Applied Clay Science xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Research paper

Characterisation of Andalusian peats for skin health care formulations

Fátima García-Villén[a], Rita Sánchez-Espejo[b], Esperanza Carazo[a], Ana Borrego-Sánchez[c], Carola Aguzzi[a], Pilar Cerezo[a], César Viseras[a,c,*]

[a] Department of Pharmacy and Pharmaceutical Technology, University of Granada, Campus of Cartuja, s/n, 18071 Granada, Spain
[b] Aguas Termales de Graena, S.A. C/San Antonio, 5, 18517 Cortes y Graena, Granada, Spain
[c] Andalusian Institute of Earth Sciences, CSIC-University of Granada, Avda. de Las Palmeras 4, 18100 Granada, Spain

ARTICLE INFO

Keywords:
Peats
Clay minerals
Pelotherapy
Rheology

ABSTRACT

Composition and properties of three different peat strata from "El Padul" peatbog have been studied and peat pastes have been formulated to prepare skin health care products. As for composition, the main phase of each stratum was constituted of smectites (outer stratum), organic matters (intermediate) or carbonates (inner). Pristine strata and their aqueous dispersed systems were characterized for such properties (pH, rheology and cooling kinetics) that are considered determinant in view of their topical application. Main phases of each stratum influenced pH and rheology but not cooling kinetics. Combination of the strata in different w/w ratios led to peat pastes with improved performance for skin administration.

1. Introduction

Peat pastes are semisolid systems used in medical hydrology and cosmetic treatments on the basis of chemical and physical mechanisms derived from their composition (Dudare and Klavins, 2013; Gomes de Melo et al., 2015). Typical peat pastes applications imply temperatures between 42 and 44 °C for 15–30 min (Flaig, 1992). Peats have demonstrated adsorptive, estrogenic, astringency, antioxidant and revulsive actions (Beer et al., 2000, 2001, 2002, 2003; Suárez et al., 2011). Fungicidal, antibacterial and antiviral properties, UV absorption as well as influences on smooth muscles and prostaglandin synthesis are also been reported (Klöcking and Helbig, 2005; Fioravanti et al., 2007; Sławinska et al., 2007; Khil'ko et al., 2011; Gomes de Melo et al., 2015).

Peats are complex mixtures of organic and inorganic components. Organic fraction comes from vegetable wastes transformed under anaerobic and waterlogged conditions for extended periods and includes humic acids, humin and fulvic acids as principal compounds. Organic compounds have demonstrated biologic activities, which make them potentially useful in topical health care and cosmetology (Summa and Tateo, 1999; Beer et al., 2003). Mineral fraction of peats is composed of clay minerals such as illite and chlorite as well as gypsum, muscovite and quartz (Summa and Tateo, 1999; Romão et al., 2007; Orru et al., 2011). The presence and the type of minerals in peats hugely depend on the deposit location (Summa and Tateo, 1999). Inorganic components, and in particular clay minerals, may greatly influence the technological and biopharmaceutical properties of peats, as for example, stability and rheology of the solid/water systems or bioavailability of the organic actives (Aguzzi et al., 2007; Viseras et al., 2007). Consequently, detailed identification of the mineral phases associated with organic substances in peat deposits must be considered in the design of semisolid health care formulations with these materials.

With these premises, the aims of the present study were i) to characterise three different peat strata from a deposit located in El Padul (Granada), ii) to prepare dispersed systems with the aforementioned strata in order to determine the technological properties and iii) to study dispersed systems feasibility as potential semisolid health care formulations.

2. Materials and methods

2.1. Materials

Peat samples were extracted from the peatbog "Turbera del Agia" located in El Padul (Granada, Spain). Peat is currently extracted from an area of approximately 20,000 m2 (Fig. 1). The actually exploited peat (P2), mainly commercialized as fertilizer, is characterized by deep black chrome and appears as a stratum of ~5 m thickness, delimitated by two other non-commercialized peat strata (P1 and P3). Details of sample position and depth are included in Fig. 1. Each stratum was separately extracted and hermetically sealed to prevent loss of natural moisture and preserved at room temperature.

* Corresponding author at: Department of Pharmacy and Pharmaceutical Technology, University of Granada, Campus of Cartuja, s/n, 18071 Granada, Spain.
E-mail address: cviseras@ugr.es (C. Viseras).

https://doi.org/10.1016/j.clay.2017.12.017
Received 10 October 2017; Received in revised form 7 December 2017; Accepted 10 December 2017

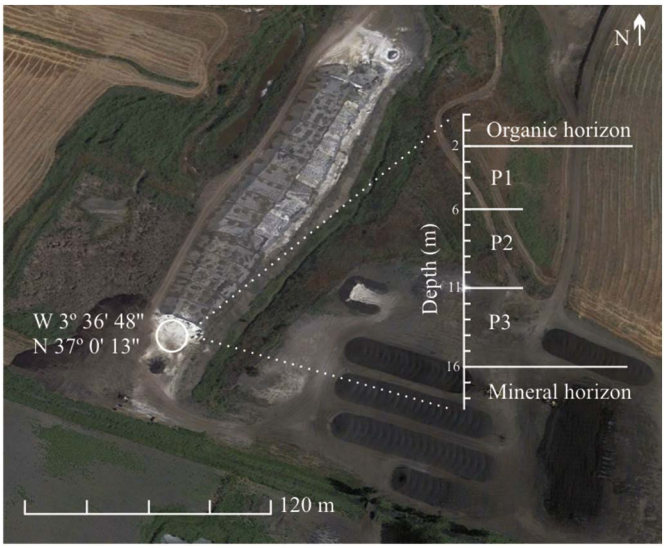

Fig. 1. Location of sampling position in "Turbera del Agia" and vertical-cross section of the samples (Photo from Google©2017).

2.2. Methods

2.2.1. X-ray powder diffraction

Peat samples were dried at 40 °C for 24 h and grounded previous X-ray powder diffraction analysis (XRPD). Mineralogical study was carried out using a PANalytical X'Pert Pro diffractometer equipped with an X'Celerator solid-state detector and a sample holder spinning. X-ray powder diffraction patterns were recorded using random oriented mounts with CuKα radiation, at 45 kV, 40 mA, in the range 3 to 50°2θ. The estimation of the solid composition in crystalline phases was obtained by X'Pert HighScore Plus (PANalytical, 2005). Chemical analysis by X-Ray fluorescence (XRF) was performed using a Bruker® S4 Pioneer equipment working at 60 kV and 150 mA.

2.2.2. Elemental analysis

Elemental analyses (EAN) were performed in order to determine the content of carbon, hydrogen, nitrogen and sulfur in P1, P2 and P3. These determinations were carried out once samples were dried after 24 h at 40 °C. Elemental analyser used was THERMO SCIENTIFIC, Flash 2000 model, equipped with a thermal conductivity detector and a precision microbalance (precision 0.01).

2.2.3. Thermal analysis

Thermogravimetric Analysis (TGA and DTG) of peat samples was carried out by using a METTLER TOLEDO mod. TGA/DSC1 with FRS5 sensor and a microbalance (precision 0.1 μg) (Mettler-Toledo GMBH). Samples were heated in air atmosphere at 10 °C/min, in the range of temperature 30–950 °C. All the experiments were run in triplicate.

2.2.4. Preparation of peat dispersed systems

Raw peats and their mixtures in different w/w ratios were dispersed in purified water to obtain a final solid concentration of 60% (w/w) (Table 1). The systems were manually homogenized until the disappearance of heavy lumps and then by a high speed agitation of 3000 rpm for 10 min by using a Silverson® L4RT (Silverson Machines, UK). All systems were packed inside hermetic containers and preserved at room temperature.

Table 1
Composition of dispersed systems.

Dispersed system	S1	S2	S3	S4	S5	S6	S7
Solid phase (60% w/w)	P1	P2	P3	P1:P2 (20:80)	P1:P2 (30:70)	P2:P3 (80:20)	P2:P3 (70:30)

2.2.5. Determination of pH

Values of pH for each peat strata and the aforementioned dispersed systems were determined by using a Crison 25 + pH-meter, equipped with a solid electrode (code 5053T), with a pH tolerance range between 2 and 11.

2.2.6. Rheological properties

Rheological analysis was carried out by means a viscometer (Thermo Scientific HAAKE, RotoVisco 1; HAAKE RheoWin software) with a plate/plate combination (Plate Ø 20 mm serrated PP20/S sensor) as measuring system. Measurements were carried out at 25 °C (TCP/P, HAAKE unit control temperature system), 90 s of rest time and 0–800 s^{-1} of shear rate. Six replicates were performed on each sample.

2.2.7. Cooling kinetics

Cooling curves were obtained following the procedure described by Sánchez-Espejo et al. (2015). Experimental cooling data were fitted by using the Newton law, describing thermal exchange between two bodies in contact at different temperatures:

$$(T - T_{min}) = (T_{max} - T_{min})e^{-kt} \quad (1)$$

where T_{min} was the room temperature (25 °C), T_{max} was the initial temperature (50 °C), t was the time in minutes and k was a constant that depends on the material and apparatus, given by:

$$k = \frac{P}{C} = \frac{P}{mC_p} \quad (2)$$

where P is the instrumental constant of the apparatus, C the heat capacity of the heated material, m the heated mass and C_p the specific heat. The apparatus constant was obtained by fitting of cooling data obtained with a known amount of a reference water dispersion of TiO_2. Experimental thermal parameters of the studied samples were then obtained by using the aforementioned equations.

3. Results and discussion

3.1. X-ray powder diffraction

X-powder diffractograms and X-ray fluorescence results were used to identify the mineral composition of the samples. Main mineral phases in sample P1 were smectites, quartz and mica (Fig. 2). Other minerals presented were calcium carbonates (calcite and aragonite) as well as pyrite in minor proportion. The studied samples came from a sedimentary basin and the minor presence of pyrite was ascribed to microbial sulphate reduction. The presence of smectites is positive in terms of technological properties due to their swelling and rheological properties in water dispersions (Viseras et al., 2007). Presence of calcium carbonate must be considered in the interpretation of EAN results. Sample P2 contained high amounts of amorphous organic matter, causing a lower crystallinity pattern. Nevertheless, presence of quartz, mica and pyrite was clearly stated. The presence of pyrite (FeS_2) in higher amount than P1 confirmed its biogenic origin. Sample P3 was mainly constituted by calcium carbonates with absence of quartz, smectites and organic matter.

3.2. Elemental analysis

P2 presented high amounts of carbon and nitrogen, clear indicators of its organic composition (Table 2). Sulfur content was in agreement with the pyrite presence discussed previously. The C/N ratio is used to measure the degree of decomposition of the organic matter in peat. During the evolution of peat, the organic matter suffers a mineralization