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Research paper

Green synthesis and characterization of colored Tunisian clays: Cosmetic applications

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ABSTRACT

Colored clays are prepared by a solid state reaction of dried leaves of flowers with a Tunisian clay used for pharmaceutical and cosmetic applications. The structural properties, photo- and thermal stability of the resulting samples were characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, Differential scanning calorimetry analysis (DSC) and UV–visible spectroscopy. The mineralogical structure, physicochemical properties and pharmacopoeial tests of the purified clay suggested that this clay mineral can function in cosmetic products. The XRD results of colored clays revealed a slight difference in values of basal spacing d_{001} when compared to values obtained from purified clay. FTIR analysis confirmed changes in functional groups and surface properties of purified clay. DSC results proved a high thermal stability for purified and modified clays. UV–visible spectra of colored materials displayed a new band compared to purified clay in 400–700 nm wavelength region. The microbiological tests revealed the suitability of all clays for the cosmetic products.

1. Introduction

Green chemistry is the design, development, and implementation of chemical products and processes to reduce or eliminate the use and generation of substances hazardous to human health and the environment (Moulton et al., 2010). Strategies to address mounting healthy concerns with current synthetic approaches include: the use of green synthesis, biodegradable materials and nontoxic chemicals. Clays are biocompatible and are highly desirable in pharmaceutical and cosmetic applications. For cosmetic purposes, they are widely used for cleansing the skin, UV radiation protection, anti-inflammatory processes and trans-dermal nutrient supplementation of elements such as calcium, iron, magnesium and potassium (Carretero, 2002; Carretero and Pozo, 2010; Matike et al., 2011; Adejumoke et al., 2016). Many cosmetic clay products are in the form of powders, pastes, creams and gels. The ability of clays to perform these various functions is influenced by their color, particle size, pH surface, specific surface area, cation exchange capacity, swelling property, hydration ability, rheological property, structural plasticity and chemical composition (Lopez-Galindo and Viseras, 2004; Choy et al., 2007; López-Galindo et al., 2007; Karakaya et al., 2010; Silva et al., 2011; Sánchez-Espejo et al., 2014; Roselli et al., 2015a).The color of clay is used to identify its function: yellow clay is believed to be effective against bacterial infections, red clay is used for cleansing skin and reducing aches in the joints, blue clay is effective against acne, green clay is used to reduce the amount of oil secreted by sebaceous glands and black clays are used for general skin nourishment (Mpuchane et al., 2010). The small size of the clay particles accords it large surface areas over which adsorption of cations and microorganisms in the soil takes place. The average particle size of the clay can induce the microcirculation of the skin (Dário et al., 2014). The pH surface of the clay is similar to that of the skin. This property helps prevent skin irritation (Carretero et al., 2006). The SSA of clay refers to the surface area per unit volume or unit mass of the particles; and the ability of clay colloids to attract and hold positively charged ions, is referred to as the CEC. The important rheological properties allow the formation of a viscous and consistent cosmetic product and the good plastic properties easy the application and adherence the cosmetic product during the skin treatment. 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 (López-Galindo et al., 2007; Gomes and Silva, 2007; Viseras et al., 2007; Matike et al., 2011; Roselli et al., 2015b). Clay minerals used in cosmetic formulations are kaolinite, bentonite, illites and palygorskite (Abrahams, 2002; Carretero and

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Pozo, 2010; Williams and Haydel, 2010; Dário et al., 2014; Khiari et al., 2014; Mattioli et al., 2016).

The aim of the work is to prepare biocosmetic products (colored clays) in powder form. These products were prepared using a natural clay and natural flower. The green synthesis of colored clays by state solid-reaction was described. The samples were characterized samples by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, Differential scanning calorimetric analysis (DSC) and UV–visible solid spectroscopy.

2. Materials and methods

2.1. Materials

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. For experiments, the smectite was processed to $< 2\,\mu m$ 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 smectite obtained was noted Na^+-Sm. Sixteen flowers are used in this study.

2.2. Preparation of colored clays

The preparation of colored samples was carried by solid–solid reaction. In the first, the leaves of flowers were washed with bi-distilled water and dried in a ventilated environment. The mixtures of Na^+-Sm clay and dried flowers were ground manually with an agate pestle and mortar at room temperature for 10 min. The mass ratio was 1:1 (smectite: flower).

2.3. Characterization of samples

2.3.1. X-ray diffraction

X-ray diffraction (XRD) patterns of the sample were recorded between 5° and 15° (2θ) at a scanning speed of 2°/min, using a «PANalytical X'Pert High Score Plus» diffractometer with monochromated $CuK\alpha_1$ radiation (30 mA and 40 kV).

2.3.2. FTIR analysis

Infrared (IR) spectra were obtained using a Perkin-Elmer FT-IR (model 783) spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the 4000–400 cm^{-1} range were obtained by the co-addition of 64 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 $cm\ s^{-1}$. KBr pellets were prepared by mixing anionic clay with KBr at 5 wt% concentration.

2.3.3. Differential scanning calorimetry analysis (DSC)

Thermal decomposition spectra of the samples were recorded via differential scanning calorimetry DSC technique, using instrument DSC Q10 analyser (produced by Setaram Inc.). Approximately 10 mg of clay was placed in aluminum sample boats, and heated from 25 to 600 °C with 10 $°C{\cdot}min^{-1}$ heating air condition.

2.3.4. UV–Visible solid analysis

UV–Visible diffuse reflectance spectra of the powders were recorded on a Cary Varian 5E spectrophotometer equipped with a PTFE-coated integration sphere. The optical absorption spectra of the sols were measured in a transmission mode on the same spectrophotometer using a quartz tube.

2.3.5. Pharmaceutical tests

Swelling capacity, Sedimentation volume and pH value were measured according to the European Pharmacopoeia (2005). (Gamoudi and Srasra, 2017).

2.3.6. 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). (Gamoudi and Srasra, 2017).

3. Results and discussions

3.1. Characterization of purified clay

3.1.1. Mineralogical and chemical characterization

According to the diffractogram of purified clay, the d_{001} reflection appears at 12.57 Å indicating the presence of Na^+-smectite. Representative structural formula of exchanged smectite derived from the chemical composition is $(Si_{7.76}\ Al_{0.24})(Al_{0.93}Fe_{0.39}Mg_{0.68})Na_{0.62}K_{0.2}O_{22}$. This formula showed that Na^+ was the most abundant exchangeable cation. The cation exchange capacity (CEC), and BET surface area of the sample are 80.0 meq/g_{clay} and 94.93 m^2/g_{clay} (Gammoudi et al., 2012).

3.1.2. Pharmaceutical tests

All pharmaceutical results are presented in Table 1, the supernatant volume prepared for sedimentation volume measurement, swelling capacity and pH value of the Tunisian smectite Na^+-Sm meets the pharmacopoeia requirements.

3.1.2.1. pH measurement. A pH value of Na^+-Sm purified clay is 9.7. This pH value is appropriate for topical uses of the studied material (Abdel-Motelib et al., 2011; Modabberi et al., 2015).

3.1.2.2. Sedimentation volume measurements. The value of sedimentation volume obtained was 1.9 mL (Table 1), corresponding to good value of pharmaceutical clay dispersions. Moreover, the purified sample was also usable to formulate pharmaceutically acceptable dispersions because no compact sediment formation was observed (Modabberi et al., 2015).

3.1.2.3. Swelling capacity. The swelling property of Na^+-Sm clay was 21.8 mL, which was lower than the pharmacopoeia minimum required swelling power of 22–24 mL (Table 1). This is attributed to the fact that the sample smectite requires an extensive purification (Abdel-Motelib et al., 2011).

3.2. Colored clays

The mixtures of Na^+-Sm and dried flowers prepared by solid–solid reaction are shown in Fig. 1. The results provide the modification of clay's color. Different colored powders were obtained: yellow, red, blue, pink, grey and purple powders. These samples can be used as natural eye shadow or blush powder. Only three flowers F1, F5 and F8 were selected to characterize the obtained powders by DRX, IR, DSC and UV-solid spectroscopy. The choice of three flowers is based on the following factors: the selected flowers are available in Tunisia, nontoxic and used in the pharmaceutical and health field. Some characteristics of these used flowers are presented in Table 2.

Table 1
Pharmacopeial values and specifications of purified sample.

Pharmaceutical properties	Na^+-Sm	Pharmacopoeia specification
pH values (2 g/100 mL)	9,7	9.0–10.5
Swelling capacity	21.8	≥ 22 mL
Sedimentation volumes	1.9	≤ 2 mL