J 1998;70:115–24.

[45] Lagergren S. Zur theorie der sogenannten absorption gelöster stoffe. PA Norstedt & Söner; 1898.

[46] Low M. Kinetics of chemisorption of gases on solids. Chem Rev 1960;60:267–312.

[47] Chao H-P, Chen S-H. Adsorption characteristics of both cationic and oxyanionic metal ions on hexadecyltrimethylammonium bromide-modified NaY zeolite. J Chem Eng 2012;193–194:283–9.

[48] Bhardwaj D, Sharma M, Sharma P, Tomar R. Synthesis and surfactant modification of clinoptilolite and montmorillonite for the removal of nitrate and preparation of slow release nitrogen fertilizer. J Hazard Mater 2012;227:292–300.

[49] Chen A, Ma X, Sun H. Decolorization of KN-R catalyzed by Fe-containing Y and ZSM-5 zeolites. J Hazard Mater 2008;156:568–75.

[50] Özcan A, Öncü EM, Özcan AS. Kinetics, isotherm and thermodynamic studies of adsorption of Acid Blue 193 from aqueous solutions onto natural sepiolite. Coll Surf A 2006;277:90–7.

[51] Ozdemir O, Turan M, Turan AZ, Faki A, Engin AB. Feasibility analysis of color removal from textile dyeing wastewater in a fixed-bed column system by surfactant-modified zeolite (SMZ). J Hazard Mater 2009;166:647–54.

[52] Wang Y-F, Lin F, Pang W-Q. Ammonium exchange in aqueous solution using Chinese natural clinoptilolite and modified zeolite. J Hazard Mater 2007;142:160–4.

[53] Armağan B, Özdemir O, Turan M, Celik M. The removal of reactive azo dyes by natural and modified zeolites. J Chem Technol Biotechnol 2003;78:725–32.

[54] Bowman RS. Zeolite '06. In: Bowman RS, Delap, SE, editors. Proceedings of the 7th international conference on the occurrence, properties, and utilization of natural zeolites; Socorro, NM, USA; 2006. p. 56.

[55] Wang Z, Xiang B, Cheng R, Li Y. Behaviors and mechanism of acid dyes sorption onto diethylenetriamine-modified native and enzymatic hydrolysis starch. J Hazard Mater 2010;183:224–32.

[56] Ip A, Barford J, McKay G. Production and comparison of high surface area bamboo derived active carbons. Bioresour Technol 2008;99:8909–16.

[57] Wong Y, Szeto Y, Cheung W, McKay G. Adsorption of acid dyes on chitosan—equilibrium isotherm analyses. Process Biochem 2004;39:695–704.

[58] Sun X-F, Wang S-G, Cheng W, Fan M, Tian B-H, Gao B-Y, et al. Enhancement of acidic dye biosorption capacity on poly (ethylenimine) grafted anaerobic granular sludge. J Hazard Mater 2011;189:27–33.

[59] Cheng R, Xiang B, Li Y, Zhang M. Application of dithiocarbamate-modified starch for dyes removal from aqueous solutions. J Hazard Mater 2011;188:254–60.

[60] Cheung W, Szeto Y, McKay G. Enhancing the adsorption capacities of acid dyes by chitosan nano particles. Bioresour Technol 2009;100:1143–8.

[61] Qiao S, Hu Q, Haghseresht F, Hu X, Lu GQM. An investigation on the adsorption of acid dyes on bentonite based composite adsorbent. Sep Purif Technol 2009;67:218–25.

[62] Vargas AM, Cazetta AL, Martins AC, Moraes JC, Garcia EE, Gauze GF, et al. Kinetic and equilibrium studies: adsorption of food dyes Acid Yellow 6, Acid Yellow 23, and Acid Red 18 on activated carbon from flamboyant pods. Chem Eng J 2012;181:243–50.

[63] Dotto G, Moura J, Cadaval T, Pinto L. Application of chitosan films for the removal of food dyes from aqueous solutions by adsorption. J Chem Eng 2013;214:8–16.

[64] Fan C, Dang N, Ma H. Adsorption of methylene blue from aqueous solutions onto fly ash. Proceedings of the international symposium on water resource and environmental protection (ISWREP), 2011. IEEE; 2011. p. 2217–20.

[65] Chao H-P, Chen S-H. Adsorption characteristics of both cationic and oxyanionic metal ions on hexadecyltrimethylammonium bromide-modified NaY zeolite. Chem Eng J 2012;193–194:283–9.

[66] Torabian A, Kazemian H, Seifi L, Bidhendi GN, Azimi AA, Ghadiri SK. Removal of petroleum aromatic hydrocarbons by surfactant-modified natural zeolite: the effect of surfactant. CLEAN—Soil Air Water 2010;38:77–83.