

ASSESSMENT OF ORGANOCLAY STRUCTURAL PROPERTIES AFTER GASOLINE ADSORPTION PROCESS

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ABSTRACT – The removal of organic contaminants from water and wastewater is a key problem of environmental remediation which can be solved by adsorption process, especially with the use of organoclays for their abundance, variety and low cost. Therefore, this study aimed the evaluation of modifications on the structure of a commercial bentonite organoclay named Spectrogel due to the adsorption process with gasoline and isooctane. The characterization of the organoclay was accomplished through TGA, DSC, FT-IR, SEM/EDX, XRD and Helium pycnometry analyzes before and after the process of gasoline removal. Modifications in the organoclay structure were verified and could be attributed to the adsorption process of the organic compounds.

1. INTRODUCTION

According to the Environmental Company of State of São Paulo (CETESB) 80% of municipality of São Paulo are totally or partially dependant on underground water. Annual reports from CETESB (2012) shows that nearly 77% of identified contaminated areas of the state are due gas station activities. This follows up what the Environmental Protection Agency from USA (USEPA) surveyed on late 80's. These contaminations are from expired underground fuel storage tanks and without proper maintenance according to Tiburtius *et al.* (2005).

According to Wang *et al.* (2013) fuels like gasoline and diesel have highly toxic, carcinogenic and mutagenic additives like BTX, and if it was not bad enough the presence of alcohol worsen the risk of contamination by enhancing the mobility of all petroleum hydrocarbons on soil as studied by Adam *et al.* (2002). These fuels also damage the environment by changing soil permeability to water and harm the flora according to Zhang *et al.* (2006).

Among the treatments of oily water a very promising one is the adsorption process using organoclays due their high capability to remove hydrophobic contaminants from aqueous solutions. As clays are a very abundant in nature and cheap this represents an economic advantage in the process as well.

According to Grim (1968) clays have an interlamellar cation that plays a great role on its

physicochemical properties like viscosity, tixotropy, plasticity, mechanical resistance and affinity to polar or organic matter. Therefore, the organoclays are chemically modified clays by the exchange of its natural interlamellar inorganic cation for an organic cation, usually a quaternary alkylammonium salt, which provides the clay a high capability to remove hydrophobic contaminants from aqueous solutions according to Kwolek *et. al.* (2003) and Alther (1995).

This study assessed the organoclay's chemical and structural properties after sorption of gasoline and isooctane for better understanding of the process and for the next studies of regeneration of this adsorbent.

2. MATERIALS AND METHODS

The commercial organoclay used was kindly provided by SpectroChem®. This clay was milled and sieved to the average size of 0.655 mm of diameter for use on the sorption process.

The proportion used for sorption was 5 mL of contaminant per gram of organoclay while the initial concentration was 16.66% in volume. After the sorption process the organoclay was removed from solution by filtering and kept on fume hood at 20 °C till dry.

The contaminated organoclay was milled and sieved to the sizes of 0.655 mm for Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) analysis and smaller than 0.075 mm for X-ray Diffraction (XRD), Thermogravimetric (TGA/DTG) and Differential Scanning Calorimetry (DSC) analyses.

2.1 Equipments and Conditions

Thermogravimetric Analyses (TG/DTG): Both analyzes were performed on equipment Shimadzu TGA-50 under a heating rate of 10 °C/min from room temperature to 1000 °C and a N₂ flow of 50 mL / min. Alpha alumina was used as the reference material for DSC analysis.

Differential scanning calorimetry (DSC): This analysis was performed using a detector Mettler-Toledo model DSC1 at a flow rate of 50 mL / min from room temperature to 500 °C and a heating rate of 10 °C/min in nitrogen atmosphere.

X-ray diffraction (XRD): The equipment used was a Philips X'Pert model with copper Ka radiation, voltage of 40 kV and 40pA current, wavelength of 1.5406 Å and 2θ ranging from 3 ° to 90 ° at 0.02 ° per second.

Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX): The clay was immobilized on carbon tape and coated with 9.2 nm of gold in Sputter Coater Polaron device, Model SC7620 brand VG Microtech (Uckfield, England). Then, the sample was analyzed in Scanning Electron Microscope with Energy Dispersive Detector X-ray, Model SEM LEO 440i and EDX Model: 6070 Brand SEM / EDX: LEO Electron Microscopy under accelerating voltage 20 kV and beam current of 100 pA at the micrographs and 600 pA for EDX.

Fourier Transform Infrared Spectroscopy (FT-IR): The powder samples were compressed into KBr pellets and analyzed in a Thermo Scientific spectrometer model Nicolet 6700 on transmittance mode ranging from 4000 to 400 cm^{-1} with resolution of 4 cm^{-1} .

3. RESULTS AND DISCUSSION

Figure 1 shows the thermogravimetric curve (TGA) and its derivative (DTG). All curves showed a similar pattern on temperature. According to Bertagnolli *et al.* (2012) the first peak for DTG, under 100 °C shows the loss of moisture. This shows a lessening on the hydrophobic property after isooctane sorption due higher amount of water. The second peak, between 100 °C and 200 °C, is related to interlayer water. It shows that more water was retained on interlayer spaces after gasoline adsorption while the other samples had almost none. The third and major peak for all samples, around 350 °C, is due the decomposition of the organic compound according to Almeida Neto *et al.* (2012). It similarity suggests that the organic salt is still there, but is affected by the sorbed compounds. The isooctane, as a pure component, showed a thinner peak under the usual temperature of decomposition, while gasoline made a wider peak. The fourth peak, close to 650 °C, refers to the alumino-silicate dehydroxylation and decarbonation, common for smectite clays.

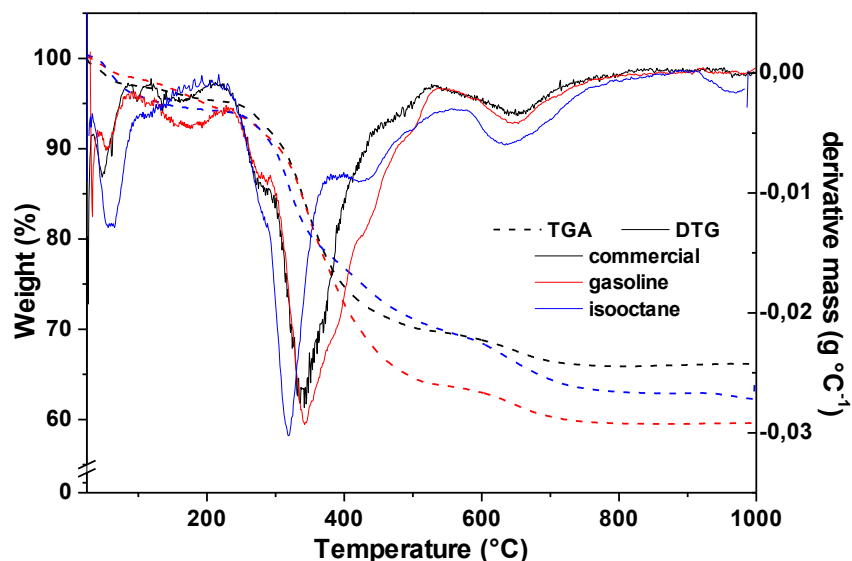


Figure 1 – Thermogravimetric analysis of commercial organoclay and contaminated organoclays.

The differential scanning calorimetry shown on Figure 2 exhibits three endothermic events. According to Almeida Neto *et al.* (2012) the first two peaks refers to dehydration of the clay, as observed in thermogravimetric analysis. The first peak at 50 °C is due the surface moisture and the second peak refers to interlayer moisture. The third peak, near 400 °C, according to Bertagnolli *et al.* (2011), is due to degradation of the organic compound present in the organoclay. The gasoline curve for this region was rather flat probably due its lower vapor pressure requiring less energy to change its state.

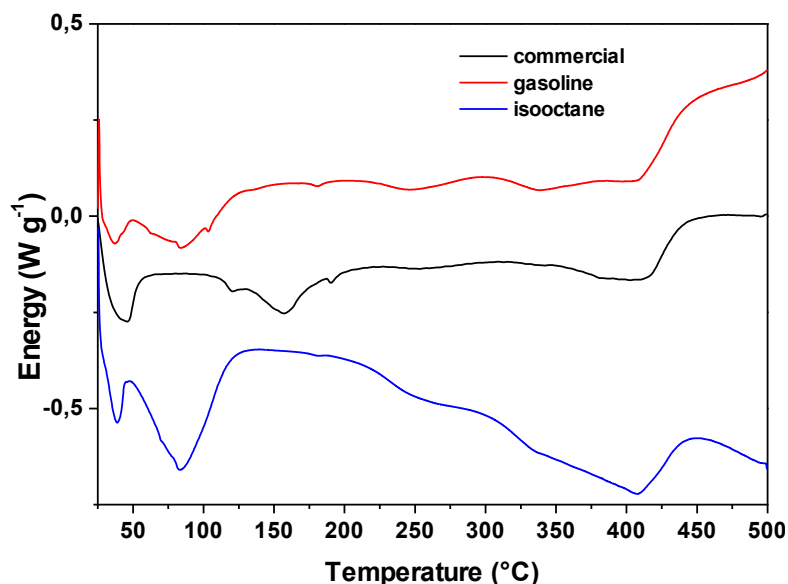


Figure 2 – Differential scanning calorimetry of commercial organoclay and contaminated organoclays.

Figure 3 shows the diffractogram for commercial organoclay and contaminated with gasoline and isooctane. As can be observed all peaks were weakened for both contaminated organoclays. The basal spacing d_{001} reduced from 2.05 nm to 1.392 nm after gasoline adsorption and to 1.314 nm after isooctane adsorption. All other peaks remained unchanged. The d_{010} (0.44 nm) peak is typical of montmorillonite clay while the d_{060} (0.149 nm) means a dioctaedral arrangement. The peaks of 0.33 nm and 0.25 nm belong to quartz while 0.28 nm and 0.20 nm are from mica according to Marcos *et al.* (2009) and Gillot (1968).

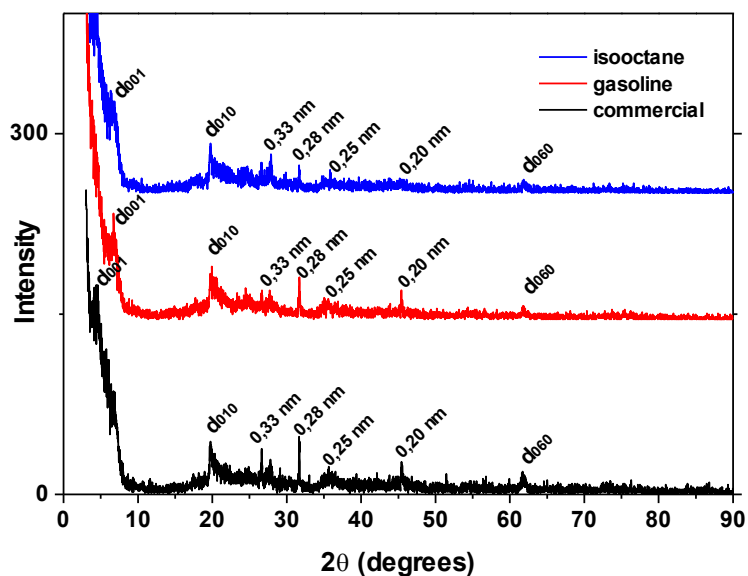


Figure 3 – Diffractograms of contaminated commercial organoclay and contaminated organoclays.

The spectrogram is shown on Figure 4. It can be noticed the peaks of CH stretching band (2920 cm^{-1}), the symmetrical stretching band of CH_3 (2850 cm^{-1}) and the peak of scissor vibration of CH_2 (1470 cm^{-1}) accordingly with Bala *et al.* (2002) and Xi *et al.* (2007). According to Pereira *et al.* (2004), the peaks inherent of smectites (3630 , 3440 , 1040 , 519 and 461 cm^{-1}) relatives to OH and SiO can be also seen. In this aspect there were not any changes after adsorption process, but the reduction of absorbance on infrared spectrum.

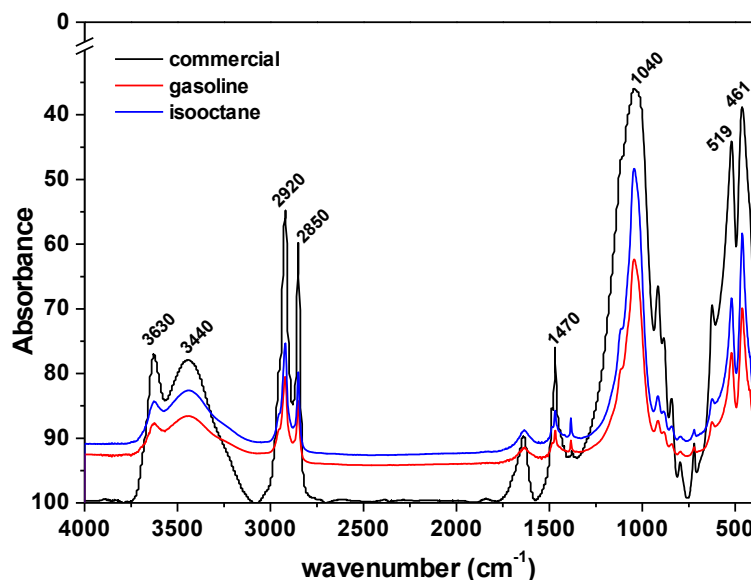


Figure 4 – FTIR spectra of the commercial clay and organoclay after sorption process.

The SEM micrographs of commercial organoclay and contaminated organoclay are shown in Figure 5. It can be observed a higher surface roughness for gasoline and isooctane compared to the commercial one.

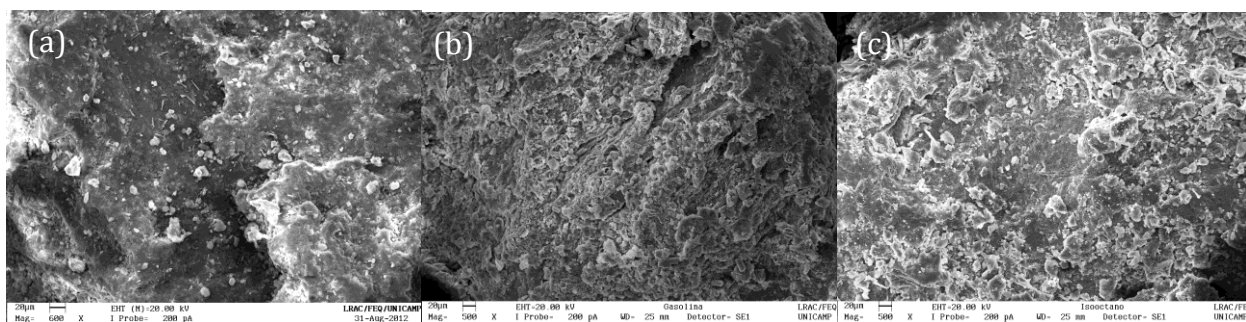


Figure 5 – Micrographs of (a) commercial, (b) gasoline and (c) isooctane organoclays at magnification of 600x.

Table 1 shows the mean chemical composition of organoclays assessed. As expected for montmorillonite clay, all samples are mainly composed of silica and aluminum. It can be observed a

rise on the proportion of Sodium that might be due the homogeneity of the sample as crystals of sodium chloride were present on the commercial's SEM micrographs, but not on the contaminated ones.

Table 1 – Chemical composition of organoclay samples by EDS.

Sample	Composition (%)					
	Si	Al	Cl	Fe	Na	Mg
Commercial	59.32	17.54	7.54	6.37	6.31	2.93
Gasoline	51.00	17.30	8.87	5.97	13.92	2.95
Isooctane	56.48	19.52	3.24	6.31	10.98	3.47

The He picnometry showed an increasing density being 1.6516 g.mL^{-1} the commercial, 1.6858 g.mL^{-1} the organoclay with isooctane and 1.7384 g.mL^{-1} the organoclay with gasoline. This could be attributed to the sorbed organic as gasoline has a higher density compared to isooctane.

The regeneration of the adsorbent contaminated of gasoline and isooctane was carried out with chemical eluents. The eluents tested were acetonitrile, methanol and ethanol (pure and diluted with water at different proportions). These eluents are compounds which have properties to desorb the contaminants. However, acetonitrile and methanol are toxic to the environment and human health. Thus, the eluent chosen to regenerate the clay was ethanol (desorption data not shown in this paper).

4. CONCLUSIONS

The sorbed compounds reduced the interlayer (d_{001}) basal spacing meaning it replaced completely or partially the organic salt or changed the arrangement of molecules in the interlayer. The contaminated organoclays showed reduced absorbance on FT-IR. The micrographs showed a rougher surface with gasoline. The picnometry of He showed higher densities after the sorption process as expected. The TGA curves showed more humidity for isooctane and a thinner peak on degradation of organic compound compared to commercial organoclay, while the gasoline contaminated organoclay showed a wider peak for being a mixture of hydrocarbons. The DSC curves showed a more intense exothermic peak for the organic decomposition for organoclay with isooctane and confirmed its higher humidity while the organoclay with gasoline showed a more steady demand of energy. This study will help in the next essays for the regeneration of this adsorbent using ethanol (diluted with water) as eluent.

5. ACKNOWLEDGEMENTS

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