Technological Evaluation of Cubati/Brazil Montmorillonite

Avaliação Tecnológica da Montmorillonita de Cubati/Brasil

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ABSTRACT
The aim of this work was the technological characterization of sample fraction from Cubati region, Pedra Lavrada – Paraíba State, Brazil, in order to evaluate its further applications as drug adsorber and as oil drilling fluid. The sample had been properly processed and characterized by X-ray diffractometry, X-ray fluorescence spectroscopy,

cation exchange capacity, thermo-differential and thermogravimetric analysis, determination of textural properties by BET and B.J.H. methods, Fourier transform infrared spectroscopy and surface charge measurements by means of Zeta potential. The results obtained showed that the studied sample is essentially composed by montmorillonite (smectite), kaolinite, quartz and dolomite, with high contents of silica (37.4%), alumina (17.2%), calcium oxide (5.7%) and iron oxide (7.5%). The CEC value obtained (41.0 meq 100 g^{-1}), is due to the presence of kaolinite, which was confirmed by XRD, DTA-TG/DTG and FTIR results. BET and B.J.H. models showed that it is a mesoporous clay mineral, with a surface area of 84.81 m^2 g^{-1}. The surface charge measurement by Zeta Potential showed that this clay mineral is negatively charged in almost all of pH range studied. Thus, it has high adsorptive potential of drugs cationic species, while activation with sodium carbonate associated with organophilization process allow its application as oil drilling fluid.

Keywords: Montmorillonite, Cubati, Characterization, Properties.

RESUMO
O intuito deste trabalho consistiu na caracterização tecnológica de uma amostra de montmorillonita da região de Cubati, Pedra Lavrada – Paraíba, Brasil, de forma a avaliar suas futuras aplicações como adsorvedor de fármacos e como fluido de perfuração de petróleo. A amostra fora devidamente beneficiada e caracterizada por difratometria de raios X, espectroscopia de fluorescência de raios X, capacidade de troca catiônica, análise termodiferencial e termogravimétrica, determinação das propriedades texturais por meio dos métodos BET e B.J.H., espectroscopia de infravermelho por transformada de Fourier e medidas de carga superficial por meio do potencial Zeta. Os resultados obtidos mostraram que a amostra estudada é composta essencialmente por montmorillonita (esmectita), caulinita, quartzo e dolomita, com teores de sílica (37,4%), de alumina (17,2%), de óxido de cálcio (5,7%) e de óxido de ferro (7,5%). O baixo valor de CTC encontrado (41,0 meq/100g), deve-se à presença de caulinita, confirmada pelos resultados de DRX, DTA-TG/DTG e FTIR. A determinação das propriedades texturais indicou que o argilomineral é mesoporoso, com uma superfície de 84,81 m^2 g^{-1}. Além disso, a amostra apresentou carga superficial negativa em praticamente toda a faixa de pH estudada. Assim, possui elevado potencial adsortivo de espécies catiônicas presentes nos fármacos, enquanto a ativação com carbonato de cálcio associada ao processo de organofilização, permitem a sua aplicação como fluido de perfuração de petróleo.

Palavras-chave : Montmorillonita, Cubati, Caracterização, Propriedades.

1 INTRODUCTION

Clay minerals are defined as hydrated aluminum silicates with fine granulometry (less than or equal to 45 µm) that occur due to rocks hydrothermal alteration, and may present magnesium, calcium and iron cations substituted in its crystalline structure, being the main constituents of clayey rocks, providing them some specific mineralogical and chemical characteristics [1]. They are classified as phyllosilicates with crystalline

structure in the form of lamellae or fibers, which provides several properties and application possibilities.

The different clay minerals are classified based on similarities in chemical composition and crystalline structure, which can be divided into groups such as 1:1 type layer (kaolinite), 1:1 type tube (halloysite), 2:1 type layer (montmorillonite, smectite, vermiculite), the regular mixed layer type (chlorite group) and 2:1 type layer-chain type (attapulgite, sepiolite) [2].

Within the group of clay minerals, there is the smectite class, which includes clay materials, such as, montmorillonite, nontronite, beidellite, saponite, hectorite and sauconite. Smectites have been the most used, both in academic research and in industrial applications due to their cation exchange capabilities and surface acidity [1]. Smectite clays are found mixed or associated with other materials such as illite, kaolinite and chlorite, quartz, feldspar, carbonates, and oxides; in addition to organic matter and other impurities [3], which can interfere in its properties.

Montmorillonite, for example, stands out the most abundant hydrated aluminum silicate type 2:1 of the rock called bentonite, a term designated to a product with a high content of smectite [4]. This clay has a general chemical formula equal to $M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$, with "M" indicating exchangeable monovalent ions and "x" is the degree of isomorphic substitution. It has particle diameter sizes that can vary from 2 µm to very small sizes such as 0.1 µm, with an average size of 0.5 µm and format of plates or blades [5]. Other properties that enhance the use and application of this clay mineral consist of its high cation exchange capacity, which varies from 60 to 150 meq 100 g^{-1} [1] and its specific surface area ranging from 75 to 150 m^2 g^{-1}.

The mean interest in these compounds is due to the possibility of modifying the interlamellar region in order to accommodate species of different natures, providing new properties to the system based on the guest-host interaction that is established between the parts [6], allowing more noble applications to this type of material. For this reason, the scientific community has dedicated itself to the study its adsorptive potential, as well as the benefits that organophilization brings to these materials when it comes to its use as oil drilling fluid.

The adsorption of potentially toxic metals [7–10], herbicides [11–15] and dyes [16–18] has often been found in literature, since clay minerals consist of a low cost and high availability raw material, especially if compared to the usual adsorbent. Currently, some studies have focused on the adsorption of drugs present in water sources [19–29],

due to the harmful effects on flora, fauna and, consequently, on population. Thereby, it is necessary to use methods that are capable of removing these pollutants, where the adsorptive process using clay minerals has been pointed out as a viable solution [30,31].

When it comes to the use of clay minerals as oil and gas drilling fluid, bentonite is widely used because of its swelling characteristic in water. This characteristic favors the formation of stable suspensions, that are capable to maintain the cuttings from the drilling of the well in suspension and prevent the sedimentation of these particles during and after operation. This ability to keep particles suspended is directly related to the rheological properties of the fluid, such as: viscosity, thixotropy and yield stress [32]. To use bentonite as a viscosifying agent in oil-based drilling fluids, it is necessary to carry out a process of organophilizing the surface of the bentonite to facilitate the dispersion of these in organic solvents [33]. The organophilization process is carried out by the ion exchange of the cationic clays interlamellar cations for organic cations contained in quartenary ammonia surfactants. Thus, the surface of the individual clays of the clays becomes hydrophobic. Another way to hydrophobize the surface of the lamellae is to use ethoxylated non-ionic surfactants that interact electrostatically with interlamellar cations [34]. Several studies have focused on the use of bentonite as oil drilling fluid and the results obtained confirm its effectiveness for this purpose [32-36].

According to the authors [37], about 62% of Brazilian bentonite reserves are located at municipality of Boa Vista, Paraíba state. Thus, the clays of this region were intensely studied and explored, causing its depletion of reserves in this region. To solve this issue, several studies are turning to the study of clay minerals from other regions of Paraíba, which present impurities, however with a simple ore dressing proposal, such as grinding, granulometric classification and magnetic separation, could become industrially attractive. Smectites from Cubati region are generally used for pottery, a regional application that allow the trade and regional livelihood. Thus, the study and ore dressing of these clay minerals enable greater knowledge about its properties, allowing more noble application of them, adding value to these raw materials that are devalued in market.

In this context, the aim of this research was the ore dressing and technological characterization of a sample from Cubati region, Pedra Lavrada - Paraíba, Brazil, in order to obtain a better understanding of its properties, aiming its further application as drug adsorber and oil drilling fluid.

2 MATERIALS AND METHODS

Sample preparation: Brazilian montmorillonite sample from Fazenda Campos Novos, Cubati region, previously crushed and ground was submitted to wet granulometric classification in a 20 µm opening sieve. Then, the sample below 20 µm was forwarded to wet magnetic separation in BOXMAG RAPID equipment with a high intensity field (15 kGauss) and ferromagnetic matrix. The sample below 20 µm non-magnetic, the sample of interest, was filtered through a filter press at a pressure of 5 bar and subjected to oven drying at 60 °C. After drying, it was comminuted in a disc mill.

For the confirmation of the smectitic clay in the sample, it was necessary to carry out the classification by suspension in 2 µm to separate the clay fraction (<2 µm), according to the methodology used by [38]. For this, before carrying out the suspension, it is necessary to decarbonate the sample using the methodology described by [39]. For that, between 8.0 and 12.0 g of the clay of interest were added in 1.0 L kitassate containing 350 mL of a buffer solution of sodium acetate (Sigma Aldrich®, ≥ 99.0 % purity) and acetic acid (Sigma Aldrich®, ≥ 99.0 % purity) both 2.0 mol L^{-1}. After the addition, the sample was placed on a thermal stirrer at a temperature of approximately 150 °C with constant stirring for 1 hour. Then, the sample was filtered through a vacuum funnel and washed with distilled water to avoid precipitation of other compounds, followed by oven drying at 60 ° C.

The sample dried after decarbonation was treated with the methodology according to [40], in which 100 mL beaker containing an equal volume of distilled water and 5.0 g of the sample was used. For the dispersion of the material, the suspension was submitted to an ultrasound bath with a tip was used in the conditions of 50 of amplitude for 1 minute. The procedure was performed according to Stokes' law with an equation as a function of time. The clay fraction (<2 µm), due to its smaller particle size, will tend to remain in suspension, while the non-clay fraction (> 2 µm) settles in the beaker due to its larger particular size. Obeying the adaptation to the method, in the 100 mL beaker, after placing the suspension, the surface 80 mL of the 100 mL beaker was collected after 19 hours, in order to guarantee the removal of the clay fraction.

Clay mineral characterization: ore dressed montmorillonite was characterized by X-ray diffractometry (XRD), X-ray fluorescence spectroscopy (XRF), cation exchange capacity (CEC), differential thermal and thermogravimetric analysis (DTA-TG/DTG), determination of textural properties using BET and B.J.H. models, Fourier transform infrared spectroscopy (FTIR) and surface charge measurements by Zeta Potential.

X-ray Diffractometry (XRD): X-ray diffractogram was obtained using the powder method, in Bruker D4 Endeavor diffractometer with CoKα radiation (λ = 1.78897 Å) at Technological Characterization Sector laboratory of CETEM, operated with 40 kV and 40 mA, goniometer speed of 0.01 (2θ) per step with counting time of 1 second. The analysis range was 4 to 80 (2θ), with a LynxEye position sensitive detector. Qualitative spectrum interpretations were performed by comparison with standards contained in the PDF4 + database with Bruker Diffrac EVA software. For the characterization of the clay fraction (< 2 µm), oriented slides naturally dried (at room temperature), treated with ethylene glycol (Sigma Aldrich®, ≥ 99.8 % purity) for 16 hours and calcined in muffle at 550 ºC for 2 hours were produced [38]. The diffractograms were obtained using a Bruker D4 Endeavor diffractometer with CoKα radiation (λ = 1.78897 Å) under 40 kV and 25 mA conditions, goniometer speed of 0.01 (2θ) per step with a counting time of 0.5 seconds. The analysis interval was 1 to 40 (2θ), with a LynxEye position sensitive detector. Subsequently, the interplanar distance was converted to d (Å).

X-ray fluorescence spectroscopy (XRF): The analysis was carried out in an X-ray fluorescence spectrometer (WDS-1), AXIOS MAX (Panalytical) model from X-ray Fluorescence Spectrometry Laboratory of CETEM. The sample was properly milled in a disc mill until it reached a particle size below 100 µm. Three procedures were performed on each sample: determination of loss by calcination; pressing and analysis on the X-ray fluorescence spectrometer.

Fourier transform infrared spectroscopy (FTIR): The analysis by vibrational spectroscopy in the infrared region was performed in a spectrophotometer with Fourier transform, Nicolet 6700 FT-IR, with records from 4,000 to 400 cm^{-1} (medium infrared), resolution of 4 cm^{-1}, in KBr tablets, at the Laboratory of Instruments and Research of the Institute of Chemistry at UFRJ (IQ-UFRJ).

Cation Exchange Capacity (CEC): The CEC of the sample was determined using the methylene blue titration method, according to ASTM C837-09 [41].

Differential thermal and thermogravimetric analysis (DTA-TG/DTG): The sample was analyzed in the TA INSTRUMENTS Q600 Series equipment, model DSC/TGA Standard of the Laboratory of Thermal Analysis of the School of Chemistry (EQ/UFRJ). The curves of the thermogravimetric analyzes were obtained under the following operating conditions: temperature range ranging from 25 to 1,000 °C, heating rate of 10 ºC.min^{-1}, alumina sample port, in an inert atmosphere (nitrogen) and in an

atmosphere non-inert (air), both with a flow rate of 100 mL.min^{-1}. The results were analyzed using the TA Instrument Universal Analysis 2000 software.

Determination of textural properties (BET/B.J.H.): This determination was carried out at Technological Characterization Sector laboratory of CETEM by means of nitrogen physisorption (N_2) at -196 ºC (77 K). The analysis was performed on TriStar II Plus equipment (Micrometrics®), using approximately 900 mg of sample. The pre-treatment of the sample consisted of drying at 120ºC under a vacuum of 1×10^{-6} mmHg for 24 hours to eliminate physical water. Then, the analysis itself was carried out, a step in which the adsorption and desorption isotherms were obtained by varying the partial pressure of N_2. With the isotherms in place, the specific areas were calculated using B.E.T. (Brunauer-Emmett-Teller) model and the pore size and volume distribution was obtained from the N_2 desorption isotherm by B.J.H. (Barret-Joyner-Halenda) model.

Surface charge measurements (Zeta potential): Determination of the surface charge by means of Zeta potential was performed at Laboratory of Surface and Nanometric Analysis of CETEM on the Zetasizer Nano ZS equipment. Approximately 0.05 g of the sample was weighed and 10 mL of the KCl 10^{-3} mol L^{-1} was added. pH adjustment was done manually using HCl 1.0 mol L^{-1}, in order to obtain pH equivalent to 1.5. For the automatic pH adjustment in the equipment, solutions of KOH and HCl 0.1 and 0.5 mol L^{-1} were used, in order to promote a run initially acid towards the alkaline (pH 1.5 to 12).

3 RESULTS AND DISCUSSION

The sample from Cubati region was characterized by XRD and according to the results presented in Fig. 1, it is mainly composed by smectite (15.50, 9.89, 4.45 and 4.06 Å), kaolinite (7.13, 3.57, 2.49, 2.34 and 1.66 Å), quartz (4.25 and 3.33 Å) and dolomite (more intense peaks at 2.89, 2.19 and 2.06 Å), also presenting characteristic peaks of spinel (2.54 and 1.48 Å) and orthoclase (3.24 and 3.51 Å).

In order to determine which smectitic clay mineral is predominantly present in the sample, X-ray diffractometry with oriented blade of the natural, glycolated and calcined sample was performed. According to [42], depending on the clay and the type of treatment applied, the main peak (001) of it undergoes changes in terms of expansion or collapse, which allow its determination. For montmorillonite clay, for example, when it is glycolated, its peak expands to approximately 17 Å, due to the fact that ethylene glycol

is concentrated between the smectite lamellae, causing its expansion. When calcined, it collapses to 10 Å, and the characteristic kaolinite peak disappears.

Thus, the presence of montmorillonite was confirmed by the use of ethylene glycol, with the expansion of the interplanar basal distance from approximately 15 Å to 17 Å, and by calcination with its breakdown to 10 Å, as shown in Fig. 2. Besides that, there is the presence of illite in both natural and glycolated samples. Similar results were found by [37,43,44,45,46], in which the main minerals found in bentonite clays from the same region were montmorillonite and kaolinite.
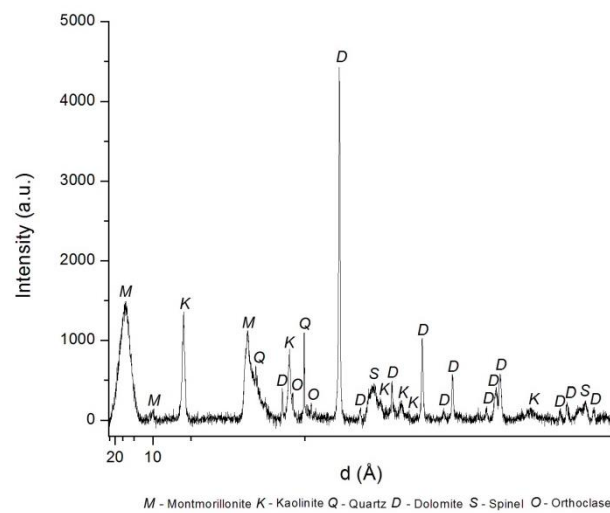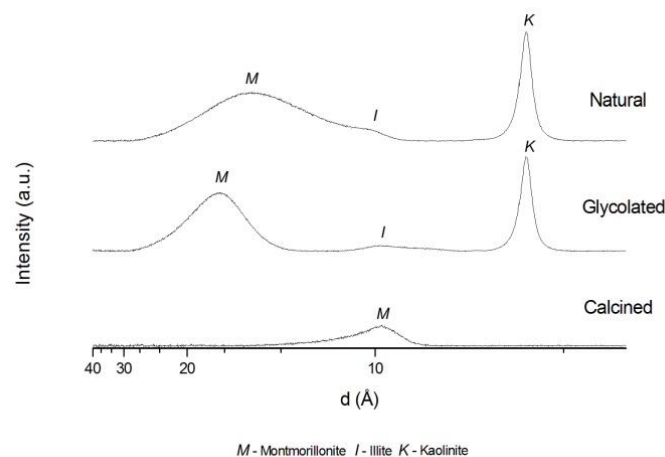
Figure 1 - X-ray diffractogram, Co Kα, of Cubati's sample.

M - Montmorillonite K - Kaolinite Q - Quartz D - Dolomite S - Spinel O - Orthoclase

Figure 2 - X-ray diffractogram, Co Kα, of Natural, Glycolated and Calcined samples.

M - Montmorillonite I - Illite K - Kaolinite

X-ray fluorescence (XRF) is a complementary technique to XRD and allows to obtain the chemical composition in percentage of oxides of the studied sample. Thus, XRF of the sample fraction is presented in Table I. The sample has a chemical

composition rich in silica (SiO_2) and alumina (Al_2O_3), as well as significant levels of magnesium, typical of this clay minerals. In addition, it is identified polycationic, by the presence of calcium, potassium and sodium oxides, as also the presence of iron oxide (Fe_2O_3). This high iron content is probably due to its presence in clay mineral structure. The other cations present may be associated with the isomorphic substitutions inherent to the clay mineral.

The evaluation of these results is important for the understanding of the sample, since, depending on its application, and modifications must be made. Due to its polycationic feature, with regard to the application as a drilling fluid, it is necessary to promote its activation with sodium carbonate, since sodium montmorillonite presents a greater volume expansion when in contact with water, producing gel aspect [47], increasing the clay mineral interplanar distance in order to allow greater efficiency of its use.

Table I - Chemical Composition of Cubati's sample.

Oxide	(%w/w)
SiO_2	37.4
Al_2O_3	17.2
MgO	6.1
CaO	5.7
K_2O	0.93
Na_2O	0.16
MnO	0.37
TiO_2	0.54
Fe_2O_3	7.5
LOI*	23.8
Total	99.70

LOI – Loss on ignition

Compared to the literature [37,43,44,45,46], silica and alumina percentages of the studied sample were lower, while magnesium, calcium and iron oxides content were higher. This fact can be associated to the increase in isomorphic substitutions at studied sample octahedral sites due to the presence of iron in kaolinite structure, while higher contents of magnesium and calcium are explained to the presence of carbonates.

Another characterization technique is the Fourier transform infrared spectroscopy (FTIR), that aims to identify the functional groups of the sample surface, being, therefore, a complementary characterization to XRD and XRF. The infrared spectrum of Cubati's sample is shown in Fig. 3. In the infrared spectrum, bands of 3697, 3621 and 3428 cm^{-1} are observed, which can be attributed to the vibrational stretching of the hydroxyl

structural group (O-H) proper to the clay [2,37,48]. The absorption band at 1637 cm^{-1} refer to the stretching of the hydroxyl groups that are related to the adsorbed water and the hydration water present in the clay [37]. The bands at 913 and 793 cm^{-1} are characteristic of montmorillonite, with regard to the octahedral layers present in the aluminosilicate [37,48]. 1034 cm^{-1} band refers to the Si-O group vibration, and the 538 and 469 cm^{-1} bands are attributed to the Al-O-Si and Si-O-Si bendings, which are characteristic of montmorillonite [37,48]. According to [49], the absorption between 400 and 1200 cm^{-1} refers to the Si-O vibrations of the kaolinite and the reflections close to 900 cm^{-1} correspond to the deformation vibration of the connections Al-OH-Fe, indicative of Al substitution by Fe, in the crystalline structure of kaolinite. Table II summarizes the characteristic bands of sample fraction. Thus, the results obtained by FTIR are in agreement with the results obtained by XRD and XRF, indicating that the sample of interest is constituted predominantly by the smectitic clay montmorillonite, associated with kaolinite.

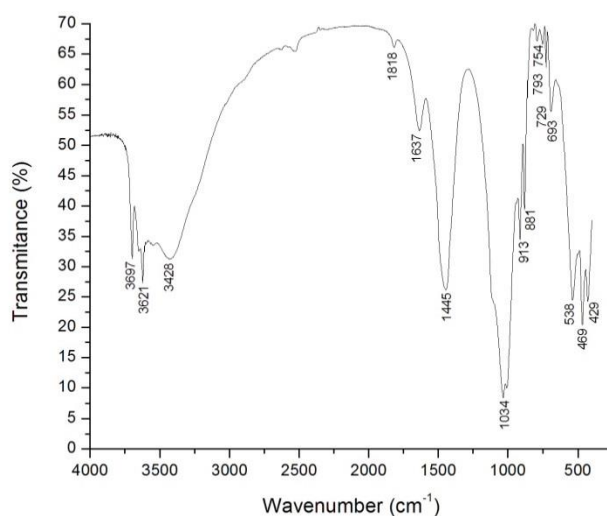Figure 3 - Infrared spectrum of Cubati's sample.

Table II – Main absorption bands of the studied clay mineral.

Wavenumber (cm^{-1})	Attribution
3697	O-H stretching
3621	O-H stretching
3428	O-H stretching
1637	O-H stretching
1034	Si-O stretching
538	Al-O-Si bending
469	Si-O-Si bending

Cationic Exchange Capacity (CEC) determination aims to evaluate the capacity of a material to adsorb and fully exchange cations present in its structure, thus evaluating its saturation point. CEC of the studied sample was determined by calculating the methylene blue index (MBI), which considers the volume (V) spent in titration as presented in Equation 1.

$$\text{MBI} = \frac{0{,}01 \text{ x V}}{2} \text{ X } 100$$

(1)

The volume spent in this test was 82.0 mL. Thus, the CEC of the studied sample was 41.0 meq 100 g^{-1}. However, this value of CEC obtained does not fit the CEC found in literature, which is from 60 to 150 meq 100 g^{-1} of sample [1]. This fact can be explained due to the presence of other associated minerals (see results of XRD and XRF), such as kaolinite, which presents CEC between 3 to 15 meq 100 g^{-1} [50]. Similar result was found by [37], in which bentonite clay from the same region presented CEC value of 41.67 meq 100 g^{-1}. Although CEC value found is below compared to the literature, several studies using clay minerals with similar characteristics showed high adsorptive potential with even lower CEC values [3,9,51].

Thermogravimetric and Differential Thermal analyses aim to monitor the changes in mass and energy variations that a substance presents when subjected to a temperature variation over time. Thus, they allow a greater knowledge about the chemical and physical processes that occur with the samples when subjected to such variations. Fig. 4 presents the thermogravimetric and thermo-differential curves of the sample fraction in both inert (N$_2$) and non-inert (air) atmosphere. Through the results of TG/DTG curves and according to literature [52,53], it is possible to observe three mass losses: the first referring to the loss of hydrated or adsorbed water and the water associated with exchangeable cations up to approximately 225ºC; the second attributed to the dehydroxylation of kaolinite (Al$_2$O$_3$.2SiO$_2$.2H$_2$O) going to metakaolinite (Al$_2$O$_3$.2SiO$_2$) in the range of 225 to 550ºC and the third characteristic of sample decarbonation between the temperature of 550 to approximately 800ºC.

It is noteworthy that, by analyzing the thermodifferential curve (Figure 4), for both atmospheres studied, all processes were endothermic (Exo up), indicating that there is no organic matter in the sample of interest, since its presence would present an exothermic

peak in DTA curve (W/g) when analyzed in air. A summary of obtained data is illustrated in Table III.

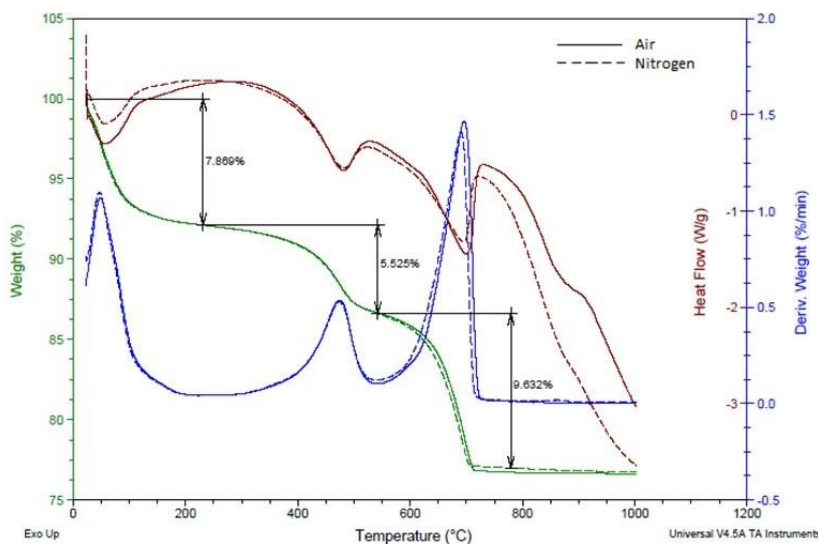Figure 4 - TG/DTG and DTA curves for sample fraction.


Table III – Summary of thermal events occured.

Events	Process	Mass loss (%)	Event Type
1°	Loss of hydration water and exchangeable cations	7.800	Endothermic
2°	Dehydroxylation of kaolinite	5.525	Endothermic
3°	Decarbonation	9.632	Endothermic

According to [52,53], in the range of 400 to 750 °C there is dehydroxylation of both kaolinite and montmorillonite, with kaolinite from 400 to 650 °C and montmorillonite from 405 to 685 °C, with variations dependent on the presence of associated minerals. The second loss of mass, according to the result obtained, occurs in the range of 225 to 550 °C, below those provided by the references.
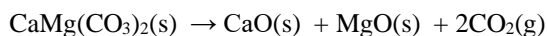
The temperature depends on the ions that are part of the octahedral layer of the mineral clay, due to the isomorphic substitutions of Al^{3+}. The increase in isomorphic substitutions causes a reduction in the dehydroxylation temperature, whose behavior is influenced by the presence of Fe^{3+} ions in the structure of the mineral clay, corroborating with the results obtained by XRD and XRF [53]. In addition, the authors observed that samples containing kaolinite also had a lower dehydroxylation temperature, attributing this reduction to the presence of silica related to this mineral.

Besides that, knowing the mass losses and the molar masses of the substances, it is possible to calculate the mass percentage of kaolinite and dolomite in the studied sample, as presented below.

Dehydroxylation of kaolinite

$$Al_2O_3.2SiO_2.2H_2O(s) \rightarrow Al_2O_3.2SiO_2(s) + 2H_2O(g)$$
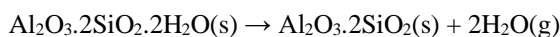
Decarbonation of Dolomite

$$CaMg(CO_3)_2(s) \rightarrow CaO(s) + MgO(s) + 2CO_2(g)$$

Thus, by stoichiometric calculation and taking into account the molar ratio (1:2 in both cases), there is 40.82% of kaolinite (which may be underestimated by the loss, in the same temperature range, related to the dehydroxylation of montmorillonite) and 20.14% of dolomite. These results are in agreement with those obtained by XRD and XRF.

The determination of textural properties aims to obtain the value of surface area (by BET model) and volume and average pore size (by B.J.H. model), properties that influence and help in understanding the adsorptive process of porous materials, such as clay minerals. The results obtained for the determination of textural properties are shown in Table IV.

Table IV – Determination of textural properties of Cubati's sample.

| Surface area $(m^2\ g^{-1})$	Average pore size (Å)	Average pore volume $(cm^3\ g^{-1})$
84.81	68.46	0.10

Thus, from the results obtained, it is observed that the sample has a surface area equal to 84.81 $m^2\ g^{-1}$, average pore size of 68.46 Å and average pore volume of 0.10 $cm^3\ g^{-1}$. The average pore size of 68.46 Å indicates that this clay mineral is mesoporous, since it is in the range between 20 to 500 Å (or 2 to 50 nm), which classifies the materials as mesoporous [1]. The value obtained from surface area is within the parameters found in the literature (from 75 to 150 $m^2\ g^{-1}$) and the values of average pore size and volume depend on the beneficiation process of the treatment performed.

The authors [54], for example, investigated and compared the effect of montmorillonite content in a natural Arabian clay with a bentonite, and the results showed that the natural clay presented 20.83 $m^2\ g^{-1}$ of surface area against 44.28 $m^2\ g^{-1}$ of bentonite surface area. Others authors [55] studied the modification of commercial montmorillonites with lanthanum (III) and iron (III), obtaining values of average pore size and pore volume in the range of 59.0 to 74 Å and 0.09 to 0.16 $cm^3\ g^{-1}$, respectively. Also [56], used a commercial montmorillonite as a study sample, with an average pore size of 65.74 Å and a total pore volume of 0.27 cm^3/g. These authors [57] evaluated the

benefits of a commercial montmorillonite pillarization with titanium oxide in pharmaceuticals adsorption and the values obtained for montmorillonite before and after modification were 65 and 216 m^2 g^{-1} of surface area and 0.001 and 0.08 cm^3 g^{-1} of micropore volume, respectively. All the studies above presented satisfactory results regarding the adsorption of their respective contaminants. Thus, the results obtained for the sample fraction from this study, which is a real sample and containing associated minerals, show its adsorptive potential.

The characteristic surface charge of sample fraction was evaluated using Zeta potential curve (mV) as a function of solution pH, illustrated in Fig. 5. For this purpose, the measurements were carried out in a pH range of approximately 1.50 to 12. Thus, the sample has a negative charge in practically the entire pH range, presenting an isoelectric point between pH 11 and 12. This negative charge can be attributed to the isomorphic substitutions that can occur in its crystalline structure, promoting a charge deficiency, justifying its negativity in practically the entire pH range studied. It is worth mentioning that no study was found on surface charge measurements by means of zeta potential for bentonites or montmorillonites from Cubati region. The negative surface charge is in agreement with studied by [58,59], in which bentonites presented high negative charge, although montmorillonite sample studied is less negative. According to [59] the presence of Ca^{2+} reduce the magnitude of Zeta potential negative charge, which is in agreement with XRD and XRF results, which presented significant amounts of dolomite and calcium oxide. Besides that, the presence of kaolinite confirmed by the other characterization techniques, may be influencing in its surface charge measurement, since it does not have a very negative charge like bentonite. Nevertheless, the negative surface charge makes this sample conducive to adsorption of cations.

Figure 5 - Surface charge measurements (Zeta Potential) of sample fraction.
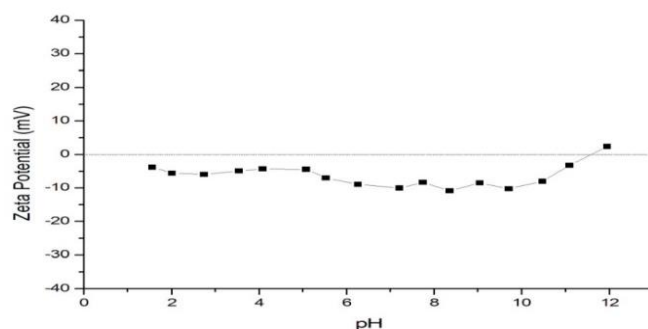
4 CONCLUSIONS

From the results obtained by the characterization of the sample fraction from Cubati region, Pedra Lavrada - Paraíba, it is possible to conclude that it is essentially composed by montmorillonite (smectite), kaolinite, quartz and dolomite, with high contents of silica (37.4%), alumina (17.2%), calcium oxide (5.7%) and iron oxide (7.5%). The low CEC value obtained (41.0 meq 100 g^{-1}), is due to the presence of kaolinite, which was confirmed by XRD, DTA-TG/DTG and FTIR results. BET e B.J.H. models showed that it is a mesoporous clay mineral, with a surface area of 84.81 m^2 g^{-1}. The surface charge measurement by Zeta Potential showed that this clay mineral is negatively charged in practically the entire pH range studied. Thus, its high surface area associated with its mesoporosity and negative charge indicates that this sample has high adsorptive potential to drugs cationic species and due to its polyatomic feature, activation with sodium carbonate and organophilization are necessary for application as oil drilling fluid. It is believed that this study will collaborate with a productive arrangement in the region, since these characterizations evidenced nobel applications of this material, which contributes to local economical and scientific knowledge development.

CREDIT AUTHORSHIP CONTRIBUTION STATEMENT

B.L. Novo: Writing - Original Draft, Writing – Reviewing and Editing, Investigation, Formal analysis, Conceptualization, Visualization. F.A.G. Brasileiro: Writing – Reviewing, Investigation, Formal analysis, Conceptualization. C.N. Barbato: Supervision, Writing – Reviewing and Editing, Resources, Formal analysis, Conceptualization. Fernanda A. N G. Silva: Supervision, Writing – Reviewing and Editing, Resources, Formal analysis, Conceptualization. Luiz C. Bertolino: Supervision, Writing – Reviewing and Editing, Resources, Formal analysis, Conceptualization. L. Yokoyama: Supervision, Writing – Reviewing and Editing, Resources, Formal analysis, Conceptualization.

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