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Interactions of ammonium-smectite with volatile organic compounds from leachates

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ABSTRACT

The percolation of water through waste landfills produces leachates with high ammonium concentrations which can generate ammonium-exchanged clays within geochemical barriers. These leachates also contain several volatile organic compounds (VOCs) that can interact with the clay barrier. The aim of this study was to characterize the sorption of eight short-chain VOCs (acetonitrile, methyl tert-butyl ether, dichloromethane, benzene, phenol, ethanol, acetone, and aniline) on ammonium-smectite, and to identify their sorption mechanisms. The treated samples were characterized by carbon and nitrogen elemental analysis, infrared spectroscopy, powder X-ray diffraction, and thermo-gravimetric analyses. For acetonitrile, methyl tert-butyl ether, dichloromethane, and benzene, no sorption was detected. Phenol, ethanol, and acetone were very weakly sorbed, through Van der Waals interactions. Aniline molecules were strongly sorbed on ammonium-smectite mainly with hydrogen bonds between aniline and interfoliar water molecules. However, aniline sorption decreased the hydrophilic character of the ammonium-smectite, which may increase the permeability of the clay barrier.

Keywords: ammonium, aniline, clay barrier, infrared spectroscopy, montmorillonite, short-chain, sorption, volatile organic compounds, waste landfill, FTIR.

1. INTRODUCTION

In 2013, 30% and 53% of municipal waste was landfilled in Europe (Eurostat, 2015) and the US (EPA, 2015), respectively. The percolation of water through waste landfills, together with the degradation of wastes, produces leachates with high amounts of pollutants. Clay barriers are used in the bottom of these sites to mitigate any pollution in the soil and groundwater. Smectites are mainly selected due to their strong adsorption properties, their low permeability after compaction, their expansion capacity, and their high cation exchange capacity (CEC). The physicochemical composition of the leachates is strongly influenced by the nature of the buried wastes and the age of the site. A young landfill (< 5 years old) produces biodegradable acidic leachates ($4.5 < \text{pH} < 6.5$), a middle-age landfill (5–10 years) is characterized by intermediate neutral leachates ($6.5 < \text{pH} < 7.5$), whereas an old landfill (> 10 years) is identified by stabilized basic leachates ($7.5 < \text{pH} < 9$) (Ghayaza *et al.*, 2011). Leachates are highly loaded with cations, organic matter, inorganic salts, adsorbable halogenated organics, and heavy metals. Among the cations, ammonium, which is mainly produced by bacterial degradation, is present in excess (Lo, 1996; Kruempelbeck & Ehrig, 1999; Kjeldsen *et al.*, 2002; Öman & Junestedt, 2008; Van Nooten *et al.*, 2008). Ammonium concentrations in leachates vary from 4.2 to 870 mg L⁻¹ in 12 Swedish municipal landfills (Öman & Junestedt, 2008), and ammonium is expected to be present in high concentrations (> 100 mg L⁻¹) in leachates for decades (Christensen *et al.*, 2001; Renou *et al.*, 2008). A natural cationic exchange can thus be anticipated in the clay barrier between the original exchangeable cations (mainly Na⁺ and Ca²⁺) and NH₄⁺, reducing the hydrophilic character of the starting clay barrier (Pironon *et al.*, 2003; Gautier *et al.*, 2010). A study dedicated to ammonium-exchanged clay must then be conducted to investigate this specific interaction with leachates.

In fact, leachate interactions with clay liners are probably far more complicated due to co-sorption, formation of organoclays (due to the occurrence of proteins, amino acids, humic materials, and other organic compounds in household wastes), and other chemical processes. The sorption and the degradation of organic pollutants in the clay liner materials can also increase the chemical attenuation of organic pollutants in leachates (Bright *et al.*, 2010). The present study focusses only on ammonium-exchanged clay, which simulates the possible evolution of the clay liner after interaction with landfill leachates. In addition to the waste landfill context, the study of NH_4^+ intercalation has particular importance in other environmental issues. For example, ammonium concentrations up to 40 mg/L were regularly found in domestic wastewater (Kim *et al.*, 2014; Kim *et al.*, 2015; Paing *et al.*, 2015) and even higher in farm effluent (Bolan *et al.*, 2004; Bouwman *et al.*, 2013). Clays can be used to remove ammonium from aqueous solution (Çelik *et al.*, 2001; Eturki *et al.*, 2012; Zadinelo *et al.*, 2015). Moreover, ammonium-smectite interaction plays a key role in better understanding sedimentary rocks (Mingram & Bräuer, 2001; Gieskes & Mahn, 2007), silicates from the Earth's mantle (Watenphul *et al.*, 2009), and meteorite matrices (Bishop *et al.*, 2002; Pizzarello *et al.*, 2012).

Landfill leachates contain large amounts of volatile organic compounds (VOCs) identified as individual pollutants, such as aromatic hydrocarbons, halogenated hydrocarbons, and phenol (Jensen & Christensen, 1999; Kjeldsen & Christophersen, 1999; Christensen *et al.*, 2001; Öman & Junestedt, 2008). Biodegradation, which occurs during anaerobic digestion, degrades organic pollutants and transforms long-chain molecules into shorter-chain molecules (Öman & Junestedt, 2008). Several authors have studied the diffusive transport in aqueous phase of VOCs through natural clays or geosynthetic clay liners (Myrand *et al.*, 1992; Kowalska *et al.*, 1994; Edil, 2003; Lake & Rowe, 2004). These studies highlighted that the diffusion may play an important role in transport of VOCs through the clay barriers and that much more research

is needed on the sorption and reaction of clays and organic pollutants to meet the future environmental challenges. Amongst VOCs, experimental sorption studies with smectites were performed on methyl tert-butyl ether (MTBE) (Sim *et al.*, 2009), phenol (Janík *et al.*, 2013), ethanol (Clausen, 2013), acetone (Amarasinghe *et al.*, 2009), dichloromethane and benzene (Lake & Rowe, 2005), and aniline (Mohammed-Azizi *et al.*, 2011; Vasudevan *et al.*, 2013). However, none of these studies were conducted on ammonium-exchanged clays. To our knowledge, only Gautier *et al.* (2009) have investigated the interaction of ammonium-clay with VOCs, in the case of low-molecular-weight carboxylic acids. They showed a cationic exchange of NH_4^+ to H_3O^+ with all the studied acids and a partial exchange to Al^{3+} only with chloroacetic and oxalic acids for which adsorption of molecules on the clay sample occurs mainly through H-bonding with the cation. Oxalic acid was found intercalated in the interlayer space.

This study aims to characterize the sorption of eight short-chain VOCs (acetonitrile, MTBE, dichloromethane, benzene, phenol, ethanol, acetone, and aniline) on ammonium-smectite after drying, and to identify their sorption mechanisms. These eight VOCs are common in landfill leachates and represent a range of functional groups (nitrile, ether, halogenated aliphatic hydrocarbon, aromatic hydrocarbon, aliphatic alcohol, aliphatic cetone, and aromatic amine, respectively). We ensured that the pHs of the organic solutions were in the order of those in landfills. Their values corresponded to the pH existing in young and medium-aged landfills. This study was performed on a wide range of VOC concentrations above the concentrations measured in landfill leachates. The choice of high VOC concentrations made it possible to emphasize the sorption of VOCs on ammonium-smectite, in order to determine the main sorption mechanisms.

2. MATERIALS AND METHODS

2.1. Ammonium-smectite preparation

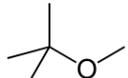
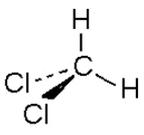
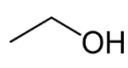
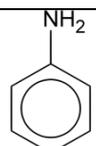
The smectite sample used for this study was SWy-2 Wyoming montmorillonite (Crook County, Wyoming, United States) supplied by the Source Clays Repository of the Clay Minerals Society. The impurities identified as quartz, feldspar, gypsum, mica, and illite in the untreated smectite sample represented 5 wt% after purification by $< 2\mu\text{m}$ size separation (Chiperá & Bish, 2001). The structural formula of the $< 2\mu\text{m}$ size fraction obtained from the chemical analysis (Gautier *et al.*, 2010) is:

$(\text{Ca}_{0.13}\text{Na}_{0.34}\text{K}_{0.03})[\text{Al}_{3.04}\text{Fe(III)}_{0.41}\text{Mg}_{0.49}\text{Ti}_{0.01}][\text{Si}_{7.98}\text{Al}_{0.02}]\text{O}_{20}(\text{OH})_4$. Approximately 2 g of the Wyoming montmorillonite were poured into a Nalgene centrifuge tube and mixed with 50 mL of 1M ammonium chloride solution (Fisher Scientific, Normapur). The sample was rotated on a SRT1 Stuart Scientific roller mixer for 12h. After centrifugation at 2795 g for 5 mn, the supernatant chloride solution was removed and the tube was refilled with a fresh 1M NH_4Cl solution. This process was repeated five times. The sample was then introduced in a dialysis membrane tubing and placed in deionized water to remove chlorides. The water was changed daily until the disappearance of chlorides (AgNO_3 test). After dialysis and decantation, the $< 2\mu\text{m}$ size fraction of ammonium-smectite was extracted, dried and finely hand ground in an agate mortar. Particle-size separations are based on Stokes's law. The detailed protocol is given is given by Moore & Reynolds (1997).

2.2 Sorption experiments

The organic solutions (Table 1) were prepared from mixtures of reagent-grade organic compounds (Fisher Scientific, Normapur) in deionised water (milli-Q/18.2 $\text{M}\Omega\text{ cm}^{-1}$). Three

Table 1: Physico-chemical characteristics of the selected landfill leachate contaminants.

Compound	Functional group	Formula	pKa	Density at 20°C (g/cm ³)	Solubility in water at 20°C
Water H ₂ O		H-O-H	15.74	1.00	-
Acetonitrile C ₂ H ₃ N	Nitrile		25	0.79	soluble
Methyl- <i>tert</i> -butyl-ether C ₅ H ₁₂ O	Ether		-	0.74	42 g L ⁻¹ 0.476 mol L ⁻¹
Dichloromethane CH ₂ Cl ₂	Halogenated aliphatic hydrocarbon		-	1.33	17.6 g L ⁻¹ 0.207 mol L ⁻¹
Benzene C ₆ H ₆	Aromatic hydrocarbon		43	0.88	1.77 g L ⁻¹ 0.023 mol L ⁻¹
Phenol C ₆ H ₆ O	Aromatic alcohol		9.95	1.07	70 g L ⁻¹ 0.74 mol L ⁻¹
Ethanol C ₂ H ₆ O	Aliphatic alcohol		16	0.79	soluble
Acetone C ₃ H ₆ O	Aliphatic ketone		19.3	0.79	soluble
Aniline C ₆ H ₇ N	Aromatic amine		4.6	1.02	34 g L ⁻¹ 0.365 mol L ⁻¹

concentrations were chosen for each organic molecule: a relatively low concentration (0.01 mol L⁻¹), a moderate concentration directly dependent on the solubility limit of the molecule, and the pure liquid. Phenol, which is available in solid form, was only studied at the 0.01 mol L⁻¹ concentration and for the saturated solution (about 0.7 mol L⁻¹). For each batch experiment, a mass of 200 mg of finely dispersed < 2 μm ammonium-smectite was introduced

in centrifuge tubes and rotated at room temperature in 20 mL of distilled water or in the organic solutions. No buffer was used. After seven days, the solution was recovered by centrifugation at 2795 g for 5 mn and the pH was measured with a pH-microelectrode (Mettler Toledo, InLab 423). The suspension aliquots were filtered through a Millipore filter (0.45 μm) and stored at 277 K before analyses. Then the treated samples were recovered for analysis without additional rinsing and gently dried at 313 K in a Memmert oven until constant weight.

To estimate the reversibility of aniline sorption onto ammonium-smectite, three successive rinsings with milli-Q water were performed on ammonium-smectite samples treated with pure aniline.

2.3 Sample characterizations

Carbon and nitrogen analyses

Total carbon and nitrogen contents in clay samples were quantified by combustion of about 40 mg of sample at 1573 K using an elemental analyzer CNS 2000 LECO. The combustion process converted any elemental carbon into CO_2 which was quantified with an infrared spectroscopy cell. Nitrogen was converted into oxidized forms then reduced to N_2 and quantified by conductivity measurements. Measurements were done in triplicate for each sample. The uncertainties on the concentrations of carbon ($\Delta\bar{C} = \pm 0.5 \text{ mg g}^{-1}$) and nitrogen ($\Delta\bar{N} = \pm 0.8 \text{ mg g}^{-1}$) were statistically determined on a set of measurements.

Infrared spectroscopy

Fourier Transform Infrared (FTIR) spectra were recorded using a NICOLET Magna-IR 760 Fourier transform spectrometer. To avoid K^+ -clay cation exchange within the sample during

analysis (Pelletier *et al.*, 1999) and to eliminate the contribution of water absorbed by the KBr pellets in the stretching O-H band, a NICOLET Nic-Plan microscope was used. The spectrometer and the microscope were purged with dry air to remove most of the atmospheric H₂O and CO₂. The powder sample was spread over the NaCl window of the microscope stage. The sample area analyzed was a 100 μm diameter circle chosen under the microscope 15 X Cassegrainian objective. The operating conditions were 128 scans and 2 cm⁻¹ resolution with no ambient CO₂-H₂O corrections. The wave number range studied was 650 – 4000 cm⁻¹ according to the spectrometer beam splitter and the microscope detector (NICOLET MCT-A). The analyses were performed in transmission mode. Experimental data were obtained by acquisition of spectra over different areas.

Powder X-ray diffraction

X-ray diffraction (XRD) patterns were recorded using a Thermo Electron ARL'XTRA diffractometer equipped with a Cu anode and a Si(Li) solid detector, filtering the CuK α radiation of a standard European type X-ray tube (40 kV and 40 mA). The vertical θ : θ goniometer supported two Sollers slits. A VTI RH 200 Relative Humidity generator device coupled to an Anton Paar HTK 1200R chamber allowed us to work with a constant humidity rate. Experimental measurement parameters were 10 s counting time per 0.05°2 θ step, from 2 to 64°2 θ . The divergence, the incident beam scatter, the diffracted beam scatter, and the receiving slits were 1.00, 1.50, 0.45, and 0.30 mm wide, respectively. XRD analysis used between 30 and 60 mg of random powdered sample and data collection was performed at 303 K and 50 % relative humidity (RH) after establishing an equilibrium period of one hour prior to each measurement.

Thermo-gravimetric analyses

The differential thermo-gravimetric analyses (DTG) were recorded with a SETARAM TGA 92 microanalyzer, from 293 to 1273 K with a heating rate of 5 °C.mn⁻¹ under a flow of argon.

Between 30 and 50 mg of sample were used for each measurement. All samples were held at the same relative humidity before the measurements to allow comparison between the dehydration peak values.

3. RESULTS

Carbon and nitrogen analyses of the treated clay samples revealed three different behaviors of the studied organic molecules towards ammonium-smectite (Table 2). A first group of molecules showed a total absence of sorption onto the clay. Indeed, after interaction with acetonitrile, MTBE, dichloromethane, or benzene, the carbon content of the ammonium-clay remained constant within the experimental errors or decreased. For the second group, three organic molecules (phenol, ethanol, acetone) revealed a relatively weak sorption, as demonstrated by an increase in the quantity of carbon after interaction. Finally, the third behavior highlighted was the strong sorption of aniline onto the ammonium-smectite.

3.1. Interaction with acetonitrile, MTBE, dichloromethane, or benzene

The FTIR spectra of ammonium-smectite samples after interaction with acetonitrile, MTBE, dichloromethane, or benzene solution, respectively, were identical to those obtained with the starting ammonium-smectite (data not shown). These results confirmed the absence of sorption revealed by carbon and nitrogen analyses (Table 2). A small decrease in carbon concentration was even measured for some treated clays (pure acetonitrile, 0.1 mol L⁻¹ and pure MTBE, pure dichloromethane, and pure benzene) in comparison with the sample interacted with water. The strong solvation capacity of these molecules seems to have led to the dissolution of the organic matter and/or carbonates present in the initial clay.

Table 2: pH of the solution and carbon and nitrogen concentrations in treated clay samples after 7 days of interaction with water or the selected organic solutions.

Compounds	Initial concentration mol L ⁻¹	pH	C mg g ⁻¹	N mg g ⁻¹	Estimated sorbed amount of organic compound mg g ⁻¹
Water		6.4	2.9 ± 0.5	7.8 ± 0.8	-
Acetonitrile	0.01	6.1	2.6 ± 0.5	7.0 ± 0.8	-
	1	6.7	2.5 ± 0.5	7.4 ± 0.8	-
	pure	n.d.	1.2 ± 0.5	8.7 ± 0.8	-
Methyl-tert-butyl-ether (MTBE)	0.01	5.7	2.5 ± 0.5	6.9 ± 0.8	-
	0.1	7.0	1.4 ± 0.5	7.1 ± 0.8	-
	pure	n.d.	1.9 ± 0.5	6.9 ± 0.8	-
Dichloromethane	0.01	6.8	3.3 ± 0.5	7.2 ± 0.8	-
	0.1	7.1	2.0 ± 0.5	7.3 ± 0.8	-
	pure	n.d.	1.3 ± 0.5	6.7 ± 0.8	-
Benzene	0.01	6.0	3.0 ± 0.5	7.2 ± 0.8	-
	pure	n.d.	1.6 ± 0.5	6.6 ± 0.8	-
Phenol	0.01	6.2	1.8 ± 0.5	6.3 ± 0.8	-
	saturated solution	5.3	15.9 ± 0.5	7.1 ± 0.8	17.0
Ethanol	0.01	4.5	8.7 ± 0.5	7.2 ± 0.8	11.2
	1	6.6	2.2 ± 0.5	7.2 ± 0.8	-
	pure	n.d.	1.1 ± 0.5	6.5 ± 0.8	-
Acetone	0.01	5.2	6.3 ± 0.5	7.3 ± 0.8	5.5
	1	7.1	1.7 ± 0.5	7.5 ± 0.8	-
	pure	n.d.	1.0 ± 0.5	6.5 ± 0.8	-
Aniline	0.01	7.3	6.2 ± 0.5	8.3 ± 0.8	4.3
	0.1	7.2	17.5 ± 0.5	10.1 ± 0.8	18.9
	pure	n.d.	42.8 ± 0.5	13.7 ± 0.8	51.5

n.d. = not determined

3.2. Interaction with phenol, acetone, and ethanol

At low concentration (0.01 mol L^{-1}), no significant sorption of phenol was revealed by carbon analysis (Table 2) or by the comparison of FTIR spectra after interaction with water and with 0.01 mol L^{-1} phenol solution (Figs. 1a,b, respectively). A weak sorption was only detected at the saturation concentration in water (approximately 0.7 mol L^{-1}), as shown by the measurement of a moderate quantity of carbon, which corresponds to *ca* 0.18 mmol of adsorbed phenol by gram of clay. The FTIR spectrum of the ammonium-smectite after interaction with the saturated phenol solution confirmed the presence of adsorbed molecules (Figure 1c). The stretching vibrations of the aromatic cycle were observed at 1489 and 1594 cm^{-1} (Ovadyahu et al, 1998a). The band at 1684 cm^{-1} was assigned to the $\nu_{\text{C=O}}$ bond stretching of the phenol ketone form. The formation of this isomer was certainly favoured by the acidic character of the NH_4^+ ion. The deformation band of water H-O-H , initially at 1630 cm^{-1} , shifted towards higher frequencies, around 1645 cm^{-1} , whereas the deformation band of NH_4^+ (1431 cm^{-1}) remained at the same wavenumber. The band around 3390 cm^{-1} , assigned to the $\nu_{\text{O-H}}$ phenol stretching band, was difficult to identify, due to the presence of the stretching $\nu_{\text{N-H}}$ bands of NH_4^+ and the stretching $\nu_{\text{O-H}}$ of H_2O (Fig. 1c). The sorption of ethanol and acetone was revealed at low concentration (0.01 mol L^{-1}) but no sorption was observed at higher concentrations (1 mol L^{-1} and pure solution) (Table 2). The quantity of ethanol fixed on the clay at 0.01 mol L^{-1} concentration was relatively low (around 0.24 mmol g^{-1}), and was not detected by FTIR spectroscopy (data not shown).

The quantity of adsorbed acetone deduced from carbon analysis was approximately 0.10 mmol g^{-1} of clay at 0.01 mol L^{-1} concentration (Table 2). FTIR spectra of the ammonium-smectite sample after interaction with water or a 0.01 mol L^{-1} acetone solution are presented in Figs 2a,b, respectively. A very weak band was detected at 1720 cm^{-1} , characteristic

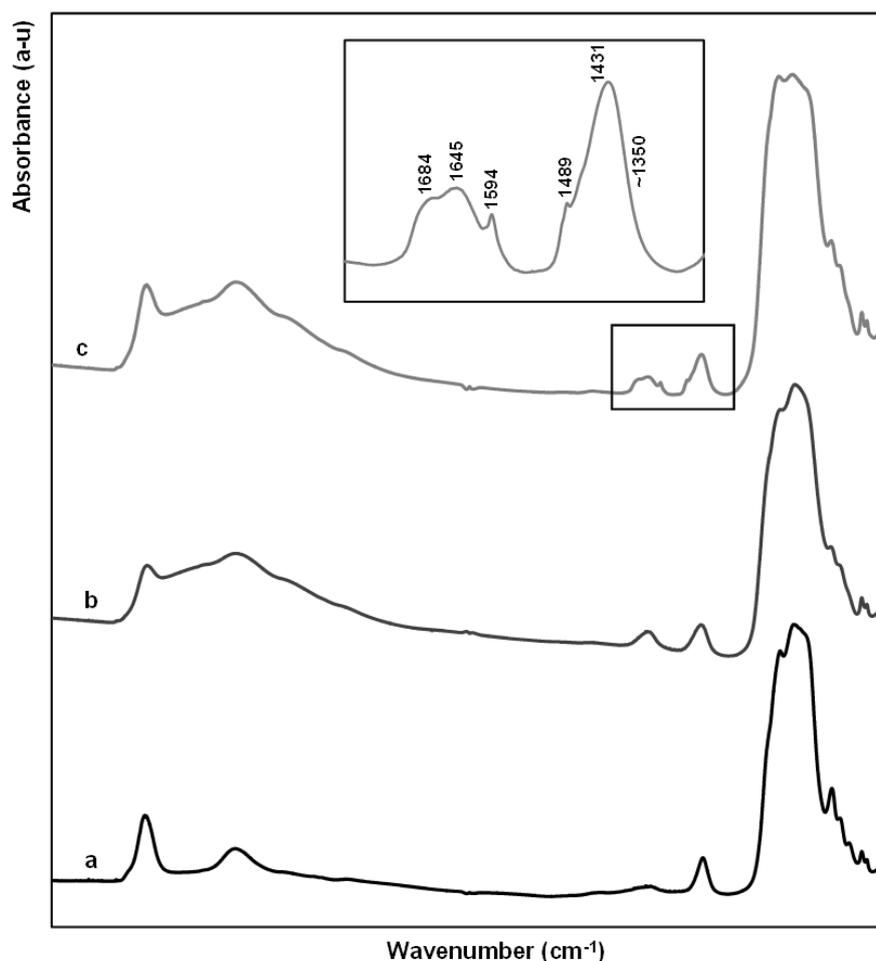


Figure 1: FTIR spectra of NH₄-smectite after 7 days interaction with (a) water used as reference, (b) a 0.01 mol L⁻¹ phenol solution, and (c) a saturated phenol solution.

of the C=O stretching band $\nu_{\text{C=O}}$ (Doner & Mortland, 1969) suggesting the binding of acetone on ammonium-smectite (Fig. 2b). The C–C stretching band ($\nu_{\text{C-C}}$) with a weak intensity was generally observed around 1200 cm⁻¹ for ketones but was not identified in this study because of the presence of Si–O vibrations in the same range. Similarly, the NH₄⁺ deformation band at 1431 cm⁻¹ overlap the CH₃ deformation bands (δ_{CH_3}), generally expected with a weak intensity around 1380 and 1440 cm⁻¹ (Parfitt & Mortland, 1968).

For these three organic molecules (phenol, ethanol, and acetone) at all three concentrations, X-ray diffraction patterns were similar before and after interaction (data not shown).

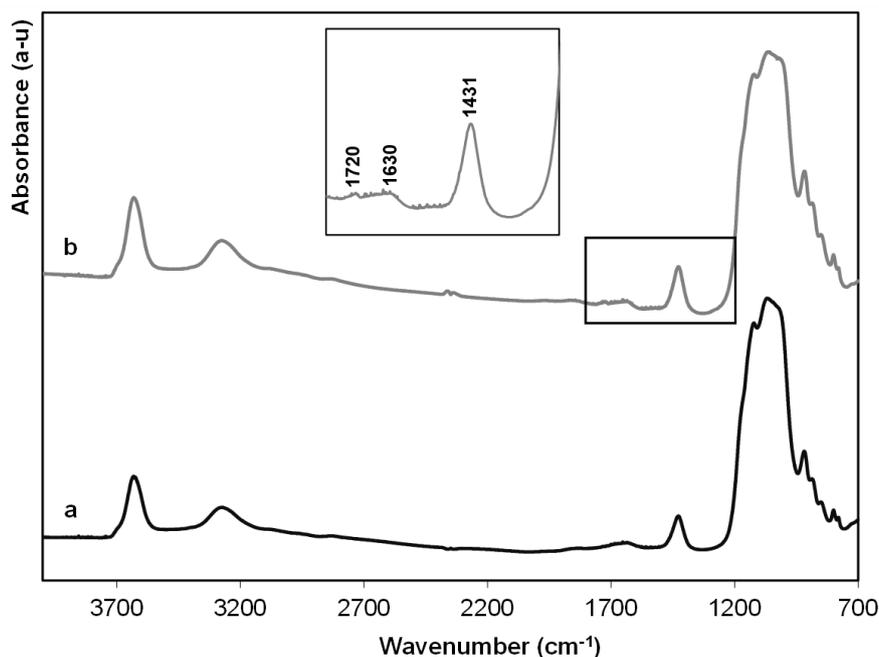


Figure 2: Infrared spectra of NH₄-smectite after 7 days interaction with (a) water as reference, and (b) a 0.01 mol L⁻¹ acetone solution.

3.3. Interaction with aniline

After interaction with aniline solution, C and N concentrations significantly increased in the clay, and particularly in the case of pure aniline solution (Table 2). These results clearly showed the sorption of aniline onto the ammonium-smectite. The comparison between the FTIR spectra of the reference ammonium-smectite sample and the one obtained after interaction with aniline solutions confirmed the chemical results (Fig. 3). No significant difference appeared between the interaction with water (Fig. 3a) and with 0.01 mol L⁻¹ aniline solution (Fig. 3b), whereas new bands appeared in the case of 0.1 mol L⁻¹ and especially 11 mol L⁻¹ aniline solutions (Figs. 3c and 3d). Some characteristic bands of aniline were identified from the study of Akalin & Akyüz (1999). The FTIR spectrum of the ammonium-smectite after interaction with pure aniline solution (Fig. 3d) showed two bands at 3386 and 3312 cm⁻¹ characteristic of the asymmetric and symmetric stretching vibrations of

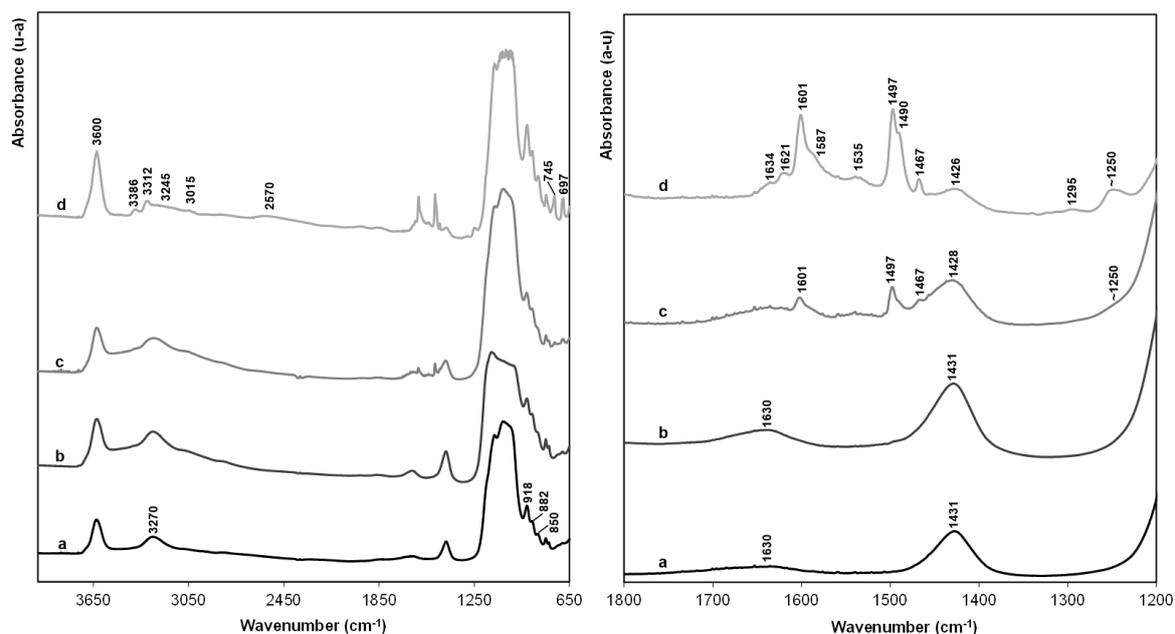


Figure 3: Infrared spectra with a specific zoom in the range 1200-1800 cm^{-1} of NH₄-smectite after 7 days interaction with (a) water used as reference, (b) a 0.01 mol·L⁻¹ aniline solution, (c) a 0.1 mol·L⁻¹ aniline solution and (d) a pure (11 mol·L⁻¹) aniline solution.

the N–H bonds of NH₂. The stretching vibrations of the C–H bonds of the aromatic cycle were also observed at 3015 cm^{-1} ($\nu_{\text{C-H}}$ symmetric). A large band around 2570 cm^{-1} , characteristic of a small quantity of the aniline-anilinium ion (Yariv *et al.*, 1968) was also identified. Additionally, the (Al, Al)–OH (918 cm^{-1}), (Al, Fe)–OH (882 cm^{-1}) and (Al, Mg)–OH (850 cm^{-1}) vibrations were not modified (Figs. 3a and 3d). The two new bands at 745 cm^{-1} and around 700 cm^{-1} (Fig. 3d) were assigned to the out of plane deformation bands of the C–H bonds ($\gamma_{\text{C-H}}$) and of the aromatic cycle (γ_{cycle}), respectively. Further information was obtained in the range 1200-1800 cm^{-1} of the FTIR spectra. The intensity of the bands that are characteristic of aniline increased along with the aniline concentration in solution. In comparison with FTIR spectra of water and 0.01 mol L⁻¹ aniline solution (Figs. 3a and 3b), the FTIR spectrum of 0.1 mol L⁻¹ aniline solution showed stretching bands of the C=C bonds ($\nu_{\text{C=C}}$ stretching) at 1601, 1497, and 1467 cm^{-1} , and a $\nu_{\text{C-NH}_2}$ shoulder around 1250 cm^{-1} (Fig. 3c). The deformation vibration of NH₂ (δ_{NH_2} scissoring) was only identified by an

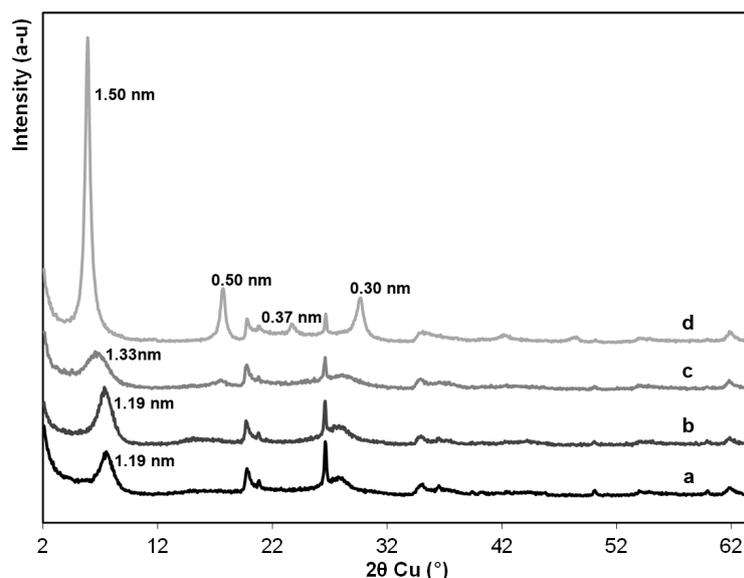


Figure 4: Differential thermo-gravimetric curves of NH_4 -smectite after 7 days interaction with (a) water and (b) pure aniline solution.

intense band at 1621 cm^{-1} in the case of the pure aniline solution (Fig. 3d). Additional bands were identified in Fig. 3d: the asymmetric and symmetric stretching bands of the C=C bonds ($\nu_{\text{C=C}}$ stretching) at 1601 and 1497 cm^{-1} (with respective shoulders at 1587 and 1490 cm^{-1}), the 1535 cm^{-1} band attributed to the vibration of NH_3^+ angular deformation ($\delta_{\text{NH}_3^+}$) (Yariv & Cross, 2002) and characteristic of the anilinium ion, a weak band around 1295 cm^{-1} assigned to the H-C-H deformation vibration band ($\delta_{\text{H-C-H}}$), and the stretching band of the C-N bonds ($\nu_{\text{C-NH}_2}$) around 1250 cm^{-1} . The deformation band of NH_4^+ (δ_{HNNH}) in the range 1426 - 1431 cm^{-1} , characteristic of the ammonium interlayer cation, had a lower intensity after interaction with pure aniline compared with water (Figs. 3a,d).

The DTG curves of ammonium-smectite after interaction with water and pure aniline solution are reported in Fig. 4. The small peak at 600 K was attributed to the thermal decomposition of NH_4^+ (Gautier *et al.*, 2010) (Figure 4a). The treated smectite contained a lower water content, as shown by the small dehydration peak at 341 K (Fig. 4b). The large intense peak at 503 K , which appeared after aniline interaction, is characteristic of the thermal decomposition of aniline complexes (Yariv, 2003). The dehydroxylation peak shifted from 878 K after

interaction with water to 848 K after interaction with pure aniline (Fig. 4). X-ray diffraction patterns were performed on the ammonium-smectite after interaction with water and the different aniline solutions (Fig. 5). The basal spacing (d_{001} value) shifted from 1.19 nm (Fig. 5a) to 1.50 nm (Fig. 5d) with the increase of aniline concentration. After interaction with the 0.1 mol L^{-1} aniline solution, the ammonium-smectite revealed a broader 001 reflection with a higher basal spacing (1.33 nm) (Fig. 5c). In the case of pure aniline (Fig. 5d), the 001 reflection was sharper and more intense, as well as the 003 (0.50 nm), 005 (0.30 nm) and 004 (0.37 nm) reflections.

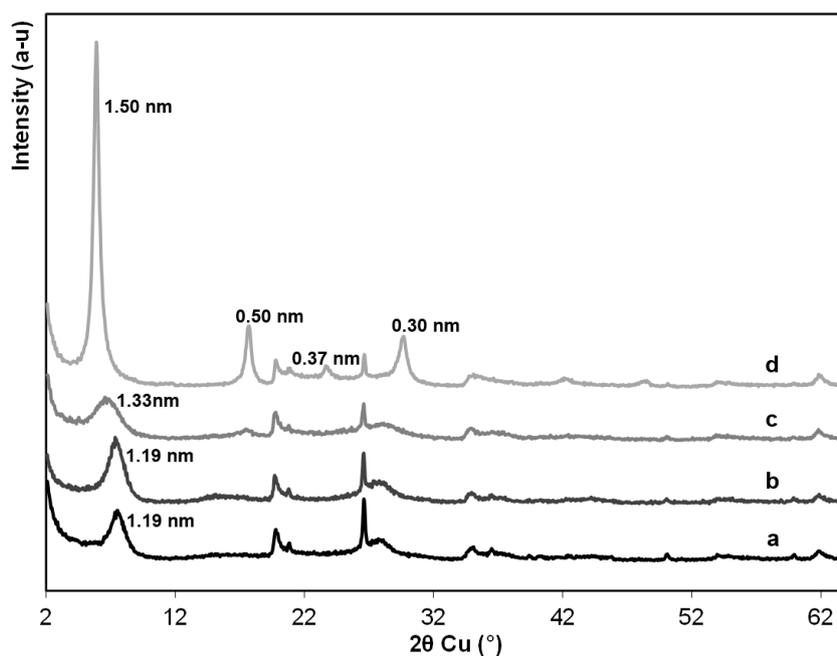


Figure 5: X-ray diffraction patterns of NH_4 -smectite after 7 days of interaction with (a) water used as reference, (b) a 0.01 mol L^{-1} aniline solution, (c) a 0.1 mol L^{-1} aniline solution and (d) a pure (11 mol L^{-1}) aniline solution.

The infrared spectrum of the clay treated with pure aniline solution was compared to the one obtained after three successive rinsings with milli-Q water (Fig. 6). After rinsing (Fig. 6b) a general decrease in the intensity of the bands characteristic of binding with aniline

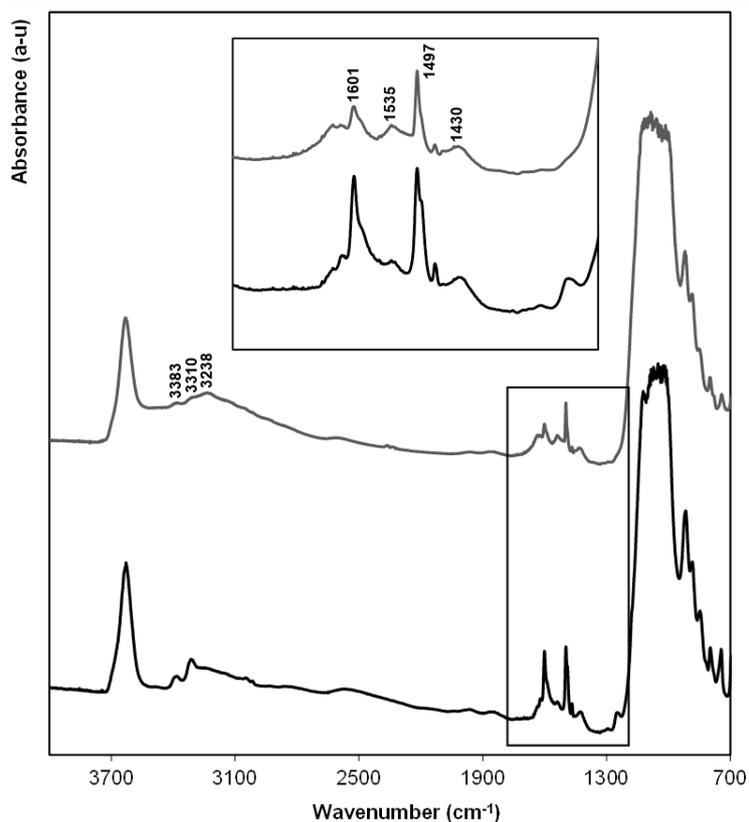


Figure 6: Infrared spectra of ammonium-smectite after 7 days interaction with (a) pure aniline and (b) pure aniline then rinsed with milli-Q water.

molecules was observed (3383, 3310, 1601, 1497 and 1469 cm^{-1}). The X-ray diffraction pattern of the clay treated with pure aniline solution was compared to the one obtained after three successive rinsings with milli-Q water (Fig. 7). The basal spacing of the treated sample shifted from 1.50 to 1.35 nm after rinsing, the 001 reflection became wider and the 003 reflection disappeared.

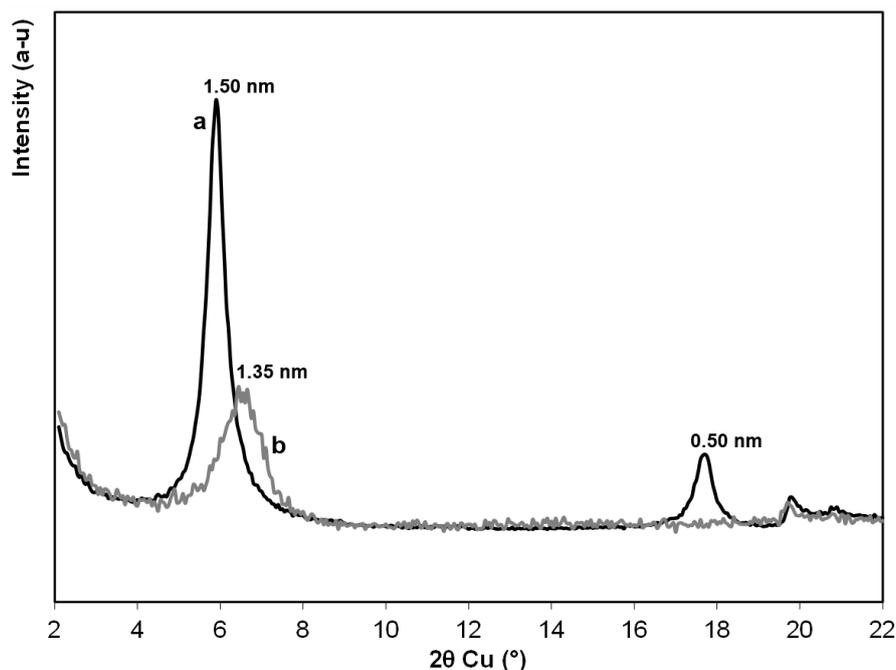


Figure 7: X-ray diffraction patterns of ammonium-smectite after 7 days interaction with (a) pure aniline and (b) pure aniline then rinsed with milli-Q water.

4. DISCUSSION

4.1. Non retained molecules

The absence of sorption onto ammonium smectite observed with acetonitrile, MTBE, dichloromethane, and benzene is in good agreement with previous studies performed on smectites with other interlayer cations. Hoffmann & Brindley (1960) studied the adsorption of non-ionic aliphatic compounds in solution onto a Ca-montmorillonite, in particular nitrile, ether, and alcohols. They showed that the length of the chain had a great influence on the adsorption of these molecules, and that a minimum chain length of 5 or 6 CH₂ units was necessary to obtain sorption. Acetonitrile and MTBE are constituted of short chains, which prevented them from being sorbed in the ammonium-smectite. Furthermore, the weak and easily reversible sorption of acetonitrile on K-, Na-, Ca-, and Mg-exchanged montmorillonites was already demonstrated by FTIR spectroscopy (Zhang *et al.*, 1990b, 1990c). Similarly, Greenwood *et al.* (2007) highlighted the very weak sorption of MTBE on clays. Among the

compounds studied, dichloromethane has the highest vapor pressure and a very fast evaporation in ambient conditions, which easily explains the absence of binding in aqueous solution. The absence of benzene adsorption onto ammonium smectite is in accordance with the results of Jaynes & Vance (1999) onto Na-, K-, Ca- and Mg-montmorillonites. The dipole moment of benzene is zero, due to its symmetry, which considerably limits the dipole-dipole interactions with the hydrophilic surface of the smectites and leads to a very low adsorption.

4.2. Weakly retained molecules

Phenol

Phenol sorption onto clays has been extensively described in the literature, both on clays with inorganic interlayer cations (Isaacson & Sawhney, 1983; Ovadyahu *et al.*, 1998a, 1998b; Viraraghavan & de Maria Alfaro, 1998; Yapar & Yilmaz, 2005; Richards & Bouazza, 2007; Djebbar *et al.*, 2012; Janík *et al.*, 2013), and with organoclays (Zhang & Sparks, 1993; Dentel *et al.*, 1995; Koh & Dixon, 2001; Yilmaz & Yapar, 2004; Richards & Bouazza, 2007; Alkaram *et al.*, 2009; Díaz-Nava *et al.*, 2012), but never on ammonium-exchanged clays. Phenol adsorption is known to be pH-dependent (Viraraghavan & de Maria Alfaro, 1998, Yilmaz & Yapar, 2004, Yapar & Yilmaz, 2005) also showed that the adsorption of phenol is dependent on the pH. In our batch experiments, the pH of the solution after interaction with phenol varied between 5.3 and 6.2 (Table 2), which imposed the neutral form of the phenol molecule ($pK_a = 9.95$), preventing the formation of electrostatic bonds. The stretching vibrations of the aromatic cycle observed at 1489 and 1594 cm^{-1} can be attributed to hydrogen bonds between the neutral phenol molecules and the water molecules in the hydration shell of the interlayer cations (Ovadyahu *et al.*, 1998a, 1998b). Two binding configurations involving a hydrogen bond between the phenol group and water molecules were suggested (Fig. 8).

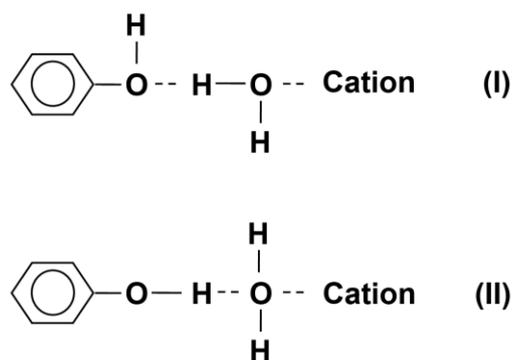


Figure 8: Possible configurations of binding involving a hydrogen bond between phenol group and water molecule.

Configuration (I) requires the breaking of the H-bond between the hydration water molecules and the oxygen atoms of the clay layers. In configuration (II), the hydrogen of the phenol group binds with the oxygen atom of the water molecule. Because of the weak polarizing power (Z/r where Z is the charge and r the ionic radius of the cation) of monovalent interlayer cations (1.02 for Na^+ , 0.75 for K^+ and $\cong 0.69$ for NH_4^+), the H-bond between hydration water and clay layers will be easy to break, and configuration (I) will be generally the most common case (Fenn & Mortland, 1972). The similar XRD patterns obtained after interaction with water and with phenol solution indicated that the aromatic groups of phenols were placed parallel to the layers as already observed in sodium and potassium montmorillonite by Saltzman & Yariv (1975). The adsorption of phenol molecules onto the surface of natural clay, through hydrogen bonds between OH group of the phenol and the silanol groups of the clay surface could also be possible. Moreover Djebbar et al. (2012) measured enthalpy values and suggested a physisorption at the surface conducted with Van der Waals forces. The sorption of phenol remained very weak and easily reversible, because it was totally desorbed after a few days at 313 K.

Ethanol and acetone

Dissociation forms of ethanol and acetone are negligible for the pH values of the solution (Table 1) because of their high pKa values (16 and 19.3 for ethanol and acetone respectively, Table 2). Configuration (I) shows a hydrogen bond between the nitrogen from aniline and the hydrogen from water molecule. Configuration (II) shows a hydrogen bond between a hydrogen from aniline and the oxygen from water molecule. There are several possible explanations why small quantities of acetone and ethanol fixed on the NH_4^+ -smectite at low concentration (0.01 mol L^{-1}). German & Harding (1969) showed that the adsorption of aliphatic alcohols onto a kaolinite or a montmorillonite saturated with calcium and sodium cations depended on the length of the carbonaceous chain and on the nature of the cation. Hoffmann & Brindley (1960) observed that a minimum chain length of five carbon units (methyl and/or methylene groups) was necessary to obtain a significant adsorption from the aqueous phase. The sorption capacity of ethanol with only two carbon units is therefore likely to be very low. Zhang *et al.* (1990a) demonstrated that ethanol was not fixed by a chemical bond to the layer surface but with Van der Waals forces which are much weaker.

As in the case of ethanol, the adsorption of acetone molecules was partly due to Van der Waals interactions, as shown by Bissada *et al.* (1967). They studied the adsorption of ethanol and acetone in liquid state on dehydrated montmorillonites. The authors demonstrated the possibility of a cation-dipole interaction and showed an increase in adsorption depending on the nature of the cation in the order $\text{K}^+ < \text{Na}^+ < \text{Ba}^{2+} < \text{Ca}^{2+}$. Because the ionic radius of ammonium is larger than that of potassium, the interaction energy will be weaker and adsorption on ammonium-clay with cation-dipole interaction should be very weak. Moreover Van der Waals forces can also occur with layer surface.

A hypothesis to explain the presence of ethanol and acetone fixed at weak concentration and their absence at stronger ones is the difference between the boiling point or vapour pressure between water and organic compounds. Ethanol and acetone, with vapour pressures of 5.9 and

23.3 kPa at 293 K, respectively, are more volatile than water vapour pressure of 2.34 kPa at 293 K. Regarding the binary diagrams water-ethanol and water-acetone it is well established that the energy needed to reach the boiling point of a mixture rich in water is higher than one with higher organic compounds content. In these conditions the drying at 313 K might explain the difference in residual fixed molecules and why more energy was needed in the case of low concentration.

4.3. Strongly retained molecule: aniline

With a pKa value of 4.6 for the anilinium/aniline couple, anilinium exists in small proportions in aqueous solution (pH = 7.3; Table 2) and cationic exchange with NH_4^+ must be considered. The FTIR spectrum for pure aniline clearly highlighted the presence of a small quantity of the anilinium and aniline-anilinium ions (Yariv *et al.*, 1968) and reported in Fig. 9. These authors also showed that the formation of anilinium may occur directly in the interlayer space by the reaction: $\text{C}_6\text{H}_5\text{NH}_2 + \text{NH}_4^+ \Leftrightarrow \text{C}_6\text{H}_5\text{NH}_3^+ + \text{NH}_3$.

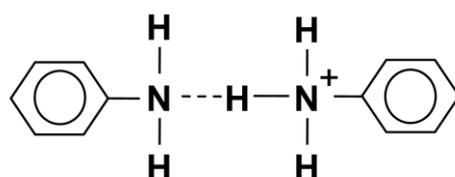


Figure 9. Structure of binding for aniline-anilinium ion.

The intercalation of aniline in the interlayer was clearly shown by FTIR analyses. The shift of the dehydroxylation peak observed in the DTG study indicated the position of aniline near the OH groups and confirmed this result. The similar basal spacing after interaction with water and with 0.01 mol L^{-1} aniline solution ($d_{001} = 1.19 \text{ nm}$, Figs. 5a and 5b) indicated that the

aniline molecules were placed parallel to the layers. This arrangement was already observed by Saltzman & Yariv (1975) in the case of a plane aromatic molecule (phenol) with a d_{001} value of 1.18 nm. After interaction with the 0.1 mol L⁻¹ aniline solution, the broader 001 reflection with a higher basal spacing ($d_{001} = 1.33$ nm, Fig. 6) is characteristic of a disorder in the inter-layered clay stack. Some molecules occupied intermediate positions between parallel and perpendicular orientation to the sheets (Theng, 1974). In the case of pure aniline, the better organization of the smectite observed by XRD and the $d_{001} = 1.5$ nm suggests that the aniline molecules were intercalated perpendicular to the clay layers (Farmer & Mortland, 1966). Yariv *et al.* (1969) studied the intercalation of aniline into montmorillonite exchanged with Al, Mg, H, Na, or K cations. They showed that aniline formed hydrogen bonds with the interlayer water molecules connected to interlayer cations and proposed two binding configurations (Fig. 10). In the case of NH₄ exchanged montmorillonite, which has a low polarizing power ($Z/r \cong 0.69$ where Z is the cation charge and r its radius), the H-bond between hydration water and clay layers will be easy to break. So configuration I will be dominant, where both hydrogen atoms of aniline are free in comparison with configuration II where a hydrogen of the NH₂ group binds with the oxygen atom of the water molecule. The symmetric and asymmetric NH₂ stretching bands, respectively at 3312 cm⁻¹ and 3386 cm⁻¹ (ν_{N-H} , Fig. 3d) confirmed this predominance (Yariv *et al.*, 1969). Another configuration in which the aniline molecule was directly bound to NH₄⁺ was proposed by Yariv & Cross (2002). This configuration only concerned very weakly hydrated environments and high aniline concentrations.

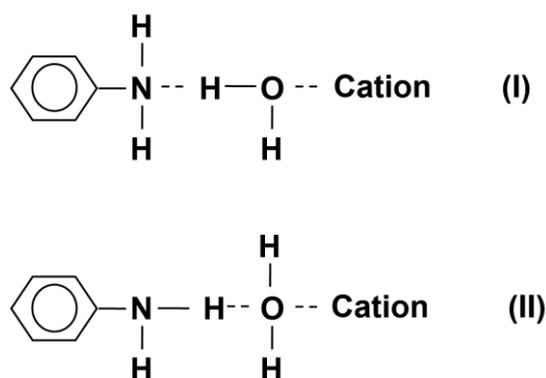


Figure 10: Possible configurations of binding involving a hydrogen bond between aniline and interfoliar water molecule.

The fixation of aniline molecules on the ammonium interlayer cations was strengthened by the shift of the main stretching vibration bands ($\nu_{\text{N-H}}$ of a NH_4^+ group) from 3270 cm^{-1} in the starting sample (Fig. 3a) to around 3245 cm^{-1} after interaction with pure aniline (Fig. 3d), and corresponding to a decrease in the N–H bond strength of the interlayer cation. The shift of some bands characteristic of the FTIR spectrum of pure aniline to lower wavenumbers after interaction with the ammonium-smectite also confirmed the sorption of aniline on ammonium-smectite: the asymmetric and symmetric stretching bands ($\nu_{\text{N-H}}$ of NH_2) shifted from 3500 and 3418 cm^{-1} in pure liquid aniline (Akalin & Akyüz, 1999) to 3386 and 3312 cm^{-1} after interaction with ammonium-smectite (Fig. 3d), and the stretching vibration band of the C–N bond ($\nu_{\text{C-NH}_2}$) decreased from 1279 cm^{-1} in pure liquid aniline (Akalin & Akyüz, 1999) to approximately 1250 cm^{-1} (Fig. 3d). Note that a small proportion of aniline may also adsorb onto the surfaces and the edges of the clay particles (Yan & Bailey, 2001; Vasudevan *et al.*, 2013). The intercalation of aniline on ammonium-smectite was accompanied by a decrease in the hydrophilic character of the material as shown by the strong decrease in the intensity of the dehydration peak in DTG analyses (Fig. 4b). The decrease in the intensity of the bands characteristic of the binding between aniline and ammonium-smectite after rinsing the ammonium-smectite treated with aniline solution (Fig. 6) indicated a partial desorption of

aniline. The basal spacing shifted from 1.50 to 1.35 nm after rinsing the ammonium-smectite treated with aniline solution (Fig. 7) confirmed the partial desorption of aniline.

5. CONCLUSION

This study focused on eight short chain VOCs contained in landfill leachate interacting with ammonium-smectite. The sorption success for these organic compounds on ammonium-smectite mainly depends on the magnitude of the interactional processes that ensure both cohesion and stability in the resulting materials. The absence of sorption observed with acetonitrile, methyl tert-butyl ether, dichloromethane, and benzene, is in agreement with previous studies. Phenol, ethanol, and acetone were very weakly sorbed. Van der Waals interactions with clay layers and cation-dipole interactions allowed the sorption of ethanol, acetone and phenol. For phenol sorption hydrogen bonds between hydroxyl groups and interlayer water molecules, whereas The higher volatility of both ethanol and acetone in comparison with water led to a decrease in the amount of molecules fixed with the increase in the solvent concentration. In contrast, aniline was strongly sorbed on ammonium-smectite, and only partially desorbed after rinsing. The proposed model of sorption was a binding of aniline on the NH_4^+ cations, with the formation of H-bonds through interlayer water molecules. Moreover, aniline can be retained by other processes: (i) by cationic exchange of NH_4^+ by anilinium ions in small proportions; (ii) by anilinium formation following the reaction $\text{C}_6\text{H}_5\text{NH}_2 + \text{NH}_4^+ \Leftrightarrow \text{C}_6\text{H}_5\text{NH}_3^+ + \text{NH}_3$; and (iii) by the formation of the aniline-anilinium ion in the clay interlayer. The sorption models for phenol, ethanol, acetone, and aniline in an ammonium smectite were identical to those proposed in the literature for smectites containing Ca^{2+} or Na^+ as interlayer cations.

The interaction processes involved in the sorption of these eight VOCs on ammonium smectite can be transposed to clay barriers. Only an easily reversible physisorption was possible for acetonitrile, methyl tert-butyl ether, dichloromethane, and benzene. These four molecules contained in leachates will not be retained by the engineered clay barriers, and therefore present a potential hazard for the pollution of groundwaters. Phenol, ethanol, and acetone will not be strongly retained by the clayey barrier and may also migrate towards groundwaters, as previously shown by Zhang *et al.* (1990a) for phenol and ethanol in water/soil systems. The clay barrier proved to be effective for aniline sorption. However, this sorption decreased the hydrophilic character of the ammonium-smectite, which may reduce its swelling capacity, and therefore may increase the permeability of the clay barrier.

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