Organophilic clays and their application in atrazine adsorption

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Abstract

Atrazine's adsorptive capabilities make the use of clays practical and effective. Three types of organophilic clays modified by cationic surfactants with the ability of one of these clays to adsorb atrazine in an aqueous medium are discussed in this work. The modification in clays was done with the surfactants cetyltrimethylammonium bromide, cetyltrimethylammonium chloride, and dodecyltrimethylammonium chloride. The X-ray diffraction data indicated different lamellar expansions for the three organophilic clays obtained when compared to *in natura* clay, proving the presence of quaternary ammonium salts in the interlamellar space. There was also a decrease in the specific surface area showing less accessibility to the lamellar spaces due to the presence of surfactants. The thermogravimetric analysis showed a negative variation profile in all the clays. The adsorption test showed a better capacity for atrazine adsorption in the organophilic clay of 64% when compared with 36% of *in natura* clay, and it followed the Freundlich isotherm model.

Keywords: adsorption, atrazine, organophilic clays, surfactants, wastewater.

INTRODUCTION

Clays are very versatile and abundant materials and used as raw material for various applications, such as building materials, ceramics, paper, petroleum drilling, pharmaceutical industry, as well as adsorbents, catalysts or catalyst carriers, ion exchangers, and others, depending on the specific property that it presents [1, 2]. Many materials developed in the most diverse fields of science become applicable through the improvement of technologies and the acquisition of new materials. From this point of view, clay materials present a great promise in the optimization of new materials due mainly to their low cost and availability. Some studies have shown the application of adsorption systems to phenolic compounds in which alginate inserted nanocomposites using calcium chloride solution for the removal of phenolic compounds in aqueous systems were developed [3]. In this study, it was shown that the organophilic clay modified with the cationic surfactant hexadecyltrimethylammonium bromide resulted in a good organophilization efficiency. In addition, adsorption results were obtained in agitation systems with different times, obtaining the maximum adsorption capacity of 0.334 and 0.118 mg/g for phenolic compounds 4-chlorophenol (4CF) and phenol, respectively. Another application for organophilic clays was studied by Iannuccelli et al. [4], with the aim of modifying and improving the biological activity of gentamicin (GM) on the evaluation of crude bentonite (Bt) for the development of new gentamicin, a clay hybrid material for topical use. For this, the bentonite was treated with sodium chloride and subsequently, dispersions of bentonite and gentamicin were prepared. Controlled X-ray powder diffraction, thermogravimetry coupled to mass spectrometry, and molecular dynamics simulations indicated monolayer arrangement of gentamicin within the montmorillonite structure without producing substantial effects on the layer periodicity. Concerning skin biomedical application, unlike the pure antibiotic permeating along the transfollicular pathway across stratum corneum, the organo-modified Bt/GM would favor the trans-epidermal route along inter-cluster corneocyte region, as *in vivo* skin penetration studies by means of tape stripping test indicated. The GM intercalation could represent a potential advantageous approach in the contribution to a new antibiotic material [4].

Pandey and Ramontja [5] presented a review on the application of modified bentonites as adsorbents in the remediation of wastewater, given the importance of these materials in the organic and inorganic removal of several pollutants, evaluating different parameters of physical processes such as the impact of pH, the adsorption mechanism and the applicability of several kinetic and thermodynamic models of adsorption. It was verified that the great majority of the results showed that the adsorption for several pollutants followed a pseudo-second-order and the isotherms conformed to the Langmuir model. In addition, the great potential of bentonite in relation to other existing materials was highlighted, however with a disadvantage of the small pore size, suggesting that the diameters for the

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selective adsorption of pollutants should be improved. The authors concluded that the research should be focused in the coming years on bentonite and modified bentonites due to the high interest in water treatment in removing traces of organic, inorganic, and pathogenic contaminants [5].

Among its diverse applications, the use of clay as an adsorbent in the clarification of oils, treatment of wastewater, and retention of agrochemicals has stood out in recent years. In this sense, this work aimed to prepare and characterize organophilic clays and verify their application in the removal of atrazine in wastewater. Atrazine was chosen because there is still no efficient method for removing it from the wastewater. Atrazine is a low-cost herbicide, widely applied in the cultivation of corn, sugarcane, coffee, pineapple, banana, lettuce, and other fruits and vegetables. According to the plan for the years 2017-2020 of the Brazilian Health Regulatory Agency (ANVISA), atrazine is classified as toxicity class III, which means medium-toxic compounds. The maximum value for this compound in drinking water is 2 µg/L and the World Health Organization (WHO) sets the value of 100 µg/L, corresponding to the sum of atrazine and its chloro-s-triazine metabolites [6, 7].

MATERIALS AND METHODS

Preparation of organophilic clays: a bentonite clay (Bentogel, Campina Grande-PB, Brazil) was prepared by organophilization by the addition of three different surfactants, cetyltrimethylammonium bromide (CTAB), cetyltrimethylammonium chloride (CTAC), and dodecyltrimethylammonium chloride (DTAC), all from Sigma-Aldrich (99% pure). The method used for the organophilization was according to Valenzuela-Díaz [8, 9], using the ratio of 60 g of bentogel clay to 1500 mL of distilled and deionized water. For the sodification, 20% m/m Na_2CO_3 (Vetec) and 50% m/m ammonium quaternary salt solution were used for the organophilization; in both steps, the surplus was worked around 150% m/m of CTAC (80 meq/100 g of clay). After organophilization, the suspension was vacuum filtered, washing with plenty of deionized and distilled water. The retained product was oven dried at 60 °C for 48 h, disintegrated in the mortar, sifted below 200 mesh, and identified as organophilic clays A1 (cetyltrimethylammonium bromide), A2 (cetyltrimethylammonium chloride), and A3 (dodecyltrimethylammonium chloride).

Determination of the ion exchange capacity (IEC) of clay: IEC was determined using the traditional Kjeldahl distillation method, also called the ammonia nitrogen method. For this procedure, 5 g of *in natura* clay was transferred to a 500 mL conical flask containing 200 mL of a 3 mol/L ammonium acetate aqueous solution. This mixture was stirred for 12 h at 100 rpm, then centrifuged for 5 min at 1000 rpm. The supernatant was removed, and the remaining clay was washed with ethyl alcohol to remove the excess ammonium acetate and centrifuged again. The final solid was oven dried at 60 °C for 24 h. Then, 1.5 g of this solid was placed in a Kjeldahl flask together with 50 mL of deionized

water, 3 drops of phenolphthalein, and 20% NaOH solution until the medium turned slightly pink. The flask was coupled to a distillation system. With heating, the ammonia was released from the mixture and collected in a conical flask containing 50 mL of 4% boric acid, 3 drops of bromocresol red, and 3 drops of methyl red. The solution went from red to green. After distillation was completed, the green-colored solution was titrated with 0.1 mL/L HCl, whose correction factor is f=1.05 and the IEC was calculated by:

$$IEC = \frac{[\text{Concentration of acid (mol/L)}.f.\text{Volume of acid (mL)}].100}{\text{Mass of clay (g)}} \quad (A)$$

X-ray diffraction (XRD): XRD data of *in natura* and organophilic clays were collected using a diffractometer (D8 Discover, Bruker) operating with CuKα radiation (λ=1.54056 Å) at 50 kV and 100 mA. Powder XRD patterns were obtained in step scanning mode, 2θ=2-90° with a step of 0.01°. *Fourie transform infrared spectroscopy (FTIR)*: the analyses were performed using a spectrometer (Spectrum 400 FT-IR, Perkin Elmer) in the range of 400 to 4000 cm⁻¹, in attenuated total reflectance (ATR) mode, using a ZnSe crystal with a resolution of 4 cm⁻¹ and recording the average of 16 scans. *Thermogravimetric analysis (TG)*: TG was performed using a thermal analyzer (SDT Q600, TA Instr.) in an oxidizing atmosphere with synthetic air with a heating rate of 20 °C/min and final temperature of 1000 °C. *Brunauer-Emmett-Teller (BET) specific surface area analysis*: BET analysis was performed with a gas sorption analyzer (Autosorb, Quantachrome) at 77 K and N_2 flow as the adsorbate.

In natura and organophilic clay adsorption tests: the adsorption tests were performed with atrazine (Sigma-Aldrich, 99.1%) using a shaker with thermostatized bath at constant ambient temperature (25 °C) for 24 h under stirring at 100 rpm. In this assay, the adsorption efficiency per unit mass of the adsorbents was determined by high-performance liquid chromatography (HPLC). The adsorbents to be evaluated were chosen based on the results of characterization of the organophilic clays obtained in this study, prevailing the one that had better efficiency in the organophilization, considering the analyses of XRD, TG, and surface area. Thus, the adsorption tests were carried out for an organophilic clay and for the clay *in natura*. The method used to carry out the adsorption tests and the preparation of the isotherms was the bottle-point method [9, 10]. Previously, 0.5 g of each adsorbent (*in natura* and A1) and 200 mL of the atrazine solution in concentrations ranging from 200 to 900 µg/L with pH 6.5±0.5 were added to Erlenmeyer flasks. Then, the flasks were placed on a shaking thermostatic bath at 25 °C for 24 h and stirred at 100 rpm. The samples were centrifuged for 15 min at 4000 rpm and the supernatants were properly packaged and analyzed by HPLC. For the HPLC, it was used a column C18 ACE 5 C18 with internal diameter dimensions of 250x4.6 mm, a mobile phase of acetonitrile and water (1:1) operating in an isocratic elution mode (1 mL/min), an injection volume of 20 µL and a wavelength of 220 nm. The adsorption tests were performed in duplicate.

RESULTS AND DISCUSSION

The analysis of cation exchange capacity was important for modified clays, due to the significant exchange of sodium present between the lamellar structure of clays by surfactant ions. According to the volume of titrant acid (V=11.4 mL) and applying Eq. A, IEC value of 79.8 meq/100 g of clay was obtained for the *in natura* clay. This result was consistent with the IEC data of smectite clay minerals found in the literature, which show for the Brazilian smectite clays IEC values ranging from 22 to 151 meq/100 g of clay [9, 10]. The variation in the IEC of the same clay mineral is also related to the degree of impurity; the higher it is, the lower the IEC [10, 11]. From the X-ray diffractograms presented in Fig. 1, the *in natura* clay presented the basal plane reflection at 6.57° and the organophilic clays A1, A2, and A3 presented this reflection peak at 4.17°, 4.34°, and 4.08°, respectively. So, comparing the diffractograms of the organophilic clays with the *in natura* clay, it was observed that the 2θ angle of the peak corresponding to (001) basal reflection was displaced to lower values, indicating the presence of the organic molecules of quaternary ammonium surfactants in the interlamellar spaces of the clay, increasing the basal distance between the layers of clay minerals. In fact, the basal distance (d_{001}) was increased, being 13.4, 21.1, 20.4, and 21.7 Å to *in natura*, A1, A2, and A3 clays, respectively. The increase in the basal distance occurs according to the type of surfactant and its concentration, being possible to obtain different basal increases and, consequently, organophilic clays with different characteristics, allowing to adsorb molecules with different or specific dimensions [8, 12]. For the organophilic clays studied, there were no significant differences between them, probably due to the similar structure of the surfactants used. According to Bertagnolli [10], the differences in the values of the interplanar distances are related to the positioning and type of density of the intercalated quaternary ammonium cation.
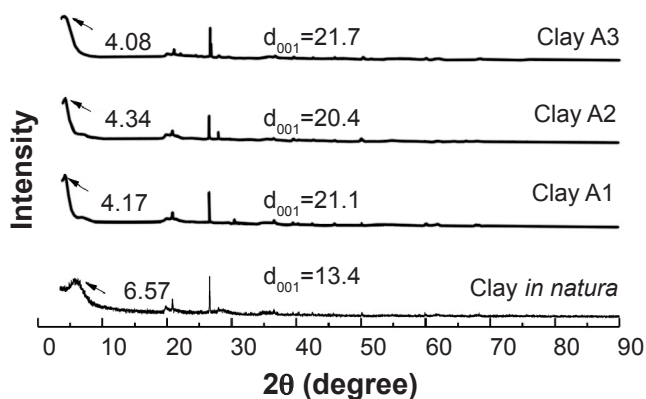

Figure 1: X-ray diffractograms of *in natura* and organophilic A1, A2, and A3 clays.

The results of the analysis by infrared spectroscopy for the *in natura* and the organophilic clays are shown in Fig. 2 and display characteristic bands of the smectite group in all spectra, indicating the permanence of the clay structure even after the modifications. The spectra of the organophilic clays presented additional bands, characteristic of the intercalated surfactants. The FTIR spectra (Fig. 2) of the *in natura* and the modified A1, A2, and A3 clays presented the OH stretching as a broad band in the 3600-3660 cm^{-1} range, involving the contributions of the OH groups coordinated to different octahedral cations. The Si-O stretching band at 1003 cm^{-1} had the contributions of in-plane Si-O-Si stretching vibrations, and the band at 1113 cm^{-1} was assigned to perpendicular Si-O vibration. A single band at 914 cm^{-1} in the spectra confirmed the dominance of Al-O within octahedral sites. As reported [8], and shown in Table I, the two bands at 2850 and 2930 cm^{-1} that appeared in the spectra of A1, A2 and A3 modified clays were assigned to the CH$_2$ group and the band at 1480 cm^{-1} referred to the CH$_3$ group from the quaternary ammonium surfactant molecules, evidencing the effective organophilization of the *in natura* clay.
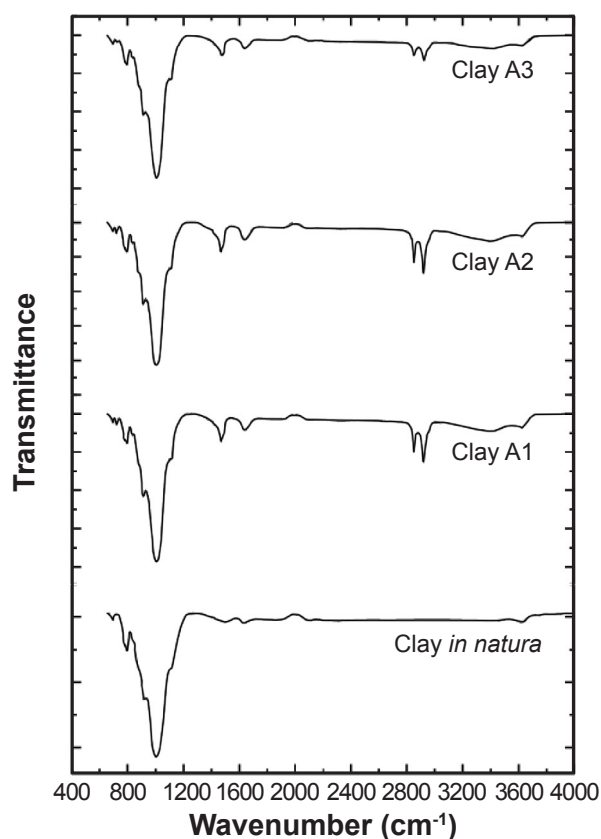

Figure 2: FTIR spectra of *in natura* and organophilic A1, A2, and A3 clays.

Table I - FTIR bands for *in natura* and organophilic A1, A2, and A3 clays.

Binding	Band (cm^{-1})	Clay
Si-O	1007	*In natura*, A1, A2, A3
Al-O	915	*In natura*, A1, A2, A3
O-H	3700	*In natura*, A1, A2, A3
CH$_2$	2920, 2850	A1, A2, A3
CH$_3$	1470	A1, A2, A3

From the TG curves shown in Fig. 3, all samples exhibited a mass loss between 25 and 150 °C, attributed to the loss of water molecules adsorbed on the surface of the clays and the water molecules of hydration around the interchangeable cations in the interlamellar space. Subsequently, the samples A1, A2, and A3 underwent a mass loss between 250 and 400 °C, attributed to the decomposition of the organics from the quaternary ammonium salt [13-16]. Finally, the last decomposition step occurred due to the dehydroxylation of the clay structure characterized by slopes between 600 and 700 °C for the organophilic samples and between 400 and 600 °C for the *in natura* clay. The temperature range of the mass loss of the structural hydroxyls for the *in natura* clay agreed with the one found by Santos [14], which was 400 to 700 °C.
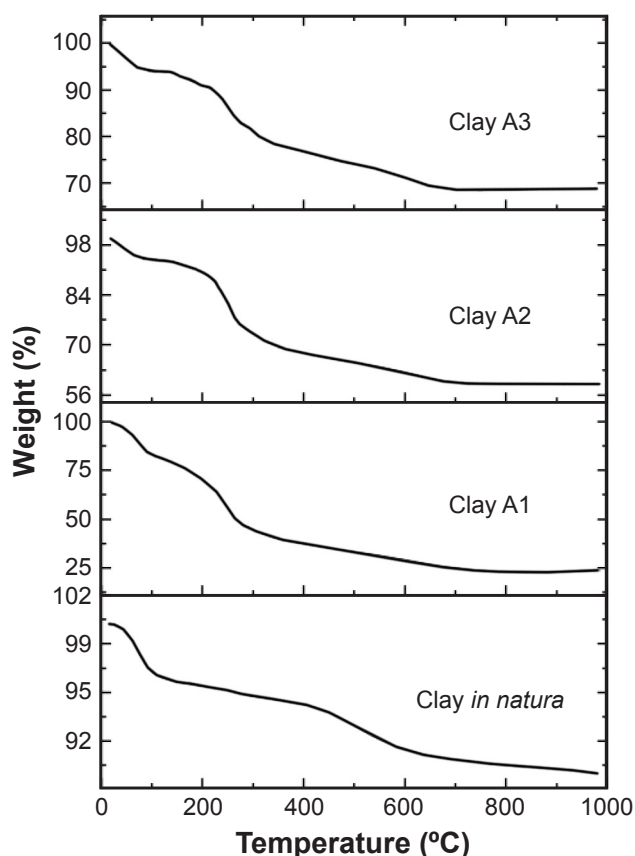

Figure 3: TG curves of *in natura* and organophilic A1, A2, and A3 clays.

Table II - BET surface area (m²/g) of *in natura* and organophilic clays.

In natura	A1	A2	A3
50.76	5.56	7.68	6.54

The results of the surface area measurements are shown in Table II. For the organophilic clays, a decrease of the surface area in relation to the value of the *in natura* clay occurred due to the presence of the molecules of the quaternary ammonium salts between clay lamellae, characterizing a good organophilization. The cation salts can block this space by preventing the passage of N_2 molecules and occupying clay active sites that could be available for N_2 [8, 10].
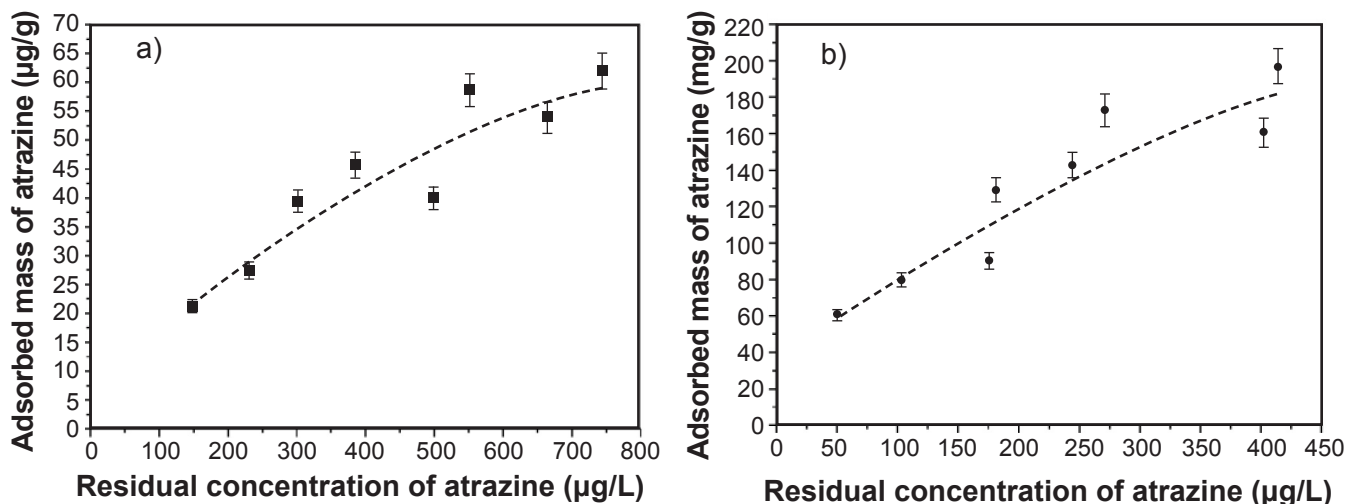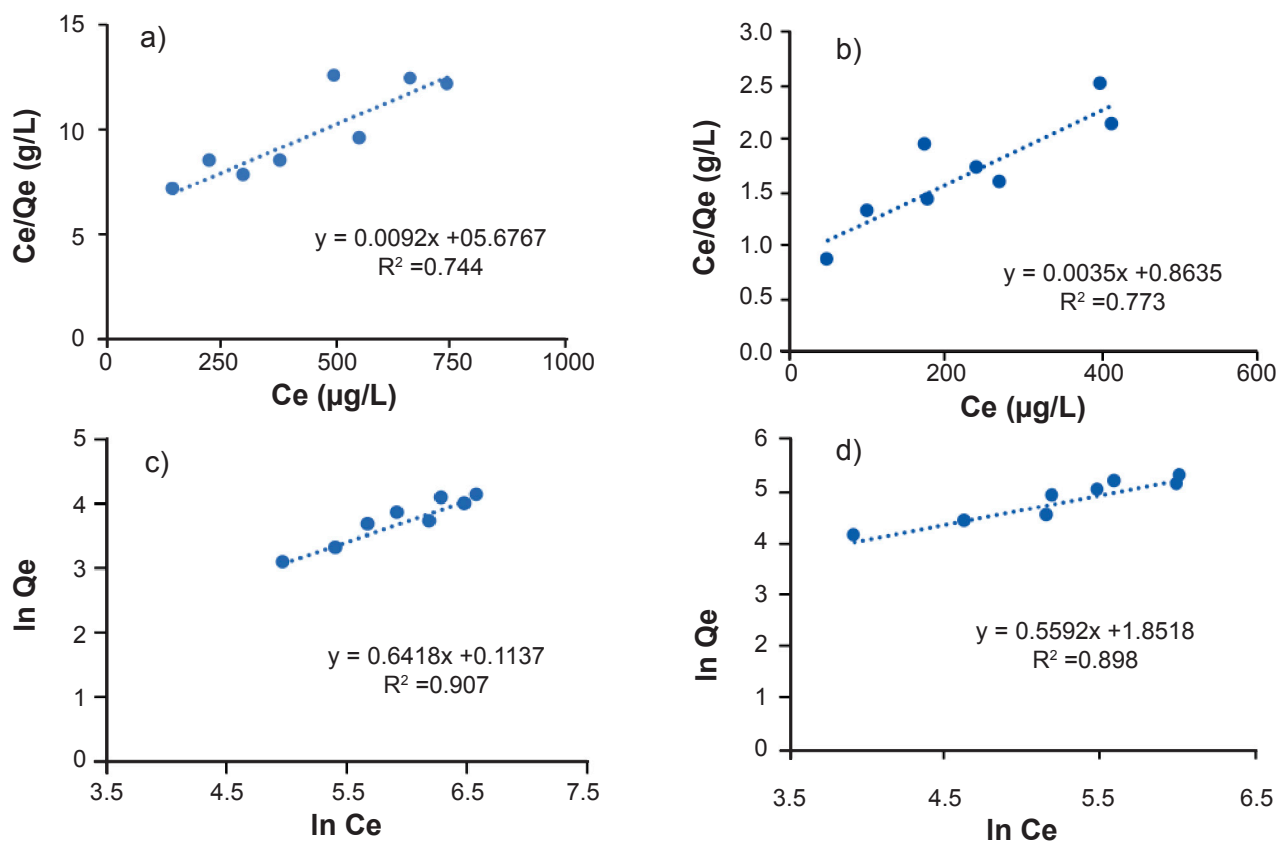
Adsorption results of atrazine by in natura and organophilic clays: the organophilic clay selected for the adsorption of atrazine was A1 and its adsorption capacity was compared with the *in natura* clay. The amount of atrazine adsorbed by the mass of the adsorbents is presented by the adsorption isotherms shown in Fig. 4a (*in natura* clay as adsorbent) and Fig. 4b (A1 clay as adsorbent). The adsorptive capacities (Qe), calculated by Eq. B [17-21] for each point, were obtained from the initial concentrations (Ci) and the residual concentrations of atrazine (Ce), which were detected in HPLC. From Fig. 4, it is observed that A1 clay exhibited an adsorption capacity much higher than *in natura* clay. Subsequently, the isotherms in Fig. 4 were studied from the linearized equations for the Langmuir (Eq. C) and Freundlich (Eq. D) isotherm models [21, 22] of the clay adsorption assays. K_L (L/g) is the Langmuir constant, Qe is the amount of adsorbate per unit mass of adsorbent, b is the constant of proportionality and K_F is the Freundlich constant. The linearized results for the atrazine adsorption by the *in natura* and A1 clays are displayed in Figs. 5a and 5b for Langmuir equation, and in Figs. 5c and 5d for the Freundlich equation.

$$Qe = \frac{(Ci-Ce).\ Volume\ of\ solution}{Mass\ of\ clay} \qquad (B)$$

$$\frac{Ce}{Qe} = \frac{1}{b.K_L} + \frac{1}{K_L}\ Ce \qquad (C)$$

$$\ln Qe = \ln K_f + \frac{1}{n}\ \ln Ce \qquad (D)$$

Table III shows the adsorption parameters for the linear adjustment of these isotherms obtained for the *in natura* and organophilic A1 clays. The model that best fitted the experimental data was the Freundlich model, which suggested that the adsorption of atrazine occurred in multilayers by both *in natura* and A1 clays. According to the literature, the constant 1/n indicates how spontaneous and strong the adsorption is, that is, the existence of affinity between the adsorbate and the adsorbent. Thus, the lower 1/n, the greater the adsorption force. In addition, their values must be between 0 and 1, for the adsorption to be considered favorable [23-25]. The 1/n value of A1 clay was the lowest, indicating that it adsorbed atrazine more strongly than *in natura* clay. The K_F value (Table III) was greater for A1 clay, indicating that its atrazine adsorption capacity was higher than *in natura* clay. Therefore, the organophilic A1 clay proved to be an adsorbent with a performance far superior to the *in natura* clay, validating and confirming the importance of the organophilization process. Reported studies [25-27] show that the Freundlich isotherm is the function that best fits the data related to the adsorption of contaminants in water treatment processes, in line with the obtained in this study.

Figure 4: Adsorption isotherms of: a) *in natura* clay; and b) A1 clay.

Figure 5: Linearization by Langmuir model (a,b) and Freundlich model (c,d) for the adsorption of atrazine by *in natura* clay (a,c) and A1 clay (b,d).

Table III - Parameters of isotherms *in natura* and organophilic A1 clays.

Clay	Langmuir		Freundlich		
	b	R^2	K_F	1/n	R^2
In natura	108.7	0.74	0.892	0.6418	0.91
A1	285.7	0.77	6.379	0.5592	0.90

CONCLUSIONS

Organophilic clays prepared from the *in natura* bentonite clay were investigated. It is concluded that the clays were obtained satisfactorily and the XRD analysis showed an increase in the basal distance (d_{001}) after the organophilization treatment, confirming the intercalation of quaternary ammonium salt molecules between the lamellae of the clays. The bands shown in the FTIR spectra were characteristic of quaternary ammonium salts and the TG analysis indicated the appearance of an additional mass loss stage, which was associated with the decomposition of organic molecules. Thus, changes in the clays, due to the exchange of inorganic cations for organic cations, led to interlamellar spaces

available for the adsorption of organic contaminants, whose affinity for the clays was confirmed in the adsorption tests. In the study of isotherms for the adsorption of atrazine in aqueous solutions, a higher adsorption performance was achieved by A1 (cetyltrimethylammonium bromide) organophilic clay than the *in natura* clay, pointing to the potential use of this clay for the removal of the organic compounds.

ACKNOWLEDGMENTS

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(Rec. 03/05/2020, Rev. 19/08/2020, 07/12/2020, Ac. 12/12/2020)