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Research Article

Portuguese Lagoon Clay Sediments for Pelotherapy Applications: The Study of Technological Properties

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Abstract

Background and Objective: Sediments from Ria de Aveiro Lagoon (Portugal) are mainly composed of recent alluvium materials, subjected to chemical contamination by industrial discharges in the past. The study aims to characterize the technological properties of these clay sediments and evaluate their potential application in pelotherapy. **Materials and Methods:** Six sediment samples were collected, in four climatic seasons, on an artificial beach and in saline pounds areas of an open-air saline health facility SPA (Sanitas per aquam). Technological (abrasiveness index, expandability, oil absorption, Atterberg limits and specific surface area), chemical (cation exchange capacity), thermal (specific heat and cooling time) and rheological (viscosity) tests were performed in samples <63 µm fraction. **Results:** Lagoon clay sediments showed technical properties values of 393-1115 g m^{-2} for abrasiveness index, 18.1-20.8% for expandability, 31.0-40.1% for oil absorption, 32.6-39.3% for liquid limit, 23.8-30.1% for plastic limit, 6.9-12.0% for plastic index and 5.8-14.6 m^2 g^{-1} for specific surface area. **Conclusion:** The two study areas revealed distinct properties, varying especially due to SPA improvement works, but also the influence of tides and climate over time that were restoring the previous properties of the lagoon clay sediments.

Key words: Sediments, technological properties, pelotherapy, dermal application, thalassotherapy, Ria de Aveiro

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Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Clays have been used by humans, for healing purposes, for longer than most other geological materials. The use of clay minerals for human curative purposes and cosmetic applications is almost as old as mankind and is commonly used for the preparation of thermal muds, applied in pelotherapy treatments[1]. Clays and clay minerals may enter the human system through inhalation, ingestion or dermal absorption and the health benefits of clays are well documented in several scientific studies[2-5]. According to Carretero[1], the composition, properties, preparation and maturation and therapeutic applications of peloids (pelotherapy) started being characterized in the XX century. The primary or secondary mixture of clayey materials with salty thermos mineral waters, accompanied by organic products generated by the biological-metabolic activity of microorganisms that grow during the maturation process originates the hydrothermal pastes named thermal muds[6]. Maturation, which consists of mixing clay materials with salty or (thermo) mineral waters for a certain time, gives rise to peloids, applied in therapeutic treatments generally related to rheumatic and skin diseases[6,7]. Pelotherapy is, commonly, the use of peloids for therapeutic and cosmetic purposes[8] and is being applied to treat specific rheumatologic and dermatological pathologies, in thermal, thalassotherapy and rehabilitation centers[9]. Medical supervision and prescription should be required by health and medical centers for the application of peloid treatments[4], such as mud or peloid packs directly on the skin[9]. Recently, the use of peloids as thermal agents in SPAs, health resorts and medical centers became common, but it is since ancient times that they have been used for different therapeutic purposes[8]. Gomes *et al.*[4] defined the term peloid as "a matured mud or muddy dispersion with healing and/or cosmetic properties, composed of a complex mixture of fine-grained natural materials of geologic and/or biologic origins, mineral water or seawater and common organic compounds from biological metabolic activity". While pharmacological and cosmetic industries require quality control before using clays, which must meet specifications regarding user safety and technological resources, peloids are used without any certification or control[10]. However, there is a need for quality criteria and certification of clay products intended to be used in pelotherapy, mainly thermal muds which have a therapeutic function[6,11]. Studies have contributed to the scientific understanding of peloid, supporting the beneficial effects of mud application on pain control and improvement of functional capacity and life quality[12-14]. Barhoumi *et al.*[15] and Khalil *et al.*[16] studied cosmetic and polytherapeutic applications of clays and Codish *et al.*[17], analyzed extensively the therapeutic effects of peloids, particularly for rheumatology purposes. Viseras *et al.*[18], highlighted the importance of technological properties of the pastes prepared from peloids. According to Carretero *et al.*[2] and Veniale *et al.*[6], major factors such as low cooling time, high absorption capacity, high cation exchange capacity, good adhesion and high swelling and plasticity, that contribute to a pleasant sensation when applied on the skin, with easy handling, determine the nature of a given peloid and its suitability for polytherapeutic applications. de Sousa Figueiredo Gomes[9] underlined that paste properties for human healing, are necessarily represented by absorption/adsorption capacity, cation exchange capacity, plastic properties, rheology, grain size and cooling index.

The main objective of this study was, as a starting point, to evaluate the Portuguese clay sediments of Ria de Aveiro and their potential application in pelotherapy treatments and cosmetic purposes through the characterization of their technological properties.

MATERIALS AND METHODS

Study area: A former saltpan at Ria de Aveiro (Portugal), was recently adapted to an artificial peri-urban SPA with two distinct areas (Fig. 1). Area 1 was adapted to a shallow limited artificial beach influenced by tides and Area 2 is a recovered artificial shallow saltpan pond being used by users for the direct application of salts[19].

Ria de Aveiro is a shallow coastal lagoon located on the NW Portuguese coast[20], occupying an area of ~45×10 km. According to Dias *et al.*[21], Ria de Aveiro is connected to the Atlantic Ocean, separated by an artificial channel with the influence of Vouga river flow and by a sand bar, occurring a mixture of sea and fresh waters[21,22]. The climate in the region is classified as temperate maritime, with long and warm summers, with average temperatures of about 20°C and mild but rainy winters, with minimum temperatures that rarely reach freezing level[23].

The study area, geologically, is located in the Aveiro Sedimentary Basin, deployed in the Lusitanian Basin, with Quaternary stratigraphic formations. Ria de Aveiro has a predominance of recent alluviums composed of silt, sandy and micaceous silt, silt with shells and muddy and coarse sands that are settled on the existing substrate[19].

Fig. 1: Study area location and surrounding environmental context (adapt. Google® maps, 2022)

The complex balance between pollutants emissions from the natural and anthropogenic origins and the water auto-depuration capacity regulates the water quality of Ria de Aveiro[24]. Chemical anthropogenic inputs contributed to Ria de Aveiro water and sediments quality degradation[24], due to past unmonitored industrial direct discharges to the lagoon coming from the Estarreja Chemical Complex (ECC), the second largest active chemical area in Portugal, located 10 km North of Aveiro urban area. These discharges, without environmental concerns, contributed to contamination by tidal transport of potentially toxic elements (PTEs). Even distant ECC areas registered high PTEs concentrations (e.g., As, Pb and Zn)[25], revealing the impact of human activities in Ria de Aveiro waters and sediments[26]. According to Pereira *et al.*[27], highly contaminated effluent discharges from EEC, occurred between 1950 and 1994, resulting in the accumulation of PTEs in the Ria de Aveiro.

Sampling, samples preparation and analysis: Technological tests were performed in six samples from SPA locations (Fig. 1): Area 1 (samples A1a, A1b, A1c and A1d) and Area 2 (samples A2a and A2d), collected in different climatic seasons between spring 2020 and autumn 2021, on a total of four sampling campaigns. In the first (spring) and last (autumn) sampling campaigns, were collected samples groups A1a, A2a and A1d, A2d, respectively. Before the collection of sample A1c (summer), an anthropogenic intervention occurred in Area 1, with the introduction of allochthonous sand on its margins, while Area 2 was not submitted to any beneficiation works. The collection of sample groups A1a, A1b and A1c, A1d occurred before and after beach improvement works, respectively. Samples were stored in individual referenced polyethylene bags until laboratory preparation and analysis, being only considered silt fraction (<63 μm) obtained by wet sieving. This study was carried out between January, 2020 to September, 2022.

Mineralogical and chemical analysis tests: These tests have been performed in all samples[19]. Technological properties of the sediment samples included abrasiveness index (AI), cation exchange capacity (CEC), expansibility, oil absorption (OA), plasticity index (PI), specific heat (SH), specific surface area (SSA) and viscosity. The abrasiveness index was determined using the Einlehner AT-1000 Abrasivimeter instrument apparatus adapted according to the procedure of Quintela *et al.*[28], after stirring and conversion to 43500 revolutions (~30 min). The ammonium acetate method for expandability was used to estimate cation exchange capacity, by the LNEC E200-1967 norm (the Portuguese version of ASTM D4829-95 standard test method for expansion index of soils). Oil absorption capacity was calculated by the ratio between the amount of linseed oil absorbed by the sediment sample and its weight. Determination of plastic and liquid limits and plasticity index was done according to the Atterberg limits

(Portuguese norm NP 143-1969). The plasticity index corresponds to the difference between the liquid limit (LL) and the plastic limit (PL). An STA 300 analyzer (Hitachi) was used at a rate of 10°C min^{-1} to a temperature limit of 500°C to estimate the specific heat of the sediment samples. The differential scanning calorimeter (DSC) analysis reveals the amount of heat recommended for 1 g of sample to increase its temperature by 1°C. The adopted method for specific surface area determination was the Brunauer-Emmett-Teller (BET) using Micromeritics Instrument Corporation Gemini II 2370 equipment[29]. This is the most widely used procedure for evaluating the SSA of porous and finely divided materials[30]. Viscosity was determined using a viscosimeter HAAKE™ Viscotester™ iQ Rheometers, accompanied by a bath thermostat Thermo Scientific A10 Circulating Chiller at different shear rates (10, 30, 50 and 70 rpm). The dried sample was heated in a small Teflon container until it reached 60°C and the temperature drop to room temperature of 30°C (cooling time) was measured with a Lutron TM-906A Dual LT Thermometer.

RESULTS AND DISCUSSION

The abrasiveness index (AI) of a material is defined as the weight loss (g m^{-2}) of a standard bronze mesh when subjected to contact with a suspension of the material after a certain number of rotations[28]. This clay's property is related to its mineralogical composition, essentially, with the existence of abrasive minerals (like quartz), decreasing in thinner materials. Sediment samples AI was ranked A1b>A1c = A2a>A1a>>A1d = A2d (Table 1), being quartz the dominant mineral phase in all sediment silt fraction samples (Fig. 2). Comparing the mineralogy of all samples, sample A1c, collected after improvement works, contained the lowest but significant quartz content and highest halite abundance. High IA of sample A1c can be linked to the abundance of quartz and also halite that has been used for skin exfoliation[31], due to the abrasive properties. The application of peloids with low AI is recommended, providing a softer and more comfortable feeling to patients[2,6]. According to Gomes *et al.*[32], poor abrasiveness and hardness are important properties to provide a pleasant sensation of touch when a peloid comes in contact with the skin and is spread on it. Microdermabrasion is a physical method used to increase skin permeability, with low damage to deeper tissues and is commonly used for the treatment of acne, scars and other dermo-cosmetics therapies[33]. In pelotherapy, the use of peloids with high abrasiveness index can be potentiated by smoothing the skin's thick outer layer safely[28]. Some commercial peloids used

Table 1: Technical properties of the studied samples

			Technical				
ID	AI* (g m^{-2})	Expandability (%)	OA (%)	LL (%)	PL (%)	PI (%)	SSA ($m^2\ g^{-1}$)
A1a	984	18.5	31.0	39.3	27.3	12.0	14.6
A1b	1115	20.1	38.3	32.6	25.7	6.9	10.5
A1c	1049	-	38.2	-	-	-	5.8
A1d	393	20.8	40.0	38.0	30.0	8.0	9.5
A2a	1049	18.3	40.1	37.7	30.1	7.5	9.7
A2d	393	18.1	38.7	34.4	23.8	10.6	6.6

AI: Abrasiveness Index, OA: Oil absorption, PL: Plastic limit, LL: Liquid limit, PI: Plasticity index, SSA: Specific surface area and *at 174000 rpm

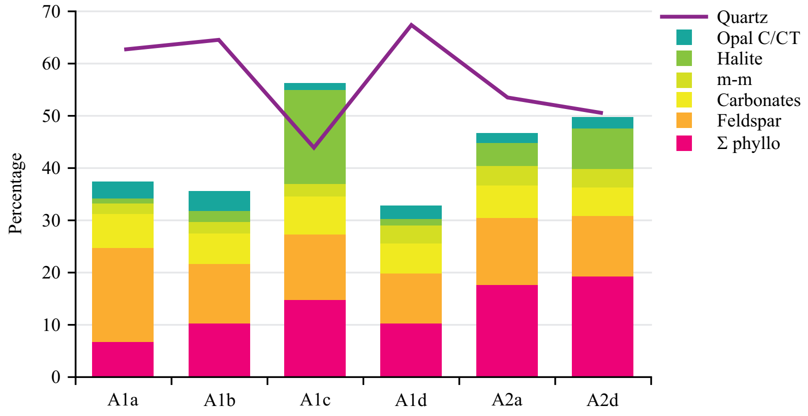

Fig. 2: Sediment samples mineral content[19]

in pelotherapy treatments present AI >200 g m^{-2}, between 310 and 370 g m^{-2} [10] and 300 g m^{-2} [28]. According to Rebelo *et al.*[34], the abrasiveness index should be <200 g m^{-2} (at 43500 rpm). Present study samples, only A1d and A2d met this requisite, with other samples revealing AI close to the guidelines proposed (at 43500 rpm: A1a = 246, A1b = 279, A1c = 262, A1d = A2d = 98 and A2a = 262 g m^{-2})[34].

Clays tend to absorb water which, consequently, increases their volume. The swelling behavior of clays, after water absorption, is defined by their expandability or swelling capacity and constitutes a relevant property to determine water retention capacity and the ability to retain heat[29]. According to Rebelo *et al.*[29], 20% is the minimum recommended expansibility value in materials for application in dermal treatments, to contribute to a higher heat retention capacity. The studied sample expansibility ranged from 18.1 to 20.8%, with samples A1b and A1d revealing 20.1 and 20.8%, respectively (Table 1). The lowest expansibility result was related to the samples' mineralogical content[35]. Rebelo *et al.*[29], presented similar results and related the small swelling values, including illitic materials, with the presence of a high content of non-clayey components.

Oil absorption (OA) is an important property of clay materials for pelotherapy applications. This property aids to eliminate excessive skin oil and toxins. Increasing oil absorption percentage, the greater product effectiveness[2]. Karakaya *et al.*[36] obtained OA values ranging from 26.51 and 59.95% in peloid samples from different SPAs in Turkey, similar to the present study results (31.0-40.1%) (Table 1). Bastos *et al.*[37] study equines rehabilitation with peloid formulations, revealing OA values between 39 and 63%, considered with good oil absorptive capabilities to clean skin impurities.

Consistency limits and plasticity index are tests used to classify materials according to plasticity[38]. The plasticity index (PI) is defined as the ability of clay materials to deform beyond yield stress without cracking or changing volume[39]. The adherence of a peloid to the skin is influenced by its plasticity[1], therefore, for a peloid to be easily handled should have high plastic capacity. Considering PI ranges proposed by de Sousa Figueiredo Gomes[9], ranging from 7<PI<15, the studied samples showed a medium plasticity index, varying from 6.9 to 12.0%, in samples A1a and A1b, respectively (Table 1). The separation of semi-solid and plastic phases and the delimitation of the latter from the viscous behavior are defined as the plastic limit (PL) and liquid limit (LL), respectively[34]. It is important to mention that values of the plastic limit between 23.8 and 30.1% were in agreement with the 5.1 and 41.5% obtained by Karakaya *et al.*[36] in a study conducted in Turkish thermal muds from different SPAs and lower than the limit values proposed by Mitchell[40]. The liquid limit of studied sediment samples, ranging from 23.8 and 30.1%, was similar to the studied peloids by Mefteh and Medhioub[39], with LL between 27.0 and 71.5%. Peloids for therapeutic purposes, such as pelotherapy, must be sufficiently plastic, with adequate adherent properties and easy removal after skin treatment[11]. Studied samples most suitable for manipulation and spreading were A1a and A2d, presenting PL results that will allow the production of pastes with better consistency.

Specific surface area (SSA) is directly related to clay content, i.e., expresses clay fraction content or relative content of fine, medium and coarse particles and the degree of particle dispersion/aggregation[41]. Higher clay-sized particle content implies higher SSA[6]. According to these authors, SSA determines the clay's reactivity, i.e., the quantity of particles surface reacting with the cutaneous area. The studied samples' SSA ranged from 5.8 to 14.6 m^2 g^{-1}, in samples A1c and A1a, respectively (Table 1). Low SSA in sample A1c was linked to the textural sand classification and mineralogical composition, revealing a high abundance of quartz and low clay minerals content and high A1a SSA in agreement with its clay-loam textural classification[19]. The guideline of SSA for use in pelotherapy is >10 m^2 g^{-1} [34], being the minimal value of commonly used clays. High clay SSA implies additional interaction between the skin area to be treated and the material applied. Results obtained in this study, showed that samples A1a and A1b meet the application requirements, with samples A1d and A2a presenting values near the guideline, of 9.5 and 9.7, respectively.

In pelotherapy, cation exchange capacity (CEC) controls the exchange of mobile elements released between skin sweat and peloid[42], increasing with reduced average particle size, since thinner particles are more susceptible to structural weaknesses responsible for the decompensation of electric charge[9]. Rebelo *et al.*[34], suggested that materials to be used in pelotherapy must have a minimum CEC of 10 meq/100 g, as it represents the minimum acceptable value for illitic clays used in therapy. Studied samples CEC ranged from 6.2 to 15.2 meq/100 g (Table 2), in A1c and A2a samples, respectively, in agreement with peloid Turkish SPAs, between 9.55 and 32.26 meq/100 g[11]. Low CEC found in sample A1c was attributed to its textural classification of sand given[19]. Considering expected CEC for clay minerals, studied samples were within the range of kaolinite (3-15 meq/100 g) and illite (10-40 meq/100 g)[9], in agreement with the abundance of kaolinite and illite found in the <2 μm fraction mineralogical content[19]. Except for sample A1c, all samples presented CEC results suitable for pelotherapy application.

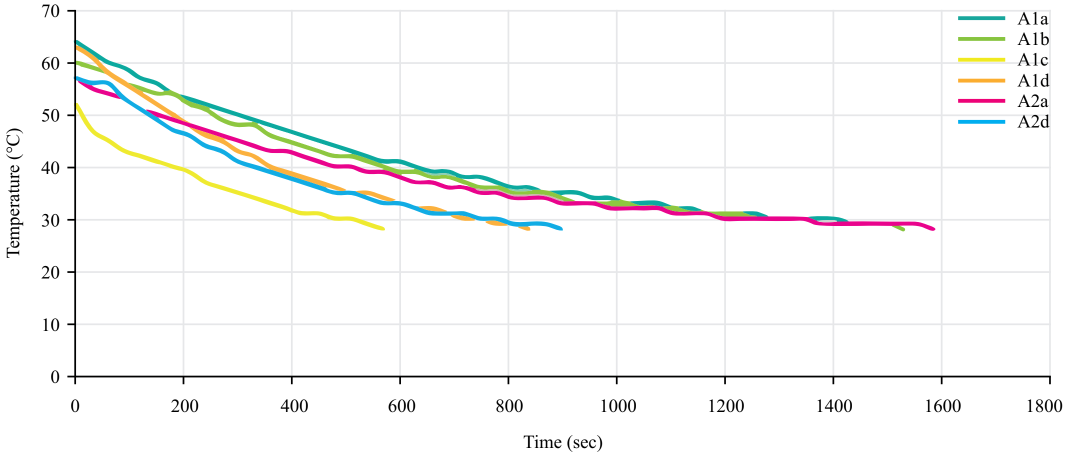

Fig. 3: Temperature cooling curves of sediment samples

Table 2: Chemical, thermal and rheological properties of the studied samples

ID	Chemical CEC (meq/100 g)	Thermal SH (J/g°C)	Thermal Cooling time (min)	Rheological Viscosity* (Pas)
A1a	11.4	0.60	21.5	35.0
A1b	12.4	0.53	21.0	24.5
A1c	6.2	0.76	8.0	-
A1d	10.6	0.58	12.0	24.0
A2a	15.2	0.58	20.0	25.0
A2d	12.8	0.60	12.5	28.0

CEC: Cation exchange capacity, SH: Specific heat and *at 10 rpm

Specific heat (SH) presented low variability on studied samples, with the highest (0.76 J/g°C) and lowest (0.53 J/g°C) results corresponding to samples A1c and A1b, respectively (Table 2). Karakaya *et al.*[43], found SH between 0.60 and 1.41 J/g°C in matured peloid samples from SPAs in Turkey, results related to clay minerals' higher purity. Clays with SH >0.5 J/g°C are considered to have better conditions for therapeutic purposes, requiring less energy to heat[34]. Studied samples SH showed acceptable values, above the minimum required. According to Carretero[1] and Karakaya *et al.*[43], in pelotherapy applications, the temperature of prepared peloid paste must be 5 to 10°C above the human body temperature and should maintain this temperature for 15 to 20 min. Clay materials, to be used in skin therapies, the temperature should be 40 to 45°C and cool down gradually, preserving a temperature above 30°C for 20 to 30 min after application on the skin[44]. Samples A1a, A1b e A2a revealed an ideal cooling time between 20 to 30 min, with the remaining samples not presenting cooling temperature rates for application in therapeutic treatments (Table 2, Fig. 3). Gámiz *et al.*[45] indicated a relationship between cooling time, pore size and particle size aggregates, like as Sánchez *et al.*[46] a decrease in cooling time with the increase of particle size. Sample A1c was the sample with the lowest cooling time, due to its sandy texture[19].

Viscosity is an important property for clay topical application since directly affects the interactions between film and skin by heat transfer and material properties[34]. Samples A1a and A2d presented higher viscosity at 10 rpm, with 35 and 28 Pas, respectively. Remaining samples presented, at 10 rpm, lower and similar viscosity values (Table 2). All samples showed a similar trend, reflecting a decrease in viscosity as rpm increased, i.e., became more fluid as viscosity decreased. Viscosity was related to clay particle size, the main factor that controls viscosity[47]. According to this author, materials with a large percentage of fine particles have higher viscosity. Sample A1a, with a higher content in the fine fraction, classified as frank clay[19], showed higher viscosity. Rebelo *et al.*[34] and Cara *et al.*[48] revealed that clay pastes used for pelotherapy purposes exhibited viscosities ~3-4 Pas, suggesting that sediment samples presented a higher potential to form clay pastes with suitable rheological behavior.

The present study aims to increase scientific knowledge in the selection of natural materials for application in thalassotherapy treatments. The SPAs must access specific materials' properties before application, selecting them from areas with studies that confirm their potential beneficial outcomes. More studies are needed to confirm their efficacy and to assess dermal exposure risk. COVID-19 restrictions influenced this research development, e.g., sampling campaigns.

CONCLUSION

The study area clayey materials revealed distinct properties, varying especially after SPA improvement works. The influence of tides and climate over time aids in restoring the previous properties of the lagoon clay sediments. In general, samples collected before human intervention were the most suitable for application in pelotherapy. Further studies will be conducted to further evaluate the material's properties and composition for skin applications, e.g., elemental dermal bioaccessibility.

SIGNIFICANCE STATEMENT

Understanding the influence of natural materials' technological properties to be used in therapeutical treatments is important for the expansion of scientific knowledge. Diverse natural products, such as clayey sediments, have been increasingly applied to promote human health and well-being. The study location, a former saltpan in Ria de Aveiro (Portugal), was recently adapted to an artificial beach with two SPA areas, being very popular where its users enjoy treatments with materials not studied. To understand the suitability and effectiveness of these clay sediments in pelotherapy (e.g., application in skin and bone disorders), is necessary to assess the characteristics of these materials, in particular the technological properties. Results showed the influence of SPA improvement works, tides and climate on the materials.

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