

## Removal of fulvic acid from aqueous media by adsorption onto modified vermiculite

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### Abstract

Clay minerals are low cost materials that can be structurally modified and exploited for removal of natural organic matter from freshwaters. The present study shows that vermiculites modified by ion exchange with hexadecyltrimethylammonium or intercalation with poly(hydroxy iron) cations are potential adsorbents for removal of fulvic acid, whereas the adsorption on the raw clay mineral is negligible. The efficiency of the modified vermiculite was evaluated by measuring adsorption isotherms by the batch technique using initial fulvic acid concentrations between 2.5 and 50.0 mg L<sup>-1</sup>, with one hour of contact time. At least 94% of the fulvic acid initially present in a 20 mg L<sup>-1</sup> solution was sorbed onto either the intercalated poly(hydroxy iron) cations or the organically modified vermiculite. Up to an initial concentration of 5.0 mg L<sup>-1</sup> the adsorption is irreversible, and no quantifiable fulvic acid was measured in the desorption experiments. For initial fulvic acid concentrations between 10.0 and 50.0 mg L<sup>-1</sup>, desorption was between 2.3% and 4.9% for Fe(III) intercalated vermiculite, and between 1.4% and 9.2% for the organoclay. The adsorption percentages on intercalated poly(hydroxy iron) cations increased upon lowering pH and increasing the ionic strength, indicating the occurrence of strong binding mechanisms such as ligand exchange. Adsorption percentage of fulvic acid onto the organoclay also increased with lowering of pH, but in this case the adsorption percentages showed a small decrease at high ionic strength, suggesting that electrostatic attraction plays an important role in the adsorption process.

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### 1. Introduction

The removal of natural organic matter (NOM) components from water supplies has demanded great attention because they are precursors of potentially carcinogenic chlorinated disinfection by-products in chlorine disinfection processes (Rook, 1974, 1977; Carvalho et al., 2004; Nikolaou et al., 2004). Besides to adsorption onto activated carbon, adsorption onto clay minerals is

among the main processes that have been studied aiming the removal of NOM from aqueous medium (Teermann and Jekel, 1999; Hagare et al., 2001; Kaneco et al., 2003; Abate and Masini, 2003; Juhna et al., 2003; Katsumata et al., 2003, 2004). Humic and fulvic acid (HA and FA) are the major components of NOM, but HA is more easily removed from waters. This fact has been explained by the intrinsic characteristics of humic substances such as the higher molar volume of humic acids (Vermeer and Koopal, 1998). Contrary to humic acids, fulvic acids do not coagulate even under low pH values, increasing the difficulty of their removal from aqueous medium. The

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lesser extent of fulvic acids adsorption in comparison to humic acids has been reported for tobermorite (Kaneco et al., 2003), xonotlite (Katsumata et al., 2003), and vermiculite (Jelinek et al., 1999).

Interactions between organic substances and raw clay minerals are weak and reversible, so that structural modifications have been described to enhance the adsorption capacity and bond strength. Structural modifications can be achieved by replacing the common interlayer cations, for instance,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Ca}^{2+}$ , by another suitable cation. Typical modifications of clay minerals are the insertion of polynuclear hydroxo iron or aluminum cations, known as pillaring (Wibulswas et al., 1998; Matthes and Kahr, 2000; Jiang et al., 2002), and the ion exchange with organic cations (Sharmasarkar et al., 2000; Jiang and Zeng, 2003; Lee et al., 2004; Cruz-Guzmán et al., 2004). Many of these modified clay minerals have been developed aiming the removal of herbicides from water, or the development of herbicide formulations with controlled release of the active component in soils (Bergaya and Lagaly, 2001).

Vermiculite is available in several commercial mines around the world. Few studies concerning adsorption properties of organic compounds (both natural and synthetic) onto crude (Tarasevich et al., 1996; Jelinek et al., 1999; Abate and Masini, 2003) or structurally modified vermiculites have been described (Hermosin and Cornejo, 1992; Martins and Fernandes, 1992; Vimond-Laboudigue et al., 1996; Dekany et al., 1996). At our best knowledge, no studies have been performed with modified vermiculite aiming the removal of fulvic acid from waters. The present study investigates the adsorption of fulvic acid onto a potassium homoionic vermiculite in comparison with modified vermiculites that were obtained by intercalating poly(hydroxy iron) cations or the hexadecyltrimethylammonium (HDTMA) cation.

## 2. Materials and methods

### 2.1. Apparatus and reagents

The determination of the soluble fraction of fulvic acid (FA) was automated by Sequential Injection Analysis (SIA) (Ruzicka and Marshall, 1990) using a Fialab 3500 (Fialab Instruments, Inc., Bellevue, WA) instrument controlled by the Fialab 5.0 software. The SIA system was coupled to an SPD 6 AV UV ultraviolet flow detector from Shimadzu for fulvic acid (FA) quantification employing the Workstation Class-LC 10 software for data acquisition and peak area integration. A Metrohm 654 potentiometer (precision of 0.1 mV or 0.001 units of pH), coupled to an Ag/AgCl combination glass electrode, was utilized for all pH range. Water used in all experiments was distilled and deionized using the Simplicity

185 system from Millipore coupled to an UV lamp. All reagents used in this work were of analytical grade from Merck, Sigma or Aldrich.

### 2.2. Fulvic acid

The humic material was extracted from a soil rich in organic matter according to the following procedure, which was adapted from the protocol described by the International Humic Substances Society (Thurman and Malcolm, 1981). The soil was grounded to pass through a 2.0 mm sieve, and then equilibrated to a pH value between 1 and 2 with 1 mol  $\text{L}^{-1}$  HCl at room temperature. The solution volume was adjusted with 0.1 mol  $\text{L}^{-1}$  HCl to provide a final concentration that had a ratio of 10 mL of liquid per 1 g of dried sample. The suspension was shaken for 1 h and the supernatant was separated from the residue by centrifugation. The supernatant was saved and labeled “FA Extract 1,” and was further used the isolation of fulvic acid.

The soil residue was neutralized with 1 mol  $\text{L}^{-1}$  NaOH to pH 7.0. Then 0.1 mol  $\text{L}^{-1}$  NaOH was added under a  $\text{N}_2$  atmosphere to give a final extractant to soil ratio of 10 : 1. Extraction was performed by intermittent shaking of the suspension under  $\text{N}_2$  for a minimum of 4 h. The alkaline suspension was allowed to settle overnight, and the supernatant was collected by means of centrifugation at 2600 g. The supernatant was acidified with 6 mol  $\text{L}^{-1}$  HCl with constant stirring to pH 1.0 and then allowed to stand overnight (a period of at least 12 h). The humic acid (precipitate) was separated by centrifugation at 2600 g and the supernatant containing the fulvic acid was saved and labeled “FA Extract 2.”

Supernatant extracts labeled “FA extract 1” and “FA extract 2” were combined and passed through a column of XAD-7 adsorption resin (1.0 mL of resin per gram of initial sample dry weight), which was previously conditioned by 3 successive washings with 0.1 mol  $\text{L}^{-1}$  NaOH and HCl solutions, followed by exhaustive washing with deionized water. The effluents were discarded; as well the washing waters (one column volume of deionized water). The sorbed fulvic acid was back eluted with one column volume of 0.1 mol  $\text{L}^{-1}$  NaOH, followed by two column volumes of deionized water. To protonate the ionizable sites, the FA solution was passed through a strongly acid Amberlyst 15 cation exchange column in the  $\text{H}^+$  form. The concentration of FA stock solution was  $1.07 \pm 0.05$  g  $\text{L}^{-1}$ , determined by dry weight of 20.00 mL aliquots.

### 2.3. Vermiculite

It was supplied by Eucatex Química e Mineral Ltda, from the Massapê mine located in Paulistana, PI, Brazil, with grains <1 mm. This material was ground, and the fraction between 0.27 and 56  $\mu\text{m}$  was separated by decantation according to previously described (Abate and Masini, 2003). A mass of approximately fifteen grams of vermiculite was treated with 0.05 mol  $\text{L}^{-1}$  HCl under agitation in an orbital shaker for 30 min. The solid phase was centrifuged, washed with 80 mL

of deionized water and then equilibrated with 50 mL of 1.0 mol L<sup>-1</sup> KCl solution for 30 min. The solid phase was separated by centrifugation and treated a second time with 50 mL of 1.0 mol L<sup>-1</sup> KCl solution in order to obtain the K<sup>+</sup> homoionic clay mineral (denoted by KVT). Finally, the excess of KCl was eliminated by washing the solid phase with deionized water. The sample was dispersed in approximately 100 mL of deionized water and the concentration of the stock suspension was determined by the dry weight of 1.00 mL homogenized aliquots, resulting 139 g L<sup>-1</sup>. The cation exchange capacity (CEC) was determined by the method of sodium saturation (Hesse, 1971), resulting the value of 1.17 ± 0.01 mmol g<sup>-1</sup> (*n*=3).

#### 2.4. Intercalated vermiculite

An intercalating Fe(III) dispersion was prepared by pumping 50 mL of 0.8 mol L<sup>-1</sup> NaOH solution into 50 mL of 0.4 mol L<sup>-1</sup> FeCl<sub>3</sub> solution at a flow rate of 1.0 mL min<sup>-1</sup> using a peristaltic pump. The reaction medium was maintained under stirring while the NaOH solution was pumped, providing a 2 : 1 molar ratio of [OH<sup>-</sup>] : [Fe(III)]. The solution was maintained at 50 °C for 48 h. Next, the KVT suspension was heated at 50 °C and the intercalating dispersion was added at a flow rate of 1.0 mL min<sup>-1</sup> under strong stirring, providing 10 mmol of Fe(III) per gram of clay mineral. The suspension was left to rest for 72 h. A similar procedure was carried out to provide an intercalating Fe(III) suspension of 0.75 : 1 molar ratio of [OH<sup>-</sup>] : [Fe(III)], and 10 mmol of Fe(III) per gram of KVT. The dispersions in presence of KVT were centrifuged at 1000 *g* for 10 min and the solid phases were washed five times with deionized water. The modified clay minerals were freeze-dried, crushed, dried in an oven at 100 °C for 24 h, and stored in a desiccator. The modified clay minerals prepared with [OH<sup>-</sup>] : [Fe(III)] molar ratios 0.75 : 1 and 2 : 1 were identified as VT-OH / Fe<sub>0.75</sub> : 1 and VT-OH / Fe<sub>2</sub> : 1, respectively (Abate and Masini, 2005).

#### 2.5. Organic vermiculite

This modified clay mineral was prepared by cation exchange with a 10 mmol L<sup>-1</sup> hexadecyltrimethylammonium bromide (HDTMA) solution. A suitable volume of homogenized KVT suspension was added, under vigorous stirring, to a volume of HDTMA solution to provide relations of 0.5 : 1 and 1 : 1 of the Cation Exchange Capacity (CEC) of vermiculite, previously determined as 1.17 mmol g<sup>-1</sup>. The resulting materials obtained with HDTMA:CEC relations of 0.5 : 1 and 1 : 1 were denoted by HDTMA-VT<sub>0.5</sub> and HDTMA-VT<sub>1.0</sub>, respectively. The suspensions were kept under agitation in an orbital shaker for 24 h at room temperature. Next, the supernatant was discarded, and the products were washed five times with 40 mL of deionized water, separating the solid phase by centrifugation. These organoclays were freeze-dried, crushed and dried at 60 °C for 48 h. The last step was repeated for the KVT suspension after a proper separation of the solid phase by centrifugation. The solids were stored in a desiccator.

#### 2.6. Characterization

Surface area and pore volume were obtained by BET measurements of N<sub>2</sub> adsorption isotherms using a Gemini 2375 V5.00 instrument from Micromeritics Instr. Corp. The basal spacing was determined by X-ray diffraction (XRD) using a Siemens D-5000 diffractometer. Iron contents of VT-OH / Fe<sub>0.75</sub> : 1, VT-OH / Fe<sub>2</sub> : 1 and KVT were determined to evaluate the amount of Fe(III) that was incorporated in the modified materials. Iron content in starting and modified vermiculite was determined by flame atomic absorption spectrometry using a Perkin-Elmer 703 spectrometer after proper treatment with 5% (v/v) HCl (Abate and Masini, 2003). Carbon, hydrogen and nitrogen contents of HDTMA-VT<sub>0.5</sub> and HDTMA-VT<sub>1.0</sub> were determined by elemental analysis using a Perkin-Elmer analyzer 2400.

#### 2.7. Contact time

A mass of 30 mg (±0.1 mg) of KVT, VT-OH / Fe<sub>0.75</sub> : 1, VT-OH / Fe<sub>2</sub> : 1, HDTMA-VT<sub>0.5</sub> and HDTMA-VT<sub>1.0</sub> was weighed in seven 4 mL glass vials, and 3.00 mL of a 10.0 mg L<sup>-1</sup> FA solution was added to each one. The flasks were kept under gentle agitation between 1 and 24 h in a closed orbital shaker programmed at 140 rpm and 25.0 ± 0.1 °C. After the programmed contact time was reached, the solids were separated by centrifugation for 10 min at 2600 *g*, and the supernatant phases were filtered using a 0.45 μm Millex Durapore membrane from Millipore. The solution concentration of FA was determined by the monitoring the absorbance peak area at 254 nm. To perform this analysis an aliquot of 20 μL of the sample solution is aspirated by the automated SIA system and then pumped at a flow rate of 16 μL s<sup>-1</sup> toward the detector flow cell using as carrier a 2.5 mmol L<sup>-1</sup> acid acetic/ ammonium acetate buffer with pH 4.5. The sample solution is buffered by overlapping with the carrier solution as it travels through the flow channel toward the detector cell (Ruzicka and Marshall, 1990). The system was previously calibrated with FA solutions prepared in deionized water at concentrations 0.10, 0.25, 0.50, 1.00, 5.00 and 10.0 mg L<sup>-1</sup>.

#### 2.8. Influence of ionic strength and pH

Both parameters were evaluated using 4.0 mL of 50.0 mg L<sup>-1</sup> FA solution and 2.5 g L<sup>-1</sup> of KVT, VT-OH / Fe<sub>0.75</sub> : 1 and HDTMA-VT<sub>1.0</sub>. The pH value was adjusted with 0.1 mol L<sup>-1</sup> HCl or KOH solution. Potassium chloride was used to obtain an ionic medium of 0.010 or 0.10 mol L<sup>-1</sup>. All FA standards were prepared at the same ionic concentration of the adsorption experiment. The vials were kept under shaking for one hour, centrifuged, and analyzed by the sequential injection method (item 2.7).

#### 2.9. Adsorption and desorption isotherms

These experiments were performed in a closed thermostatic orbital shaker programmed at 25.0 ± 0.1 °C. An appropriate

Table 1  
BET specific surface area, porosity, basal spacing  $d(001)$ , iron contents and elemental analysis of the vermiculite materials

Sorbent	Area ( $\text{m}^2 \text{g}^{-1}$ )	Porosity ( $\mu\text{L g}^{-1}$ )	$d$ (001) ( $\text{\AA}$ )	Iron (%)	Elemental analysis (%)		
					C	H	N
VT-OH / $\text{Fe}_{0.75:1}$	48.8	21	14.5	$11.5 \pm 0.6$	–	–	–
VT-OH / $\text{Fe}_{2:1}$	52.1	22	14.5	$10.7 \pm 0.6$	–	–	–
HDTMA- $\text{VT}_{0.5}$	13.7	5.2	13.7	–	11.5	2.78	0.70
HDTMA- $\text{VT}_{1.0}$	11.4	4.2	14.4	–	18.9	4.11	1.18
KVT	31.4	14	10.8	$4.0 \pm 0.1$	–	–	–

mass of the sorbents KVT, VT-OH /  $\text{Fe}_{0.75:1}$  and HDTMA- $\text{VT}_{1.0}$  was weighted in seven glass vials, providing concentrations of  $2.5 \text{ g L}^{-1}$  of each sorbent in the final volume of 4.00 mL. Fulvic acid solutions were added to provide the following initial concentrations: 0.00; 2.50; 5.00; 10.0; 20.0; 35.0 and  $50.0 \text{ mg L}^{-1}$ . This range implies in dissolved organic carbon concentrations (DOC) between 1.2 and  $25.0 \text{ mg L}^{-1}$ , which are within the DOC values found in most river waters around the world (Buffle, 1990). The vials were maintained under agitation for one hour and centrifuged for 10 min at 2600 g. The pH was not controlled, but it was measured two times: just after mixing the FA solution and the sorbent material, and after 1 h of contact time, before centrifuging the samples. After that, 3.80 mL of the supernatants was withdrawn, filtered and analyzed in the sequential injection system. To assess the desorption degree, 3.80 mL of deionized water was added (OECD, 2000) and the vials were closed and

maintained under agitation for 24 h. They were centrifuged, and the supernatant solutions were also analyzed as described in the item 2.7. To construct the desorption isotherm, the equilibrium concentration of adsorbed fulvic acid was computed discounting the mass remaining in the 0.2 mL of solution left in the tube.

### 3. Results

#### 3.1. Characterization

Table 1 shows the characterization parameters for the materials studied. The specific surface area and pore volume of the intercalated clays, VT-OH /  $\text{Fe}_{0.75:1}$  and VT-OH /  $\text{Fe}_{1:1}$ , were enhanced in comparison with KVT. Similarly, the basal spacing increased from 10.8 to 14.5  $\text{\AA}$ , indicating that the vermiculite interlayer space was occupied by the poly(hydroxy iron) cations. This expansion is consistent with the expected behavior of vermiculites (McBride, 1994) although expansion to 18  $\text{\AA}$  has been reported (del Rey-Perez-Caballero and Poncelet, 2000), using Al pillaring solutions. Expansion to 18  $\text{\AA}$  is more common for other smectites such as hectorite, montmorillonite and nontronite (Dramé, 2005). The iron contents of VT-OH /  $\text{Fe}_{0.75:1}$  and VT-OH /  $\text{Fe}_{1:1}$  are almost three times larger than in KVT.

The basal spacing of HDTMA- $\text{VT}_{0.5}$  and HDTMA- $\text{VT}_{1.0}$  were 13.7 and 14.4  $\text{\AA}$ , respectively, suggesting a monolayer of HDTMA, but with contributions of 29 and 39  $\text{\AA}$  (Fig. 1), indicating the presence of paraffin-like interlayer arrangements. The coexistence of both

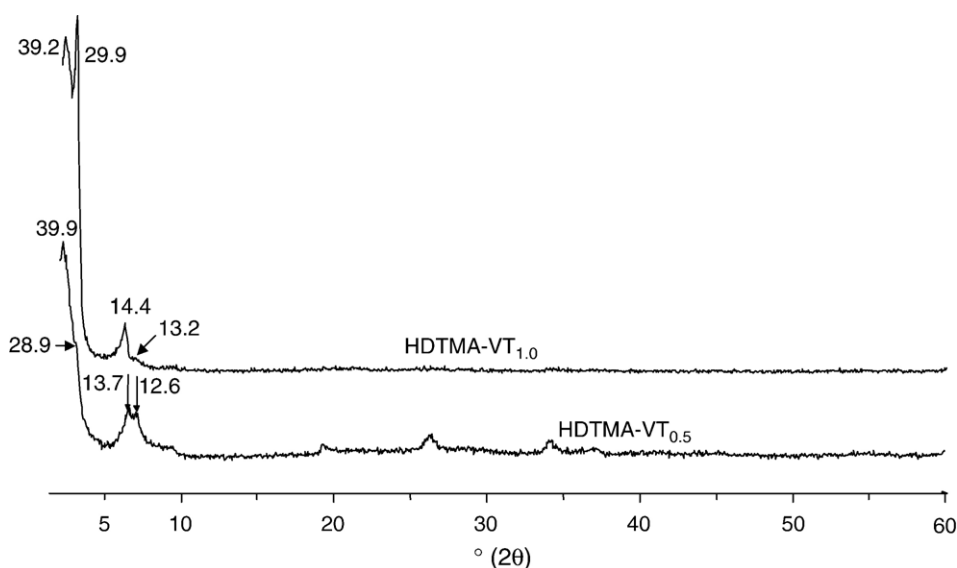


Fig. 1. X-ray diffractogram of organic vermiculites.

reflections may also indicate that the intercalated cations are distributed at the periphery of the vermiculite platelets, leaving the central region un-intercalated by the HDTMA cations. The basal reflections of 2 : 1 minerals with surfactant concentrations of 0.75–1.0 CEC is usually  $>18 \text{ \AA}$  (Lee and Kim, 2002; Slade and Gates, 2004; He et al., 2004). The results obtained in the present work may be a consequence of the procedure used to prepare the modified vermiculite. We used a 24 h equilibration time at room temperature, while other authors have performed the reaction of the vermiculite suspension with HDTMA solutions for time periods from 2 days (Lee and Kim, 2002) at room temperature, up to 14 days under reflux at  $40 \text{ }^\circ\text{C}$  (Slade and Gates, 2004). Thus, it is possible that the HDTMA materials prepared in the present study are not completely intercalated. The surface area and porosity of organically modified vermiculite were greatly reduced because of the incorporation of the HDTMA cations, which clog up the interlayer space, hindering the  $\text{N}_2$  access to the internal surface during the BET experiments. This finding is in agreement with Bartelt-Hunt et al. (2003), who determined surface areas of bentonite samples prepared using several HDTMA ratios, verifying that the surface area decreased with the increase of carbon uptake. The elemental analysis is consistent with the incorporation of C, H and N in the mineral structure because these elements were not detected in the starting material (KVT). The carbon percentages indicate that there is no excess of organic cations in relation to the CEC value.

The elemental analysis of FA resulted 46.8% C, 4.0% H and 1.1% N, with an ash content  $<1\%$ . The absorptivity of the FA at 254 nm was  $(0.0331 \pm 0.0003) \text{ L mg}^{-1} \text{ cm}^{-1}$ . The acid–base properties were studied using a discrete site distribution model (Masini et al., 1998), revealing five kinds of ionizable groups, with  $\text{p}K_a$  values of  $1.9 \pm 0.1$ ,  $4.2 \pm 0.3$ ,  $5.9 \pm 0.1$ ,  $8.2 \pm 0.2$  and  $9.7 \pm 0.1$ . The concentrations of these ionizable groups were  $5.8 \pm 0.4$ ,  $3.2 \pm 0.3$ ,  $1.5 \pm 0.2$ ,  $0.50 \pm 0.08$  and  $0.52 \pm 0.09 \text{ mmol g}^{-1}$ , respectively. Ionizable species with  $\text{p}K_a < 7$  can be assigned to carboxylic groups and species with  $\text{p}K_a > 7$  were assigned to phenolic or amine groups.

### 3.2. Fulvic acid adsorption onto KVT and modified vermiculite

An initial study was performed with the five materials using contact time intervals between 1 and 24 h (Fig. 2). This experiment revealed that the adsorption of FA onto KVT was negligible, and that the apparent equilibrium time for the other materials is reached within less than 1 h. Furthermore, it was verified that intercalated VT–OH /  $\text{Fe}_{0.75 : 1}$  and VT–OH /  $\text{Fe}_{2 : 1}$  retained more than 95% of the  $10.0 \text{ mg L}^{-1}$  FA initial concentration, so that the different  $[\text{Fe}] : [\text{OH}]$  ratios used in the intercalation process did not modify significantly the adsorption performance of the materials. The organically modified HDTMA–VT<sub>0.5</sub> and HDTMA–VT<sub>1.0</sub> adsorbed, respectively, 74% and 98% of the FA initially present in a  $10 \text{ mg L}^{-1}$  solution,

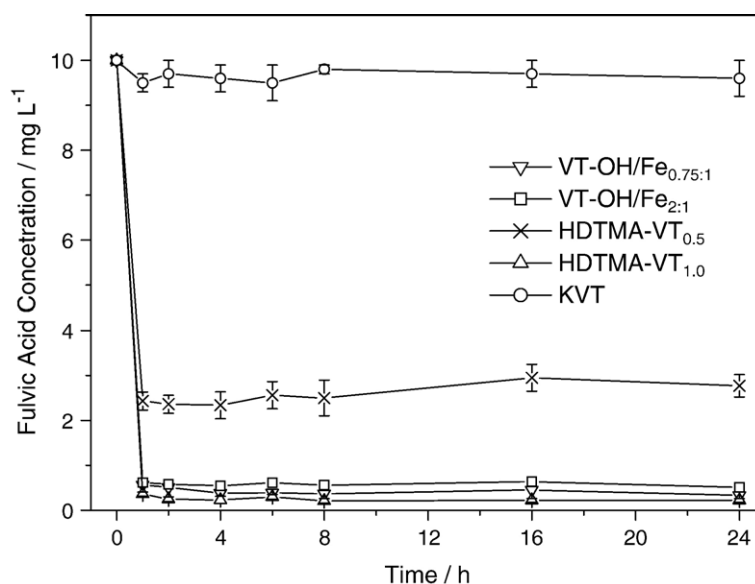


Fig. 2. Solution concentration of fulvic acid after preset contact times with  $10.0 \text{ g L}^{-1}$  suspensions of the five clay minerals studied. Initial fulvic acid concentration =  $10.0 \text{ mg L}^{-1}$ . Error bars are the standard deviation estimate for the average of three experiments.

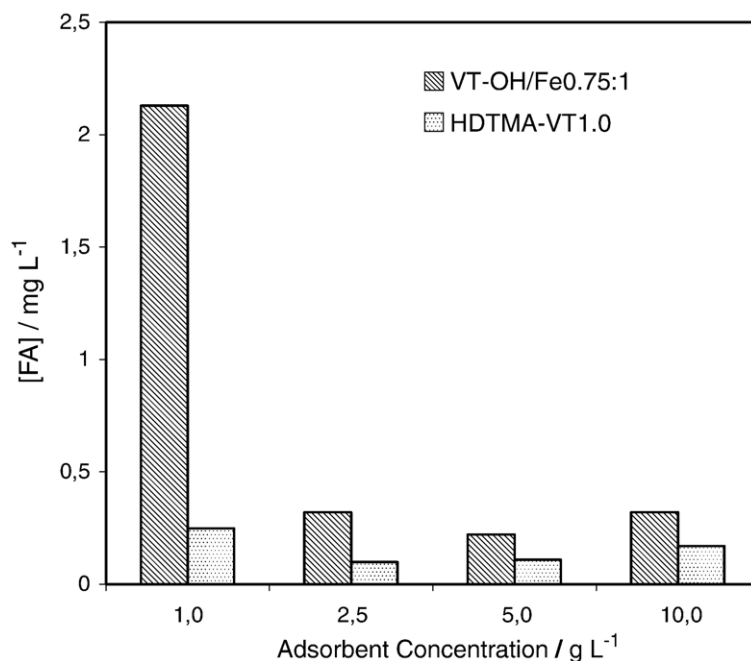


Fig. 3. Influence of adsorbent concentrations on the adsorption percentages observed for an initial FA concentration of  $10.0 \text{ mg L}^{-1}$ .

indicating that the higher amount of HDTMA incorporated in HDTMA–VT<sub>1.0</sub>, compared to HDTMA–VT<sub>0.5</sub>, played a key role in the performance of the material for FA adsorption.

### 3.3. Sorbent concentration

Because of the high efficiency of the  $10 \text{ g L}^{-1}$  suspensions of both VT–OH / Fe<sub>0.75</sub> : 1 and HDTMA–VT<sub>1.0</sub> to remove FA, an experiment was carried out with the suspensions concentrations ranging from  $1.0$  to  $10.0 \text{ g L}^{-1}$  to assess the minimum amount of material that can be used. A contact time of 60 min was used in these experiments. For suspension concentrations between  $2.5$  and  $10.0 \text{ g L}^{-1}$ , the remaining FA solution concentrations were independent of the amount of sorbent (Fig. 3). The FA solution concentration in all experiments was smaller for the suspensions of HDTMA–VT<sub>1.0</sub> material, especially at the sorbent concentration of  $1.0 \text{ g L}^{-1}$ .

### 3.4. Influence of pH and ionic strength on adsorption

Table 2 shows the pH of the suspensions measured just after mixing the protonated FA solution and the vermiculite materials, as well as the pH of the suspensions after 60 min of contact time. Adsorption of FA from a  $50.0 \text{ mg L}^{-1}$  in a  $2.5 \text{ g L}^{-1}$  KVT suspension was less than 2% in any pH studied in the range between

3 and 7 (Fig. 4). Increasing the ionic concentration lead to an increase in adsorption: in ionic medium of  $0.010 \text{ mol L}^{-1}$  KCl, 4.6% of FA was adsorbed onto KVT, but the increase of the ionic concentration to  $0.10 \text{ mol L}^{-1}$  KCl enhanced the adsorption to 16.6% (at pH 4.1). This fact is consistent with mechanism such as ligand exchange rather than electrostatic interactions. The lowering of pH in comparison to the blank is a consequence of the large proportion of FA not adsorbed by KVT.

For both modified vermiculites, VT–OH / Fe<sub>0.75</sub> : 1 and HDTMA–VT<sub>1.0</sub>, the adsorption percentages increased with lowering the solution pH (Fig. 4), a fact that has been observed by other authors studying diverse clay minerals and oxides (Abate and Masini, 2003; Murphy et al., 1990; Schlautman and Morgan, 1994;

Table 2  
pH values of VT–OH / Fe<sub>0.75</sub> : 1, VT–HDTMA<sub>1.0</sub> and KVT suspensions in presence of some FA concentrations

FA concentration (mg L <sup>-1</sup> )	VT–OH / Fe <sub>0.75</sub> : 1		VT–HDTMA <sub>1.0</sub>		KVT	
	pH <sup>a</sup>	pH <sup>b</sup>	pH <sup>a</sup>	pH <sup>b</sup>	pH <sup>a</sup>	pH <sup>b</sup>
Blank	4.35	3.83	7.09	6.06	7.42	7.10
5.0	4.37	3.78	6.55	5.45	7.42	6.78
20	4.38	3.69	5.83	4.37	6.85	5.56
50	4.35	3.46	5.10	3.81	6.41	4.51

<sup>a</sup>pH measured just after mixing the solutions with the clay minerals;

<sup>b</sup>pH measured after 60 min of contact time.

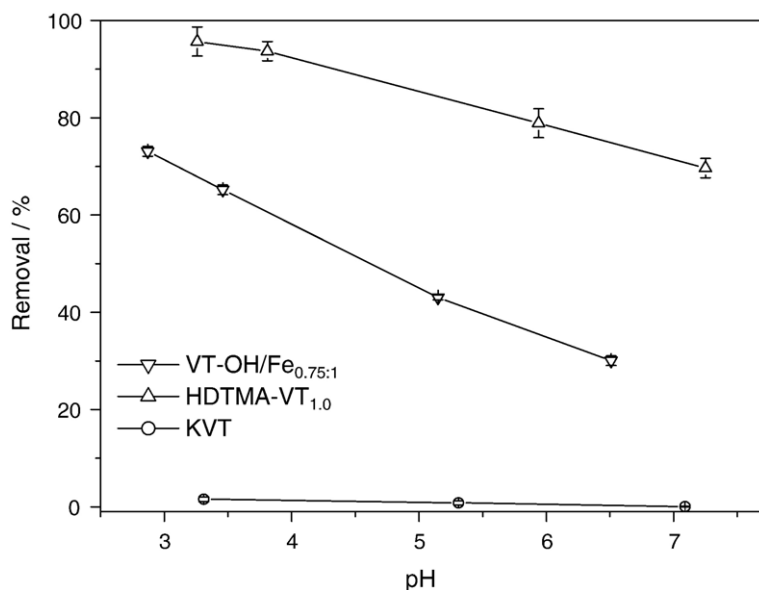


Fig. 4. Influence of pH on the adsorption of FA onto  $2.5 \text{ g L}^{-1}$  suspensions of VT-OH /  $\text{Fe}_{0.75} : 1$ , HDTMA-VT<sub>1.0</sub> and KVT. Initial FA concentration =  $50.0 \text{ mg L}^{-1}$ .

Murphy and Zachara, 1995; Jelinek et al., 1999; Christ and Kretzschmar, 2001). For the VT-OH /  $\text{Fe}_{0.75} : 1$  material the adsorption percentages of FA from a  $50 \text{ mg L}^{-1}$  solution in absence of KCl (pH 3.5) was 65.2%, but this percentage increased to 76.5% and 80.1% upon increasing the ionic concentration to 0.01 and  $0.10 \text{ mol L}^{-1}$  KCl, respectively. For the HDTMA-VT<sub>1.0</sub> material, the adsorption of FA was more intense than observed for VT-OH /  $\text{Fe}_{0.75} : 1$  (Fig. 4). However, whereas the adsorption percentages in absence of KCl was 93.7%, in 0.010 and  $0.10 \text{ mol L}^{-1}$  KCl the adsorption percentages were 94.8% and 89.5%, respectively (at pH 4).

### 3.5. Adsorption and desorption isotherms

Adsorption of FA on the intercalated VT-OH /  $\text{Fe}_{0.75} : 1$  was very strong up to the initial FA concentration of  $5.0 \text{ mg L}^{-1}$ . The remaining solution concentrations of FA were below the limit of quantification of the analytical method ( $0.066 \text{ mg L}^{-1}$ ), implying in more than 98% of adsorption. Adsorption remained high, 98% and 94% for initial FA concentrations 10 and  $20 \text{ mg L}^{-1}$ , respectively. For initial FA concentrations 30 and  $50 \text{ mg L}^{-1}$  the adsorption isotherm shows a significant decrease in the slope (Fig. 5A), with adsorption percentages of 75% and 65%, respectively. Fig. 5A also shows the desorption isotherms. For the experiments performed with initial FA concentrations between 10 and  $50 \text{ mg L}^{-1}$ , the desorption percentages from VT-OH /  $\text{Fe}_{0.75} : 1$  ranged from 2.3% to 4.9% of

the initially amount of adsorbed FA. For the experiments performed with initial FA concentrations up to  $5.0 \text{ mg L}^{-1}$ , no measurable desorption was verified.

The adsorption of FA onto HDTMA-VT<sub>1.0</sub> has an L-type profile (Fig. 5B), reflecting a high affinity between the sorbate and sorbent. The removal of FA was near 94%, even for the most concentrated  $50 \text{ mg L}^{-1}$  FA solution, denoting an excellent adsorption capacity. Despite the more intense adsorption of FA onto HDTMA-VT<sub>1.0</sub>, desorption from this material was also more intense, with percentages ranging between 1.4% and 9.2% (initial fulvic acid concentration between 10.0 and  $50.0 \text{ mg L}^{-1}$ ). As a consequence of the high adsorbed initial concentration and the significant desorption percentage, the desorption isotherm showed an atypical profile, being located below the adsorption isotherm (Fig. 5B).

## 4. Discussion and conclusions

### 4.1. VT-OH / $\text{Fe}_{0.75} : 1$

The intercalation with polyhydroxy cations of Fe(III) caused a significant enhancement of FA adsorption in comparison with the starting KVT material, for which the FA adsorption was negligible. This enhancement may be explained by the increase of the specific surface area, basal spacing and porosity of the modified vermiculite (Table 1). It is worth noticing that even with the decrease of pH at the higher FA concentrations

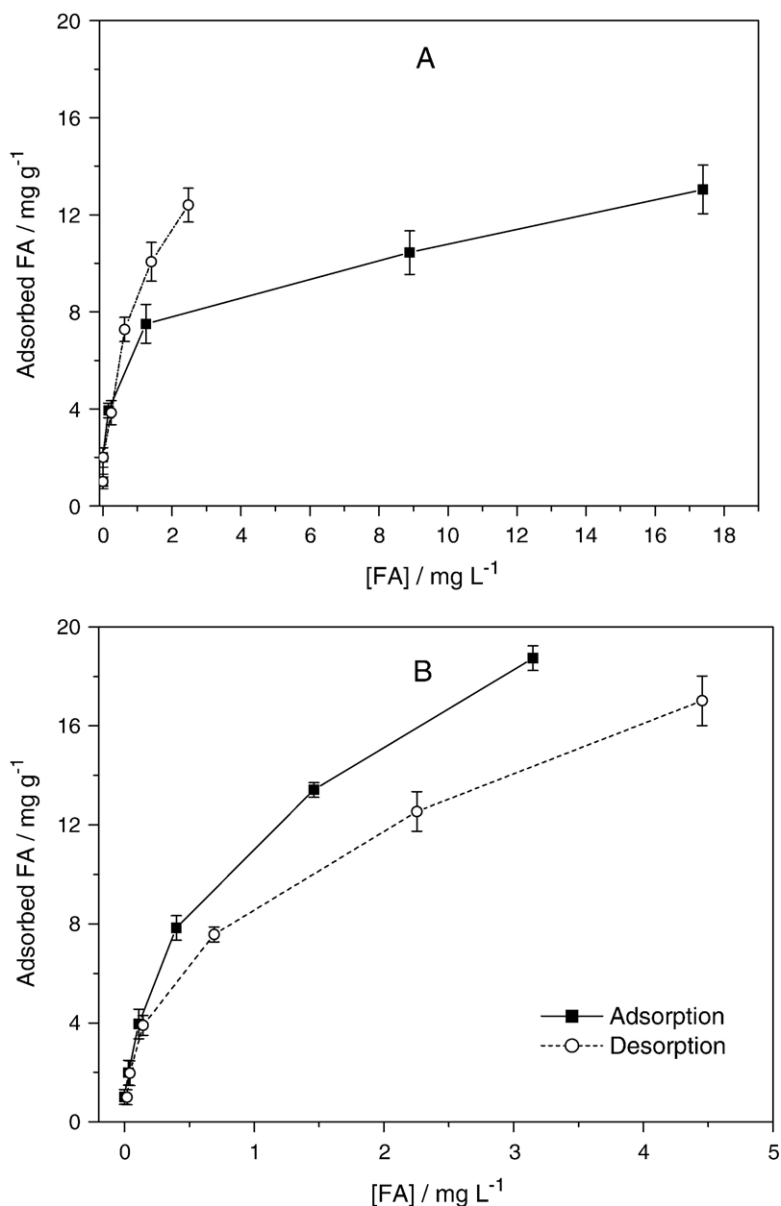


Fig. 5. Fulvic Acid adsorption and desorption isotherms onto VT-OH / Fe<sub>0.75</sub> : 1 (A) and HDTMA-VT<sub>1.0</sub> (B). Results are mean values of three experiments.

(Table 2), a condition that was shown to favor the interactions between FA and both modified vermiculites (Fig. 4), the adsorption isotherm is significantly flattened. The profile of the adsorption isotherm of FA onto VT-OH / Fe<sub>0.75</sub> : 1 (Fig. 5A) is typical for heterogeneous interactions between adsorbate and adsorbent, that is, upon saturation of the stronger binding sites (higher slope) the adsorption is governed by weaker ones, or by non-specific partition mechanisms. This behavior is indicative of a limited number of strong adsorption sites. Hydrogen bonding and coordination of

carboxylic and phenolic groups to the intercalated iron oxide in the interlayer of the clay mineral are possible mechanisms, so that the results suggest that interactions between FA and VT-OH / Fe<sub>0.75</sub> : 1 are governed mostly by chemisorption.

Increase of FA adsorption onto VT-OH / Fe<sub>0.75</sub> : 1 with the increase of ionic strength and decrease of pH may be a consequence of minimizing the electrostatic repulsion between negative segments of FA and the surface of the clay. This finding also suggests that the possible mechanism governing the adsorption is



surface complexation of carboxylic and phenolic groups with the Fe(III) species in the interlayer space, as well as hydrogen bonding between hydroxyl surface groups and carboxylates of FA. The hypothesis of chemisorption is also supported by the low desorption degree, as can be verified in Fig. 5A. For the 20.0 mg L<sup>-1</sup> FA solution, the adsorption percentage of FA onto VT-OH / Fe<sub>0.75</sub> : 1 is near to 94% (pH between 4.4 and 3.7) which is significantly higher than reported for adsorbents such as tobermorite (~60%), Zeolite (~20%) and molecular sieves (~5%) (Kaneco et al., 2003).

#### 4.2. HDTMA-VT<sub>1.0</sub>

Adsorption of the hydrophilic humic and fulvic acids onto HDTMA modified montmorillonite has been attributed to a slight excess of the organic cation retained by the organic clay mineral via hydrophobic bonding, causing charge reversal (Xu and Boyd, 1995; Zhao and Vance, 1998). The extra positive charge would contribute to retention of hydrophilic and negatively charged fulvic acid by the organoclay minerals. In the present study, an excess of organic cations was not measured (Table 1), but this possibility should not be ruled out. This statement is based on the findings of Xu and Boyd (1995), who demonstrated that for HDTMA to CEC ratios higher than 0.5 a significant contribution of hydrophobic adsorption is likely to occur because of the limited access of HDTMA molecules to interlayer sites, resulting in dense packing of HDTMA even at low loading levels, leading to lateral tail to tail HDTMA interactions. Thus, even for HDTMA to CEC ratios lower than 1, the occurrence of these tail to tail hydrophobic interactions is possible, resulting free positive charges that can interact with the negative carboxylate groups of FA. This hypothesis may be represented by the reaction:



where HDTMA-VT represents the organic cation surface exchange complex. One positive charge in the product is developed for each organic cation adsorbed by hydrophobic bonding. These positive charges are neutralized by electrostatic interaction with the carboxylate anions of the fulvic acid:



For the HDTMA-VT<sub>1.0</sub> material, the adsorption of FA was more intense than observed for VT-OH/Fe<sub>0.75</sub> : 1

(Figs. 2–4). However, whereas the adsorption percentages in absence of KCl was 93.7%, in 0.010 and 0.10 mol L<sup>-1</sup> KCl the adsorption percentages were 94.8% and 89.5%, respectively (at pH 4). The small decrease of adsorption measured in 0.10 mol L<sup>-1</sup> KCl can be explained by charge screening, which may weaken the electrostatic attraction between HDTMA and FA with opposite charges. Additionally, adsorption of FA on HDTMA-VT<sub>1.0</sub> was less dependent on pH than VT-OH / Fe<sub>0.75</sub> : 1. This behavior may be related to the high concentration of carboxylic groups with low pK<sub>a</sub>, contributing with permanent negative charges in the range of pH studied.

Both materials studied were very effective to remove FA from solutions with concentrations up to 5.0 mg L<sup>-1</sup> (remaining soluble FA < 0.066 mg L<sup>-1</sup>). Despite the higher adsorption percentages of FA onto the HDTMA-VT<sub>1.0</sub>, the VT-OH / Fe<sub>0.75</sub> : 1 material seems to be more interesting for potential technological applications. This statement is based on the lower desorption of FA from VT-OH / Fe<sub>0.75</sub> : 1 than from HDTMA-VT<sub>1.0</sub>. Additionally, modification of KVT by intercalation with the highly available poly(hydroxy iron) cation is less expensive than using the quaternary ammonium salts.

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