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Research paper

Characterization of Tunisian clay suitable for pharmaceutical and cosmetic applications

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ABSTRACT

The aim of this study is to assess the suitability of purified Tunisian clay for its possible pharmaceutical and cosmetic uses. Mineralogical, chemical and physicochemical characterization was performed with the aid of tools like X-ray diffraction (XRD), Chemical composition, DTA/TGA analysis, Cation exchange capacity (CEC), particle size distribution by laser dispersion (PSD), surface area (BET method), Point of zero charge (PZC) and surface charge density σ_H. Pharmacopoeia tests were also carried: Swelling capacity, sedimentation volume and pH measurement. For microbiological tests, the absence of *Salmonella* species, *Escherichia coli*, *Staphylococcus aureus* and *Pseudomonas aeruginosa* was tested.

The X-ray diffraction data revealed that the Tunisian sample is an interstratified illite-smectite. The percentage of smectitic fraction is estimated to be 78%. The chemical, textural and porosimetric results show important values suggesting that this mineral clay can function in creams, powders and emulsions.

In view of the fundamentals of major pharmacopoeias for use of bentonite in pharmacy and considering the swelling capacity and sedimentation volume values, and microbiological results we could designate a pharmaceutical acceptable denomination for Tunisian purified clay.

1. Introduction

The use of clay minerals for cosmetic and pharmaceutical purposes has increased in the past few years, due to the increasing success of natural remedies. Furthermore, clays are regarded as essentially non-toxic and non-irritant materials at the levels used in pharmaceutical and cosmetic products. For cosmetic purposes, clays are used for external applications such as facial (Ngomo et al., 2014), and skin treatment (Pusch, 2014). For pharmaceutical applications, clays are used as active principals or excipients (Sanchez-martin et al., 1988; Joshi et al., 2009; Chen et al., 2010; Carretero et al., 2006; Carretero and Pozo, 2009, 2010). As active principals, clays may be gastrointestinal, antidiarrhoeal and dermatological protectors, antacid and anti-inflammatory. As excipients, clays are used as lubricants, desiccants, disintegrants and emulsifying, thickening and anticaking agents. Among all members of clay minerals, kaolinite, talc, smectites, sepiolite and palygorskite are used in cosmetic and pharmaceutical formulations (Viseras and Lopez-Galindo, 1999; Park et al., 2008; Tateo et al., 2006). The fundamental properties that needs to be considered and maintained for use of a material in cosmetic and pharmaceutical formulations are: colloid size, crystalline structure plasticity, mineralogical composition, high cation exchange capacity, swelling capacity, high specific surface area, and consequential strong adsorption and absorption capacity (Lin et al., 2002; Tateo and Summa, 2007; Karakaya et al., 2010; Abdel-Motelib et al., 2011; Silva-Valenzuela et al., 2013).

The aim of the present work is to characterize a Tunisian clay and to study the suitability of this clay to be used in new fields such as pharmaceutical and cosmetic applications.

2. Materials and methods

2.1. Preparation of purified-smectite

A sample clay used in this study came from Elfahs (North-east Tunisia). This clay was naturally Ca^{2+}-smectite with quartz and calcite as impurities, which were determined by X-ray diffraction (Fig. 1). For experiments, the smectite was processed to < 2 μm size fraction by sedimentation in deionized water and was purified using the classical method of Van Olphen (1963). This purification greatly decreased the associated impurities. The purified clay obtained was noted Na^{+}-EP.

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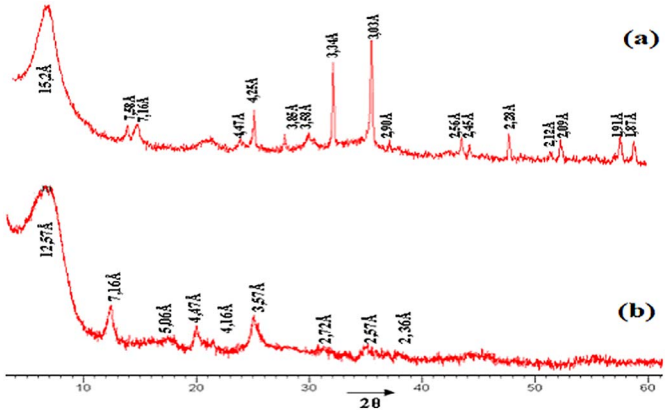

Fig. 1. XRD patterns of (a) raw clay and (b) purified clay Na^+-EP.

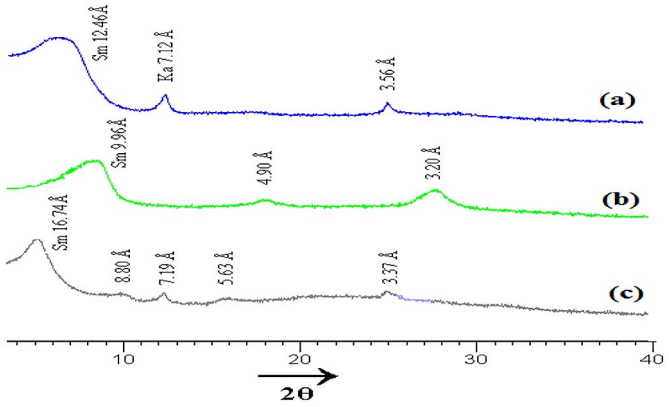

Fig. 2. XRD diffractograms of Na^+-EP, (a) purified clay; (b) heated at 823 K; (c) treated by ethylene glycol.

Table 1
Chemical composition of the studied sample.

%M_xO_y	SiO_2	Al_2O_3	MgO	Fe_2O_3	Na_2O	K_2O	CaO	LOI	Total
Raw clay	43.44	12.32	2.96	2.92	1.14	0.62	12.52	24.30	100.22
Na^+-EP clay	52.62	18.44	3.09	3.56	1.92	1.12	0.52	18.67	99.97

2.2. Characterization of samples

2.2.1. Mineralogy and chemical characterization

2.2.1.1. XRD analysis. XRD patterns of the sample were recorded between 1° and 60° (2θ) at a scanning speed of 2°/min, using a «PANalytical X'Pert High Score Plus» diffractometer with monochromated CuKα$_1$ radiation (30 mA and 40 kV). Two types of diffractograms were studied: diffractograms with disorientated powder where all the (*h k l*) peaks appear and diffractograms of plate oriented obtained by sedimentation. This makes it possible to determine the stacking periodicity of the layers, with the identification based on the (d_{001}) reflection. Test of ethylene glycol is used to identify swelling clays and also interstratified illite-smectite (Srodon, 1980). The dried purified clay is solvated with ethylene glycol and then analyzed by XRD. For the heat treatment, the sample was heated at 823 K for 2 h.

2.2.2. Chemical composition

The clay sample was attacked by a mixture of three acids (HCl, H_2SO_4, and HNO_3). All the elements passed into solution, except the silica (SiO_2) which was determined by gravimetry. The other elements, such as Al, Fe, Mg, Ca, Na and K were analyzed by Atomic Absorption Spectrophotometer (AAS).

2.2.3. Thermal analysis

The thermal analysis was performed by TGA/DTA SETSYS EVOLUTION model 1740, in temperature range from ambient to 1173 K. All experiments were carried out by placing about 30 mg of each sample under the dynamic atmosphere of air with a constant heating rate of 10 °C/min.

2.2.4. Physical and physicochemical characterization

2.2.4.1. Cation exchange capacity (CEC). CEC was determined by the method of copper ethylenediamine$(EDA)_2CuCl_2$ complex (Bergaya and Vayer, 1997).

2.2.4.2. BET surface analysis. Nitrogen adsorption measurements were performed at 77 K with an Autosorb-1 unit (Quantachrome, USA) for the determination of sample textural properties using the multipoint Brunauer-Emmet-Teller (BET) method. The samples were out gassed at 393 K under a vacuum at 10–3 mm Hg for 3.5 h.

2.2.4.3. The particle size distribution (PSD). The particle size distribution (PSD) of the natural and purified samples was measured by means of a Laser granulometer Microtrac S3500.

2.2.4.4. Point of zero charge (PZC). Point of zero charge (PZC) was determined using mass titration, this method was described by Noh and Schwarz (1989). Our experiments on mass titrations were performed. Approximately 0.05 g of dry Na^+-EP was added to 50 mL of a NaCl solution at different ionic strengths (0.5 M and 0.1 M) and different pH values (4, 5, 8 and 10).

2.2.4.5. Surface charge density σ_H. Surface charge density σ_H was determined by potentiometric acid-base titration using NaCl as background electrolyte at constant ionic strengths for 0.5 M, 0.1 M and 0.01 M concentration (Schroth and Sposito, 1997):

$$\sigma_H(\text{mol}\cdot\text{m}^{-2}) = \frac{V}{m}S\left\{([H^+]_b - [H^+]_s) - \left(\frac{K_w}{[H^+]_b} - \frac{K_w}{[H^+]_S}\right)\right\}$$

where, V is the volume of the electrolyte solution equilibrated with the clay mineral (mL); $[H^+]$ is the solution proton concentration; K_w is the dissociation product of water; subscripts "s" and "b" refer to sample and blank solution; m is the mass of sample used (g) and S is the specific surface area ($m^2\,g^{-1}$).

2.2.5. Pharmaceutical tests

2.2.5.1. Swelling capacity. Swelling capacity was measured in dispersions of 2 g clay in 100 mL by quantifying the apparent sediment volumes after 2 h.

2.2.5.2. Sedimentation volume. Sedimentation volume was measured according to the European Pharmacopoeia (2005). The dispersion of 6 g of each bentonite sample in 200 mL of water was prepared with a high-speed mixer operating at 10,000 RPM. Transferred 100 mL of each dispersion to 100 mL graduated cylinder and allowed to remains undisturbed. The sedimentation volume was then measured by quantifying the clear supernatant volume of water after 24 h.

2.2.5.3. pH measurement. According to US Pharmacopoeia (2007), the pH values of clay water dispersions (1 g/50 mL) were measured after 2 min of continuous stirring.

2.2.6. Microbiological tests

The tested species were *Salmonella* species and *Escherichia coli* for products intended for pharmaceutic use and *Staphylococcus aureus* and *Pseudomonas aeruginosa* for products intended for cosmetic use. All tests were carried according to the US Pharmacopoeia (2007).