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BRAZILIAN BENTONITE SUBMITTED TO MILD ACID TREATMENT UNDER MODERATED CONDITIONS

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ABSTRACT

The present paper presents the study of light green smectite clay, from Paraiba, Brazil, submitted to mild acid attack under moderated conditions. Usually, clays are subjected to treatment with strong inorganic acids at temperatures near the boiling point and at high acid concentrations and then, widely used as bleaching agents. The treatment occurred under bellow boiling temperature and at short times of reaction (90°C, reaction times of 1, 6, 12, 18 and 24 hours in close reactor, concentration of the aqueous solution of hydrochloric acid 1.5 M, clay/acid solution ratio of 1g/10mL). The purpose of these attacks is 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 as cosmetics and polymer/clay nanocomposites. The raw clay and the attacked samples were characterized by X-ray diffraction (XRD), cation exchange capacity (CEC), stereomicroscopy, scanning electron microscopy (SEM) and energy dispersive X-ray detector (EDS).

1 INTRODUCTION

The industrial application of bentonites is vast, mostly used in oil industry as drilling fluids, in pharmaceutic and cosmetics as dissecant, in the food industry as oil bleaching, among others applications. For those aplications, bentonites needs to be clean of mineral impurities. Acid attack is a common method that provides a specific area increased by structure disorganization, mesopores and mineral impurities cleaning. Other benefit of acid attack is improving of acid sites with more porosity, excellent properties when apply in catalysis [1-6]. Several groups have studied the clays preparation using acid attack with high concentration aiming to obtain bleaching, producing a clear color clay, or similar, mostly used in bleaching process or oil, grease and organic, minerals and animals fat. The industrial use for clays is also based on exchangeable cations and clay minerals properties [7-9].

Geologic origin of clays determinates a classification as bentonites, however, there is a common agreement that if the smectite clays presents the same properties of traditional bentonites and/or is commercialized to the same use, those clays can be classified as bentonites, which have a high grade of colloidal material, absolving capacity and activation capacity [10-13].

Among the bentonites for industrial use there are bentonites with highly water absorvation and non-water absorvation. The sodium interlayer is responsible for the capacity of bentonites absorvation instead those not, have calcium as a preponderate cation [14,15].

The polycathionic bentonite from Paraiba, Brazil is smectite clay with non-preponderate interlayer cation with light color providing by low iron concentration [16].

The light green smectite within methodologies for the production of bleaching clays may be a good alternative to material raw. The economic advantages over imported clays used in processes to obtain products with high value as cosmetics and nanocomposites.

2 MATERIALS AND METHODS

Start Materials

The light green smectite clay, in its natural form, was from Paraíba´s State, Brazil was submitted to mild acid attack using a concentration of the aqueous solution of hydrochloric acid 1.5 M, clay/acid solution ratio of 1g/10mL, at 90°C under bellow boiling temperature and at short times of reaction 1, 6, 12, 18 and 24 hours in close reactor.

The attacked clay was washed, by filtration, with distilled water until pH 7-8, and then subjected to drying at 60°C for 24 hours.

After drying, the clay was grounded using a manual mortar and vibratory ball mill until completely pass through #200 mesh sieve.

Materials Characterization

The raw clay and the attacked samples were characterized by X-ray diffraction (XRD), cation exchange capacity (CEC), stereomicroscopy, energy dispersive X-ray detector (EDS) and scanning electron microscopy (SEM).

The XRD were performed on diffractometer model X'Pert Pro MPD (Panalytical) with Cu anodes; scan from 5° to 90° 2Θ; 40kV and 35mA.

The scanning electron microscopy (SEM) and energy dispersive X-ray detector (EDS) was performed on scanning electron microscopy, Philips - EDAX INSPECT 50 with energy dispersive x-ray detector (EDS).

To observe the clay was used a stereomicroscopy Zeiss, model Stemi 2000C.

CEC was performed using the ammonium acetate method.

3 RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction curves of light green smectite submitted only to H_2O for 24h at 90^{o}C, we observe that the $d_{(001)}$ characteristic smectitic peak at 15,05Å with intensity of 120 counts. As impurity the sample presents quartz with a peak at 3,3Å and an intensity of 255 counts.

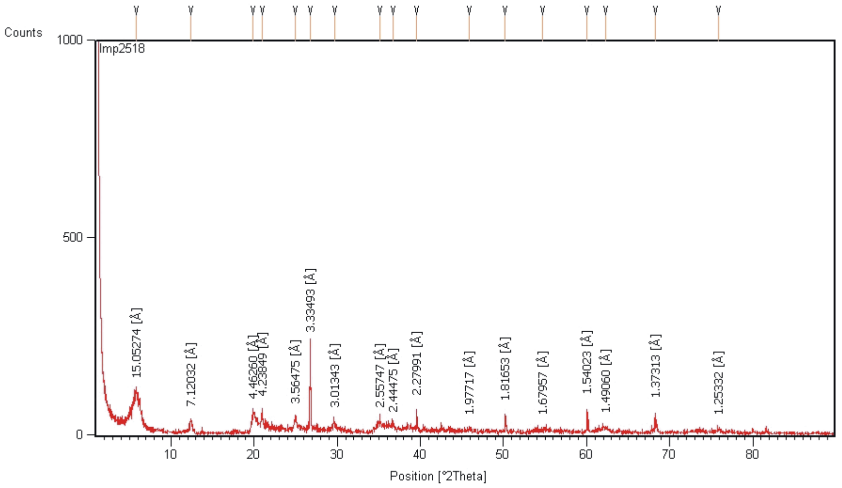

Figure 1. X-ray diffraction curve of Light green smectite, H_2O 24h at 90^{o}C.

Figure 2 shows the XRD curve of Light green smectite submitted to mild acid attack during 24h at 90°C. The $d_{(001)}$ smectitic peak is present at 15,62Å with an intensity of 100 counts. The quartz, with peak at 3,33Å presents intensity of 340 counts.

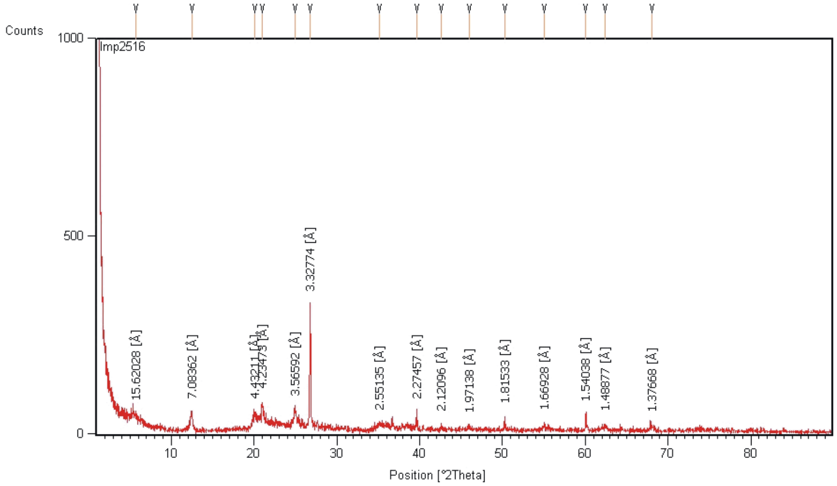

Figure 2 – X-ray diffraction curve of the Light green smectite, HCl 24h at 90°C.

Table I 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.

Table 1. $d_{(001)}$ smectitic peaks, smectitic peaks intensities, and intensities of the quartz peaks for the samples of Light green bentonite attacked for different times.

Sample	Smectitic peak $d_{(001)}$ (Å)	Smectitic peak intensity (counts)	Quartz peak at 3,33 Å intensity (counts)
24h in water	15,05	150	255
1h attack	14,53	100	290
6h attack	15,14	90	590
12h attack	15,38	80	250
18h attack	15,31	70	300
24h attack	15,62	100	340

The intensity of the smectitic $d_{(001)}$ peak tend to diminish its intensity with the time of attack as the acid have more time to destroy the octahedral sheet of the clay mineral. The increase of the quartz peak with the time of acid attack is a possible indicative of the dissolution of part of the clay minerals. It was verified that the clays submitted to mild acid attack during long times presented more bleaching than others.

The figures 3 and 4 presents the EDS results for samples treated with water for 24h and HCl for 24h at 90°C. Is possible to observe the peak reduction of metals, that indicates a good result of purification at sample treated with HCl for 24h.

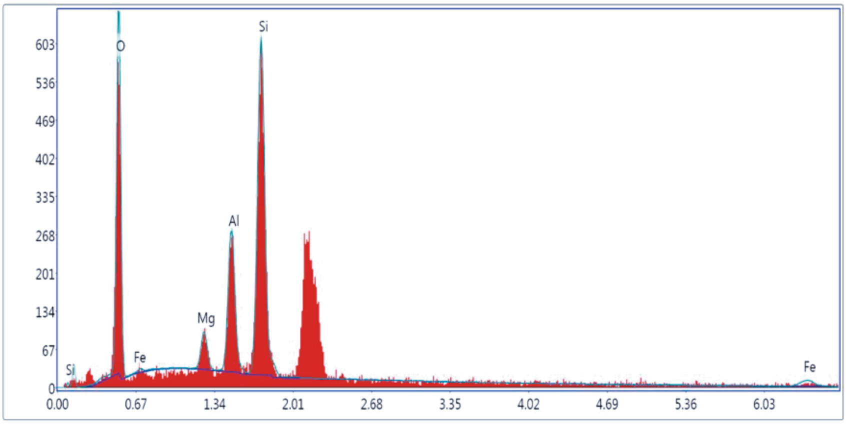

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Figure 3 – EDS results of light green smectite treated with H_2O for 24h

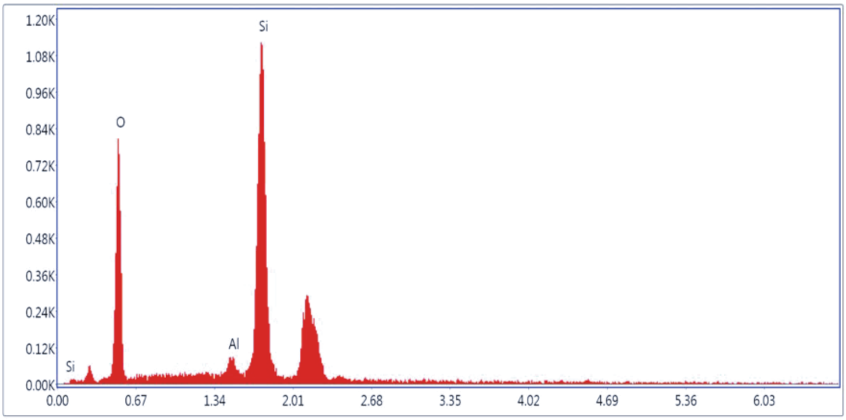

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Figure 4 – EDS results of light green smectite treated with HCl for 24h

Table 2 presents the CEC values, that tends to diminish after treatment, with the time of attack with the 24 hours attacked sample having only 70% of the original value.

Table 2 - CEC results of light green smectite treated.

Sample	CEC (meq/100g)	% of the no attacked sample
24h in water	41,30	100
1h attack	38,29	92,72
6h attack	37,63	91,11
12h attack	33,27	80,55
18h attack	31,33	75,86
24h attack	28,99	70,20

At the stereomicroscopy image 1 is possible observe the impurity particles into the sample treated with water for 24h.

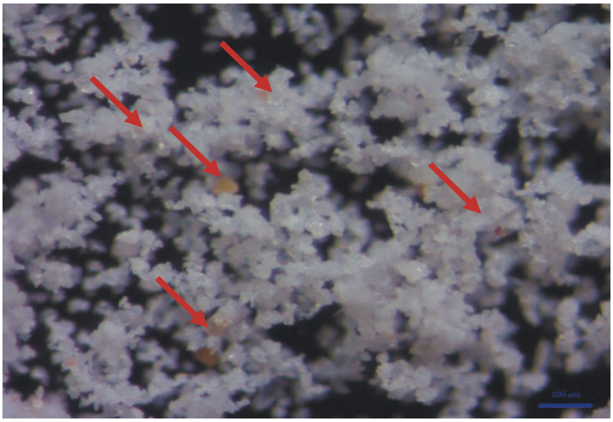

Image 1 - Micrographic of light green smectite treated with H_2O for 24h

At the stereomicroscopy image 2 the sample, treated with HCl for 6h, is clean of impurity particles.

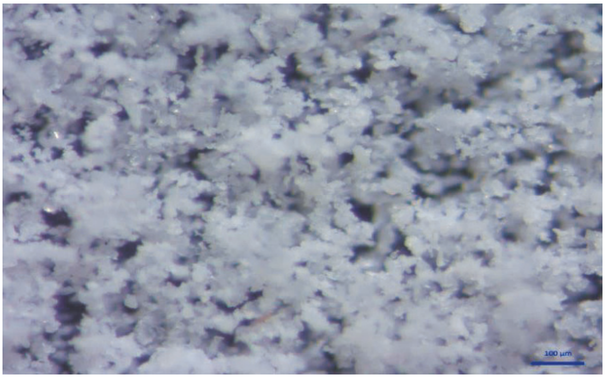

Image 2 - Micrographic of light green smectite treated with HCl for 6 h

The images of SEM micrographic are the sample treated with water and with HCl, both for 24h at 90°C.

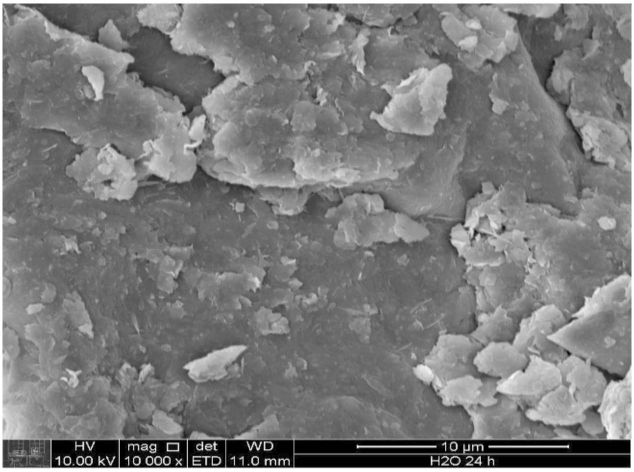

Image 3 – SEM micrographic of light green smectite treated with H_2O for 24h

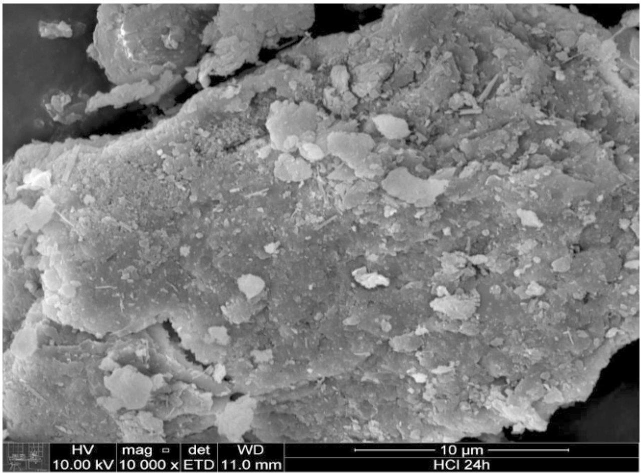

Image 4 – SEM micrographic of light green smectite treated with HCl for 24h

The lamellar structure of the samples is agglomerated in layers, mostly in same size. This is a possible indicator of the no complete destruction of crystal structures of smectite.

4 CONCLUSIONS

The light green smectite sample submitted to mild attack acid demonstrated a good response to the bleaching and purification at reaction time of 6 hours with a good preservation of crystalline structure and a significant bleaching and quartz purification.

The most evident modifications in decolorizing and CEC occurred in the first 12 hours of acid treatment.

In accordance with the methodology presented and from the results acquired, decrease the concentration of impurities that provides color, with no great change in the clay minerals structure, aiming at use in products of high value such as cosmetics and polymer/clay nanocomposites revealed an economical and environment efficient alternative.

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