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Removal of red 2 and yellow 6 by Zn- and-Na modified zeolitic tuffs in the presence of H_2O_2

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ABSTRACT

The adsorption of red-2 and yellow-2 dyes from aqueous solution was evaluated using both Na and Zn zeolitic materials in the absence and presence of hydrogen peroxide. The adsorbents were characterized by scanning electron microscopy, X-ray diffraction, and their specific surface areas were determined. Sorption kinetic and isotherms, in the absence and presence of hydrogen peroxide, were determined. The kinetic adsorption behavior of red-2 and yellow-2 by Na-zeolitic tuff and in presence of H_2O_2 was similar. The experimental data of the adsorption of red-2 were best adjusted to the kinetic model of Lagergren and the data of yellow-6 to the pseudo-second-order model indicating chemisorption. The adsorption isotherms in the absence of H_2O_2 showed low adsorption capacities, however sodium zeolitic tuff in the presence of hydrogen peroxide showed to be an efficient material for the removal of these dyes.

Keywords: Red 2; Yellow 6; Zeolitic tuff; Adsorption; Zinc

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1. Introduction

Water pollution produced by various kinds of synthetic dyes discharged from textile and other industrial facilities is a serious environmental problem. Colored wastewater is particularly associated with reactive dyes that are used as the most common dyes due to their bright colors, excellent colorfastness, and ease of application [1].

The dyes are widely used for coloring various consumer products, however large amounts of water are used during production processes, which are discharged directly into water bodies causing serious environmental problems such as eutrophication because dyes adsorb and reflect sunlight entering the water, which interferes with the growth of bacteria, impede photosynthesis process in aquatic plants, and the balanced growth of micro-organisms comprising aquatic biota [2,3].

The sorption behaviors of different dyes by natural- and iron-modified aluminosilicates have been reported, one advantage of these adsorption systems is that they may oxidize the dyes if hydrogen peroxide is added to the saturated adsorbents [4–8].

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The removal of remazol yellow from aqueous solution was reported using a Fe-zeolitic tuff. Kinetic pseudo-second-order and Langmuir–Freundlich models were successfully applied to the experimental results, indicating chemisorption on a heterogeneous material. The regeneration of the material was best accomplished using a H_2O_2 solution and the sorption capacity of the Fe-zeolitic tuff increased when the saturated samples were treated with a H_2O_2 or $FeCl_3$ solution [7].

The effect of pH, contact time, dye concentration, and temperature was considered for the sorption of brilliant blue FCF dye by natural clay and modified with iron. The results showed that pH influences the sorption of the dye in the unmodified clay, but this effect was not observed in the iron-modified clay. The sorption capacity for the unmodified material was lower than the iron-modified clay. Sorption kinetics results were best adjusted to the pseudo-first-order and pseudo-second-order models and sorption isotherms were best adjusted to the Langmuir model, indicating homogeneous surfaces [4]. The same dye was removed from aqueous solution using an iron-modified zeolitic tuff, the results were fitted to the pseudo-first-order kinetic model and Langmuir–Freundlich isotherm model which indicated that the sorption mechanism was physisorption on a heterogeneous material [6].

The removal of red-5 and yellow-6 used in foodstuff has been reported by the adsorption on an iron-modified zeolite, the regeneration of the dyes saturated materials was also considered. The sorption kinetics showed that the sodium-modified zeolitic material removed neither red-5 nor yellow-6 dyes while the iron-modified zeolitic material removed both dyes, the removal percentage for red-5 was 89.4% and for yellow-6 was 96.7% and the saturated adsorbents were regenerated by Fenton's reagent [5].

The removal of dyes using surfactant-modified aluminosilicates, iron-modified clays and zeolites have been used and no other metal has been used for these modifications. Therefore, the purpose of this paper was to investigate the effects of H_2O_2 on the adsorption of red-2 and yellow-6 from aqueous solutions by sodium- and zinc-modified zeolitic tuffs.

2. Materials and methods

2.1. Zeolitic tuff (Ze)

The clinoptilolite-rich tuff from Parral, Chihuahua, Mexico, was milled and sieved. The grain size used in this work was 0.841 mm (20 mesh, ASTM). The zeolitic material was treated with a solution of sodium chloride and refluxed for 3 h (100 g of material with 1 L of 0.5 M NaCl solution), the phases were separated and a fresh solution was again added, this procedure was repeated twice, the zeolitic material (Na-Ze) was washed with distilled water until no presence of chloride ions was indicated in the washing solution using a $AgNO_3$ test.

Zn-zeolitic tuff samples (Zn0.1-Ze and Zn0.5-Ze) were prepared by refluxing 50 g of Na-Ze with 0.1 or 0.5 M $ZnCl_2$ solutions; the procedures were similar to the treatment with sodium chloride.

2.2. Dyes

Red-2 (trisodium (4E)-3-oxo-4-[(4-sulfonato-1-naphthyl)hydrazono]naphthalene-2,7-disulfonate) and yellow-6 (disodium 6 hydroxi-5-[(4-sulfophenyl)azo]-2-naftalen sulfonic acid) were obtained as commercial dyes from SENSIET Co. The general characteristics for red 2 are: molar mass 604.47 $\mathrm{g\ mol^{-1}}$, CAS 915-67-3 and for yellow 6 are: molar mass 452.37 $\mathrm{g\ mol^{-1}}$, CAS 2,783-94-0. Red 2 is a dark red to purple azo dye once used as a food dye and to color cosmetics, but since 1976 it has been banned in the United States by the food and drug administration (FDA) as it is a suspected carcinogen. Yellow 6 may be responsible for causing an allergic reaction in people with an aspirin intolerance, resulting in various symptoms, including gastric upset, diarrhea, vomiting, nettle rash (urticaria), swelling of the skin (angioedema), and migraines.

2.3. Characterization

2.3.1. Scanning electron microscopy

For scanning electron microscopy (SEM) observations, the samples were mounted directly on the holders then observed at 10 and 20 kV in a JEOL JSM-5900-LD electron microscope. The microanalysis was done with an EDS (energy X-ray dispersive spectroscopy) system.

2.3.2. X-ray diffraction (XRD)

Powder diffractograms of the zeolitic samples were obtained with a Siemens D500 diffractometer coupled to a copper anode X-ray tube. The conventional diffractograms were used to identify the compounds and to verify crystalline structure.

2.3.3. Surface areas, BET (S_{BET})

The BET specific surface areas were determined by standard multipoint techniques of nitrogen adsorption, using a Micromeritics Gemini 2360 instrument. The samples were heated at 373 K for 2 h before specific surface areas were measured.

2.4. Sorption kinetic

Kinetic removal of dyes by the Na-Ze was performed as follows: 100 mg of adsorbent, 10 mL aliquots of a 10 mg/L dye solution, and 1 mL of H_2O_2 solution at 30% were placed in centrifuge tubes and shaken for different times (15, 30, and 45 min, 1, 2, 3, 5, 8, 12, 18, 24, 36, 48, 60, and 72 h) at 100 rpm and 25°C, later the phases were separated. The dyes concentrations in the solutions were determined by using an ultraviolet-visible spectrophotometer analyzer UV/vis Perkin Elmer Lambda 10 at 521.7 and 481.8 nm for red 2 and yellow 6, respectively.

2.5. Sorption isotherms

One hundred milligrams samples of Na-Ze, Zn0.1-Ze or Zn0.5-Ze were put in contact with 10 mL of different concentrations of dyes solutions (1, 3, 5, 7, 10, 15, 20, and 25 mg/L), for 24 h at 25°C and shaken at 100 rpm. Later the samples were centrifuged and decanted, dye concentrations were determined in the remaining liquid phases. Isotherms were determined in absence and presence of 1 mL of H_2O_2 solution at 30% in the mixtures.

3. Results and discussion

3.1. Scanning electron microscopy

The morphology of the natural-, sodium- (Fig. 1), zinc- (Fig. 2) modified zeolitic tuffs, and the modified zeolitic tuffs saturated with red 2 (Fig. 3) and yellow 6 are very similar, they show the typical morphology coffin and cubic-like crystals [7], characteristics of rich clinoptilolite tuffs. The chemical compositions of the unmodified zeolitic tuff, Na-Ze, Zn0.5-Ze, and Na-Ze saturated with red 2 or yellow 6 are shown in Table 1. The main elements, Si, Al, and O, corresponding to aluminosilicates, were identified. Iron, magnesium, potassium, and calcium were found in all samples, sodium was not observed in the unmodified sample and zinc was found only in the sample Zn0.5-Ze.

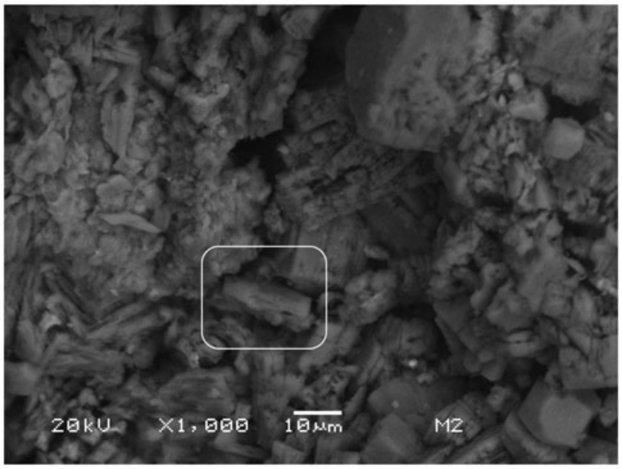

Fig. 1. Scanning electron micrograph of the Na-zeolitic tuff.

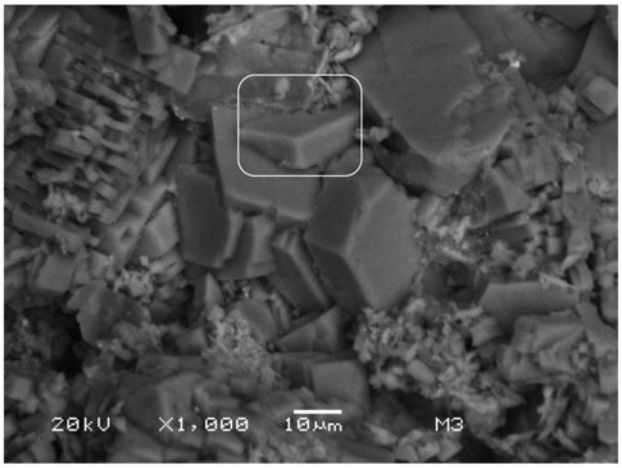

Fig. 2. Scanning electron micrograph of the Zn0.5-zeolitic tuff.

3.2. X-ray diffraction (XRD)

In general, the components of clinoptilolite tuffs are mordenite, estilbite, erionite, quartz, natrolite,

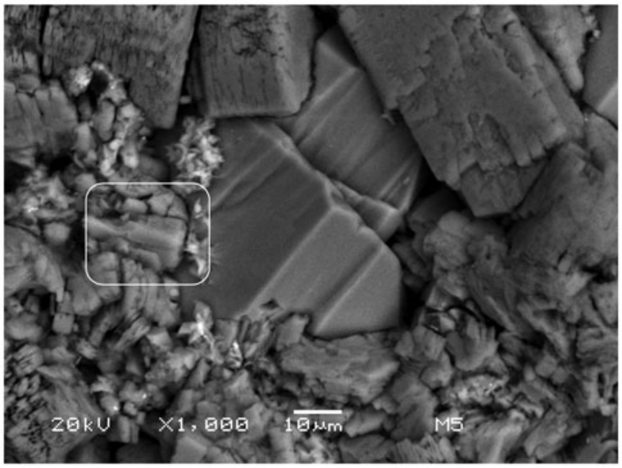

Fig. 3. Scanning electron micrograph of Red 2 saturated Na-zeolitic tuff.

Table 1
Chemical compositions of the unmodified zeolitic tuff, Na-Ze, Zn0.5-Ze, and Na-Ze saturated with red-2 or yellow-6 determined by EDS

Element	Natural	Na-Ze	Zn0.5-Ze	Na-ZeSat$_{R2}$	Na-ZeSat$_{Y6}$
O	36.55 ± 1.59	37.50 ± 2.00	34.28 ± 0.29	36.44 ± 3.31	36.04 ± 1.86
Mg	0.77 ± 0.53	0.52 ± 0.40	0.23 ± 0.42	0.42 ± 0.51	0.84 ± 0.23
Al	5.07 ± 0.78	5.43 ± 0.28	6.52 ± 0.05	5.33 ± 0.98	5.76 ± 0.22
Si	28.94 ± 3.64	28.21 ± 1.03	27.68 ± 1.47	25.74 ± 2.17	29.53 ± 0.59
K	6.38 ± 1.14	4.37 ± 4.11	4.27 ± 3.92	4.18 ± 5.89	6.26 ± 3.20
Ca	1.02 ± 0.30	1.39 ± 2.16	0.32 ± 2.39	0.94 ± 3.17	0.85 ± 1.03
Fe	3.70 ± 1.19	2.62 ± 0.58	2.12 ± 0.07	1.73 ± 1.19	2.53 ± 0.06
Na	–	1.40 ± 1.42	0.76 ± 0.77	1.17 ± 0.56	0.82 ± 0.61
Zn	–	–	4.89 ± 1.53	–	–

cristobalite, celadonite, sanidine, chabazite, ferrierite, laumontite, analcime, calcite, and clinoptilolite [8]. The X-ray powder diffraction patterns of the natural zeolitic tuff (Fig. 4), Na-Ze, Zn0.5-Ze, and Na-Ze saturated with red 2 or yellow 6 were similar. The diffractograms were compared with the Joint Committee on Powder Diffraction Standards (JCPDS); calcium clinoptilolite (083-1261), quartz (70-7344), and sanidine (73-1117).

3.3. Specific surface areas, BET (S_{BET})

The BET specific surface areas were 4.775, 4.414, and 4.600 m^2/g and pore volumes were 1.097, 1.014, and 1.057 cm^3/g for the natural zeolitic tuff, Na-Ze and Zn-Ze0.5, respectively, all of them of the same order of magnitude. The specific surface areas were 1.310 and 1.527 m^2/g and the pore volumes were 0.301 and 0.351 for the Na-Ze saturated with red-2 or yellow-6, respectively, as it is observed the specific surface areas and the pore volumes decreased when the materials were treated with the dyes solutions, this indicates that the dyes molecules close the pores of the zeolitic tuffs.

3.4. Sorption kinetics

Figs. 5 and 6 show the relationship between contact times and the sorption capacities of Na-Ze in the presence of 30% H_2O_2 solution for red 2 and yellow 6, respectively. The adsorption behavior for both dyes

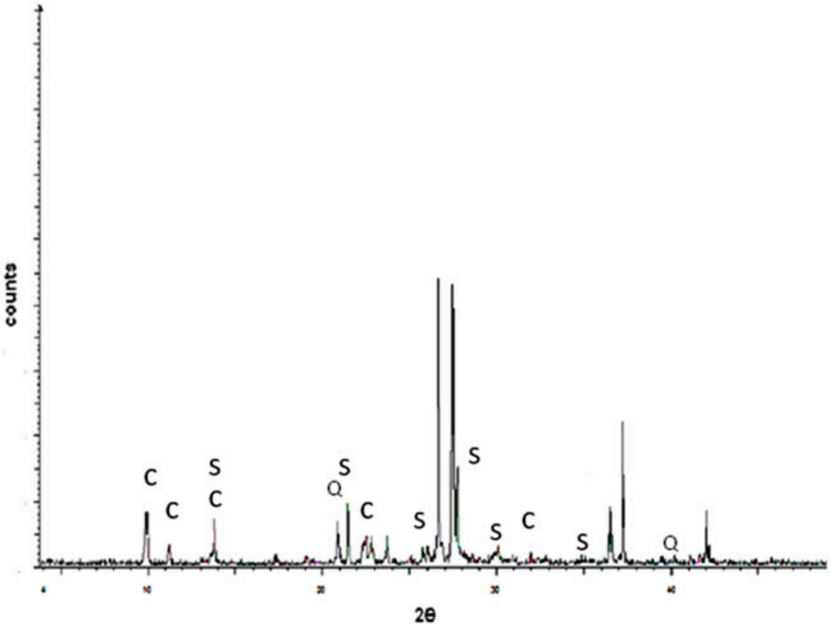

Fig. 4. XRD patterns of natural zeolitic tuff (C) calcium clinoptilolite, (Q) quartz, and (S) sanidine.

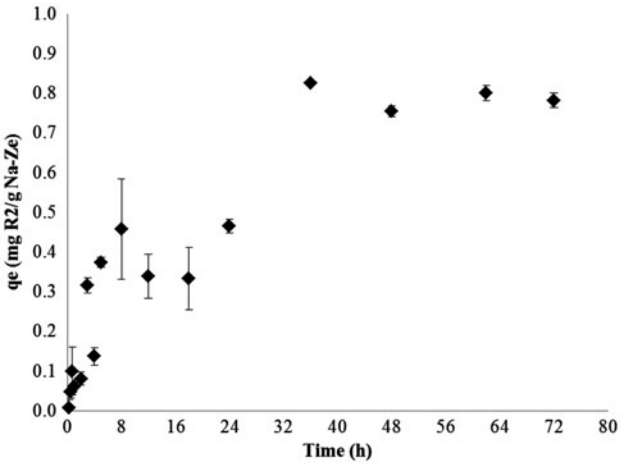

Fig. 5. Kinetic adsorption behavior of red-2 in presence of H_2O_2 by Na-Ze.

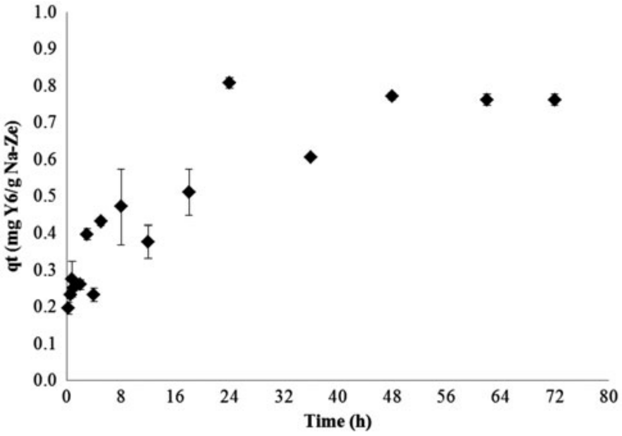

Fig. 6. Kinetic adsorption behavior of yellow-6 in presence of H_2O_2 by Na-Ze.

was similar, the adsorption rates were fast at the beginning of the processes and then a first plateau was reached, then the process was repeated up to a second plateau was reached, this behavior is not commonly found and it may be attributed to the presence of H_2O_2, one may think that oxidation of the dyes takes place in the system, iron present in the adsorbent (Table 1) may act as catalyst in the oxidation of dyes. The adsorption capacities at equilibrium were about 0.8 mg/g. The experimental data were fitted to the kinetic models of Lagergren, Ho, and Elovich with the help of STATISTICA® version 6.0 software.

3.4.1. Pseudo-first-order model (Lagergren)

This model is commonly used for homogeneous sorbents and physical sorption; the sorption rate is proportional to the solute concentration. If the sorption behavior is of the first order, then the experimental results could be adjusted to the following equation:

$$q_t = q_e\left(1 - e^{-K_L t}\right) \tag{1}$$

with the linear form being:

$$\ln\left(1-\left(q_t/q_e\right)\right) = -K_L t \tag{2}$$

where q_t and q_e are the amounts of adsorbed dye (mg/g) in the equilibrium and at time t (h), respectively, and K_L (h^{-1}) is the rate sorption constant of Lagergren [9]. The calculated K and q_e parameters are found in Table 2.

3.4.2. Second-order model (Elovich)

This model has been used suitably in chemisorptions on highly heterogeneous materials [10] and is represented by the following equation:

Table 2
Parameters obtained from kinetic models applied to the red-2 and yellow-6 (with H_2O_2) adsorption by Na-Ze samples

Dye	Kinetic model	Parameters	r^2
R2	Largergren	q_e = 0.7936 (mg/g)	0.8664
	Pseudo-first-order	K_L = 0.0601 h^{-1}	
	Elovich	α = 12.8809 (mg/g min)	0.8511
	Second-order	β = 0.1494 (g/mg)	
	Ho	q_e = 0.9794 (mg/g)	0.8747
	Pseudo-second-order	k = 0.0614 (g/mg h)	
Y6	Elovich	α = 126.91 (mg/g min)	0.7909
	Second-order	β = 0.1013 (g/mg)	
	Ho	q_e = 0.7735 (mg/g)	0.9442
	Pseudo-second-order	k = 0.2510 (g/mg h)	

$$q_t = \beta \ln(\alpha\beta) + \beta \ln(t) \tag{3}$$

where q_t is the amount of adsorbed dye at time t, α is the sorption constant of the dye (mg/g), and β is the desorption constant (mg/g). Thus, the constant can be obtained from the slope and intercept of the linear plot of q_t vs. ln (t). Table 2 shows the kinetic constants obtained with this model.

3.4.3. *Pseudo-second-order model (Ho)*

The pseudo-second-order model, proposed by Ho and McKay [11], is based on the assumption that the rate-limiting step may be chemisorption involving valence forces through the sharing or exchange of electrons between adsorbent and adsorbate. This model can be represented in the following form:

$$t/q_t = \left(1/k_2 q_e^2\right) + (1/q_e)t \tag{4}$$

where q_t and q_e are the amount adsorbed at time t and at equilibrium (mg/g), respectively, and k_2 is the pseudo-second-order rate constant for the sorption process (g/mg h).

Table 2 shows the kinetic constants obtained applying these models, according to the calculated value of q_e and r^2, the experimental data were best fitted to the Lagergren model for the case of red 2 and to the pseudo-second-order model for yellow 6.

3.5. *Sorption isotherms in the absence of H_2O_2*

Figs. 7 and 8 show the isotherms obtained with Na-Ze, Zn0.1-Ze, and Zn0.5-Ze tuffs for the adsorption of red-2 and yellow-6, respectively, for the first case the data could not be fitted to any model and for yellow-6 the isotherm behaviors was lineal (Table 3). The adsorptions capacities for red-2 were lower than the adsorption capacities for yellow-6. The maximum capacities found for red-2 were about 0.15 mg/g for Na-Ze and about 0.06 mg/g for Zn0.1-Ze, this value was similar for Zn0.5-Ze (Fig. 7). For yellow-6, the adsorption capacities were similar for the three zeolitic tuffs (Fig. 8).

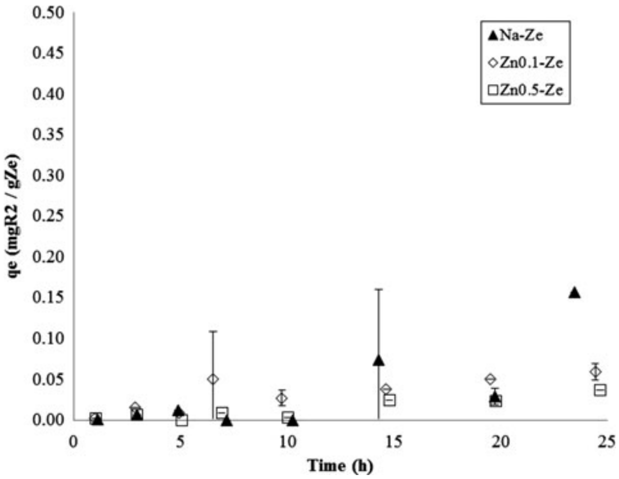

Fig. 7. Adsorption isotherms of red-2 from aqueous solutions by Zn and Na zeolite samples.

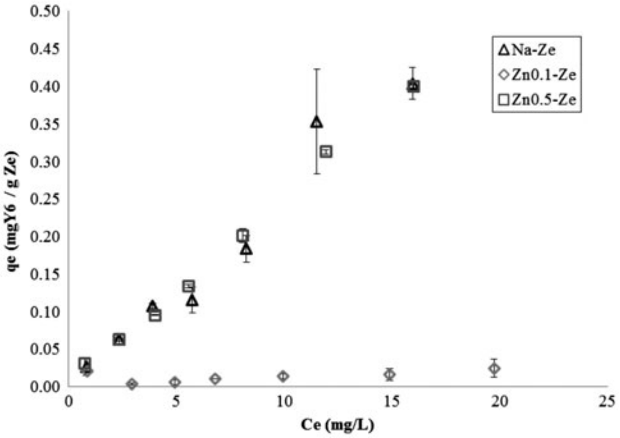

Fig. 8. Adsorption isotherms of yellow-6 from aqueous solutions by Zn and Na zeolite samples.

Table 3
Linear equations of the fitting of the isotherms adsorption of yellow-6 (without H_2O_2) by Na-Ze samples

Sample	Lineal equation	r^2
Na-Ze	$y = 0.0261x$	0.9595
Zn0.1-Ze	$y = 0.0012x$	0.9668
Zn0.5-Ze	$y = 0.0232x$	0.957

3.5.1. *Adsorption isotherms in the presence of H_2O_2*

Figs. 9 and 10 show the adsorption isotherms for red-2 and yellow-6 by Na-Ze in presence of H_2O_2.

The adsorption capacities of Zn-Ze0.1 and Zn-Ze0.5 tuffs were 0.17 and 0.07 mg/g for red-2 and 0.29 and 0.07 for yellow-6, respectively. The sodium zeolitic tuff shows to be an efficient material for the adsorption of red-2 and yellow-6 dyes (Figs. 9 and 10) and the isotherms show to be lineal.

In general, it is observed that the presence of zinc in the zeolitic tuff does not improve the removal of dyes by this material and an opposite behavior has been observed with the presence of iron in

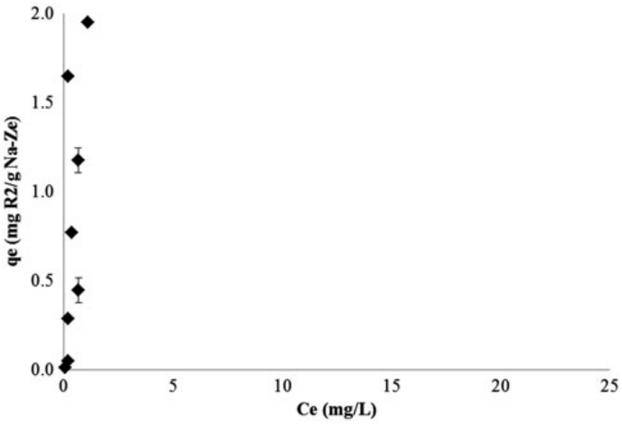

Fig. 9. Adsorption isotherm of red-2 by ZeNa in presence of H_2O_2.

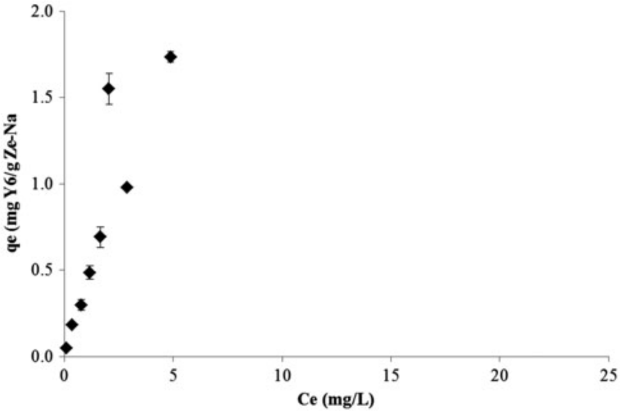

Fig. 10. Adsorption isotherm of yellow-6 by ZeNa in presence of H_2O_2.

aluminosilicates (probably due to the catalytic properties of iron in oxidation reactions) [4–6,12,13], in these papers the maximum adsorption capacity reported was 1.87 mg/g for the removal of red 5 by an iron-modified zeolite. Although the sodium-modified zeolitic tuff is not an efficient material for the removal of neither red-2 nor yellow-2 dyes, the presence of H_2O_2 makes the zeolitic tuff more efficient than the iron-modified aluminosilicates as shown in Figs. 9 and 10.

4. Conclusions

The adsorption kinetic processes of red-2 and yellow-6 by Na-Ze in presence of H_2O_2 were similar, although for the first case the best adjusted was to the kinetic model of Lagergren and the second to the pseudo-second-order model indicating that the sorption mechanism is chemisorption. The presence of Zn did not improve the adsorption efficiency of the zeolitic tuff for the dyes; however, hydrogen peroxide showed to be a very important agent to remove these dyes from aqueous solutions by a sodium zeolitic tuff.

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