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Characterization of Brazilian Bentonite Organoclays as Sorbents of Petroleum-derived Fuels

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This work focused on preparing and characterizing Brazilian bentonite clay through the use of quaternary ammonium salt so as to apply it as a sorbent for petroleum-derived fuels. Bentonite clay was organophilizated by the intercalation of quaternary ammonium salts such as cetyl-pyridinium chloride and benzalkonium chloride. The resulting materials were characterized by X-ray diffraction, scanning electron microscopy, energy dispersive X-ray spectroscopy, N_2 physisorption and infrared spectroscopy techniques. The clay similarity with petroleum-derived fuels, gasoline and diesel oil were defined by sorption and swelling tests. The increase in basal spacing and the appearance of absorption bands related to the CH_2 and CH_3 groups confirm the efficiency of Brazilian organoclays. Removal percentages between 50 and 60 for benzene, toluene and xylene indicate the potential of organoclay in the remediation of areas contaminated by petroleum-derived fuels.

Keywords: *"Verde-Lodo" clay, quaternary ammonium salt, X-ray diffraction, infrared spectroscopy*

1. Introduction

The exploration, refining, and transportation of petroleum and its derivatives have become largely responsible for the pollution of soil and water by organic compounds due their increased scale of production and use. Gas stations represent a potential source of contamination of soils and groundwater due to the products they manipulate (gasoline, diesel oil and ethanol) and the manner in which these are stored and sold. Although large accidental oil spills are troubling, Tiburtius et al. (2005)[1] consider small and continuous leaks as well as fuel distribution depots as the main source of contamination. Fuelling activities and vehicle washing cause fuel loss which is carried by rain - reaching rivers, groundwater and pluvial sewers - in addition to contamination from leaks in old, cracked and corroded storage tanks[2].

In Brazil, there are no statistics for underground fuel tank contamination, although the São Paulo state environmental company has estimated that gas stations are responsible for 78% of all contaminated areas[3].

Petroleum-derived fuels contain highly toxic compounds to human health including aromatic fractions (benzene, toluene, ethyl benzene and xylene - BTEX). As BTEX have the physico-chemical properties that make them more soluble in water, major pollution problems have been attributed to them[4,5]. Aromatic hydrocarbons from gasoline, for example, have greater mobility in water and water-soil systems due to the lower partition coefficient between octanol-water[6]. Several processes are available to treat groundwater impacted by petroleum hydrocarbons, such as bioremediation, air spray and monitored natural attenuation[7]. These treatment processes are complex and relatively long. Therefore, the use of organoclays for sorption of organic compounds, either as a reactive barrier or as adsorption systems has been found effective for containment of leaks from underground fuel storage tanks, preventing or controlling environmental pollution[8-11]. Many studies have evaluated the use of organoclays in contaminant remediation. Cationic surfactants controlled migration of nonionic organic compounds[12]. Burns et al. (2003)[13] investigated the adsorption capacity and retention of hydrocarbons of gasoline by bentonite clay modified with hexadecyltrimethylammonium and triethylbenzylammonium. Although a mixture of hydrocarbons can be found at polluted sites, sorption using organoclay was evaluated for a single contaminant in most studies.

Clay minerals can change their naturally hydrophilic character into organophilic, acting as sorbents for organic compounds derived from petroleum such as gasoline, diesel oil, xylene and toluene[14]. The organophilization consists of quaternary ammonium salt addition with a chain of twelve or more carbon atoms to aqueous dispersions at an inorganic cation change for alkylammonium cations[15]. The salt molecules reduce the clay superficial tension when it disperses into organic medium[16]. According Kowalska et al. (1994)[17], clay interactions with organic compounds involve the electrostatic charge on the surface of silicate, being influenced by molecular weight, chain length and functional group of the adsorbed organic molecule.

The bentonite group is largely used in the preparation of organoclay, due to small crystal dimensions, high superficial area and cation exchange capacity[18]. Moreover, the clays, particularly those from the Northeast of Brazil, occur superimposed on other mineral deposits of great commercial

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interest, such as gypsum. This fact could help reduce the extraction costs of that mineral in these deposits.

Thus, this work was aimed at preparing and characterizing Brazilian organoclays in order to evaluate their interactions with petroleum-derived fuels so as to use them in the remediation of contaminated areas. Several characterization techniques were employed to identify the changes in clay that enable its applicability as a sorbent.

2. Material and methods

2.1. *Clay preparation*

Bentonite "Verde-Lodo" clay from Paraíba, located in the Northeastern region of Brazil, was used. The cation exchange capacity (CEC) is of 87.53 mEq.100 g^{-1} (estimate determined through ammonium cation exchange[19]). Initially, clays were purified through sodium exchange: carbonate sodium solution and clay were mixed under heat, being stirred until boiling. This first pre-treatment is performed with sodium ions, which are easily exchangeable as they are a monovalent ion and are usually found in large numbers between clay layers. After heating, the dispersion was stirred for another 20 minutes for cooling and subsequent benzalkonium chloride or cetyl-pyridinium chloride surfactant addition at 1:1 ratio of CEC's clay[20]. The clay samples were identified as VL-natural, VL-benzal (with benzalkonium chloride salt) and VL-cetyl (with cetyl-pyridinium chloride salt).

2.2. *Clay characterization*

The obtained material was characterized through several techniques and the organoclay swelling and sorption in petroleum-derived fuels were measured. The Bragg angular zone was explored by X-ray diffraction (XRD) in Shimadzu equipment, XDR 7000, Kα cooper radiation (λ = 1.54 Å), monitoring the diffraction 2θ angles, 0.02 degree step size from 1.5 to 30°, 1 second signal accumulation time, 40 kV voltage and 30 mA current. In order to evaluate the adsorbent morphology, a scanning electron microscopy (SEM) using LEO equipment, LEO 440i, with 500 × power was performed. The energy dispersive X-ray technique (EDX) enables qualitative evaluation of chemical compositions. The surface area and the volume of pores and micropores were obtained through N_2 physisorption (BET method) at 77 K, using a special sample tube with bulb. These analyses were performed using a Micromeritics® Gemini III 2375 Surface Area Analyzer device using the BET method. Infrared spectra were collected using a Spectrum One - FT-IR spectrometer, Perkin Elmer. Spectra were collected over the spectral range 4000-400 cm^{-1}. Samples consisted of anhydrous KBr pellets mixed with clay.

2.3. *Petroleum-derived sorption*

Organoclay swelling into petroleum-derived fuels was measured in gasoline and diesel oil. 1.0 g of clay was gradually added to 50 mL of petroleum-derived fuels contained into a graduated cylinder, without stirring. After 24 hours, clay column volume was measured; after the stirring dispersion and another 24 hours, swelling was measured again. This test was performed in conformity with Foster (1953)[21], with some adjustments proposed by Diaz (1994)[15].

The organic liquids sorption capacity was measured following a method based on ASTM® 716-82 and ASTM® F726-99 standard[22,23]. At sorption tests, 1.0 g of clay was placed into a small metal basket of a certain known weight, and subsequently, in contact with the petroleum-derivative for 15 minutes, suspended for 15 seconds to remove its derivative excess and measured again. The organic sorption was obtained through the difference between initial and final weight.

In addition to sorption and swelling tests, the removal percentage of benzene, toluene and xylene (BTX) in gasoline by organoclay was also evaluated. 100 mL of 15% volume of gasoline in water was placed in contact with 1 g of organoclay for 48 hours[24] and the initial and final concentrations of benzene, toluene and xylene compounds were determined by headspace gas chromatography (Shimadzu, 2010, detector GCMS-QP plus). BTX removal was determined due to the presence of large amounts of these compounds in petroleum-derived fuels and high toxicity. The tests were kept under constant stirring of 250 rpm, with temperature control at 25 °C. To minimize vaporization losses, the tops of the tubes were covered with aluminum foil before caps were screwed onto them.

3. Results and Discussion

3.1. *Characterization*

3.1.1. Basal spacing evaluation by X-ray diffraction

The diffractograms obtained from natural and organophilic clay were shown in Figure 1. Thus, it is possible to observe the presence of montmorillonite and quartz, typical of this type of clay in which smectite is the predominant clay mineral[18]. The basal spacing of the natural clay changed from 15.2 to 23.9 Å for VL-benzal and to 21.6 Å for VL-cetyl. The significant increase in d_{001} of organoclays shows the effective quaternary ammonium

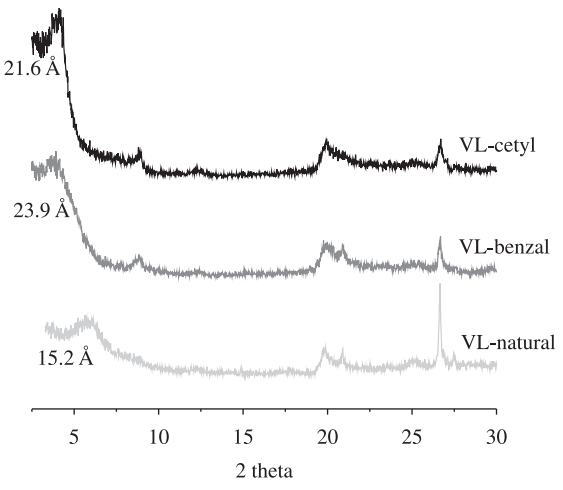


Figure 1. Clay diffractograms.

cation intercalation in the layers. According to the measured basal spacing, intercalated alkylammonium cations in VL-benzal acquire a paraffin-type orientation, while the VL-cetyl clay was a pseudo-trimolecular layer[25].

3.1.2. Morphology and qualitative chemical composition

The scanning electron microscopy (SEM) results for natural and organoclay samples are presented in Figure 2. The solid porous nature was verified through various sized irregular blades and many similar aspects, even after the samples had been treated with quaternary salt.

Bentonite qualitative chemical analysis is shown in Figure 3. The significant Si and Al presence could be observed in all clays. These are the main components of clay minerals[18]. Mg and Fe were isomorphous substitution elements and Na was the exchange cation. C and Cl peaks appear in organoclays (Figure 3b,c), coming from intercalated quaternary salt. Na peaks disappeared, confirming that most Na cations had been replaced by alkylammonium cations, and were eliminated during clay filtration and washing.

3.1.3. Surface area and pore characteristics

The obtained values for surface area through BET method for natural and organoclay samples are found in Table 1. Using BET adsorption isotherms, micropore (V_{mi}) and mesopore (V_{mes}) volumes were obtained by reading adsorbed volume (V_{ads}) at $P/P_0 = 0.10$ and 0.95, expressed by Equations 1 and 2[26].

$$V_{mi} = V_{ads} (P/P_0 = 0.10) \quad (1)$$

$$V_{mes} = V_{ads} (P/P_0 = 0.95) - V_{ads} (P/P_0 = 0.10) \quad (2)$$

The organoclay surface area, as well as micro- and mesopore volumes were drastically reduced after organophilization. These decreases were attributed to the organoclay microstructure, since the quaternary salt intercalation caused an interlayer expansion, as seen on X-ray diffraction analysis, so that salt ions blocked the passage of N_2 molecules, occupying active clay sites which might be available for N_2[27,28]. Differences among modified clay areas are due to organic cations, which had been layered, and to their interlayer orientation.

3.1.4. Infrared spectroscopy

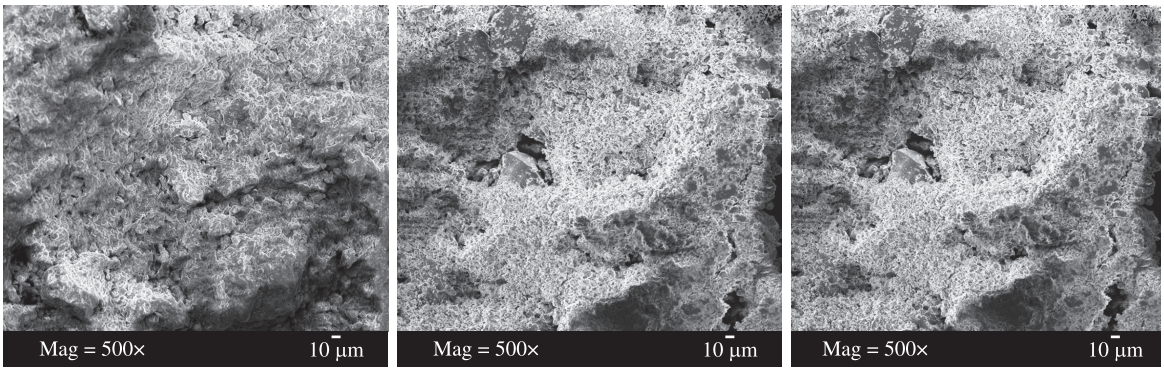
The FTIR spectra for clays are shown in Figure 4. The adsorption bands with the corresponding groups or bonds for each spectrum are found in Table 2. The characteristic vibration peaks of VL-natural were at 470 and 1120 cm^{-1} corresponding to the clay structure and Si-O-Si and Si-O-Al stretching and bending. The peaks at 1040 cm^{-1} (Si-O stretching) and 523 cm^{-1} (Si-O bending) were also presented[29]. Sorbed water contributed to H-O-H bending region (1600-1700 cm^{-1}) and to O-H asymmetric and symmetric stretching region (3100-3700 cm^{-1})[30]. These bands were presented in all studied clays, as shown in Table 2. The intensity of these bands was reduced with organophilization, because the quaternary salt intercalation, which modified the montmorillonite surface, was modified from hydrophilic to hydrophobic[31].

Table 1. Specific superficial area and volume of pores of clays by BET method.

Samples	Superficial Area ($m^2.g^{-1}$)	R^2	V_{mi} ($cm^3.g^{-1}$)	V_{mes} ($cm^3.g^{-1}$)
VL-natural	65.414	0.999	17.024	16.711
VL-benzal	5.659	0.999	1.128	2.514
VL-cetyl	0.123	0.998	0.029	0.027

Table 2. Bonds identified on the FTIR spectrum.

Groups (bond)	Wavenumber (cm^{-1})		
	VL-natural	VL-benzal	VL-cetyl
O-H asymmetric stretching	3625	3623	3627
O-H symmetric stretching	3427	3435	3427
C-H asymmetric stretching	-	2925	2920
C-H symmetric stretching	-	2853	2852
H-O-H bending	1643	1643	1636
CH_2 scissoring	-	1469	1470
N-CH_3 scissoring	-	1483	1487
Si-O stretching	1030	1032	1032
Octahedral sheet	915	915	915
Octahedral sheet	792	783	775
Si-O-Al bending	695	703	685
Si-O bending	532	527	531
Si-O-Si bending	470	470	471



(a) (b) (c)

Figure 2. a) VL-natural; b) VL-benzal; and c) VL-cetyl micrographics clay 500 × amplified.

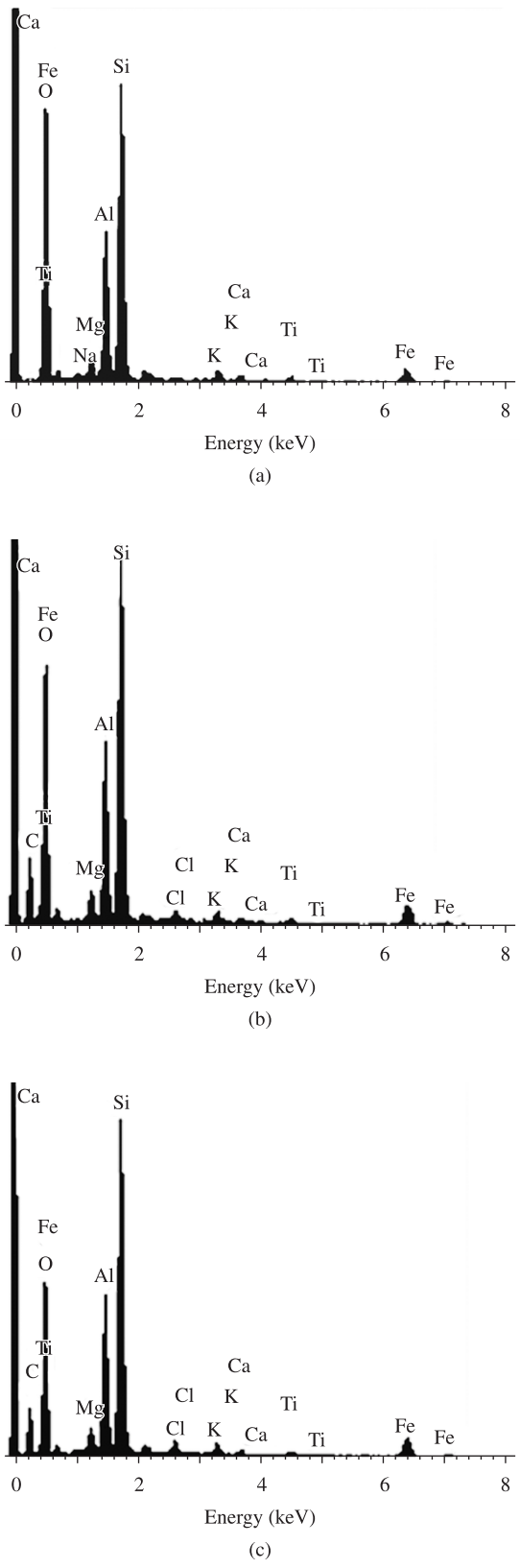


Figure 3. Chemical composition by energy dispersive X-ray spectroscopy of a) VL-natural; b) VL-benzal; and c) VL-cetyl.

The organoclays presented new characteristic vibrations at 2917 and 2850 cm^{-1}, corresponding to asymmetric and symmetric CH_2 stretching modes, and at 1400 cm^{-1}, corresponding to CH_2 scissoring[32]. Several studies[32-34] have related frequency and width of asymmetric CH_2 stretching and sensitive to *gauche/trans* conformer and methylene packing density. Highly ordered characteristic alkylammonium cations (*trans* conformations) corresponded to C-H stretching shift band location in lower frequencies, low wave number and usually high salt concentrations, whereas low salt concentrations, band location in high frequencies and high wave number corresponded to *gauche* conformations (chain disorder). Table 2 presents C-H stretching band position, where we can observe changes for higher wave number with maximum variations of 8 cm^{-1} at the asymmetric stretching and 3 cm^{-1} at the symmetric stretching for VL-benzal clay. The increase in the stretching frequency has indicated *gauche* chain conformation. This has occurred in both modified clays. The smallest variation in clay symmetric wave number stretching showed this largest band sensibility; similar behavior was observed by He et al. (2004)[35]. The CH_2 scissoring, corresponding to 1470 cm^{-1}, was also chain disorder indicative.

He et al. (2004)[35], Xue et al. (2007)[31] and Li et al. (2008)[36] had obtained spectra for organoclays with different salt amounts, observing intensity and band position with the cation exchange capacity. CH_2 and CH_3 best vibration definition increased with CEC, especially for salt amounts corresponding to twice the amount of clay CEC. The relation 1:1 CEC used in salt amounts for the clays produced in this work, allowed the identification of a 1487 cm^{-1} band in Table 2, corresponding to N-CH_3 scissoring, a group of alkylammonium chain extremity[37].

3.2. *Petroleum-derived sorption*

Swelling was not present before the clays were mixed, in contact with petroleum-derived hydrocarbons. This indicates that the stirring is an important factor for compound sorption. VL-natural did not present an expansion for any petroleum derivative, due to the fact that it does not

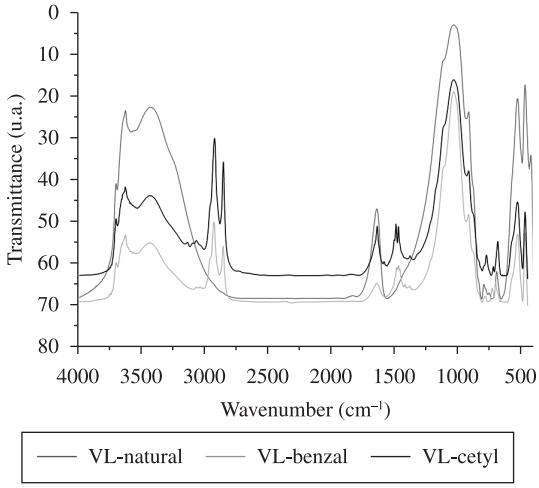


Figure 4. Infrared curves of a) VL-natural; b) VL-benzal; and c) VL-cetyl clays.

present natural affinity with organic compounds. VL-cetyl clay presented intermediate value (from 6 to 8 mL.g^{-1})[15] for swelling in gasoline and VL-benzal clay presented intermediate value for swelling in diesel oil after 48 hours and after mixing (Figure 5). This analysis characterized organoclays hydrophobicity/organophilicity and the natural clay hydrophilicity/organophobicity.

Gomes (1988)[38] considers sorption or interaction as dependent on the structure and property of the pollutant, besides the characteristics of clay minerals and exchange cations. While working with clays from Paraiba, Pereira et al. (2005)[39] also obtained intermediate values in gasoline expansion, whereas Vianna (2005)[40] attained improved expansion levels reaching high levels for some of the treatments and quaternary ammonium salts used in the preparation of his clays.

Figure 6 shows sorption test results. VL-cetyl showed the largest sorption capacity for gasoline. The sorption value was 3.7 times higher when compared to the VL-natural sorption value for gasoline. The affinity order for VL-natural and VL-cetyl clays was: gasoline > diesel oil, while for VL-benzal clay is reversed (diesel oil > gasoline).

Removal percentage of benzene, toluene and xylene through VL-cetyl was performed, as optimal affinity was assessed at swelling and sorption experiments. The best results of VL-cetyl may be related to linear chain of cetyl-pyridinium chloride salt in comparison with the benzalkonium chloride, as assumed by Jaynes and Vance (1996)[41].

Table 3 shows removal percentage of compounds by VL-cetyl. The values, considered to be high, indicate the affinity of organophilic clay with the compounds. As gasoline contains approximately 200 different hydrocarbons, aside from additives[4], and clay interacts with many of these compounds, only BTX have been measured in the present work, with a view to represent the existing affinity between organic compounds and clay. Gasoline sorption test with metal basket resulted in 5.5 g gasoline/g VL-cetyl, after 48 hours.

Removal percentages correspond to a total of 0.687 mg BTX/g organoclay. This value is close to the capacities obtained by Carvalho et al. (2011)[42] in the removal

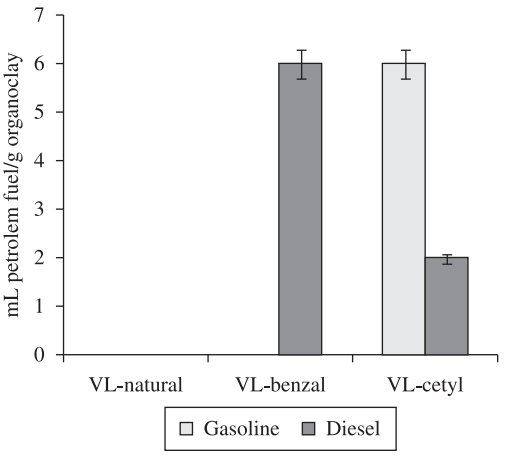


Figure 5. Swelling values after stirring.

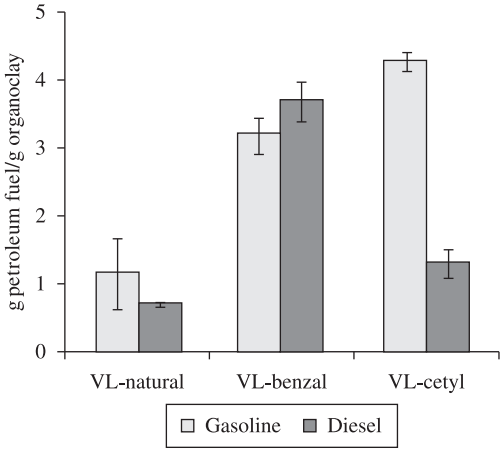


Figure 6. Sorption test.

Table 3. Removal percentage of BTX by VL-cetyl.

Compounds	% removal	mg.g^{-1} adsorbed
Benzene	60.28 ± 0.32	0.216
Toluene	60.12 ± 0.11	0.346
Xylene	50.38 ± 0.74	0.125

of m- and p-xylene separately using clays modified with cetyltrimethylammonium chloride, 0.758 mg de m-xylene/g organoclay and 0.765 p-xylene/g organoclay.

The relatively high affinity between BTX and organoclay is probably the result of BTX molecules interacting favorably with the pyridinium ring through π–π interactions[43].

The removal percentage test shows good results and the potential use of Brazilian organoclays for sorption of petroleum-derived fuels. The obtained values do not correspond to the maximum sorption capacity of organophilic clays - which should be based on sorption isotherms - although they confirm affinity.

4. Conclusions

The results have confirmed the synthesis effectiveness of "Verde-Lodo" organoclay, verified through basal spacing increase, CH_2 and CH_3 group bands at infrared spectroscopy and carbon and chlorine peaks in the energy dispersive X-ray spectroscopy. The organophilization altered the natural hydrophilic character to hydrophobic and organophilic. Modifications occurred in clays due to inorganic cations changes into organic cations, which caused interlayer space features to enable the organic compound interaction, whose likeness for the clays was confirmed at swelling and sorption tests. The removal percentages of BTX show that the organoclays presented potential for environmental remediation, such as petroleum-derived fuels sorption in the form of barrier systems or adsorption systems.

Acknowledgements

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