

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 concentrations of NH_4^+ which can generate NH_4^+ -exchanged clays within geochemical barriers. These leachates also contain several volatile organic compounds (VOCs) which can interact with the clay barrier. The aim of the present study was to characterize the sorption of eight short-chain VOCs (acetonitrile, methyl tert-butyl ether, dichloromethane, benzene, phenol, ethanol, acetone and aniline) on NH_4^+ -smectite, and to identify their sorption mechanisms. The samples treated were characterized by carbon and nitrogen elemental analysis, infrared spectroscopy, powder X-ray diffraction, and thermogravimetric analysis. For acetonitrile, methyl tert-butyl ether, dichloromethane and benzene, no sorption was detected. Phenol, ethanol and acetone were sorbed very weakly, through Van der Waals interactions. Aniline molecules were sorbed strongly on NH_4^+ -smectite mainly with hydrogen bonds between aniline and interlayer water molecules. However, aniline sorption decreased the hydrophilic character of the NH_4^+ -smectite, which may increase the permeability of the clay barrier.

KEYWORDS: NH_4^+ , aniline, clay barrier, montmorillonite, short-chain, sorption, volatile organic compounds, waste landfill, FTIR.

In 2013, 30% and 53% of municipal waste was transported to landfill sites in Europe (Eurostat, 2015) and the US (EPA, 2015), respectively. The percolation of water through waste landfills, together with the degradation of wastes, produce leachates with large amounts of pollutants. Clay barriers are used at the base of these sites to mitigate any pollution in the soil and groundwater. Smectites are selected mainly due to their adsorption properties, their low permeability after compaction, their swelling capacity and their large cation exchange capacity (CEC). The physicochemical compositions of the leachates are influenced strongly by the nature of the buried wastes and the age of the

site. A young landfill (<5 y old) produces biodegradable acidic leachates ($4.5 < \text{pH} < 6.5$), a medium-age landfill (5–10 y) is characterized by intermediate neutral leachates ($6.5 < \text{pH} < 7.5$), whereas an old landfill (>10 y) is identified by stabilized basic leachates ($7.5 < \text{pH} < 9$) (Ghayaza *et al.*, 2011). Leachates are rich in cations, organic matter, inorganic salts, adsorbable halogenated organic compounds and heavy metals. Among the cations, ammonium (NH_4^+), which is produced mainly by bacterial degradation, is present to 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

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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 Ca^{2+}) and NH_4^+ , reducing the hydrophilic character of the starting clay barrier (Pironon *et al.*, 2003; Gautier *et al.*, 2010). A study dedicated to NH_4^+ -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 focuses on NH_4^+ -exchanged clay only, 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, NH_4^+ concentrations of up to 40 mg/L have been found in domestic wastewater (Kim *et al.*, 2014, 2015; Paing *et al.*, 2015) and even higher concentrations in farm effluents (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, NH_4^+ -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 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 the 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 suggested that the diffusion may play an important role in transport of VOCs through the clay barriers and that more work is needed on the

sorption and reaction of clays and organic pollutants to meet future environmental challenges. Amongst VOCs, experimental sorption studies with smectites have been 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 was conducted on NH_4^+ -exchanged clays. To the present authors' knowledge, only Gautier *et al.* (2009) have investigated the interaction of NH_4^+ -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 acids studied and a partial exchange to Al^{3+} with chloroacetic and oxalic acids only 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.

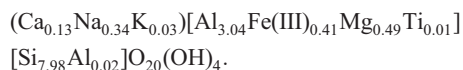
The present study aims to characterize the sorption of eight short-chain VOCs (acetonitrile, MTBE, dichloromethane, benzene, phenol, ethanol, acetone and aniline) on NH_4^+ -smectite after drying, and to identify their sorption mechanisms. These eight VOCs are common in landfill leachates and represent a range of functional groups (nitrile, ether, halogenated aliphatic hydrocarbon, aromatic hydrocarbon, aliphatic alcohol, aliphatic ketone and aromatic amine, respectively). The pH values of the organic solutions were maintained at levels similar to those in landfills and corresponded to the pH of young and medium-aged landfills. The sorption 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 NH_4^+ -smectite in order to determine the main sorption mechanisms.

MATERIALS AND METHODS

NH₄⁺-smectite preparation

The smectite sample used for this study was SWy-2 Wyoming montmorillonite (Crook County, Wyoming, USA) 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 μm size separation (Chipera & Bish, 2001). The structural formula of the <2 μm size fraction obtained from the chemical analysis (Gautier

et al., 2010) is:




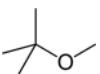
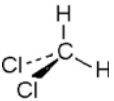

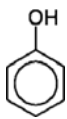



Approximately 2 g of the Wyoming montmorillonite was poured into a Nalgene centrifuge tube and mixed with 50 mL of 1 M NH₄Cl solution (Fisher Scientific, Normapur). The sample was rotated using an SRT1 Stuart Scientific roller mixer for 12 h. After centrifugation at 2795 × g for 5 min, the supernatant chloride solution was removed and the tube was refilled with a fresh 1M NH₄Cl solution. This process was repeated five times. The sample was then introduced to a dialysis membrane tubing and placed in deionized water to remove chlorides. The water was changed

daily until chloride free (AgNO₃ test). After dialysis and decantation, the <2 μm size fraction of NH₄⁺-smectite was extracted, dried and hand ground in an agate mortar. Particle-size separations are based on Stokes' law. The detailed protocol was given by Moore & Reynolds (1997).

Sorption experiments

The organic solutions (Table 1) were prepared from mixtures of reagent-grade organic compounds (Fisher Scientific, Normapur) in deionized water (milli-Q/18.2 MΩ cm⁻¹). Three concentrations were chosen for each organic molecule: a relatively low concentration (0.01 mol L⁻¹), a moderate concentration which

TABLE 1. Physicochemical 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

depends on the solubility limit of the molecule, and the pure liquid. Phenol, which is available in solid form, was studied at the 0.01 mol L^{-1} concentration only and for the saturated solution (at $\sim 0.7 \text{ mol L}^{-1}$). For each batch experiment, a mass of 200 mg of finely dispersed $<2 \mu\text{m}$ NH_4^+ -smectite was introduced in centrifuge tubes and rotated at room temperature in 20 mL of distilled water or in organic solutions, without the use of a buffer. After seven days, the solution was recovered by centrifugation at $2795 \times g$ for 5 min and the pH was measured with a pH-microelectrode (Mettler Toledo, InLab 423). The suspension aliquots were filtered through a Millipore filter ($0.45 \mu\text{m}$) and stored at 277 K before analysis. Then the samples treated were recovered for analysis without additional rinsing and dried gently at 313 K in a Memmert oven until constant weight.

To estimate the reversibility of aniline sorption onto NH_4^+ -smectite, three successive washings with milli-Q water were performed on NH_4^+ -smectite samples treated with pure aniline.

Sample characterizations

Carbon and nitrogen analyses. Total carbon and nitrogen contents in clay samples were quantified by combustion of $\sim 40 \text{ mg}$ 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 using an IR spectroscopy cell. Nitrogen was converted to oxidized forms and then reduced to N_2 and quantified by means of 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 determined statistically on a set of measurements.

Infrared spectroscopy. Fourier Transform Infrared (FTIR) spectra were recorded using a NICOLET Magna-IR 760 Fourier transform IR 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 H_2O and CO_2 . The powder sample was spread over the NaCl window of the microscope stage. The sample area analyzed was a $100 \mu\text{m}$ diameter circle chosen under the microscope using a $15\times$ Cassegrainian objective. The operating conditions

were 128 scans and 2 cm^{-1} resolution without ambient CO_2 - H_2O corrections. The wavenumber range studied was $650\text{--}4000 \text{ cm}^{-1}$ 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 Cu- $K\alpha$ radiation of a standard European type X-ray tube (40 kV and 40 mA). The vertical θ : θ goniometer supported two Soller slits. A VTI RH 200 Relative Humidity generator device coupled to an Anton Paar HTK 1200R chamber provided for operation at a constant humidity rate. Experimental measurement parameters were 10 s counting time per $0.05^\circ 2\theta$ step, from 2 to $64^\circ 2\theta$. 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. X-ray diffraction 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 1 h prior to each measurement.

Thermogravimetric analyses. Differential thermogravimetric analyses (DTG) were done using a SETARAM TGA 92 microanalyzer, from 293 to 1273 K at a heating rate of 5°C min^{-1} under argon flow, using 30–50 mg of sample for each measurement. All samples were kept at the same relative humidity before measurement to allow comparison between the dehydration peak values.

RESULTS

Carbon and nitrogen analyses of the clay samples treated revealed three different behaviours of the organic molecules studied toward NH_4^+ -smectite (Table 2). A first group of molecules showed a complete absence of sorption onto the clay. Indeed, after interaction with acetonitrile, MTBE, dichloromethane or benzene, the carbon content of the NH_4^+ -clay remained constant, within the experimental error of the methods, or decreased. For the second group, three organic molecules (phenol, ethanol, acetone) had relatively weak sorption, as demonstrated by an increase in the quantity of carbon after interaction.

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		C (mg g ⁻¹)	N (mg g ⁻¹)	Estimate of the amount of organic compound sorbed (mg g ⁻¹)
	(mol L ⁻¹)	pH			
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.

Finally, the third behaviour highlighted was the strong sorption of aniline onto the NH₄⁺-smectite.

Interaction with acetonitrile, MTBE, dichloromethane or benzene

The FTIR spectra of NH₄⁺-smectite samples after interaction with acetonitrile, MTBE, dichloromethane or benzene solution, respectively, were identical to those obtained with the starting NH₄⁺-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 might have led to the dissolution of the organic matter and/or carbonates present in the initial clay.

Interaction with phenol, acetone and ethanol

At a 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 (Fig. 1a,b, respectively). A weak sorption was only detected at the saturation concentration in water (~0.7 mol L⁻¹), as shown by the measurement of a moderate quantity of carbon, which corresponds to ~0.18 mmol of phenol adsorbed g⁻¹ of clay. The FTIR spectrum of the NH₄⁺-smectite

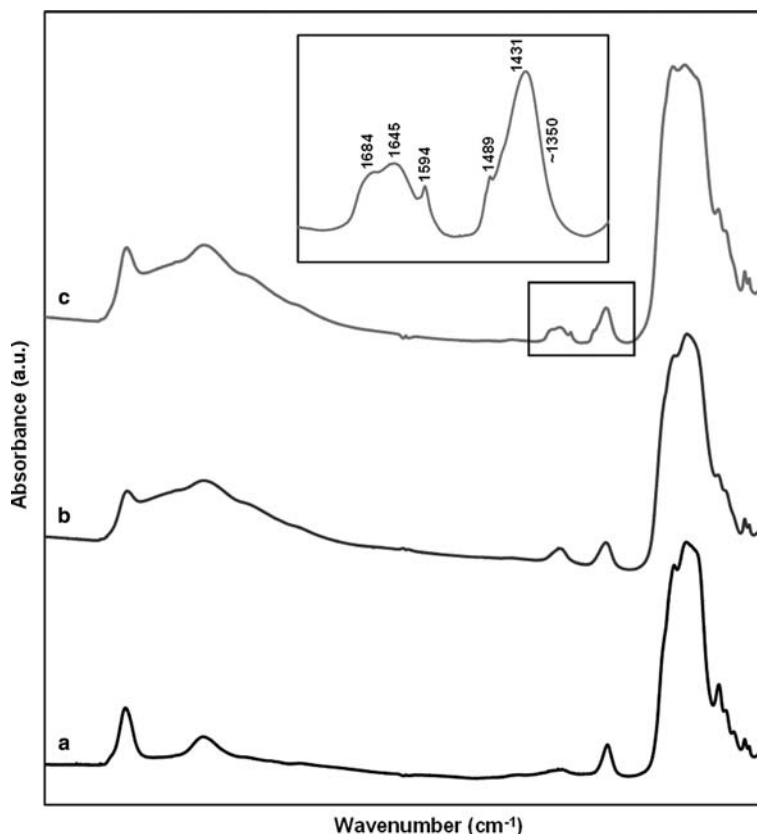


FIG. 1. FTIR spectra of NH_4^+ -smectite after 7 days of interaction with: (a) water used as reference; (b) a 0.01 mol L^{-1} phenol solution; and (c) a saturated phenol solution.

after interaction with the saturated phenol solution confirmed the presence of adsorbed molecules (Fig. 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, $\sim 1645 \text{ cm}^{-1}$, whereas the deformation band of NH_4^+ (1431 cm^{-1}) remained unaffected. The band at $\sim 3390 \text{ cm}^{-1}$, assigned to the $\nu_{\text{O-H}}$ phenol stretching, 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 concentrations (0.01 mol L^{-1}) but no sorption was observed at higher concentrations (1 mol L^{-1} and pure solution) (Table 2). The

amount of ethanol fixed on the clay at 0.01 mol L^{-1} concentration was relatively small ($\sim 0.24 \text{ mmol g}^{-1}$), and was not detected by FTIR spectroscopy (data not shown).

The amount of acetone adsorbed, as deduced from carbon analysis, was $\sim 0.10 \text{ mmol g}^{-1}$ of clay at 0.01 mol L^{-1} concentration (Table 2). The FTIR spectra of the NH_4^+ -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 of the C=O stretching band $\nu_{\text{C=O}}$ (Doner & Mortland, 1969) suggesting the binding of acetone to NH_4^+ -smectite (Fig. 2b). The weak C–C stretching band ($\nu_{\text{C-C}}$) generally observed at $\sim 1200 \text{ cm}^{-1}$ in ketones, was not identified in this study because of the presence of Si–O vibrations in the same range. Similarly, the NH_4^+ deformation band at 1431 cm^{-1} overlaps the CH_3 deformation bands (δ_{CH_3}), generally expected with a

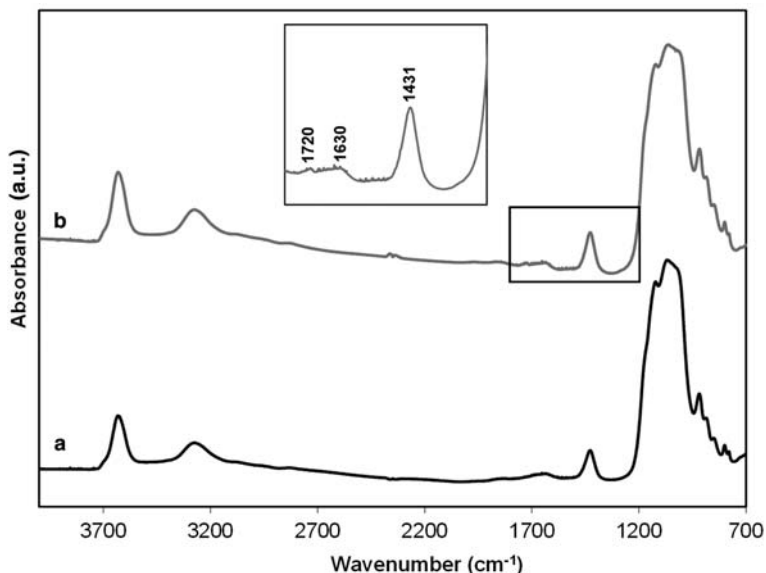


Fig. 2. IR spectra of NH₄-smectite after 7 days of interaction with: (a) water used as reference; and (b) a 0.01 mol L⁻¹ acetone solution.

weak intensity at ~ 1380 and 1440 cm⁻¹ (Parfitt & Mortland, 1968).

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

Interaction with aniline

After interaction with aniline solution, the C and N concentrations increased significantly in the clay and particularly in the case of pure aniline solution (Table 2). These results showed clearly the sorption of aniline onto the NH₄⁺-smectite. The comparison between the FTIR spectra of the reference NH₄⁺-smectite sample and that 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 (Fig. 3c,d). Some characteristic bands of aniline were identified from the study of Akalin & Akyüz (1999). The FTIR spectrum of the NH₄⁺-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 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 (ν_{C-H} symmetric). A large band at ~ 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 (Fig. 3a,d). The two new bands at 745 cm⁻¹ and at ~ 700 cm⁻¹ (Fig. 3d) were assigned to the out-of-plane deformation bands of the C–H bonds (γ_{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 the FTIR spectra of water and 0.01 mol L⁻¹ aniline solution (Fig. 3a,b), the FTIR spectrum of 0.1 mol L⁻¹ aniline solution showed stretching bands of the C=C bonds ($\nu_{C=C}$ stretching) at 1601, 1497 and 1467 cm⁻¹, and a ν_{C-NH_2} shoulder at ~ 1250 cm⁻¹ (Fig. 3c). The deformation vibration of NH₂ (δ_{NH_2} scissoring) was only identified by an 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 ($\nu_{C=C}$ stretching) at 1601 and 1497 cm⁻¹ (with shoulders at 1587 and 1490 cm⁻¹, respectively), the 1535 cm⁻¹ band

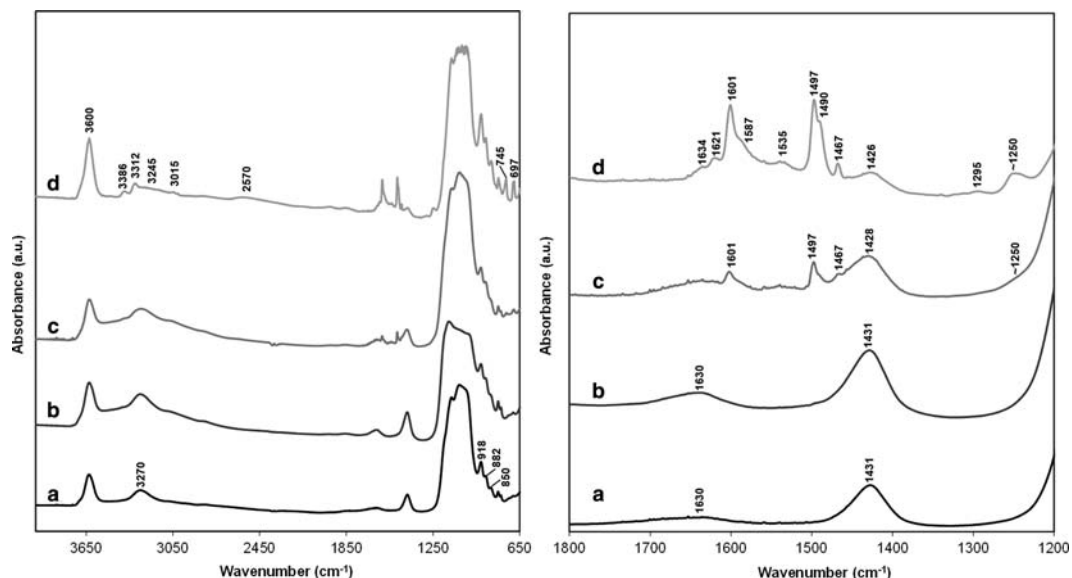


FIG. 3. IR spectra with a specific zoom in the range 1200–1800 cm^{-1} of NH_4 -smectite after 7 days of interaction with: (a) water used as reference; (b) a 0.01 mol L^{-1} aniline solution; (c) a 0.1 mol L^{-1} aniline solution; and (d) a pure (11 mol L^{-1}) aniline solution.

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 at $\sim 1295 \text{ cm}^{-1}$ assigned to

the H–C–H deformation vibration band ($\delta_{\text{H-C-H}}$), and the stretching band of the C–N bonds ($\nu_{\text{C-NH}_2}$) at $\sim 1250 \text{ cm}^{-1}$. The deformation band of NH_4^+ (δ_{HNH}) in

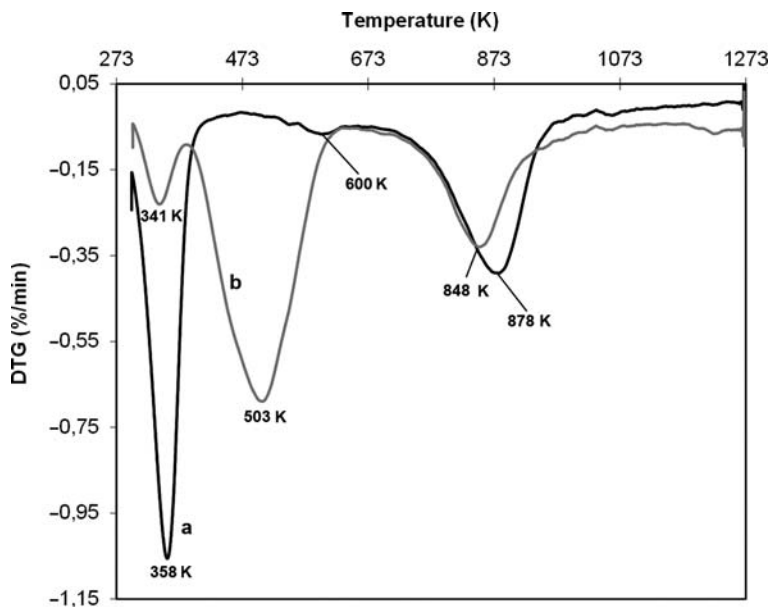


FIG. 4. Differential thermo-gravimetric curves of NH_4 -smectite after 7 days of interaction with: (a) water and (b) pure aniline solution.

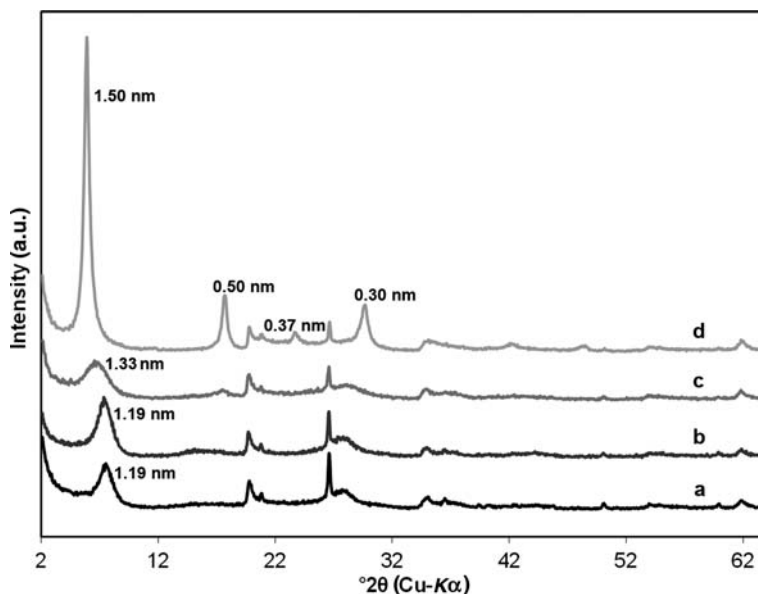


Fig. 5. XRD patterns of NH₄-smectite after 7 days of interaction with: (a) water used as a reference; (b) a 0.01 mol L⁻¹ aniline solution; (c) a 0.1 mol L⁻¹ aniline solution; and (d) a pure (11 mol L⁻¹) aniline solution.

the range 1426–1431 cm⁻¹, characteristic of the NH₄⁺ interlayer cation, had a lower intensity after interaction with pure aniline compared with water (Fig. 3a,d).

The DTG curves of NH₄⁺-smectite after interaction with water and pure aniline solution are reported in Fig. 4. The small event at 600 K (Fig. 4a) was attributed to the thermal decomposition of NH₄⁺ (Gautier *et al.*, 2010). The smectite treated had a smaller 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 collected on the NH₄⁺-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 increase in the aniline concentration. After interaction with the 0.1 mol L⁻¹ aniline solution, the NH₄⁺-smectite revealed a broader 001 reflection with a larger basal spacing (1.33 nm) (Fig. 5c). In the case of pure aniline (Fig. 5d), the 001 reflection was sharper and more intense, and so were the 003 (0.50 nm), 005 (0.30 nm) and 004 (0.37 nm) reflections.

The IR spectrum of the clay treated with pure aniline solution was compared to that obtained after

three successive washings with milli-Q water (Fig. 6). After rinsing, a general decrease in the intensity of the bands characteristic of binding with aniline molecules was observed (3383, 3310, 1601, 1497 and 1469 cm⁻¹) (Fig. 6b). The XRD pattern of the clay treated with pure aniline solution was compared to that obtained after three successive washings with milli-Q water (Fig. 7). The basal spacing of the sample treated shifted from 1.50 to 1.35 nm after rinsing, the 001 reflection became wider and the 003 reflection disappeared.

DISCUSSION

Non-retained molecules

The absence of sorption onto NH₄⁺-smectite observed for 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 particular nitrile, ether and alcohols, in solution, onto a Ca-montmorillonite. Those authors showed that the length of the chain had a significant 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 consist of

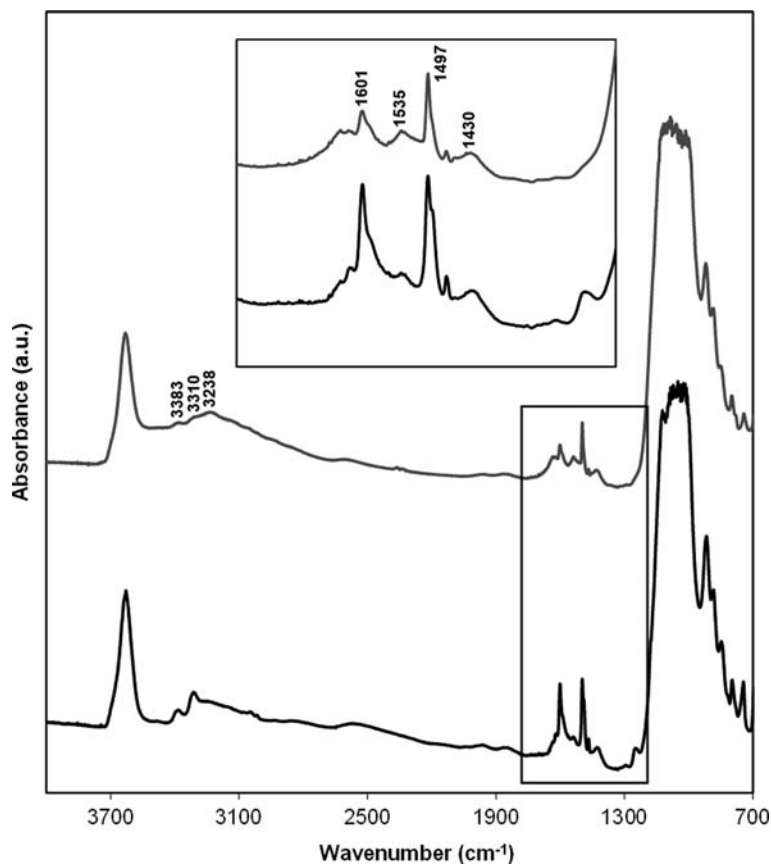


FIG. 6. IR spectra of NH_4 -smectite after 7 days of interaction with: (a) pure aniline; and (b) pure aniline rinsed with milli-Q water.

short chains, which prevented them from being sorbed to the NH_4^+ -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 greatest vapour 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 NH_4^+ -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 limits the dipole-dipole interactions with the hydrophilic surface of the smectites and leads to a very limited adsorption.

Weakly retained molecules

Phenol. Phenol sorption onto clays has been described extensively in the literature, both for clays with inorganic interlayer cations (Isaacson & Sawhney, 1983; Ovadyahu *et al.*, 1998a,b; Viraraghavan & de Maria Alfaro, 1998; Yapar & Yilmaz, 2005; Richard & Bouazza, 2007; Djebbar *et al.*, 2012; Janík *et al.*, 2013), and for organoclays (Zhang & Sparks, 1993; Dentel *et al.*, 1995; Koh & Dixon, 2001; Yilmaz & Yapar, 2004; Richard & Bouazza, 2007; Alkaram *et al.*, 2009; Díaz-Nava *et al.*, 2012), but never on NH_4^+ -exchanged clays. Adsorption of phenol is known to be pH-dependent (Viraraghavan & de Maria Alfaro, 1998; Yilmaz & Yapar, 2004; Yapar & Yilmaz, 2005). 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

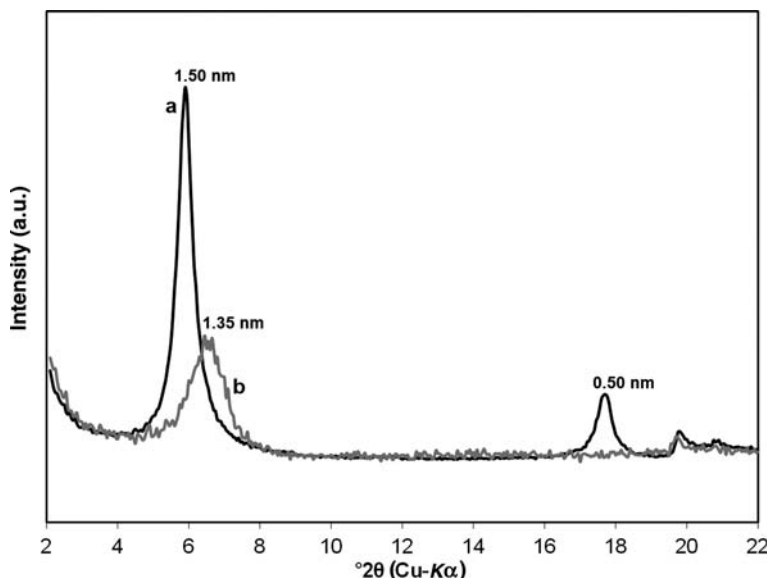


FIG. 7. XRD patterns of NH₄-smectite after 7 days of interaction with: (a) pure aniline; and (b) pure aniline rinsed with milli-Q water.

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,b). Two binding configurations involving a hydrogen bond between the phenol group and water molecules were suggested (Fig. 8). 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

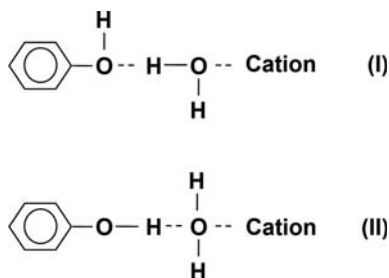


FIG. 8. Possible binding configurations involving a hydrogen bond between a phenol group and a water molecule.

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 ≈ 0.69 for NH_4^+), the H-bond between hydration water and clay layers will be easy to break, and configuration I will generally be 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 Na^+ - and K^+ -montmorillonite by Saltzman & Yariv (1975). The adsorption of phenol molecules onto the surface of natural clay, through hydrogen bonds between the 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 pK_a 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 the water molecule. Configuration II shows a hydrogen

bond between a hydrogen from aniline and oxygen from the water molecule. There are several possible explanations why small quantities of acetone and ethanol were 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 Ca^{2+} and Na^+ 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 due partly to Van der Waals interactions in a study of the adsorption of ethanol and acetone in liquid state on dehydrated montmorillonites (Bissada *et al.*, 1967). 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 NH_4^+ is larger than that of K^+ , the interaction energy will be weaker and adsorption on NH_4^+ -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 in 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 a water-vapour pressure of 2.34 kPa at 293 K. With respect to the binary diagrams of water-ethanol and water-acetone, the energy needed to reach the boiling point of a mixture rich in water is greater than that for a mixture with more organic compounds present. 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 concentrations.

Strongly retained molecule: aniline

With a pKa value of 4.6 for the anilinium/aniline couple, anilinium exists in small proportions in aqueous solution ($\text{pH} = 7.3$; Table 2) and cationic

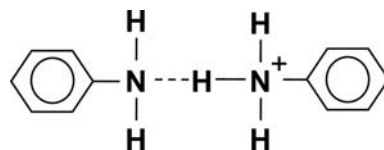
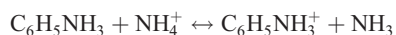


FIG. 9. Binding structure for an aniline-anilinium ion.

exchange with NH_4^+ should be considered. The FTIR spectrum for pure aniline has highlighted the presence of a small quantity of the anilinium and aniline-anilinium ions (Yariv *et al.*, 1968) (Fig. 9). Those authors also showed that the formation of anilinium may occur directly in the interlayer space by the following reaction:



The intercalation of aniline in the interlayer was shown by FTIR analyses. The shift in 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 ($d_{001} = 1.19 \text{ nm}$, Fig. 5a,b) indicated that the aniline molecules were coordinated parallel to the smectite layers. This arrangement was 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 larger basal spacing ($d_{001} = 1.33 \text{ nm}$, Fig. 6) is characteristic of disorder in the interlayered 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 $d_{001} = 1.5 \text{ nm}$ suggests that the aniline molecules were intercalated

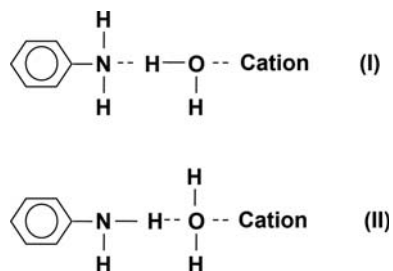


FIG. 10. Possible binding configurations involving a hydrogen bond between aniline and an interlayer water molecule.

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 ($Z/r \approx 0.69$ where Z is the cation charge and r its radius), the H bond between hydration water and clay layers will be easy to break. Hence, configuration I will be dominant, with both hydrogen atoms of aniline being 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 at 3312 cm⁻¹ and 3386 cm⁻¹ respectively ($\nu_{\text{N-H}}$, Fig. 3d) confirmed this predominance (Yariv *et al.*, 1969). Another configuration in which the aniline molecule was bound directly to NH₄⁺ was proposed by Yariv & Cross (2002). This configuration concerned only very weakly hydrated environments and high aniline concentrations.

The fixation of aniline molecules on the NH₄⁺ interlayer cations was strengthened by the shift of the main stretching vibration bands ($\nu_{\text{N-H}}$ of a NH₄⁺ group) from 3270 cm⁻¹ in the starting sample (Fig. 3a) to ~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 in some bands characteristic of the FTIR spectrum of pure aniline to lower wavenumbers after interaction with the NH₄⁺-smectite also confirmed the sorption of aniline on NH₄⁺-smectite: the asymmetric and symmetric stretching bands ($\nu_{\text{N-H}}$ of NH₂) shifted from 3500 and 3418 cm⁻¹ in pure liquid aniline (Akalin & Akyüz, 1999) to 3386 and 3312 cm⁻¹ after interaction with NH₄⁺-smectite (Fig. 3d). Also, 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 ~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 NH₄⁺-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 NH₄⁺-smectite after rinsing the NH₄⁺-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 NH₄⁺-smectite treated with aniline solution (Fig. 7) which confirmed the partial desorption of aniline.

CONCLUSIONS

The present study focused on eight short-chain VOCs contained in landfill leachate interacting with NH₄⁺-smectite. The degree of sorption of these organic compounds on NH₄⁺-smectite depends mainly on the magnitude of the interaction processes which ensures both cohesion and stability in the resulting materials. The absence of sorption observed for acetonitrile, methyl tert-butyl ether, dichloromethane and benzene is in agreement with previous studies. Phenol, ethanol and acetone were sorbed very weakly. Van der Waals interactions with clay layers and cation-dipole interactions allowed the sorption of ethanol, acetone and phenol. For phenol sorption, hydrogen bonds formed between hydroxyl groups and interlayer water molecules, whereas the greater 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 sorbed strongly on NH₄⁺-smectite, and only partially desorbed after rinsing. The proposed model of sorption was binding of aniline on the NH₄⁺ cations, with the formation of H-bonds through interlayer water molecules. Moreover, aniline might be retained by other processes: (1) by cationic exchange of NH₄⁺ by anilinium ions in small proportions; (2) by anilinium formation following the reaction $\text{C}_6\text{H}_5\text{NH}_2 + \text{NH}_4^+ \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+ + \text{NH}_3$; and (3) by the formation of the aniline-anilinium ion in the clay interlayer. The sorption models for phenol, ethanol, acetone and aniline in an NH₄⁺ smectite were identical to those proposed in the literature for smectites containing Ca²⁺ or Na⁺ as interlayer cations.

The interaction processes involved in the sorption of these eight VOCs on NH₄⁺-smectite can be extended to clay barriers. Only an easily reversible physisorption was possible for acetonitrile, methyl tert-butyl ether, dichloromethane and benzene. Hence, these 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 retained strongly by the clayey barrier and may also migrate towards groundwaters, as shown previously 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 NH_4^+ -smectite, which may reduce its swelling capacity, and therefore may increase the permeability of the clay barrier.

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