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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 cethyltrimethylammonium 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_2O, 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%.