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BRAZILIAN CLAY SUBMITTED TO MILD ACID TREATMENT

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ABSTRACT: Smectite clays are widely used as bleaching agents after subjected to acid attack treatment using strong inorganic acids. These treatments are usually proceed at temperatures near the boiling point and at high acid concentrations. In this paper a sample of Chocobofe, a polycathionic bentonite, from Boa Vista, Paraíba, Brazil, was submitted to mild acid attack under bellow boiling temperature and at short times of reaction (90°C, reaction times of 1, 6, 12, 18 and 24 hours in closed reactor, concentration of the aqueous solution of hydrochloric acid 1.5 mo / L, acid solution/clay ratio of 1 g / 10 mL). These acids attacks have the objective to reduce the concentration of impurities providing color, with minimal change in the clay minerals structure, aiming at use in products of high value such polymer/clay nanocomposites and as cosmetics. The raw clay and the attacked samples were characterized by X-ray diffraction (XRD), cation exchange capacity (CEC), stereomicroscopy and oil absorption.

KEYWORDS: clays, bentonite, acid attack, nanocomposites

1. INTRODUCTION

Clays are hydrated aluminosilicates of alkali and alkaline earth metals that have a characteristic crystalline structure formed by combination of silica tetrahedra $[SiO_4]^{4-}$ and alumina $[AlO_4]^{5-}$, joined together by oxygen atoms (Breck, 1974).

A rock formed mostly by smectite clay mineral originated generally from volcanic ashes by devitrification is defined as bentonite (Souza Santos, 1992).

The polycathionic Chocobofe bentonite from Boa Vista, Paraiba, Brazil is smectite clay with non-preponderate interlayer cation, with high iron concentration that provides a dark color (Valenzuela-Diaz, 1994).

Bentonites can have high activation possibilities sorption capacities. The industrial application is vast, proportioned mostly by a diverse chemical composition (Abreu, 1973).

The sodium interlayer is responsible for the capacity of bentonites absorption. Bentonites with calcium preponderate interlayer population or with polycationic interlayer population are usually submitted to attack with strong acids to improve bleaching capacity (Pereira, 2003 and 2004, Valenzuela-Diaz and Souza Santos, 2001).

To provide specific area increased by structure disorganization, mesopores and mineral impurities leaching the usually method is an acid attack. Other benefit of acid attack is improving of acid sites with more porosity, excellent properties when applied in catalysis (Vaccari, 1999).

Another important property for industrial use of clays is the exchangeable cations capacity and minerals properties (Grim, 1978).

The industrial application of bentonites has a large range, the most part as well drilling fluids in the oil industry, as dissecant, in pharmaceutic and cosmetics, as bleaching agent in the food and vegetable oil industries among others applications

(Gomes et al, 1988, Murray, 2000; Amorim et al, 2005; Pereira et al, 2005; Ferreira et al, 2008).

Vegetable oils are important raw materials for industry, and offer the possibility of a large number of uses, for example, in the cosmetic and pharmaceutical industries. Clays are also important raw materials for industry and are having an increase use in the cosmetic and pharmaceutical industries.

The chocobofe bentonite studied in this work is an abundant cream clay found in the state of Pariba, Brazil. The aim of this work is reduce by mild acid attack the quantity of color impurities of the clay without a severe destruction of the clay mineral structure and test the sorption capacity of almond oil of the purified clay.

2. MATERIALS AND METHODS

2.1 Start Materials

Natural from Boa Vista County, Paraíba´s State, Brazil, raw Chocobofe bentonite was dried at 90°C and grounded (passing 200 mesh). The clay was treated bellow boiling temperature (90 °C) at short times of reaction: 1, 6, 12, 18 and 24 hours, in close reactor with mild acid attack using a low concentration of hydrochloric acid (1.5 mol/L), and clay/acid solution ratio of 1g/10mL. Distilled water was used to wash the clay, by filtration until pH 5-6. The washed clay was dried at 60 °C for 24 hours.

2.2 Materials Characterization

The starting material was characterized by cation exchange capacity (CEC), stereomicroscopy, X-ray diffraction and almond oil absorption capacity.

CEC was performed using the ammonium acetate method (Grim, 1978).To observe the clay was used a stereomicroscop Zeiss, model Stemi 2000C.

The XRDs were performed on diffractometer model X'Pert Pro MPD (Panalytical) with Cu anodes; scan from 2° to 90° 2ϴ; 40 kV and 35 mA.

Absorption capacity was performed using sweet almond oil. The ability of absorption (g oil/100 g clay) was determined by adding oil to 5,00 g of clay, mixing and rubbing with spatula and repeating the operation until the formation of a brilliant film on the surface of the clay indicates the saturation of clay by oil. With the total quantity of oil added the capacity of the clay to incorporate oil was calculated.

3. RESULTS AND DISCUSSION

As expected the cation exchange capacity (CEC) values (Table 1) tends to diminish with the time of attack with the 24 hours attacked sample having only 59% of the original value.

Table 1. Cation Exchange Capacity values.

Sample	CEC (meq / 100 g)	% of the no attacked
24h in water	63	100
1h attack	52	82
6h attack	58	92
12h attack	47	74
18h attack	14,6	95
24h attack	37	59

The attacked samples presented an increase in color reduction with time of acid attack. Figure 1 shows a stereomicroscopy image with 100.000nm zoom of a chocobofe sample- treated with water for 24 h. It is possible to observe some impurities in the sample.

In Figure 2 is possible to observe a decrease of impurities in the sample submitted to mild attack for 6h. Samples with attack times from 12 to 24 h showed a continuous but small decrease of impurities (that is lighter colors) compared with the sample attacked by 6 hours

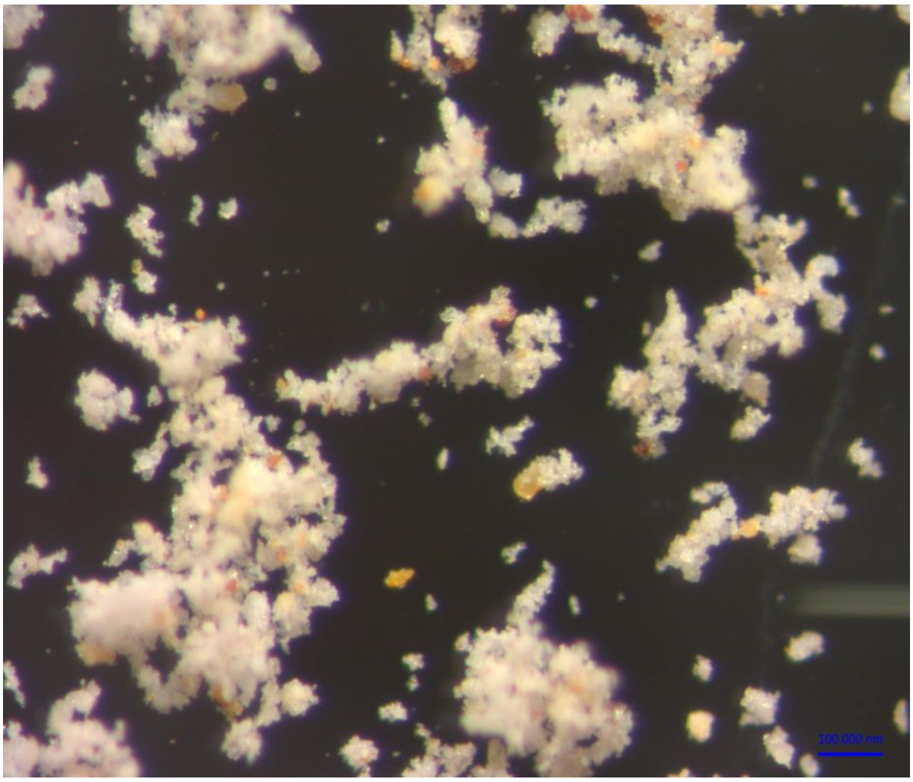

Figure 1 - Image of Chocobofe **-** treated with water for 24h. 1 cm corresponds to 1.3 micron.

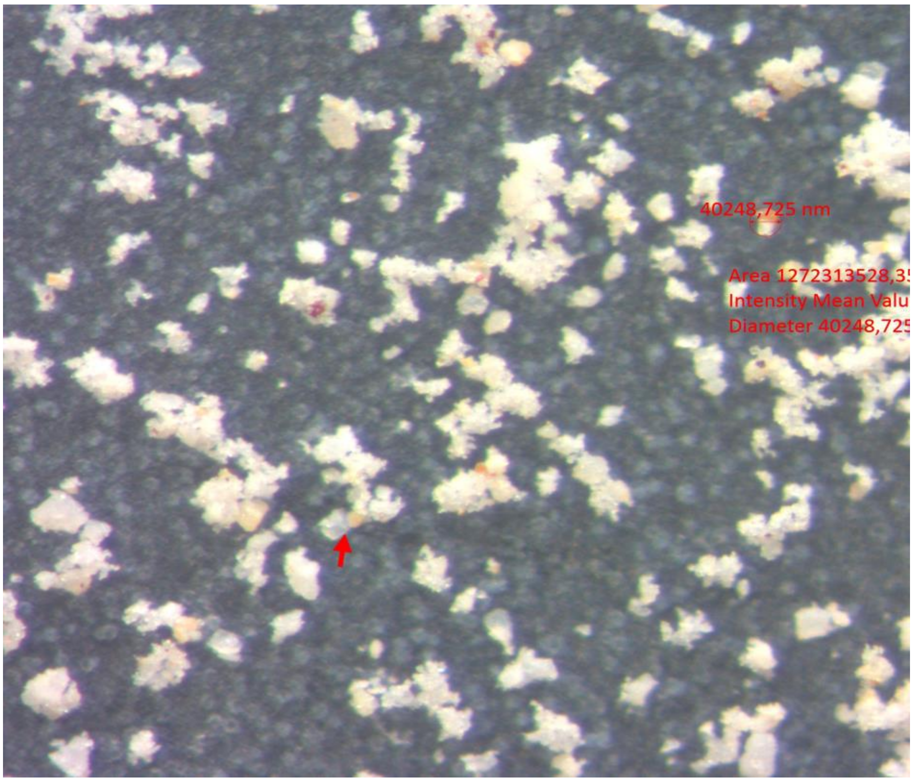

Figure 2 - Image of Chocobofe **-** treated with HCl for 6 h. 1 cm corresponds to 1.3 micron.

Figure 3 shows the X-ray diffraction curves of chocobofe submitted only to H20 for 24h at 90oC. The d(001) characteristic smectitic peak at 14,6 Å presents an intensity of 120 counts. As impurity the sample has quartz with a peak at 3,3 Å and an intensity of 500 counts.

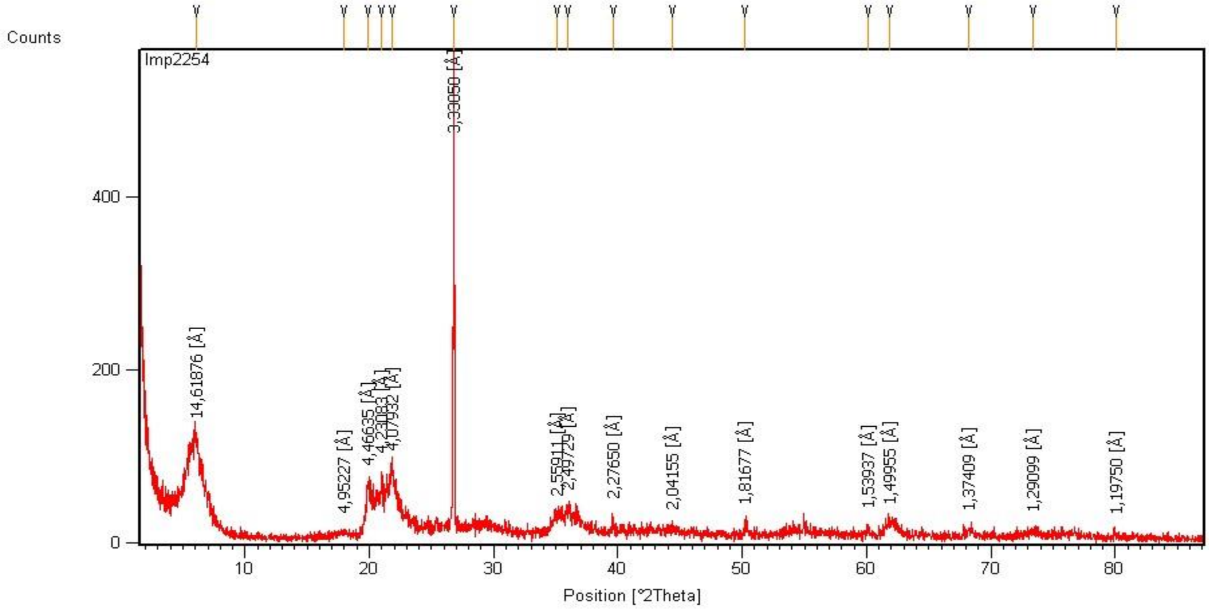

Figure 3. XRD curve of Chocobofe H_2O 24h

Figure 4 shows the XRD curve of chocobofe submitted to mild acid attack during 1h at 90°C. The smectitic d(001) peak appears at13,6 Å with an intensity of 100 counts. The quartz peak at 3,33 Å presents an intensity of 420 counts.

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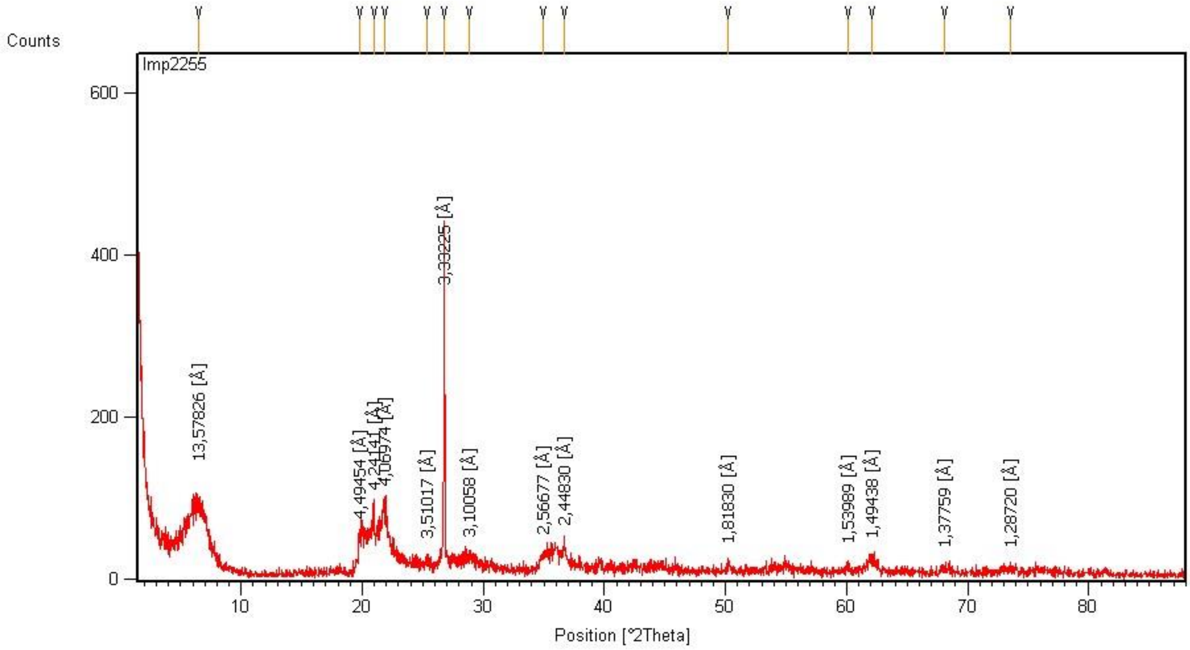

Figure 4 – XRD curve of the Chocobofe, HCL 1h at 90°C.

Figure 5 shows the XRD curve of Chocobofe submitted to mild acid attack during 24h at 90°C. The d(001) smectitic peak is present at 14,8 Å with an intensity of 90 counts. The quartz, with peak at 3,33 Å presents intensity of 200 counts.

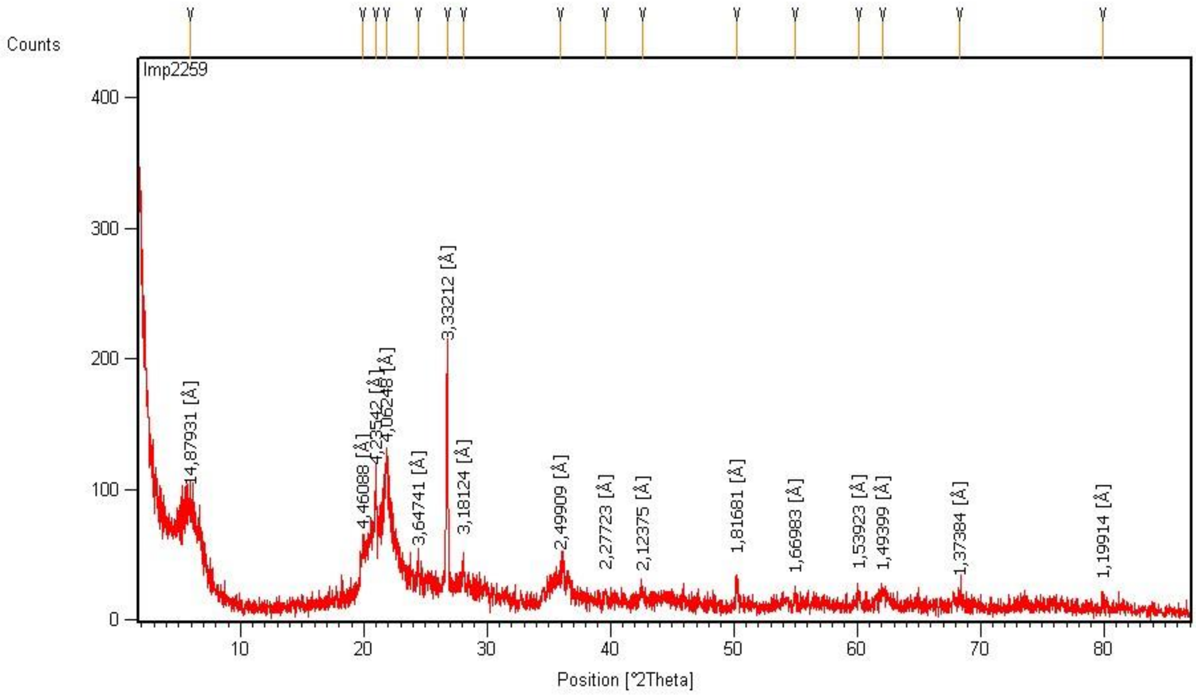

Figure 5 - XRD curve of the Chocobofe HCL 24h at 90°C.

Table 2 presents the interplanar distance of the d(001) smectite peaks for the samples attacked at different times and its intensities. The table shows also the intensities of the quartz peaks at 3,33Å for the samples of Chocobofe bentonite attacked for different times.

Table 2. d(001) smectitic peaks, smectitic peaks intensities, and intensities of the quartz peaks

Sample	Smectitic d001 peak (Å)	Smectitic peak intensity. (counts)	Quartz peak at 3,33 Å intensity (counts)
24h in water	14,6	120	571
1h attack	14,6	100	441
6h attack	14,0	128	226
12h attack	14,2	97	259
18h attack	14,6	95	188
24h attack	14,9	90	205

The intensity of the smectitic d(001) peak tends to diminish with the time of attack as the acid have more time to destroy the octahedral sheet of the clay mineral. Diminish of the quartz peak intensity with the time of attack is an evidence of the purification of the sample by the mild acid attack procedures. It is verified that the clays submitted to mild acid attack during long time presents more clear colors than others.

Table 3 presents the oil absorption capacity of chocobofe, after different times of attack, using sweet almond oil. Surprisingly the 1 hour attacked sample presents a near 300% increase of oil sorption capacity over the no attacked sample. That shows the importance of the leaching impurities and the preservation of the clay mineral structure on the sorption capacity. The 6 h and the 12 h attacked sample showed a near 200% increase of oil sorption over the no attacked sample.

Table 3. oil absorption capacity

Sample	Oil sorption (g oil/100g sample)
24h in water	5,4
1h attack	20,5
6h attack	9,00
12h attack	10,2
18h attack	4,2
24h attack	7,8

4. CONCLUSIONS

The sample chocobofe bentonite subjected to mild acid attack demonstrated a good bleaching response from reaction times of 6 hours. The crystalline structure of the clay mineral presented no significantly modifications, otherwise was observed a good color reduction and quartz purification.

The best oil absorption capacity was identified in sample with 1hour of acid attack, with an impressive improvement over the no attacked sample. In accordance with the methodology presented and from the results obtained, the present purified clay can be an alternative to use in products of high value such as cosmetics and polymer/clay nanocomposites; showing an efficient option, more economical and less aggressive to the environment.

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