



Organofunctionalized Amazon smectite for dye removal from aqueous medium—Kinetic and thermodynamic adsorption investigations

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ABSTRACT

The objective of this study is to examine the adsorption behavior of Sumifix Brilliant Orange 3R textile dye from aqueous solution on smectite sample, an abundant Amazon clay. The original smectite clay mineral has been collected from Amazon region, Brazil. The compound 2-aminomethylpyridine was anchored onto smectite surface by heterogeneous route. The ability of these materials to remove the Sumifix Brilliant Orange 3R textile dye from aqueous solution was followed by a series of adsorption isotherms, using a batchwise process. The maximum number of moles adsorbed was determined to be 1.26 and 2.07 mmol g⁻¹ for natural and modified clay samples, respectively. The energetic effects caused by dye cations adsorption were determined through calorimetric titrations. Thermodynamics indicated the existence of favorable conditions for such dye–nitrogen interactions.

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1. Introduction

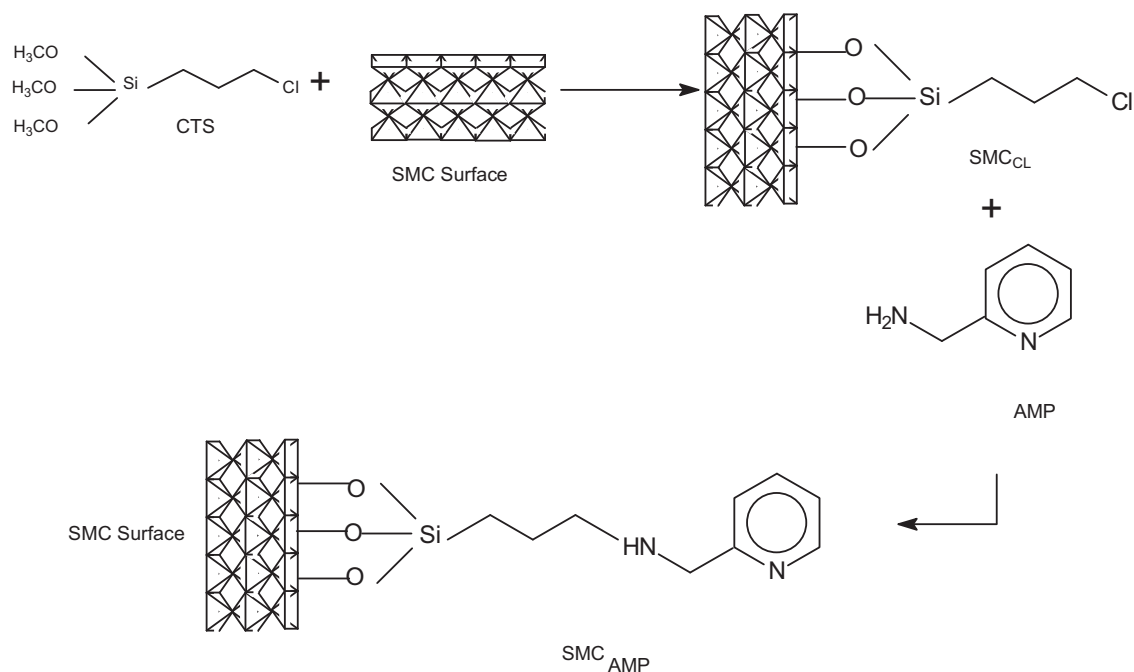
Agrosystems, which are the important consumers of fresh water in many regions around the world, currently face the challenge of developing new approaches to water management that will insure the protection groundwater resources and their integrity for the future use [1]. A wide range of procedures for removal of synthetic dyes from industrial effluents are based on the decolorization by activated sludge containing some additives such as powdered smectite clay [2]. The insertion process of organic neutral polar molecules into the nanospace void of sheets of layered insoluble nanocompounds leads to well-organized inorganic/organic structural layer materials. The advances in the organofunctionalization field are closely associated with development of new silylating agents, which pendant organic chains can display non-hydrolyzable silicon–carbon bond, to prevent the leaching of the immobilized reagent to solution. However, as the pendant chains incorporate donor basic atoms, an improvement on adsorption and exchange properties are normally increased [2,3]. Various conventional and non-conventional adsorbents have been explored for removal of different metal ions from aqueous. For example, materials containing micro and macropores, such as pillared and intercalated clays, are often employed in such

operations, smectite clays have continuously attracted attention also for the possibility of modifying their layered structure by functionalization, thus creating new hybrid materials with high reactivity [4,5].

The adsorption of dye ions onto phyllosilicate is an important process not only in soil chemistry but also in the treatment of industrial wastewaters. Aqueous effluents containing dye ions contaminants continue to be discharged into the environment from the industries. Adsorption capacity depends on activated clay properties, adsorbate chemical properties, temperature, pH, ionic strength, etc. Bearing in mind this proposal, new adsorbent materials are now being employed for removal of toxic and valuable compounds from water and other solvents. Covalent immobilization onto solid supports of a desired chelate moiety, with the specific purpose of obtaining selectively adsorbent materials, is one of the most important procedures to develop highly selective matrices [5,6]. The immobilization of the 2-aminomethylpyridine (AMP) has been explored by different immobilization methodologies in the preparation of hybrid materials with high adsorptive capacity [7], although some of these amino-functionalized adsorbents can exhibit specific interactions with hard Lewis acids, the selectivity of these materials are usually unremarkable, because many dyes have great ability to bind amine ligands. The possibility of an organofunctionalization reaction prior to dye adsorption would increase the capacity of adsorption by the chemically modified materials [8–13]. For this purpose, natural Amazon smectite was chosen as a source of layered silicate, since its surface

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Scheme 1. Incorporation of the 2-aminomethylpyridine onto smectite surface by heterogeneous route.

contains a high degree of regularly distributed silanol groups in the space interlayer that favor organomodification reactions [3].

In this paper, we investigated the use of original (SMC) and modified smectite (SMC_{AMP}) clay samples as alternative adsorbents for extraction of toxic dyes, which are commonly present in waters from a variety of sources and industrial effluents. For this purpose, the adsorption isotherms of Sumifix Brilliant Orange 3R (SBO3R) from aqueous medium at room temperature were explored, bearing in mind the influence of different parameters such as solution pH, dye concentration, temperature, and contact time. Amazon smectite clay sample has been chemically modified with 2-aminomethylpyridine (AMP). From calorimetric determinations the quantitative thermal effects for SBO3R/reactive center interactions gave exothermic enthalpy, negative Gibbs free energy and positive entropy. These thermodynamic data confirmed the energetically favorable condition of such interactions at the solid/liquid interface for both systems.

2. Materials and methods

2.1. Raw material and reagents

The clay sample used in this investigation was obtained from the Manacapuru area, Amazonas state, North of Brazil, Amazon region. A natural smectite sample, named SMC, with less than 2 μm particles, was separated by sedimentation. The natural clay sample was activated in a stream of dry nitrogen by heating at 423 ± 1 K for 10 h and used immediately.

Reagent grade solvents were used. The compounds 2-aminomethylpyridine (AMP) (C₆H₈N₂) (Sigma) and 3-chloropropyltrimethoxysilane (CTS) (C₆H₁₅ClO₃Si) (Aldrich) were used without purification. Other chemicals such as methanol and ethanol were of reagent grade. The reactive dye Sumifix Brilliant Orange 3R (SBO3R) textile dye also known as Reactive Orange 16 (C.I. 177577; C₂₀H₁₇N₃O₁₀S₃Na₂, 601.54 g mol⁻¹, $\lambda_{\text{max}} = 493$ nm) was obtained from Sigma with a dye content of 50.0%. It was used without further purification. SBO3R has one sulfonate group and

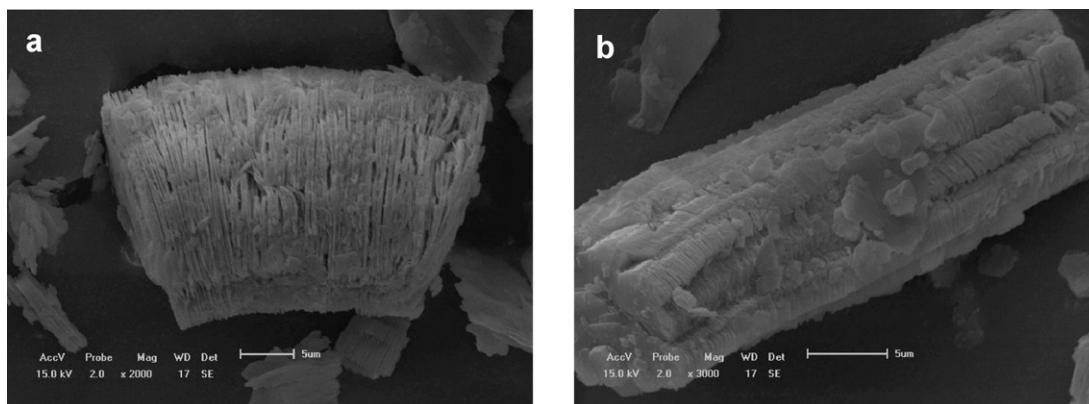


Fig. 1. SEM of the smectite samples: SMC (a) and SMC_{AMP} (b).

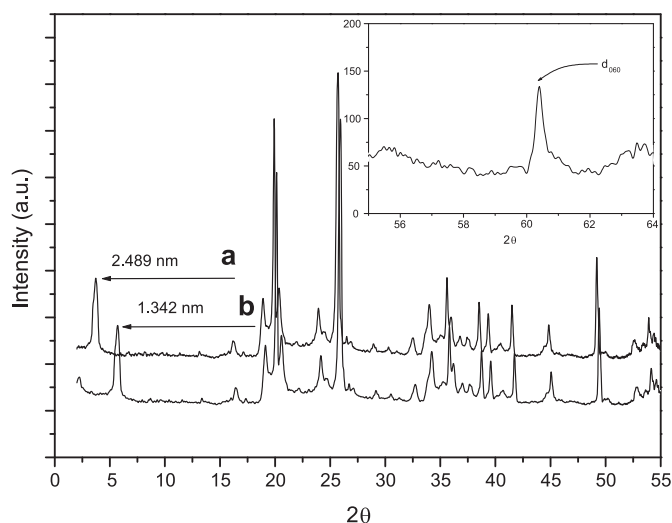


Fig. 2. X-ray diffraction patterns for unmodified and modified smectite samples: SMC (a) and SMC_{AMP} (b).

one sulfato-ethyl-sulfone groups; both have negative charges even in highly acidic solutions, because their pK_a values are lower than zero. Doubly distilled deionized water (DDW) was used for the preparation of solutions, wherever required. Solutions of dye were by dissolving accurately weighed dye in DDW to a concentration of $5000.0 \text{ mg dm}^{-3}$.

2.2. Organofunctionalization of smectite clay

A sample of 20.0 g of activated smectite was suspended in 100.0 cm^3 of dry toluene and 20.0 cm^3 (108.0 mmol) of CTS was added to this suspension. The mixture was mechanically stirred under reflux of the solvent in an inert atmosphere for 72 h. The suspension was filtered and the solid was washed with toluene and dried under vacuum at $230 \pm 1 \text{ K}$ for several hours, to give the modified smectite, named SMC_{CL} [4].

A sample of 5.0 g of SMC_{CL} reacted with 3.50 cm^3 (0.034 mmol) of the compound AMP in 50.0 cm^3 of toluene, containing 5.0 cm^3 of triethylamine in order to favor the reaction equilibrium [4]. The suspension was kept under reflux and mechanically stirred for 72 h at 363 K . The final product, SMC_{AMP}, was filtered, washed with toluene and ethanol, and dried under vacuum at 230 K for 15 h.

The attachment of the 2-aminomethylpyridine onto original smectite followed a sequence of two distinct steps. The first one consisted in grafting 3-chloropropyltrimethoxysilane (CTS) onto SMC to yield the new surface, SMC_{CL}. In the next stage, this precursor was reacted with 2-aminomethylpyridine (AMP) to give the product SMC_{AMP}, as represented in Scheme 1.

2.3. Characterization methods

The natural smectite clay was analyzed by inductively couple plasma optical emission spectrometry (ICP OES) using a Perkin Elmer 3000 DV instrument. The oven-dried powdered sample weighing 230.0 mg was placed on weighed glass dishes and transferred quantitatively to pre-cleaned nitric acid digestion bottles. The sample was then digested with 7.0 cm^3 of concentrated nitric and hydrochloric acids in 1:3 proportions in volume, with an identical volume of hydrofluoric acid over 5 days. The smectite sample were cooled in an ice-bath and 25.0 cm^3 of 0.10 mol dm^{-3} boric acid was added with stirring, followed by 50.0 cm^3 of DDW, and the solution was then diluted to 100.0 cm^3 . A blank and a set of elemental standards were run to calibrate the instrument.

The natural and modified smectite clays were analyzed by scanning electron microscopy (SEM) in JEOL microscope, model JEOL JSM 6360LV, using an acceleration voltage of 15 kV and magnification ranging from 300 to 3000 fold.

X-ray powder diffraction (XRD) patterns were recorded with Philips PW 1050 diffractometer using $\text{CuK}\alpha$ (0.154 nm) radiation in the region in the between 2° and 65° (2θ) at a speed of 2° per min and in steps of 0.050° .

The infrared spectra of the clay samples in KBr pellets were obtained by accumulating 32 scans on a Bomen spectrophotometer, MB-Series, in the $4000\text{--}400 \text{ cm}^{-1}$ range with 4 cm^{-1} of resolution.

The amount of organic pendant chains attached onto the inorganic layers formed were calculated based on carbon, hydrogen and nitrogen percentages, determined through elemental analysis on a PerkinElmer, model 2400, elemental analyzer, and at least two independent determinations were performed for modified clay sample.

The cation exchange capacities (CEC) of natural and modified smectite clay samples were followed by the ammonium acetate method with a concentration of 2.0 mol dm^{-3} at pH 8.0.

Brunauer–Emmett–Teller (BET) surface area, pore diameter and pore volume were obtained from nitrogen adsorption/desorption in a Micromeritics ASAP 2000 BET surface analyzer system. The mesopore size distribution was obtained by applying the Barret–Joyner–Halenda (BJH) method to the adsorption branch of the isotherm.

2.4. Batch adsorption study

The adsorption experiments were performed through the batch-wise method by suspending a series of 20 mg samples of the natural smectite clay (SCM), in 20.0 cm^3 aqueous solutions of cation at concentrations varying from 0.125 to $3.50 \text{ mmol dm}^{-3}$, under orbital stirring for 24 h at $298 \pm 1 \text{ K}$ [14,15]. The solid was separated by centrifugation and from the supernatant were carefully pipetted samples for cation determination. 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 SBO3R dye 493 nm [14].

Profiles of the obtained adsorption isotherms were represented by the number of moles adsorbed (N_f), versus the number of moles at equilibrium per volume of solution (C_s), for series of isotherms, the data reveal that the adsorption process conforms to the Sips model [16] (Eq. (1)). The Sips isotherm is a three parameter fitting equation and combines the features of both Langmuir and Freundlich models.

$$N_f = \frac{N_S K_S C_s^{\frac{1}{n}}}{1 + K_S C_s^{\frac{1}{n}}} \quad (1)$$

where C_s is the concentration of solution at equilibrium (mol dm^{-3}), N_f is defined as before (mmol g^{-1}) and N_S is the maximum number of moles of adsorbed per gram of the adsorbent (mmol g^{-1}), which also depends upon the number of adsorption sites, K_S is the equilibrium constant and n is the Freundlich exponent. The effect of pH on adsorption for all clay samples was evaluated by varying this parameter over the range from 1.0 to 8.0, with addition of 0.10 mol dm^{-3} of nitric acid or sodium hydroxide. The pH of the solutions was measured using a pH/Ion Analyzer, model 450M. In the investigation of the influence of contact time in the adsorption process, the kinetic parameters were analyzed by pseudo second-order model [17].

2.5. Thermodynamic of adsorption

The thermal effects from adsorption reaction were followed by calorimetric titrations using an isothermal calorimeter, Model LKB 2277, from thermometric. In this titration, the dye solution is added to a suspension of about 20 mg of the clay samples in 2.0 cm³ of water, under stirring at 298 ± 1 K. For each calorimetric titration about 20 mg of original and modified smectite samples was suspended in a steel ampoule and stirred at room temperature. After equilibrium was established, as demonstrated by the base line, the cation solution was incrementally added in a previously programmed procedure at intervals of 2 h, using a microsyringe coupled to the calorimetric vessel. For each increment, the thermal effect of interaction (ΣQ_t) was recorded, and after a sequence, constant thermal effects were obtained as expected for the end of such operation. The same procedure was employed to monitor the thermal effect cation dilution (ΣQ_d) in the calorimetric solvent. The thermal effect cation dilution (ΣQ_h) (effect of water) on the anchored surface was noted as null values. By combining these two output thermal effects, the net (ΣQ_r) value was determined using the expression (Eq. (2)) [18]:

$$\sum Q_r = \sum (Q_t) - \sum (Q_d) \quad (2)$$

3. Results and discussion

3.1. Characterization

The bulk geological material used for investigation was massive greenish clay stone consisting of 26.5% smectite clay, 69.0% silt and 4.5% sand. Elemental analyses from the ICP OES technique for the original smectite sample, SMC, gave results consistent with smectite with silicon and aluminum being the major components. The total mineralogical composition is given by 46.26%; 39.62%; 0.47%; 0.28%; 0.27%; 0.21 and 0.17% of SiO₂, Al₂O₃, Fe₂O₃, MgO, Na₂O, CaO, and K₂O respectively, and 12.73% of mass was lost in the ignition process. The composition of the original smectite sample was calculated through the chemical analysis, to give the formula (Eq. (3)):



The cation exchange capacity of clay mineral is attributed to structural defects, broken bonds and structural hydroxyl transfers [19]. Intercalation process increases the total number of exchange sites marginally in smectite. The cation exchange capacity is relatively high compared to other smectite clay samples. For comparison, Table 1 also summarizes some physical properties of clay fraction and reference smectite [20–22]. The CEC of natural smectite was found to be 95.0 meq/100 g of clay, and modified smectite was found to be 175.5 meq/100 g of clay, as listed in Table 1.

Morphologies as well as structural ordering of the natural and modified smectite clays, presented in Fig. 1a and b, were analyzed by SEM. The individual crystals presented themselves as flakes in an irregular morphology, as confirmed by SEM image of the modified smectite clay. The presence of agglomerated particles of nanodimensions was also noted in the natural smectite sample. Small aggregates of rounded crystal coexisted with irregular smectite particles with particle size mostly smaller than 5.0 μm as illustrated in Fig. 1a. This aggregation was similar to that described by Keller [23] for weathered hydrothermal kaolin samples, with particles and 'books' randomly oriented. In general, smectite crystals of large size (>1.0 μm) showed pseudo-hexagonal form and well defined edges, whereas the edges of crystals of small sizes were rounded.

Different experiments were performed using bridged organosilane 2-aminomethylpyridine as an intercalating agent to synthesize

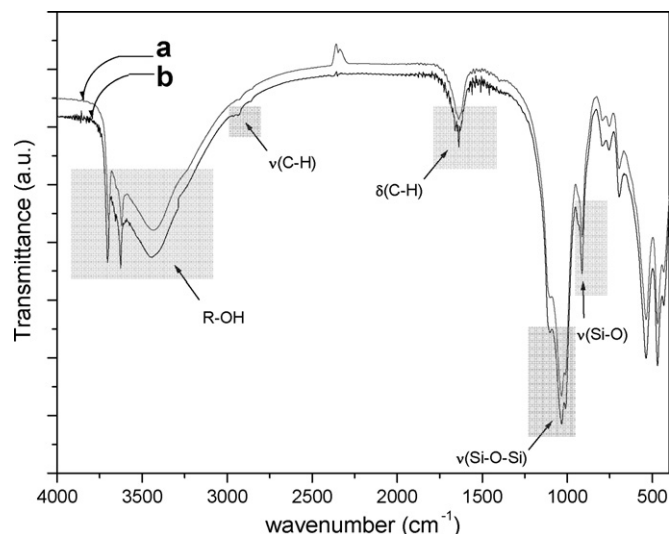


Fig. 3. Infrared spectra of unmodified and modified smectite samples: SMC (a) and SMC_{AMP} (b).

inorganic–organic hybrid layered material. In the modified smectite structure, the organic linkers present in the initial organosilane could be incorporated into the interlayer space of layered phyllosilicates, covalently bonded to the surfaces of smectite-type inorganic layers. Indeed, XRD patterns of natural and modified smectite (Fig. 2a and b) exhibit 001 reflections corresponding, in the case of original smectite, to a basal spacing of 1.342 nm due to the presence of Na⁺, Mg²⁺, and K⁺ cations and water molecules present between the smectite layers, the thickness of which is ~0.860 nm (Fig. 2a), whereas, after the chemical modification process, the basal spacing increased to 2.489 nm because of the effective intercalation of the AMP molecules in the interlayer space (Fig. 2b). Taking into account the thickness (0.860 nm) of the smectite layers, the space occupied by the bridged polysiloxane corresponds to 1.629 nm, confirming that the organic–inorganic precursor was successfully intercalated into the interlayer space with the 2-aminomethylpyridine units oriented perpendicular to the phyllosilicate layer. The great influence of the number of 2-aminomethylpyridine ions on the surface and on the constitution and distribution of the ions has been reported previously [24]. The mass fraction of intercalated phyllosilicate can be estimated as the relative intensities of the reflection originating from the 'unchanged' and the 'expanded' layers. In the intercalated sample, the degree of intercalation reaction could be estimated as ~88%, indicating that the AMP molecules are arranged in monolayers between the phyllosilicate layers. The smectite was characterized as a dioctahedral montmorillonite after analysis of the 060 reflection ($d_{060} = 0.1467$ nm) [25].

From infrared spectra obtained for clay samples was possible to conclude the success of the immobilization by heterogeneous route, as presented in Fig. 3a and b. A small difference is observed in relation to wave number and intensities of the bands in comparing immobilized clay and the natural clay. The main features of two clay samples spectra are connected to the similarity of bands associated with the inorganic backbone such as (i) a large broad band between 3400 and 3200 cm⁻¹, which is assigned to R-OH stretching mode of silanol groups and also to the remaining adsorbed water, (ii) The intense band related to siloxane (Si–O–Si) stretching of these groups at 1100 cm⁻¹, (iii) a band assigned Si–O stretching mode of silanol groups at 900 cm⁻¹ and (iv) the band around 1675 cm⁻¹, assigned to water bending mode. However, the modified clay sample presented a characteristic peak at 2950 cm⁻¹ and 1900 assigned to ν(C–H) and δ(C–H), respectively, stretching of the

Table 1

Textural proprieties of smectite samples, quantification of anchored organic molecules in the modified smectite sample and comparison of the properties of some smectite clays.

Sample	Surface area-S _{BET} (m ² g ⁻¹)	Micropore area (m ² g ⁻¹)	Average pore diameter (nm)	Pore volume (cm ³ g ⁻¹)	L ₀ (mmol g ⁻¹)	d (molecules nm ⁻²)	I (nm)	CEC (meq/100 g of clay)	Reference
SMC	48.4 ± 0.12	9.7 ± 0.11	1.1 ± 0.17	0.12 ± 0.13	–	–	–	95.0	Current research
SMC _{AMP}	872.3 ± 0.12	48.4 ± 0.12	8.3 ± 0.12	0.47 ± 0.11	1.52 ± 0.12	0.95 ± 0.15	1.32 ± 0.17	175.5	Current research
Smectite (SWy-1)	335.5	–	–	–	–	–	–	75.0	[13]
Smectite (BO1)	29.23	2.77	–	0.0417	–	–	–	–	[14]
Smectite (BO2)	56.56	15.30	–	0.0781	–	–	–	–	[14]
Smectite (NaS)	61	–	–	0.11	–	–	–	1.08 (mol kg ⁻¹)	[15]

tetrahedral carbon, which confirms the anchoring of the organic molecule onto clay smectite sample [24].

The quantity of molecules attached to the smectite surface was calculated from the percentage of nitrogen in the functionalized smectite sample, as estimated by elemental analysis, using the following Eq. (4) [26]:

$$L_0 = \frac{\%N \times 10}{\text{nitrogen atomic weight}} \quad (4)$$

The C/N molar ratio calculated from the elemental analysis of SMC_{AMP} indicates a 1:1 stoichiometry between the silanol groups on the silicate surface and the ligand. Taking into account L₀ (mmol g⁻¹) and surface area (m² g⁻¹) (S_{BET}) of the modified smectite clay, the average surface density (molecules nm⁻²), d, of the attached molecules and the average intermolecular distance (nm), I, can be calculated by applying the following Eqs. (5) and (6) [26]:

$$d = N_A \frac{L_0}{S_{BET}} \quad (5)$$

$$I = \left(\frac{1}{d}\right)^{\frac{1}{2}} \quad (6)$$

where N_A is Avogadro's number (mol⁻¹). The results obtained confirm a high efficiency in the chemical modifications of the original smectite sample. Thus, the high functionalization degree obtained in the modified smectite sample can be explained as a consequence of its modification of physical–chemical properties (Table 1).

The surface area of a porous organoclay is one of the most useful microstructural parameters for defining properties. The BET surface areas of the natural and modified clay samples demonstrated that chemical modification caused the formation of micropores in the solid particles, resulting in a higher surface area, revealing 872.3 m² g⁻¹ for SMC_{AMP} and relative to the natural SMC sample with 48.4 m² g⁻¹. The pore diameters change in the same direction, varying from 1.1 nm for the natural to 8.3 nm for the anchored clay. The textural properties of natural and modified smectite samples are reported in Table 1, which depends on particle size shape, and distribution of cracks and pores in the material. The SMC_{AMP} has a significantly higher surface area than the SMC and has pores <2 nm in diameter (micropore) in addition to some mesopores (>4 nm diameter). The smectite have small N₂ BET surface areas and only mesopores because N₂, as opposed to H₂O, –OH, and H₃O⁺, is unable to penetrate into the interlayer spaces of the lamellar silicate.

3.2. Effects of dye concentration and pH

The available reactive atoms from the organic molecules and the maximum adsorption values are listed in Table 2. The mesoporous hybrid materials have been used to evaluate the maximum adsorption capacity for uptaking dye ions, such as SBO3R, from aqueous solutions. In fact, these species act as acidic Lewis centers that interact with the nitrogen basic Lewis centers attached to the pendant molecules covalently bonded to the clay surface, as presented in Fig. 4a. The influence of the silylating agents covalently bonded on the inorganic structure is clearly reflected in adsorption isotherms due to different basic center attached to the pendant chains, as outlined by the saturation process [27,28]. The molecules anchored onto the oxides containing nitrogen basic atoms on pendant chains favor a dye interaction, mainly of soft cations, due to the presence of the basic reactive centers [29]. Based on the structural features presented by basic groups on the natural or modified clay surfaces, the adsorption can be related directly to the available nitrogen atoms. The Sips non-linear adsorption model was used to explain the significant capacity of these clays to quantify SBO3R interactions on these polymeric inorganic structures.

The large capacity of modified smectite sample was confirmed through constant values obtained with this model in the non-linear form, whose results gave the best approximation to the experimental data, as illustrated in Fig. 4a. The values are listed in Table 2. The large capacity of adsorption of the anchored smectite is represented by these constant values, which can be attributed to the immobilization of reactive basic groups on the pendant chains. Thus, the attached groups are the reactive basic center that contributes directly to the adsorption property of the anchored smectite sample.

Fig. 4b shows the influence of pH in adsorption process of SBO3R onto natural and modified matrices. The data reveals maximum values of N_f^{max} around pH 4.0 for two matrices. The amount adsorbed increased as the pH of the solution was changed to lower values (<4.0) and the amount adsorbed increased for pH values >4.0. The smectite cation adsorption capacity for all these matrices depends on the nature of the complex formed on surface and also on the affinity of the dye for any particular attached ligand [6,29]. These N_f^{max} values reflect the good affinity of the nitrogen donor atoms attached to the inorganic backbone for bonding SBO3R. Favorable nitrogen/SBO3R interactions were previously observed for these silylating agents when immobilized on natural smectite clay sur-

Table 2

Equilibrium and thermodynamic data for SBO3R dye onto natural and modified smectite samples.

Sample	N _f ^{max} (mmol g ⁻¹)				N _{s(298 K)} (mmol g ⁻¹)	–Δ _{int} h (J g ⁻¹)	–Δ _{int} H (kJ mol ⁻¹)	n _(298 K)	K _S × 10 ⁻³	–Δ _{int} G (kJ mol ⁻¹)	Δ _{int} S (JK ⁻¹ mol ⁻¹)
	298 K	303 K	308 K	313 K							
SMC	1.26 ± 0.12	1.46 ± 0.14	1.56 ± 0.16	1.59 ± 0.11	1.51 ± 0.12	11.48 ± 0.11	7.61 ± 0.17	0.89	6.6 ± 0.2	21.8 ± 0.3	49 ± 1
SMC _{AMP}	2.07 ± 0.08	2.27 ± 0.11	2.57 ± 0.10	2.77 ± 0.12	2.12 ± 0.01	15.45 ± 0.16	7.31 ± 0.02	0.99	10.7 ± 0.4	22.8 ± 0.2	52 ± 2

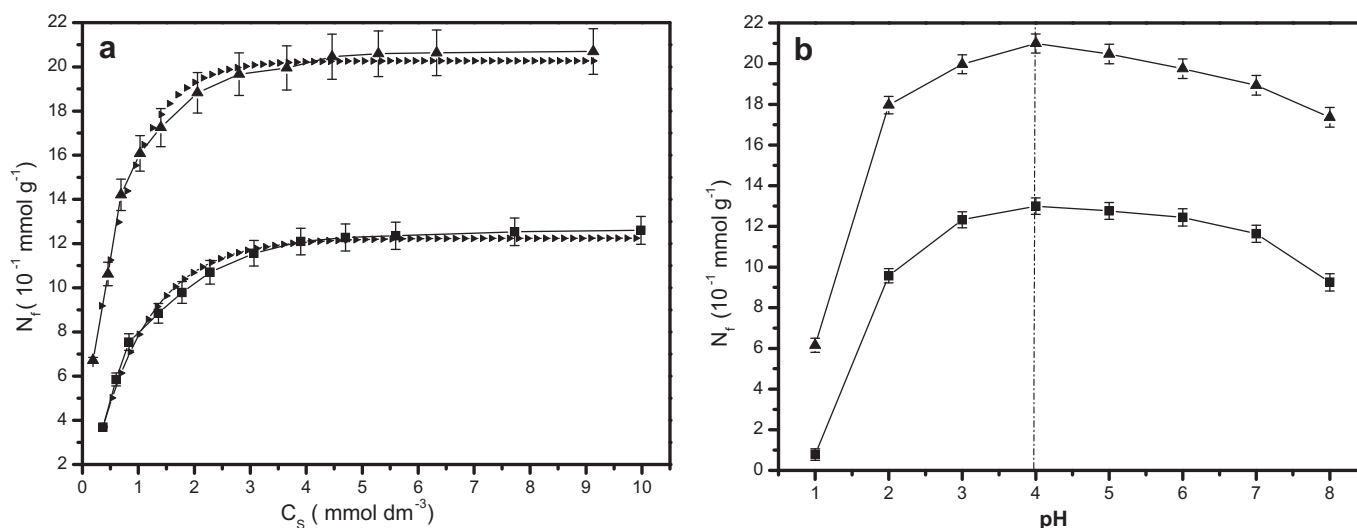


Fig. 4. Effect of concentration (a) and pH (b) on cations adsorption onto unmodified and modified smectite samples from aqueous solution: SMC (■) and SMC_{AMP} (▲) isotherms calculated with non-linear method (▶).

faces. Results emphasize that with increase in pH of solution, the N_f adsorbed increases for two systems. Therefore the efficiency of SBO3R on unmodified and modified phyllosilicates can be controlled by the initial pH of the solid/liquid reaction. At low pH, the number of available hydrogen ions is high in medium and SBORR ions have to compete with them for the adsorption sites on the adsorbent surface. The reactive sites on the adsorbent surface are weakly acidic in nature and with increase in pH, they are gradually deprotonated favoring more and more dye uptake.

3.3. Effects of temperature, contact time, and kinetic of adsorption

Amount of SBO3R adsorbed at four different temperatures of 298, 303, 308, and 313 K showed an increasing trend with increase in temperature. Typical results are shown in Fig. 5a and b and Table 2 with the highest pronounced adsorption for modified smectite in 313 K. It is likely that adsorption of dye on smectite clay surfaces requires activation energy and rise in temperature helps more dye ion to overcome this energy barrier and get attached to the clay surfaces. Another possibility is the creation of additional adsorption reactive sites on smectite surfaces arising due dissociation of some of the surface components of natural and modified smectite samples at a temperature higher than the ambient which increase dye uptake, for example, ions present in the interlayer region of phyllosilicate, as potassium, phosphorus, and magnesium, these ions does not directly contribute to increase of the adsorption capacity of clay. These influences may operate independently of one another or may be operational simultaneously in reactive clay surfaces.

The adsorption data for dye uptake versus contact time for a fixed adsorbent amount at 298 K is shown in Fig. 5c and Table 3 at four different temperatures of 298, 303, 308, and 313 K, giving identical abrupt increases in adsorption at low times before reaching the plateaus. According to these data, equilibrium is achieved at around 12 and 16 min for SMC_{AMP} and SMC, respectively. However, to be sure on the best adsorption conditions at higher concentrations levels, to obtain equilibrium at the solid/liquid interface, all the experiments were carried out with approximately 40 min of contact time. This short time period required to attain equilibrium suggests an excellent affinity of the SBO3R for these adsorbents from aqueous solutions. In order to study the specific rate constant of SBO3R – phyllosilicates systems, was used a pseudo-second-

order rate equation to simulate the kinetic adsorption of dye on the silicates [17,30]. When the rate of reaction of an adsorption reaction is controlled by chemical exchange, then a pseudo-second-order model can be better adjusted to the experimental kinetic data [10], as expressed by Eq. (7).

$$\frac{t}{N_f} = \left(\frac{1}{k_2 N_{fEQ}^2} \right) + \left(\frac{1}{N_{fEQ}} \right) t \quad (7)$$

where k_2 is the pseudo-second-order rate ($\text{mmol g}^{-1} \text{min}^{-1}$). The values of k_2 can be obtained from the non-linear regression plot of N_f versus t . Carrying out a set of experiments at constant temperature and monitoring the amount adsorbed with time, the kinetics of the adsorption process should be known. The values of k_2 and N_{fEQ} are shown in Table 3 for SMC and SMC_{AMP}. The correlation coefficient of the pseudo-second-order rate equation (r^2) for the regression non-linear is 0.999, which suggest that the kinetic adsorption can be described by the pseudo-second-order rate equation very well for all systems.

3.4. Thermodynamic of adsorption

The applicability of these kinds of porous materials depends on a series of physicochemical properties like as the degree of molecules immobilized, mainly when the adsorption is considered [30]. The adsorption process was also calorimetrically monitored by titration process. From this value, the thermal effect related to

Table 3

Second-order rate constant data for SBO3R dye onto natural and modified smectite samples at 298, 303, 308, and 313 K.

Sample	N_{fEQ} (mmol g^{-1})	k_2 ($\text{mmol g}^{-1} \text{min}^{-1}$)
298 K		
SMC	1.20 ± 0.11	28.01 ± 0.01
SMC _{AMP}	2.05 ± 0.11	91.14 ± 0.05
303 K		
SMC	1.36 ± 0.11	31.02 ± 0.02
SMC _{AMP}	2.25 ± 0.11	95.15 ± 0.04
308 K		
SMC	1.48 ± 0.13	35.01 ± 0.03
SMC _{AMP}	2.67 ± 0.10	98.13 ± 0.08
313 K		
SMC	1.69 ± 0.14	38.11 ± 0.02
SMC _{AMP}	2.91 ± 0.12	99.01 ± 0.05

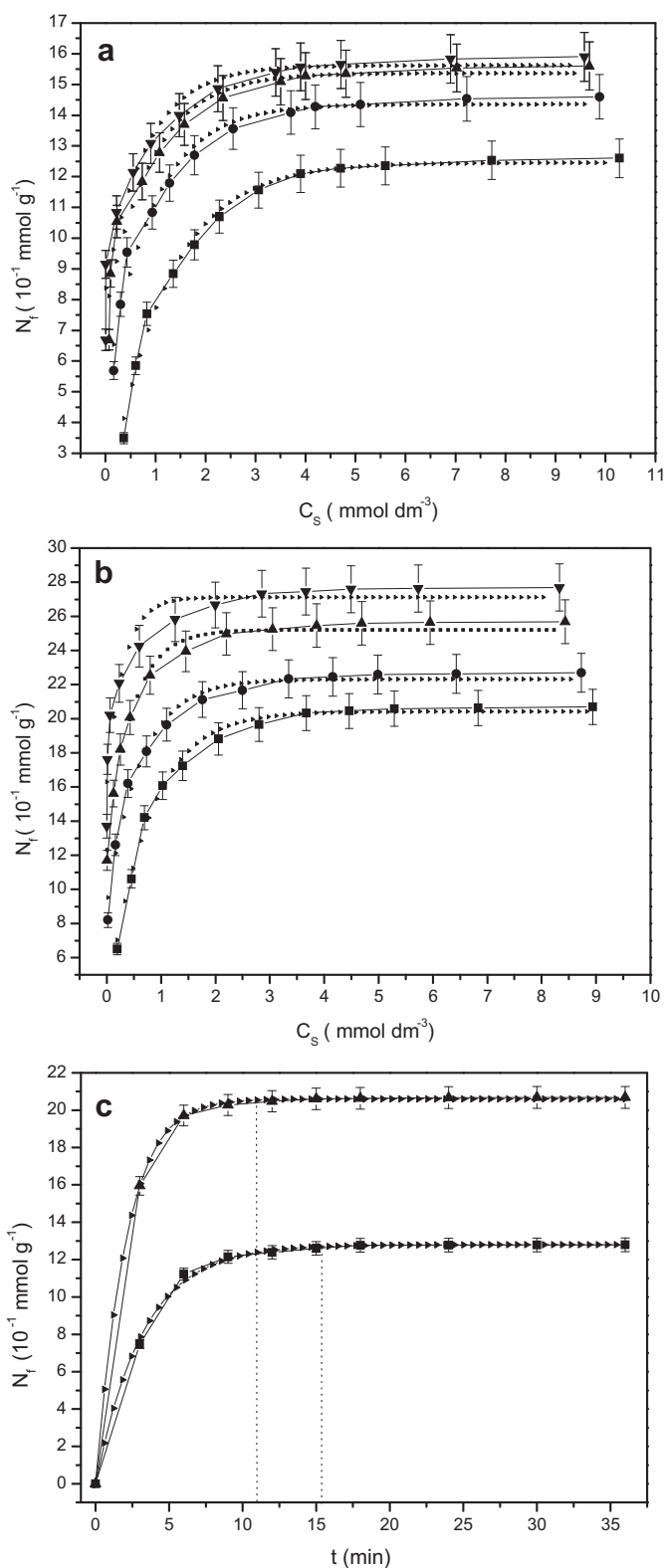


Fig. 5. Effect temperature of adsorption SBO3R on natural and modified smectite clays at 298 K (■), 303 K (●), 308 K (▲), and 313 K (▼). SMC (a) and SMC_{AMP} (b) and effect of contact time: SMC (■) and SMC_{AMP} (▲) (c) isotherms calculated with non-linear method (▶).

cation-basic center interactions on the natural and modified surfaces is obtained. An illustration of all the steps of calorimetric titration of 20.0 mg of the modified smectite with 0.050 mol dm⁻³ of SBO3R solution is shown in Fig. 6a. This value was adjusted to

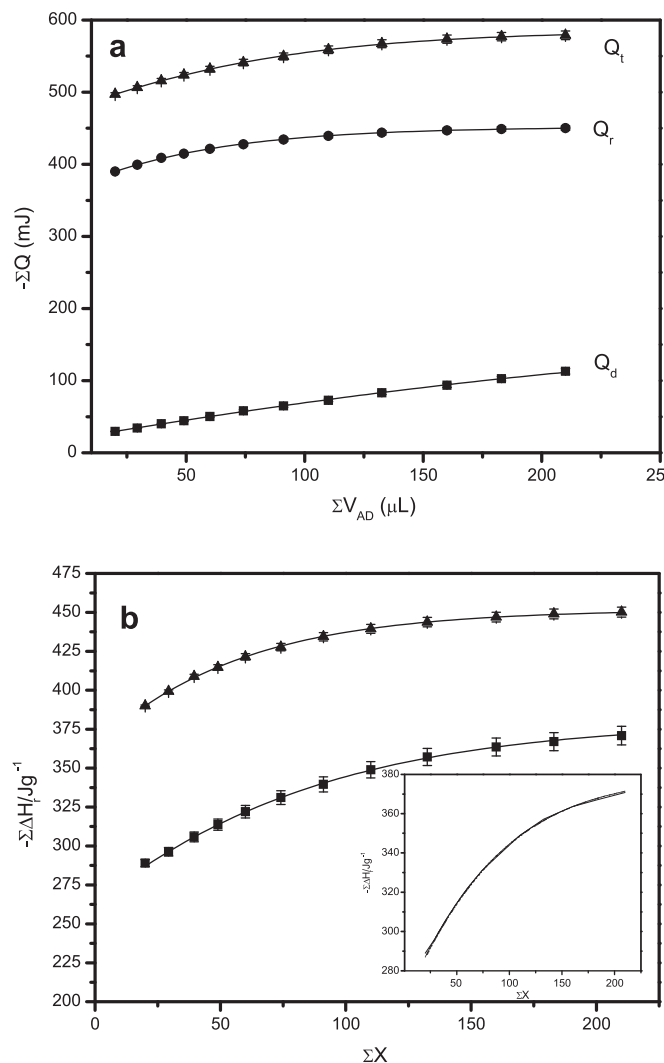


Fig. 6. The resulting thermal effect of adsorption SBO3R on modified smectite at 298 ± 1 K. The experiment points represent the thermal effect of cation titration $\sum Q_t$ (▲), cation dilution $\sum Q_d$ (■) and the net thermal effect of interaction $\sum Q_r$ (●), $\sum Q_t$ and V_{ad} values are the sum of detected thermal effect and total injected volume of SBO3R solution (a) and the net calorimetric data plotted in non-linear form for SMC (■) and SMC_{AMP} (▲) (b).

the modified Langmuir model (Eq. (8)), which is:

$$\frac{\sum X}{\sum \Delta_r H} = \frac{\sum X}{\Delta_{\text{mon}} H} + \frac{1}{\Delta_{\text{mon}} H (K_L - 1)} \quad (8)$$

where $\sum X$ is the sum of the mole fraction of each SBO3R cation in solution, after adsorption, obtained for each experimental point of titrand addition. $\Delta_r H$ is the integral enthalpy of adsorption for each point of the calorimetric titration obtained by dividing the thermal effect resulting from adsorption by the number of moles of adsorbate, K_L is proportionality constant that also includes the equilibrium constant. $\Delta_{\text{mon}} H$ is the thermal effect of formation of a monolayer on the surface. A plot of $\sum X / \sum \Delta_r H$ versus $\sum X$ gave the values of $\Delta_{\text{mon}} H$ and K_L , respectively, obtained from non-linear fitting method of the calorimetric isotherms, as shown in Fig. 6b. The enthalpy of adsorption $\Delta_{\text{ads}} H$ is calculated using the expression (Eq. (9)) [31].

$$\Delta_{\text{ads}} H = \frac{\Delta_{\text{mon}} h}{N_s} \quad (9)$$

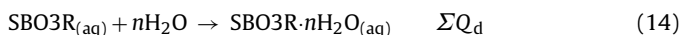
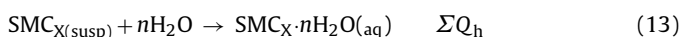
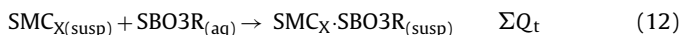
From K_S values, the Gibbs free energies were calculated by expression and the entropy value can be calculated through (Eqs.

(10) and (11)).

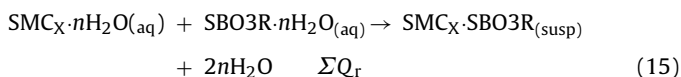
$$\Delta_{\text{mon}}G = -RT \ln K_s \quad (10)$$

$$\Delta_{\text{mon}}G = \Delta_{\text{mon}}H - T\Delta_{\text{mon}}S \quad (11)$$

The thermodynamic cycle for this series of adsorptions involving a suspension (susp) of smectite samples (SMC_X) in aqueous (aq) solution with dye cation (SBO3R) can be represented by the following calorimetric reactions. Reactions (12)–(14) represent calorimetric titration experiment carried out in duplicate for each determination:



The thermal effects of reactions (12)–(14) for each experimental point of the calorimetric titration were considered in the calculation of the net thermal effect (ΣQ_r) of these interactions, as represented by reaction (15).



A resume of the thermodynamic data is listed in Table 2. From the thermodynamic point of view, the obtained exothermic and positive entropic values establish the set of favorable results for the thermodynamic of SBO3R–nitrogen center interactions. Thus, the spontaneity of such reactions is expressed by the negative Gibbs free energy with a great contribution of the positive entropy due to the solvent displacement from the smectite sample and those initially hydrogenated bonded to amine groups of the attached organic chains, as the SBO3R/nitrogen basic center interactions at the solid/liquid interface [31].

4. Summary

The adsorption capacities of the natural clay sample with respect to the removal of Sumifix Brilliant Orange 3R dye are predominantly high under optimized condition which is indicative of its physicochemical properties. The adsorption of the dye ion depended on pH and shaking contact time. The optimum pH for the adsorption of the SBO3R ion ranged from 4.0 to 5.0 for all systems and the minimum shaking contact time necessary for reaching the equilibrium was about 12–16 min, for SMC_{AMP} and SMC , respectively. Through calorimetric investigation information about all systems was obtained, resulting in exothermic enthalpy, negative Gibbs free energy and positive entropy. This series of thermodynamic data reflects the favorable cation/base center interaction at the solid/liquid interface.

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