A useful organofunctionalized layered silicate for textile dye removal

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ABSTRACT

The octosilicate Na-RUB-18 has the ability to exchange its original sodium with cetyltrimethylammonium cations. This procedure leads to interlayer space expansion, with the aim of obtaining inorganic–organic nanostructured hybrids by chemical modification reactions. The silylating agent 3-trimethoxysilylpropylurea was attached to the inorganic layer using heterogeneous methodology. The new organofunctionalized material was characterized by elemental analysis, X-ray diffraction, ^{13}C and ^{29}Si nuclear magnetic resonances in the solid state, infrared spectroscopy, thermogravimetry and scanning electron microscopy. The amount of silylating agent immobilized on surface was 2.03 mmol g^{-1}, with a basal distance of 2.43 nm. Nuclear magnetic resonance of ^{13}C and ^{29}Si nuclei evidenced covalent bond formation between organosilyl and silanol groups at the surface. The new synthesized nanostructured layered material was able to remove the textile dye Reactive Black 5 from aqueous solution, followed through a batchwise process. The effects of stirring time, adsorbent dosage and pH on the adsorption capacity demonstrated that 150 min is enough to reach equilibrium at 298 ± 1 K at pH 3.0. Based on error function values the data were best fitted to fractional-order kinetic models and compared to pseudo-first-order, pseudo-second-order and chemisorption kinetic models. The equilibrium data were better fitted to the Sips isotherm models.

1. Introduction

Industrial activities are responsible for generating large volumes of hazardous species contaminating wastewater effluents [1]. Even more pronounced is the effluent contamination by colored rejects, which cause serious problems of environment pollution [2,3]. As a result, the interest in textile dye removal from aqueous solution has grown, as has the development of synthetic materials that could be used for this purpose [1–4]. These materials must have wide applicabilities, not only for discoloring different industrial wastewater, but also due to interesting structural aspects that lead to better results compared to natural and other commonly used sorbents [5,6].

Normally the sorption process was carried out by conventional ion exchange procedure [7]. The possibility of chemically modified different surfaces increases capability of dye sorption presented by those synthesized organofunctionalized materials, as previously assigned [2,4].

RUB-18 is a member of the hydrous layered silicate family, also composed of makatite, kanemite, kenyaite and magadiite [8]. With

the exception of RUB-18, these silicates were first discovered in nature. From the synthetic point of view this set of silicates is also synthesized in the laboratory in the sodic form. For example, $Na_8Si_{32}O_{64}(OH)_8 \cdot 32H_2O$ with a basal distance of 1.10 nm, with structural lamella composed of four rings connected by other five silicon atoms [9]. The [5^4] cage model was first investigated with this layered silicate. Makatite and kanemite also had their structures determined, but those for the other members of the family, magadiite and kenyaite, remain unknown [8,10]. These silicates present charge neutrality maintained through the hydrated sodium counter ion distributed inside the layered framework [8,9].

The silanol groups disposed on the layered surface of the RUB-18 structure enable silylating agents bonding, after prior exchange of sodium with cetyltrimethylammonium cations, with the objective to expand the interlayer cavity to obtain a greater organophillic character, favoring by this procedure covalent bond formation between the silylating agent and the layered surface [11]. Examples of chemical organofuncionalization of surfaces are conventional procedures used for synthesis of natural talc phyllosilicates and other layered materials [3,12]. On the other hand, the organofunctionalized materials can be obtained by different methodologies, such as the sol–gel process, solvent evaporation and conventional reflux methodology [13]. The procedure leads to the design of chosen molecules to be grafted to nanostructured materials that

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Nomenclature

a_{RP}	Redlich–Peterson constant $(mg\,dm^{-3})^{-g}$
C	constant related with the thickness of the boundary layer $(mg\,g^{-1})$.
C_f	dye concentration at the end of the adsorption $(mg\,dm^{-3})$
C_e	dye concentration at equilibrium $(mg\,dm^{-3})$
C_o	initial dye concentration put in contact with the adsorbent $(mg\,dm^{-3})$
g	dimensionless exponent of Redlich–Peterson equation
h_o	the initial sorption rate $(mg\,g^{-1}\,min^{-1})$ of the pseudo-second-order equation
k_{AV}	Avrami kinetic constant (min^{-1})
k_f	pseudo-first-order rate constant (min^{-1}).
K_F	the Freundlich constant related to adsorption capacity $[mg\,g^{-1}(mg\,dm^{-3})^{-1/n_F}]$.
k_{id}	intra-particle diffusion rate constant $(mg\,g^{-1}\,min^{-0.5})$
K_L	Langmuir affinity constant $(dm^3\,mg^{-1})$.
K_{RP}	Redlich–Peterson constant $(dm^3\,g^{-1})$
K_S	the Sips constant related to the affinity constant $((mg\,dm^{-3})^{-1/n_S})$
k_s	the pseudo-second-order rate constant $(g\,mg^{-1}\,min^{-1})$
m	mass of adsorbent (g)
n_{AV}	a fractional reaction order (Avrami) which can be related to the adsorption mechanism
n_F	dimensionless exponent of the Freundlich equation
n_S	dimensionless exponent of the Sips equation
q	amount of the dye absorbed by the adsorbent $(mg\,g^{-1})$
q_e	amount of adsorbate adsorbed at the equilibrium $(mg\,g^{-1})$
Q_{max}	the maximum adsorption capacity of the adsorbent $(mg\,g^{-1})$
q_t	amount of adsorbate adsorbed at time t $(mg\,g^{-1})$
t	time of contact (h)
V	volume of dye put in contact with the adsorbent (dm^3)

Greek letters

α	the initial adsorption rate $(mg\,g^{-1}\,min^{-1})$ of the Elovich equation
β	Elovich constant related to the extent of surface coverage and also to the activation energy involved in chemisorption $(g\,mg^{-1})$

present established functionalities and different practical applications.

The silicate RUB-18 presents a regular layered surface and high capacity for organofunctionalization reactions. Recently, the interlayer space of RUB-18 has been modified by different methoxy and chlorosilanes and the synthesized inorganic–organic nanostructured materials were successfully used for removal of divalent cation and heavy metal from aqueous solution [13,14].

The present investigation deals with a synthesized organofunctionalized RUB-18 for use as a sorbent for Reactive Black 5 textile dye removal. Consequently, the natural and chemical aspects related to the silylating agent grafted on the layers are presented, together with the application of this material as sorbent for dye removal from aqueous effluents.

2. Experimental

2.1. Synthesis of Na-RUB-18

The hydrated sodium silicate RUB-18 was synthesized by a hydrothermal procedure [14]. Briefly, suspension of silica gel (Fluka) and a sodium hydroxide (Nuclear) solution in the molar ratio of SiO_2:0.5NaOH:7.0H$_2$O, that corresponds to 25.0 g of amorphous silica gel, 8.32 g of sodium hydroxide and 53 cm^3 of deionised water was transferred to a Teflon-lined autoclave with autogeneous pressure and treated at 378 K for 9 days. The as-synthesized Na-RUB-18 was filtered, washed with deionised water until neutral pH and dried at 323 K for 24 h [14–16].

2.2. Synthesis of CTA-RUB-18

A sample of 2.0 g of Na-RUB-18 was dispersed in 200 cm^3 of 0.10 mol dm^{-3} of an aqueous solution of cetyltrimethylammonium bromide (CTAB). The mixture was stirred for 3 days at room temperature. The procedure was repeated 3 times until completing the intercalation process, which was followed by X-ray diffraction. Finally, the solid obtained (CTA-RUB-18) was centrifuged, washed with ethanol and dried at 323 K for 24 h [14,16].

2.3. Organofunctionalization

A sample of 2.0 g of the as-synthesized CTA-RUB-18 was suspended in 100 cm^3 of toluene under nitrogen flow at 343 K for 1 h. Then, 2.0 cm^3 of the silylating agent 3-trimethoxysilylpropylurea (TPU, $(CH_3O)_3Si(CH_2)_3NHCONH_2$) was added to the reaction medium, which remained for another 96 h. The obtained product (C-RUB-U) was filtered, washed with ethanol (Synth), dried under vacuum at 343 K for 24 h [4,14,15].

2.4. Characterization

Carbon, nitrogen and hydrogen amounts were determined on a Perkin-Elmer 2400 Series II microelemental analyzer and two independent determinations were performed. X-ray diffraction patterns were collected on a Shimadzu model XRD 7000 diffractometer, varying 2θ from 1.4 to 50°, with CuKα radiation (corresponding to 1.54 nm). Thermogravimetric curves were obtained on a TA Instruments 5100, with heating rate of 0.167 K s^{-1}, under 1.67 cm^3 s^{-1} of argon flow, from room temperature to 1273 K, and initial mass of at least 10.0 mg of the solid.

Nuclear magnetic resonance spectra were recorded with a Bruker AC300/P solid state high-resolution spectrometer, by cross-polarization and magic angle spinning (CP-MAS). The frequencies were 79.4 and 100.6 MHz, with rotational frequencies of 10 kHz and delay times of 6.0 ms and 8.0 ms for ^{29}Si and ^{13}C nuclei, respectively. Chemical shifts were referenced to tetramethylsilane. Infrared spectra were performed on a Bomem model MB FTIR spectrophotometer, with KBr pellets in the 4000–400 cm^{-1} region and resolution scan of 4 cm^{-1}, accumulating 32 scans. The micrographs were measured on a JEOL 6360-LV scanning electron microscope. The samples were first suspended in acetone and the micrograph was obtained after sputter coating a thin conducting layer of gold for 400 s.

2.5. Solutions and reagents

Deionised water was used throughout the experiments for all solution preparations.

The Reactive Black 5 textile dye (RB-5), (C.I. 20505; $C_{26}H_{21}N_5O_{19}S_6Na_4$, 991.82 g mol^{-1}, λ_{max} = 590 nm, as shown in Scheme 1) was obtained from Sigma with a dye content of 55%.
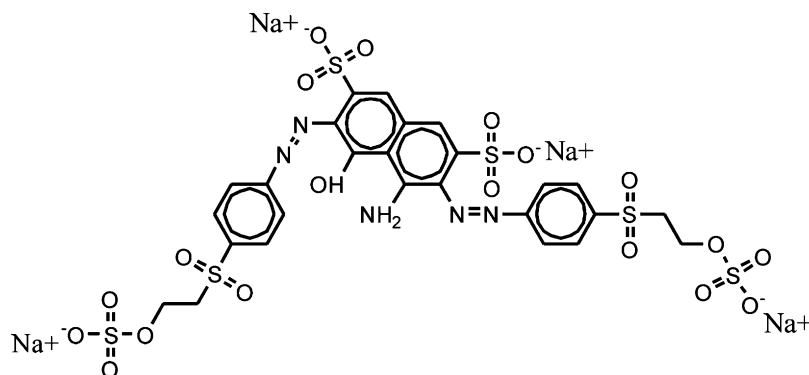
Scheme 1. Structural formula of Reactive Black 5 dye (RB-5).

It was used without further purification. The dye has two sulfonate groups and another two sulfato-ethyl-sulfone group, with negative charges even in highly acidic solutions, due to their pK_a values are lower than zero [17].

The stock solution was prepared by dissolving accurately weighed dye in distilled water at a concentration of $5000\,mg\,dm^{-3}$. The working solutions were obtained by diluting the dye stock solution to the required concentrations. In order to adjust the pH of the solutions, $0.10\,mol\,dm^{-3}$ sodium hydroxide or hydrochloric acid solutions were used, using a Hanna (HI 255) pHmeter.

2.6. Batchwise adsorption procedure

The adsorption studies to evaluate the C-RUB-U for RB-5 dye removal from aqueous solutions were carried-out in triplicate using a batch adsorption procedure. For these experiments, fixed amounts of adsorbent varying from 20.0 to 200.0 mg were suspended in a series of $50\,cm^3$ glass flasks containing $20.0\,cm^3$ of dye solution with concentrations that varied from 2.00 to $1000.0\,mg\,dm^{-3}$. These suspensions were stirred for suitable times from 5 to 360 min. The isotherms clearly demonstrated that a well-established plateau was obtained and the equilibrium studies determined in these optimized conditions were 150 min at $298 \pm 1\,K$, with the initial pH of the dye solutions ranging from 2.5 to 8.5. Subsequently, in order to separate the adsorbents from the aqueous solutions, the flasks were centrifuged at 3600 rpm for 10 min, as already described in other publications [17,18], and aliquots of $1.0–10.0\,cm^3$ of the supernatant were properly diluted. The final concentrations of the dye remaining in solution were determined by visible spectrophotometry, using a Femto spectrophotometer provided with 1.0 cm path length optical-glass cells. Absorbance measurements were made at the maximum wavelength of the dye, 590 nm, and the detection limit using the spectrophotometric method, determined according to IUPAC [19], was $0.14\,mg\,dm^{-3}$. The amount of the dye uptake and percentage of dye removal by the adsorbent were calculated by applying Eqs. (1) and (2), respectively:

$$q = \frac{(C_o - C_f)}{m} V \tag{1}$$

$$\%Removal = 100\frac{(C_o - C_f)}{C_o} \tag{2}$$

where q is the amount of dye uptake by the adsorbent ($mg\,g^{-1}$); C_o is the initial RB-5 concentration in contact with the adsorbent ($mg\,dm^{-3}$), C_f is the dye concentration ($mg\,dm^{-3}$) after the batch adsorption procedure, V is the volume of dye solution (dm^3) in contact with the adsorbent and m is the mass (g) of adsorbent.

2.7. Kinetic and equilibrium models

The kinetic equations corresponding to the Avrami, pseudo-first-order, pseudo-second-order, and Elovich models are given in Table 1 [20]. The isotherm equations corresponding to the Langmuir, Freundlich, and Sips models are listed in Table 2 [21].

2.8. Statistical evaluation of the kinetic and isotherm parameters

The kinetic and equilibrium models were fitted by employing a nonlinear method, with successive interactions calculated by the method of Levenberg–Marquardt and also interactions calculated by the Simplex method, using the nonlinear fitting facilities of the software Microcal Origin 7.0. In addition, the models were also evaluated by an error function, which measures the differences in the amount of dye uptake by the adsorbent predicted by the models and the actual q measured experimentally [22]

$$F_{error} = \sqrt{\left(\frac{1}{n-p}\right) \sum_{i}^{n} (q_{i,exp} - q_{i,model})^2} \tag{3}$$

where $q_{i,exp}$ is the value of q measured experimentally, $q_{i,model}$ is the value of q predicted by the fitted model, n is the number of experiments performed, and p is the number of parameter of the fitted model.

Table 1
Kinetic adsorption models.

Kinetic model	Nonlinear equation
Avrami	$q_t = q_e\{1 - \exp[-(k_{AV}t)]^{n_{AV}}\}$
Pseudo-first-order	$q_t = q_e[1 - \exp(-k_f t)]$
Pseudo-second-order	$q_t = \frac{k_s q_e^2 t}{1 + q_e k_s t}$
	$h_o = k_s q_e^2$
	Initial sorption rate
Elovich	$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t)$

Table 2
Isotherm models.

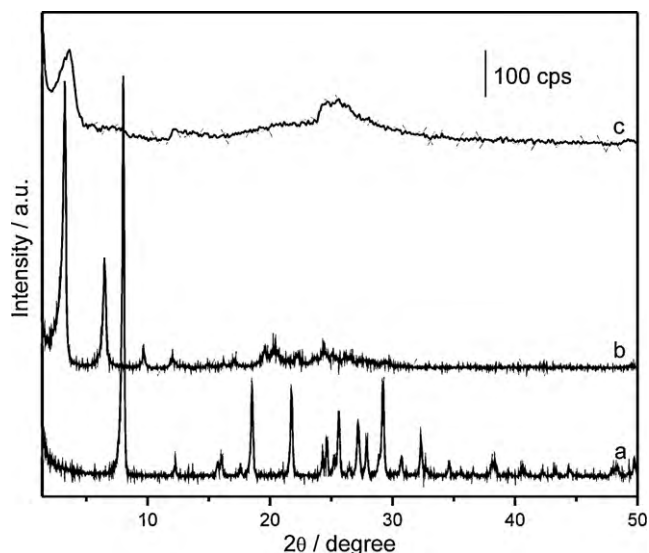| Isotherm model	Equation
Langmuir	$q_e = \frac{Q_{max}K_L C_e}{1 + K_L C_e}$
Freundlich	$q_e = K_F C_e^{1/n_F}$
Sips	$q_e = \frac{Q_{max}K_S C_e^{1/n_S}}{1 + K_S C_e^{1/n_S}}$

Fig. 1. X-ray diffraction patterns of Na-RUB-18 (a), CTA-RUB-18 (b) and of the organomodified C-RUB-U (c) materials.

3. Results and discussion

3.1. Sorbent characterization

X-ray diffraction pattern of the Na-RUB-18, intercalated CTA-RUB-18 and organofunctionalized C-RUB-U compounds are shown in Fig. 1. As observed at the curve a, Na-RUB-18 shows lamellar domains revealed by peaks for 2θ at 8.1 and 16.1°, related to the diffraction of the [0 0 1] and [0 0 2] planes of the solid surface, respectively [9,14]. The first peak is attributed to the basal distance of 1.09 nm and after exchanging the interlayered sodium ions by the cetyltrimethylammonium cations the basal distance increased 2.70 nm, 2θ being 3.3°, as expected, favoring the step of organofunctionalization [12,14]. The attachment of the silylating agent N-trimethoxysilylpropylurea to the layered RUB-18 surface causes a decrease of the precursor silicate basal distance, from 2.70 to 2.43 nm, easily viewed by the shift in the d_{001} reflection to greater 2θ value at 3.6°, showing also that the intercalated cation was removed after the attachment [14]. Covalent bond formation between silanol groups on the layered surface and the silylating agent in the organofunctionalization process, disposes attached pendant chains that could be protonated in aqueous solutions, adding potential capability for dye sorption [2]. The elemental analysis results for synthesized modified material gave: C, 9.84%; H, 2.12%; N, 5.68%, with the immobilized amount of pendant organic groups being 2.03 mmol g^{-1}, based on the amount of nitrogen obtained. This result reflects the amount of anchored organic groups able to interact with the RB-5 textile dye. The result obtained by elemental analysis is very near from that obtained through thermogravimetry, that gave an amount of 2.09 mmol g^{-1} of organic groups, which decomposed upon heating the sample. The agreement between elemental analysis and thermogravimetry shows a well behaved system [15].

Through ^{29}Si CP-MAS NMR it is possible to determine the connectivity of the layers [23]. The spectrum obtained for the Na-RUB-18 shows two signals, at −99.9 and −111.1 ppm, from the units Q^3, (SiO)$_3$Si–O$^-$, and Q^4, (SiO)$_4$Si, respectively, due to silanol and siloxane groups on the structure of the layered silicate, as shown in Fig. 2A (a). For the intercalated form CTA-RUB-18, the spectrum in Fig. 2A (b) gave the same set of signals, with little displacement to −101.4 and −112.3 ppm, due to Q^3 and Q^4 groups, respectively.
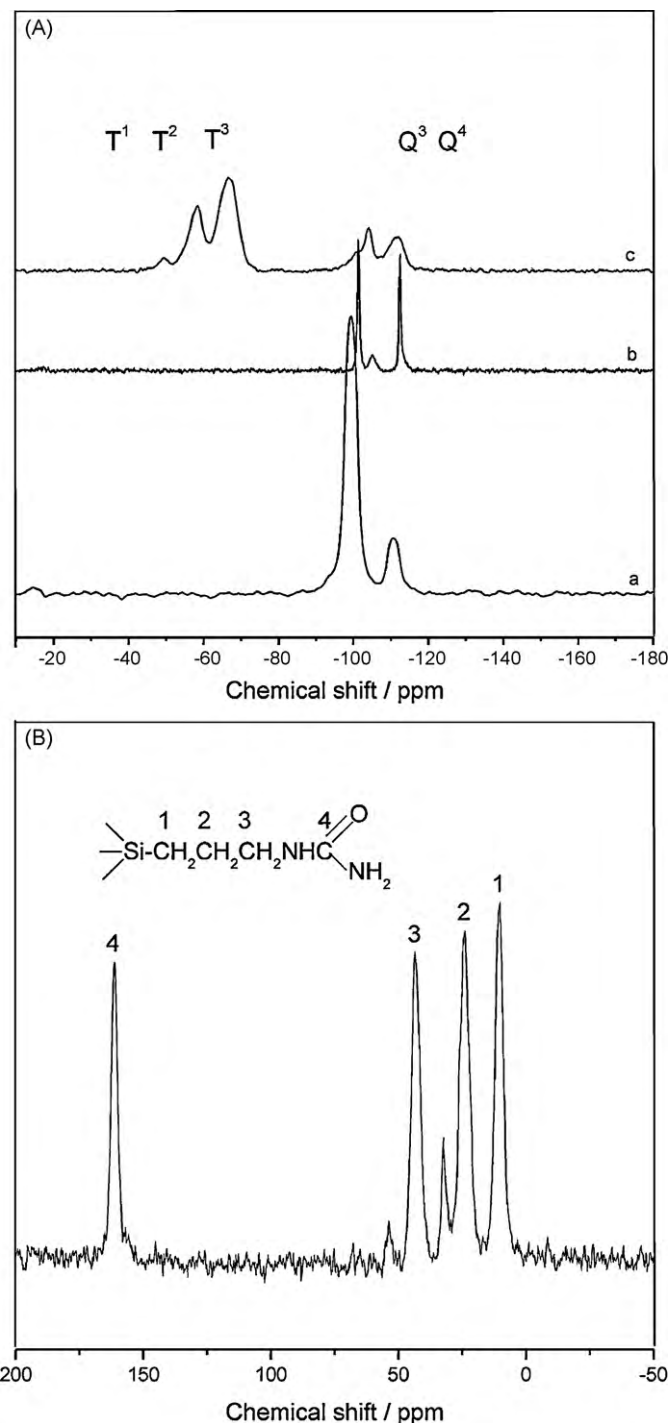

Fig. 2. (A) ^{29}Si MAS NMR of Na-RUB-18 (a), CTA-RUB-18 (b), C-RUB-U (c) and (B) ^{13}C MAS NMR of C-RUB-U materials.

The signal between at −104.8 ppm may occur when two forms of intercalation changes silicon environment [9,14].

The spectrum of the organofunctionalized inorganic–organic hybrid, as shown in Fig. 2A (c), shows signals from Q^3 and Q^4 groups at −104.2 and −111.7 ppm, respectively. The reduction of the Q^3 signal intensity was observed together with an increase in the signal intensity related to the Q^4 signal, confirming the reaction of the organic molecule with the silanol groups of the silicate surface, being converted to Q^4 sites [13]. In addition, upon covalent bond formation, three new signals are related to T^1, T^2 and T^3 environments, at −49.4, −58.3 and −66.6, respectively. Those
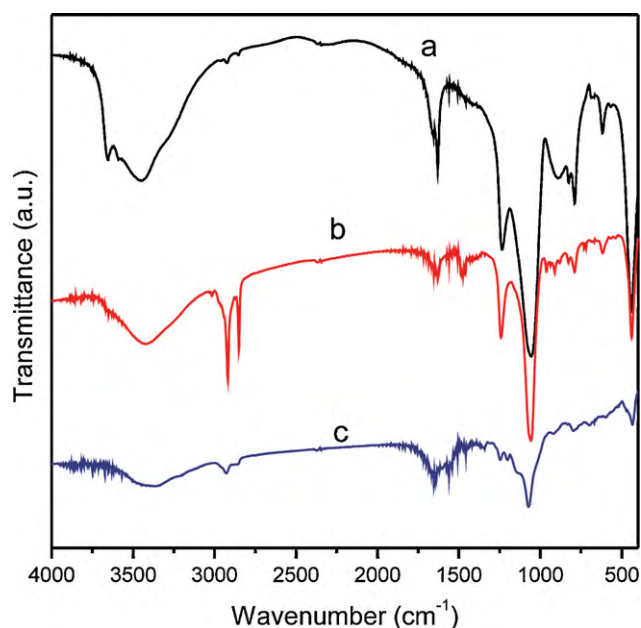
Fig. 3. FTIR spectra of Na-RUB-18 (a), CTA-RUB-18 (b) and C-RUB-U (c).

signals indicate different attachments, since T^1 corresponds to $[Si(OSi)(OH)_2R]$ to T^2 $[Si(OSi)_2(OH)R]$ and T^3 to $[Si(OSi)_3R]$, being R an organic chain [2,14,24].

^{13}C CP-MAS NMR spectrum of C-RUB-U material is shown in Fig. 2B, with the inserted structure of the organic chain covalently bonded to the inorganic framework [25]. The spectrum confirms the presence of the carbon from the silylating agent anchored to the silicate layer, and also that the surfactant was completely removed during the washing process. The signals from the organic pendant groups were seen at 12.4, 23.8, 43.9 and 161.5 ppm, in agreement with the attributions, for carbon (1) attached to the silicate sheet and chain intermediate carbons (2) and (3), with carbon (4) corresponding to the functional group, respectively.

The infrared spectrum of the Na-RUB-18 layered silicate shows the expected bands of the physisorbed water molecules on the inorganic material, represented by $\nu(OH)$ stretching frequency at 3650 cm^{-1} and the $\delta(OH)$ deformation band near 1630 cm^{-1} (see Fig. 3a). The band that appeared at 3650 cm^{-1} is also attributed to available silanol groups on the surface. The bands at the interval of 1000–500 cm^{-1} are due to frequency $\nu(Si–O)$ vibrations, from the inorganic framework. Absorption bands at 797 and 670 cm^{-1} are related to the symmetric stretching $\nu(SiO)$ of Si–O–Si groups [2]. The intercalated compound infrared spectrum shows the same bands related to the inorganic structure of the layer, with new bands detected at 2920 and 2855 cm^{-1}, associated with symmetric and asymmetric stretching $\nu(CH_2)$ respectively, and at 1474 cm^{-1} for the symmetric deformation $\delta(CH_2)$ vibrations for the intercalated organic cation $[C_{16}H_{33}N(CH_3)_3]^+$ [13,16] (see Fig. 3b). The organically modified RUB-18 structure presented bands at 2967 and at 1620 cm^{-1}, due to $\nu(C–H)$ stretching and $\delta(NH)$ deformation vibrations, respectively, and the band at 1650 cm^{-1} is attributed to $\nu(C=O)$ carbonyl stretching vibration, from the silylating agent attachment at the surface [2,14,15] (see Fig. 3c).

The scanning electron microscopy of the as-synthesized samples of CTA-RUB-18 and of the organofunctionalized C-RUB-U are shown in Fig. 4. The morphologies are similar, showing that the particles were organized forming plates typical for a layered structure [8].

3.2. Effects of acidity on adsorption

One of the most important factors in adsorption studies is the effect of the acidity of the medium [26]. Different species being adsorbed on diverse adsorbents will present divergent ranges of suitable pH regions for adsorption. The effects of initial pH on RB-5 dye adsorption capacity using C-RUB-U adsorbent was evaluated within the pH range from 2.5 to 8.5, as shown in Fig. 5A. The amount of dye adsorbed (q) was constant in the pH range from 2.5 to 3.0. From pH 3.0 to 4.0 the percentages of RB-5 dye removal decreased by 7%. With values ranging from 4.5 to 6.0, the percentages were practically constant. From pH 6.0 to 8.5, the percentages decreased on the order of 32%. Based on the present data, the initial pH of all adsorbate solutions were kept at 3.0.

The major adsorption capacity of C-RUB-U adsorbent for RB-5 adsorption occurs at pH 2.5–3.0, because at this pH range, the amino groups of the adsorbent are protonated, facilitating the adsorption of the negative charged dye (see Scheme 2).

3.3. Adsorbent mass

The investigation of the mass of adsorbent for dye removal from aqueous solution was carried out using adsorbent masses ranging from 20.0 to 200.0 mg, by fixing the initial concentration and volume of RB-5 solutions at 60.0 mg dm^{-3} and 20.0 cm^3, respectively. The highest amount of dye removal was attained for adsorbent masses of at least 50.0 mg of adsorbent, as shown in Fig. 5B (at left). For adsorbent masses higher than these values, the dye removal remained almost constant. The increase in the percentage of dye removal with adsorbent mass can be attributed to increases in
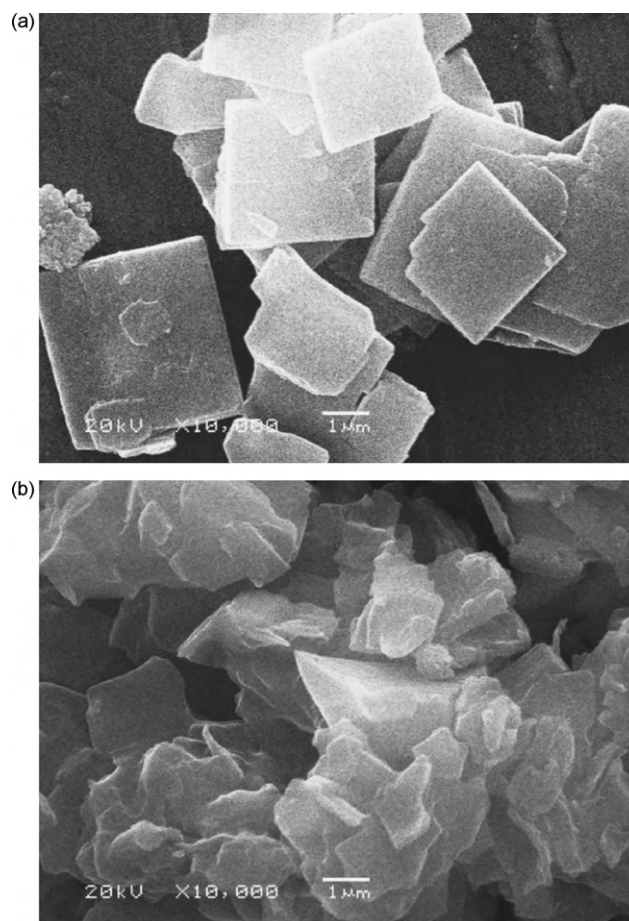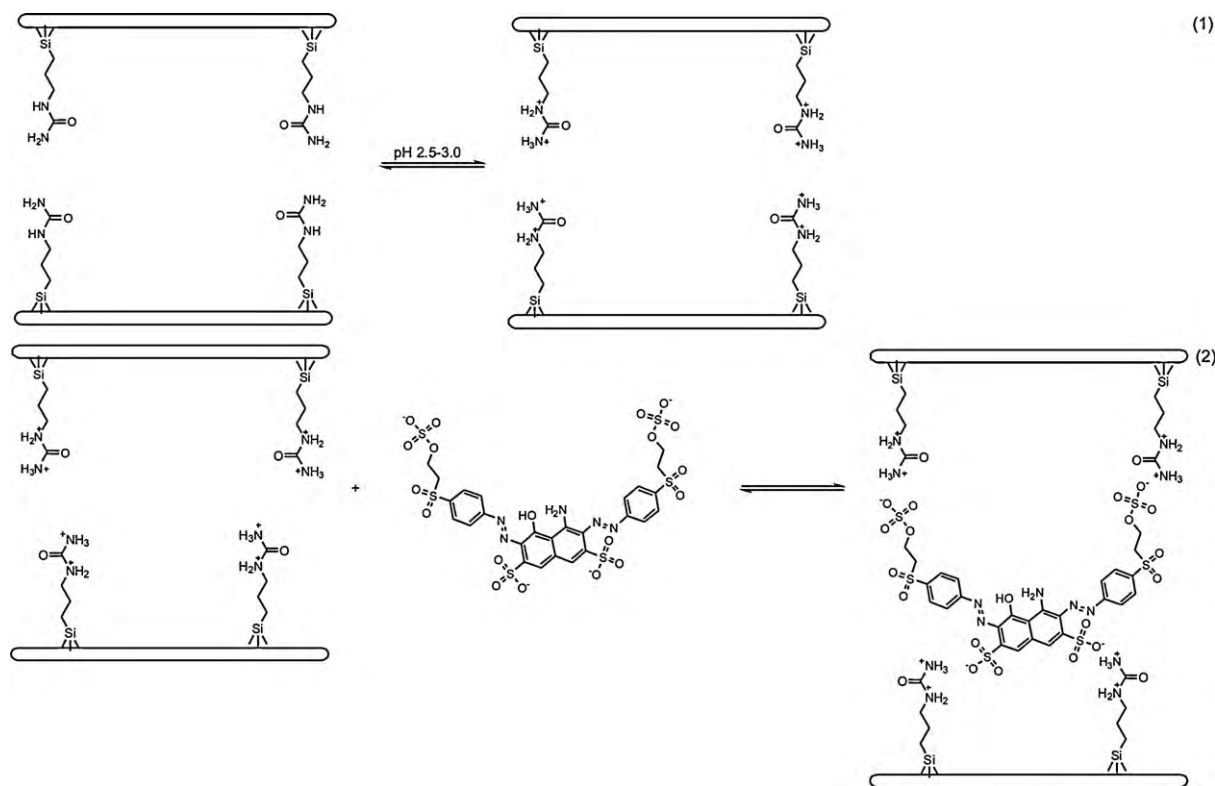

Fig. 4. Scanning electron microscopy of CTA-RUB-18 (a) and C-RUB-U (b) samples.

Scheme 2. Mechanism of adsorption of RB-5 by C-RUB-U adsorbent.

the adsorbent surface areas, augmenting the number of adsorption sites available for adsorption [4,5,18]. On the other hand, the increase in the adsorbent mass promotes a remarkable decrease in the amount of dye uptake per gram of adsorbent (q), as shown in Fig. 5B (at right), an effect that can be mathematically explained by combining Eqs. (1) and (2):

$$q = \frac{\%\text{Removal} \cdot C_0 \cdot V}{100m} \tag{4}$$

As observed from Eq. (4), the amount of dye uptake (q) and the mass of adsorbent (m) are inversely proportional. For a fixed dye percent removal, an increase of adsorbent mass leads to a decrease in q values, since the volume (V) and initial dye concentrations (C_0) are always fixed. These values clearly indicate that the adsorbent mass must be fixed at 50.0 mg, which corresponds to the minimum amount of adsorbent that leads to constant dye removal.

3.4. Kinetic studies

Studies of adsorption kinetics are an important feature to be considered in aqueous effluent treatments as they provide valuable information on the mechanism of adsorption processes [20]. In attempting to describe RB-5 dye adsorption by the adsorbent, four kinetic models were tried, as shown in Fig. 6A and B. The kinetic parameters for the models are listed in Table 3. Based on the F_{error} values, it was observed that the Avrami the Avrami model provides the best fit to the data. The pseudo-first-order, pseudo-second-order and chemisorption kinetic models presented F_{error} values at least 3.7 times higher than the Avrami fractional kinetic model.

Additionally, it was verified that the q_e values found in the fractional-order were in good agreement with the experimental data (see Table 3). For the pseudo-first-order, pseudo-second-order and chemisorption models, the q_e fitted values were not so coincident with the q_e experimental value. This result indicates that

the fractional-order kinetic model better explains the adsorption process of RB-5 uptake by C-RUB-U adsorbent.

Analyzing the values of the kinetic parameters presented in Table 3 indicates that the k_{AV} values showed a variation of 5.8%, when the initial concentration of the adsorbate increased from 60.0 to 120.0 mg dm^{-3}. On the other hand, the percentage of variation of k_S was 68.1%, when the initial concentration levels of the RB-

Table 3
Kinetic parameters for RB-5 removal using C-RUB-U as adsorbent. Conditions: temperature 298 K; pH 3.0; adsorbent mass: 50.0 mg.

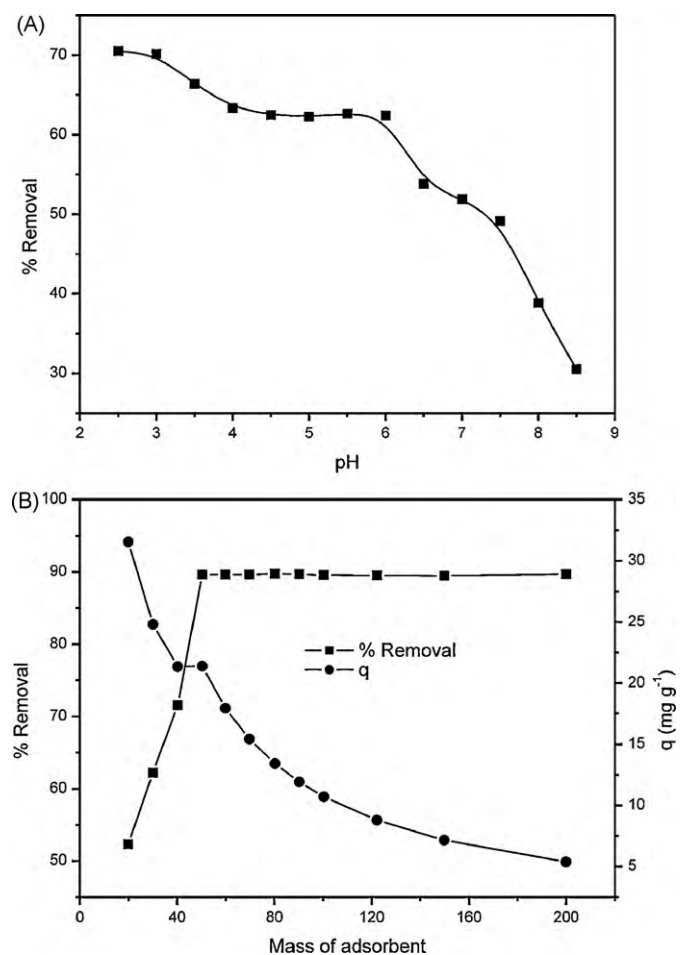|	C_0 (mg dm^{-3})	
	60.0	120.0
q_e experimental (mg g^{-1})	24.25	44.85
Fractional order		
k_{AV} (min^{-1})	0.01898	0.02008
q_e (mg g^{-1})	24.33	44.91
n_{AV}	0.8876	0.8738
R^2 adjusted	0.9998	0.9998
F_{error}	0.1139	0.2241
Pseudo-first-order		
k_f (min^{-1})	0.02047	0.02182
q_e (mg g^{-1})	23.78	43.82
R^2 adjusted	0.9975	0.9968
F_{error}	0.4200	0.8677
Pseudo-second-order		
k_s (g mg^{-1} min^{-1})	7.900×10^{-4}	4.700×10^{-4}
q_e (mg g^{-1})	28.29	51.72
h_0 (mg g^{-1} min^{-1})	0.6321	1.257
R^2 adjusted	0.9968	0.9971
F_{error}	0.4764	0.8255
Elovich chemisorption		
α (mg g^{-1} min^{-1})	1.488	2.942
β (g mg^{-1})	0.1734	0.09513
R^2 adjusted	0.9817	0.9825
F_{error}	1.132	2.208

Fig. 5. (A) Effect of pH on the adsorption. (B) Effect of mass of adsorbent on the percentage removal and amount of RB-5 dye adsorbed. Initial RB-5 concentration was 40.0 and 60.0 mg dm^{-3}, for Fig. 4A and B, respectively.

5 dye were increased from 60.0 to 120.0 mg dm^{-3}. Therefore, the fractional kinetic model provides a constant rate parameter which is much better for comparison of different kinetic constants, using several adsorbates and adsorbents, as already observed in other publications [2,4,5,17,20,21,27,28].

3.5. Equilibrium studies

The adsorption isotherm describes the amount of adsorbate uptake by the adsorbent and the adsorbate concentration that should remain in solution [21]. Therefore, many equations for analyzing experimental adsorption equilibrium data are available. The equation parameters of these equilibrium models often provide some insight into the adsorption mechanism, the surface properties and the affinity of the adsorbent. For this purpose the Langmuir [21], Freundlich [21], and Sips [29] isotherm models were assayed.

The isotherms of RB-5 adsorption on C-RUB-U adsorbent were obtained, by using the best experimental conditions, as shown in Fig. 7, and the data of the fitted models are presented in Table 4. Based on F_{error}, the equilibrium data was well fitted by Sips isotherm model when using this adsorbent for sorption of this dye. On the other hand, the Langmuir and Freundlich models failed to fit the isotherm curve, as shown by the low adjusted R^2 as well as high F_{error} values, indicating that for this specific case the Langmuir and Freundlich isotherm models were not suitable fitted. The lower the error function (F_{error}) is, the smaller will be the difference of the q calculated by the model from the experimentally measured
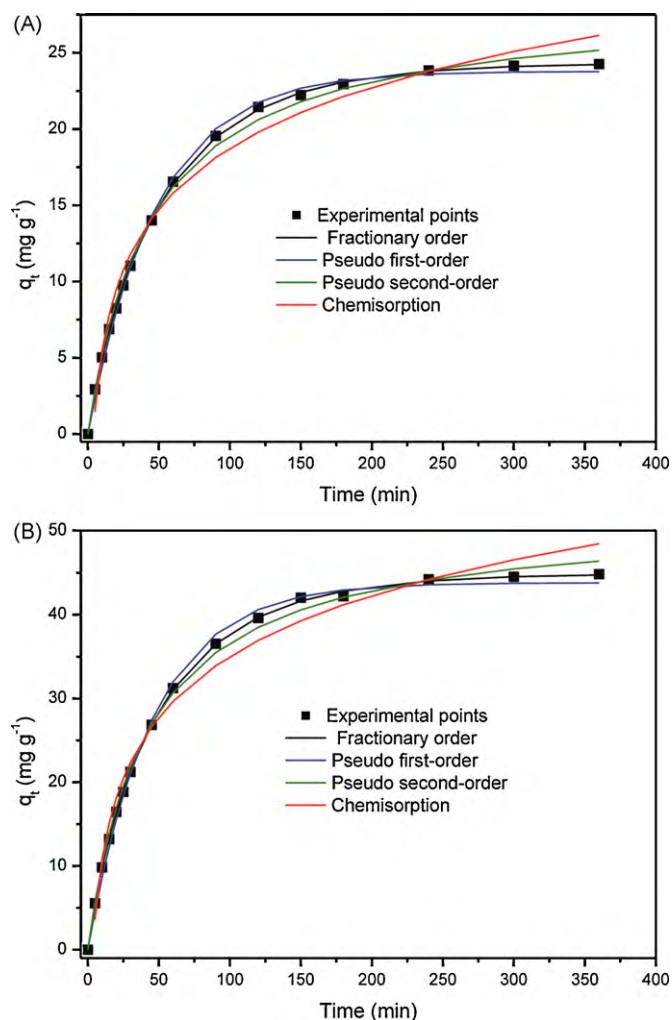

Fig. 6. Kinetic curves. (A) 60.0 mg dm^{-3}, (B) 120.0 mg dm^{-3}. Conditions: temperature 298 K; pH 3.0; mass of adsorbent 50.0 mg.
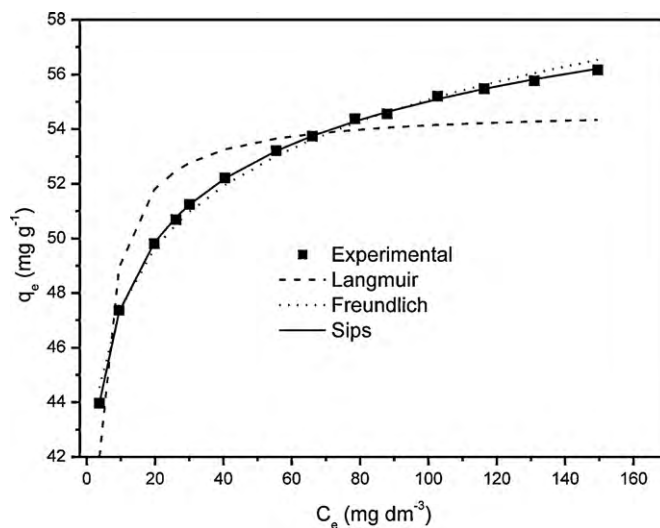

Fig. 7. Isotherm of adsorption. Conditions: temperature 298 K; pH 3.0; mass of adsorbent 50.0 mg, time of contact 300 min.

Table 4
Isotherm parameters for RB-5 adsorption, using C-RUB-U as adsorbent. Conditions: temperature 298 ± 1 K, contact time 300 min, pH 3.0 and mass of adsorbent 50.0 mg.

	C-RUB-U
Langmuir	
Q_{max} (mg g^{-1})	54.75
K_L (dm^3 mg^{-1})	0.8833
R^2 adjusted	0.8271
F_{error}	1.465
Freundlich	
K_F (mg g^{-1}(mg dm^{-3})$^{-1/n_F}$)	40.91
n_F	15.49
R^2 adjusted	0.9943
F_{error}	0.2656
Sips	
Q_{max} (mg g^{-1})	76.77
K_S ((mg dm^{-3})$^{-1/n_S}$)	1.040
n_S	5.181
R^2 adjusted	0.9997
F_{error}	0.06109

q [20–22]. Only analysis of R^2 values for the establishment of a given model is not enough, the use of the error function that evaluates the differences associated with each individual point fitted by the model, is also necessary [20–22].

Taking into account the Sips isotherm, the maximum amount of dye uptake was 76.77 mg g^{-1}, which corresponds to 0.0774 mmol g^{-1}. From the point of view of the exchange process at the solid/liquid interface, the RB-5 dye has negative sulfonate and sulfate-ethyl-sulfonate groups to ionically interact with the protonated nitrogens attached to the pendant chain covalently grafted on the silicate layer, as shown in Scheme 2. This interactive process is favored at pH < 3, as shown in Fig. 5A, when the basic nitrogen atoms are easily protonated to acquire a positive charge. In general for the adsorption process, the degree of adsorption depends both on the active sites of the adsorbent and the adsorbate properties. The results obtained suggest that the textile dye uses more than one basic center of the grafted trimethoxysilylpropylurea molecule, during the interactive process [30], as might be expected for a favorable adjustment of its size inside the pores of the adsorbent to counteract the opposing charges. When saturated an amount of 2.03 mmol g^{-1} is retained.

4. Conclusion

The synthesized crystalline layered silicic compound intercalated with surfactant, CTA-RUB-18, demonstrated efficiency in coupling a silylating agent into the free interlayer cavity. Thus, the success in grafting organic molecules depends firstly on prior basal distance expansion, which favors the intercalation process. Structural features related to silicon nuclear magnetic resonance in the solid state clearly illustrated carbon-(oxygen silicon) covalent bond formation, supporting the attachment of the pendant organic chains to the inorganic layer, by reaching the final interlayer distance of 2.43 nm. The available protonated basic atoms extract the Reactive Black 5 textile dye from aqueous solution through a batchwise process. The dye adsorption data was adjusted to the Sips isotherms model and the kinetic data was fitted to a fractional-order kinetic model. For this interactive process the basic protonated nitrogen atoms were saturated to give plateaus represented by the maximum number of moles adsorbed, for example, 76.77 mg g^{-1} (0.0774 mmol g^{-1}), given by the Sips isotherm. Based on these results, it is supposed that the textile dye uses more than one basic center of the grafted urea molecule when interacting with the available basic nitrogens to reach 0.310 mmol g^{-1}. This is expected, since the dye has two sulfonate and also two sulfato-ethyl-sulfone groups, all of them possessing negative charges to interact with the positive amine groups of the organomodified material. However, this interaction may happen with different protonated amine groups of the urea, it is also necessary to consider the size of the dye molecules.

Acknowledgements

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