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Research paper

Characterization of Egyptian kaolins for health-care uses

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ABSTRACT

This work aimed to evaluate by first time the suitability of the Egyptian Abu Zenima (Sinai Peninsula) kaolins to be used in pharmaceutical and cosmetic applications. Sixty five kaolin samples were collected from six stratigraphic sections: Wadi Khaboba, Gabal Hazbar and Wadi Abu Natash sections, belonging to the Abu Thora Formation (Carboniferous age), and Gabal El Dehessa, Gabal Farsh El Ghozlan and Wadi Budra sections, belonging to the Malha Formation (Lower Cretaceous), and characterized by mean of X-ray diffraction and fluorescence, electron microscopy, spectrophotometry and rheometry.

Most of the samples were dominated by kaolinite, and half of the samples contained >75% of this mineral, reaching up to 96%. Quartz was the main impurity, with very variables quantities; it was always present except in some parts of the Wadi Abu Natash and Wadi Budra sections. Mica, anatase and hematite were frequently present, but they normally did not exceed 10%. Other detected impurities were carbonates (calcite, dolomite, ankerite), sulfates (gypsum, alunite), smectite, feldspars, magnetite, pyrite, halite and heulandite, but in lesser amounts and only in some samples.

Carboniferous kaolinites exhibited a high crystallinity (Hinckley Index >1), while most of Cretaceous kaolinites were medium to poorly crystallized (Hinckley Index normally <1). CIELAB colorimetric parameters put into evidence the general grayish color of the samples, some of which showing light tints of redness and yellowness in correlation with their iron content.

The rheological characterization of the 31 purest kaolin samples revealed that their dispersion exhibited similar and good pseudoplastic flow behavior at 50% W/W solid concentrations. The apparent viscosity and yield stress values of Carboniferous samples showed a widest range of variations when compared to Cretaceous ones. The observed variations were interpreted to be correlated with both, the kaolinite content as well as microtexture and the dimensions of kaolinite particles.

With these premises, some of the studied kaolins are considered to have a very high economic potential, once the detected impurities are removed easily by the appropriate process, and then suitable for pharmaceutical and cosmetic purposes. Even if there were zones rich in kaolinite in all the studied sections, the highest quality for the target purposes is found at the lower part of the Wadi Abu Natash section, where quartz was absent and include the samples with the highest viscosities.

1. Introduction

Kaolinite is a planar hydrous 1:1 dioctahedral clay mineral with an ideal structural formula of $Al_2Si_2O_5(OH)_4$. It is the most common mineral of the kaolin-group, which includes other members as halloysite, nacrite and dickite. These minerals exhibit many excellent physical, chemical, mechanical and structural properties (rather simple structure, plasticity, alkaline pH, thixotropic and colloidal properties, influence on the viscosity of organic polymer dispersions, relatively low specific surface area and low sorption capacity) that make them very useful for many pharmaceutical applications, like drug excipients (e.g., diluent and binder, emulsifying, thickening and anticaking agent, flavor corrector and carrier-releaser) or active ingredient in many solid and semisolid drug products administered orally or topically such as gastrointestinal protector, antidiarrhoeaic product, dermatological protector, anti-inflammatory and local anesthetic, cosmetic creams, powders and emulsions (Braun, 1994; Bolger, 1995; Wenninger et al., 2000; Carretero, 2002; López-Galindo and Viseras, 2004; Carretero et al., 2006, 2013; Droy-Lefaix and Tateo, 2006; Sweetman, 2007; Ferrell, 2008; Carretero and Pozo, 2009, 2010; Rowe et al., 2009).

In addition to the classic pharmaceutical uses, new advanced biopharmaceutical strategies are focusing on applying clay nanoparticles

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as vectors for drug and gene delivery, based on their interactions with drugs and biochemical molecules, bioadhesion and cellular uptake (Aguzzi et al., 2007). Moreover, modified clays and clay-biopolymer nanocomposites offer further capabilities for improvement of drug loading and release properties and also the specificity of targeted drug delivery, and minimize toxicity (Viseras et al., 2010).These interesting advancements have also paid attention to apply kaolinite in many biomedical innovation areas, such as development of products used for treating antibiotic-resistant bacteria, antiviral activity against hepatitis C virus and anticancer activity (Shi et al., 2011; Vergaro et al., 2012; Cervini-Silva et al., 2013; Ali et al., 2014; Pasbakhsh and Churchman, 2015).

Egypt has numerous and big sedimentary kaolin deposits, ranging in age from Carboniferous to Neogene (Zaghloul et al., 1982; Saied, 1990; Boulis and Attia, 1994; Baioumy and Gilg, 2011; Baioumy, 2014). The most important deposits are located at Abu Zenima and El Tih plateau (West-Central Sinai), Abu El Darag area (approximately 85 km south of Suez city), Wadi Qiseib area (about 90 km south of Suez city), Wadi Abu Sanduk area (94 km south of Suez city), Wadi Abu Had area (at 80 km west of Ras Gharib city), Wadi Abu Sobeira area (15 km north east of Aswan city), and Wadi Kalabsha area (105 km southwest of Aswan city). The reserves are estimated to be around 120 million tons in west central Sinai deposits (Abd El-Razik, 1972), about 17 million tons in the Wadi Kalabsha area, and 5 million tons in the Wadi Abu Sobeira area (Qusa, 1986). The exploited Egyptian kaolins are used in ceramics, refractories, white ware, heavy-clay products, Portland cement, paints and paper on the basis of the great demand and importance of such industries in Egypt (Abdel Shafy, 1967; Soliman and El Fetouh, 1969; Amer et al., 1971; Abd El-Razik, 1972; Hegab et al., 1992; Abdel Razek, 1994; Boulis and Attia, 1994; Rashed and Amer, 1994; Kamel et al., 1997). However, these kaolins have never been submitted to special characterizations to evaluate their suitability for pharmaceuticals, cosmetics and other health care applications, even if the output value of kaolinite in pharmaceutical industries is enormous, because the price of pharmaceutical grade quality may be up to ten times that of the same grade dedicated to the above mentioned uses. The kaolinite materials have to completely correspond to stringent and precise chemical, physical, toxicological and microbiological specifications regulated by the Pharmacopoeias (EP. 8.0, 2014; USP 39-NF34, 2015).

The quality of industrial kaolinite is influenced, among other factors, by the quantities of mineral impurities such as quartz, anatase, rutile, mica, feldspar, calcite, dolomite, magnetite, hematite, illite, smectite or pyrite. The economic value of kaolinite upgrades as the purity increases, because this minimizes the processing cost. Pharmaceutical grade kaolin is mined, powdered and freed of coarse gritty particles either by elutriation or by screening. Impurities such as ferric oxide, calcium carbonate, and magnesium carbonate, that usually accompany kaolinite, are removed easily with an electromagnet and by treatment with hydrochloric acid and/or sulfuric acids.

This study aims to characterize samples from Abu Zenima kaolin deposits, located at West Central Sinai, with the highest reserves and purist grade amongst all the Egyptian kaolin deposits (Rashed and Amer, 1994), in order to evaluate their general potentialities in pharmaceutical and/or cosmetic industries and other health care applications. The results will be used to propose those samples that could be exploited for health care application, to increase the market of Egyptian kaolinites and to call attention of the Egyptian Mineral Resources, Industry and Investment authorities for the high quality of the selected samples.

2. Geological context

The studied kaolin deposits are located in the Abu Zenima district (Eastern coast of the Gulf of Suez, West Central Sinai Peninsula), in an area of around 333 Km^2. They belong to both Carboniferous and Lower Cretaceous sedimentary units. The Carboniferous (Upper Visean) kaolin deposits occur within the Abu Thora Formation (Kora, 1989), and the Lower Cretaceous (Albian) kaolin deposits occur within the fluvial-continental Malha Formation (Abdallah et al., 1963).

As regards to the studied sections, the Abu Thora Formation is a siliciclastic sequence with a thickness ranging from 65 to 188 m, made up of pinkish white sandstones intercalated by multicolored siltstones and mudstones. The "Wadi Khaboba" section (named K, at 29°05′01″ N and 33°14′46″ E) includes three dark grey to yellowish grey kaolinitic horizons each one of around 5 m thickness, alternating with three multicolored cross bedded medium to coarse grained sandstone beds. The "Gabal Hazbar" section (named H, at 29°04′45″ N and 33°22′05″ E) includes two light to dark grey laminated kaolin horizons intercalated by a yellow fine-grained sandstone bed and overlaid by a white and laminated sandstone bed. In "Wadi Abu Natash" section (named N, at 28°56′45″ N and 33°19′24″ E) there are three light gray, grey and reddish brown kaolinitic claystone beds intercalated with four ferruginous laminated and cross-bedded sandstone layers.

The Malha Formation, which ranges between 70 and 130 m in thickness, is composed mainly of thin cross-bedded, very fine to coarse-grained "Nubian-type" sandstones with intercalations of red to grey, fine-grained claystones and siltstone beds, and sporadic thin kaolinitic lenses. The "Gabal El Dehessa" section (named D, at 28°55′55″ N and 33°17′59″ E) exhibit three grey and pinkish grey massive kaolinitic siltstone and claystone intercalated with cross-bedded white and ferruginous sandstone layers. In "Gabal Farsh El Ghozlan" section (named F, at 28°55′40″ N and 33°18′10″ E), the kaolin deposits occur in the form of white, pinkish grey and reddish brown lenticular beds intercalated within the sandstone. The "Wadi Budra" section area (named B, at 28°55′06″ N and 33°19′16″ E) is characterized by its varicolored sandstones intercalated by lenses of massive kaolin, kaolinitic clays and siltstone beds.

3. Materials and methods

3.1. Mineralogy and chemistry

Sixty five samples (dried, milled and sieved under 125 μm) were studied by means of X-ray diffraction (XRD), using a PANalytical X'Pert Pro diffractometer (CuKα radiation, 45 kV, 40 mA) equipped with an X'Celerator solid-state linear detector, using a step increment of 0.008° 2θ and a counting time of 10 s/step. The diffraction data were analyzed using the XPOWDER® computer program (Martín-Ramos, 2004). Semi-quantitative analysis were performed following Moore and Reynolds (1989), and the final contents of the different mineral phases were calculated by combining XRD and chemical analytical data, following Torres-Ruiz et al. (1994) and López-Galindo et al. (1996).

The Hinckley Index (Hinckley, 1963) was measured by using the reflections (02l) and (11l) in the range from 19° to 24° 2θ in random oriented powdered samples, that are very sensitive to the structural defects (random and interlayer displacements) in kaolinite structure. The maximum intensity ratio of (020), (0-10) and (11-1) reflections were determined using the XPOWDER® software.

Elements were analyzed using a commercial wavelength dispersive X-ray fluorescence instrument (Bruker S4 Pioneer) equipped with an Rh anode X-ray tube (60 kV, 150 mA); three analyzer crystals (OVO-55, LiF 200 and PET) and a flow proportional counter for light element detection and a scintillation counter for heavy elements. Quantification was made by the fundamental parameters method using the software linked to the equipment (SpectraPlus). Five grams of each powdered sample was mixed with 0.5 g of a binder (Hoechst wax C micropowder) and homogenized in agate mortar. To obtain a XRF-pellet, a small metallic sample holder made of aluminum with a diameter of about 4 cm was used. The pellets were pressed at 90 bars in a Nannetti hydraulic press for 30 s. To determine loss on ignition (LOI), samples were heated to 900 °C for 1 h.

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