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PALYGORSKITE FROM PIAUÍ, BRAZIL: TECHNOLOGICAL INVESTIGATION OF A NEW MINERAL OCCURRENCE WITH INDUSTRIAL AND ENVIRONMENTAL APPLICATIONS

PALYGORSKITA DO PIAUÍ, BRASIL: INVESTIGAÇÃO TECNOLÓGICA DE UMA NOVA OCORRÊNCIA MINERAL PARA APLICAÇÕES INDUSTRIAIS E AMBIENTAIS

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RESUMO - A pesquisa relaciona-se a uma investigação tecnológica de uma amostra *run-of-mine* de palygorskita proveniente de uma nova ocorrência em Guadalupe, estado do Piauí, Brasil e consistiu em beneficiamento e classificação granulométrica a úmido em 45 e 20 µm, com posterior separação magnética da alíquota com tamanho de partícula inferior a 20 µm. As frações obtidas foram caracterizadas por difratometria de raios X, espectrometria de raios X, microscopia eletrônica de varredura, determinação da capacidade de troca catiônica (CTC), medição de carga superficial (potencial Zeta) e análise das propriedades texturais do argilomineral através da fisissorção de N_2 usando a determinação de área superficial BET. De acordo com os resultados a amostra consiste em palygorskita, caulinita, goethita e quartzo, apresenta 41 meq $100g^{-1}$ de CTC, carga superficial negativa em uma faixa de pH de 2,2 a 14, área superficial específica de $142{,}08 m^2g^{-1}$ e tamanho médio do diâmetro dos poros em 52,77 Å. A nova ocorrência de palygorskita possui características para aplicações adsorventes, como adsorventes.
Palavras-chave: Argilomineral. Investigação tecnológica. Aplicações industriais.

ABSTRACT - This research reports the technological investigation of a run-of-mine sample of palygorskite from a new occurrence in the Guadalupe, state of Piauí, Brazil and consisted of ore dressing of the sample and wet size classification in 45 and 20 µm, with subsequent wet magnetic selection of the aliquot with particle size smaller than twenty µm. The fractions obtained were characterized by X-ray diffraction, X-ray spectrometry, scanning electron microscopy, cation exchange capacity (CEC), surface charge measurement (zeta potential) and analysis of the textural properties of the clay mineral through N_2 nitrogen physisorption using BET surface area determination. According to results this sample consisted of palygorskite, kaolinite, goethite, and quartz, had 41 meq 100 g^{-1} of CEC, negative surface charge for a pH range of 2.2 to 14, specific area of 142.08 m^2g^{-1} and average pore diameter size of 52.77 Å. The new occurrence of palygorskite has characteristics for adsorbents and industrial applications.
Keywords: Clay mineral. Technological investigation. Industrial applications.

INTRODUCTION

Clay minerals are commonly used for environmental remediation purposes because they are inexpensive, easy to mine and nontoxic (Murray, 2007; Hess, 2013; Khoury, 2018; Moraru, 2018). However, based on the region of occurrence and distance from industrial centers, some ore is not dressed after extraction, so some clay minerals have more common applications such as to pharmaceuticals, make ceramics and fillers for paints, paper and coatings (Murray, 2007; Carretero & Pozo, 2010; Hess, 2013; Harvey & Lagaly, 2013; Suárez & García-Romero, 2013; Khurana et al., 2015; Campos et al., 2019; Otunola & Ololade, 2020).

Palygorskite is a type 2:1 layered clay mineral composed of an octahedral sheet shared with two tetrahedral sheets, with chemical formula $(Mg,Al)_5Si_8O_{20}(OH)_2(OH_2)_4.4H_2O$. Its structural arrangement allows the formation of microchannels and micropores, resulting in high specific surface area (125 to 210 m^2g^{-1}) with excellent sorption capacity (Murray, 2007; Galan & Singer, 2011). In comparison with bentonite clays (rich in smectite), palygorskite has a fibrous morphology (elongated fibers) and stable structure, hindering swelling (Carretero & Pozo, 2010; Galan & Singer, 2011; Lobato-Aguiar et al., 2018).

Natural clays have impurities that directly affect their physicochemical characteristics, so inorganic and organic chemical treatments are necessary to expand their applicability (He et al., 2018; Zhang et al., 2018a, b). In this context, palygorskite can have several industrial uses, such as adsorbent materials, additives for aqueous bases and nanomaterials, carriers for agriculture and rheological additives for water-based systems. It also can be applied in synergetic combinations to improve the physicochemical characteristics of compounds to which it is added (Liu et al., 2013; Jiang et al., 2014; Middea et al., 2015; Oliveira et al., 2015; Gueye et al., 2017; Simões et al., 2017; Zhang et al., 2018a, b; Zhu et al., 2016; Cui et al., 2020; Mohammed et al., 2020; He et al., 2020).

Besides Brazil, palygorskite deposits occur in the United States, Mexico, Senegal, and Greece, with reserves estimated at 2,000, 260, 188 and 108 Mt, respectively (Willet, 2020). In Brazil, its occurrences are located in the municipalities of Alcântara, (Maranhão state) (Rodrigues et al., 2014) and Guadalupe (Piauí) (Middea et al., 2015; Simões et al., 2017; Assis et al., 2019), with estimated yearly production of 3,000 t (Willet, 2020). The main industrial application, after acid treatment, is for the clarification of vegetable oils, animal tallow and carnauba wax, with values close to US$ 130.00 t^{-1}, while the USA exports it at an average value of US$ 40 t^{-1} for industrial applications such as adsorbents (West, 2020; Willet, 2020).

Currently, the palygorskite occurrences located in Guadalupe are being studied for many applications, such as adsorption of potentially toxic metals and herbicides for pollution remediation, for production of pharmaceuticals and as additives for the formation of nano-composites (Middea et al., 2015; Oliveira et al., 2015; Simões et al., 2017; Assis et al., 2019; Santanna et al., 2020). Thus, this study reported the technological investigation of a sample from a new occurrence of palygorskite, in the municipality of Guadalupe, to evaluate future industrial and environmental applications.

MATERIALS, METHODS AND TECHNIQUES

The technological investigation was conducted at the Center for Mineral Technology (CETEM). A run-of-mine (ROM) palygorskite sample was crushed, ground, homogenized and quarting, followed by wet size classification to sizes of 45 and 20 µm (PA>45 µm and PA>20 µm, respecttively), with the smaller fraction (PA<20 µm) being subjected to wet magnetic separation in a high intensity field (14,000 Gauss) (PA<20 µm n-mag) (Simões et al., 2017; Assis et al., 2019).

Mineralogical characterization through X-ray diffractometry (XRD) was performed using the powder method with a Bruker-D8 diffractometer under following operating conditions: Cokα radiation (40 kV/40 mA); goniometer speed of 0.02° (2θ) per step, with counting time of 0.5 second per step and collection from 4 to 80 (2θ), with a LynxEye position sensitive detector. Qualitative spectrum interpretations were performed using the PDF02 database (ICDD, 2006) and the Bruker DiffracPlus software.

The chemical composition was determined by X-ray fluorescence (PANalytical Axios MAX WDS-1 X-ray fluorescence spectrometer), in a VANEOX automatic press, using H_3BO_3 as binder in the ratio of 1:0.1. Semiquantitative results are expressed as %, calculated as 100% normalized oxides.

The morphological characteristics of the palygorskite were observed by scanning electron microscopy (SEM-EDS, FEI Quanta 200i microscope). The determination of the cation exchange capacity (CEC) was calculated using methylene blue method as the titrant, with a dispersion prepared with deionized water containing the sample.

The pH was adjusted between 3 and 4 using a solution of H_2SO_4 to 0.1 mol.L^{-1} and subsequently titration was conducted until the indicator turned, according to American Society for Testing and Materials, ASTM (2003).

The surface charge was determined by measuring the zeta potential in the with a Zetasizer Nano ZS particle size analyzer, with a suspension containing 0.05 g of sample and 10 mL of 0.001M KCl, and the pH adjustment was performed with HCl solutions (0.1 and 0.5M) and KOH (0.1M).

The analysis by nitrogen physisorption (N_2) at 77K was performed with a Micromeritics TriStar II Plus analyzer running the MicroActive version 2.03 software to obtaining the isotherms, which were calculated by the BET method while the pore size distribution was determined by desorption isotherm of N_2 using the BJH method.

RESULTS AND DISCUSSION

The diffractograms of the ROM sample and the fractions obtained after ore dressing are shown in figure 1. The results indicate crystalline phases corresponding to palygorskite at 9.77º (2θ), kaolinite at 14.33º (2θ), quartz at 25.00º (2θ) and goethite at 31.05º (2θ). As indicated in Figure 1, there was an increase in peak intensity for the palygorskite, showing that the decrease in particle size and magnetic separation increased the concentration of palygorskite (Simões et al., 2017; Assis et al., 2019), since it has fine granulometry, with concentration in the fraction below 45 µm. Goethite (FeO(OH)) corresponded to the isomorphic substitutions of Si^{4+} by Fe^{3+} in the crystalline structure of the palygorskite. The decrease in peak intensity is related to quartz impurity. This was expected since this mineral has particle size above 45 µm. The relationship between the intensity of the characteristic peaks of palygorskite and quartz, as well as the presence of quartz in the sample, does not affect its industrial uses and other applications (Rodrigues et al., 2014; Middea et al., 2015; Oliveira et al., 2015; Gueye et al., 2017; Simões et al., 2017; Zhuang et al., 2017; He et al., 2018; Khoury, 2018; Zhang et al., 2018a, b; Mohammed et al., 2020; Zhu et al., 2016; Cui et al., 2020; He et al., 2020; Santanna et al., 2020).

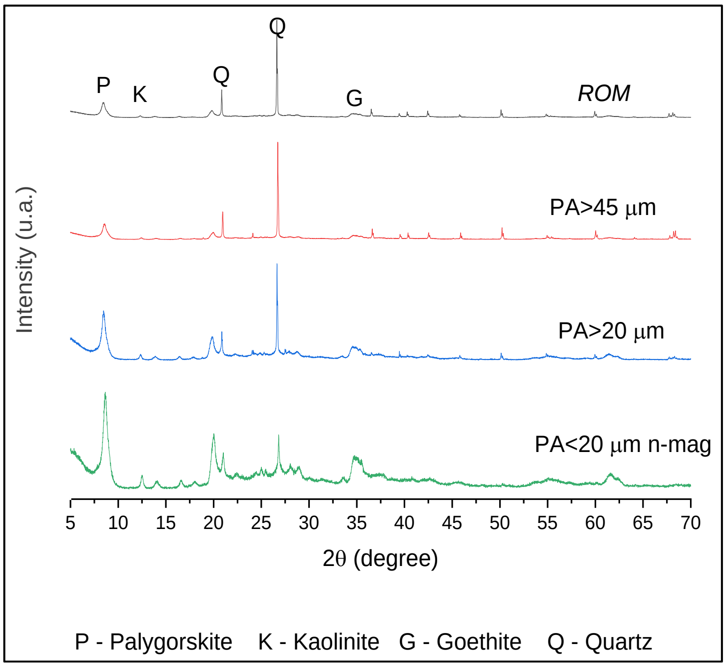

Figure 1 - X-ray diffractograms (Cokα) of palygorskite samples - Run-of-mine (ROM); after ore dressing: aliquot above 45 µm (PA>45 µm), aliquot above 20 µm (PA>20 µm), aliquot below 20 µm after wet magnetic selection (PA<20 µm n-mag).

The results of the chemical analyses performed by XRF (Table 1) corroborate those obtained through XRD.

The increase in the contents of Al_2O_3 and Fe_2O_3 supported the hypotheses about the concentration of the clay mineral and the isomorphic substitution of Fe^{3+}. The presence of Ca, K and Na corresponded to the exchangeable cations present in the palygorskite channels, as also observed in palygorskite samples used for adsorption of Eu(III) and U(IV) (Zuo et al., 2019), as well as for pharmaceuticals, additives for the formation of nanocomposites, adsorbent materials, environmental and industrial applications (Rodrigues et al., 2014; Middea et al., 2015; Gueye et al., 2017; Simões et al., 2017; Assis et al., 2019; Cui et al., 2020; Santanna et al., 2020).

The SEM analyses (Figure 2) showed nanoparticles between 20 and 100 nm, in the form of rods, characteristic of the fibrous nature of palygorskite, showing that the ore dressing (crushing, grinding and wet magnetic separation) did not alter the characteristic of the clay mineral (Jiang et al., 2014; Rodrigues et al., 2014; Middea et al., 2015; Oliveira et al., 2015; Gueye et al., 2017; Simões et al., 2017; Zhuang et al., 2017; He et al., 2018; Zhang et al., 2018a, b; Lobato-Aguiar et al., 2018; Mohammed et al., 2020; He et al., 2020; Zhang et al., 2020). This morphology in nanometric size was studied to prepare silica nanorods for use as carriers and reinforcing agent for fabrication of various composites (Wang et al., 2019).

Table 1 – Chemical analysis by XRF of oxides (%p/p) of palygorskite samples - Run-of-mine (ROM); after ore dressing: aliquot below 20 µm after wet magnetic selection (PA<20 µm n-mag).

	XRF (%p/p)									
Sample	Al_2O_3	SiO_2	MgO	Fe_2O^3	CaO	Na_2O	K_2O	TiO_2	*LOI	Total
ROM	15.3	54.8	5.2	6.7	0.17	0.14	2.4	0.64	14.6	99
PA<20 µm n-mag	16.4	51.5	5.5	7.1	0.25	0.12	2.4	0.70	16.0	99

**Loss on ignition.*

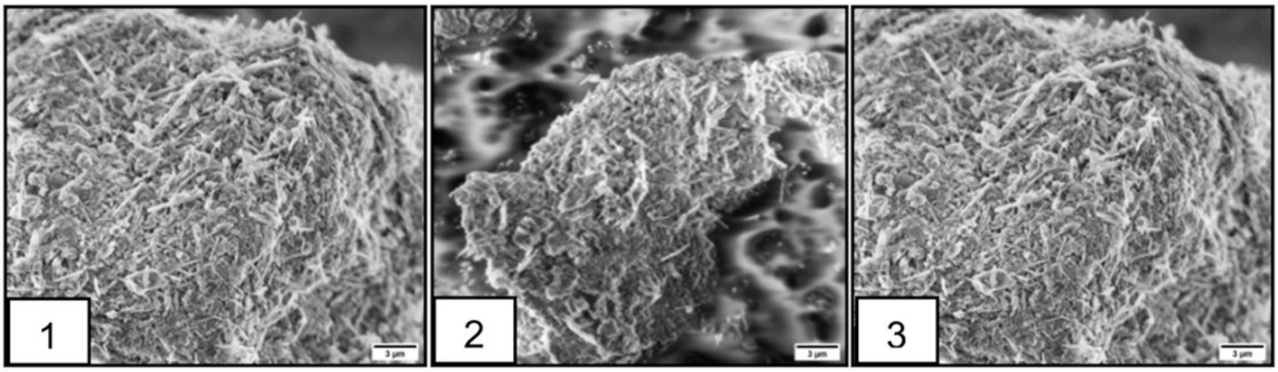

Figure 2 - Images obtained by SEM (3 µm scale), showing the fibrous nature characteristic of the palygorskitesamples after ore dressing: (1) aliquot above 45 µm (PA>45 µm), (2) aliquot above 20 µm (PA>20 µm), (3) aliquot below 20 µm after wet magnetic selection (PA<20 µm n-mag).

The CEC result of the PA<20 µm n-mag fraction was 41 meq 100 g^{-1}, showing that the ore dressing increased the purity of the palygorskite compared to the CEC value of the ROM, which was 28.5 meq 100 g^{-1}. This result is close to the value found for another ore sample studied by other authors, in which they compared different palygorskite samples from Guadalupe (Simões et al., 2017; Assis et al., 2019). It is considered promising with regard to the application of palygorskite in adsorption processes, where the size should vary from 20 to 50 meq 100 g^{-1} (Gueye et al., 2017). Recent studies have investigated application of palygorskite for synthesis of inorganic gel composites for multiple applications (Cui et al., 2020), formation of organic polymeric composites to improve the performance of physicochemical and electrical properties (Oliveira et al., 2015), support for perylene bisimide to sense fluorescence in the solid state in order to detect polar organic vapors (He et al., 2020) , and synthesis of hybrid clay-drug materials for antibacterial applications (Lobato-Aguiar et al., 2018). In all these investigations, the CEC values were lower than in the palygorskite studied here, even after purification treatments to improve industrial applications.

The values of the Zeta potential (mV) (Figure 3) showed that the palygorskite had a negative surface charge over the entire pH range studied (Middea et al., 2015; Simões et al., 2017; He et al., 2018; Zhang et al., 2018a, b; Cui et al., 2020). This was due to the deprotonation of the Si-OH that accumulates on the surface of palygorskite and the isomorphic substitutions that occur in its structure (He et al., 2018).

The results obtained through the nitrogen physisorption N_2 (BET) test of palygorskite (Table 2) allowed identifying the textural properties, such as specific surface area, average pore diameter and average pore volume of ROM and PA<20 µm n-mag samples. There was a considerable increase in the specific area after ore dressing, corroborating the results obtained that indicated the concentration of palygorskite in the fine fraction. The results related to BJH indicated the material is mesoporous (Hess, 2013).

The BET and BJH results agreed with those obtained by other researchers investigating industrial applications of palygorskite, such as the adsorption of methylene blue (Gueye et al., 2017; He et al., 2018) and heavy metals (Simões et al., 2017; Mohammed et al., 2020), the synthesis of organophilized palygorskites for removal of heavy metals (Zuo et al., 2019; Wang et al., 2020) and in the synthesis of carbon nanotubes with palygorskite as a source of silica (Jiang et al., 2014).

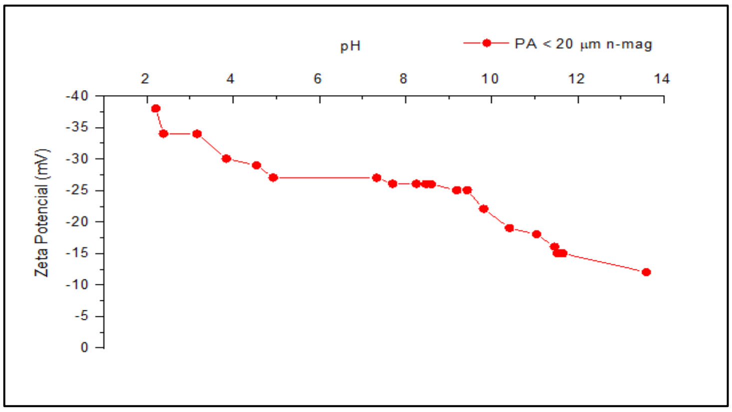

Figure 3 - Zeta potential curve (mV) versus pH for the palygorskite samples aliquot below 20 µm after wet magnetic selection (PA<20 µm n-mag).

Table 2 - Textural properties of palygorskite samples - Run-of-mine (ROM); after ore dressing: aliquot below 20 µm after wet magnetic selection (PA<20 µm n-mag).

Surface area measurements			
Sample	Surface area (BET)	BJH adsorption	BJH desorption
	(m2 g-1)	Average pore diameter (Â)	
ROM	97.44	52.05	51.33
PA<20 µm n-mag	142.078	52.77	52.77

CONCLUSIONS

The technological investigation conducted for palygorskite from the new occurrence in the region of Guadalupe indicated that the sample consisted of palygorskite, kaolinite, goethite, and quartz.

However, the proposal for a simple ore dressing route promoted the concentration of the clay mineral in the fine fraction. The palygorskite sample has a composition rich in SiO_2 and Al_2O_3, the Al^{3+} and Fe^{3+} cations may be present in the octahedral layer of the clay mineral and Fe^{3+}. Ti^{4+} is also associated with impurities, CaO indicates the presence of carbonates and K^+ is a compensation cation of the palygorskite crystalline structure. The images obtained by SEM revealed the presence of palygorskite nanoparticles, characteristic of its fibrous nature.

The investigations of its physicochemical characteristics, negative surface charge, average pore diameter and surface area of 52.77Å and 142.08 m^2g^{-1}, respectively, indicate this new palygorskite found in Guadalupe could be applied for several industrial and environmental remediation purposes, contributing to the economic development of the region with a noble application of this clay.

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