

Evaluation of Brazilian Organoclay Synthesized in the Laboratory and Commercial

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Bentonite clays organically modified with quaternary ammonium salt, of which features enable to interact with organic compounds, have great potential use for environmental remediation, such as adsorption of organic compounds from wastewater. In this study, the natural clay 'bofe' had its properties modified by the organophilization with cation exchange linked to quaternary ammonium salt (benzalkonium chloride). The commercial clay Spectrogel, provided by Spectrochem, was also studied for comparison with sample modified in laboratory. The clays had been characterized by use of x-ray diffraction, scanning electron microscopy, energy dispersive x-ray techniques, thermogravimetric analysis, and differential scanning calorimetry. The organophilic character was evaluated by swelling capacity test in water. There was an increase in the basal spacing, in the presence of carbon and chlorine, and in the new decomposition stage for modified clays, attributed to the organic matter released from quaternary ammonium salt. Such fact confirms how effective is the synthesis of the organoclay and similar behavior for the organoclays modified in laboratory and commercial. The potential for removal of petroleum derived from wastewaters was verified, showing potential use for environmental remediation.

1. Introduction

The group of smectite clays has a high adsorption capacity and high content of colloidal matter, or even a high likelihood of activation, and may be modified or subjected to processes to improve its properties (Abreu, 1973). In aqueous dispersions of smectite the lamellae are more separated, facilitating the addition of quaternary ammonium salts to produce organoclay due to the exchange of inorganic cations originally present in the natural clay by alkylammonium cations (Barbosa et al., 2006). These clays have been used to control the viscosity of organic products suspensions, to control opacity and viscosity of paints, pharmaceuticals and cosmetics products, and more recently to produce polymer nanocomposites (Yariv and Cross, 2002; Patel et al., 2006).

A change from hydrophilic characteristic to organophilic clays allows the use as adsorbent of organic compounds, especially to separate mixture of oil and water.

In this work, bentonite 'bofe' clay was organophilized and their properties were compared with a commercial clay. These samples have hydrophobic properties and thus

increase the affinity with organic compounds, seeking to use it into petroleum derived removal from wastewaters.

2. Material and methods

2.1 Sample preparation

Bentonite 'bofe' clay from Boa Vista city, state of Paraíba, in the northeastern region of Brazil, was used. The cation exchange capacity (CEC, determined through ammonium cation exchange (Guarino et al., 1997)) was 87.53 meq/100 g. At the first treatment, clays were purified by sodium exchange: carbonate sodium solution and clay were mixed under heating with stirring until boiling. After heating, the dispersion was stirred for another 20 minutes for cooling and benzalkonium chloride surfactant addition at 1:1 ratio of CEC's clay (Pereira, 2008). The clays were untreated Natural, Benzal (with benzalkonium chloride salt), and Commercial (provided by Spectrochem).

2.2 Characterization

The obtained material had been characterized by using several techniques. In the present study, the Bragg angular zone was explored by x-ray diffraction (XRD) in Shimadzu equipment, XDR 7000, K α cooper radiation ($\lambda=1.54 \text{ \AA}$), observing the diffraction angle of 2θ , step size of 0.02 degrees ranging between 3° and 30° . Bragg's law (Eq. 1) establishes the relationship between the diffraction angle and the distance between planes that originated it in each crystalline phase.

$$d = \frac{n\lambda}{2\sin\theta} \quad (1)$$

where: d - distance between the atoms layers; n - positive integer number (usually equal to 1); λ - X-rays wavelength and θ - diffraction angle.

In order to evaluate the adsorbent morphology, a scanning electron microscopy (SEM) with LEO equipment, LEO440i, with 500X power was performed. Energy dispersive x-ray techniques (EDX) were used to identify the total chemical composition of the clay. The thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) allowed us to establish the relationship between physical property and chemical property and the temperature. The first was carried out ranging from room temperature to 1000°C in nitrogen atmosphere and using equipment Shimadzu, model TGA-50, while the second was carried until 500°C , in Shimadzu, model DSC-50.

2.3 Water swelling

The hydrophobic property was evaluated with 0.5 g of Natural, Benzal, and Commercial clays in 10 mL test tube, and their contents were completed with deionized water. Each sample was stirred and allowed to rest for a few minutes to check their behavior in the presence of water.

3. Results and Discussion

3.1 Basal spacing evaluation by x-ray diffraction

In the diffractograms from Natural, Benzal, and Commercial clays, Figure 1, are possible to observe montmorillonite (M) and quartz (Q) presences, typical of this clay type in which smectite is the predominant clay mineral (Santos, 1992). The basal spacing of the Natural clay was changed from 15.5 Å to 23.9 Å for Benzal and to 19.8 Å for Commercial. The significant increase in d_{001} of organoclays shows the effective quaternary ammonium cation intercalation in the layers. According to the measured basal spacing, intercalated alkylammonium cations in Benzal acquire a paraffin-type orientation (Lagaly, 1982).

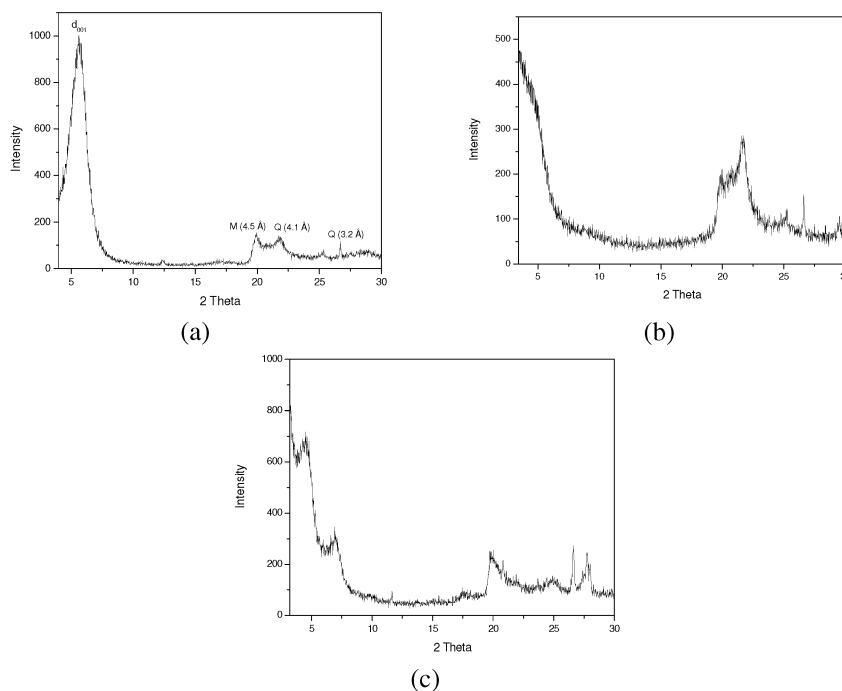


Figure 1: Diffractograms of (a) Natural, (b) Benzal and (c) Commercial.

3.2 Morphology and qualitative chemical composition

The scanning electron microscopy results for natural and organoclay samples are presented in Figure 2. The solid porous nature has verified through various sized irregular blades and many similar aspects, whether the samples have been treated with quaternary salt.

The chemical composition by EDX shows the significant Si and Al presence could be observed in all clays. They are principal components of the clay minerals (Santos, 1992). Mg and Fe were isomorphous substitution elements and Na was the exchange cation. The C and Cl peaks appear at the organoclays coming from intercalated quaternary salt. The Na peaks disappeared, confirming that most of Na

cations had changed by alkylammonium cations, and were eliminated during clay filtration and washing. The Commercial sample shows Na traces, which shows that some cations are not exchanged or presence of impurities are not eliminated with a washing step due to treatment suffered by the clay, which is not known.

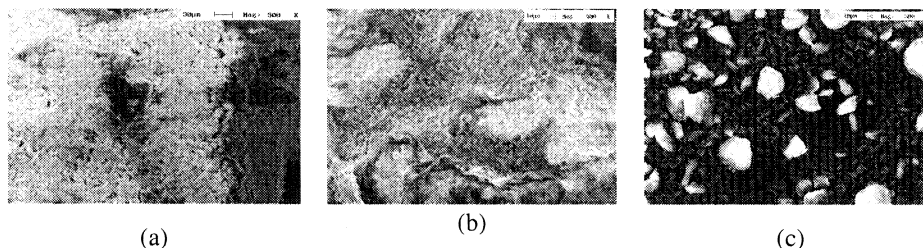


Figure 2: (a) Natural, (b) Benzal and (c) Commercial micrographics clays 500X amplified.

3.3 Thermal analysis

The Figure 3 shows the thermogravimetric curve and its derivative for Natural, Benzal and Commercial clays. All clays have a region of water loss around 50 °C (P1). There are two types of water losses: the first, water adsorbed with high mobility, being easily removed; and the second loss, hydration water around the exchangeable cations, whose presence depend on the number of hydrated cations in the interlayer. This type occurs in natural clays, which contains very hydratable cations such as Na⁺, K⁺ and Ca²⁺ (Yariv, 2004). Dehydroxylation peak (P2) appears roughly 400 °C and 480 °C. The range of structural hydroxyl loss for natural clay is in agreement with those found by Santos (1975), i.e., 400 °C to 700 °C. For Benzal and Commercial clays, besides (P1) and (P2) losses, a new stage of weight loss appears (P3) regarding quaternary ammonium salt, interspersed with the clay structure during organophilization. This peak reaches between 200 and 300 °C. The organic weight losses of the organophilic clays (P2), regarding the initial mass, were 15.6% for Benzal and 32.3% for Commercial clay. Differences in percentage weight loss of samples indicate variations in the amount and type of salt intercalated.

The DSC analysis has been used in applications where typically the differential thermal analysis (DTA) was used, indicating the occurrence of thermal reactions in the sample due to the difference in heat flow. Yariv (1991) defines the DTA curves in three regions, which were observed in DTG of the samples, referring to the curves of DSC: region with endothermic peaks of dehydration (water interlayer or external) below 200 °C. A thermal reactions region of organic matter, with an endothermic peak, characteristic of evaporation and decomposition of organic compounds in the case of an inert atmosphere, usually above 200 °C. The last region was not observed in the analysis of the clays under study, since it occurs in temperatures higher than the limit of the analysis (500 °C). The endothermic peak of organic salt decomposition was almost 250 °C for the Benzal clay, and in the form of two small peaks 200 °C and 260 °C for Commercial clay. The thermal effect of this curve depends on atmosphere used,

characteristics of organic compounds in the clay and in changing the position of the chains of salt in the clay structure. The presence of more than one peak in this region indicates the presence of salt in more than one preferred position with respect to the surface of clay (Pereira, 2008).

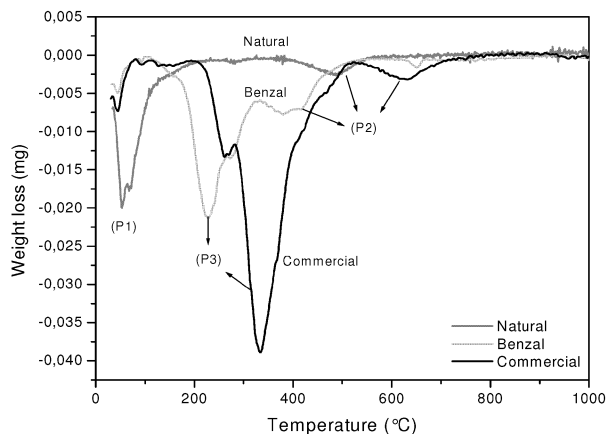


Figure 3: Derivative of thermogravimetric curve from clays.

3.4 Water swelling

The hydrophobic character of the organoclays was evidenced by the contact of clay with water. After stirring the samples, was realized a faster settling of the organoclay, compared with the Natural clay which was more delaminated, Figure 4. Natural clay undergo expansion due to adsorption layers of water molecules by exchangeable cations present between the clay layers, lithium and sodium cations, , i.e. it can consist of from 11 to 12 water molecules weakly linked by bridges hydrogen (Santos, 1992; Wersin et al., 2004). The expansion of Natural clay allows the use in the process of organophilization; thus, water entering the galleries of clay has favored the exchange of cations. The dynamic behavior of separation is due to the hydrophobic character that was acquired during its modification. The change from inorganic cations to organic decrease the sorption of water in two ways: the alkylammonium cation is not strongly hydrated and the hidden part of the surface silicate invalidates the water interaction with such surface (Mortland, 1970).

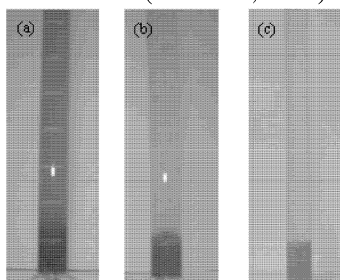


Figure 4: Behavior of clays in water. (a) Natural, (b) Benzal, and (c) Commercial.

4. Conclusions

The results confirm the effectiveness of the synthesis of organoclay 'bofe' with similar characteristics compared to those ones observed in the Commercial clay. The features were obtained by a simple process and enable interaction with organic compounds.

Acknowledgments

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