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Characterization of clays from the State of Paraíba, Brazil for aesthetic and medicinal use

(Caracterização de argilas do estado da Paraíba para uso estético e medicinal)

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Abstract

This study aimed to evaluate the potential of clays from the State of Paraíba to be used for medicinal, therapeutic and aesthetic treatments. The samples were characterized by X-ray diffraction, X-ray fluorescence chemical composition, thermogravimetry, differential thermal analysis, laser diffraction granulometric analysis, cation exchange capacity, and antimicrobial activity. Based on the study, it was concluded that the clays from the State of Paraíba had properties similar to those of commercial clay. The antimicrobial evaluation revealed that the samples showed no activity against the three bacterial strains of clinical interest: *Staphylococcus epidermidis* ATCC 12 228, *Staphylococcus aureus* ATCC 25 923, and *Escherichia coli* ATCC 25 922. Finally, it was concluded that the clays studied have the potential for technological applications in medicinal, therapeutic, and aesthetic treatments, and as raw material for obtaining biomaterials, due to their stability and biological safety.

Keywords: clays, biominerals, characterization, medical treatment.

Resumo

Este trabalho teve como objetivo avaliar a potencialidade das argilas do estado da Paraíba, visando suas aplicações em tratamentos medicinais, terapêuticos e estéticos. As amostras das argilas foram caracterizadas pelas técnicas de difração de raios X, composição química por fluorescência de raios X, termogravimetria, análise térmica diferencial, análise granulométrica por difração a laser, capacidade de troca catiônica e atividade antimicrobiana. Com base no estudo, concluiu-se que as argilas do estado da Paraíba apresentaram propriedades similares à argila comercial. A avaliação antimicrobiana revelou que as amostras não apresentaram atividade frente a três cepas bacterianas de interesse clínico: Staphylococcus epidermidis ATCC 12 228, Staphylococcus aureus ATCC 25 923 e Escherichia coli ATCC 25 922. Por fim conclui-se que as argilas estudadas possuem potencial tecnológico para aplicações em tratamentos medicinais, terapêuticos, estéticos e como matéria-prima para obtenção de biomateriais, em virtude da sua estabilidade e segurança biológica.

Palavras-chave*: argilas, biominerais, caracterização, tratamento medicinal.*

INTRODUCTION

Clays are fine-grained, earthy materials chemically formed from hydrated aluminum, iron, and magnesium silicates. They consist of extremely small crystalline particles of a restricted number of minerals known as clay minerals, and may also contain organic matter, soluble salts, quartz particles, pyrite, calcite, and other residual and amorphous minerals [1-3]. They are found in nature in a variety of types and colors and have many useful applications. Clays are some of the oldest materials used for healing purposes in traditional medicine [4-10]. Clay minerals have been used throughout the world for curative and preventive purposes. In traditional medicine, clay minerals have been used primarily in external applications such as clay baths, which aims to cure skin diseases, and for simple gastrointestinal diseases such as diarrhea [10]. In addition, clays were also used in nutrition and veterinary medicine [11-13]. The healing properties of clay minerals, passed down from ancient cultures, continue to be applied in modern life for the treatment of various topical and internal diseases. With emerging modern technologies, the advantages of using clay minerals for various industrial applications have also been explored. Clay minerals have specific physicochemical characteristics, such as high adsorption capacity, cation exchange capacity, colloidal and swelling capacity, optimum rheological behavior, and high dispersibility in water, which make them suitable for various biological applications, including pharmaceutical products, cosmetics, veterinary medicine, biomaterials, and biosensors, and are used as active ingredients or excipients. The qualitative and quantitative mineralogical composition, as well as the particle size distribution, are the main factors controlling the physicochemical properties of a particular clay [14, 15].

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The basic classification types for clays come from the decomposition over millions of years of feldspar and sedimentary rocks and are classified into two categories: primary and secondary. Primary clays are attacked poorly by atmospheric agents, have coarser particles and lighter coloration, are less plastic and have a high degree of purity with high refractoriness, an example being kaolinite. Secondary clays, however, are finer and more plastic and may contain aggregated impurities when mixed with organic matter [16]. Hydromicas (illites, montmorillonites, bentonites) are classes of clay having a structure of octahedral gypsum layers between two tetrahedral silica layers. This structure allows for higher water adsorption and ion exchange, with the most common substitution being Al^{3+} by Si^{4+} in the tetrahedral layers. They present a higher degree of plasticity (when compared to kaolinite) because they contain an extra sheet having weak intralayer bonds and a high specific area [17].

A material to be used in pharmaceutical formulations must have low or zero toxicity. The presence of some elements, even in trace amounts, can pose a potential threat for the patient [18]. Research on the interaction of clay minerals for medicinal, therapeutic, and aesthetic uses and the influence of these minerals on the cosmetic and therapeutic properties of clay are very important for people's well-being, since these clays must be adapted to a number of safety and stability requirements and should be chemically and microbiologically safe. This includes the selection of earthy materials containing clay minerals with suitable chemical, colloidal, and rheological properties, any water purification processes to increase the purity of these minerals, as well as control of the of heavy metal (arsenic, lead) content, granulometry, and microbial load. Studies on this subject in the literature are scarce, only being found in books containing technical definitions of the chemical composition of clay. Few papers on its therapeutic and aesthetic uses can be found [5, 18-32]. Papers about clay are dedicated almost exclusively to other areas, forgetting about other possible alternatives of using the clay. The objective of this study was to analyze the properties of clays from the State of Paraíba and compare them with commercially available clay for aesthetic use, highlighting their structural, thermal, chemical, granulometric, and antimicrobial characteristics.

MATERIALS AND METHODOLOGY

To carry out this study, the clays used were: one commercially available (AC - Commercial Clay, green in color, used for cosmetic purposes), one from an area located in the municipality of Boa Vista/PB (Cho - Chocolate clay, yellow in color), one from an area located in the municipality of João Pessoa/PB (BC - ball clay, white) and one industrialized clay (Cau - kaolinite clay, white). The samples were dried in an oven at approximately 60 °C, then ground in a ball mill and passed through an ABNT n° 200 (75 μm) sieve.

The characterization of the clays was carried out using the following techniques: granulometric analysis (GA, 1064, Cilas); cation exchange capacity (CTC) determined by the methylene blue adsorption method described in [33]; X-ray fluorescence spectroscopy (EDX 720, Shimadzu); X-ray diffraction (XRD 6000, Shimadzu) with CuKα radiation (40 kV/30 mA) and goniometer rotation of 2 °/min and interval of 0.02° over the range 5°-35°; thermogravimetric analysis (TG) and differential thermal analysis (DTA) (TA 60H, Shimadzu, and RB-3000, BP Eng.), with a heating rate of 12.5 °C/min in air (the maximum temperature for both cases was 1000 °C). The reference used for the DTA was calcinated aluminum oxide (Al_2O_3) and antimicrobial activity was determined in a sterile environment and performed against three bacterial strains of clinical interest: *Staphylococcus epidermidis* ATCC 12 228, *Staphylococcus aureus* ATCC 25 923, and *Escherichia coli* ATCC 25 922. For the antimicrobial activity assay, Mueller-Hinton broth (Kasvi) and Bacto agar (BD, Sparks) culture media were used on 90x15 mm plates. Samples were exposed to ultraviolet light for 30 min and diluted in sterile injection water before being added to the medium for analysis.

RESULTS AND DISCUSSION

Fig. 1 shows the particle size distribution curves of the samples used. It can be seen that the samples presented bimodal behavior. It was also possible to verify a concentration of particles having sizes between 2 and 5 μm. The samples presented a similar distribution of particles, with a higher percentage in the size range of 1 to 20 μm, with values close to those of the clay fraction percentage. With regard to the accumulated volume, D50 (diameter for 50%) was found at 2.27 μm for the AC sample, 2.47 μm for the Cho sample, 5.15 μm for the BC sample, and 5.35 μm for the Cau sample. Table I shows the granulometric composition values for the clays studied. Knowledge of particle size distribution features of the raw materials is essential for the right pre-formulation steps of cosmetic and pharmaceutical products. Based on the literature [34] the powder particle size distribution applicability can vary. Finer powders have higher skin adhesion and provide better softness when applied on the skin. From Table I, it can be observed that the studied samples had clay fractions between 26-46% and an average particle diameter of 3.98 and 4.63 μm for the AC and Cho samples, respectively, with larger diameter particles (10.48 and 11.60 μm) for the Cau and BC clays. AC and Cho clays showed only small differences for all of the parameters studied. This reduced particle size range suggested the application of clays in cosmetics. According to literature, particles smaller than 63.00 μm may have anti-inflammatory effects and may assist in the skin hydration, retaining moisture due to the high skin adhesiveness [25]. Comparing the particle size distribution results of the samples under study with results obtained in [35-48], it was verified that the presented values were similar, showing that these samples had similar physical and granulometric characteristics. All samples had higher mean diameters than that of commercial clay (AC).

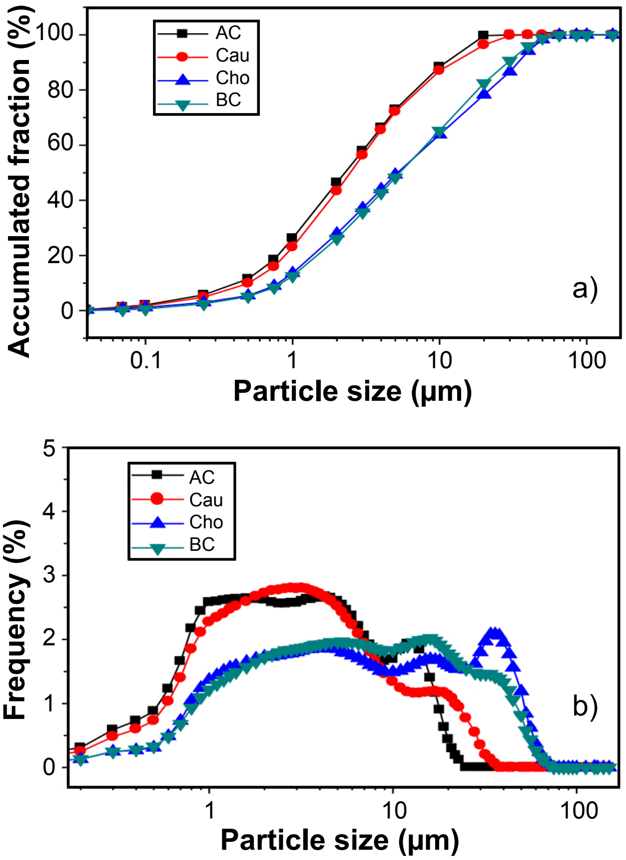

Figure 1: Particle size distribution curves of the studied clays: a) accumulated volume; and b) histogram.
[Figura 1: Curvas de distribuição granulométrica das argilas estudadas: a) volume acumulado; e b) histograma.]

Table I - Granulometric composition of the clays studied.
[Tabela I - Composição granulométrica das argilas estudadas.]

Sample	D<2 µm (%)	2<D<20 µm (%)	D>20 µm (%)	Average diameter (µm)
AC	46.42	53.26	0.32	3.98
Cho	43.30	53.06	3.64	4.63
BC	27.93	50.32	21.75	11.60
Cau	26.13	56.40	17.47	10.48

Table II contains the cation exchange capacity (CEC) results determined by the methylene blue method [33]. It was verified that samples AC and Cho presented only small differences between their CEC values, with clay Cho having a value within the range of the smectite group of clay minerals (80 to 150 cmol/kg) [49]. The AC clay produced a value lower than the range required by the group of smectites (60 cmol/kg), due to the presence of accessory minerals in large quantities. The CEC results of the smectic clay of 88 cmol/kg of dry clay is a typical value for bentonite clays from the State of Paraíba, determined by the methylene blue methodology and compatible with data found in [41, 44, 50]. According to [51], a CEC so high, of more than 70.0 cmol/kg, indicates the presence of a greater amount of montmorillonite mineral. The BC and Cau clays presented values within the range for clay minerals of the kaolinite group (3 to 15 cmol/kg), compatible with the literature [46, 47]. The kaolinite clays had a lower CEC than the smectite clays, because the stacking of the montmorillonite layers is governed by van der Waals forces, with negative charges between these plates generated by isomorphic substitutions that occur in the lattice, giving smectites a greater ability to exchange cations. The kaolinites have almost no isomorphic substitution because the layers are bound by hydrogen bonds, which are stronger bound, producing lower CEC.

Table II - Cation exchange capacity (cmol/kg)of the clays studied.
[Tabela II - Capacidade de troca de cátions (cmol/kg) das argilas estudadas.]

AC	Cho	BC	Cau
60.0	88.0	3.2	3.8

Table III shows the chemical composition of the clays studied. The analysis showed that they were rich in silicon and aluminum oxides (47.99% for AC, 55.42% for Cho, 44.98% for BC, and 45.39% for Cau), referring to both oxides present in the tetrahedral layer of the clay minerals and the free silica, an accessory mineral, as well as alumina. According to [6, 28], high amounts of silicon mean that the clay should be used in the reconstruction of skin tissues, besides providing tissue hydration and mitigation of possible skin inflammatory processes, and aluminum would inhibit the growth of microorganisms in a culture. In this way, the Cho clay, due to its higher silica content, should show a greater hydration effect, and the BC and Cau clays should be better microorganism growth inhibitors, due to their higher amount of alumina. Two of the samples were also observed to have high levels of iron oxide (AC clay: 10.59%, Cho clay: 8.69%), characteristic of the clay minerals from the smectite group, as observed in [49]. These values were associated with the isomorphic substitutions of the octahedral layer of bentonites and with accessory minerals and exchangeable cations in the basal layers of smectite and kaolinitic clay minerals, respectively. According to [6], iron, through electron transfer, would act on cellular respiration, and potassium would act on cellular ionic balance, aiding in their hydration. Therefore, AC, BC, and Cau clays, due to their potassium oxide content, should aid cell hydration, and AC and Cho should assist in respiration of the skin, due to their high iron content. According to [16], the AC (green) and Cho (yellow) clays have the greatest diversity of elements such as iron oxide associated with magnesium, calcium, potassium, manganese, phosphorus, aluminum, and silicon because they belong to the montmorillonite group. It was observed that the samples had a loss on ignition of 11.45% for AC clay, 8.97% for Cho clay, 14.70% for BC clay, and 14.87% for Cau clay, related to the loss of coordinated

Table III - Chemical composition (%) of commercial clay (CA), kaolin (Cau), chocolate (Cho) and ball clay (BC).
[Tabela III - Composições químicas (%) das argilas comercial (AC), caulim (Cau), chocolate (Cho) e ball clay (BC).]

Sample	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	TiO_2	K_2O	Other oxides	LOI
AC	47.99	23.56	0.67	10.59	2.62	1.43	1.41	0.76	11.45
Cau	45.39	37.94	-	0.53	-	0.04	1.14	0.10	14.87
Cho	55.42	18.11	2.38	8.69	3.24	1.00	0.63	2.19	8.97
BC	44.98	37.56	-	0.41	0.88	-	1.35	0.12	14.70

LOI: loss on ignition; '-' absent

and adsorbed waters, hydroxyls of clay minerals, organic matter, and other materials. Comparing against the values determined for clays from other municipalities [36-38, 41, 45, 52-57], it was verified that the Cho sample and even the AC commercial clay had values similar to the bentonite clays. The values obtained were also corroborated in [23, 58]. Comparing the values determined for the clays studied in [46, 47, 52], it was verified that the samples under study had values similar to those of kaolinite clays.

Fig. 2 illustrates the thermogravimetric curves and mass loss of the clays studied. The results for the thermal decomposition steps of the clays are shown in Table IV. The values observed in the decomposition stages are initial temperature - T_i (°C), final temperature - T_f (°C), mass loss (mg and %), and total mass loss (%). It can be verified in Fig. 2 that three stages of thermal decomposition occurred for the clays studied. The first stage was between 25 and 274 °C, resulting in a mass loss of 13.83% for AC clay. For Cho clay, the value was very similar, with a mass loss of 13.86% between 27 and 210 °C. The Cau and BC samples also had similar stage in the range of 22 to 197 °C with mass loss of 0.85% and 23 to 130 °C with mass loss of 0.70%, respectively. The second decomposition stage of the AC and Cho clays was between 274 and 553 °C with a mass loss of 5.69%, and 210 and 591 °C with loss of 4.38%, respectively. For the Cau and BC clays, the decomposition was between

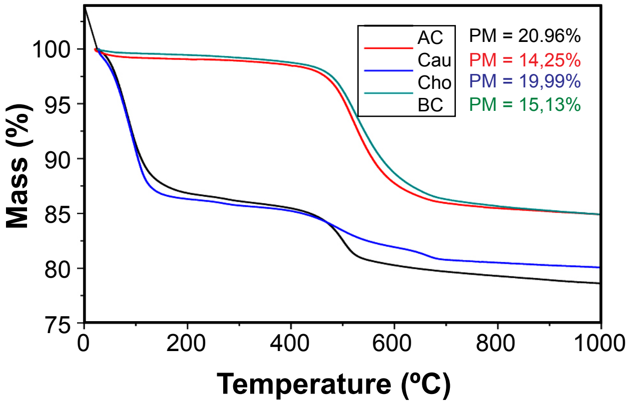

Figure 2: Thermogravimetric curves of commercial clay (CA), kaolin (Cau), chocolate (Cho), and ball clay (BC).
[Figura 2: Curvas termogravimétricas das argilas comercial (AC), caulim (Cau), chocolate (Cho) e ball clay (BC).]

Table IV - Values obtained from the thermogravimetric curves of commercial clay (CA), kaolin (Cau), chocolate (Cho) and ball clay (BC).
[Tabela IV - Valores obtidos das curvas termogravimétrica das argilas comercial (AC), caulim (Cau), chocolate (Cho) e ball clay (BC).]

Sample	Loss stage	T_i (ºC)	T_f (ºC)	Mass loss (mg) / (%)	Total mass loss (%)
AC	1st	25	274	4.79 / 13.83	20.96
	2nd	274	553	2.12 / 5.69	
	3rd	553	1000	0.52 / 1.44	
Cau	1st	22	197	0.22 / 0.85	14.25
	2nd	197	599	1.59 / 11.10	
	3rd	599	1000	0.61 / 2.30	
Cho	1st	27	210	5.24 / 13.86	19.99
	2nd	210	591	1.92 / 4.38	
	3rd	591	1000	0.38 / 1.75	
BC	1st	23	130	0.11 / 0.70	15.13
	2nd	130	638	1.73 / 12.70	
	3rd	638	1000	0.26 / 1.73	

197 and 599 °C with a mass loss of 11.10%, and 130 and 638 °C, with a loss of 12.70%, respectively. Finally, the third stage of decomposition was from 553 to 1000 °C with a mass loss of 1.44% for AC clay, and from 591 to 1000 °C with a mass loss of 1.75% for Cho clay. For the Cau clay, the mass loss was 2.30% from 599 to 1000 °C, and for BC clay the mass loss was 1.73% over the range from 638 to 1000 °C. The total mass lost was 15.13% and 14.25% for the BC and Cau clays, and 19.99% and 20.96% for the Cho and AC clays, respectively, corresponding to water loss, organic matter loss, hydroxylation, and mullite nucleation.

Fig. 3 illustrates the curves and the events of the differential thermal analysis of the clays under study. The peak temperatures of the first event were 137 and 147 °C for AC and Cho clays, respectively, and 82 and 86 °C for Cau and BC clays, respectively. These were attributed to the temperatures of the endothermic event caused by the loss of free and adsorbed water and the combustion of raw material. The second event peak temperatures for the Cho and AC clays were 562 and 570 °C, respectively, and for the Cau and BC clays were 572 and 601 °C, respectively. These were attributed to the presence of hydroxyls from the octahedral layer of smectite and kaolinite. In the DTA curves it was possible to observe a phase change at the temperatures of the exothermic event at approximately 918 and 910 °C, for the AC and Cho clays, respectively, and at 992 and 996 °C for BC and Cau clays, respectively. These were attributed to nucleation of the mullite. In short, the AC and Cho samples presented similar thermograms typical of smectic clays, while the BC and Cau clays also had similar results, characteristic of kaolinite materials. Comparing the results of these thermograms with those found in previous studies [36-38, 42, 45-47, 52, 57, 59], the typical behavior of bentonite and kaolinite clays from the State of Paraíba was observed. However, it is important to note that in the literature there are few studies on clays for medicinal and cosmetic purposes, making it difficult to relate these thermal transformations to their uses. In the literature, only a relationship between colors and possible therapeutic uses is found.

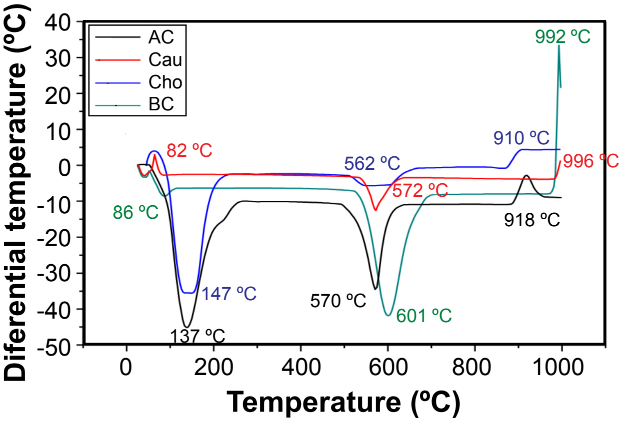

Figure 3: DTA curves of commercial clay (AC), kaolin (Cau), chocolate (Cho), and ball clay (BC).

[Figura 3: Curvas de DTA das argilas comercial (AC), caulim (Cau), chocolate (Cho) e ball clay (BC).]

Fig. 4 shows the X-ray diffraction patterns for the clays studied. The mineralogical composition of the samples was as follows: smectite (JCPDS 29-1497) at interplanar distances 14.10, 4.41, and 3.10 Å for Cho clay, and 15.19 and 4.45 Å for AC clay; kaolinite (JCPDS 14-0164) at interplanar distances of 7.09, 4.43, and 4.15 Å for Cau clay, 7.16 and 3.57 Å for BC clay, and 7.18 and 2.33 Å for AC clay; mica (JCPDS 42-1339) at interplanar distances of 9.00 Å for Cau clay, and 9.94 and 4.98 Å for BC clay; and the presence of accessory minerals such as quartz (JCPDS 46-1045), characterized by interplanar distances of 4.25, 3.33, and 2.24 Å. The diffractogram of the AC clay was found to be similar to the studies performed in [22, 58], where the kaolinite phase was predominant, with the presence of quartz and an expansive mineral, smectite. Because it is a green clay, according to [16], its qualitative mineralogical composition corresponds to a mixture of quartz, smectite, and kaolinite. The results of the Cho and BC clays were similar to other studies [36-38, 42, 45-47, 52, 57, 59], with smectic and kaolinite clays from the municipalities of the Boa Vista region, such as Pedra Lavrada/PB, Cubatí/PB, Sossego/PB, and João Pessoa/PB. The four samples studied presented similarities among themselves making them usable for the same purposes. These results were consistent with the mineralogical compositions reported in the literature for commercial clays samples used in pharmaceutical and cosmetic products [22, 60]. Smectites and kaolinites are widely used in cosmetic products, such as cosmetic creams, powders and emulsions, and pharmaceutical products, including gastrointestinal protectors, antidiarrheals, dermatological protectors and anti-inflammatories [10].

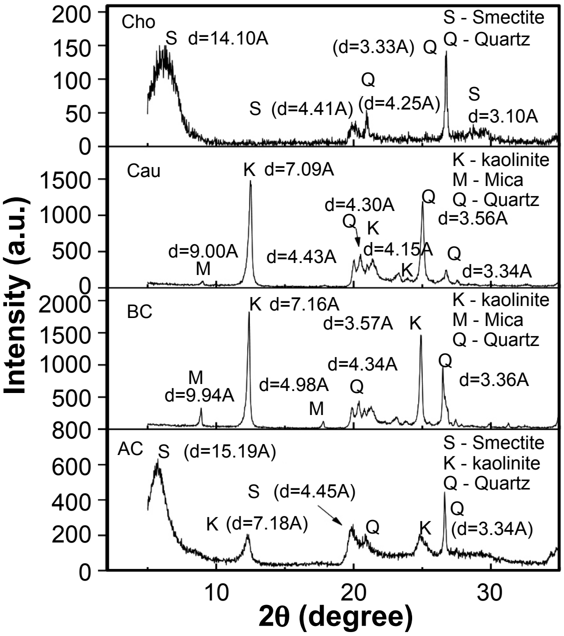

Figure 4: XRD patterns of the chocolate clay (Cho), kaolin (Cau), ball clay (BC), and commercial clay (AC).

[Figura 4: Difratogramas de raios X das argilas chocolate (Cho), caulim (Cau), ball clay (BC) e comercial (AC).]

Fig. 5 shows the antimicrobial activity of AC, Cho, Cau, and BC clays in a sterile environment and performed against three bacterial strains of clinical interest: *Staphylococcus epidermidis* ATCC 12 228, *Staphylococcus aureus* ATCC 25 923, and *Escherichia coli* ATCC 25922. The results of the antimicrobial activity point to the absence of contaminating microorganisms. The images show the absence of bacteria, demonstrating that there was no risk of bacterial contamination in any of the clays studied that may compromise the system, making them biologically safe and without antimicrobial activity. The same results were obtained in [20, 23, 26], using cosmetic formulations based on bentonite clays.

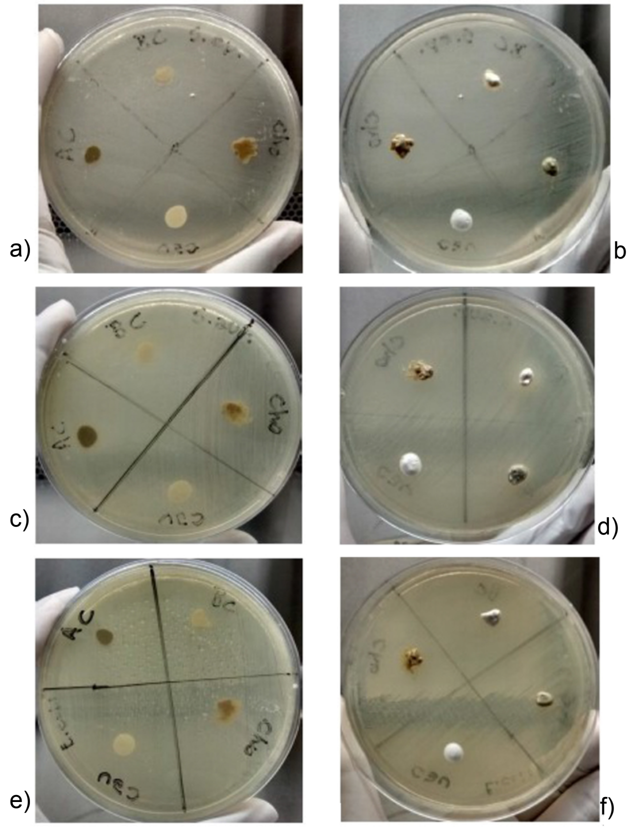

Figure 5: Antimicrobial activity of ball clay (BC), Chocolate (Cho), kaolin (Cau), and commercial clay (AC) against strains of *Staphylococcus epidermidis* ATCC 12 228 (a,b), *Staphylococcus aureus* ATCC 25 923 (c,d), and *Escherichia coli* ATCC 25 922 (e,f). *[Figura 5: Atividade antimicrobiana das argilas ball clay (BC), chocolate (Cho), caulim (Cau) e comercial (AC) frente às cepas de Staphylococcus epidermidis ATCC 12 228 (a,b), Staphylococcus aureus ATCC 25 923 (c,d) e Escherichia coli ATCC 25 922 (e,f).]*

CONCLUSIONS

After the characterization studies on the clays from the State of Paraíba for application in medicinal treatments, it was concluded that the samples studied presented results similar to those of commercial clay. The antimicrobial evaluation revealed that the samples did not present antimicrobial activity against the three bacterial strains of clinical interest tested, without the possibility of microorganisms compromising the system, as the results were negative for bacterial growth. Therefore, it is concluded that the clays present potential for technological applications in medicinal, therapeutic and aesthetic treatments.

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