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Article

Solid-state properties of pink clay from Jequitinhonha Valley in Brazil for pre-formulation study

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Clay minerals are still widely used in pharmaceutical products for human health and cosmetic purposes. Pre-formulation studies were conducted to identify solid-state properties of pink clay, a sample from Diamantina, Brazil. Among the solid properties to be analyzed, we have selected type identification, iron phases, crystallinity, powder flow characteristics, thermal behavior, and non-isothermal phase transition kinetics. The pink clay is composed of (1:1) clay type and kaolinite as the main component. The Mössbauer spectrum of pink clay shows Fe^{3+}(α-Fe_2O_3) hematite, Fe^{2+}, and Fe^{3+} with large $\Delta/2\xi q$ of about 2.80 and 2.69 $mm.s^{-1}$ respectively, related to iron silicates, most likely pyroxene, and a superparamagnetic Fe^{3+}. Pink clay exhibits poor flow properties. The thermal behavior indicates a phase-transition between 400 - 600 ºC associated with the dehydroxylation of the pink clay system requiring ~300 kJ mol^{-1}, being constant until the process reaches a conversion of ~50% when the energy is enhanced to ~530 kJ mol^{-1}, concluding the whole dehydroxylation process (α=80%). Solid-state properties and characteristics found for the pink clay must be considered for the proper design of formulations. This type of clay shows unique pharmaceutical properties that can be favorably exploited by the cosmetic industry.

Keywords: Pink clay mineral. Thermal behavior. Iron phases. Powder technology. Solid-state stability. Kinetic study.

INTRODUCTION

Minerals are widely used in the pharmaceutical industry as active ingredients or excipients, performing functions such as lubricants, desiccants, disintegrants, diluents, binders, pigments, and opacifiers, as well as emulsifiers, thickeners, isotonic agents, skin oil controllers, anti-cracking agents, flavor correctors and drug delivery (Bejaoui, Kalfat, Galai, 2021; Carretero, Pozo, 2010, 2009; Silva, Fortes, Tomé, Silva Filho, Freitas, Soares-Sobrinho *et al*., 2021; Yendluri, Lvov, de Villiers, Vinokurov, Naumenko, Tarasova *et al*., 2017). Pharmaceutical grade clay minerals usually applied in human health are kaolinite, talc, smectites (montmorillonite, saponite, and hectorite), and fibrous clays (palygorskite and sepiolite) (Silva, Fortes, Tomé, Silva Filho, Freitas, Soares-Sobrinho *et al*., 2013).

Clay minerals are primarily composed of silicates, alumina, magnesia, water, and a varied concentration of potassium, sodium, and calcium, among other metal ions. The three-dimensional structure and mineralogical composition determine the plastic properties of a clay (Moore, Reynolds, 1989) and, consequently, its designation in the pharmaceutical industry (Carretero, Pozo, 2010).

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Clays are abundant, low-cost, and sustainable materials, presenting high specific surface area and adequate ion exchange capability (Moore, Reynolds, 1989). In semi-solid pharmaceutical formulations, clays are used to stabilize dispersed systems and ajust the preparations rheological patterns. In solid pharmaceutical formulations clays are applied to the dispersion on the formation of the physically stable amorphous system (Bejaoui, Kalfat, Galai, 2021). For a proper pharmaceutical formulation, the physical and chemical properties must be well established (Aulton, Taylor, 2016; Browne, Feldkamp, White, Hem, 1980; Iwasaki, Onodera, Torii, 1989).

With advances in cosmetology, clays received recognition as materials with active properties, instead of the traditional contributions in the formulation base (Silva Favero, dos Santos, Weiss-Angeli, Gomes, Veras, Dani *et al*., 2019; Gamoudi, Srasra, 2018, 2017; López-Galindo, Viseras, Cerezo, 2007; Silva-Valenzuela, Chambi-Peralta, Sayeg, de Souza Carvalho, Wang, Valenzuela-Díaz, 2018). Clays with Fe, Zn, and silicon are essential in the cosmetic skin treatment, as iron acts as antiseptic and a cell renewal catalyst, silicon reconstructs skin tissues, providing hydration and a smoothing effect, while zinc and magnesium are invigorating (Matike, Ekosse, Ngole, 2011; Mattioli, Giardini, Roselli, Desideri, 2016).

The solid-state properties of clays can be modified to suit their purpose (Marosz, Kowalczyk, Gil, Chmielarz, 2020), including cosmetics. For instance, changes in the hydrophilic-lipophilic aspects (Silva, Oliveira, Farias, Fávaro, Mazzilli, 2011) allow the clays to incorporate active pharmaceutical ingredients (API) of different polarities and modulate their capacity of sorption in the control of the skin oiliness. This clay–API association is often possible through heat treatment; therefore, thermal decomposition is not desired along this process. Furthermore, the kinetics of the whole pink clay thermal degradation by dehydroxylation is now investigated using the traditional Vyazovkin isoconversional method, whose application for clay minerals characterization is still unknown at present. Four heating rates dynamic thermogravimetry (TG) curves were obtained in the inert atmosphere, and the activation energy (Ea) along the conversion degree is determined (Vyazovkin, Chrissafis, Di Lorenzo, Koga, Pijolat, Roduit *et al*., 2014). Several studies have been published using the Vyazovkin method from data on the thermal behavior of pharmaceutical systems (Silva, Fialho, Barbosa, Araujo, Carneiro, Sebastião *et al.* 2021; Freitas-Marques, Araujo, da Silva, Fernandes, Mussel, Sebastião, Yoshida, 2019; Freitas-Marques, Araujo, Fernandes, Mussel, Sebastião, Yoshida, 2020; Freitas-Marques, Araujo, Mussel, Sebastião, Yoshida, 2021). The Vyazovkin method is applied at short intervals, allowing an indirect analysis of multiple steps, as the activation energy varies according to the α degree (conversion process). Therefore the thermal phenomenon that involves mass loss can have its kinetics determined by isoconversional treatment (Vyazovkin, 2015) to give full support in the understanding of the changes in solid-state properties, development, and chemistry of the materials, as proposed.

Brazil has a diversified geological formation, such as pink clay, whose samples were collected in Diamantina, Jequitinhonha Valley. Another clay system has been studied for pre-formulation of face masks applied in cosmetics, evidencing the advantages of using natural specific clays systems in the cosmetics industry (López-Galindo, Viseras, Cerezo, 2007).

MATERIAL AND METHODS

The pink clay sample from Diamantina city, Jequitinhonha Valley in Brazil was used.

Powder X-ray diffraction (PXRD)

The PXRD data for pink clay were obtained using a Shimadzu diffractometer, XRD-7000, under 40 kV, 30 mA, using Cu Kα, measured from 5 - 40° 2θ with a step size of 0.02° and a time constant of 1.2 s step^{-1}, using a graphite monochromator, in a parallel focusing geometry under 30 rpm to minimize any remained preferred orientation. Rietveld refinement was performed using the FullProf Suite 2019.

The ethylene glycol swelling clay test

The swelling property for the pink clay system was evaluated using ethylene glycol (Moore and Reynolds, 1989); 20 mg of widely spread clay over a watch glass was

conditioned in a glass vat containing 50 mL of ethylene glycol in an open becker. The system remained closed for inner atmosphere saturation for 24 h. After this period, the sample was analyzed by PXRD for comparison to the untreated pink clay.

Mössbauer spectroscopy

The Mössbauer spectrum was collected at room temperature (~298 K) in the constant acceleration transmission mode with a ~20 mCi ^{57}Co/Rh gamma-ray source. Data were stored in a 512-channel MCS memory unit, with Doppler velocities ranging between approximately ±12.0 mm s^{-1}. Isomer shift values are quoted relative to an α-Fe foil at room temperature. The experimental data were least square-fitted to Lorentzian-shape resonance lines, with the WinNormos™ fitting program.

Powder Flow

Powder flow properties of pink clay were assessed accordingly with the British Pharmacopoeia (The British Pharmacopoeia Commission, 2021) and the United States Pharmacopeia (United States Pharmacopeial Convention, 2018).

Compressibility index and Hausner ratio

First, a 250 mL graduated cylinder was filled with 100 g deagglomerated clay powder, which was carefully leveled without compacting, if necessary. The initial unsettled apparent volume (V_0) was then determined. The cylinder was then tapped 100, 500, 1250, and 2500 times and the tapped volume (V_f) was determined in each stage up to constant volume, i. e., the difference between these stages was < 2%. Bulk density (ρ_{bulk}) and tapped density (ρ_{tapped}) were directly calculated from V_0 and V_f after 1250 cycles, respectively.

Compressibility index and Hausner ratio were respectively determined from the equations:

$$Compressibility\ index = \frac{\rho_{tapped} - \rho_{bulk}}{\rho_{tapped}}$$

$$Hausner\ ratio = \frac{\rho_{tapped}}{\rho_{bulk}}$$

Powder with Hausner ratio 1.00-1.11, 1.12-1.18, 1.19-1.25, 1.26-1.34, and >1.35 indicates excellent, good, fair, passable, and poor flow, respectively. In the same way, powders with compressibility index ≤10, 11-15, 16-20, 21-25, 26-31, 32-37, >38 are associated with excellent, good, fair, passable, and poor flow, respectively.

Angle of repose

The angle of repose was determined by the flow of the powder from a funnel to a vibration-free circular base. The funnel height was varied to carefully build up a symmetrical cone of powder, maintaining the distance of approximately 2-4 cm from the top of the powder pile as it was being formed. The height of the powder cone was measured and the angle of repose was calculated from the following equation:

$$tan(\alpha) = \frac{height}{0.5base}$$

The angle of repose values 25-30°, 31-35°, 36-40°, 41-45°, and >46° indicate powder with excellent, good, fair, passable, and poor flow, respectively.

Thermal Analysis

Thermogravimetry (TG) and Differential Thermal Analysis (DTA) simultaneously evaluated the thermal behavior of the pink clay sample. The obtained TG/DTA curves use a Shimadzu DTG60H, with a heating rate of 10 ºC min^{-1} in the temperature range of 30 up to 1100 ºC, under a dynamic nitrogen atmosphere at 50 mL min^{-1} in an alumina crucible with sample mass of about 2.5 mg accurately weighted. This temperature range is essential for proper physical-chemical characterization. It is important in the identification of the whole sample and all thermal phenomena, from a mineral composition, requiring higher temperature ranges, usually above 1000ºC. The heat-treated sample undergoes a temperature program control, and the

residue is analyzed for following up any phase changes by PXRD.

Non-isothermal kinetic study

Four TG curves were obtained using a Shimadzu DTG60H, with a heating rate (β; i =1,...,n) of 5, 7.5, 10, and 15 ºC min^{-1}, in the temperature range (T) of 30 up to 1100 ºC. These curves were treated by the traditional isoconversional nonlinear Vyazovkin method (Vyazovkin, 2015) to determine activation energy (Ea) along with the extent of the reaction (α). The equation of this method is represented as:

$$\sum_{i=1}^{n}\sum_{j\neq 1}^{n}\frac{I(E_\alpha,T_{\alpha 1})\beta_j}{I(E_\alpha,T_{\alpha 1})\beta_i}=minimum$$

RESULTS AND DISCUSSION

For the proper characterization of clays, it is necessary to define the types of silicate coexisting in the sample. Using basal PXRD reflections of an oriented aggregate make it almost impossible to distinguish between one or all occurrences in the same sample. The Rietveld refinement exhibited the quality index R-factor (Rwp) of 0.091 (Figure 1).

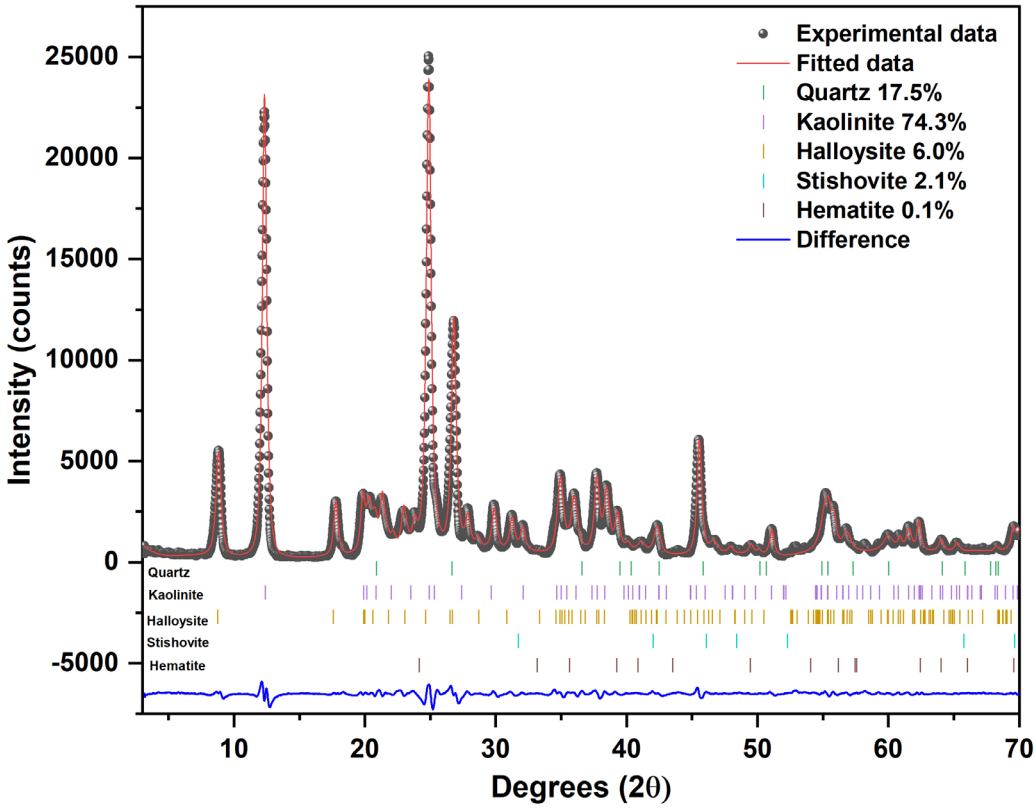

FIGURE 1 - X-Ray Rietveld refinement of the raw pink clay sample.

The ethylene glycol expansion experiment aimed to help in the identification of the silicate mixture in the sample. As observed in Figure 2, there is an overlay between both patterns of the raw pink clay (black line) and pink clay treated with ethilenoglycol (red line), which is indicative that the clay has not expanded. The result is characteristic of a whole clay sample mainly composed of (1:1) clay type only.

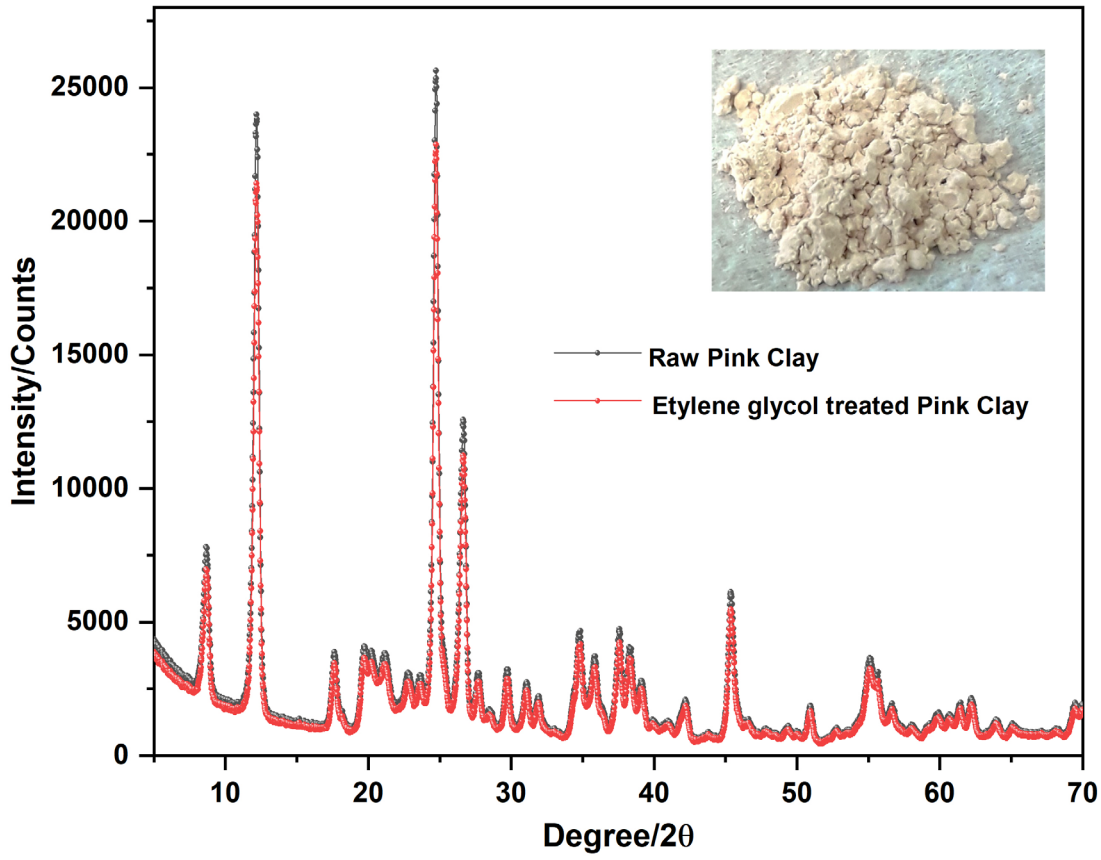

FIGURE 2 - The PXRD of raw pink clay sample (black line) and treated with ethilenoglycol (red line). In detail, a real sample image.

For cosmetic applications, the clay color plays an important role. The pink color is due to the small number of iron compounds, such as hematite and goethite, or ion substitution on the original clay structure. For a complete characterization, Mössbauer spectroscopy was applied. Mössbauer spectroscopy provides quantitative information on the oxidation state of Fe species, being a powerful tool to determine the contribution of Fe ions in a sample. The Mössbauer spectrum of the pink clay system shows four components, identified as Fe^{3+}(α-Fe_2O_3) hematite, Fe^{2+} and Fe^{3+} with large $\Delta/2\xi q$ of about 2.80 and 2.69 $mm.s^{-1}$ respectively, related to silicate iron, most likely pyroxene, and a superparamagnetic Fe^{3+}. The superparamagnetic iron could be related to the small amount of nano-goethite, ferrihydrite not directly identified by X-ray diffraction in the sample, lepidocrocite, and the Fe^{3+} in pyroxene. Due to the small particle size, not visible at the X-ray experiment, the presence is confirmed in the intense inner duplet at the Mössbauer spectroscopy, suggesting a superparamagnetic behavior. Some of them were already identified in the X-ray experiment, as well as the tiny crystalline size of hematite, one of the two main color components (Figure 3, Table I).

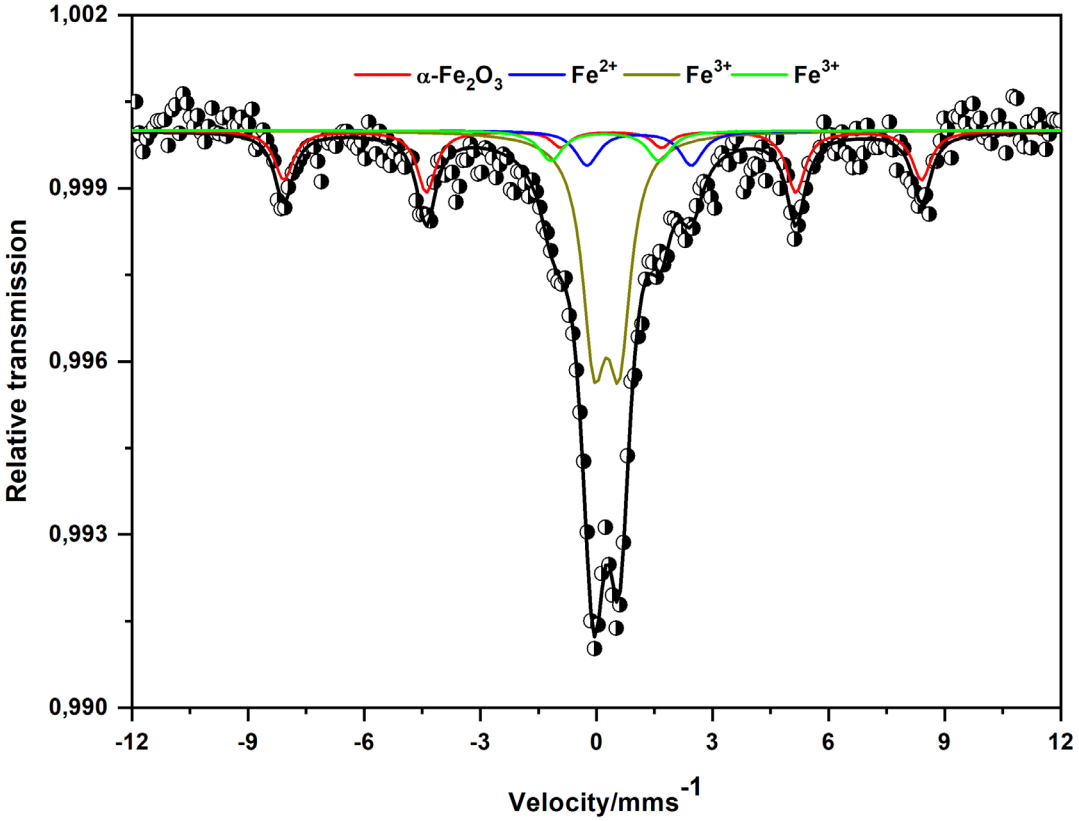

FIGURE 3 - The Mössbauer spectrum at room temperature for pink clay sample.

TABLE I - The fitted Hyperfine parameters for all iron contributions identified in the pink clay sample

Ion/compound	δ (± 0.05) mm/s	Δ/2ξq (± 0.05) mm/s	BHF (± 0.5) Tesla	Area (%)
$Fe^{3+}(\alpha\text{-}Fe_2O_3)$	0.37	-0.22	51.1	24
Fe^{3+}	0.36	0.66	-	57
$Fe^{3+(*)}$	0.31	2.80	-	9
$Fe^{2+(*)}$	1.20	2.69	-	10

*Large **Δ/2ξq** associated with a silicate Mössbauer typical parameters.

Usually represented by the formulae $XY(Si,Al)_2O_6$, pyroxene is formed by a net of silicon oxide octahedrons, usually monoclinic or orthorhombic, with X represented by Ca^{2+}, Na^{+}, Fe^{2+}, and Mg^{2+}, while Y is equivalent to smaller ions such as Al^{3+}, Fe^{3+}, and Mg^{2+}.

The very fine particles suggest some amount of superparamagnetic Fe atoms, as evidenced by the Mössbauer experiment. PXRD shows the presence of hematite ($\alpha\text{-}Fe_2O_3$) as well as a small amount of goethite (α-FeOOH), both minerals being associated with the pink color of the clay. Kaolinite is present as the primary phase associated with a small amount of halloysite. In the geoformation of kaolinite, some Fe^{3+} may be present in the structure, as an isomorphic or interstitial substitution, usually found in the mineral, demanding the necessity of iron extraction, increasing the whiteness of the kaolinite, especially used in the paper industry as filler.

The high $\Delta/2\xi q$ = 2.80 mm/s associated with low δ = 0.31 mm/s suggests the presence of Fe^{3+} from the epidote family, a sorosilicate mineral, formula $Ca_2(Al, Fe)_3(SiO_4)3(OH)$. The δ of 1.2 mm/s and $\Delta/2\xi q$ of 2.69 mm/s also indicate some complex aluminum silicate containing iron, such as $Al_{2-x}Fe_xO_5Si$ family compounds. Mössbauer spectroscopy is not a routine technique applied to pre-formulation studies and quality control in pharmaceutical materials, due to the analytical peculiarity. However, as observed, it is an essential tool for the identification of iron phases in pink clay minerals.

A direct correlation between the Rietveld and Mössbauer fitting results needs to consider at least two crucial points. The PXRD shows only the detectable crystalline phases, whether it contains or not iron in the structure. The Mössbauer Fe57 spectroscopy is an iron probe technique evidencing only the components that contain iron atoms. Therefore, both technics are complementary, not straightly related. Not all crystalline phases detected by PXRD will contain iron atoms. The Mössbauer spectrum may present iron phases not detected by PXDR mainly due to dilution effects, the limit of detection, or even due to low crystallinity. As seen in the whole studied sample, only 0.1 mass % is hematite, responsible for the pink color of the raw clay sample, which will represent the main Mössbauer spectrum phase and which is consistent with what is found in other natural clays with shades of pink. Tiny amounts of silicate phases not resolved from the significant overlap of the PXRD are present as Fe phases in the Mössbauer spectrum with high $\Delta/2\xi q$. The silicate analysis is very complex in PXRD analysis due to superpositions of the reflection planes. They differentiate in the Mössbauer spectra. By Mössbauer spectroscopy, it is not possible to assure the crystallinity of the components. The occurrence of a small amount of hematite seen by Mössbauer spectroscopy is enough to generate color to the clay. Another feature is the small amount of goethite detectable in the Mössbauer fitting. This small amount is not visible in the PXRD as an isolated phase. The whole clay sample PXRD shows between 20 – 30 degrees 2θ an amorphous fingerprint, as broad background. The observation suggests that goethite detected in the Mössbauer fitting is an amorphous phase, therefore not visible in the PXRD as a crystalline phase. It may also indicate that part of the observable goethite could be responsible for some superparamagnetic contribution in the inner duplets on the Mössbauer spectrum (Olowe, Refait, Genin, 1990).

Studies have been conducted to obtain atomic coordinates and to propose a model that describes the structure of the main components of clays such as dickite (Dera, Prewitt, Japel, Bish, Johnston, 2003; Yan, Wang, 2018), nacrite (Jaafar, Rhaiem, Ben, Amara, 2016), and kaolinite (Teixeira, Brandão, Nunes, 2017). Our results show kaolinite as the main component of the studied pink clay, 1:1 layer (Figure 4), inner hydroxyl groups (red and light pink), a tetrahedron (dark blue), and octahedron (light blue), iron atoms replaces silicate and aluminum sites in kaolinite.

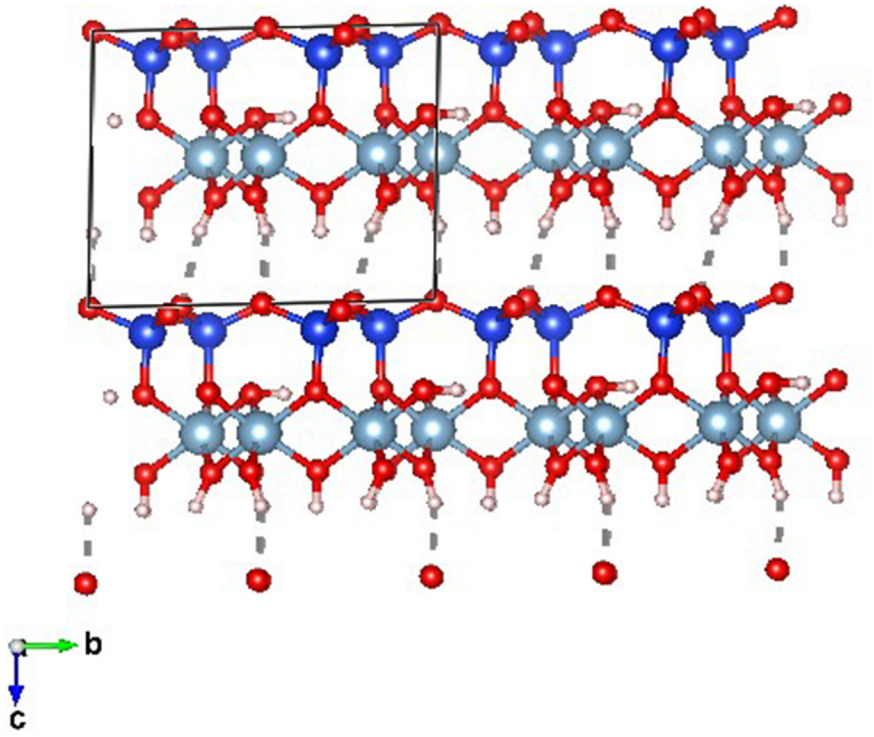

FIGURE 4 - Ball-and-stick model of kaolinite, the main component of pink clay. In the square is represented the 1:1 layer. Color scheme: tetrahedron - dark blue, octahedron - light blue, oxygen - red, hydrogen - light pink.

Knowledge of the flowability properties of powders is crucial in the manufacturing process as it directly impacts the choice of excipients, adequate quantities, unit operations, equipment, and process parameters (Patel, Patel, Patel, 2009). The powder flow properties of pink clay for the pre-formulation study are described in Table II. As observed, pink clay does not have satisfactory flow properties for use in the solid-state. The poor flow of the clay powder is expected. This can be justified by the small particle size, which increases the contact surface and favors its cohesion. The poor flow is directly associated with the primary cosmetic action of the clay, which is as adsorbent for skin oils (Browne, Feldkamp, White, Hem, 1980). For cosmetic use, the face mask is semi-solid, so the impacts of the flow properties of the pink clay will be relevant in the mixing stage with the possible components of the formulation, information to be considered in powder technology manipulation.

TABLE II - Powder flow properties of pink clay

Parameter	Value	Flow property
Compressibility index	41.2 %	Poor
Hausner ratio	1.70	Poor
Angle of repose	43.6°	Passable

Another important property of clays is the ability to swell. Non-expansive clays are not suitable for adsorptive applications (Chauhan, Saini, Suthar, 2019); nevertheless, the thermal activation can be applied for physicochemical tunning of the laminar clays (Ilić, Radonjanin, Malešev, Zdujić, Mitrović, 2016; Padilla-Ortega, Medellín-Castillo, Robledo-Cabrera, 2020; Yan, Wang, 2018), as observed for the raw pink clay system in this study. The TG/DTA followed the thermal phase transition. TG curve of pink clay showed a significant mass loss effect, between 400 – 600 ºC, about 9% (Figure 5A), region I to II. This temperature range is characteristically associated with kaolinite dehydroxylation (Brindley, Nakahira,

1956; Silva-Valenzuela, Chambi-Peralta, Sayeg, de Souza Carvalho, Wang, Valenzuela-Díaz, 2018), in full accordance with the X-ray diffraction shown in Figure 5B, I, and II. At 600 ºC an "arch band" pattern could be observed between 15 to 33° 2θ in the PXRD pattern, indicating the occurrence of an amorphous contribution of meta-dickite, an occurrence also found by Yan, Wang (2018) (Figure 5B, II). The dehydroxylation of the main component generates aluminum silicates and SiO_2 polymorphs such as silimanite, quartz and SiO_2 polymorphs. Further heating generates quartz and sillimanite (Figure 5A, III) for instance, in a full dehydroxylation process of kaolinite (Figure 5B, III). The peaks positions and identification were obtained by Le Bail peak extraction and search match (Le Bail, 2005; Peterson, 2005).

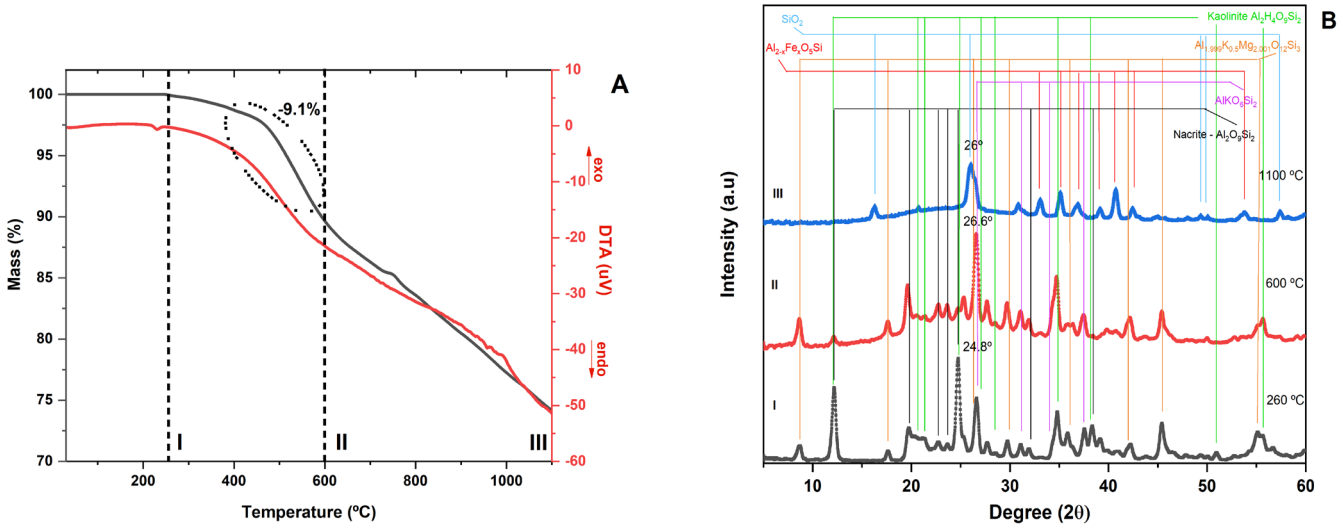

FIGURE 5 - Thermogravimetry and Differential Thermal Analysis TG/DTA simultaneous (A) and X-ray diffraction after heat treatment at 260 (I), 600 (II), and 1100 ºC (III) (B) of pink clay sample.

The determination of the dehydroxylation kinetics of clays has been studied for a long time (Brindley, Nakahira, 1956). Factors relating to the form of the specimen, (shape, size, compaction, container, etc.) and geological formation can influence the dehydroxylation process. Figure 5 presents the conversion degree along with the temperature, $\alpha(T)$, calculated from the four TG curves with heating rates of 5, 7.5, 10, and 15 ºC min^{-1} in the temperature range of 400 up to 600 ºC, corresponding to the dehydroxylation phenomenon, as observed in Figure 6. The conversion degree was determined using $\alpha_i = m_i - m_t/m_i$ being m_i the initial mass, m_t the mass at time t, and m_f the final mass.

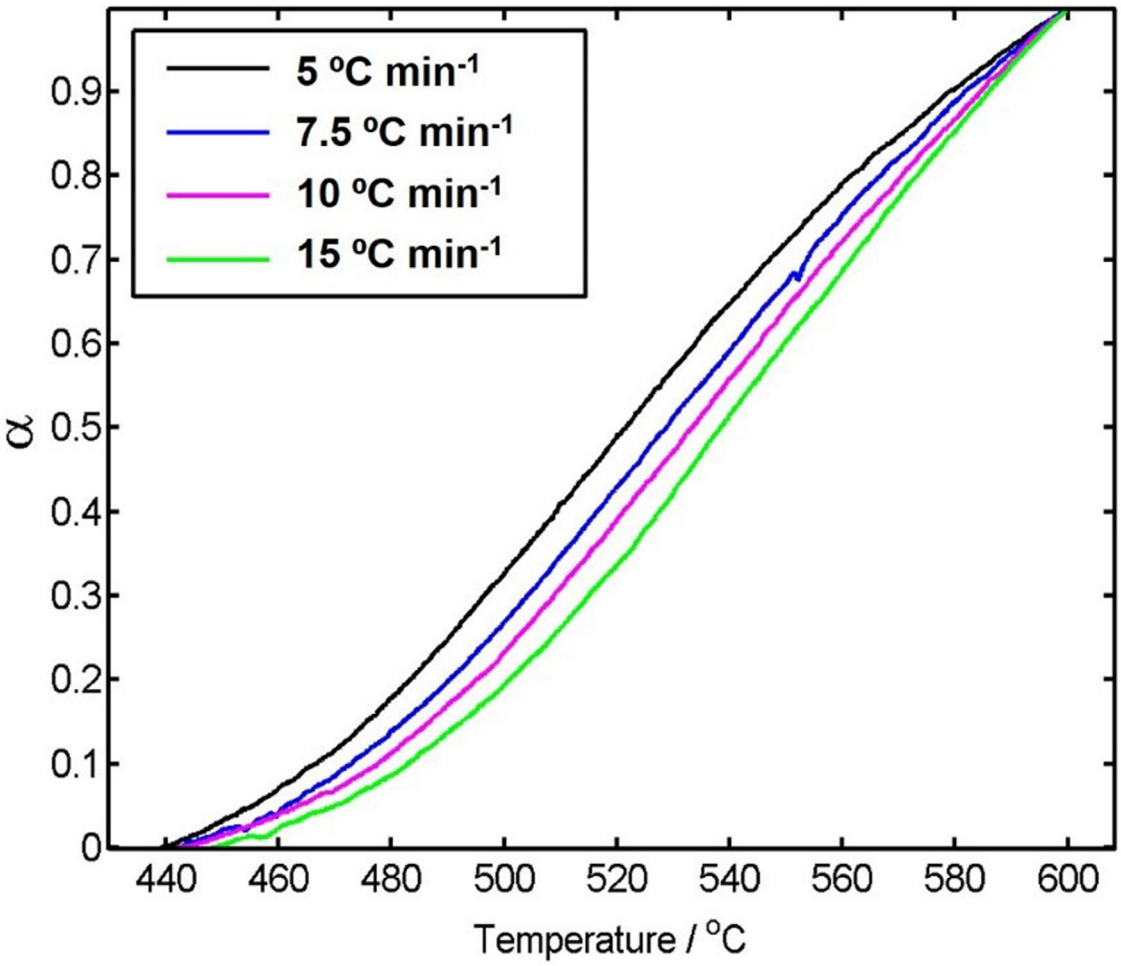

FIGURE 6 - Dehydroxylation fraction (α) of the pink clay system at different heating rates between 400 – 600 ºC.

A displacement of the curves was observed according to the heating rate, 5, 7.5, 10 and 15 ºC min^{-1}, as expected (Cavalheiro, Ionashiro, Breviglieri, Marino, Chierice, 1995) and the separation between the curves attest the experimental suitability, as previously described (Carvalho, Braga, Freitas-Marques, Sebastião, 2020; Freitas-Marques, Araujo, Fernandes, Mussel, Sebastião, Yoshida, 2020).

From these TG curves, the traditional Vyazovkin method was applied, Figure 7 presents the Ea (kJ mol^{-1}) determined according to the conversion (α). It is possible to note that the dehydroxylation process begins with Ea of about 300 kJ mol^{-1}. This energy is constant until the process reaches 40-50% conversion when the energy is enhanced to conclude the whole dehydroxylation process, ~530 kJ mol^{-1} (α=80%). This higher value of activation energy is indicative of the thermal stability of this material, corroborating its safety after being submitted to processing technologies. Also, these results confirmed that it is possible to modify the physical-chemical properties of the pink clay systems through heat treatment according to the intended industrial-purpose, in this case, the cosmetic industry.

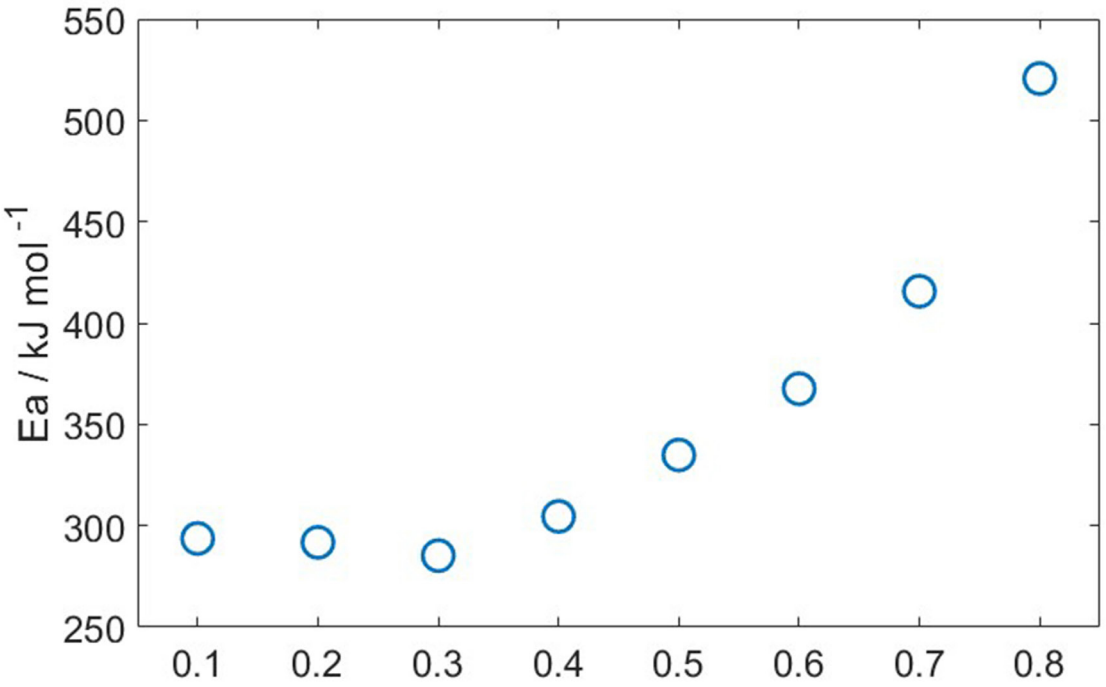

FIGURE 7 - The activation energy (kJ mol-1) according to conversion degree (α) of pink clay under heating.

Table III shows the standard deviations found in the Vyazovkin method and their small values (maximum of 3%) indicate the accuracy of the results (Vyazovkin, 2015; Vyazovkin, S., Chrissafis, Di Lorenzo, Koga, Pijolat, Roduit *et al*, 2014). This nonlinear method for isoconversional data treatment from TG curves was previously used for the characterization of solid-state pharmaceutical reactions (Brito, Leite, Duarte, Ostrosky, Ferrari, de Lima, 2019; Silva, Fortes, Tomé, Silva Filho, Freitas, Soares-Sobrinho *et al* 2021; Freitas-Marques, Araujo, Fernandes, Mussel, Sebastião, Yoshida, 2020) and can be considered a suitable and reliable procedure to determine the activation energy of the pink clay whole dehydroxylation process.

TABLE III - The standard deviation of the Vyazovkin method

Conversion degree (α)	Standard deviation
0.1	0.00443
0.2	0.00417
0.3	0.00690

TABLE III - The standard deviation of the Vyazovkin method

Conversion degree (α)	Standard deviation
0.4	0.00224
0.5	0.01363
0.6	0.02124
0.7	0.03414
0.8	0.02912

CONCLUSION

The pink clay system sample from Diamantina is mainly composed of kaolinite, 1:1 layer hydroxy-silicate. The pink color is due to the presence of Fe^{3+}(α-Fe_2O_3) hematite, Fe^{2+}, and Fe^{3+} related to silicate iron, a small amount of goethite, and a superparamagnetic Fe^{3+} as precisely described by Mössbauer spectroscopy, an important characterization tool for clay minerals applied in pharmaceutical products. Pink clay does not have satisfactory flow properties, an aspect that does not compromise its use in facial masks. The commonly accepted

concept of kaolinite and associated hydrous silicates dehydroxylation results from the reaction of the hydroxyl groups in a two-steps process to form a water molecule by proton transfer. Thermal phase transition followed by X-ray diffraction confirmed this phenomenon of the whole sample. The heating rates applied to the kinetic study corroborate experimental data suitability for the described occurrence. The kinetics of the dehydroxylation process, Ea ~300 – 530 kJ mol^{-1}, was determined by nonlinear isoconversional Vyazovkin method using four TG curves, which experimentally attested the high stability of this material together with its possibility to incorporate API of different polarities. It consequently modulate its capacity of sorption in the control of the skin oiliness, unique pharmaceutical properties that can be favorably exploited by the cosmetic industry.

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