

Influence of Thermal Treatment Applied to Fe(III) Polyhydroxy Cation Intercalated Vermiculite on the Adsorption of Atrazine

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Intercalation of vermiculite with Fe(III) polyhydroxy cations at 1:1 and 2:1 [OH⁻]/[Fe(III)] molar ratios increases the affinity of the clay mineral toward atrazine in comparison with potassium saturated vermiculite. The present paper describes the effects of thermal treatments applied to Fe(III) polyhydroxy cations modified vermiculite on the adsorption properties of the clay mineral. Only small changes in the textural characteristics were observed for the materials intercalated with either 1:1 or 2:1 [OH⁻]/[Fe(III)] molar ratios treated at 100 and 250 °C. In comparison with potassium saturated vermiculite, or intercalated vermiculite treated at 100 °C, a significant enhancement in the adsorption of atrazine was observed for the materials treated at 250 and 400 °C, which removed more than 95.8 and 99.5% of the herbicide initially present in a 50.0 μg L⁻¹ aqueous solution, respectively. In comparison with potassium saturated vermiculite and intercalated vermiculite treated at 100 °C, a lower desorption degree of preadsorbed atrazine was observed for both intercalated materials treated at 250 and 400 °C. These findings suggest that the thermal treatment produced modified vermiculite materials with a high adsorption capacity and high affinity toward atrazine, with potential application in the removal of this herbicide, as well as other triazines, from aqueous medium.

KEYWORDS: Clay minerals; intercalation; herbicide; adsorption

INTRODUCTION

Clay minerals in soils play a key role in the geochemical mobility of nutrients and pollutants, as well as in the bioavailability of these compounds to plants and microorganisms. Because of their high surface area and high cation exchange capacity (CEC), clay minerals exert an important control in the runoff of toxic species such as heavy metal ions and agrochemical residues to surface and groundwaters. Several studies have been dedicated to the use of these minerals to remove toxic species from water (1–5). Notwithstanding, low adsorption degrees between the adsorbent and the pollutant (adsorbate) are frequently observed because sometimes both have the same electrical charge or the adsorbent has no specific adsorption sites to interact with the pollutant. Thus, the modification of clay minerals is often an attractive approach to improve their adsorption properties by the insertion of a suitable cation or compound in the interlayer space, aiming to increase the affinity between adsorbent and adsorbate (6–10). Intercalations of either organic cation or polyhydroxy cations derived from trivalent metal ions in the interlayer space are among the most common procedures to modify clay minerals (11).

Celis et al. (8) modified two samples of montmorillonite with several ammonium organic cations to promote the adsorption of the herbicide hexazinone. Insertion of the organic cations provided slow release of the active herbicide, minimizing the leaching of highly mobile herbicides and decreasing the risk of groundwater contamination. Similar modification of montmorillonite with organic ammonium salts was carried out by Carrizosa et al. (12) to remove the ionizable organic pollutants bentazon and dicamba from aqueous samples. Hydrogen bonding between herbicides and monosubstituted amino groups in organoclays produced hydrophobic interactions, suggesting that the organoclays can be used to remove these pollutants from waters or soils. El-Nahhal and Lagaly (13) studied the adsorption of the herbicide linuron onto organobentonites in the presence of several salts. Not only was an increase of linuron uptake verified in comparison with calcium bentonite, but the reduction of the desorption degree also was verified. Saline solutions caused a reduction of the linuron adsorption, but NaI, CsBr, and CsI solutions enhanced the adsorption, a fact that was attributed to the structure breaking properties of iodide or cesium in these salts. Some modified clay minerals work as hybrid sorbents, as demonstrated by Andini et al. (14), who used an organophillic bentonite for the simultaneous adsorption of 2-chlorobenzene, Cd²⁺, and Pb²⁺.

Natural vermiculite has been exploited for the adsorption of heavy metal ions (4, 5, 15), humic substances (16, 17), and oils

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(18, 19). Nevertheless, little attention has been dedicated to the modification of this clay mineral for environmental and agricultural purposes (9, 10, 18–21). Abate and Masini (9) studied the adsorption of the herbicide atrazine and its main metabolites deethylatrazine, deisopropylatrazine, and hydroxyatrazine onto Fe(III) polyhydroxy cations intercalated vermiculite and montmorillonite. Montmorillonite showed an excellent performance, even in its natural form without intercalation, being useful to extract and concentrate the herbicide from aqueous solutions (22). On the other hand, the natural potassium monoionic vermiculite exhibited only poor adsorption affinity by atrazine and metabolites. Intercalation of vermiculite with Fe(III) polyhydroxy cations increased the adsorption of the studied compounds, but this enhancement was not so meaningful. Besides, desorption percentages of atrazine were significantly high from the intercalated vermiculite.

This paper evaluates the influence of thermal treatment applied to vermiculite samples intercalated with Fe(III) polyhydroxy cations with two different $[\text{OH}^-]/[\text{Fe(III)}]$ molar ratios to remove atrazine from aqueous solutions, aiming at the development of materials capable of minimizing the leaching of this herbicide to surface or groundwaters.

MATERIALS AND METHODS

Apparatus and Reagents. An LC 9A Shimadzu (Tokyo, Japan) high-performance liquid chromatograph (HPLC), equipped with an SPD 6 AV UV detector adjusted at the wavelength of 220 nm, and the LC Workstation Class-LC 10 software, was employed in all experiments for atrazine quantification. An SB C18 Zorbax (Santa Clara, CA) column (3.5 μm , 150 mm \times 4.6 mm) connected to a C18 Phenomenex (Torrance, CA) guard column was used. Sample injection was made with a rotary Rheodyne (Rohnert Park, CA) valve using a 0.020 cm^{-3} sample loop. A Metrohm 654 (Herisau, Switzerland) potentiometer (resolution of 0.1 mV or 0.001 units of pH), coupled to an Ag/AgCl (KCl saturated) combination glass electrode, was utilized for the preparation of the buffer ammonium acetate and acetic acid and for all pH measurements. An orbital shaker from Marconi (Piracicaba, São Paulo, Brazil) with thermostatic control at 25.0 ± 0.1 °C was used in the batch adsorption experiments. Surface area and pore volume were obtained from BET measurements of N_2 adsorption isotherms using a Gemini 2375 V5.00 instrument from Micromeritics Instrument Corp. (Norcross, GA). The basal spacing was determined by X-ray diffraction (XRD) using a Siemens D-5000 diffractometer (Munich, Germany).

The analytical standard of AT (99.2%) was purchased from Riedel-de Haën (Honeywell Riedel-de Haën, Seelze, Germany). A 500.0 mg dm^{-3} stock solution of the atrazine standard was prepared in methanol and stored in a freezer at -18 °C. Acetonitrile (ACN) and methanol, both of HPLC grade, were supplied by JT Baker (Mallinckrodt Baker do Brasil Ltda., São Paulo, Brazil). Ammonium acetate and acetic acid were purchased from Merck (Rio de Janeiro, Brazil). Water used in all experiments was distilled and deionized using the Simplicity 185 system from Millipore (São Paulo, Brazil) coupled to a UV lamp. All other reagents used in this work were of analytical grade.

Vermiculite Sample. Vermiculite clay mineral was supplied by Eucatex Química e Mineral Ltda. from the Massapê mine located in Paulistana, Brazil, in grain sizes of <1 mm. The preparation and purification of this sample were performed according to Abate and Masini (17). The CEC was determined by the method of sodium saturation (23), resulting in a value of 1.17 ± 0.01 mmol g^{-1} . This CEC value is consistent with the range between 1.0 and 1.5 mmol g^{-1} that has been reported for vermiculites (31). For comparison purposes, CEC of illites ranged from 0.10 to 0.40 mmol g^{-1} , whereas smectites, another 2:1 clay mineral such as vermiculite, had CEC values between 0.7 and 1.2 mmol g^{-1} (31).

Intercalation Procedure. Crude vermiculite was ground, and the particles with sizes between 0.27 and 56 μm (17) were washed with 0.050 mol dm^{-3} HCl and treated with 1.0 mol dm^{-3} KCl solution to obtain a potassium homoionic clay mineral (KVT). All details of these

operations are described elsewhere (9, 10). KVT was dispersed in deionized water, and the concentration of the stock suspension was determined by the dry weight of 1.00 cm^3 homogenized aliquots. The modification of KVT was performed under two conditions, using intercalating suspensions prepared with 1:1 and 2:1 $[\text{OH}^-]/[\text{Fe(III)}]$ molar ratio suspensions, as described by Abate and Masini (9). Both modified clay minerals and KVT were freeze-dried, crushed, and dried in an oven at 100 °C for 24 h. A part of the modified adsorbent phases was treated in a muffle furnace at 250 or 400 °C for 3 h. All samples including KVT were stored in a desiccator. Intercalated vermiculites prepared with a 1:1 $[\text{OH}^-]/[\text{Fe(III)}]$ molar ratio suspension, treated at 100, 250, or 400 °C, were identified by VT–OH/Fe1:1₍₁₀₀₎, VT–OH/Fe1:1₍₂₅₀₎, and VT–OH/Fe1:1₍₄₀₀₎, respectively. Analogously, VT–OH/Fe2:1₍₁₀₀₎, VT–OH/Fe2:1₍₂₅₀₎, and VT–OH/Fe2:1₍₄₀₀₎ were the notations assigned to the clay minerals prepared with the 2:1 $[\text{OH}^-]/[\text{Fe(III)}]$ molar ratio suspensions.

Adsorption and Desorption Experiments. A mass of 30 mg (± 0.1 mg) of each adsorbent was weighed in seven glass vials with a capacity of 4 mL. After that, 3.00 cm^3 of atrazine solution, with concentrations between 50.0 and 1000 $\mu\text{g dm}^{-3}$, was added to glass vials, which were closed, protected from light, and kept under gentle agitation for 24 h in an thermostatic orbital shaker programmed at 140 rpm and 25.0 ± 0.1 °C. A blank solution and five standards with concentrations between 5.00 and 500 $\mu\text{g dm}^{-3}$ were treated in the same way, simultaneous to the samples. After 24 h of contact time, the pH of the suspensions was measured, and the solid phases were separated by centrifugation for 15 min at 2600g. Next, 2.70 cm^3 of the supernatant was withdrawn and filtered through a 0.45 μm Durapore membrane Millex from Millipore (São Paulo, Brazil). These solutions were buffered with 1.0 mol dm^{-3} ammonium acetate buffer (pH 4.5) using a volume suitable to give a final concentration of 2.5 mmol dm^{-3} . The atrazine concentrations were determined by HPLC under isocratic elution using a mobile phase composed of 50% (v/v) acetonitrile/water, with the aqueous phase being constituted by 2.5 mmol dm^{-3} ammonium acetate buffer (pH 4.5). The UV detector was set at a wavelength of 220 nm. Under these HPLC conditions, the retention time observed for atrazine was 4.19 min.

To evaluate the desorption degree, 2.70 cm^3 of deionized water was added to each one of the vials containing the solid phases and the remaining 0.30 cm^3 of atrazine solution was used to construct the adsorption isotherm. A second 24 h agitation cycle was carried out. This step is analogous to the approach proposed by Moorman et al. (24) to evaluate the atrazine desorption from soils and sediments. Quantification of atrazine was performed by the previously described HPLC method. Adsorption data were treated by the linearized Freundlich equation

$$\log_{10} Y = \log_{10} K_f + \frac{1}{n} \log_{10} c \quad (1)$$

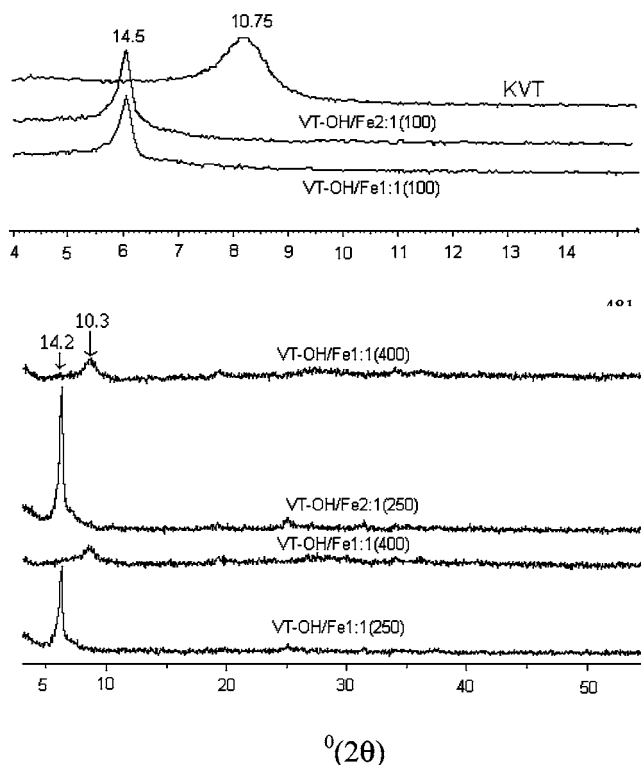
In eq 1, K_f and $1/n$ are empirical constants related to adsorption capacity and heterogeneity, respectively, c is the concentration of atrazine in solution ($\mu\text{mol dm}^{-3}$) after 24 h of contact time, and Y is the amount of adsorbed atrazine (μmol) per amount of adsorbent mass (kg).

RESULTS AND DISCUSSION

Sample Characterization. Table 1 shows the results of surface area, pore and micropore volumes, and basal spacing, $d(001)$, of the studied materials. An increase in the basal spacing is verified as a consequence of the interaction with Fe(III) polyhydroxy cations, followed by thermal treatments at 100 and 250 °C. The XRD spectra of these materials (Figure 1) exhibit well-defined narrow peaks, suggesting that vermiculite was intercalated by the polyhydroxycations of Fe(III), without the occurrence of heterogeneous structures. At 400 °C, an unambiguous diminution of the basal spacing to 10.3 Å was verified, as well as decrease in the peak intensity (Figure 1). This behavior at high temperatures was also observed for pillared smectites (25, 26) and vermiculites treated above 400 °C, a fact

Table 1. Surface Area (BET), Pore and Micropore Volumes, and Basal Spacing $d(001)$ of the Adsorbents

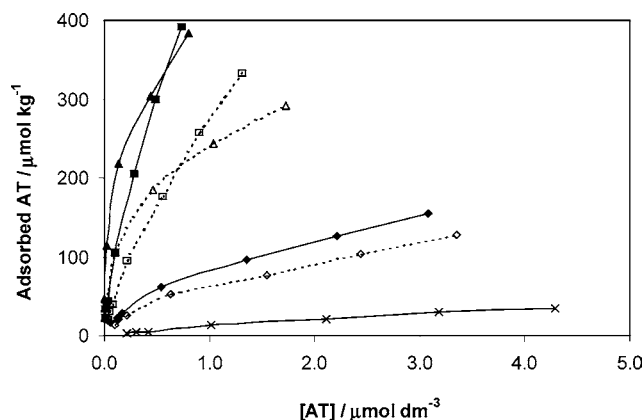
material	BET ($\text{m}^2 \text{g}^{-1}$)	pore volume ($\text{cm}^3 \text{g}^{-1}$)	micropore volume ($\text{cm}^3 \text{g}^{-1}$)	$d(001)$ (\AA)
KVT ^a	31.4 ± 0.1	0.014	0.002	10.8
VT-OH/Fe1:1 ₍₁₀₀₎ ^a	43.1 ± 0.1	0.019	0.004	14.5
VT-OH/Fe1:1 ₍₂₅₀₎	50.5 ± 0.1	0.022	0.004	14.2
VT-OH/Fe1:1 ₍₄₀₀₎	49.2 ± 0.1	0.021	0.003	10.3
VT-OH/Fe2:1 ₍₁₀₀₎ ^a	52.1 ± 0.1	0.022	0.004	14.5
VT-OH/Fe2:1 ₍₂₅₀₎	46.3 ± 0.1	0.020	0.003	14.2
VT-OH/Fe2:1 ₍₄₀₀₎	44.1 ± 0.1	0.019	0.003	10.3

^a Results from ref 9.**Figure 1.** X-ray diffractograms of the potassium homionic vermiculite (KVT) in comparison with the vermiculite materials modified with Fe(III) polyhydroxy cations (VT-OH/Fe) prepared by interaction with 1:1 or 2:1 [OH⁻]/[Fe(III)] molar ratio intercalating suspensions. The obtained solid materials were thermally treated at 100, 250, or 400 °C.

that has been attributed to dehydration and dehydroxylation of the pillars during the thermal treatment (27). According to Pergher et al. (28), the thermal treatment of an aluminum-pillared montmorillonite sample at temperatures higher than 750 °C caused complete structural destruction at 900 °C. The authors suggest 450 °C as the suitable temperature for pillarization.

Interaction with Fe(III) polyhydroxy cations increased the surface area and pore and micropore volumes in comparison with KVT (Table 1), but this increase was modest as compared with the ones observed by del Rey-Perez-Caballero and Poncet (27) for Al-pillared vermiculites. These authors found about a 10-fold increase in surface area as a consequence of the development of microporosity accompanying the introduction of Al pillars between the layers.

Increasing the temperature from 100 to 250 °C caused an unambiguous increase in the BET surface area from 43 $\text{m}^2 \text{g}^{-1}$ for VT-OH/Fe1:1₍₁₀₀₎ to 51 $\text{m}^2 \text{g}^{-1}$ for VT-OH/Fe1:1₍₂₅₀₎, but

**Figure 2.** Adsorption isotherms of AT onto vermiculite materials. (x) KVT; (◆,◇) VT-OH/Fe1:1₍₁₀₀₎ and VT-OH/Fe2:1₍₁₀₀₎; (■,□) VT-OH/Fe1:1₍₂₅₀₎ and VT-OH/Fe2:1₍₂₅₀₎; and (▲,△) VT-OH/Fe1:1₍₄₀₀₎ and VT-OH/Fe2:1₍₄₀₀₎. Continuous and dotted lines refer to VT-OH/Fe1:1 and VT-OH/Fe2:1, respectively, except for KVT. Initial concentrations of atrazine between 50.0 and 1000 $\mu\text{g L}^{-1}$; concentration of the vermiculite suspensions 10.0 g L^{-1} ; contact time 24 h at 25.0 ± 0.1 °C. The points are mean values of adsorption experiments made in duplicate.

increasing the temperature to 400 °C caused a non-distinct diminution to 49 $\text{m}^2 \text{g}^{-1}$ in VT-OH/Fe1:1₍₄₀₀₎ (Table 1). This behavior was not verified for VT-OH/Fe2:1, for which a clear reduction in the surface area was observed with the increase in temperature. The pore volume did not show significant variation as a consequence of thermal treatment, while a small decreasing of micropore volume was observed at 400 °C, at least for VT-OH/Fe2:1. This effect may be related to the sintering of the pillars (29), although there is no information if this temperature is high enough to promote this effect. Khalaf et al. (26) did not verify variations in the textural characteristics of Al-pillared bentonites until 310 °C, but the heating at 505 °C caused a slight reduction in the microporosity as a consequence of a decrease in the interlayer spacing. According to del-Rey-Perez-Caballero and Poncet (27), increases in surface area, pore volume, and microporosity were observed for aluminum-pillared vermiculites up to 500 or 600 °C, depending on the sample. Notwithstanding, above these temperatures, a structural rearrangement of the interlayer material takes place because of dehydroxylation processes.

Adsorption and Desorption of Atrazine with Vermiculite. Initial atrazine concentrations between 50.0 and 1000 $\mu\text{g dm}^{-3}$ (0.232 and 4.64 $\mu\text{mol dm}^{-3}$) were used to construct the adsorption isotherms shown in Figure 2. Adsorption on KVT was weak, with a maximum removal of approximately 10% of atrazine from a 50.0 $\mu\text{g dm}^{-3}$ solution. A significant increase in adsorption can be verified for the intercalated samples treated at 100 °C, for which adsorption percentages between 74 and 34% (VT-OH/Fe1:1₍₁₀₀₎) and between 60 and 30% (VT-OH/Fe2:1₍₁₀₀₎) were observed for initial atrazine concentrations of 50.0 and 1000 $\mu\text{g dm}^{-3}$, respectively. The adsorption mechanism of atrazine onto soils and clay minerals has been assigned to the protonation of atrazine either in the interlayer or in the surface waters of the clay minerals, followed by electrostatic interaction of an atrazine cation with negative charges of the mineral surface (30). This hypothesis has been confirmed for other weak bases (8). Figure 3 shows the reaction scheme for atrazine protonation (31).

Heating at 250 and 400 °C enhanced the adsorption of atrazine onto the modified vermiculite in comparison with the materials heated at 100 °C (Figure 1). VT-OH/Fe1:1₍₂₅₀₎ and

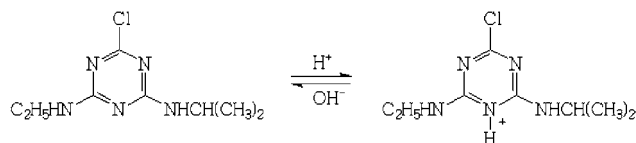


Figure 3. Reaction scheme showing atrazine protonation.

Table 2. Results^a of Atrazine Adsorption Percent onto KVT and Modified Vermiculite

samples	adsorption (%)	
	first point (50.0 g dm ⁻³)	last point (1000 g dm ⁻³)
KVT ^b	10 ± 1	7.5 ± 0.4
VT-OH/Fe1:1 ₍₁₀₀₎ ^b	74 ± 6	34 ± 1
VT-OH/Fe1:1 ₍₂₅₀₎	95.8 ± 0.1	84.2 ± 0.2
VT-OH/Fe1:1 ₍₄₀₀₎	>99.0 ^c	82.7 ± 0.1
VT-OH/Fe2:1 ₍₁₀₀₎ ^b	60 ± 4	30 ± 1
VT-OH/Fe2:1 ₍₂₅₀₎	86.8 ± 0.1	71.8 ± 0.1
VT-OH/Fe2:1 ₍₄₀₀₎	99.1 ± 0.6	62.8 ± 0.2

^a The results are the average of duplicate of experiments and express the adsorption of atrazine between the first and the last point of the adsorption curves.

^b Results from ref 9. ^c Result limited by the limit of detection (0.50 μg dm⁻³) of the HPLC method.

VT-OH/Fe1:1₍₄₀₀₎ showed the best results, with the isotherms resembling a hybrid case between H-type (high affinity) and L-type (Langmuir), indicative of chemisorption (31). Also, VT-OH/Fe2:1₍₂₅₀₎ and VT-OH/Fe2:1₍₄₀₀₎ showed high adsorption percentages, exhibiting L-type isotherms. Both modified materials treated at 400 °C have a higher adsorption at the outset of the curves. However, a clear diminution of their slopes is observed, especially for VT-OH/Fe2:1₍₄₀₀₎. This behavior indicates that the materials treated at 250 °C have a higher number of available adsorption sites, although materials prepared at 400 °C have higher affinity by atrazine, at least for initial concentrations up to 100 μg L⁻¹, which is denoted by the higher slope of the adsorption isotherms (Figure 2). Table 2 shows the percentage of atrazine adsorption for the first (50.0 μg dm⁻³) and last point (1000 μg dm⁻³) of the isotherms, evidencing the better performance of the modified materials treated at 250 and 400 °C in comparison with the ones treated at 100 °C, even for the initial concentration of 1000 μg dm⁻³.

As mentioned before, protonation of atrazine plays a key role in the adsorption process. The pH of the VT-OH/Fe1:1₍₁₀₀₎, VT-OH/Fe2:1₍₁₀₀₎, and KVT suspensions after a contact time of 24 h were 3.67, 4.31, and 7.14, respectively. Abate and Masini (9) verified that the diminution of pH by adding a strong acid to KVT suspensions caused a significant increase in the adsorption of atrazine, at levels comparable to the ones shown by intercalated VT-OH/Fe1:1₍₁₀₀₎ and VT-OH/Fe2:1₍₁₀₀₎ materials. This fact corroborates with the hypothesis that the adsorption enhancement of the intercalated vermiculites is a consequence of the increased acidic intensity caused by the highly hydrolyzable Fe(III) species either in the interlamellar spacing or adsorbed on the external surface.

After 24 h of contact time, the suspension pH of VT-OH/Fe1:1₍₂₅₀₎, VT-OH/Fe1:1₍₄₀₀₎, VT-OH/Fe2:1₍₂₅₀₎, and VT-OH/Fe2:1₍₄₀₀₎ was 3.56, 4.72, 4.23, and 5.62, respectively. Higher temperatures imply dehydration and dehydroxylation of the pillars, as well as of silanol and aluminol groups of the clay surface, having as a consequence, a decreasing in Brönsted and Lewis acidity (32). On the other hand, extremely high surface acidity is expected in clay surfaces that have been dried, especially if the clay is intercalated with highly hydrolyzable polyhydroxy cations of Fe(III) or Al(III). As a result, the surface

Table 3. Adsorption Freundlich Parameters for Interaction between Atrazine and Adsorbent Phases

adsorbents	K_f (mol ^{1-1/n} dm ^{3(1/n)} kg ⁻¹)	1/n	r
KVT ^a	10.5 ± 0.7	0.90 ± 0.05	0.992
VT-OH/Fe1:1 ₍₁₀₀₎ ^a	78 ± 4	0.61 ± 0.04	0.992
VT-OH/Fe1:1 ₍₂₅₀₎	475 ± 5	0.66 ± 0.01	0.997
VT-OH/Fe1:1 ₍₄₀₀₎	434 ± 27	0.38 ± 0.06	0.994
VT-OH/Fe2:1 ₍₁₀₀₎ ^a	62 ± 3	0.63 ± 0.03	0.996
VT-OH/Fe2:1 ₍₂₅₀₎	277 ± 1	0.75 ± 0.01	0.999
VT-OH/Fe2:1 ₍₄₀₀₎	236 ± 7	0.39 ± 0.04	0.992

^a Results from ref 9.

hydrogen ion activity is much higher than suggested by the pH measured in the bulk suspension (31). Thus, the clay surface and associated water molecules may work as proton donors to a greater extent than indicated by the pH of the clay suspension. These protons react with the amino groups of s-triazines, even when the pH of the aqueous solution is above the pK_a of the herbicide (33), as shown in Figure 3. Therefore, under this situation, atrazine protonation is the mechanism responsible for the adsorption process, even if the basal spacing and textural characteristics are not suitable, as observed in the present results. Bandoz and Cheng (25) studied a smectite modified with Fe(III) polycations, verifying that the materials did not suffer chemical changes with the thermal treatment at 200 °C, having two pK_a values of 5.2 and 8.5, which were assigned to hydroxyl-iron complexes and mineral layers, respectively. Heating at 400 and 600 °C caused a dramatic increase in the variety of acidic groups in the surface of the clay along with an increase in their strength. Sites with pK_a values near 3.2–3.7 with relatively high concentrations were formed upon heating, being assigned to inner-sphere complexes between Fe(III) with oxygen atoms from silicate layers. Bandoz and Cheng (25) reported an increase in the pH of the bulk suspension from 3.5 or 3.6 for materials treated at 200 °C and to 6.4 or 6.8 for treatment at 600 °C, even after the generation of the sites with pK_a values between 3.2 and 3.7. Similar processes may be occurring with the thermally treated intercalation Fe(III) polyhydroxy cation vermiculite, explaining the strong interaction with atrazine even without a significant increase in the basal spacing.

Table 3 shows the Freundlich parameters related to adsorption capacity (K_f) and heterogeneity (1/n), together with the correlation coefficients (r), which were >0.99, denoting good fitting of the experimental data to the Freundlich equation. KVT markedly shows the lowest K_f , confirming the negligible adsorption process with atrazine, as well as the 1/n value approaching the unity because of the small heterogeneity of the adsorption sites. The K_f values for VT-OH/Fe1:1 were higher than the ones determined for VT-OH/Fe2:1, denoting the larger adsorption capacity of the former. This finding is consistent with the higher acidity of the 1:1 [OH⁻]/[Fe(III)] molar ratio intercalating suspension, as well as with the hypothesis of atrazine protonation on the clay mineral surface. A slight decrease in the adsorption capacity parameter is verified for both modified materials treated at 400 °C in comparison with the ones treated at 250 °C, a fact that may be related to the decrease in basal spacing and an increase of pH. For materials obtained at higher temperatures, the 1/n values were near 0.4, suggesting an increase in the site heterogeneity, in agreement with the findings of Bandoz and Cheng (25).

Atrazine desorption from KVT was not studied because of the weak interaction between the clay mineral and the herbicide (9). Figure 4 shows desorption percentages obtained in relation

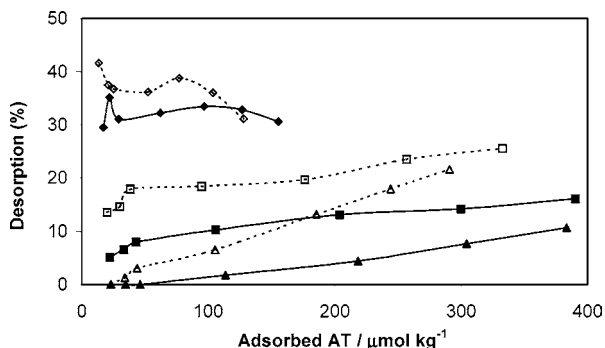


Figure 4. Desorption curves of AT from vermiculite materials. (◆,◇) VT-OH/Fe1:1₍₁₀₀₎ and VT-OH/Fe2:1₍₁₀₀₎; (■,□) VT-OH/Fe1:1₍₂₅₀₎ and VT-OH/Fe2:1₍₂₅₀₎; and (▲,△) VT-OH/Fe1:1₍₄₀₀₎ and VT-OH/Fe2:1₍₄₀₀₎. Initial concentrations of atrazine in the adsorption study between 50.0 and 1000 $\mu\text{g L}^{-1}$; concentration of the vermiculite suspensions 10.0 g L^{-1} ; contact time 24 h at 25.0 ± 0.1 °C. The points are mean values of desorption experiments made in duplicate.

Table 4. Desorption Freundlich Parameters for Interaction between Atrazine and Adsorbent Phases

adsorbents	K_f ($\text{mol}^{1-1/n}$ $\text{dm}^{3(1/n)} \text{kg}^{-1}$)	$1/n$	r
KVT ^a	not studied	not studied	not studied
VT-OH/Fe1:1 ₍₁₀₀₎ ^a	145 ± 13	0.86 ± 0.05	0.990
VT-OH/Fe1:1 ₍₂₅₀₎	417 ± 4	0.69 ± 0.01	0.999
VT-OH/Fe1:1 ₍₄₀₀₎	449 ± 1	0.36 ± 0.01	0.999
VT-OH/Fe2:1 ₍₁₀₀₎ ^a	135 ± 13	0.96 ± 0.04	0.995
VT-OH/Fe2:1 ₍₂₅₀₎	265 ± 3	0.78 ± 0.01	0.998
VT-OH/Fe2:1 ₍₄₀₀₎	256 ± 3	0.40 ± 0.01	0.995

^a Results from ref 9.

to the atrazine amount previously adsorbed on the intercalation vermiculites. The most irreversible adsorption was observed for the VT-OH/Fe1:1₍₄₀₀₎ material, for which no detectable atrazine was desorbed in the first three points of the desorption isotherm. Comparing desorption from VT-OH/Fe2:1₍₄₀₀₎ with VT-OH/Fe1:1₍₂₅₀₎, one can observe that the former shows lower desorption percentages at lower amounts of adsorbed atrazine, but the situation is reversed for larger amounts of adsorbate. Comparing materials prepared with similar $[\text{OH}^-]/[\text{Fe(III)}]$ molar ratios, one can observe that, at low degrees of site occupation, lower desorption percentages are obtained from the materials prepared at 400 °C, but the slope of the desorption percentages as a function of adsorbate concentration (Figure 2) is smaller for the materials prepared at 250 °C. This is consistent with the larger adsorption capacities of the materials prepared at 250 °C (Table 3) and with a higher adsorption intensity at low degrees of site occupation for materials prepared at 400 °C. Desorption data were fitted to the Freundlich equation, generating the K_f and $1/n$ parameters shown in Table 4. From the K_f parameter, one can depict the following desorption order: VT-OH/Fe1:1₍₁₀₀₎ \sim VT-OH/Fe2:1₍₁₀₀₎ > VT-OH/Fe2:1₍₂₅₀₎ \sim VT-OH/Fe2:1₍₄₀₀₎ > VT-OH/Fe1:1₍₂₅₀₎ > VT-OH/Fe1:1₍₄₀₀₎. The heterogeneity parameter determined from desorption isotherms is consistent with the ones obtained for adsorption, that is, the modified vermiculites prepared at 400 °C are more heterogeneous than the material prepared at 250 °C, which are more heterogeneous than the materials prepared at 100 °C.

Summarizing, the thermal treatment of the Fe(III) polyhydroxy cations modified vermiculite obtained with 1:1 and 2:1 $[\text{OH}^-]/[\text{Fe(III)}]$ molar ratios enhanced the adsorption of atrazine

in comparison with the natural K homoionic clay mineral. Materials obtained with the 1:1 $[\text{OH}^-]/[\text{Fe(III)}]$ intercalating suspension showed better performance in comparison with the ones prepared using a 2:1 molar ratio, probably as a consequence of the greater acidity conferred to the surface of the modified clay mineral. Thermal treatments at 100 and 250 °C increased the basal spacing, but at 400 °C, the structure may have collapsed, losing its crystallinity, as evidenced by XRD (Figure 1). Although the increase in basal spacing was small or even inexistent, the chemical modification on the vermiculite surface allowed us to obtain adsorbents with strong interactions with atrazine. Therefore, the materials obtained at either 250 or 400 °C have a potential application in the removal of atrazine and other *s*-triazines from waters as well as for soil remediation.

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