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Sorption of Azo Dyes onto a Mexican Surfactant-Modified Clinoptilolite-Rich Tuff

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Abstract: The selectivity of a Mexican surfactant-modified clinoptilolite-rich tuff to retain azo dyes (red-40, yellow-5 and a mixture of them) from aqueous solutions has been investigated. The zeolitic material was modified with hexadecyltrimethylammonium bromide and then left in contact with azo dyes. The uptake was determined at different contact times and concentrations of dyes solutions. First order Elovich, and pseudo second order models as well as the lineal, Langmuir, and Freundlich isotherms were used to describe the experimental data. It was found that in single and binary solutions, under the experimental conditions, the modified zeolitic material retain preferentially the dye red-40 in comparison to yellow-5. The best models to describe the reaction rate and the sorption of azo dyes red-40 and yellow-5 by Mexican surfactant modified clinoptilolite-rich tuff were pseudo-second order and Langmuir models, respectively. These results show that surfactant modified clinoptilolite-rich tuff from Villa de Reyes (San Luis Potosi, Mexico) could be considered as a potential adsorbent of azo dyes from aqueous solutions.

Keywords: Dye, modified zeolitic rock, sorption

INTRODUCTION

Hues in water may result from natural minerals, such as iron and manganese, vegetable origins-hummus material and tannins, or color wastes discharges

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from a variety of industries including mining, refining, pulp and paper, chemicals, and food processing. The true color of water is considered to be only that attributable to substances in solution after removal of suspended materials by centrifuging or filtration. In domestic water color is undesirable aesthetically and may dull clothes or stain fixtures. Stringent color limits are required for water use in many industries, beverage production, dairy and food processing, paper manufactures and textiles (1). The removal of color from textile effluents is one of the challenging problems in the field of environmental chemistry, because of the difficulty of treating such waters by conventional chemical and biological treatment methods. Azo dyes are presently the most important compounds, contributing about 20–40% of the total dyes used for coloring. These dyes are based on the azo chromogen (-N=N-) group.

Clays and zeolites have permanent negative charges on their surfaces, enabling them to be modified by cation surfactants. Such modifications results in the significant increase in total organic carbon content of the minerals and drastically raises their sorption capacity for organic compounds (2). Boyd et al. (3) proposed the use of surfactant-modified clay minerals to remove contaminants from water. Since then many parameters have been considered for the preparation of surfactant-modified clays and zeolites (4). Surfactant-modified zeolites and clays have been shown to be effective and versatile sorbents for nonpolar organics, inorganic cations and inorganic oxyanions. (5, 6). Due to their broad sorptive capabilities, physical and chemical stability, these surfactant-modified zeolites and clays should find many applications in the different branches of industry and environmental protection.

Recently the sorption for dyes removal from aqueous solutions using aluminosilicates has been reported (7–14). The sorption of a variety of dyes (Red 57, Red 3BS, Blue 294, Black B, Black 5, Red 239, Yellow 176, Yellow 3RS H/C) from aqueous solutions onto sepiolite and surfactant-modified sepiolite has been reported (8, 10, 15). It was found that the adsorption of acid dyes obeys Freundlich isotherms and the second order kinetics model, and the adsorption data for azo dyes could be fitted to the Langmuir isotherm.

Ho et al. (7) reported the sorption kinetics for Basic Red 18 and Acid Blue 9 onto an activated clay from Laporte Industry (Singapore) Pte., Ltd. They found a good compliance with the pseudo-second order equation, it means that the chemisorption reaction or an activated process were becoming more predominant in the rate-controlling step for both dye and activated clay systems.

The removal of azo dyes everzol Black, everzol Red 239, everzol Yellow (11, 12) by natural and surfactant-modified clinoptilolite show that natural zeolite have limited adsorption capacities of the reactive dyes but are substantially improved upon modifying its surface with hexadecyltrimethylammonium bromide. The results showed that the adsorption capacities of the surfactant modified clinoptilolite for the dyes followed the order of hydrophilicity of the dye molecules. The isotherms were treated with the Langmuir model.

The aim of this paper is to examine the adsorption capacities of two azo dyes onto a natural and surfactant-modified Mexican clinoptilolite-rich tuff to test kinetics and isotherm models for analyzing the sorption of the dyes on the modified material, mono and bi-component dyes solutions were considered.

EXPERIMENTAL

Material

The clinoptilolite-rich tuff from Villa de Reyes, San Luis Potosi, Mexico was milled and sieved. The grain size used in this work was from 0.8 to 1.0mm.

Treatment with Sodium Chloride

50 g of zeolitic material was treated with 250 mL of 0.125 M NaCl solution, the mixture was refluxed for 8 hours, the phases was separated and a fresh solution of NaCl was added again, this procedure was repeated 4 times. Finally the zeolitic sample was washed with deionized water until no presence of chloride ions was indicated in the washing solution using a $AgNO_3$ test. The sodium treated clinoptilolite-rich tuff was then dried at 333 K for 2 hours.

External Cation Exchange Capacities

The external cation exchange capacities of the material before and after the treatment with sodium were determined. For this purpose the materials were treated with 1M sodium acetate buffered solution of pH 5 for 18 hours to eliminate the carbonate coating on the zeolite, and then the solids were dried at room temperature for 24 hours. Samples of 250 mg were treated with 5 mL of 0.1 M hexadecyltrimethylammonium-bromide (HDTMA-Br) for 48 hours at 303 K, the phases were separated and the solids were washed twice with 5 mL of the same 0.1 M HDTMA-Br. Finally, sodium was determined in the remaining 0.1 M HDTMA-Br solutions.

The external cation exchange capacities were calculated from the quantity of sodium removed per gram of material and it was expressed in meq/g. Sodium was determined in the solutions by atomic absorption spectroscopy using a GBS 932 plus spectrometer with a potassium hollow cathode lamp in a wavelength of 404.4 nm.

Modification with HDTMA-Br

25 g of sodium treated clinoptilolite-rich tuff were mixed with 250 mL of a 0.6 M HDTMA-Br solution, the mixture was shaken for 48 hours at 303 K. Then, the zeolitic material was separated from the solution and it was washed 10 times each day for 12 days with 40 mL of distilled water each

time, until the concentration of HDTMA-Br in the washing solutions was less than 10% of the initial concentration. The surfactant retained in the zeolitic material was determined using an elemental analyzer CHNS-O, CE-Instrument, model EA-1110. The quantity of surfactant retained on the zeolitic material was calculated from the carbon determined in the sample. It is important to note that carbon was determined as well in the untreated sample with HDTMA-Br and the quantity of carbon in this last sample was negligible. Raman spectroscopy was done to verify the interaction between the HDTMA and the zeolite by a high-resolution micro-Raman system (HR LabRam 800) using the 632 nm line of a He–Ne laser in a backscattering configuration. The operation range was from 4000 to 400 cm^{-1}.

Characterization

X-Ray Diffraction

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.

Scanning Electron Microscopy

For scanning electron microscopy (SEM) observations, the natural zeolite samples before and after dyes sorption were mounted directly on the holders, covered by sputtering with gold, and then observed at 10 and 20 kV in a XL 30 Philips electron microscope. The microanalysis was done with an EDS (Energy X-ray Dispersive Spectroscopy) system.

Surface Areas (BET)

The BET surface areas were determined by standard multipoint techniques of nitrogen adsorption, using a Micromeritics Gemini 2360 instrument. The untreated and sodium treated zeolitic samples were heated at 373 K for 24 h before specific surface areas were measured.

Kinetics

Batch type experiments were performed to determine the kinetics removal of dyes by the surfactant modified zeolitic tuff. 200 mg of zeolite samples and 20 mL aliquots of a 5.5 mg/L red-40, 5.48 mg/L yellow-5 or a binary dye solutions (1:1, in the same concentrations) were placed in centrifuge tubes and shaken for different times (5, 10, 15, and 30 minutes, 1, 3, 5, 7, and 12 hours) at room temperature, later the samples were centrifuged, decanted, and washed. The dyes concentrations in solution were determined by using an ultraviolet-visible spectrophotometer analyzer at $\lambda = 499.75$ nm and 426.70 nm for red-40 and yellow-5, respectively.

Isotherms

200 mg samples of surfactant modified zeolitic tuff were put in contact with 20 mL of different concentrations of mono and bi-component dyes solutions (2.5, 5.0, 7.5, 10.0, 12.5, 15.0, 17.5, and 20.0 mg/L). The aqueous and solid phases were shaken for 5 hours at room temperature. The samples were centrifuged and decanted; dyes were analyzed in the liquid phases as described above.

RESULTS AND DISCUSSION

External Cation Exchange Capacities

The external cation exchange capacities for the clinoptilolite rich tuff and the sodium form were 0.0940 and 0.0852 meq/g, respectively. The treatment with sodium chloride does not improve the cation exchange capacity of the clinoptilolite rich-tuff from Villa de Reyes, San Luis Potosi (Mexico). These values are similar or slightly higher than those reported for other natural zeolites (16).

HDTMA Exchanged in the Natural Zeolite

The HDTMA exchanged in the sodium zeolitic material was 0.05373 meq/g, this result shows that 63% of the external ions from the surface of the material were removed by the cationic surfactant. This result was confirmed by Raman spectroscopy through the CH_2 s-stretch frequency band observed at 2860 cm^{-1}. The position of this band has been associated with the amount of surfactant adsorbed by zeolitic materials and according to Sullivan et al. (17) it corresponds between 60 and 80% of the external cation exchange capacity.

Benkli et al. (18) calculated the HDTMA coverage on zeolite surface and they found that a bilayer formation is the most viable packing that enables maximum removal of the dye. Although the surfactant amount adsorbed by the Mexican clinoptilolite-rich tuff was not enough for a bilayer formation, it was enough to have the ability to remove dyes pollutants, as it will be discussed later.

Characterization

X-ray Diffraction

Figure 1 shows the powder diffraction pattern of the natural zeolite from Villa de Reyes, San Luis Potosi (Mexico). Both, clinoptilolite (JCPDS 25-1349)

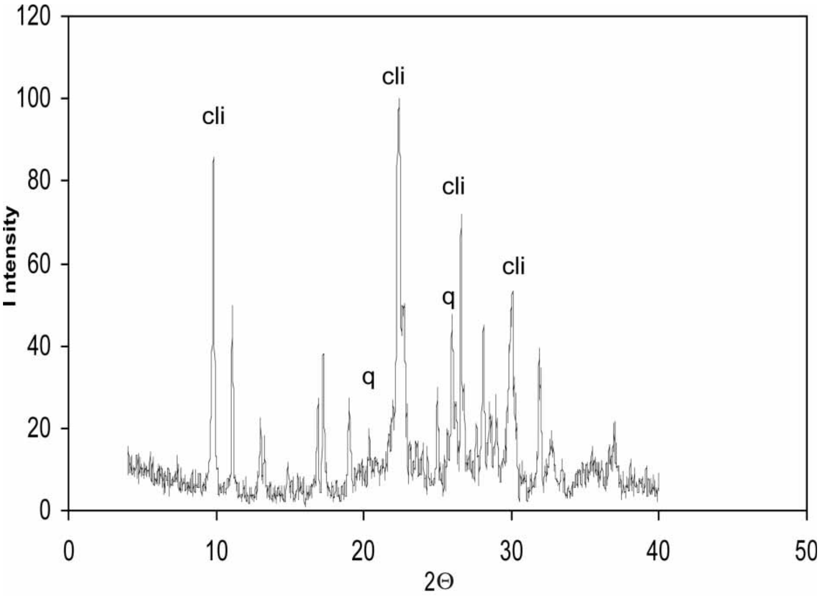


Figure 1. X-ray powder diffraction pattern of the natural zeolite from Villa de Reyes San Luis Potosi (Mexico), in comparison with clinoptilolite (cli) and quartz (q).

and quartz (JCPDS 33-1161), were the principal components found in the zeolitic samples and there was not observed any clay minerals. The diffractogram of the sodium conditioned natural zeolitic material was also compared with that of the halite (JCPDS 5-0628) and it indicated that it was NaCl free. It was observed that HDTMA modified zeolite samples showed no significant changes in the position of the most intense diffraction peaks. These results suggest that the surfactant conditioning has no effects on the structure of the zeolitic material. The powder diffraction pattern of the surfactant Mexican natural zeolite after the azo dyes sorption did not show any important changes.

Scanning Electron Microscopy

The untreated and treated natural zeolite show similar morphologies. Figure 2 shows the SEM image of the Mexican natural zeolite crystals treated with sodium, it displays a typical morphology of sedimentary clinoptilolites which occurred as euhedral plates and laths (19). EDS analysis showed that the chemical compositions of the samples (untreated an treated natural zeolite) are slightly different. The untreated samples did not contain any sodium and the contents of calcium and potassium were the highest, therefore the starting material was a K- and Ca- rich clinoptilolite. The concentration of

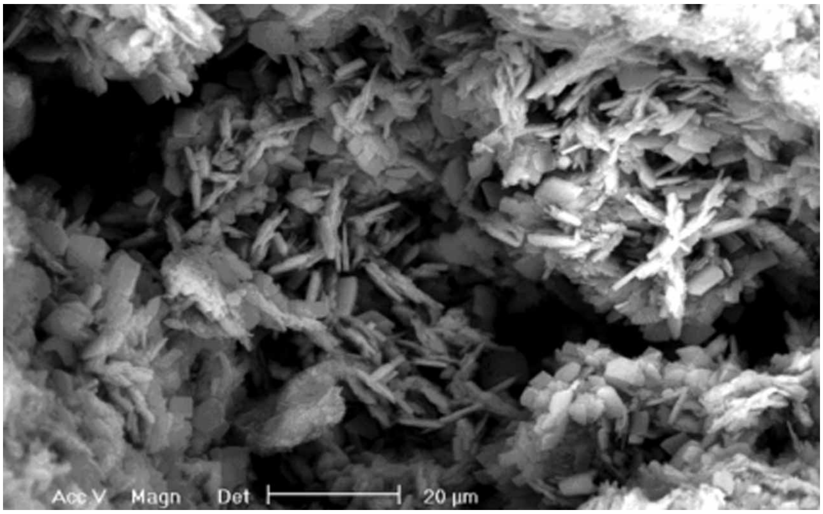


Figure 2. SEM image of the sodium modified clinoptilolite-rich tuff from Villa de Reyes San Luis Potosi (Mexico).

sodium increased in the zeolitic material after the treatment with sodium chloride (2.5 ± 0.2%wt.).

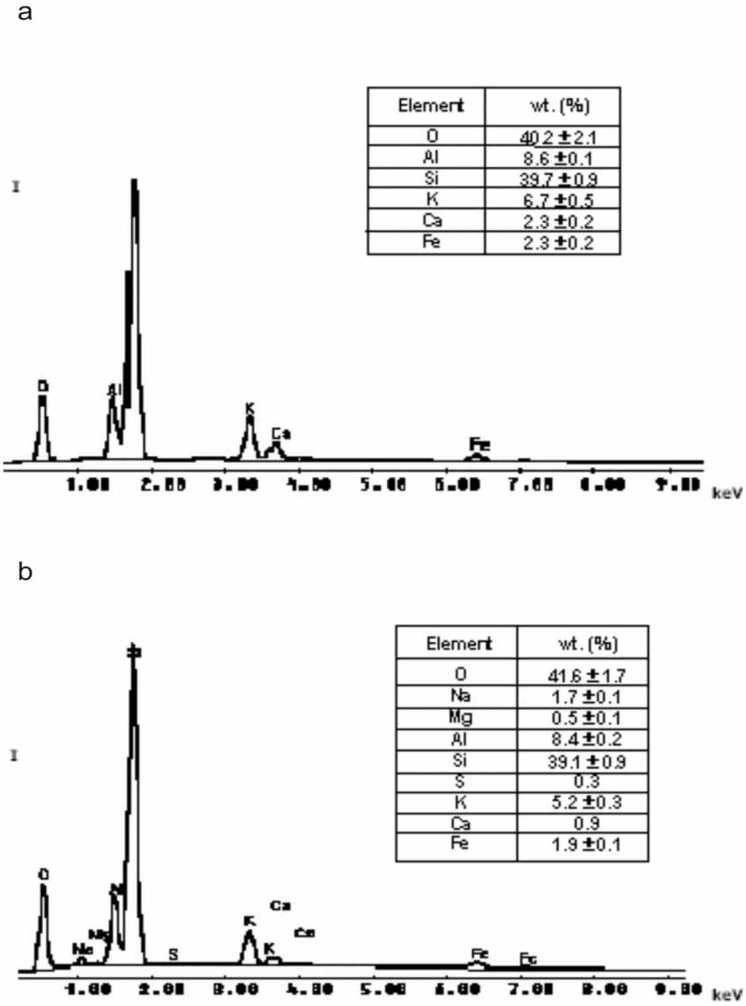
The quantity of sodium in the surfactant modified zeolite was 2.1 ± 0.1% wt. and it decreased (1.7 ± 0.1%wt.) when the samples were in contact with the azo dyes (red-40 or yellow-5). The presence of sulphur (~0.3%wt.) in the modified natural zeolite (Fig. 3) after the dye sorption processes confirms the interaction between the dye and the surfactant bonded to the zeolite surface. S is a component of the azo dyes according with their chemical formulas: $C_{18}H_{14}N_2Na_2O_8S_2$ for red-40 and $C_{16}H_9N_4Na_3O_9S_2$ for yellow-5.

Surface Areas (BET)

The BET surface areas for the untreated and sodium zeolitic samples were 18.2 and 20.3 m^2/g respectively and the total pore volumes were 0.43 and 0.48 cm^3/g respectively. As it is observed the surface area and the pore volume increase when the sample was treated with sodium chloride. It is important to note that the characterization of this zeolitic material has been reported elsewhere (20–22).

Sorption Kinetics

The equilibrium pH values of the solutions was a little higher than the initial pH values, for red-40, yellow-5 and the mixture was: 7.04 ± 0.18, 6.90 ± 0.15, and 6.94 ± 0.29 respectively. It is important to note that the



Element	wt. (%)
O	40.2 ±2.1
Al	8.6 ±0.1
Si	39.7 ±0.9
K	6.7 ±0.5
Ca	2.3 ±0.2
Fe	2.3 ±0.2

Element	wt. (%)
O	41.6 ±1.7
Na	1.7 ±0.1
Mg	0.5 ±0.1
Al	8.4 ±0.2
Si	39.1 ±0.9
S	0.3
K	5.2 ±0.3
Ca	0.9
Fe	1.9 ±0.1

Figure 3. EDS analyses of the HDTMA modified clinoptilolite-rich tuff (a) before and (b) after the red-40 sorption processes.

retention of azo dyes by natural and modified zeolites is not affected in the pH range between 5 and 8 (9).

The adsorption capacities of the untreated clinoptilolite-rich tuff from Villa de Reyes for red-40 and yellow-5 were found to be insignificant, the same behavior has been observed with other zeolitic rocks and dyes (12).

Figures 4, 5 and 6 show the kinetic sorption behavior of red-40 and yellow-5 dyes, in single and binary systems, by the surfactant modified zeolitic material. The curves show that the sorption rate is rapid at the beginning of the processes and then becomes slower as equilibriums are

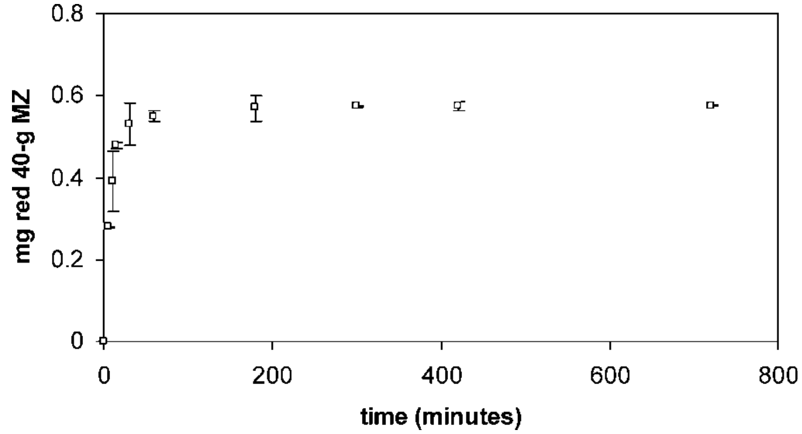


Figure 4. Red-40 adsorption from mono-component aqueous solution by HDTMA modified clinoptilolite-rich tuff (MZ) as a function of time.

approached, the time required to reach the equilibriums were about 30 and 180 minutes for red-40 and yellow-5, respectively; and when working with the binary solution the equilibrium was reached in 180 minutes.

The adsorption at equilibrium for red-40 and yellow-5 were very similar; 0.5751 ± 0.0012 and 0.5741 ± 0.0007 mg of dye/g of material, respectively. When working with the binary solution the sorption of red-40 did not change but the sorption of yellow-5 decreased in 34%. These results show that the material is more selective for red-40 than for yellow-5 when both dyes

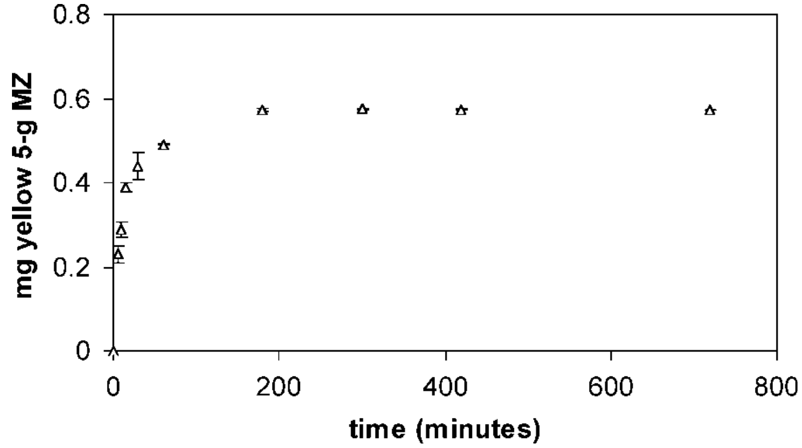


Figure 5. Yellow-5 adsorption from mono-component aqueous solution by HDTMA modified clinoptilolite-rich tuff (MZ) as a function of time.

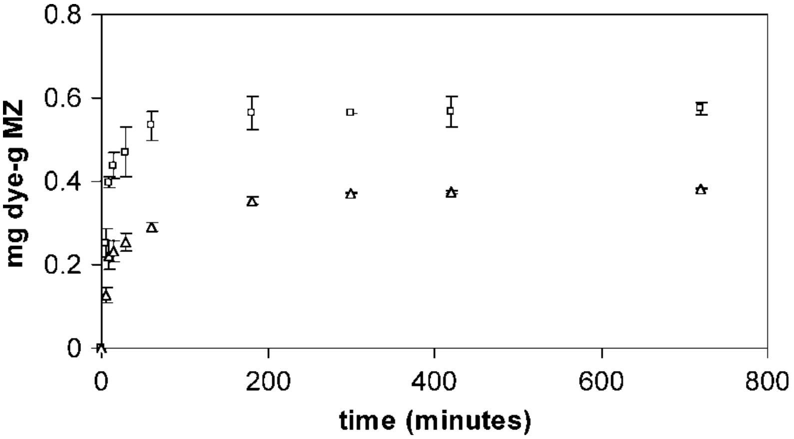


Figure 6. Red-40 (□) and yellow-5 (△) adsorption from bi-component aqueous solution by HDTMA modified clinoptilolite-rich tuff (MZ) as a function of time.

are present, although the time to reach the red-40 equilibrium sorption is longer than with single system.

The data were fitted to the following kinetic models:

Lagergren First-Order Model

The model is represented by the equation (23):

$$q_t = q_e(1 - \exp(-K_L t)) \tag{1}$$

where:

q_t (mg/g) is the amount of dye adsorbed at time t

q_e (mg/g) is the amount of dye adsorbed at equilibrium

K_L (h^{-1}) is the Lagergren rate constant

It was found that this equation provided a good description of the current data. Table 1 shows the first order kinetics equations and r^2 corresponding to dyes sorption on the modified zeolitic rock. Although, the correlation coefficients showed that this model was not the best fitted to the experimental data, the results show that the amounts of dyes adsorbed at equilibrium (q_e) were similar for both cases, red-40 and yellow-5, in single systems and this parameter was lower for yellow-5 than for red-40 in binary system. The Lagergren rate constant K_L was always higher for red-40 than for yellow-5 and they were of the same order of magnitude in both single and binary systems. These behaviors show that the modified material has more affinity for red-40 than for yellow-5, and this behavior could be explained by the hydrophobic/hydrophilic match of the zeolite surface with the dye molecule, which depends upon the way zeolite is modified with the surfactant (18).

Table 1. First order kinetic parameters of the dye sorption by the modified zeolitic rock from Villa de Reyes (San Luis Potosi, Mexico)

	First order kinetic model			
Dye	Equation	q_e (mg g^{-1})	K_L (h^{-1})	r^2
Red-40 (single system)	qt = 0.576*(1-exp(−(0.118)*t))	0. 576	0.118	0.976
Yellow-5 (single system)	qt = 0.574*(1-exp(−(0.035)*t))	0.574	0.035	0.914
Red-40 (binary system)	qt = 0.573*(1-exp(−(0.103)*t))	0.573	0.103	0.900
Yellow-5 (binary system)	qt = 0.382*(1-exp(−(0.058)*t))	0.382	0.058	0.755

Elovich Model

The Elovich rate equation has been used in the kinetics of chemisorption of gases on solids. However some researchers have applied this model to solid-liquid sorption systems. This model is represented by the following equation (24):

$$q_t = \frac{1}{t}\ln(1 + abt) \qquad (2)$$

where:

q_t (mg g^{-1}) is the amount of dye adsorbed at time t

a (mg g^{-1}) is the sorption constant of the dye

b (mg g^{-1}) is the desorption constant of the dye

Table 2 shows the equations, the sorption (a), and desorption (b) constants and r^2 obtained applying the Elovich model to the experimental data. The sorption constant (a) is 234 times higher for red-40 than for yellow-5. In the binary system, the constant for red-40 is lower that in the single system and for yellow-5 the behavior is the opposite, however, the relation red-40/ yellow-5 is lower in the binary system than in the single system, probably due to the competence for the sorption sites in the zeolite. The desorption constant (b) shows higher values for red-40 than for yellow-5 in both cases, in single and binary systems. This model has proved suitable for highly heterogeneous systems. The adsorption of dyes on modified zeolitic rocks is such a case, since they are composed by different minerals and, therefore, exhibit different activation energies for chemisorption.

Pseudo-Second Order Model

The model can be represented by the following equation (25):

$$1/(q_e - q_t) = 1/q_e + kt \qquad (3)$$

Table 2. Elovich kinetic parameters of the dye sorption by the modified zeolitic rock from Villa de Reyes (San Luis Potosi, Mexico)

	Elovich kinetic model			
Dye	Equation	a (mg g^{-1})	b (mg g^{-1})	r^2
Red-40 (single system)	qt = (1/(19.880))*ln(1 + ((16.937)*(19.880)*t))	16.937	19.880	0.745
Yellow-5 (single system)	qt = (1/(9.792))*ln(1 + ((0.072)*(9.792)*t))	0.072	9.792	0.873
Red-40 (binary system)	qt = (1/(18.164))*ln(1 + ((5.553)*(18.164)*t))	5.553	18.164	0.827
Yellow-5 (binary system)	qt = (1/(20.705))*log(1 + ((0.298)*(20.705)*t))	0.298	20.705	0.947

rearranging this equation to a linear form:

$$t/q_t = (1/kq_e^2) + t/q_e$$

where

k (g $mg^{-1}h^{-1}$) constant of pseudo-second order

q_t (mg g^{-1}) is the amount of dye adsorbed at time t

q_e (mg g^{-1}) is the amount of dye adsorbed at equilibrium

The data in straight-line plots of t/q_t against t were tested to obtain rate parameters. The pseudo-second order rate constant, k, initial sorption rate, kq_e^2, equilibrium sorption capacity, q_e, and correlation coefficients, r^2, for the dyes were calculated and compared with the adjustments of the models described above.

Figure 7 shows the adjustments of the experimental data for red-40 to the linear equation of this model and Table 3 shows the pseudo-second order kinetics equations, the pseudo-second order rate constants, k, and correlation coefficients, r^2 corresponding to red-40, yellow-5 and the mixture sorption on the modified Mexican natural zeolite.

The pseudo-second order model is based on the assumption that the rate-limiting step may be chemisorption involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate. Although, the experimental points could be fitted to the first and pseudo-second order kinetics equations, in general the best adjustments were observed with the pseudo-second order kinetics equation, which is generally applied to heterogeneous materials which is the case of natural zeolites. The kinetic constants show that the sorption rate is higher for red-40 than for yellow-5

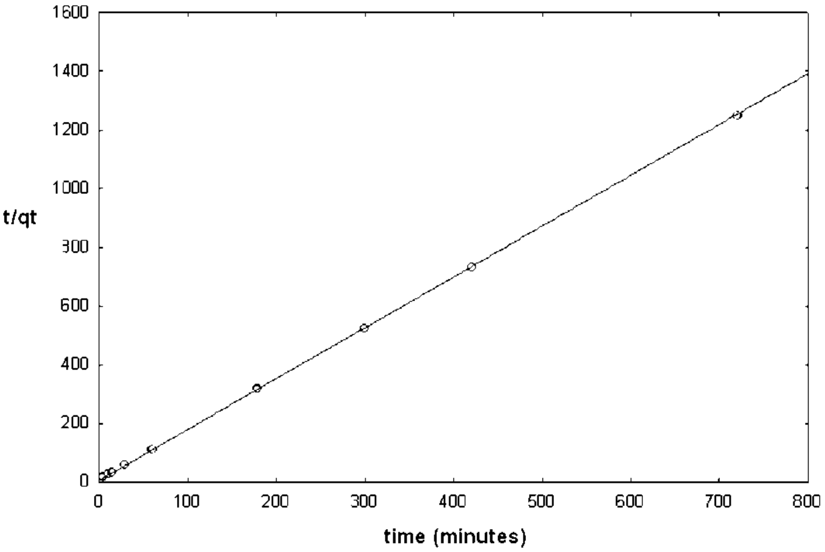


Figure 7. Kinetic pseudo-second order model applied to the red-40 sorption from mono-component aqueous solution by HDTMA modified clinoptilolite-rich tuff.

in both cases single and binary systems, it is important to note that the correlation coefficient was the lowest for the dye yellow-5 in the binary system.

Sorption Isotherms

The isotherm data obtained in this work were fitted to the Langmuir and Freundlich models in order to describe the azo dyes sorption behavior in

Table 3. Second order kinetic parameters of the dye sorption by the modified zeolitic rock from Villa de Reyes (San Luis Potosi, Mexico)

	Pseudo–second order kinetic model		
Dye	Equation	K ($g\,mg^{-1}h^{-1}$)	r^2
Red-40 (single system)	$t/qt = (1/(0.078)(0.576^2)) + (t/0.576)$	0. 078	0.999
Yellow-5 (single system)	$t/qt = (1/(0.018)(0.574^2) + (t/0.574)$	0. 018	0.997
Red-40 (binary system)	$t/qt = (1/(0.042)(0.573^2)) + (t/0.573)$	0.042	0.999
Yellow-5 (binary system)	$t/qt = (1/(0.005)(0.382^2)) + (t/0.382)$	0. 005	0.939

surfactant modified clinoptilolite-rich tuff from Villa de Reyes, San Luis Potosi (Mexico).

Langmuir Model

The Langmuir model is probably the most widely applied sorption isotherm. This model considers that the sorption energy of each molecule is the same, independently of the surface of the material, the sorption takes place only on some sites and there are no interactions between the molecules (26). It may be represented as follows:

$$q_e = \frac{Q_0 b C_e}{1 + b C_e} \tag{4}$$

and the linear form of the equation is

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{1}{Q_0} C_e$$

where

Q_o (mg g^{-1}) is the amount of dye adsorbed per unit weight of adsorbent in forming a complete monolayer on the surface

q_e (mg g^{-1}) is the amount of dye adsorbed

C_e (mg L^{-1}) concentration of the dye in the solution at equilibrium

b is the constant related to the energy or net enthalpy of adsorption.

The experimental data for red-40 were fitted to this isotherm model and the results are shown in Fig. 8. Table 4 shows the equations, Q_0, b and r for the adsorption of red-40, yellow-5 and mixture by the modified zeolitic rock.

The sorption constants, Q_o, and b are higher for red-40 than for yellow-5 in both cases binary and single components.

Armagan et al. (11), used zeolite from Turkey, as a low-cost adsorbent, to evaluate its ability to remove color from textile effluents and they reported that the natural zeolite has a limited adsorption capacity for reactive dyes but is substantially improved upon modifying its surfaces with quaternary ammonium salts. A mechanism involving electrostatic attraction of the ionic groups of dye molecules onto oppositely charged surfactant-modified zeolite surface is proposed to be responsible for the uptake of dyes (5), the degree of hydrophilicity plays an important role in the interaction of oppositely charge groups. Surface coverage as a bilayer rather than a monolayer has a strongly favorable influence on the dyes uptake. They found that natural zeolite has a limited adsorption capacity for reactive dyes but can be distinctly improved by modifying its surfaces with quaternary ammonium salt. Their comparison of natural and modified zeolites at 5% solids concentration indicated that, while the adsorption densities of Everzol dyes with natural zeolite yielded negative or slightly positive values, those with modified zeolite gave adsorption densities in the range of 2.9 to 7.6 mg/g.

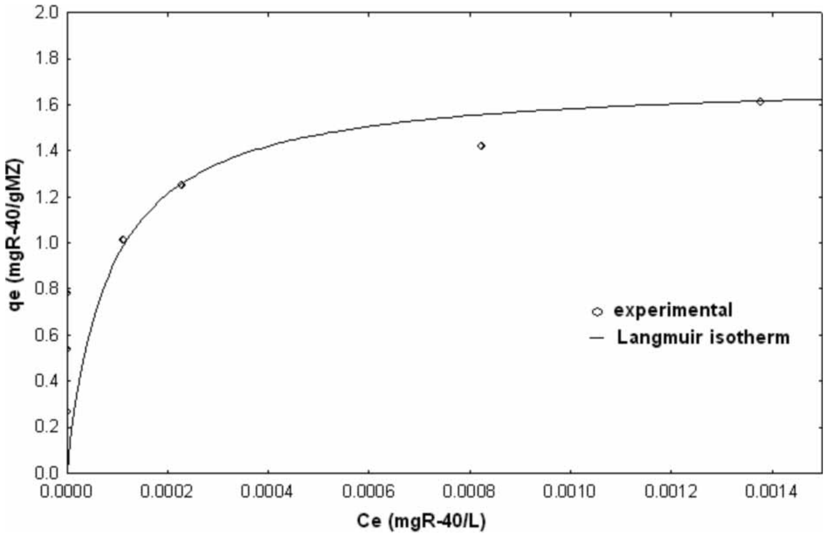


Figure 8. Langmuir isotherm applied to the red-40 sorption from mono-component aqueous solution by HDTMA modified clinoptilolite-rich tuff (MZ).

Freundlich Model

This empirical model can be applied to no ideal sorption on heterogeneous surfaces as well as multiplayer sorption and can be expressed by the following equation:

$$q_e = K_f C_e^{\frac{1}{n}} \tag{5}$$

Table 4. Langmuir parameters of the dye sorption by the modified zeolitic rock from Villa de Reyes (San Luis Potosi, Mexico)

	Langmuir isotherm model			
Dye	Equation	Q_o (mg g^{-1})	b (L mg^{-1})	r^2
Red-40 (single system)	$q_e = ((1.714)^*(12085.900)^*\ C_e)/(1 + ((12085.900)^*\ C_e))$	1.714	12085.900	0.485
Yellow-5 (single system)	$q_e = ((1.050)^*(3260.120)^*\ C_e)/(1 + ((3260.120)^*\ C_e))$	1.051	3260.120	0.918
Red-40 (binary system)	$q_e = ((1.537)^*(2982.310)^*\ C_e)/(1 + ((2982.310)^*\ C_e))$	1.537	2982.310	0.726
Yellow-5 (binary system)	$q_e = ((0.700)^*(2604.410)^*\ C_e)/(1 + ((2604.410)^*\ C_e))$	0.700	2604.410	0.963

where:

q_e (mg/g) is the amount of dye per unit weight of zeolite

C_e (mg/L) is the equilibrium concentration of dye in solution

K_f is the equilibrium constant indicative of adsorption capacity

n is the adsorption equilibrium constant whose reciprocal is indicative of adsorption intensity.

The Freundlich isotherm has been derived by assuming an exponentially decaying sorption site energy distribution. The Freundlich isotherm plot for the sorption of red-40 by the modified natural zeolite is presented in Fig. 9. Table 5 shows the Freundlich sorption isotherms equations, constants and r^2 for red-40, yellow-5 and mixture.

The experimental data of yellow-5 were better adjusted in both single and binary components than for red-40. The adsorption capacity K_f for red-40 were higher than for yellow-5 in both cases, this behavior could be due to the water solubility of the dyes, yellow-5 is more soluble in water than red-40. Bowman et al. (6) found that the sorption of p-xylene, toluene, and benzene by surfactant-modified zeolites increases as the aqueous solubility of the organic decreases, they proposed that the surfactant-modified zeolites sorbed nonpolar organic solutes from water via a partitioning mechanism. We believe that the uptake of the solutes consists of surface sorption of anionic species on the two-dimensional surface of the organic medium as discussed above.

In general the correlation coefficients were higher using the model of Langmuir than the model of Freundlich.

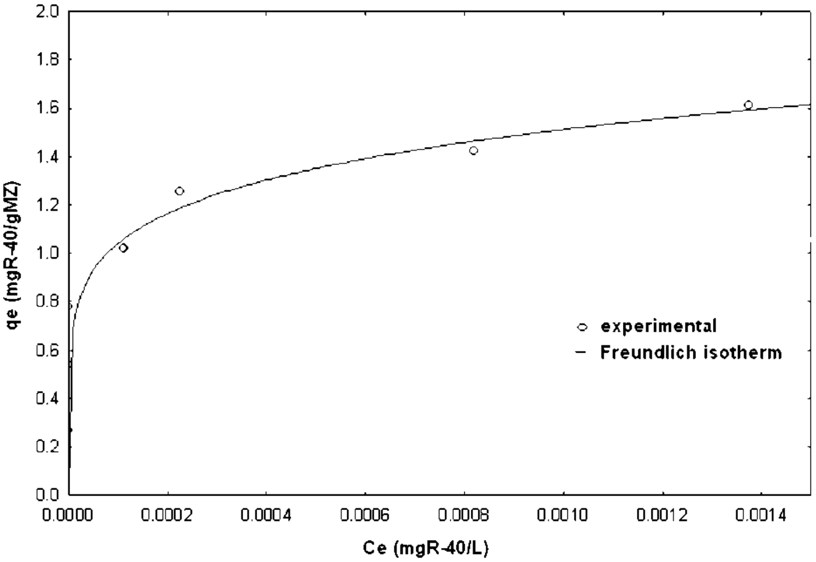


Figure 9. Freundlich isotherm applied to the red-40 sorption from mono-component aqueous solution by HDTMA modified clinoptilolite-rich tuff (MZ).

Table 5. Freundlich parameters of the sorption of the dyes by the modified zeolitic rock

Dye	Freundlich isotherm model			
	Equation	K_f (mg g^{-1})	n	r^2
Red-40 (single system)	$q_e = (4.644)Ce^{(1/6.160)}$	4.644	6.160	0.496
Yellow-5 (single system)	$q_e = (3.295)Ce^{(1/4.362)}$	3.295	4.362	0.915
Red-40 (binary system)	$q_e = (6.829)Ce^{(1/3.704)}$	6.829	3.704	0.766
Yellow-5 (binary system)	$q_e = (1.052)Ce^{(1/10.483)}$	1.052	10.483	0.868

Langmuir Competitive Model

One way to represent binary dye systems is a prediction using mathematical equations, which contain parameters obtained from single metal isotherms. The experimental data were compared with the curves obtained using an extension of the Langmuir competitive equations given elsewhere (27, 28):

$$q_1 = \frac{q_{\max 1} b_1 C_1}{1 + b_1 C_1 + \eta_2 C_2} \tag{6}$$

$$q_2 = \frac{q_{\max 2} b_2 C_2}{1 + b_2 C_2 + \eta_1 C_1}$$

where b_1, b_2, $q_{\max 1}$ and $q_{\max 2}$ are the individual Langmuir adsorption constants of the first and second dye respectively, while η_1 and η_2 are the multi-component Langmuir adsorption constants of the first and second dye respectively, which are estimated from binary adsorption data. C_1 and C_2 are the equilibrium concentrations of the first and the second dye ion respectively.

The sorption of a dye may be affected by the presence of any other component in the solution, depending on the physical and chemical characteristics of the components in the aqueous media.

The experimental data were treated with the extension of Langmuir competitive equations and the parameters obtained are shown in Table 6. In general the larger the multi-component Langmuir adsorption constant of one dye, the larger is the competition effect of this dye on the adsorption of the other. Although, the correlation values, r^2, were low, comparing the adjustable parameter for red-40 and yellow-5 it is evidenced that the multi-component Langmuir adsorption constant for red-40 is higher than that for yellow-5 evidencing the stronger depression operated by red-40 on yellow-5 adsorption when both dyes are present in solution.

Table 6. Langmuir competitive model parameters of the sorption of the dyes by the modified zeolitic rock in a binary component solution

Dye	Equation	q_{max} (mg g^{-1})	b (L mg^{-1})	η	r^2
Red-40	$q = (1.714{*}12085.900{*}\ C_1)/(1 + (12085.900{*}\ C_1) + (3260.120{*}\ ((0.003){*}\ C_2))$	1.714	12085.900	0.003	0.696
Yellow-5	$q = (1.050{*}3260.120{*}\ C_2)/(1 + (3260.120{*}\ C_2) + (12085.900{*}((-0.183){*}\ C_1))$	1.050	3260.120	−0.183	0.962

CONCLUSIONS

The major mineral component of the Villa de Reyes tuff was clinoptilolite.

The treatment of the natural zeolite from Villa de Reyes, San Luis Potosi (Mexico), with sodium chloride does not improve its external cation exchange capacity.

The HDTMA exchanged in the natural zeolite (Villa de Reyes) was 63% of the external cation exchange capacity.

The crystals morphology of the clinoptilolite-rich tuff from Villa de Reyes (San Luis Potosi, Mexico) does not change after the HDTMA surface modifications of the zeolite. Sulfur confirms the interaction between the dyes and the surfactant modified clinoptilolite-rich tuff.

The pseudo-second order rate constants for the dye sorption by Mexican natural zeolite depend of both the chemical nature of each dye in the aqueous solution and the interactions between them in a bi-component system.

The surfactant modified clinoptilolite-rich tuff from Villa de Reyes sorbs more selectively red-40 than yellow-5 from a mixture of both azo dyes in aqueous solution.

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REFERENCES

1. Hammer, M.J. and Hammer, M.J. (Jr) (1996) *Water and Waste Water Technology*. 3rd edn.; Prentice Hall Inc: USA.

2. Li, Z., Alessi, D., and Allen, L. (2002) Influence of quaternary ammonium on sorption of selected metal cations onto clinoptilolite zeolite. *Journal Environmental Quality*, 31: 1106–1114.
3. Boyd, S.A., Mortland, M.M., and Chiou, C.T. (1988) Sorption characteristics of organic compounds on hexadecyltrimethylammonium-smectite. *Soil Sci. Soc. Am. J.*, 52: 652–657.
4. Li, Z. (1999) Sorption kinetics of hexadecyltrimethylammonium on natural clinoptilolite. *Langmuir*, 15: 6438–6445.
5. Armagan, B., Ozdemir, O., Turan, M., and Celik, M. (2003) Adsorption of negatively charged azo dyes onto surfactant-modified sepiolite. *Journal of Environmental Engineering*, 129 (8): 709–715.
6. Bowman, R., Haggerty, G., Huddleston, R., Neel, D., and Flynn, M. (1995) *Sorption of Nonpolar Organic Compounds, Inorganic Cations, and Inorganic Oxyanions by Surfactant-Modified Zeolites*, Sabatani, D., Knox, R., and Harwell, J. (eds.); ACS Symposium Series 594, Surfactant-enhanced subsurface remediation, Emerging Technologies. American Chemical Society: Washington D.C.
7. Ho, Y., Chiang, C., and Hsu, Y. (2001) Sorption kinetics for dye removal from aqueous solution using activated clay. *Separation Science and Technology*, 36: 2473–2488.
8. Ozcan, A., Tetik, S., and Ozcan, A. (2004) Adsorption of acid dyes from aqueous solutions onto sepiolite. *Separation Science and Technology*, 39 (2): 301–320.
9. Armagan, B., Özdemir, O., Turan, M., and Çelik, M. (2003) The removal of reactive azo dyes by natural and modified zeolites. *Journal of Chemical Technology and Biotechnology*, 78 (7): 725–732.
10. Armagan, B., Özdemir, O., Turan, M., and Çelik, M. (2003) Clay mineral batch process for color removal of textile waste water. *Journal of Environmental Science Health A. Tox. Hazard Subst. Environ. Eng.*, 38 (10): 2251–2258.
11. Armagan, B., Turan, M., and Cęlik, M. (2004) Equilibrium studies on the adsorption of reactive azodyes into zeolite. *Desalination*, 170 (1): 33–39.
12. Armagan, B., Turan, M., Ozdemir, O., and Cęlik, M. (2004) Color removal of reactive dyes from water by clinoptilolite. *Journal of Environmental Science Health A. Tox. Hazard Subst. Environ. Eng.*, 39 (5): 1251–1261.
13. Al-Bastaki, N. and Banat, F. (2004) Combining ultrafiltration and adsorption on bentonite in a one-step process for the treatment of colored waters. *Resources, Conservation and Recycling*, 41 (2): 103–113.
14. Bouberka, Z., Kacha, S., Kameche, M., Elmaleh, S., and Derriche, Z. (2005) Sorption study of an acid dye from an aqueous solutions using modified clays. *Journal of Hazardous Materials*, 119 (1–3): 117–124.
15. Ozdemir, O., Armagan, B., Turan, M., and Çelik, M. (2004) Comparison of the adsorption characteristics of azo-reactive dyes on mezoporous minerals. *Dyes and Pigments*, 62 (1): 49–60.
16. Díaz-Nava, M., Olguín, M., Solache-Ríos, M., Alarcón-Herrera, M., and Aguilar-Elguezabal, A. (2005) Characterization and improvement of ion exchange capacities of Mexican clinoptilolite-rich tuffs. *Journal of Inclusion Phenomena and Macrocyclic Chemistry*, 51 (3–4): 231–240.
17. Sullivan, E.J., Hunter, D.B., and Bowman, R.S. (1998) Fourier transform raman spectroscopy of sorbed HDTMA and the mechanism of chromate sorption to surfactant-modified clinoptilolite. *Environmental Science & Technology*, 32: 1948–1955.

18. Benkli, Y., Can, M., Turan, M., and Çelik, M. (2005) Modification of organo-zeolite surface for the removal of reactive azo dyes in fixed-bed reactors. *Journal of Hazardous Materials*, 119 (1–3): 117–124.
19. Mumpton, F. and Clayton, O. (1976) Morphology of zeolites in sedimentary rocks by Scanning Electron Microscopy. *Clays and Clay Minerals*, 24: 1–23.
20. Hernández, S.M.V. (1999) Intercambio iónico de metales pesados presentes en solución acuosa sobre zeolitas naturales. México., UASLP, SLPTesis de Maestría, Facultad de Ciencias Químicas.
21. Leyva, R.R., Sánchez, C.M.A., Hernández, S.M.V., and Guerrero, C.R.M. (2001) Remoción de metales pesados de solución acuosa por medio de clinoptilolitas naturales. *Revista Internacional de Contaminación Ambiental*, 17: 129–136.
22. Leyva, R.R., Medellín, N.C., Guerrero, R.C., Berber, M.M., Aragón, A.P., and Jacobo, A.A. (2005) Intercambio iónico de plata (I) en solución acuosa sobre clinoptilolita. *Revista Internacional de Contaminación Ambiental*, 21: 193–200.
23. Mathialagan, T. and Viraraghavan, T. (2003) Adsorption of cadmium from aqueous solutions by vermiculite. *Separation Science and Technology*, 38: 57–76.
24. Cheung, C., Porter, J., and McKay, G. (2000) Elovich equation and modified second-order equation for sorption of cadmium ions onto bone char. *Journal of Chemical Technology and Biotechnology*, 75: 963–970.
25. Ho, Y. and McKay, G. (1999) Pseudo-second order model for sorption processes. *Process Biochemistry*, 34 (5): 451–465.
26. Slejko, F. (1985) *Adsorption Technology: A Step-Step Approach to Process Evaluation and Application*; Marcel-Decker Inc: USA.
27. Pagnanelli, F., Esposito, A., and Veglio, F. (2002) Multi-metallic modelling for biosorption of binary systems. *Water Research*, 36 (16): 4095–4105.
28. Pagnanelli, F., Mainelli, S., Centofanti, M., Veglio, F., and Toro, L. (2003) *Biosorption of Binary Metal Systems onto an Olive Pomace: Equilibrium Modeling;* The Sixth Italian Conference on Chemical and Process Engineering: Pisa, Italy.