

## Influence of Organobentonite Structure on Toluene Adsorption from Water Solution

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Due to increase water pollution by organic compound derived from hydrocarbons such as toluene, several alternative technologies for remediation of polluted water have been originated. In this work natural bentonites were modified with cetyltrimethylammonium (CTMA<sup>+</sup>) for obtaining organophilic bentonites. The obtained CTMA-bentonites would be suitable for use as adsorbents of toluene present in water. The influence of structural characteristics of CTMA-bentonites on their adsorption capacity was studied. It was shown that adsorption of toluene depended on homogeneous interlayer space associated with arrangements of CTMA<sup>+</sup> paraffin-monolayer and bilayer models, accompanied by a high degree ordering of the carbon chain of organic cation in both arrangements. However, packing density would not have an evident influence on the retention capacity of these materials. The solids obtained were characterized by chemical analysis, X-ray diffractions and infrared spectroscopy. Toluene adsorption was measured by UV-visible spectrophotometer. Adsorption capacity was studied by determining adsorption isotherms and adsorption coefficient calculation. The adsorption isotherms were straight-line indicating a partition phenomenon of toluene between the aqueous and organic phase present in organophilic bentonites.

**Keywords:** bentonites, CTMA-bentonites, toluene, adsorption

### 1. Introduction

Contaminated water, soil and air by various chemicals (arsenic, lead, zinc, chromium, copper, benzene, toluene, naphthalene, phenols, polychlorinated biphenyls, organochlorine dyes, etc.) have generated international preoccupation. Several authors have characterized and developed efficient materials to retain these pollutants<sup>1-3</sup>. Aromatic compounds, in general, have certain toxicity and are considered possible carcinogenic and dangerous in very small concentrations. Among the most notable pollutants, related almost directly to the chemical and petrochemical industry, are organic non-ionic (NOC's) such as toluene, which also is a constituent of the BTEX group (benzene, toluene, ethylbenzene and xylenes)<sup>4</sup>. Toluene concentrations in industrial wastewaters can reach values around 800 mg.L<sup>-1</sup>, depending on the manufacture type<sup>5</sup>. Some processes available to retain toluene of polluted water, include: biodegradation with bacteria<sup>6,7</sup>, combined (ceramic biofilters presence of fungi)<sup>8</sup>, activated carbon<sup>9-11</sup>, etc. Although these materials are used for adsorbing different concentrations of toluene present in water, its widespread use is limited by its high cost of manufacturing<sup>12</sup>. Ideal natural materials used as a filter or barriers to adsorb a wide variety of pollutants are the bentonite clays<sup>13-15</sup>. Bentonites have low operation cost and are also present as deposits in most continents of the world, making them economical materials. These rocks are generally composed of montmorillonite type and also contain small amounts of other minerals,

usually quartz, feldspar, volcanic glass, gypsum, pyrite and organic matter<sup>16</sup>.

Montmorillonite is a hydrated aluminum silicate, its layered structure belonging to the 2:1 type clay minerals, whose basic structure is constituted by an aluminum octahedral layer between two layers of tetrahedral silica (T-O-T)<sup>17</sup>. In both tetrahedral and octahedral layers of cations Si<sup>4+</sup> and Al<sup>3+</sup> respectively, isomorphic replacement can take place generating negative charges in the mineral structure.

The charges are compensated by exchangeable cations such as Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>++</sup>, Mg<sup>++</sup>, etc. The clay minerals are hydrophilic in nature and can be transformed in organophilic, for example, after exchanging natural cations by organic cations such as those derived from quaternary ammonium salts. In this way, the solids are generally named organoclays and these materials are capable of retaining non-polar organic compounds present in contaminated waters<sup>18-47</sup>. Cetyltrimetilamonio (CTMA)-bentonites as adsorbents for organic pollutants present in water were studied by different authors through the years<sup>48-51</sup>.

Jaynes and Boyd<sup>22</sup> retained toluene from CTMA-clays and found that the higher adsorption capacity was associated with large interlaminar spacing of the clay mineral in the presence of long carbon chain of the CTMA<sup>+</sup>. For Jaynes and Vance<sup>25</sup>, toluene present in water was efficiently adsorbed by organo-clays prepared from montmorillonite modified with organic cations of long alkyl chain as the CTMA<sup>+</sup>. They observed that the adsorption was governed by the arrangement adopted by the organic

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cation associated with important interlaminal spacing (e.g. paraffin-type). Cetyltrimethylammonium (CTMA<sup>+</sup>) generates an organophilic phase partition in the interlayer space of the montmorillonite constituent of bentonite<sup>52-54</sup>.

Sharmasarkar et al.<sup>31</sup> evaluated the adsorption of toluene and other hydrocarbons by some organo-montmorillonite and also evaluated the adsorptive capacity of these materials in relation to type of organic cation, molecular weight and interlayer spacing in the organo-clays.

Loess soils with high contents of organic carbon provided by the CTMA<sup>+</sup> cation and high cation exchange capacity were much more efficient than non-modified soils to sorbent toluene, a NOC<sup>34</sup>. According to Ramos Vianna et al.<sup>42</sup> Brazilian purified sodium bentonite in different amounts was used to prepare CTMA - organoclays and they observed that bentonite in different amounts (1% and 4%) treated with CTMA equivalent to the CEC of the original clay, showed higher adsorptive properties as tested by using toluene as the reference adsorbate. Nevertheless, the studies of adsorption of toluene in water referred to arrangement and degree of ordering chain alkyl of the cation organic in this CTMA-bentonite type are scarce. In this work adsorption isotherm of toluene by CTMA-bentonite was obtained and the influence of arrangement and ordering of carbon chain with toluene retention by bentonite, solid that can be used as potential adsorbents for toluene and environmental applications, was analysed.

2. Material and Methods

Selected bentonites for this study were two Argentines (Ja and DL) and two from the USA (B1 and B2). The bentonites contain montmorillonite (smectite- type) as the main mineralogical component with variable amounts of impurities (Table 2). Dried bentonitic clay samples were crushed to pass a sieve M:200 (<74 μm). The cation exchange capacity (CEC) of each bentonite was 0.98 meq.g<sup>-1</sup>, 1.0 meq.g<sup>-1</sup>, 1.10 meq.g<sup>-1</sup> and 0.97 meq.g<sup>-1</sup> for Ja, DL, B1 and B2 samples, respectively. The CEC was determined by using 2N ammonium acetate at pH = 8.

The CTMA<sup>+</sup>, Table 1, is a monovalent cation of cetyltrimethylammonium, containing nineteen carbon atoms. It was selected in this work for preparing organo-bentonites.

Different CTMA-bentonites were prepared adding cetyltrimethylammonium chloride equal to CEC. An amount

of 2 g of bentonite per 100 mL aqueous solutions of CTMA chloride salt was contacted for 24 hours. The solids were washed with distilled water to remove excess salt, separated, and dried at 60 °C. CTMA-bentonites samples were crushed to pass a sieve M:200 (<74 μm) and stabilized at a relative humidity of 55% (RH) before characterization. The CTMA-bentonites were named JaC, B1C, B2C and DLC.

Organic carbon (OC) contents in the samples were determined by the Solid Simple Module SSM-5000A for TOC-5000(A)/5050(A) Total Organic Carbon Analyzer, Shimadzu.

Chemical analyses of the bentonites were obtained using Inductively Coupled Plasma (ICP) and were performed on crushed sample to pass a sieve M: 200 (<74 μm).

The X-ray diffraction (XRD) of the samples were obtained by using a Philips 3020 Goniometer equipment with PW 3710 Controller, Cu Kα radiation (λ = 1.5405 Å), and Ni filter at 40 kV and 20 mA. The patterns were obtained by scanning at 1° (2θ)/min between 2.2 and 70° (2θ). Quantitative identification of crystalline phase was carried out by Rietveld method.

Fourier transform infrared spectroscopy (FTIR) spectra using KBr pressed disk technique were conducted on Spectrum One Perkin Elmer equipment. The spectra were collected for each measurement over the spectral range of 400-4000 cm<sup>-1</sup>.

Toluene concentrations in water analyzed were in the range of 50 to 1000 mg.L<sup>-1</sup>. Batch sorption experiments of toluene by CTMA-bentonites were made by weighing 200 mg organo-bentonite sample into 10 mL of aqueous solution of toluene. Toluene uptake by organo-bentonite was calculated from the difference between the quantity of toluene added and the quantity remaining in the equilibrium solution after 24 hours of contact. The amount of toluene was determined by measuring the absorbance at 261 nm in a Hewlett Packard 8435 spectrophotometer. All measurements were done in duplicate. Blank experiments (without CTMA-bentonite) were measured each time to determine possible loss in the solution of toluene by evaporation.

3. Results and Discussion

Applying the Rietveld method to the analysis by X-ray diffraction, in the Table 2, was observed that the bentonites were montmorillonite-rich samples (major component over 87%)

Table 1. Characteristics of CTMA<sup>+</sup> cation.

Name	Abbreviation	Dimensions and structure
Cetyltrimethylammonium cation	CTMA <sup>+</sup>	Side: a = 25.3 Å; b = 5.1 Å; c = 4.6 Å Up: a = 25.3 Å; b' = 6.7 Å; c' = 4.1 Å

with small, but variable, amount of quartz, calcium feldspar, sodium feldspar y cristobalite.

According to mineralogical and chemical analyses (Table 3) of the clays, the samples are typical of bentonites<sup>16,52,55-57</sup>. Bentonites, mainly composed of smectites, can be grouped in Cheto-type if the amount of magnesium expressed as oxide in the range of 5 to 6% and Wyoming-type if the amount of iron as oxide (Fe<sub>2</sub>O<sub>3</sub>) in the range of 3 to 5%<sup>58</sup>. For the bentonites selected content of magnesium expressed as oxide (MgO) is higher for samples B1 and Ja (6.91 and 6.65%), compared with samples B2 and DL (2.78 and 3.33%). However, these last two bentonites have a higher content of iron expressed as oxide (Fe<sub>2</sub>O<sub>3</sub> = 4.17 and 4.69%) compared with B1 and Ja.

The adsorption isotherms of toluene in water onto organic bentonites are shown in Figure 1. CTMA-bentonites showed linear adsorption isotherms in all the range of the study, similar to Class- C isotherm proposed by Giles et al.<sup>59</sup>.

A linear model was used for a quantitative evaluation of adsorption, according to the following equation:  $X/M = K_d C_e$ , where X = mass of toluene removed from solution (mmol), M = mass of adsorbent (kg), Ce = solution equilibrium concentration (mmol.L<sup>-1</sup>) and Kd = adsorption coefficient, linear partition or distribution (L.kg<sup>-1</sup>) of toluene between the aqueous phase and CTMA-bentonite. The adsorption coefficient K<sub>d</sub> for each series of CTMA-bentonite was calculated from the equation referred, Table 4. Linear correlation coefficient was r ≥ 0.97 for all adsorption isotherms. Linearity of the isotherms would be related to behavior known as *hydrophobic partitioning process*, which occurs mainly between organic contaminants with scarce o non-polarity and non-polar parts of a large molecule<sup>60,61</sup>. In this work, the partitioning process would be between hydrophobic parts of the organics cations in interlayer spacing and toluene in water. Table 4 shows the partition coefficients (K<sub>d</sub>) of adsorption toluene by the organobentonites. The sample JaC gave the highest K<sub>d</sub> value 258 L.kg<sup>-1</sup>, while the lowest K<sub>d</sub> value of adsorption of toluene 140 L.kg<sup>-1</sup> was obtained for B2C.

Normalized K<sub>d</sub> value (L.kg<sup>-1</sup>) by organic content present in each organic bentonite, arise organic content corrected

coefficient, K<sub>om</sub> (L.kg<sup>-1</sup> of carbon) (Table 4)<sup>62</sup>, calculated according to the Equation 1:

$$K_{om} = \left( \frac{K_d}{OC \times f_{oc}} \right) 1000, \text{ where } f_{oc} = \frac{W_{CTMA^+}}{W_C} \quad (1)$$

where OC is the organic carbon (mgC.g<sup>-1</sup> sample); W<sub>CTMA+</sub> weight of CTMA<sup>+</sup> and W<sub>C</sub> was the weight of carbon in CTMA<sup>+</sup>. It was observed that the adsorption capacity, K<sub>d</sub>, of each series CTMA-bentonites increased with increasing organic content, associated with the simultaneous increase in the K<sub>om</sub> (Table 4, Figure 2). Jaynes and Boyd<sup>22</sup>, Jaynes and Vance<sup>25</sup>, Sharmasarkar et al.<sup>31</sup>; Chen et al.<sup>34</sup>; Ramos Vianna et al.<sup>42</sup>, found similar OC, K<sub>d</sub> and K<sub>om</sub> values for smectites montmorillonite-type modified with added amounts of CTMA<sup>+</sup> equal to those of this work (Table 4).

To evaluate the apparent affinity of toluene for remaining in the organic bentonite or in aqueous phase, it was compared the values obtained for organic content corrected coefficient (K<sub>om</sub>) with octanol coefficient (K<sub>ow</sub>) of toluene (489.8 L. kg<sup>-1</sup>)<sup>63</sup>, from the following equation: log K<sub>om</sub> - log K<sub>ow</sub>. If the values obtained from this difference are positive, the affinity of toluene is for solid organic phase and if the values are negative, toluene remains in solution<sup>22,42</sup>. The log K<sub>om</sub> - log K<sub>ow</sub> values were positive for all CTMA-bentonites prepared in this paper. The JaC and B1C samples presented values similar to slightly higher than those expounded by Jaynes and Vance<sup>25</sup> for SAz-HDTMA used to retain toluene in water, Table 4. For samples DLC and B2C these values were higher than for Wyoming-type bentonites modified with CTMA<sup>+</sup> presented by Jaynes and Vance<sup>25</sup>; Sharmasarkar et al.<sup>31</sup>; Ramos Vianna et al.<sup>42</sup> (Table 4). Based on the results of Table 4, the order of log K<sub>om</sub> - log K<sub>ow</sub> for toluene was JaC > DLC > B1C > B2C.

The structure of bentonite clays modified with the CTMA<sup>+</sup> cation was studied by XDR and FTIR.

Figure 3 shows X- ray diffraction of natural bentonites (B1, Ja, B2 and DL) containing mainly montmorillonite (as smectite-type); and prepared CTMA-bentonites. It was observed that the interlayer spacing, d(001), of montmorillonite changed in a range of 18.4 Å to 23.9 Å when CTMA<sup>+</sup> was added in equivalent to the exchange capacity. The change in spacing values of the bentonites B2, DL and

Table 2. Percentage of each mineral phase in selected bentonites.

Mineralogical phase	B1 (%)	Ja (%)	B2 (%)	DL (%)
Montmorillonite	96	94	87	92
Quartz	1	1	9	3
Calcium Feldspar	-	-	4	-
Sodium Feldspar	-	4	-	4
Cristobalite	3	1	-	1

Table 3. Chemical composition (%) of selected bentonite in dry base.

Samples	SiO <sub>2</sub> (%)	TiO <sub>2</sub> (%)	Al <sub>2</sub> O <sub>3</sub> (%)	Fe <sub>2</sub> O <sub>3</sub> (%)	MgO (%)	CaO (%)	Na <sub>2</sub> O (%)	K <sub>2</sub> O (%)
B1	67.37	0.25	19.99	1.74	6.91	3.24	0.10	0.21
Ja	66.42	0.28	19.31	1.66	6.65	1.61	3.22	0.75
B2	68.12	0.12	20.57	4.17	2.78	1.91	1.63	0.59
DL	66.94	0.19	20.77	4.69	3.33	0.93	2.67	0.31

Ja, B1 are attributed to replacement of interlayer inorganic cations with organic CTMA<sup>+</sup> cation. Similar spaces were reported by Lee and Kim<sup>64</sup>; Volzone et al.<sup>65</sup>; Zhu et al.<sup>62</sup>; Vidal and Volzone<sup>45</sup> for the treatment of bentonite clays with CTMA<sup>+</sup>.

According to different models proposed by Lagaly et al.<sup>66</sup>; Vaia et al.<sup>67</sup>; Zhu et al.<sup>68,69</sup>; Bergaya et al.<sup>70</sup>; Zhu et al.<sup>71</sup>; Xu and Zhu<sup>72</sup> the arrangement of an organic cation of long carbon chain, for example CTMA<sup>+</sup>, with respect to the sheet of clay mineral would be located in monolayer when interlayer spacing are between 14.8 Å to 15.0 Å, in two successive layers (bilayer) when recorded interlayer spacing values between 17.8 Å to 18.8 Å; and pseudotrilayer if *d*(001) values are between 19.5 Å to 21 Å<sup>39,73</sup>. If the carbon chain is inclined a certain angle  $\alpha$  or near perpendicular to the sheet mineral clay, this arrangement is called paraffin-type monolayer (22.3 Å a 30 Å) and paraffin-type bilayer with basal spacing >30 Å (sen  $\alpha$  = interlayer spacing/length of CTMA<sup>+</sup>, 25.3 Å).

B2 and DL bentonites (Wyoming-type) increases the interlayer spacing values of 14.4 Å and 14.2 Å to 18.5 Å and 18.4 Å, respectively, to be modified with an amount of

CTMA<sup>+</sup> equivalent to CEC. In this case the organic cation adopts a bilayer arrangement with respect to the sheet of clay. According to Zhu et al.<sup>71</sup> and Xu and Boyd<sup>74</sup>, in this type of clay minerals the CTMA<sup>+</sup> cation never exceed beyond pseudotrilaminar arrangement, by having a low surface charge density generated by the type of isomorphic substitution in the octahedral sheet.

Cheto-type bentonites, B1 and Ja, showed a different behavior to B2 and DL with modification by CTMA<sup>+</sup>. The *d*(001) values for JaC was 23.9 Å and for sample B1C, coexisting two simultaneously interlayers values 22.8 Å and 15.6 Å. Paraffin-monolayer arrangement would be represented in the sample JaC and with 72% in the sample B1C. The 28% of sample B1C may adopt a transition conformation between monolayer and bilayer of carbon tail of organic cation<sup>71</sup>. Both percentages were determined by deconvolution of reflection 001 (Figure 3, dotted line). The heterogeneous interlayer arrangement indicate that CTMA<sup>+</sup> was distributed differently between the sheets of each clay and such situations only present in Cheto-type montmorillonite<sup>64,75,76</sup>.

For FTIR characterization, there aren't characteristic bands of montmorillonite in the selected spectral region between 3100 and 2700 cm<sup>-1</sup>, but they are shown for comparison. For CTMA-bentonites, characteristic bands of cation organic CTMA<sup>+</sup> are localized at 3020 cm<sup>-1</sup>, assigned to the symmetric stretching mode of the trimethylammonium headgroup CH<sub>3</sub>-N while the bands 2918 cm<sup>-1</sup> and 2849 cm<sup>-1</sup> are typical asymmetrical and symmetrical modes of bond C-H methylene asymmetric and symmetric, respectively (concerning CTMA<sup>+</sup> solid)<sup>77</sup>. The wavenumber of C-H methylene stretching absorption bands of CTMA<sup>+</sup> cation are extremely sensitive to the degree of ordering adopting carbon chain in each conformation<sup>78-81</sup>. When the chains are highly ordered (*all trans*) and with high packing density, these absorption bands are close to the wavenumber of the pure CTMA<sup>+</sup> solid. Nevertheless, He et al.<sup>78</sup> showed that the asymmetric C-H methylene stretching absorption mode is more sensitive to the carbon chain conformation than

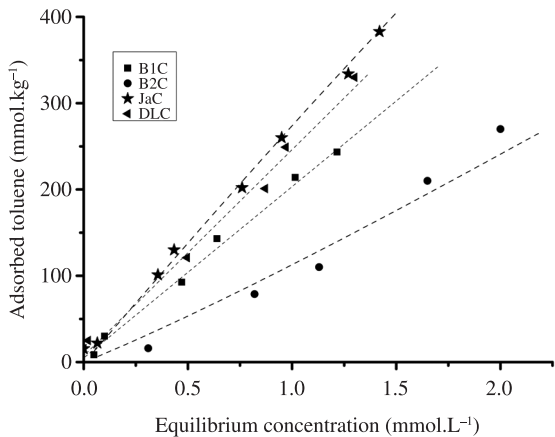


Figure 1. Sorption isotherms of toluene on the CTMA-bentonites.

Table 4. Distribution coefficients (*K<sub>d</sub>*), coefficient normalized to organic matter (*K<sub>om</sub>*) for CTMA-bentonites in this paper and different authors.

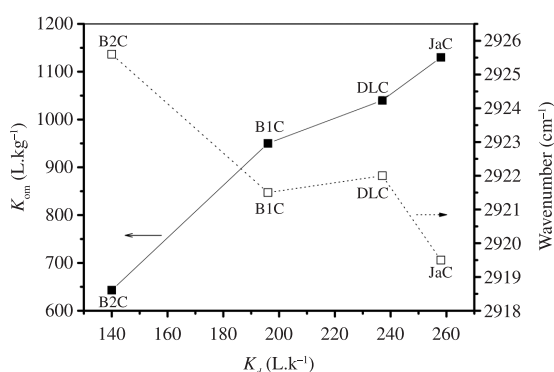
Adsorbent	<i>K<sub>d</sub></i> (L.kg <sup>-1</sup> )	Organic Carbon (OC) (mgC.g <sup>-1</sup> )	<i>K<sub>om</sub></i> (L.kg <sup>-1</sup> )	log <i>K<sub>om</sub></i> – log <i>K<sub>ow</sub></i>	References
JaC	258	183	1130	0.363	This paper
DLC	237	181	1049	0.331	
B1C	196	164	957	0.291	
B2C	140	174	645	0.120	
SWy-CTMA	74	174.6	338.84	–0.16	Jaynes and Boyd <sup>22</sup>
Saz-CTMA	319	230	1122	0.36	
SWy-CTMA	114	167	548.04	0.05	Jaynes and Vance <sup>25</sup>
Saz-CTMA	317	239	1064.84	0.34	
SWy-CTMA	79.43	168	378.67	–0.11	Sharmasarkar et al. <sup>31</sup>
Loess Soil - CTMA	11.9	8.34	nd	nd	Chen et al. <sup>34</sup>
Na-Smectite-CTMA (1%, 100)	140	156	721.57	0.17	Ramos Vianna et al. <sup>42</sup>
Na-Smectite-CTMA (4%, 100)	131	162	649.60	0.12	

\*log *K<sub>ow</sub>* toluene: 2.69

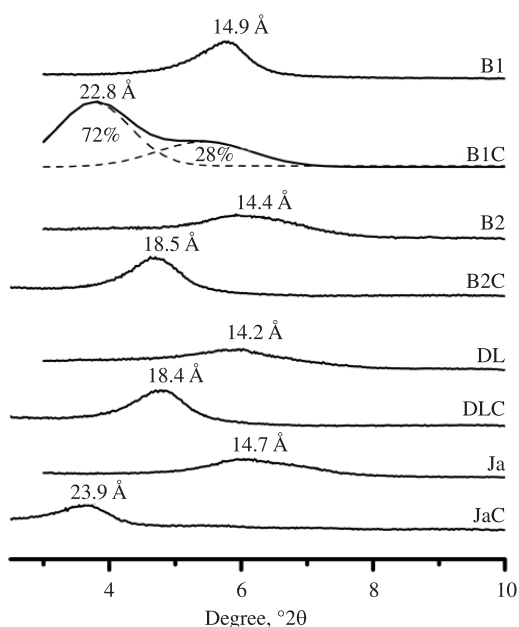


the symmetric C-H methylene stretching absorption mode is. If the band of stretching asymmetrical C-H methylene is shifted to a higher wavenumber and widens, that would indicate a tendency to disorder (*gauche*) of the amine chain of CTMA<sup>+</sup> in the conformation adopted<sup>67,81,82</sup>. In the selected CTMA-bentonites the degree of ordering increased from the sample B2C (2925.6 cm<sup>-1</sup>), followed by DLC and B1C, these last two samples being similar (2922 cm<sup>-1</sup> and 2921.5 cm<sup>-1</sup>, respectively) because their wavenumber only show a slight difference of less than 1 cm<sup>-1</sup>[83]; to the greatest ordering corresponding to sample JaC (2919.5 cm<sup>-1</sup>).

It has also been observed that the absorption band at 3020 cm<sup>-1</sup> showed a more notable intensity in the samples JaC and DLC compared to samples B1C and B2C. The presence of this band would be related to a higher ordering of the large carbon chain<sup>80</sup>. Figure 4b showed doublet for the band associated with scissoring (1490 y 1490 cm<sup>-1</sup>)



**Figure 2.**  $K_{om}$  and wavenumber of stretching asymmetric vibration modes of C-H methylene as a function of  $K_d$ .



**Figure 3.** X-ray diffraction and basal spacing of bentonites before and after cetyltrimethylammonium exchange. Deconvolution in dotted line.

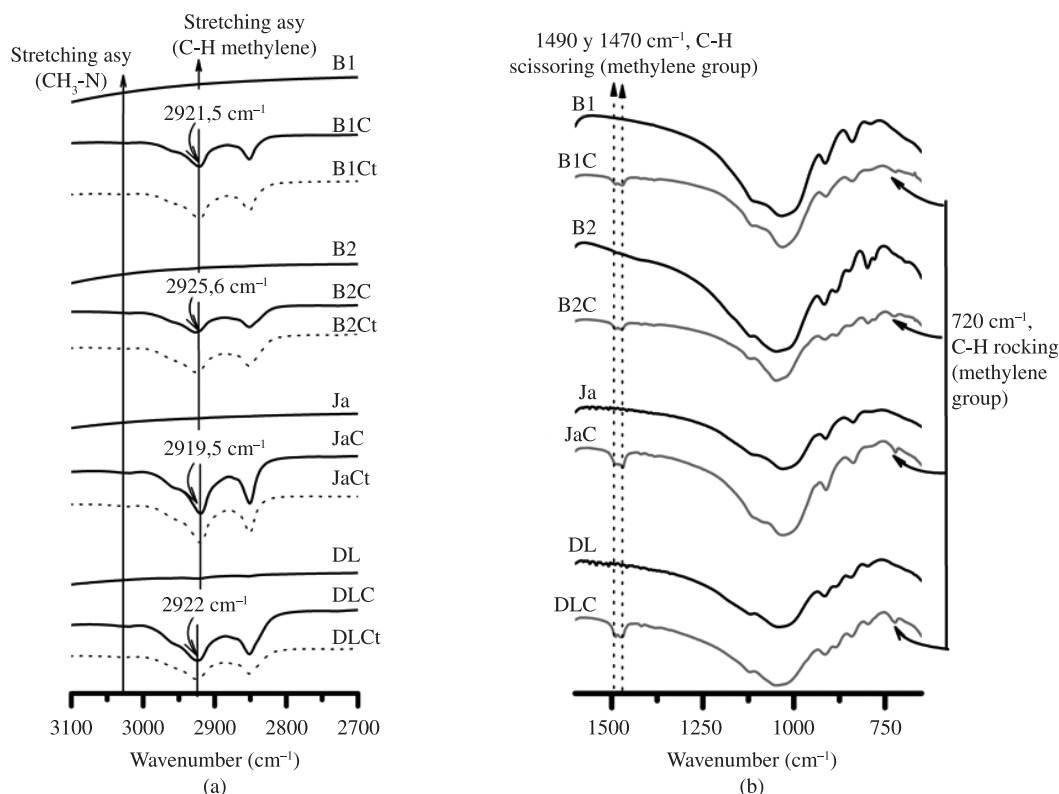
and rocking at 710 cm<sup>-1</sup> vibration modes for bond C-H methylene. Presence of the band at 710 cm<sup>-1</sup> and doublet of scissoring modes suggest the tendency to ordering that would take the carbon chain and an increase in the intensity of both bands is associated with higher carbon content<sup>78</sup>. It has been observed that these bands are present in all CTMA-bentonite, and its intensity is greater in the DLC and JaC in respect to B1C and B2C organobentonites

Figure 4a includes the IR spectrum of organic bentonite after retain toluene (B1Ct, B2Ct, JaCt, DLCt) in dotted line. Characteristic bands of toluene ranging from 3100 to 2700 cm<sup>-1</sup>, correspond to both stretching symmetric (2960 cm<sup>-1</sup> and 2854 cm<sup>-1</sup>) and asymmetric (2925 and 2919 cm<sup>-1</sup>) stretching vibration modes for C-H metal<sup>84-89</sup> but in general are overlapped by the characteristic bands of the CTMA<sup>+</sup> cation<sup>90</sup>.

Understanding the factors affecting the adsorption coefficient,  $K_d$ , for each group of CTMA-bentonite is very important for predicting and optimizing the adsorption capacity of these organic bentonites for retaining toluene present in water.

The hydrophobic environment created in the bentonite clay by the presence of the organic cation of long carbon chain (CTMA<sup>+</sup>) showed to be a good environment to retain toluene present in water<sup>91</sup>. The resulting mechanism, that controls the retention of toluene in this medium, was partition into the organic phase created by the organic bentonites (Figure 1). In the calculated  $K_d$  values for this system, it was observed that they had a direct relationship with increasing organic content of each clay, expressed as  $K_{om}$ , Table 4 and Figure 2. However, differences in retention of toluene between each CTMA-bentonite can be attributed to structural differences between them (e.g.: type of arrangement and state of ordering of CTMA<sup>+</sup> in the interlayer of the clay mineral). According to Jaynes and Boyd<sup>22</sup>; Jaynes and Vance<sup>25</sup> only the interlayer spacing values,  $d(001)$ , associated with paraffin-type monolayer arrangement of carbon chain of cation organic, demonstrated to be related to optimal adsorptive capacities of different clay minerals modified with organics to retain benzene, toluene, ethylbenzene, propylbenzene, naphthalene, biphenyls and xylenes.

The high degree of ordering of paraffin-type monolayer arrangement of cation CTMA<sup>+</sup> of the sample JaC would be consistent with the highest  $K_d$  values (258 L.kg<sup>-1</sup>). However, for sample B1C paraffin-type monolayer arrangement represented around 72% and its  $K_d$  value (196 L.kg<sup>-1</sup>) would be the same percentage (or the same proportion as a percentage) of the value of the coefficient for sample JaC. In this way, it could be inferred that transition between monolayer and bilayer arrangement, also found in B1C which corresponds to 28% of the 001 reflection, would be attributed as an inactive phase front to retention of toluene in water, causing the retention efficiency to be decreased. Although interlayer spacing value,  $d(001)$ , and bilayer arrangement are similar between samples DLC and B2C, whose  $K_d$  values were 237 L.kg<sup>-1</sup> and 140 L.kg<sup>-1</sup>, respectively, DLC organic bentonite gave the second highest  $K_d$  value with respect to the sample JaC. This behavior can be explained due to the degree of ordering



**Figure 4.** FTIR patterns: a) bentonites, and CTMA-bentonites with and without toluene in the region 3100-2700 cm<sup>-1</sup>; b) bentonites and CTMA-bentonites in the region 1550-700 cm<sup>-1</sup>.

that would adopt the CTMA<sup>+</sup> cation between the sheets of clay mineral in the bilaminar arrangement of both samples.

Some authors have observed that the retention properties of CTMA-clay type depend on the arrangement/configuration of the organic cation which is controlled by the organic carbon content between layers<sup>46,62,72</sup>. Although, Zhu et al.<sup>81</sup> observed that  $K_{om}$  value of CTMA-montmorillonite used to adsorb naphthalene in water, gradually increases to a maximum and then decreases sharply when the amount of carbon retained is equivalent to a high ordering and packing density of the tail carbon of CTMA<sup>+</sup> on the interlayer spacing. In this paper, a correlation between the increase in the *degree of ordering* that adopts the carbon chain of the CTMA<sup>+</sup> and increased  $K_d$  value of different organic bentonite, independent of the arrangement adopted by the organic cation, was observed (Figure 2). That is, the efficiency of adsorption of toluene in water would be favored in those organic bentonites in which the band corresponding to stretching asymmetric vibration modes for bond C-H metilene presented wavenumber values until close to that of CTMA<sup>+</sup> solid. The selected CTMA-bentonites showed that JaC and DLC have higher  $K_{om}$  values compared to samples B1C and B2C, according to a higher ordering of the carbon chain in each arrangement models of the CTMA<sup>+</sup> between the sheets of clay mineral (Figure 2).

In contrast to that observed by Zhu and Zhu<sup>46</sup>; Zhu et al<sup>92</sup> the packing density conformation between the alkyl chains would be a factor that would influence little on the retention

capacity of each organo-bentonite. Presence of toluene in the samples does not generate changes in the position of the band's associated stretching asymmetric vibration modes of C-H methylene (~ 2920 cm<sup>-1</sup>) to the four CTMA-bentonites. This behavior suggests it would not have a high packing density between the carbon chains of CTMA<sup>+</sup> cations present in the interlayer spacing, at the time of the adsorption of toluene, shown in dotted line in Figure 4a.

Thereby, homogeneous interlayer space associated with arrangements of CTMA<sup>+</sup> paraffin-monolayer and bilayer models, accompanied by a high order of the carbon chain of organic cation in both arrangements, increase the adsorption capacity of CTMA-bentonite prepared from natural bentonite

## 4. Conclusion

The presence of carbon in the treated bentonite with CTMA<sup>+</sup> played an important role in the retention of toluene. It was observed that homogeneous spaces corresponding to a paraffin-monolayer or bilayer arrangement, accompanied by a high ordering of the organic cation between the sheets of clay mineral, can optimize the capacity of CTMA-bentonite adsorbent for retaining toluene from water solution. The packing density of cation CTMA<sup>+</sup> in the interlayer space of the montmorillonite would not have an evident influence on the retention capacity of these materials.

Obtained CTMA-bentonites from natural bentonites with high montmorillonite content, originated an adsorbent

with potential application to remove varying concentrations of toluene present in contaminated water. The low cost of bentonite due to its abundance in nature, easy development and its modification by a simple physicochemical process with cation CTMA<sup>+</sup> makes them viable materials for application.

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