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Research paper

Physical and chemical characterization and method for the decontamination of clays for application in cosmetics

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ABSTRACT

Clays are materials originated from rock decomposition, made up of clay minerals and non-clayish minerals. Their applicability in the field of cosmetics depends on their chemical and mineralogical composition. In view of their huge bioburden there is the need to submit them to effective decontamination before they are incorporated into cosmetics. The present work involved the characterization of four different samples of clays originated from the sand extraction residue of mining activities in the hinterland of São Paulo state, Brazil. Characterization was performed with the aid of tools like X-ray fluorescence (XRF), X-ray diffraction (XRD), thermogravimetric analysis (TGA/DTA), particle size distribution by laser dispersion, surface area (BET method) and Fourier transform infrared spectroscopy (FTIR). Besides, it aims to evaluate the bioburden of these clays, as well as to propose a method for the decontamination of these samples. The average particle diameter varied from 3.6 to 24.1 μm, kaolinite and illite being the main mineralogical phases to be identified. The proposed method for decontamination employed a combination of ethanol 70% and dry heat at 120 °C in an oven for 24 h. The decontamination was effective in reducing samples bioburden, leaving the clays within the limits required for cosmetics application.

1. Introduction

Clays are usually defined as natural, earthy, fine granulated materials of diameters smaller than 2 μm. When wet they exhibit plasticity resulting from their hydrophilic nature (Srinivasan, 2011). Their constitution is basically that of a clay mineral, but they can contain variable amounts of other non-clayish minerals, for example quartz, feldspath, mica, calcite, hematite, besides organic matter (Baschini et al., 2010; López-Galindo et al., 2007; Vieira et al., 2008).

In the pharmaceutical domain, clays have been employed as carriers for organic molecules in cosmetics and drugs, as a catalyst support (Zhang et al., 2011) and as excipient in solid, liquid, and semi-solid pharmaceutical forms (Carretero, 2002; Carretero and Lagaly, 2007; López-Galindo et al., 2007). There is a growing interest in the use of clays based on the search for abundant and low-priced materials that when disposed of, do not harm the environment (Bergaya et al., 2006).

Application of clays, chiefly in the field of cosmetics, is related to their mineralogical and chemical composition. Therefore, it is paramount to be informed about their composition, both mineralogical and chemical-physical characteristics, by means of different techniques available for this purpose (Carretero et al., 2014; Khiari et al., 2014). In general, clays contain Si, Al, Fe, Zn, Mg, Ca, K and Ti. The importance of these minerals in the cosmetics field is based on the assumed role of various elements on the skin, such as iron as an antiseptic and as a cell renewal catalyst, silicon as providing reconstruction of skin tissues, hydration and a soothing effect, zinc and magnesium that are invigorating (Gomes and Silva, 2007). Calcium and potassium act on circulation and tissue invigoration. Titanium is a further mineral of interest in cosmetology, chiefly employed in photo protection formulations, being a mineral able to provide reflection of UV radiation (Carretero and Pozo, 2010).

Nevertheless, clays have a huge bioburden and therefore, according to López-Galindo et al. (2007), the control of clays bioburden is extremely relevant. Thus, before being incorporated into cosmetics formulations, they should undergo some kind of decontamination process, such as heating at 160 °C for at least 1 h or exposure to gamma radiation (Viseras et al., 2007). Besides, assessment of decontamination process effectiveness by means of microbiological tests is essential for securing inputs quality, storage processes and possibility of external contamination (El-Bazza et al., 2009; Katusin-Razem et al., 2003; Modabberi et al., 2015).

Brazilian cosmetics legislation establishes the acceptable limits for microorganisms in cosmetics and personal hygiene products through

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Resolution no. 481, of September 23, 1999, issued by the National Health Surveillance Agency (ANVISA) (Brazil, 1999), so as to preserve the product physical chemical features as well as its safety and effectiveness.

With these premises, the aim of this work was to characterize four clays produced as waste from sand extraction for the civil construction industry (São Paulo/Brazil) and propose an effective method for decontamination.

2. Materials and methods

2.1. Materials

The four clay samples (assigned as I, II, III and IV) produced as waste from sand (raw material) extraction for the civil construction industry were collected by mining companies of São Paulo state hinterland, Brazil (different locations, Fig. 1). The main activity of the mining company is extraction and trade of sand (raw material). Clays I, III and IV were extracted from rocky formations in Parana Basin. The Parana Basin covers an approximate area of 1,600,000 km^2 comprised of sedimentary and magmatic rocks (spillage and intrusive) which cover nearly 70% of the basin (Conceição et al., 2015; Ulbrich and Gomes, 1981). Clay I (Leme city) is from a region where sedimentary rocks of Santa Rita Formation and Piramboia Formation predominate (reddish and whitish, fine to medium sandstone) (Araújo et al., 2000). Clay II originates from Ibiúna, where rocks of Paranapiacaba Group (Ibiúna Batholith) occur, they are made up of quartz dioritic rock enclaves, with predominance of monzogranite and subordinate syenogranite rocks, with porphyritic faces and seconded by nonequigranular rocks (Godoy et al., 2010). Clay III and clay IV originate from the Mogi Guaçu region, where recent deposits and basic intrusive rocks occur. Extraction of raw material (sand) is performed from unconsolidated sandy and sand-clayish materials (clay III) and of unconsolidated materials of the Mogi Guaçu river floodplain (clay IV). Sampling was carried out by quartering, resulting in a final stock of about 10 kg of each kind of clay.

For the decontamination process distilled water and ethanol 96% (m/m) (Vetec Química Fina Ltda/Brazil) were used.

2.2. Clay characterization

The four *in natura* clay samples (I, II, III and IV) were dried in an oven (Fanem 315SE/Brazil) at 120 °C for 24 h and afterwards characterized.

2.2.1. X-ray diffraction

Mineralogical analyses were carried out by X-ray diffraction (XRD). XRD patterns were obtained with a Diffrac 5000 Bruker diffractometer (USA) operating at 45 kV and 40 mA using Cu-Kα monochromatic radiation (λ = 1.54 Å), 2θ angle interval of 2 to 28° (mineral clay fraction) with counting time of 5 s/pass, step size of 0.05° in 2 Theta, and slit widths of 150 μm. In order to separate the clay mineral fraction for X-ray diffraction studies, the samples were prepared as it follows: the <2 μm fraction from each sample was separated by centrifugation (XRD pattern of *in natura* clays randomly oriented powder, 2θ angle = 4 to 45°) and oriented clay aggregates were prepared by allowing clay-water suspensions to dry at room temperature on three glass slides. XRD tests were performed on the clay minerals fraction (which was separated by decantation from the coarser fraction) for the four samples. Two analyses for each sample were run: natural (untreated) and calcined at 550 °C (Poppe et al., 2001).

2.2.2. Elemental chemical analysis

This test was performed with the aid of X-rays fluorescence spectrometry (XRF) on a XRF Shimadzu (Japan), XRF 1800 sequential spectrometer and loss on ignition (LOI) was determined in accordance with the ASTM D7348-08 Method (ASTM, 2008).

In order to assess the iron II concentration (Fe^{2+}) in the samples, citric acid and ammonium citrate extraction was performed and then quantification was carried out in an Agilent Technologies, model AA-55 Atomic Absorption Spectrophotometer (AAS) instrument (USA).

2.2.3. Thermal analysis, Fourier transform infrared spectroscopy (FTIR), particle size distribution and surface area

Mass loss was determined by thermogravimetric analysis (TGA/DTA) in a Mettler Toledo, TGA/SDTA851e (Brazil) thermal balance

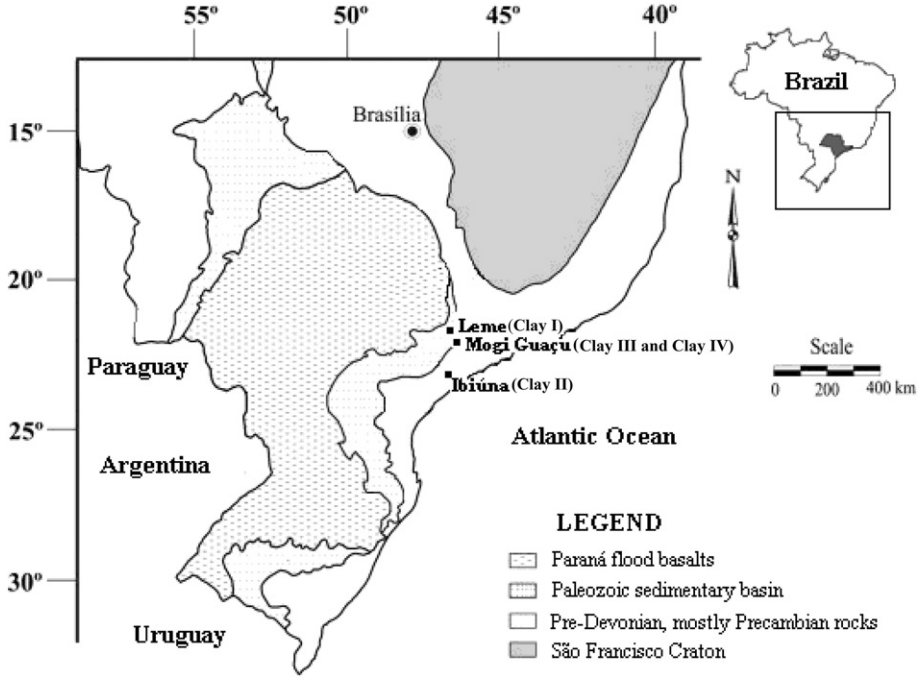

Fig. 1. Map of eastern South America, Brazil showing the extent of Paraná flood basalts relative to Paraná Sedimentary Basin and location of the study area (cities): Leme (clay I), Ibiúna (clay II) and Mogi Guaçu (clays III and IV).
Adapted from Conceição et al. (2015).