

# Characterization of organo-modified bentonite sorbents: The effect of modification conditions on adsorption performance



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## ABSTRACT

The organic modification of a natural bentonite was evaluated using two methods: exchanging the interlayer cations by hexadecyltrimethylammonium (HDTMA) and grafting with vinyltrimethoxysilane (VTMS) and  $\gamma$ -methacryloyloxy propyl trimethoxysilane (TMSPMA) on montmorillonite surface. The physicochemical characterization of all materials was made by X-ray diffraction (XRD), IR spectroscopy, thermogravimetric analysis (TGA) and Brunauer–Emmett–Teller (BET) surface area techniques. HDTMA cations and organosilanes were intercalated into the interlayer space of montmorillonite, as deduced from the increase of the basal spacing. IR spectroscopy, TGA and BET area give evidence of successful organic modification. The studies show a decrease in the IR absorption band intensity at  $3465\text{ cm}^{-1}$  with surfactant modification, and also a decrease of mass loss due to adsorbed water observed in two samples: the organoclay and functionalized bentonites, which are evidences of a lower interlayer hydrophilicity. The efficiency of aniline removal onto natural bentonite, organobentonite and functionalized bentonites from aqueous solutions was evaluated. Aniline sorption on natural bentonite was studied using batch experiments, XRD and IR spectroscopy. The hydrophobic surface of organobentonite and functionalized bentonites increased the retention capacity for nonionic organic substances such as aniline on bentonites. The sorption properties of modified bentonite, through different modification methods, enhanced the potential industrial applications of bentonites in water decontamination.

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## 1. Introduction

Bentonite is a clay mainly constituted by the clay mineral montmorillonite. Montmorillonites are swellable dioctahedral 2:1 layer silicates which consist of stacks of several so-called 2:1 layers. This clay mineral has a permanent negative charge that arises from isomorphous substitution of  $\text{Al}^{3+}$  for  $\text{Si}^{4+}$  in the tetrahedral sheet and  $\text{Mg}^{2+}$  for  $\text{Al}^{3+}$  in the octahedral sheet. This negative charge is naturally compensated by exchangeable cations (i.e.  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ) located in the interlayer space [1]. Montmorillonite has a high cation exchange capacity (CEC), marked swelling and high specific surface area leading to a strong adsorption/absorption capacity of ionic or polar compounds [2]. Along the edges of this clay

mineral, another surface having variable charge is developed where Si–O–Si and Al–O–Al bonds are ‘broken’ and may convert into Si–OH and Al–OH groups [3]. The hydration of inorganic cations at the exchange sites causes its surface to be hydrophilic and provides appropriate properties for it to act as a natural adsorbent for several pollutants in the treatment of contaminated waters [4].

Sorption has an important effect on the transport, reactivity and bioavailability of contaminants in soils and sediments. There is great interest nowadays in the removal of organic compounds from water by sorption processes. A large number of effective sorbent clays have been developed for organic contaminants retention.

Montmorillonite surface is hydrophilic in character and has low affinity for nonpolar liquids. In order to enhance their applicability, this clay mineral has to be modified or functionalized. There are different ways to modify clay minerals, i.e., adsorption, ion exchange with organic/inorganic cations and grafting with organic compounds [5,6]. Montmorillonites can suffer ion exchange reactions with long-chain or short-chain quaternary amine cations to obtain

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organobentonites [2,7,8]. Cation surfactant retention occurs within the interlayer space of clay minerals with a consequent increase of the basal spacing which provides an optimal hydrophobic environment for the retention of organic molecules. The increment of the basal spacing depends on the surfactant chain length and the charge density of the clay mineral [9,10]. X-ray diffraction (XRD) analyses are mostly conducted to elucidate the structural and mineralogical aspect of intercalated clay minerals [11–14]. The interaction between hydrophobic molecules and clay surfaces can also be greatly enhanced by simple grafting of hydrophobic groups onto the layer surfaces [15], which leads to a well-organized inorganic/organic structural layer material. In previous studies of the interaction between silane derivatives and swelling clay materials, three grafting sites (interlayer, external surface and “broken” edge) have been proposed [16]. The silane compounds interact with the hydroxylated surface groups and the organic moieties are covalently grafted to the mineral [17]. Several other authors have carried out clay modification studies to improve their ability as barriers to isolate organic compounds from gasoline storage tanks [18], landfill waste sites [19] and in the area of nanotechnology to develop polymer nanocomposites from natural clays [20,21].

Phenolic compounds and aniline are common contaminants, particularly found in effluents from pesticides, pharmaceuticals, petrochemicals and other industries. A variety of organobentonites and organosilane grafted bentonites have been applied for the removal of hydrophobic organic compounds, such as phenolic compounds and toxic metals in aquatic environments [10,22–24]. Majdan et al. [25] investigated the relationship between different structures and arrangements of hexadecyltrimethylammonium (HDTMA) and benzyldimethylhexadecylammonium (BDMHDA) surfactant cations in the interlayer space of bentonite and their phenol sorption properties. Liu et al. [26], using IR spectroscopy and X-ray diffraction (XRD) analyses, have demonstrated that phenol is adsorbed and penetrates the interlayer space of the surfactant-modified montmorillonite. Organosilane grafted clays are obtained for the removal of heavy metals and neutral and anionic pollutants from water [24]. Also, alachlor and imazquin removal by clay grafted with 3-chloropropyl-trimethoxysilane and octyltrimethoxysilane was previously studied [23].

The applications of these materials in the waste water treatment is an emerging area of interest [4], however, there are few studies that address the effects of the type of bentonite modification, organic or grafting, on the structural/surface characteristics and organic contaminant sorption performance of the resulting clay adsorbent materials.

In the North Patagonia region (Argentina) it is possible to identify numerous outcrops of commercially available sodium bentonite. Technological applications of raw clay materials mainly depend on total mineral composition, particle size distribution, processing conditions and particularly the state and distribution of the electrostatic charge of the structural layers of the clay minerals [27]. Numerous studies have been performed in our laboratory to investigate environmental applications of North Patagonian bentonites, i.e. pesticide retention [28], pharmaceutical formulation [29–31] and as liners in landfills [32,33].

The main objective of this work is to compare two methods for producing mineral surface variations in montmorillonites, and the potential of the resulting materials for hydrophobic contaminant sorption. In this study, two approaches were adopted for the organic modification of bentonite. The first is based on exchanging the interlayer cations with different concentrations of HDTMA. The other strategy is the grafting of either vinyltrimethoxysilane (VTMS) or  $\gamma$ -methacryloyloxy propyl trimethoxysilane (TMSPMA) on the montmorillonite surface (Fig. 1). The physicochemical characterization of all materials was made by X-ray diffraction (XRD), IR spectroscopy, thermogravimetric analysis (TGA) and

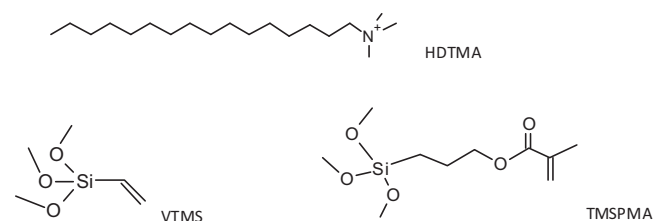


Fig. 1. Structural formulae of the surfactant cation (HDTMA) and silane compounds (VTMS and TMSPMA) used as modifiers for the Na–B.

Brunauer–Emmett–Teller (BET) surface area techniques. Subsequently, the removal efficiency of aniline from aqueous solutions onto natural bentonite, organobentonite and silane grafted bentonite was evaluated.

## 2. Materials and methods

### 2.1. Materials

The bentonite sample (Na–B) was obtained from deposits located close to the margin of the Pellegrini Lake, Río Negro province, North Patagonia, Argentina. The mineralogical composition, determined by XRD, is mainly montmorillonite (90%), with quartz, feldspars and zeolites (heulandite–clinoptilolite) as secondary phases. The structural formula, calculated from  $<2\ \mu\text{m}$  fraction, can be expressed as  $((\text{Si}_{3.85}, \text{Al}_{0.15})(\text{Al}_{1.43}, \text{Fe}^{3+}_{0.26}, \text{Mg}_{0.28}, \text{Ti}_{0.02})\text{O}_{10}(\text{OH})_2) \text{M}^{+}_{0.21}$ , where  $\text{M}^{+}$  is predominantly  $\text{Na}^{+}$ . Its cationic exchange capacity is  $105\ \text{cmol}_c/\text{kg}$  as measured by the  $\text{AgNO}_3$ /thiourea method and it has a specific surface of  $755\ \text{m}^2/\text{g}$  ( $0.755\ \text{m}^2/\text{kg}$ ) as measured by the adsorption of ethylene glycol monoethyl ether [32] (identified as sample CATAE).

Hexadecyltrimethylammonium bromide (HDTMA) was purchased from SIGMA (purity of 98%). The silane coupling agents were vinyltrimethoxysilane (VTMS) (FLUKA) and 3-(trimethoxysilyl)propyl methacrylate (TMSPMA) (ALDRICH). The reaction solvent was a mixture of isomeric xylenes (FLUKA). Aniline, used as an organic contaminant model of analytical grade with an octanol–water partition coefficient ( $\log K_{ow}$ ) of 0.9 and aqueous solubility of  $36,000\ \text{mg}/\text{L}$  at  $25\ ^\circ\text{C}$ . The  $\text{pK}_a$  value at  $25\ ^\circ\text{C}$  for the deprotonation of anilinium was 4.58 [34]. The molecule is therefore present primarily as a neutral species at slightly acidic pH values and higher.

### 2.2. Synthesis of organic modified bentonites

HDTMA intercalated montmorillonite (organobentonite) was synthesized as follows: hexadecyltrimethylammonium bromide amounts equivalent to various percentages of the CEC (0.20, 0.50, 0.70, 1.00, 1.50,  $2.00 \times \text{CEC}$ ) were dissolved in deionized water. 1 g of Na–B was added to the surfactant solutions at  $60\ ^\circ\text{C}$ . The dispersions were stirred for 4 h at  $60\ ^\circ\text{C}$  and then centrifuged at 3600 rpm during 1 h. The samples collected were washed with deionized water by centrifugation (3600 rpm, 30 min) several times until  $\text{Br}^-$  free. Na–B with various HDTMA loading amounts were denoted as  $x\text{CEC-HDTMA}$  ( $x$  means the added amount of HDTMA).

Reactive groups were introduced onto the montmorillonite surfaces by the reaction of silane with hydroxyl groups of the mineral in an anhydrous environment, following Fernández et al. [35]. The silylation reactor system consisted of a 500 mL glass reaction flask that was heated and stirred using a heating/magnetic stirring device placed in an oil bath. The Na–B loading of the solution was  $80\ \text{g}/\text{L}$ . Silylation was carried out using 10% v/v VTMS or TMSPMA solution in xylene. The reaction proceeded for 5 h at  $130\ ^\circ\text{C}$ . The temperature of the condenser was kept at  $75\ ^\circ\text{C}$  to reflux the

solvent back to the reactor while the methanol by-product is formed during the silylation reaction. The suspension was rinsed with pure xylene to remove un-reacted silane. Subsequently, the silylated material was dried under vacuum in a rotary evaporator. The materials obtained were denoted as B-VTMS and B-TMSPMA.

### 2.3. Characterization of untreated and modified bentonites

XRD patterns were recorded using a Rigaku D-Max II-C diffractometer with  $\text{CuK}\alpha$  radiation at 40 kV and 20 mA. Scans were recorded between  $2^\circ$  and  $15^\circ$  ( $2\theta$ ) with a step size of  $0.05^\circ$  and a scanning speed of  $2^\circ/\text{min}$ . The samples were prepared from bentonite suspensions (15 mg/mL) and the dispersions were deposited and oriented onto glass slides under constant 36% relative humidity. Infrared spectra were recorded over the region  $600\text{--}4000\text{ cm}^{-1}$  on a Buck 500 IR spectrophotometer equipped with a deuterated L-alanine doped triglycine sulfate (DLATGS) detector. The samples were examined in KBr pellets (3 mg/300 mg KBr). Thermogravimetric analyses were obtained using a NETZSCH 409 TGA model operating at ramp  $10^\circ\text{C}/\text{min}$  with high resolution from room temperature to  $1100^\circ\text{C}$  in a high-purity flowing nitrogen atmosphere ( $60\text{ cm}^3/\text{min}$ ). BET surface areas were measured by nitrogen adsorption at 77 K with an Asap 2000, Micromeritics Surface Area & Pore Size Analyzer. Prior to  $\text{N}_2$  adsorption, the samples were degassed in a vacuum at  $70^\circ\text{C}$  for 12 h. The relative pressure between 0.05 and 0.30 was applied for the calculation.

Aniline–bentonite sorption complexes were analysed by XRD and IR spectroscopy at a sorptive–sorbent ratio of 68 mmol/kg.

### 2.4. Sorption experiments

Sorption experiments were carried out at  $25^\circ\text{C}$  using the equilibrium technique: 0.062 g of the Na–B or modified bentonite was combined with 10 mL of aniline solution (30–270 mg/L) in deionized water using 25 mL centrifuge tubes. The pH value of the solutions in contact with adsorbents was designed to be in the range 6.5–7.0 (original pH values of the synthetic aniline solutions). The tubes were shaken at 100 rpm for 24 h. After centrifugation (3600 rpm during 1 h), the solute concentration in the supernatant was analysed with a UV–vis Nanocolor Macherey–Nagel spectrophotometer at a wavelength of 230 nm. The measurements were made in duplicate and without pH adjustment.

The amount of adsorbed aniline was calculated by the difference between the initial and the equilibrium concentration. Control experiments (without addition of sorbent) demonstrated that the loss of aniline was less than 5% during the sorption process.

## 3. Results and discussion

### 3.1. Characterization of modified bentonites

#### 3.1.1. X-ray diffraction (XRD)

Fig. 2 shows the XRD patterns of Na–B and surfactant intercalated montmorillonites at different surfactant concentrations. The XRD diagrams for the untreated Na–B produced a diffraction pattern with a first order reflection that corresponds to a basal spacing  $d(001)$  of 1.26 nm ( $6.98^\circ 2\theta$ ). This figure clearly shows the increase in the basal spacing of montmorillonite from 1.26 nm to 1.95 nm for 2.0CEC–HDTMA, indicating that the interlayer spacing of the montmorillonite was expanded by the intercalated surfactant cations. An asymmetric first order reflection for concentrations higher than 0.5CEC–HDTMA was observed, suggesting a random interstratification of surfactant molecule in the interlayer space. The orientation of the intercalated surfactant cation in the interlayer space can be determined from the dimensions of surfactant cations and the interlayer spacing, calculated by subtracting the thickness of the

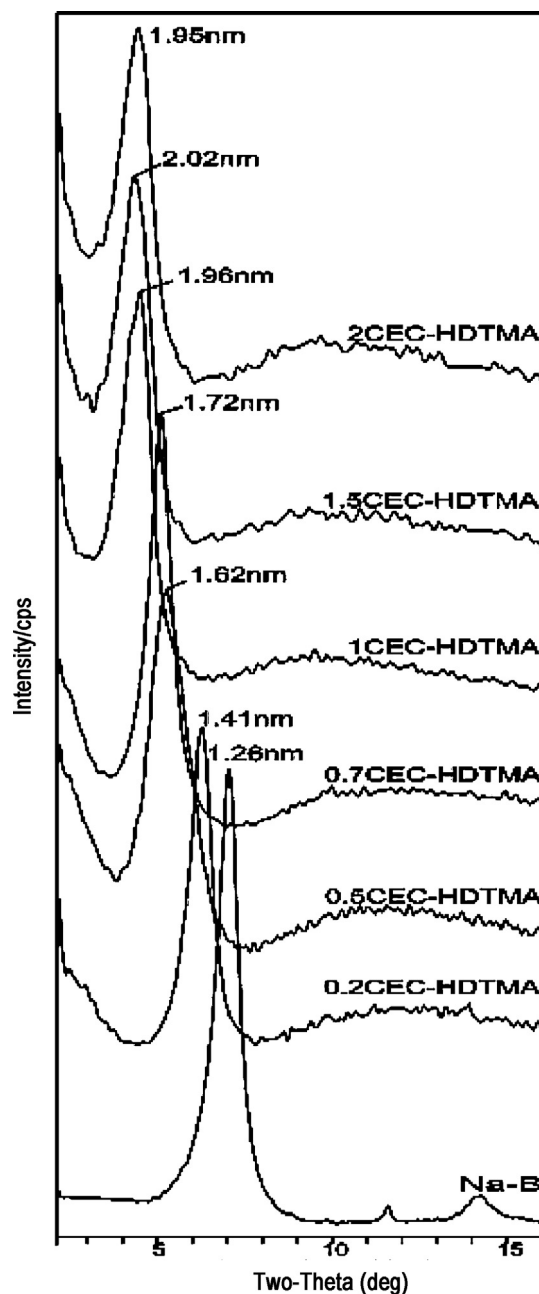


Fig. 2. XRD patterns of untreated bentonite and organobentonites.

unit-cell dimension (0.96 nm) from the basal spacing. The basal spacing value of 1.41 nm corresponding to 0.2CEC–HDTMA suggests that the HDTMA molecule adopts a lateral-monolayer arrangement model within the montmorillonite interlayer space. The XRD pattern of 0.5CEC–HDTMA shows a basal spacing value of 1.62 nm. According to He et al. [36] this would correspond to a transition structure between lateral-monolayer and lateral-bilayer for the HDTMA molecule. The basal spacing of 1.72 nm observed for 0.7CEC–HDTMA would correspond to the formation of a HDTMA lateral-bilayer in the interlayer space. Finally, an increase of the basal spacing  $d(001)$  is observed as the loaded surfactant increased from 1.0CEC–HDTMA to 2.0CEC–HDTMA. This interlayer space was smaller than the length of HDTMA and more than twice the width of HDTMA (0.4 nm), which suggests that the orientation of the surfactant molecule configuration may be a tilted bimolecular layer [34].

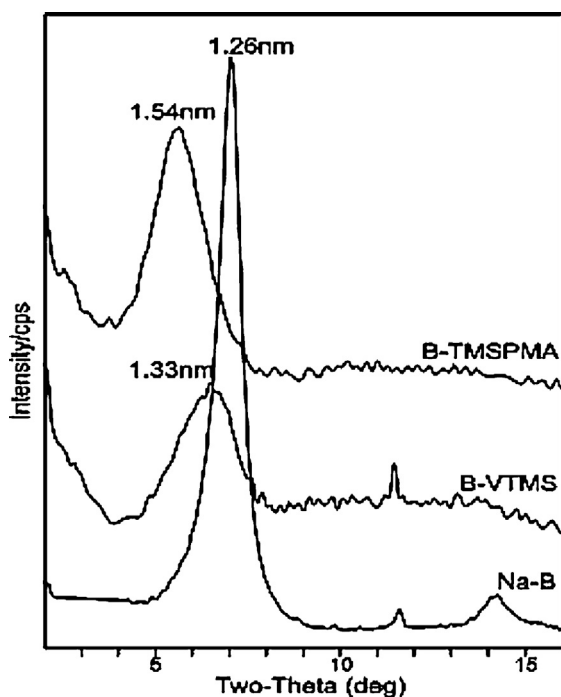


Fig. 3. XRD patterns of untreated bentonite and functionalized bentonites.

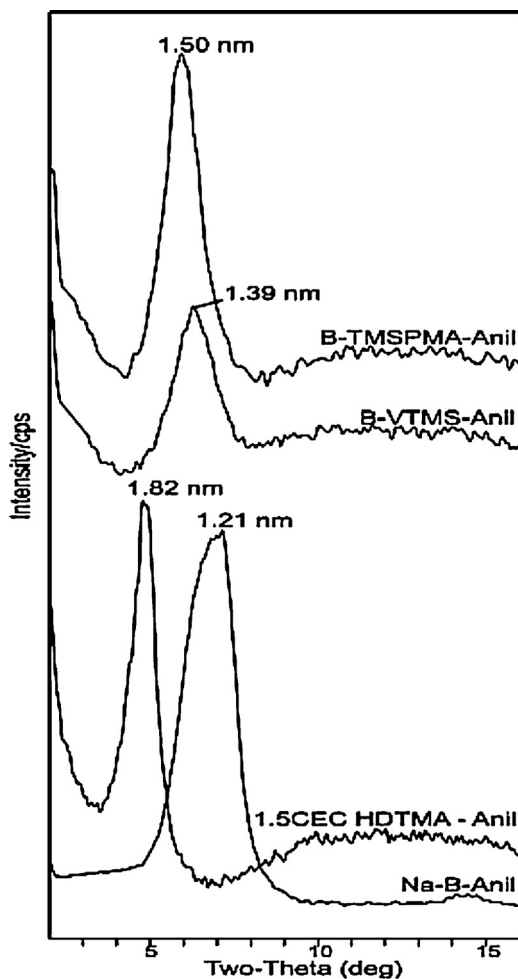


Fig. 4. XRD patterns of Na-B-aniline sorption complex, 1.5CEC-HDTMA-aniline sorption complex and functionalized bentonite-aniline sorption complex.

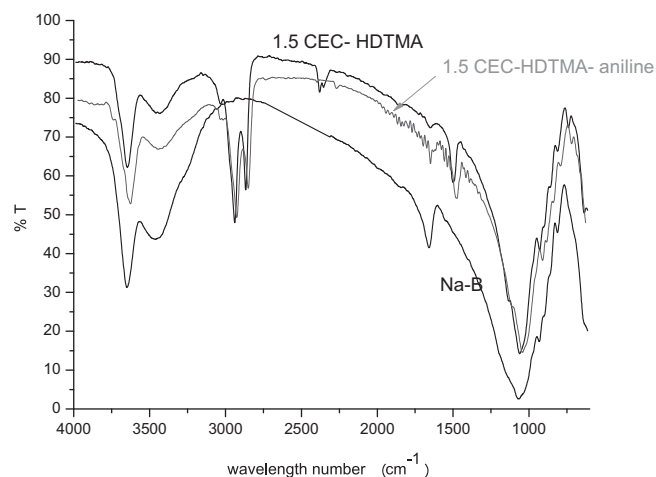


Fig. 5. IR spectra of raw bentonite (Na-B), organobentonite (1.5CEC-HDTMA) and aniline-sorption complex (1.5CEC-HDTMA-anil).

The XRD patterns of the Na-B before and after grafting are shown in Fig. 3. As shown by the XRD patterns, the basal spacing of silane-grafted bentonite is higher than that of Na-B, indicating that the silane has been intercalated into montmorillonite interlayer space. Previous studies demonstrated that the grafting reaction contained two steps, i.e., adsorption and intercalation, followed by condensation reaction between silane molecule and Si-O tetrahedral sheet of clay mineral and/or among silane molecules [15]. After the grafting reaction, the basal spacing increased to 1.33 nm for B-VTMS and to 1.53 nm for B-TMSPMA. The longer chain length and the presence of polar functional groups of TMSPMA molecule determined the higher extent of cross-link arrangement and the larger basal spacing. Therefore, the configuration of the silane has an effect on the interlayer space height of the grafting products. Similar interpretations were found for grafted montmorillonites by using 3-aminopropyltriethoxysilane and trimethylchlorosilane [6].

### 3.1.2. Infrared spectroscopy (IR)

Fig. 5 shows the IR spectrum of Na-B. For comparison, the figure also shows the spectra of the organobentonite (1.5CEC-HDTMA) and aniline sorption complex (1.5CEC-HDTMA-anil). The main bands of montmorillonite were:  $3650\text{ cm}^{-1}$  attributed to the -OH stretching vibration of structural hydroxyl groups,  $3465\text{ cm}^{-1}$  and  $1659\text{ cm}^{-1}$  assigned to the -OH stretching and -OH deformation vibration of water respectively, and  $1067\text{ cm}^{-1}$  assigned to Si-O stretching vibration [37]. The intensity of the absorption band at  $3465\text{ cm}^{-1}$  decreased with surfactant modification, which evidences a lower hydrophilicity in the interlayer region. For the organobentonite, the additional IR-bands at  $2938\text{ cm}^{-1}$  and  $2866\text{ cm}^{-1}$  correspond to -CH<sub>2</sub> asymmetric stretching,  $\nu_{as}(\text{CH}_2)$ , and symmetric stretching,  $\nu_s(\text{CH}_2)$  vibration respectively and between  $1543\text{ cm}^{-1}$  and  $1443\text{ cm}^{-1}$  for -CH<sub>2</sub> bending vibrations,  $\delta(\text{CH}_2)$ , of alkyl chains. The frequency, width and intensity of  $\delta(\text{CH}_2)$  band are sensitive to interaction with the alkyl chains and the packing arrangement of HDTMA [38,39]. Further, the split of the  $\delta(\text{CH}_2)$  band is mainly due to the lateral interchain interaction between -CH<sub>2</sub> groups of adjacent chains, which in general characterizes an orthorhombic arrangement of the -CH<sub>2</sub> chains. This splitting is absent in alkane chain assemblies of low packing density when lateral interchain interactions are weak [40]. A comparison between the IR spectrum of 1.5CEC-HDTMA and solid HDTMA (data not shown) show a lower intensity and the absence of splitting in the band corresponding to -CH<sub>2</sub> bending vibrations in 1.5CEC-HDTMA spectrum. This would indicate a lower packing density of the

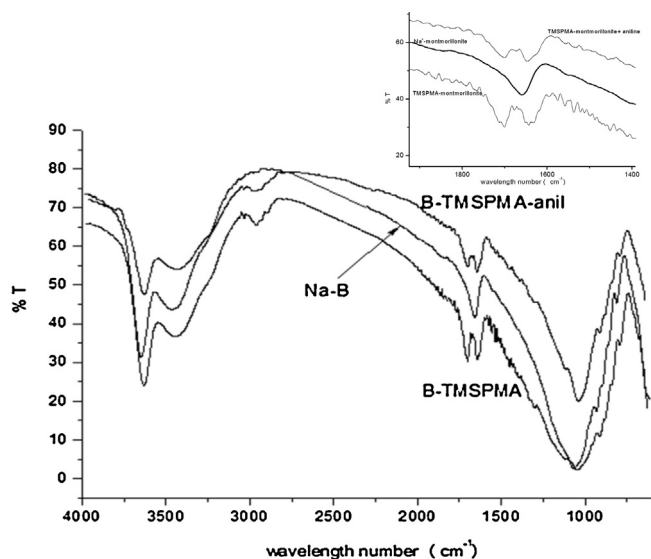


Fig. 6. IR spectra of Na-B, functionalized bentonite (B-TMSPMA) and aniline sorption complex (B-TMSPMA-anil).

surfactant chains in the organobentonite. This is in accordance with XRD pattern observations for 1.5CEC-HDTMA, which proposed that the intercalated surfactants adopted a tilted bilayer arrangement with relatively weak alkyl chains interaction.

Fig. 6 shows the IR spectra of a Na-B, functionalized bentonite (B-TMSPMA) and aniline sorption complex (B-TMSPMA-anil). The IR spectrum of B-TMSPMA evidences the presence of silanized agent on montmorillonite surface. The broad and weak bands at 2875–2980  $\text{cm}^{-1}$  correspond to the  $-\text{CH}_3$  and  $-\text{CH}_2$  stretching mode of TMSPMA and the band at 1702  $\text{cm}^{-1}$  and 1308  $\text{cm}^{-1}$  corresponding to the stretching vibration of the  $\text{C}=\text{O}$  group and  $\text{C}=\text{CH}_2$  of methacrylate, respectively. The splitting of the band at 1659  $\text{cm}^{-1}$  (inset) corresponds to the deformation band ( $\delta\text{OH}$ ) due to physisorbed water, and to the stretching vibration of the  $\text{C}=\text{C}$  double bond (1630  $\text{cm}^{-1}$ ). The band which corresponds to  $\text{C}=\text{O}$  group shows a shoulder at 1712  $\text{cm}^{-1}$  (Fig. 6) when hydrogen-bonding is generated. This suggests that the carbonyl group of TMSPMA interacts with the edge hydroxyl groups or with the water hydrating the remaining cations in the montmorillonite interlayer space. Similar results were found for the characterization of polymer/Laponite nanocomposite by organic modification using the same silane agent [41]. These authors attributed this vibration frequency to a hydrogen-bonding carbonyl group interacting with the edge hydroxyl groups of Laponite clay platelets. The shoulder observed at higher wavenumber in the absorption band corresponds to Si–O stretching vibration evidencing a successful grafting.

### 3.1.3. Thermogravimetric analysis (TGA)

Thermal stability of Na-B, organo and functionalized bentonites was determined by TGA. The mass loss of the samples and the temperature discernible from DTG is summarised in Table 1. The untreated bentonite shows the first mass loss at 148  $^{\circ}\text{C}$  due to the removal of the physisorbed water and water molecules around metal cations in the exchangeable sites of montmorillonite. The thermal decomposition at 688  $^{\circ}\text{C}$  was caused by dehydroxylation of the montmorillonite.

TG/DTG analyses of organobentonites show two peaks in the temperature range of 200–450  $^{\circ}\text{C}$  (Table 1) which correspond to the loss of the surfactant [2]. The peaks at 200–300  $^{\circ}\text{C}$  correspond to the physically adsorbed surfactants, whereas the peaks at 300–450  $^{\circ}\text{C}$  correspond to the evaporation and decomposition

of the intercalated surfactants [42]. TG analyses of organobentonites show an increase of the mass loss in the temperature range of 200–450  $^{\circ}\text{C}$  as the surfactant concentration loading increases: 14.5% (0.5CEC-HDTMA), 21.5% (1.0CEC-HDTMA) and 27.1% (1.5CEC-HDTMA).

The decrease in the mass loss of organobentonites in the temperature range 100–200  $^{\circ}\text{C}$  is mainly due to the partial replacement of hydrated cations by the surfactant (Table 1). The dehydroxylation temperature of organobentonite was also lower than that of the untreated bentonite, with a less of the corresponding mass loss.

Table 2 shows the TG/DTG results of B-VTMS and B-TMSPMA compared with Na-B. The decomposition of functionalized bentonites can be separated into five steps. The corresponding temperature ranges are: 65–130  $^{\circ}\text{C}$ , 298–315  $^{\circ}\text{C}$ , 430–490  $^{\circ}\text{C}$ , 525–600  $^{\circ}\text{C}$  and 610–640  $^{\circ}\text{C}$ . For Na-B there is no obvious mass loss in the range 200–600  $^{\circ}\text{C}$ . The peaks at second and third steps for B-VTMS and B-TMSPMA are attributed to the decomposition of the intercalated silane while the fourth step corresponds to the decomposition of the grafted silane [15]. The mass loss corresponding to intercalated silane (second and third steps) was higher for B-TMSPMA while B-VTMS showed higher mass loss of grafted silane (four step) which could be due to a higher efficiency in the silanization reaction.

### 3.1.4. Surface area measurement

As shown in Table 3, the BET surface area of untreated bentonite and organobentonites decreases in the order: Na-B > 0.5CEC-HDTMA > 1.0CEC-HDTMA > 1.5CEC-HDTMA > 2.0CEC-HDTMA. The surface area of Na-B (53  $\text{m}^2/\text{g}$ ) is that expected for sodium bentonites [43]. The slight difference between the total pore volume and mesopore pore volume indicates that all the samples consist mainly of mesopores. At higher surfactant concentrations (1.0–2.0CEC-HDTMA), organobentonites have lower BET surface area and mesopore volume, indicating that the HDTMA molecule is mainly introduced in the mesopore space. Furthermore, the average adsorption pore diameter ( $D$ ) is also related to the loading of surfactant. In general, an increase in  $D$  was observed with surfactant loadings. As proposed by Park et al. [44], in organoclay with a surfactant loading exceeding 1.0 CEC, the molecules are highly intercalated in the clay mineral interlayer space as well as in the interparticle pores, which leads to a decreased surface area and pore volume. Hence, the clay layers are almost completely enclosed, and the pores are enlarged by the loaded surfactant molecules. The  $\text{N}_2$  adsorption properties of functionalized bentonites are similar to those observed for organobentonites, indicating that in this case the silane agent is mainly reducing the mesopore space according to the length of the chains. These observations support the idea that the access of nitrogen to the surface is blocked by the organic moieties covalently linked at the edge  $-\text{OH}$  groups of individual clay platelets [45].

### 3.2. Sorption studies

Aniline was used as organic contaminants to examine the sorption characteristics of the modified bentonites. Initial concentrations of 0.32–2.90 mmol/L aniline were used for sorption studies onto Na-B, 1.5CEC-HDTMA, B-TMSPMA and B-VTMS. Fig. 7 presents the sorption isotherms of aniline on untreated and modified bentonites. The adsorption performance of the organobentonites and functionalized bentonites for aniline is superior to that of natural bentonite.

The adsorption isotherm of aniline on Na-B was nonlinear with a fit to the Langmuir equation ( $R^2 = 0.89$ ). The maximum adsorption quantity ( $Q_{\text{max}}$ ) was calculated to be 49 mmol/kg and the adsorption constant ( $K_L$ ) is 0.443 L/mmol. It has been reported that natural bentonite does not show high adsorption capacity for

**Table 1**  
TGA results of natural bentonite and organoclays.

Sample	Dehydration		Desurfactant		Desurfactant		Dehydroxylation (OH unit)	
	% Mass loss	T (°C)	% Mass loss	T (°C)	% Mass loss	T (°C)	% Mass loss	T (°C)
Na-B	10.5	148					4.1	688
0.5CEC-HDTMA	3.5	104	1.2	296	13.3	426	3.1	626
1CEC-HDTMA	4.1	110	10.2	297	11.3	422	3.2	599
1.5CEC-HDTMA	4.6	107	17.4	278	9.7	420	2.7	650

**Table 2**  
TGA results of untreated bentonite and functionalized bentonites.

Sample	First step		Second step		Third step		Fourth step		Fifth step	
	% Mass loss	T (°C)	% Mass loss	T (°C)	% Mass loss	T (°C)	% Mass loss	T (°C)	% Mass loss	T (°C)
Na-B	10.5	148	4.1	688						
B-VTMS	5.3	130	0.9	315	2.1	430	2.7	525	3	610
B-TMSPMA	3.7	65	4.1	298	2	490	1	600	640	

**Table 3**  
BET specific surface area ( $S_{BET}$ ), pore volume ( $V_T$ : total volume,  $V_{mp}$ : mesopore volume,  $V_{\mu p}$ : micropore volume) and pore diameter ( $D$ ) for natural bentonite, organoclays and functionalized bentonites.

Sample	$V_T$ (cm <sup>3</sup> /g)	$V_{mp}$ (cm <sup>3</sup> /g)	$V_{\mu p}$ (cm <sup>3</sup> /g)	$S_{BET}$ (m <sup>2</sup> /g)	$D^a$ (nm)
Na-B	0.092	0.079	0.013	53	6.943
0.5CEC-HDTMA	0.067	0.060	0.007	15	17.867
1.0CEC-HDTMA	0.027	0.022	0.005	4	27.000
1.5CEC-HDTMA	0.017	0.015	0.002	3	22.667
2CEC-HDTMA	0.016	0.013	0.003	2	32.000
B-VTMS	0.051	0.042	0.009	13	15.692
B-TMSPMA	0.033	0.033	–	9	14.667

<sup>a</sup> Adsorption pore diameter ( $4V_T/S_{BET}$ ).

nonionic organic compounds, with a negligible contribution of physical adsorption by the surface and edge groups of the silicate layers. The lower uptake of aniline at low concentrations clearly shows that solute–adsorbent interactions are quite weak.

Two types of interaction between organic compounds and organically modified bentonites were proposed: adsorption and partition. The sorption isotherms on modified bentonite were essentially linear ( $R^2 > 0.90$ ) with solid–water distribution coefficient values ( $K_d$ ) of 78 L/kg (B-VTMS), 52 L/kg (1.5CEC-HDTMA) and 31 L/kg (B-TMSPMA). This suggests partition mechanisms for nonionic organic compounds sorption on organically modified bentonites with higher loaded surfactant molecules [7,45]. The linearity of sorption isotherms evidences that the number of available sites for adsorption remains constant in the concentration range

studied. Such a situation could arise when the solute penetrates the hydrophobic region of the sorbent, as suggested by Paul et al. [23]. The B-VTMS shows higher adsorption ability than B-TMSPMA, evidencing different affinity between the pollutant molecules and the different grafted molecules.

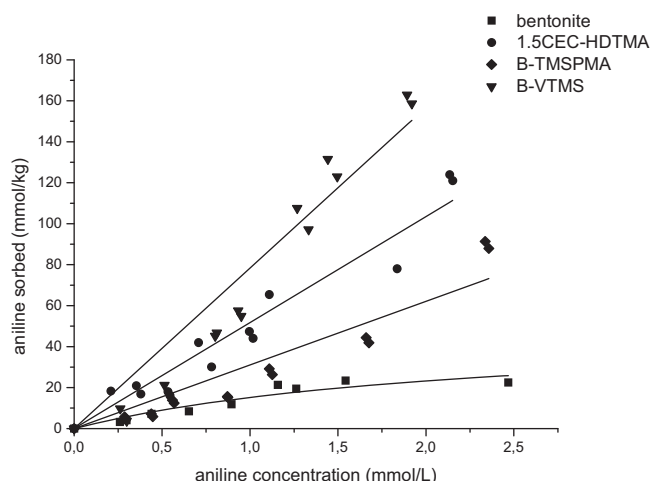
### 3.3. The effect of modification conditions on sorption performance

The adsorption results were combined with XRD data and IR spectroscopy in order to confirm the presence of aniline on the montmorillonite surface and to obtain some molecular-level information of the montmorillonite–aniline interaction.

The obtained results show that the interlaminal spacing of modified bentonites is not the decisive factor in the adsorption capacity of aniline. From XRD pattern for organobentonites, it was proposed that the intercalated surfactants produce a hydrophobic phase and the ability to van der Waals interactions between chains and later-sorbed solutes.

Fig. 4 shows XRD patterns of aniline sorption complexes where the basal spacing for aniline adsorbed on 1.5CEC-HDTMA is 1.82 nm compared with 1.96 nm for the 1.5CEC-HDTMA. The sorption on organobentonite (1.5CEC-HDTMA-anil) shows a decrease in basal spacing. Therefore, the presence of aniline in aqueous media can lead to a modification of the surfactant molecular arrangement from tilted bimolecular layer to flat bilayer, which may be responsible for the basal spacing of 1.82 nm.

The IR absorption band at 1533 cm<sup>-1</sup> evidences the aniline presence in the structure of the modified bentonite. This band is characteristic of aromatic ring stretching vibration. The absorption bands of the surfactant –CH<sub>2</sub> group also show a shift to lower frequencies in the presence of aniline (Fig. 5). These results support the XRD observations where the presence of aniline in the interlayer space leads to modification of the surfactant molecular arrangement, probably by non specific interaction of aniline molecules

**Fig. 7.** Sorption isotherms of aniline to natural and modified bentonites.

with alkyl chains of the HDTMA molecule. Furthermore, the aniline sorption complex IR spectrum (1.5CEC-HDTMA-anil) shows a shift of the vibration frequency band which corresponds to –OH structural groups from  $3647\text{ cm}^{-1}$  for 1.5CEC-HDTMA to  $3629\text{ cm}^{-1}$  for 1.5CEC-HDTMA-anil. This seems to indicate hydrogen bonding interactions between the aniline molecule and the edge –OH groups. The basal spacing  $d(001)$  of aniline sorbed by B-VTMS (B-VTMS-anil) and B-TMSPMA (B-TMSPMA-anil) was 1.39 nm and 1.50 nm, respectively. These results indicated that aniline sorption on functionalized bentonite (B-VTMS and B-TMSPMA) did not modify the basal spacing, mainly because the interlayer space is determined by interactions among silane molecules grafted and between clay mineral and special group in silane. The distribution coefficient value of aniline is evidently the highest for B-VTMS. This fact probably is a result from an increase in sorption efficiency of silane grafted to the surface of the montmorillonite.

#### 4. Conclusions

In this contribution, two strategies for organic modification of bentonite were implemented: exchanging the interlayer cations with different concentrations of HDTMA and grafting of either VTMS or TMSPMA. The materials obtained were characterized and applied to remove aniline from aqueous solution. The results obtained from XRD analyses, IR spectroscopy, TG analyses and BET surface area determination showed that organic modification through the exchange of a surfactant or grafting was successful. Surfactant molecules as well as silanized agents of functionalized bentonites are intercalated in the montmorillonite interlayer space, increasing the basal spacing. The structural properties of an untreated bentonite intercalated with a surfactant and grafted with silanized agents were changed from hydrophilic to hydrophobic, increasing the retention capacity of nonionic organic substances such as aniline. The linearity of sorption isotherms evidence that the main sorption mechanism of modified bentonites is partition. The bentonite surface functionalized with vinyltrimethoxysilane (VTMS) showed the highest adsorption ability for aniline among all the studied samples. However, 1.5CEC-HDTMA also had remarkable adsorption ability therefore we propose this as an effective bentonite organic modification, considering that it produces satisfactory adsorption results and is easier and faster to obtain.

These findings increase the potential industrial applications of bentonites in water decontamination processes.

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