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Physicochemical characteristics of organophilic clays prepared using two organo-modifiers: alkylammonium cation arrangement models

Ismail Ltifi[1] · Fadhila Ayari[1] · Dalila Ben Hassen Chehimi[1] · Malika Trabelsi Ayadi[1]

Abstract

The clay was modified by an ion exchange reaction with cetylpyridinium chloride CPC and hexadecyltrimethylammonium bromide HDTMA. The modified samples were studied by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The basal spacing of unmodified clay determined by XRD was 12.72 Å and, after modification, increased with increasing concentration; expressed as a function of the cation exchange capacity (CEC) of the clay; to reach 21.08 and 26 Å for clays modified with CPC and HDTMA successively for an equal concentration of 3CEC. FTIR studies revealed structural differences between modified and unmodified clay samples. Modified clay spectra showed C–N functional bands (1480 cm^{-1}) and C–H vibrations (near 2936 and 2871 cm^{-1}). The results of the SEM study reveal a difference between natural and modified clays. The purified clay has massive and curved plates. However, the modified clays show numerous small aggregate particles and plaques that become relatively flat. The arrangement of surfactants in clay is rather complicated. It depends on the nature of the surfactant molecules, the CEC of the clay and the method of preparation. According to these parameters, the inserted surfactants may be arranged in monolayer, paraffinic or admicelles structures.

Keywords Tunisian clay · HDTMA · HDPyridine · Arrangements

Introduction

There has been growing interest in the development of innovative adsorbent materials to solve the problem of industrial wastewater pollution (Nejib et al. 2014; Ltifi et al. 2017; Nahed and Kais 2015). Natural clays are considered among the available materials such as montmorillonite which is widely used as adsorbents because of the high cation exchange capacity (CEC), so that their swelling properties are high (Ayari et al. 2005). Montmorillonite (MMT) is a 2:1 clay mineral that has two silica–oxygen tetrahedral sheets with a central alumina octahedral layer (TOT layer).

Mixed "clay-surfactant" systems are of great interest for industrial applications. Nowadays, they are used in various fields as thickeners in inks, in the preparation of nanoparticle silver also as additives thickeners and in cosmetic formulations, as sorbents of organic compounds present (dyes, metals heavy) wastewater. Their main interest comes from the properties conferred by the intercalation of organic cations in interfolliaiary clay space. Substitution of surfactants greatly increases the hydrophobicity of interfolliaiary clay space, and therefore, clay can be swollen in non-aqueous systems. The adsorption of alkylammonium molecules or cations on the clay has different structures depending on the cation exchange capacity of clay (CEC), the size of the alkyl chain or the method of preparation. These molecules or cations can adopt various arrangements in the interlayer spacing of the clay.

The hexadecyltrimethylammonium bromide HDTMA intercalated in Na-montmorillonite has a paraffin-type monolayer arrangement parallel to the basal montmorillonite spacing. With the increase in the concentration of surfactants hexadecyltrimethylammonium bromide and cetylpyridinium chloride (0–3 CEC) in montmorillonite (Tahani et al. 1999), the adsorption of the cationic surfactant has been widely studied for several types of clay such as montmorillonite

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(Zhu et al. 2003), saponite (Ogawa et al. 1995), kaolinite (Komoria et al. 1999) and mica (Chen et al. 1992).

In contrast, few articles are devoted to the adsorption of organic ammonium cations on natural interstratified clays composed of smectite, kaolinite and illite.

The aim of the present study is to try to elucidate the mechanism by which surfactant molecules or cations are intercalated in the interlayer space of these clays, thanks to an analysis based on adsorption isotherms, spectroscopy FTIR and diffraction of rays X.

Experimental

Materials

The clay used is from the GAFSA region located south of 'TUNISIA.' Organic surfactants used were hexadecyl-trimethylammonium bromide (HDTMA, formula weight: 364.45 and chemical formula: $C_{19}H_{42}BrN$) and cetylpyridinium chloride (CPC, formula weight: 339.9 and chemical formula: $C_{21}H_{38}ClN$) was obtained from Sigma-Aldrich. The molecular structure of CPC and HDTMA is illustrated in (Fig. 1). Other chemical reagents, such as NaOH, HCl and AgNO₃, were utilized of analytical grade.

Preparation of organoclays

The organophilic clays are prepared by the procedure which takes place in two stages; on the one hand, a 20 g of the adsorbent (Gafsa Clay) is dispersed in about 500 ml of water in distilled water. On the other hand, a desired amount of surfactant (HDTMA or CPC) was stirred in 100 ml of distilled water until it was completely dissolved and then added drop wise to the clay solutions. The amounts of each surfactant were calculated on the basis of the CEC of the adsorbent. The reaction mixtures were mechanically stirred

at room temperature for 48 h. The resulting mixture was filtered through filter papers and washed with distilled water until complete breakdown of Br⁻ and Cl⁻ (AgNO₃ test). The products are dried at 80 °C for 12 h. Finally, the adsorbents were ground in an agate mortar and stored (Ltifi et al. 2017).

Characterization methods

The prepared organoclays were characterized by X-ray diffraction (XRD), surface area measurement (BET), Fourier transform infrared spectroscopy (FTIR). XRD for obtaining basal spacing d(001) values was operated, and the method was described in the paper by Park et al. (2013). The mineralogical composition was determined in the < 2 μm fraction. The proportions of species in clay were estimated by the refence intensity ratio method using the High Score software. The specific surface area (S_s) measured by the BET and the cation exchange capacity (CEC) is determined by the method of MANTIN (Mantin 1969). The zero charge point (PZNPC) of the aqueous clay adsorbent was analyzed using the solid addition method (Wibowo et al. 2007).

Characterization

X-ray diffraction

X-ray diffraction (XRD) patterns were recorded using Cu $K\alpha$ radiation ($n = 1.5418$ Å), a Philips PANalytical X' Pert PRO diffractometer operating at 40 kV and 40 mA with 0.25° divergence slit. For XRD at low angle section, it was between 1° and 30° (2θ) at a step size of 0.0167° with variable divergence slit and 0.125° anti-scatter slit.

Spectroscopy IR

Infrared spectra are collected on PERKIN ELMER 66 (Fourier transform infrared spectrometer); OPUS software allows the band intensity to be normalized by the most intense one. Spectra are collected over the spectral range 400–4000 cm⁻¹.

Measurement of the specific surface by the BET method and cation exchange capacity (CEC)

Nitrogen adsorption measurements were performed at 77 K with an Autosorb-1 unit (Quantachrome) for the determination of sample textural properties using the multipoint Brunauer–Emmett–Teller (BET) method. The samples were out gassed at 120 °C under a vacuum at 10–3 mm Hg for 3.5 h.

CEC was determined by adsorption of copper ethylenediamine $(EDA)_2CuCl_2$ complex (Bergaya and Vayer 1997).

Molecules	Molecular structure
Hexadecyltrimethylammonium bromide HDTMA $C_{19}H_{42}BrN$	Br⁻ Me–N⁺–(CH₂)₁₄Me Me Me
Cetylpyridinium chloride CPC $C_{21}H_{38}ClN$	Cl⁻ N⁺ CH₂(CH₂)₁₄CH₃

Fig. 1 Molecular structure of HDTMA, and CPC

Morphology MEB

The morphology of the prepared materials was evaluated by transmission electron microscopy (TEM); the SEM images were taken by a Hitachi S-3400N transmission electron microscopy.

Results and discussion

Chemical composition of raw and purified clay

The results of the chemical analysis given in Table 1 show:

- Silica/alumina ratios equal to 3.14 characteristics of montmorillonite. Value included in the domain (2.5, 5).
- A high content of magnesium and iron.
- The clay phase consists mainly of montmorillonite with a small amount of illite and kaolinite.

The silica to alumina SiO_2/Al_2O_3 ratio confirms montmorillonite and the essential component of GAFSA clay. These results show a decrease in the silica content (SiO_2) from 54.3% for the crude clay to 47.51% for the purified clay and sodium.

The decrease in the CaO and MgO content is due to the Ca and Mg cations exchanged by the sodium cations. In parallel during the treatment of the clay purified by sodium chloride (NaCl) during the washing operations, there is an increase in the concentration of Na_2O. This increase is due to the ion exchange between the ions of the clay and the sodium ion from the salt (NaCl).

Table 1 Chemical composition of the catalyst

Oxide elements (%)	Mass composition in % calcined clay oxides	
	ArB	ArP
SiO_2	54.30	47.51
Al_2O_3	16.42	15.13
Fe_2O_3	08.21	09.58
MgO	04.75	03.47
CaO	04.61	03.38
K_2O	01.32	00.96
Na_2O	00.75	06.34
Total	90.38	86.37
PF	10.40	11.20
SiO_2/Al_2O_3	03.30	03.14

Changes in basal spacings by organophilization

One of the most important methods for studying Interlayer displacement is X-ray diffraction (XRD). The decrease in the angle 2θ and the widening of the peak indicate an increase in interfolliairy spacing (Jahan et al. 2012). The Bragg law allows to calculate the distance of the silicate layer ($n\lambda = 2d\sin\theta$, d = interfolliairy distances). One of the most important properties of layered silicates is the distance between the clay layers (d001). This distance can be calculated with data collected from X-ray diffraction. It is also reflected in the XRD pattern of the purified clay. When the modification of substances cannot penetrate the interlayer space, the value of d001 does not change (Kozak and Domka 2004), in our study and after the ion exchange reaction, the basal spacing increases from 12.72° to 26° for HDTMA and 21.08° for CPC indicating that both cationic surfactants have been intercalated successfully within clay (Fig. 2) (Hoidy et al. 2009).

Infrared spectroscopy (IR)

Based on the results of the XRD, it was possible to confirm that the exchange of HDTMA and CPC polycations with the Na^+ alkaline cations of the interfoliairy space is successful.

Two absorption bands at 726–780 cm^{-1} correspond to the mode of vibration of deformation out of the plane of the CH_2 group (Vaia et al. 1994).

The group in the 950–1100 cm^{-1} region corresponds to the stretching vibration of the Si–O groups (Xie et al. 2001).

As shown in Fig. 3, new peaks appear at 2939 cm^{-1}; 2842 cm^{-1} for clay-CPC and at 2936 cm^{-1} and 2871 cm^{-1} for clay-HDTMA which correspond to asymmetric vibration –CH_2 and symmetric stretching –CH_2. These bands are absent in the IR spectrum of unmodified purified clay (0 CEC) which indicates the incorporation of surfactants into the organophilic clays.

Since the groups are very narrow, the variation in their intensity increases with the increase in the initial surfactant content, indicating the intercalation of a larger amount of surfactant in the studied clay with the increase in the initial amount of the surfactant.

As shown in Fig. 3, when the surfactants are sandwiched within the clays of the clays, a broad band at 1480 cm^{-1} indicating the presence of the functional group C–N corresponds to the tertiary amine as described in literature (Zhu et al. 2005).

The smectite family has spectral hydration characteristics that have been attributed to adsorption of water on the external surfaces of the clay as well as internal regions. The property of these interlayer waters greatly depends on the level of moisture and the intercalated cation.
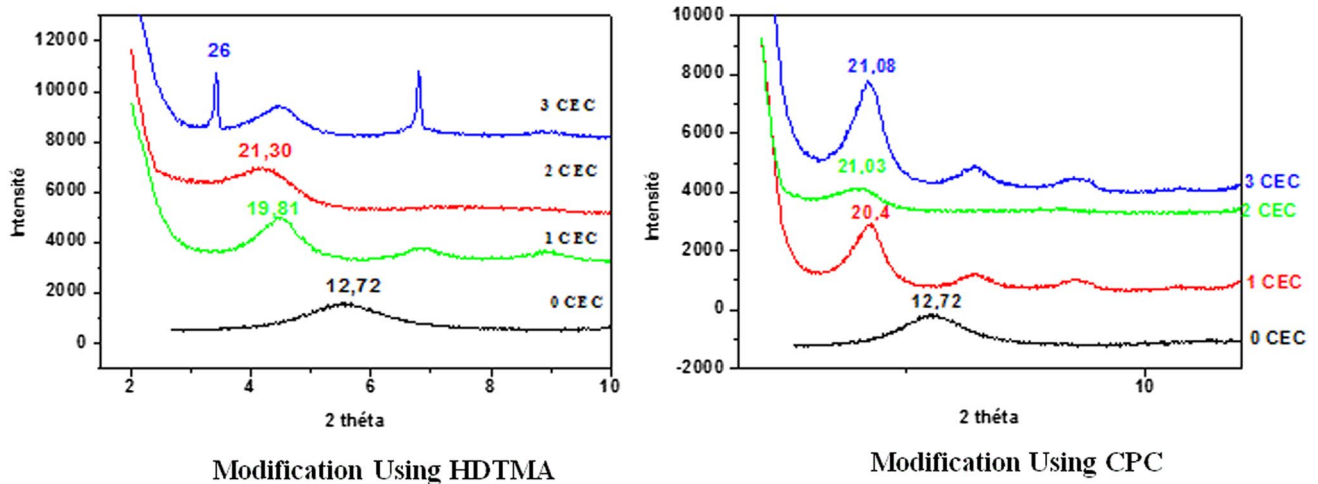
Fig. 2 X-ray diffractograms of purified clay (0 CEC) and organophilic clays by HDTMA and CPC (different concentrations 1, 2 and 3 CEC)
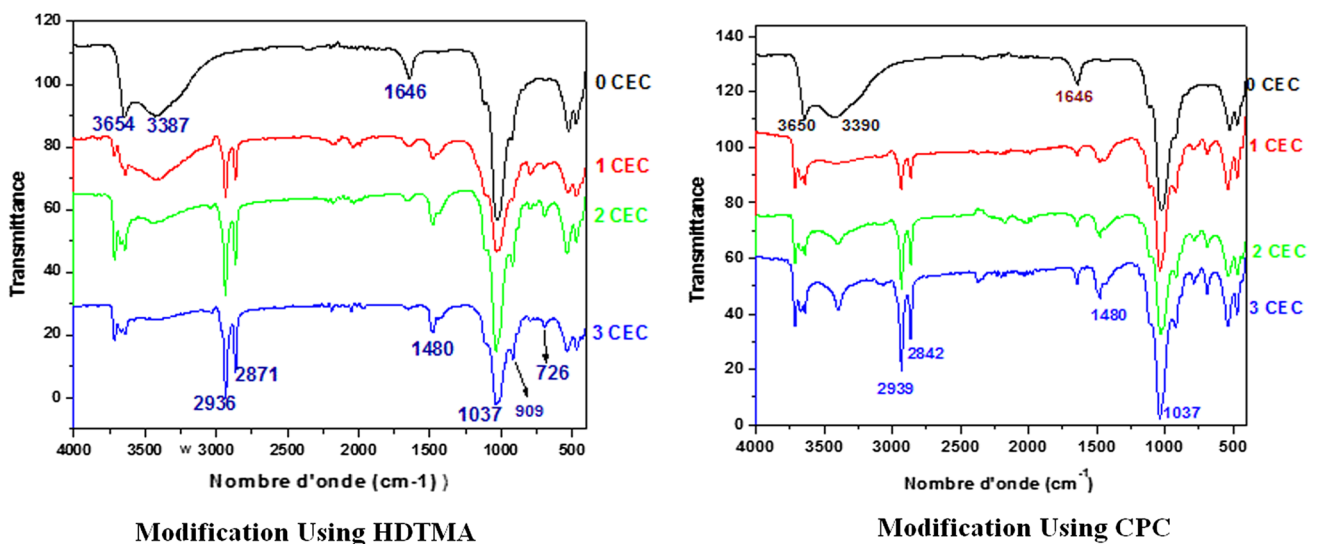

Fig. 3 FTIR spectra of purified clay (0 CEC) and organophilic clays by HDTMA and CPC (different concentrations 1, 2 and 3 CEC)

The spectra show a more obvious adsorption band at 3620 cm^{-1} due to structural stretching vibrations of OH groups independent of surfactant loading which is consistent with the result indicated in the literature.

In the region between 3100 and 3500 cm^{-1}, the spectra show a wide band around 3400 cm^{-1} corresponding to the symmetric and asymmetric overlapping of the vibrations (H–O–H).

When the surfactants are inserted in the smectite gallery, the adsorption bands detected are mainly attributed to the adsorbed water molecules, in particular with high surfactant loading. At the same time, with the intercalation of surfactants, the clay surface property is modified. As a result, the hydrophilic surface of the smectite has been

changed and becomes hydrophobic and the clay becomes organophilic(Kung and Hayes 1993; Mandalia and Bergaya 2006).

The study of the point of zero charge and cationic exchange capacity

The PZNPC or pH zero corresponds to the pH value for which the net charge of the adsorbing surface is zero (Wibowo et al. 2007). This parameter is very important in the adsorption phenomena, especially when electrostatic forces are involved in the mechanisms. A quick and easy way to determine the PZNPC is to place 50 ml of distilled water in closed bottles and adjust the pH of each (values between 2
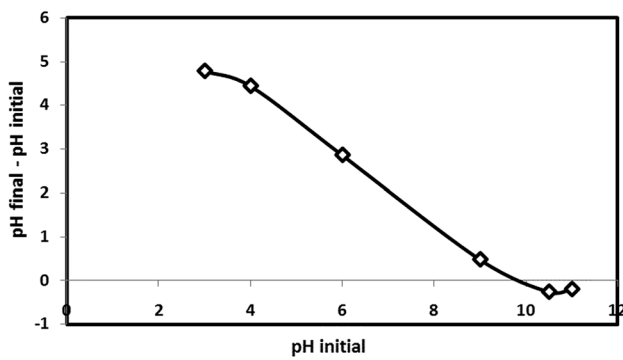
Fig. 4 Point of zero charge in clays

Table 2 The BET surface area, total pore volume and average pore diameter for clay, HDTMA-clay and CPC-clay

Adsorbent samples	S_{BET} (m²/g)	VP (cm²/g)	APD (nm)	d_{001} (nm)
Clay	54.00	0.107	4.0	1.27
HDTMA-clay	02.19	0.011	3.3	2.60
CPC-clay	01.28	0.007	2.7	2.10

S_{BET} specific surface area, *VP* pore volume determined by BJH method from N_2 desorption isotherm, *APD* average pore diameter determined by the curve of BJH desorption d*V*/d*D* pore volume, d_{001} Basal distance

and 12) by addition of NaOH solution or HCl (0.1 M). Then added to each flask, 50 mg of clay. The suspensions should be kept in agitation at room temperature for 24 h, and the final pH is then determined. It relates to a graph $pH = f(pH_i)$ where $pH = (pH_f - pH_i)$; the intersection of the curve with the axis that passes through the zero gives the isoelectric point (Fig. 4).

Regarding the value of CEC of raw and purified clays, measurements of the cation exchange capacities of the studied clay are taken by the method of MANTIN.

It should be noted that for the raw sample, the CEC is 76 meq/100 g of calcined clay and that of the purified sample is 91.04 meq/100 g of calcined clay. This difference is due to the presence of impurities in the untreated sample, which are removed after purification.

The obtained CEC values are characteristic of smectite clay.

BET analysis of clay and surfactant modified HDTMA and CPC

Table 2 shows the BET surface area (m²/g), the total pore volume (cm³/g) and the average pore diameter (nm) and the basal distance (d_{001}) of the clay, clay-CPC adsorbent and clay-HDTMA. The BET surface area decreased from 54 to 1.28 m²/g for CPC-modified clay and to 2.19 m²/g for HDTMA-clay modification, which can be attributed to blockage and pore screening of clay by surfactant alkyl chains. The average pore diameter decreases slightly from 4.0 to 3.3 nm from clay to HDTMA-clay, which is likely due to the complete removal of micropores of the adsorbent structure (Gladysz-Plaska et al. 2012).

Morphology and particle size by MEB

The SEM micrographs (Fig. 5) show the surface morphology of montmorillonite and organophilic clay samples. It can be seen that the original montmorillonite Arg-Na has massive and curved plates (Fig. 5a) (Lee and Kim 2002). However, clay treated with cationic surfactants (HDTMA and HDPy) shows significant changes in morphology.

Compared to the morphology of Na-montmorillonite, there are many small aggregated particles and the plates become relatively flat in Arg-HDTMA and Arg-HDPy organophilic clays (Fig. 5b, c).

Therefore, the present study shows that not only the basal spacing but also the morphology of the organophilic clays
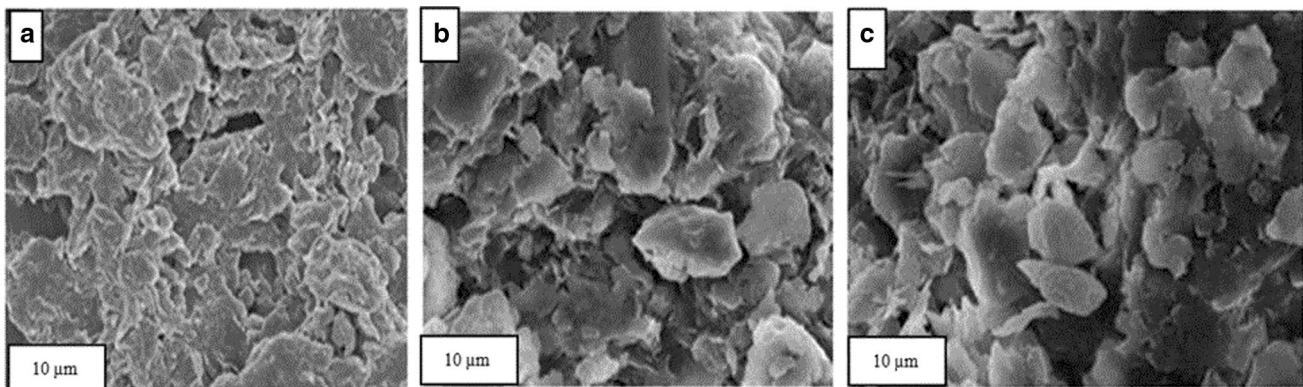

Fig. 5 SEM images of Arg-Na (**a**), Arg-HDTMA (**b**) and Arg-HDPy (**c**)

strongly depends on the packing density of the surfactants in the interspace of montmorillonite.

Alkyl chain arrangements

Calculation of the angle of inclination:

According to Zhu et al. (2003), the theoretical length of the HDTMA cation is 25.3 Å, the height of the alkyl chain is 4.1 Å, and the head of the nail is 5.1 Å; The HDTMA cation is flat between layers of montmorillonite.

According to Gamoudi et al. (2015), the theoretical length of the cation HDPy is 23.1 Å, the height of the alkyl chain is 2.8 Å, and the head of the nail is 4.9 Å.

The difference between the values of the basal space d001 affects the organization of the alkylammonium ions (HDTMA and HDPy) in the interfolliairy space, and the amount of surfactants also plays a role on the type of arrangement.

Based on the $d001$ value and the dimensions of the alkylammonium, as shown in Fig. 6, the nature of the alkylammonium ion arrangements in the interfolliairy space is determined. All XRD analysis values of various organophilic clays are summarized in Table 3.

We also calculated the angle of inclination (α) of the alkylammonium ion between the clay sheets based on the interlayer distance $d001$ and the length of the alkylammonium ion. These values were calculated assuming that the organization of ammonium ions is paraffinic.

It is important to note that the angle of inclination (α) of the alkylammonium ion between the clay layers is calculated as indicated by the following equation:

$$\sin \alpha = \frac{d001 - e}{a}$$

Fig. 6 Dimension of molecules (i) HDTMA+ and (ii) HDPy (Bors et al. 2001)
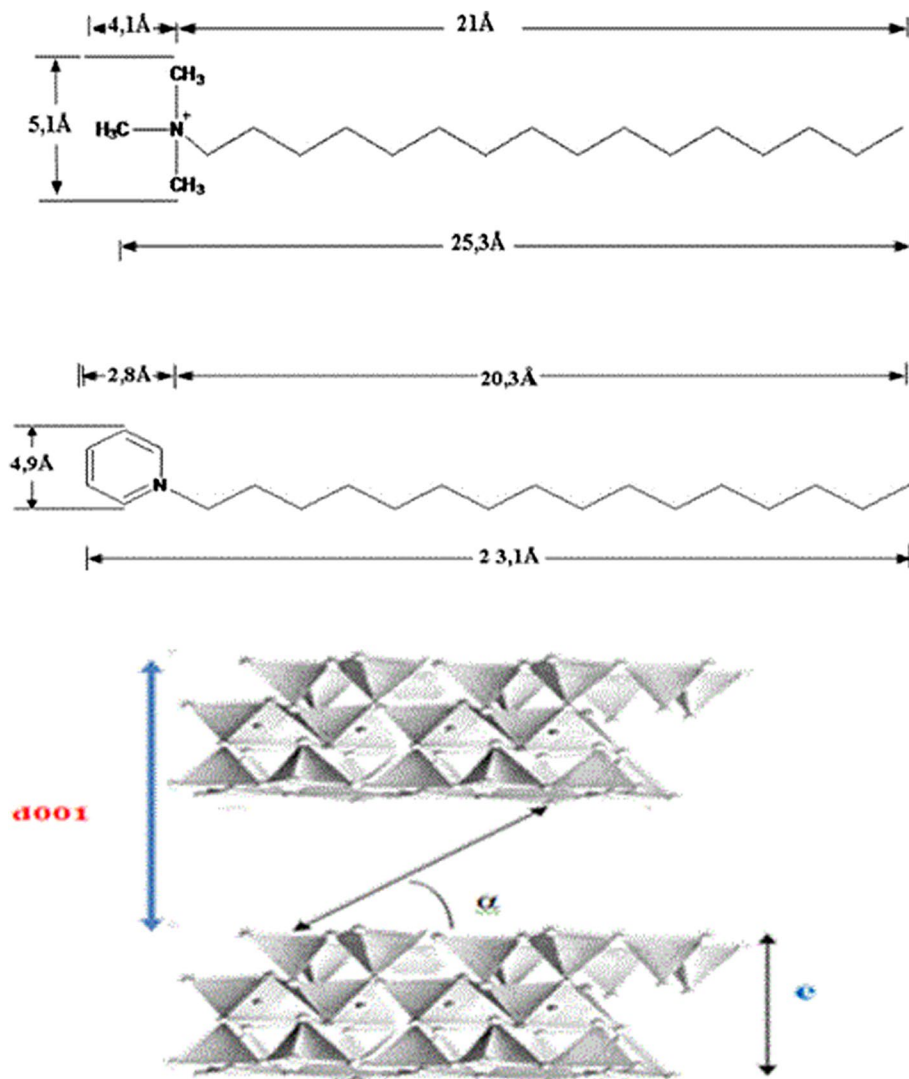
Table 3 d00l values of HDTMA, HDPy and different arrangements

CEC	HDTMA		HDPyridine	
	d/nm	Arrangements	d/nm	Arrangements
1	1.981 ($\alpha=35.45$)	Paraffine-type monolayer	2.040 ($\alpha=42.06$)	Paraffine-type monolayer
2	2.130 (39.79)	Paraffine-type monolayer	2.103 ($\alpha=43.63$)	Paraffine-type monolayer
3	2.600 ($\alpha=55.00$)	Paraffine-type bilayer	2.108 ($\alpha=44.40$)	Paraffine-type monolayer

e thickness of the surfactant (Å); a length of the surfactant (Å) (He et al. 2006).

For HDTMA: $e=5.1$ Å and $a=25.3$ Å.

For HDPyridine: $e=4.9$ Å and $a=23.1$ Å.

The spacing of organophilic clays increases with an increase in the amount of surfactant added (increase in the concentration of the alkylammonium salts).

The alkyl chains take the paraffin-type arrangement in the interfolliairy space of the clays. The angle of inclination α and the spacing d increase with the increase in the concentration of the surfactants studied, as shown in Table 3.

In the case of HDTMA, for a concentration of 3CEC, the angle of inclination α is 55°. Under this condition, the alkyl chains take the arrangement of a paraffin-type bilayer in the studied clay, as illustrated in Fig. 7.

Likewise for HDPyridine and for the same concentration (3CEC), the alkyl chains adopt the paraffin-type single-layer structure. Therefore, the type of arrangement depends on the length of the alkyl chain as well as the concentration of surfactant.

Conclusions

In this study, modified organic clays were obtained with two different quaternary ammonium salts (HDTMA and HDPyridine). X-ray diffractograms show that the interlayer distance (d001) of the organophilic clay increases after treatment

Fig. 7 Representation of modified smectite arrangements by HDTMA (**a**) and HDPy (**b**). The lateral distances between the alkylammonium units are inversely related to the charge density of the layer
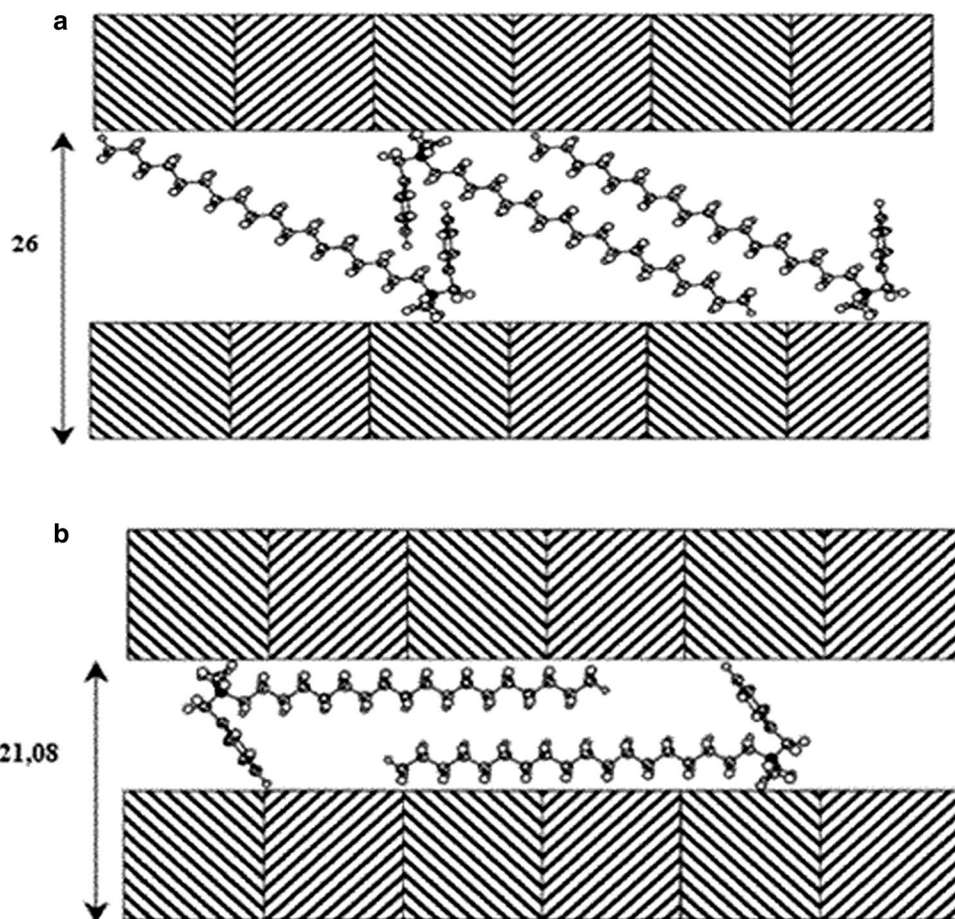
with the two quaternary ammonium salts (HDTMA and HDPyridine), confirming the intercalation of the ammonium cations within clay. The greatest interlayer distance is observed in clays treated with HDTMA salt. Infrared spectra showed new bands of vibrations CH_2 and CH_3, which correspond to the presence of ammonium salts inside the clay structure. Finally, the results of the adsorption capacity confirmed the great promise of using organophilic clays as adsorbents for the adsorption of organic solvents for the treatment of wastewater.

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