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Research paper

Thermally activated palygorskites as agents to clarify soybean oil

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ABSTRACT

Palygorskite, a fibrous clay mineral, exhibits excellent adsorbent properties. This study was conducted to assess the potential activation of palygorskite and to obtain thermally activated samples to use as clarifying agents for soybean oil. Previously, the palygorskite samples were thermally activated at various temperatures in the range of 100–900 °C for 24 h. The natural and activated samples were characterized using the following techniques, XRD, XRF, FTIR, SEM, SSA, CEC and thermal analysis, to observe the structural and morphologic alterations after thermal treatment. These characterizations indicated that the primary changes to the palygorskite surface referred to losses of structural water: physically adsorbed, zeolitic and coordination water molecules. The sample was activated above 700 °C, which potentiated the clarification of the soybean oil by the removal of the carotenoid dye and other pigments, and exhibited higher performance compared with the natural palygorskite.

1. Introduction

The of soybean oil processing industry has focused its attention on studying new technologies that are expected to attain standardization of the quality of their products in the market for human consumption. Studies have reported that the clarifying stage has become one of the most important steps in refining vegetable oils because it plays a role in eliminating the substances that confer color and instability to the oil (Rossi et al., 2003; Martinho et al., 2008; Nguetnkam et al., 2008).

Several factors can affect the performance of the clarifying procedure; among them, the clarifying adsorbent plays an important role. Activated clay minerals and other adsorbents, e.g., activated charcoal and silica-based products, are usually used as oil clarifying agents or other pollutants because of their low cost and relatively high performance (Juang et al., 2002; Nguetnkam et al., 2008; Shuali et al., 2011; Worasith et al., 2011; Xavier et al., 2014; Cheng et al., 2015; Santos et al., 2015; Toor et al., 2015). Therefore, among the seven groups of clay minerals, at least 33 different specific phases are used as adsorbents to clarify oil (Liu et al., 2008; Morales-Carrera et al., 2009; Gunawan et al., 2010). Palygorskite (Pal) is a clay mineral with a microfibrous morphology, low surface charge, high porosity and high specific surface area (SSA) (Ye et al., 2006; Bergaya et al., 2013). These characteristics confer important adsorptive properties to palygorskite and organic and inorganic cations, depending of the size of the chemical species, can easily penetrate into its structure (Haden and Schwint, 1967, Chen et al., 2007; Liu et al., 2012a,b; Cui et al., 2013; Oliveira et al., 2013; Wang et al., 2015; Yu et al., 2015).

In general, palygorskite is found almost exclusively in the soil of arid and semi-arid zones across the globe (Neaman and Singer, 2004). In Brazil, the major deposits of palygorskite are located in the state of Piauí and distributed throughout an area of nearly 700 km^2, where several investigations have been conducted into the utilization of palygorskite for various industrial uses, e.g., well-drilling fluid; a decolorizing agent for vegetable, animal and mineral oils; and applications within the pharmaceutical industry (Baltar et al., 2009).

The first structure for palygorskite, $Si_8Mg_5O_{20}(OH)_2(OH_2)_4 \cdot 4H_2O$, was proposed by Bradley (1940) (Gonzalez et al., 1989a,b). This formula shows that in the structure of palygorskite, three types of water molecules are contained: (a) coordinated water to cations of the octahedral sheet, (b) zeolitic water present in the channels that interact with both the coordinated water molecule and the tetrahedral sheet and (c) structural water, corresponding to hydroxyl groups bonded to the structure of the clay mineral in the center of the octahedral sheet (Gionis et al., 2006). Because of the limited number of zeolitic, structurally bonded, and coordinated water molecules in the octahedral sheet and in the channels of palygorskite, the adsorption capacity of this clay mineral may be improved by the removal of water molecules through thermal activation without loss of any other physicochemical properties (Bu et al., 2011).

In the current study, thermally activated palygorskites were obtained and characterized, and their use as clarifying for soybean oil was investigated to determine more effective conditions for the thermal treatment to improve the adsorptive properties of the palygorskite.

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2. Experimental section

2.1. Treatment of palygorskite

The Brazilian palygorskite, commercialized by the Itaoeste Company, originated from a deposit in the municipality of Guadalupe, which is in the state of Piauí. Initially, the natural sample was submitted to the quartering process to obtain a more homogenous sample. The disaggregation was performed with a hammer mill and macerated with a porcelain mortar and followed by sieving the sample in a 200-mesh (0.074 mm) sieve and drying at 70 ± 1 °C for 24 h to remove the excessive humidity.

2.2. Activation of palygorskite

Five dried and disaggregated natural samples were subjected to thermal treatment at temperatures between 100 and 900 °C for 24 h in a muffle furnace at a heating rate of 10 °C min^{-1} without atmosphere control. The samples were designated as Pal-Nat for the natural palygorskite sample and Pal-x (where x is the temperature used in the thermal treatment, x = 100, 300, 500, 700 and 900 °C) for the treated samples (Gan et al., 2009; Chen et al., 2011; Boudriche et al., 2012).

2.3. Characterization of the adsorbent

2.3.1. X-ray diffraction (XRD)

The samples of palygorskite before and after the thermal treatment were characterized by X-ray diffraction (XRD) using a Shimadzu LABX — XRD 600 diffractometer with Cu-Kα radiation (λ = 1.5406 Å), 2θ in the range between 5°–75° and a scan rate of 2° min^{-1} for a total exposure time of 40 min. The obtained XRD patterns were compared with the crystallographic data of the program PDF22003 to determine the crystalline phases.

2.3.2. Thermal analysis

Thermogravimetric (TG) and differential scanning calorimetry (DSC) analyses of samples with initial weights of 8.731 mg were performed using an SDT Q600 in a nitrogen atmosphere with a dynamic flow rate of 100 mL min^{-1} and a heating rate of 10 °C min^{-1}.

2.3.3. X-ray fluorescence (XRF)

The XRF analysis was performed to determine the principal mineral constituents present in the natural and modified palygorskites. The contents of the primary oxides were determined by a semi-quantitative analysis in an X-ray fluorescence spectrometer — (WDS), model BOL — FRX. The samples were prepared by fusion to a mixture of borates as a flux ($Li_2B_4O_7$–$LiBO_2$) in a 1:10 ratio. The results are expressed in percentages (%) of oxides.

2.3.4. Fourier transform infrared spectroscopy (FTIR)

The infrared spectroscopy experiment was conducted to elucidate the structural alterations of the adsorbent in a short range order. The analyses were conducted on a Varian 660 - IR spectrometer using KBr pellets in the 4000–400 cm^{-1} region with 96 scans and a resolution of 4 cm^{-1}.

2.3.5. Scanning electron microscopy (SEM)

The scanning electron microscopy (SEM) experiment was conducted to determine the particle morphology of the samples before and after the thermal treatment. The micrographs were obtained on a scanning electron microscope after the metallization of the samples in gold and palladium using the JEOL T-300 microscope.

2.3.6. Specific surface area (SSA)

The SSA of natural and thermally treated clay minerals was determined by nitrogen physical adsorption on Quantachrome NOVA® 4200 equipment. To remove adsorbed water from the palygorskite, the sample was previously outgassed for 24 h under vacuum at 90 °C.

2.3.7. Cation-exchange capacity (CEC)

The cation-exchange capacities of the natural palygorskite and the thermally activated samples were determined using the methylene blue method (Morales-Carrera et al., 2009).

2.4. Clarification assay

The crude soybean oil was provided by the Dureino® refining company, which is located in the capital city of Teresina in the state of Piauí, and it was subjected to a delecithination and neutralization process. The clarification assay was performed using a (*w*/*w*) ratio of 6% clay mineral/neutral soybean oil under heating at a constant temperature of 150 °C and atmosphere conditions and stirring at 200 rpm. Under these conditions, the adsorbent was added to the reaction after 10 min, and then the adsorbent was separated by vacuum filtration.

2.4.1. Determining the clarification capacity

The capacity of the thermally activated and natural samples to decolorize the soybean oil was determined by monitoring the β-carotene content of the oil using a UV–visible digital spectrophotometer operating at 460 nm (Varian, Cary 300). Dichloromethane was used as a ground and to dilute the samples with a V/V dichloromethane:dichloromethane ratio of 1:10. All measurements were performed in triplicate (Morales-Carrera et al., 2009).

The degree of clarification of the soybean oil was calculated by the equation $[(C_0 - C) / C_0] \times 100$, where C_0 is the concentration of beta carotene (mg/L) in the soybean oil before the clarification and C is the concentration of β-carotene after decolorization (Liu et al., 2008; Nguetnkam et al., 2008).

2.4.2. Colorimetric analysis

The color measurement of the neutral and decolorized soybean oil samples was performed using a Lovibond® Tintometer (E AF 900) by comparisons between the color of the analyzed sample and the Lovibond color scale, which regards color measurements for red and yellow. This technique involves the combination of the color of the light transmitted through a specific depth of the oil with the color of the light transmitted from the same source of the set of filters as the reference colors (Sun et al., 2001; Sampaio et al., 2013).

3. Results and discussion

3.1. Characterization of palygorskite

3.1.1. XRD analyses

The X-ray diffraction patterns of pristine sample (Fig. 1A) show reflections that are typically indexed to palygorskite and quartz, which is consistent with the crystallographic cards No 31-0783 and 1-0850794, respectively. The higher intensity reflection of palygorskite at 8.50° corresponds to the *110* plane. Other characteristic lower reflections of this clay mineral were identified as the $d_{(200)}$ at 14.00° and $d_{(400)}$ at 28.10°. The presence of quartz was implied by the reflection at 26.65° (Christ et al., 1969; Chisholm, 1992; Chen et al., 2008). The XRD patterns show that the palygorskite was a well-crystalline sample.

For the thermally activated palygorskite samples (Fig. 1B), the X-ray diffractograms show that as the thermal treatment temperature increased, a progressive decrease in the *110* reflection occurred with its disappearance at higher temperature. However, thermal treatment of approximately 300 °C did not cause any significant changes in the reflection in the *110* plane, only a slight decrease in its intensity. Above 300 °C, the total disappearance of the palygorskite *110* plane occurred, which suggested a drastic alteration of the palygorskite structure.