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Clinoptilolita cubana para la adsorción de rodamina B. Caracterización de los materiales zeolita-colorante obtenidos

Cuban clinoptilolite for rhodamine B adsorption. Characterization of the obtained zeolite-dye materials

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Resumen

En el presente trabajo se estudió la adsorción del colorante fluorescente rodamina B (RB) en una zeolita natural cubana (NZ). Se verificó que la adsorción se favorece a pH ácido y que la isoterma de adsorción puede ser ajustada por los modelos de Langmuir y Freundlich. Los estudios cinéticos indicaron que la adsorción sigue un modelo cinético de pseudo segundo orden. Más del 92 % de la RB en disolución es adsorbida por la zeolita en un amplio rango de concentraciones iniciales, lo cual constituye un resultado excelente para aplicaciones medioambientales. La caracterización de los materiales compuestos mostró que poseen una buena estabilidad térmica y una distribución homogénea de RB en la superficie de NZ. El colorante exhibe un incremento en la intensidad de fluorescencia cuando se adsorbe en NZ, por lo que las muestras NZ-RB pudieran ser buenos candidatos para su empleo como sensores y en sistemas ópticos.

Palabras clave: zeolita, clinoptilolita, rodamina B, remoción de colorante.

Abstract

In the present work, the adsorption of the fluorescent dye rhodamine B (RB) onto a Cuban natural zeolite (NZ) was studied. The isotherm adsorption could be fitted by the Langmuir and Freundlich models and it was verified that the adsorption is favored in acid pH. Kinetics studies indicated that the adsorption followed a pseudo, second order kinetic model. More than the 92 % of the RB in solution is captured by the zeolite in a wide range of initial concentrations, which constitutes an excellent result for environmental applications. The characterization of the composite materials showed a good thermal stability and homogeneous distribution of RB on NZ surface. The dye exhibits an increase in fluorescence intensity when it is absorbed onto NZ, so NZ-RB samples could be good candidates for their use as sensors and in optic systems.

Keywords: zeolite, clinoptilolite, rhodamine B, dye removal.

Introduction

The use of dyes in different industries produce highly colored waste effluents. The discard of these wastes into water may cause environmental problems, mainly because these compounds can be toxic to the aquatic flora and fauna. Several treatments such as physical separation, chemical oxidation, reverse osmosis, adsorption and biological degradation have been developed for the removal of dyes from wastewater [1]. Adsorption technologies are considered the most efficient for removing such pollutants, in terms of cost, simplicity of design and operation, and availability [2]. Activated carbon, clays, zeolites and other porous materials, alumina, and polymers, among others, have been investigated as adsorbents for dye removal [2-10]. Currently, activated carbon is considered the most effective adsorbent. However, the high cost in its production and regeneration, makes it uneconomical. This fact encourages looking for better, more efficient and regenerable adsorbents to remove such contaminants from water. In this sense, natural zeolites are promising candidates due to their ion-exchange and adsorptive properties, thermal and mechanical stabilities, and low cost. Based on such properties, natural and modified zeolites have been widely used for the adsorption of a great variety of organic compounds [11-15]. In recent years, several investigations about the adsorption of dyes from aqueous medium onto clinoptilolite have been reported in the literature [16-21].

Clinoptilolite is one of the most abundant and economically important natural zeolites. The typical unit cell formula of a clinoptilolite is given as $(Na,K,Ca,Mg)_6[Al_6Si_{30}O_{72}]$ $x{\cdot}nH_2O$ [22]. The three-dimensional crystal structure contains three types of channels interconnected in two dimensions. The channels A and B (confined by ten- and eight-membered rings, respectively), run parallel to the *c*-axis, and the channel C (confined by eight-membered ring) run parallel to the *a*-axis of the structure [23, 24]. The dimensions of the channels are about: A ≈ 7,5 x 3,1 Å, B ≈ 4,6 x 3,6 Å and C ≈ 4,7 x 2,8 Å [25]. The channels are occupied by the exchangeable cations (Na^+, K^+, Ca^{2+} and Mg^{2+}), which are partially coordinated with the structural oxygens and complete their coordination sphere with water molecules. These cations play an important role in the adsorption, ion-exchange and catalytic properties, as well as in the thermal and chemical stability of the zeolite [26, 27].

The present work aims to assess the applicability of a cuban natural clinoptilolite in the adsorption of the fluorescent dye rhodamine B, for its use in environmental remediation.

Furthermore, the characterization of the obtained materials (zeolite-dye) is carried out in view of to evaluate their potentialities in other applications such as sensors, optic and laser systems.

Experimental

Materials

The raw zeolitic material used in this study was the purified natural clinoptilolite, NZ, from Tasajeras deposit (Cuba), which was obtained by means of a mineral benefit method reported elsewhere [28]. NZ was submitted to an additional purification consisting in washing processes at 100 ^{o}C with distilled water, and the magnetic separation of iron oxides. The resulting zeolite sample was a powder of 36-56 μm particle size, mainly consisting in a mixture of clinoptilolite (70 %), mordenite (5 %), anorthite (15 %) and quartz (10 %). The oxide form chemical composition of the employed zeolite is SiO_2 (63,5), Al_2O_3 (11,2), Na_2O (1,7), K_2O (1,3), CaO (3,7), MgO (0.6), and Fe_2O_3 (0,2). The specific surface area of NZ calculated using the BET method is 70 m^2/g, while the external surface area, according to the t-plot method, is about 20 m^2/g (for the sample degassed at 300 ^{o}C). The dye rhodamine B (RB) was kindly supplied by the Department of Operative Chemical Applications, Central Laboratory of Criminalistic of Cuba (DCRIM).

Dye adsorption experiments

To perform an initial screening, adsorption experiments were carried out shaking 0,25 g of NZ with 25 mL of RB aqueous solutions at room temperature, varying the initial pH, the adsorbate concentrations and the contact time. The adsorption isotherm at 30 ^{o}C was obtained by shaking 0,25 g of NZ with 25 mL of RB solutions at different concentrations (0,1 x 10^{-5} – 25 x 10^{-5} mol/L) at pH = 2 for 24 h. The adsorption data were analyzed employing the commonly used Freundlich and Langmuir isotherms. The Langmuir isotherm, based on the assumption of the adsorption at specific homogeneous sites within the adsorbent, is expressed in its linear form by the following equation:

$$\frac{c_{eq}}{\Gamma_{ad}} = \frac{1}{\Gamma_{\max} K_L} + \frac{c_{eq}}{\Gamma_{\max}} \qquad (1)$$

where: Γ_{ad} is the amount adsorbed

Γ_{max} is the maximum sorption capacity

C_{eq} is the equilibrium concentration

K_L is the Langmuir constant related to the adsorption energy.

Plot of c_{eq}/Γ_{ad} *vs.* c_{eq} gives a straight line of slope $1/\Gamma_{max}$ and intercept $1/\Gamma_{max}K_L$.

The empirical Freundlich model, which is employed to describe heterogeneous systems, is expressed in its logarithmic form by the equation:

$$\log \Gamma_{ad} = \log K_F + \frac{1}{n}\log c_{eq} \qquad (2)$$

where: Γ_{ad} is the amount adsorbed

c_{eq} is the equilibrium concentration

K_F and *n* are Freundlich constants which are related to adsorption capacity and intensity of adsorption. Plot of $\log\Gamma_{ad}$ *vs.* $\log c_{eq}$ gives a straight line of slope 1/*n* and intercept $\log K_F$.

Kinetics experiments were performed under the same conditions at constants initial RB concentrations of 5, 10 and 20 x 10^{-5} mol/L. The RB concentration before and after the interaction was determined by UV spectroscopy by measuring absorbance at λ = 552 nm and the amount adsorbed was calculated by the depletion method.

Characterization of zeolite-dye materials

Nitrogen adsorption measurements were conducted using TriStar II 3020 equipment. Before measurements NZ was degassed at 300 °C under vacuum over the night employing a micromeritics VacPre 061 sample degas system. The NZ-RB samples were degassed at 110 °C to avoid dye decomposition. The measurement for NZ degassed at this temperature was also performed to compare.

Thermogravimetry (TG/DSC) analysis was carried out with the aid of a NETZSCH STA 409 PC/PG thermal analyzer. Samples were heated form 298 to 973 K at a heating rate of 10 K/min under dry air at a purging flow rate of 50 mL/min. The sensitivity of the thermobalance was ± 1 µg. A solid sample of about 35 mg was used in each test.

The UV–VIS diffuse reflectance spectra (UV–VIS-DRS) in the wavelength range between 190 and 850 nm were recorded at room temperature making use of a CARY SCAN 300 (VARIAN) equipped with an integrating sphere unit. The spectrum of the clinoptilolite (NZ) was taken as reference.

The fluorescence spectrum of RB was recorded in aqueous solution at a dye concentration of 1,5 x 10^{-5} mol/L. The spectra of RB adsorbed onto NZ were measured in glycerin suspensions of NZ-RB samples (exciting between 557 to 564 nm and measuring between 576 to 581 nm). A Shimadzu RF-5301PC spectrofluorimeter was employed.

The epifluorescence images were acquired employing a Zeiss fluorescence microscope with ApoTome attachment (Axio Imager 2.1) with 40x/1,3 oil immersion objective. A coolsnap HQ2 camera was employed. The excitation was performed between 532 – 558 nm and the emission was recorded between 570 – 640 nm. The ApoTome structured-illumination attachment allowed optical sectioning using the camera and the AxioVision software allowed automatic collection of multi-channel Z-stack images.

Results and discussion

Rhodamine B adsorption onto NZ

The results of the screening of the RB adsorption onto NZ, which was carried out varying the initial pH, the adsorbate concentrations and the contact time, are presented in table 1. As can be seen the adsorption of the dye is favored at acid pH. This can be explained by the electrostatic interaction between the cationic dye and the negatively charged zeolitic surface. The carboxylic group of the rhodamine B molecule (see fig. 1) can be dissociated with increasing pH of the solution. At pH values higher than its pKa value (pKa = 3,2) the molecule has a zwitterionic structure. This fact leads to the decrease of the amount adsorbed, because the electrostatic interactions between the molecule and the zeolitic surface diminish. These results are in good agreement with those reported by other authors [19, 21]. The amount of RB adsorbed also increases with the dye initial concentration, and a contact time of 24 h seems to be enough to reach the equilibrium.

TABLE 1. AMOUNT OF RHODAMINE B ADSORBED ON TO NZ AT DIFFERENT EXPERIMENTAL CONDITIONS

Sample	Time (h)	pH_i	pH_f	c_i (µmol/L)	c_{eq} (µmol/L)	Γ_{ad} (µmol/g)
NZ-RB-1	24	2,5	3,2	15	1,03	6,99
NZ-RB-2	24	6,4	9,7	5	4,18	0,41
NZ-RB-3	48	2,4	3,2	5	1,36	1,82
NZ-RB-4	48	5,5	9,2	15	9,92	2,54
NZ-RB-5	24	2,5	3,1	30	2,63	13,69

c_i: RB initial concentration, c_{eq}: RB equilibrium concentration, Γ_{ad}: amount of RB adsorbed on NZ

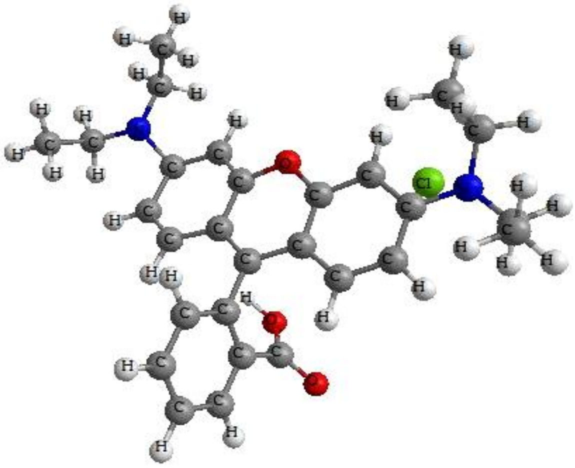


Fig. 1. Chemical structure of the dye rhodamine B

The adsorption isotherm of RB onto NZ and the percent of the dye uptake by the zeolite are shown in figure 2. The shape of the isotherm, in particular its high initial slope in the region of low concentrations, denotes the great affinity of the dye by the zeolite. It can be noted from figure 2B that the percent of RB removed by NZ is greater than 92 % in a wide range of concentrations. In the range between 0.5 - 10 x 10^{-5} mol/L it is even bigger than 99 %, which constitutes an excellent result from the point of view of environmental applications.

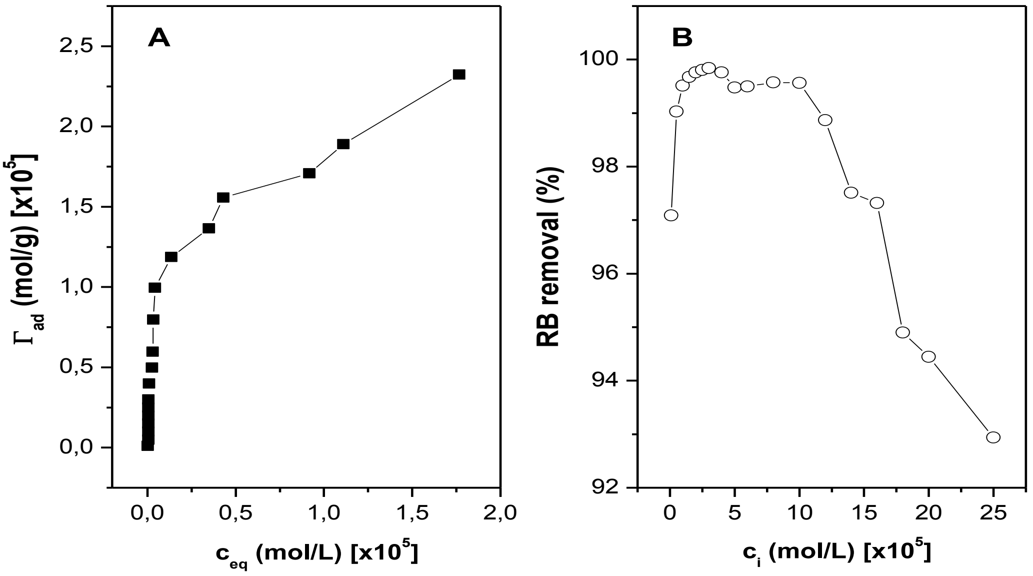


Fig. 2. Adsorption isotherm of RB onto NZ (A) and percent of RB removal by NZ as a function of the dye initial concentration (B). The adsorption experiments were performed at 30 ºC, pH = 2 and 24 h

The parameters obtained by the fit of the experimental data according to Freundlich and Langmuir isotherms are presented in table 2. As can be see the fits for the two isotherms are quite similar, although the correlation coefficient obtained from the Langmuir isotherm is slightly higher than that from the Freundlich isotherm. Based on the Langmuir adsorption constant, K_L, the standard free energy (ΔG^o) of the RB adsorption process was calculated ($\Delta G^o = -RT \ln K_L$). The adsorption process is spontaneous with ΔG^o = -31,82 kJ/mol. The values obtained for all the parameters are very similar to those reported by Wang and Zhu [19], which studied the adsorption of RB on Australian natural clinoptilolite.

TABLE 2. PARAMETERS FOR THE ADSORPTION ISOTHERM OF RHODAMINE B ONTO NZ

Langmuir isotherm			**Freundlich isotherm**		
Γ_{max}	**K_L**	**R^2**	**K_F (mol/g)**	**1/*n***	**R^2**
2,22 x 10^{-5}	3,6 x 10^{5}	0,968 6	5,68 x 10^{-4}	0.280	0,957 3

It is important to mention that the dimensions of the RB molecule are bigger than the largest clinoptilolite channel (channel A: 7,5 Å x 3,1 Å). Therefore, the molecule can't enter the zeolite channel system and the adsorption is essentially limited to the external solid surface. From the values of the maximum sorption capacity (Γ_{max}) and the external surface area per gram of adsorbent (S_{ext} = 20 m^2/g) the area occupied by an adsorbed dye molecule (A_s) can be obtained by the following equation:

$$A_s = \frac{10^{20} S_{ext}}{N_A \Gamma_{max}} \qquad (3)$$

N_A being the Avogadro's number. The obtained experimental value is A_s = 149 Å^2. If we assumes that the RB molecule is adsorbed on NZ with its polar group ($=NH^+-$) pointing to the adsorbent the theoretical area occupied by a molecule at the surface should be of 39,7 Å^2 [6]. Therefore, the degree of coverage of the NZ surface is around 0,27, indicating that it is not yet saturated with the dye, which is in good agreement with the not achievement of the plateau region in the isotherm.

Figure 3A shows the kinetic curves for RB adsorption onto NZ from aqueous solutions at different initial concentrations. In all cases there is an initial step in which the amount of adsorbed RB increases very quickly with time (about 93 % of RB is adsorbed in the first five minutes of interaction). After that, a transitional regime where the amount adsorbed slowly increases with time is observed. The plateau region is finally reached at 2, 6 and 12 h of contact for initial concentrations of 5, 10 and 20 x 10^{-5} mol/L, respectively. Farhade and Aziz [21], studied the adsorption of RB on a natural clinoptilolite and report a similar kinetic behavior at 25 °C. The authors reported an equilibration time of 200 min (≈ 3,3 h) for an initial concentration of 6 x 10^{-6} mol/L. Wang and Zhu [19] reported a much larger value (50 h) at 30 °C, but in this case, the initial RB concentration is not stated. The kinetics data were fitted in the whole time range employing the pseudo first and pseudo second order kinetic models, and the intraparticle diffusion model [8]. The obtained fitted parameters are presented in table 3.

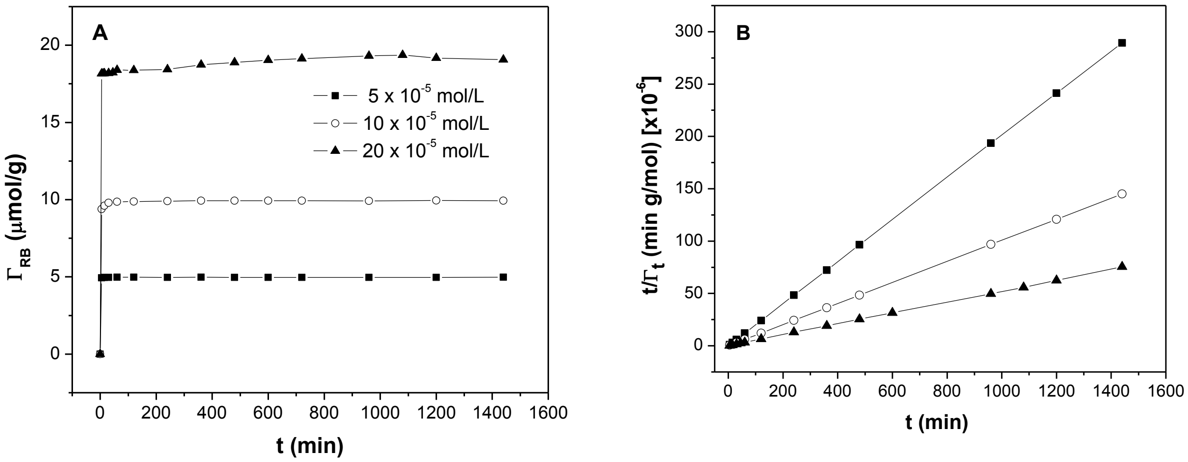


Fig. 3. Amount of RB adsorbed onto NZ from aqueous solution as a function of the time for different initial concentrations (A) and fitted of the pseudo second order model (B)

TABLE 3. KINETICS FITTED PARAMETERS FOR THE ADSORPTION OF RHODAMINE B ONTO NZ

c_i. (mol/L)	**Pseudo first order**			**Pseudo second order**			**Intraparticle**	
	Γ_{max} (μmol/g)	**k_1 (1/min)**	**R^2**	**Γ_{max} (μmol/g)**	**k_2 (mol/g min)**	**R^2**	**k_d (mol/g $min^{1/2}$)**	**R^2**
5 x 10^{-5}	0,05	10 x 10-	0,702	4,97	274 x 10^4	0,999	3,6 x 10^{-10}	0,316
10 x 10^{-5}	0,15	5 x 10^{-3}	0,941	9,94	18,7 x 10^4	0,999	94,2 x 10-	0,409
20 x 10^{-5}	1,24	2 x 10^{-3}	0,950	19,2	1,74 x 10^4	0,999	344 x 10^{-10}	0,915

Γ_t: amount of RB adsorbed at time t, Γ_{max}: amount of RB adsorbed at equilibrium, k_1, k_2 and k_d: rate constants for pseudo first order, pseudo second order and intraparticle diffusion adsorption, respectively.

The pseudo first order kinetic curves does not showed a straight line and the calculated Γ_{max} values were very different with respect to the experimental ones. Therefore, this kinetic model is not appropriate to describe the adsorption data. For the case of intraparticle diffusion model the curves showed two linear portions indicating that the dye adsorption takes place in two stages. The first one is usually attributed to external surface adsorption and the second one to the intraparticle diffusion process. The best fit of the experimental data was obtained for the pseudo second order kinetic model, with correlation coefficients close to the ideal value and with calculated Γ_{max} values very similar to the experimental ones (see fig. 3B and table 3). This suggests that the adsorption of RB onto NZ can be represented better by the pseudo second order model. In general, these results are coherent with those reported in the literature for the adsorption of different dyes on several solid adsorbents [19, 21, 29].

Characterization of zeolite-dye materials

The textural parameters of NZ and selected NZ-RB samples are presented in table 4. The specific surface area of NZ calculated using the BET method is 22 m^2/g, while the external surface area, according to the t-plot method, is about 13 m^2/g. All parameters of the zeolite-dye materials decrease due to the presence of the adsorbed rhodamine, indicating that the molecule partially blocks the entrance to the channels system of the zeolite. Such decrease is directly proportional to the amount of rhodamine adsorbed on the zeolitic surface.

TABLE 4. TEXTURAL PARAMETER FOR NZ AND NZ-RB SAMPLES

Sample	**BET surface area (m^2/g)**	**t-plot micropore area**	**t-plot ext. surface area (m^2/g)**	**t-plot micropore volume (cm^3/g)**
NZ	22	9,6	13,1	0,004 8
NZ-RB-0.5	11	4,5	6,5	0,002 2
NZ-RB-5	9	3,9	5,1	0,002 0
NZ-RB-15	9	2,7	6,3	0,001 3

Figure 4 shows the TG – DTG curves for RB, NZ, and NZ-RB sample with a loading of about 20 µmol/g. The thermogram of RB exhibits several stages of mass loss between 210 - 605 °C, which are related to different step of compound decomposition. The total mass loss in NZ, of about 12 %, occurs in two stages. The first loss of mass, at a minimum of 125 °C, is associated with desorption of physically adsorbed water. The second stage between about 300 - 750 °C is due to the release of the water molecules coordinated to the cations (that are progressively removed) and to dehydroxylation. The dye adsorption doesn’t significantly influence the thermal stability of the zeolite, as can be observed in the thermogram of the NZ-RB sample. Moreover, the dye decomposition peaks are not observed because the amount adsorbed on NZ is almost in the detection limit of the used equipment (about 1 % in weight).

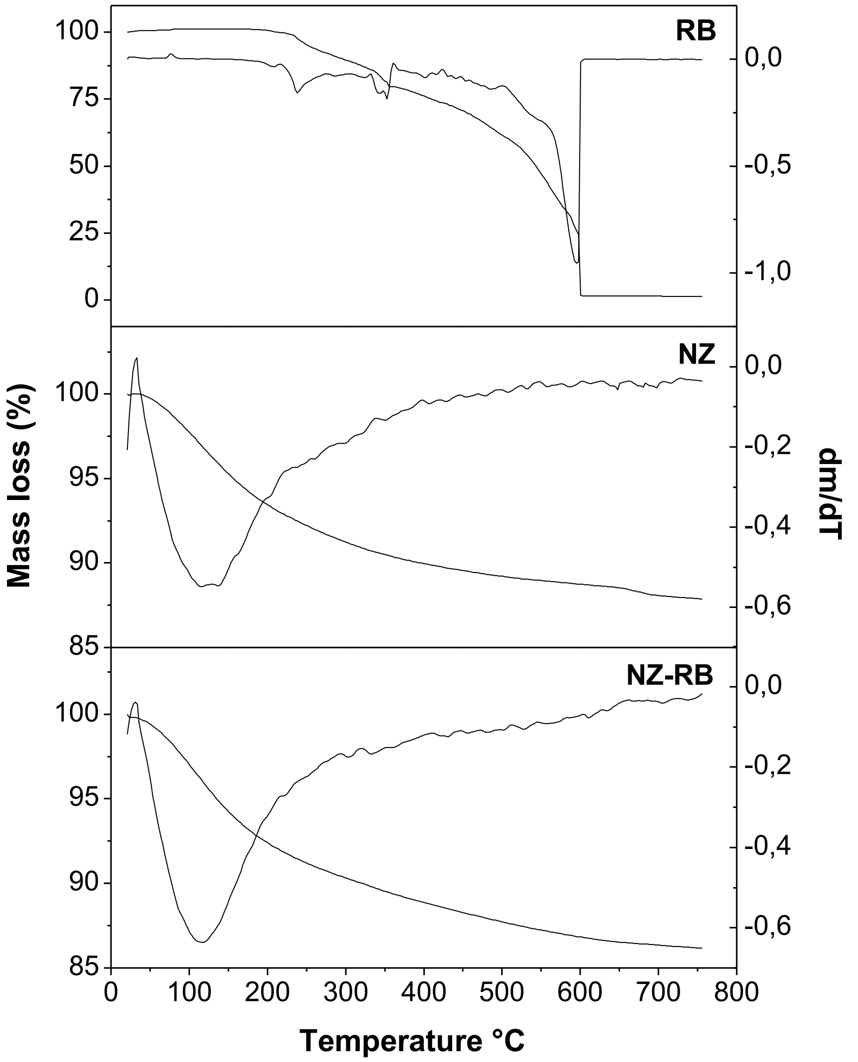
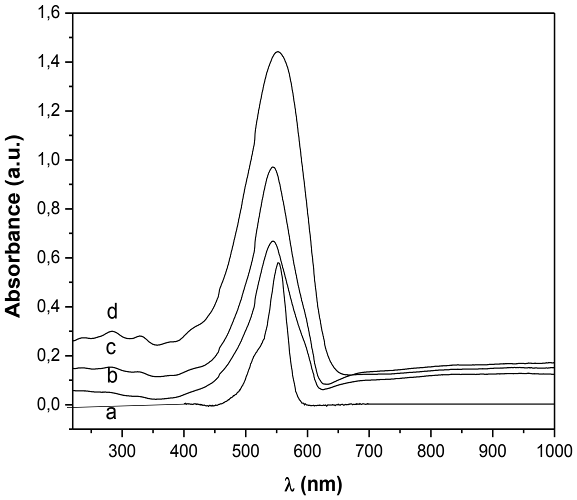


Fig. 4. TG – DTG curves for RB, NZ, and NZ-RB recorded at 10 °C/min

The UV-VIS spectrum of rhodamine B and the UV-VIS-DRS spectra of NZ-RB samples are shown in figure 5. The spectrum of RB in aqueous solution present two peaks at 522 and 554 nm, corresponding to H-dimers and monomeric species, respectively [30]. In the spectra of NZ-RB samples both bands can be observed, indicating that the dye is absorbed in its monomeric form and as aggregates. An increase in the absorbance of both peaks is observed as a function of the amount of dye adsorbed, although there is not a linear relationship. The deconvolution of the UV-VIS spectra (fig. 6) shows that in NZ-RB samples a new band with small intensity appears at around 590 nm, which could be assigned to J-dimers. The presence of J-dimers has been previously reported for RB and R3B adsorbed on different clays [29, 30]. In addition, a blue shift of the band at 554 nm in the spectra of NZ-RB samples of about 7 nm is observed, which could be due to the change in the local environment of the molecules.



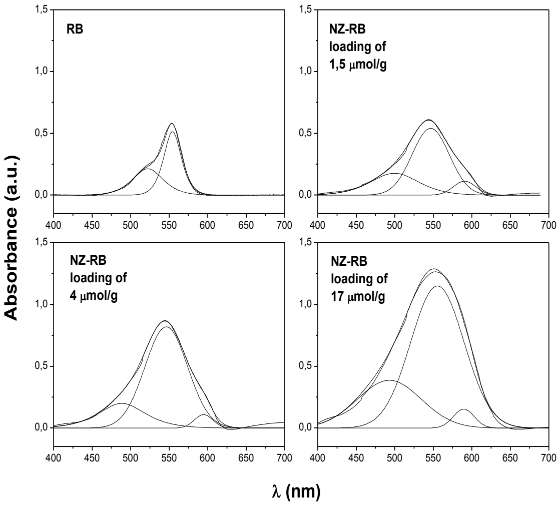


Fig. 5. UV-VIS spectrum of rhodamine B in aqueous solution (a) and UV–VIS diffuse reflectance spectra of: NZ-RB-1,5 (b), NZ-RB-4 (c) and NZ-RB-18 (d) samples

Fig. 6. Deconvolution of the UV-VIS and UV–VIS diffuse reflectance spectra of rhodamine B and NZ-RB samples

The fluorescence spectra of RB in aqueous solution and adsorbed onto NZ are presented in figure 7.

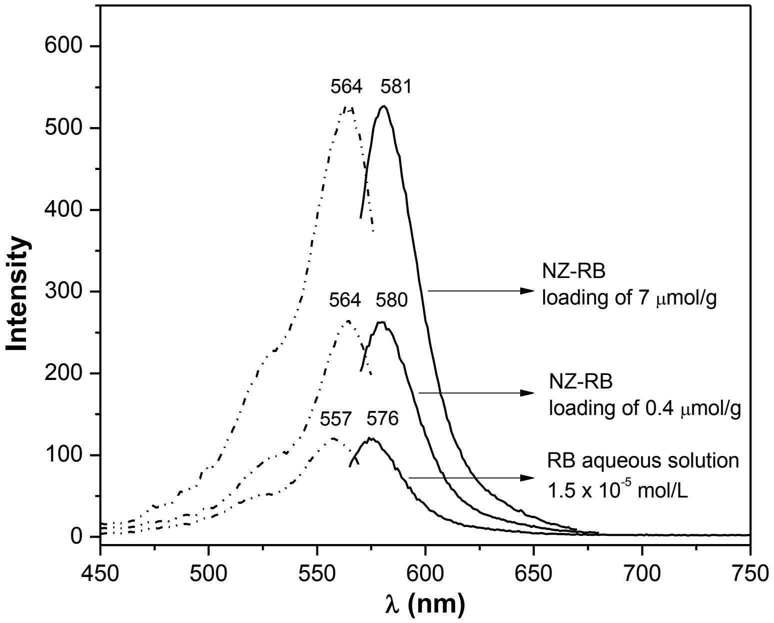


Fig. 7. Fluorescence spectra of rhodamine B in aqueous solution and adsorbed onto NZ. Dotted and continuous lines correspond to the excitation and emission spectra, respectively

It is interesting to note that the dye exhibits an increase in the fluorescence intensity when it is absorbed onto NZ. Such increase depends of the amount of dye adsorbed. This result is expected when no aggregates are formed in the zeolitic surface, because it is known that the presence of aggregates leads to fluorescence quenching. Thus, in our case, where monomers, and H- and J- dimers are present in the material, the increase in the fluorescence intensity could suggest the existence of host–guest interactions between NZ and the RB chromophore. Taking into account these facts NZ-RB samples could be good candidates for further applications such as optic and laser systems.

The Epi-fluorescence microscopy images and the 3-D reconstructed images of NZ-RB-0.5 and NZ-RB-20 are shown in figure 8. The images permit to confirm that the molecules of rhodamine B are adsorbed in the external surface of the zeolite. The distribution of the adsorbed RB is almost homogeneous. However, in NZ-RB-20 sample, with more dye loaded, dense zones of adsorbed dye can be observed.

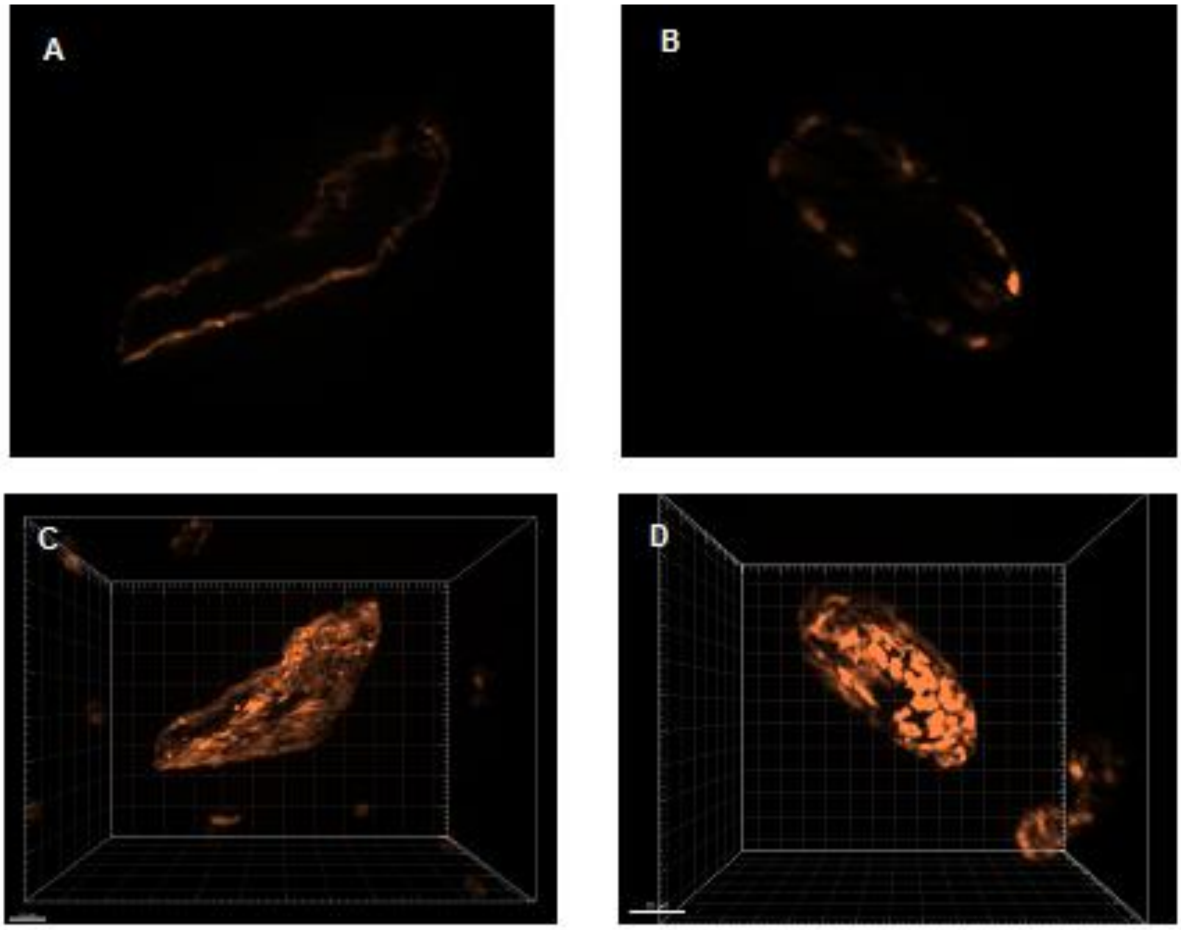


Fig. 8. Epi-fluorescence microscopy images and 3-D reconstructed images of NZ-RB-0.5 (A and C) and NZ-RB-20 (B and D), respectively

Conclusions

A Cuban natural clinoptilolite (NZ) was tested for the adsorption of the fluorescent dye rhodamine B. It was demonstrated that NZ has a great RB adsorption capacity, mainly at acid pH. The adsorption data was well fitted by the Langmuir isotherm, and kinetics of the adsorption process was better described by the pseudo second order model. More than 92 % of the RB in solution is captured by the zeolite in the range of concentrations studied, reaching only a maximum of 27 % of the material surface coverage. These facts suggests that NZ is a good candidate for the adsorption of the fluorescent dye rhodamine B, which constitutes an excellent result for environmental applications. The obtained zeolite-dye samples showed a good thermal stability and homogeneous distribution of RB on NZ surface. The dye exhibits an increase in fluorescence intensity when it is absorbed onto NZ, so NZ-RB samples could be good candidates for further applications such as sensors, optic and laser systems.

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