

# Ceramic characterization of raw material with a high content of organic matter reduced by composting

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## Abstract

The process of beneficiation of a peaty ceramic raw material extracted from the Poços de Caldas region, MG, through the composting method to reduce organic matter (OM) was analyzed. The raw materials used in separate piles were divided, keeping one of the samples pure (TP) and adding bovine wastes in the second (TB). The process lasted 6 months and, at the end of each month, the amount of OM was analyzed by the Walkley-Black method. Results of maximum degradation of 56%±6% of OM in the TB and 47%±5% of OM in the TP were obtained. The ceramic characterization of the processed raw material was then carried out. It has been proved that the proposed method is efficient for the decrease of OM in the ceramic raw material. Regarding the composting product, the results were positive, showing that this material can be used in ceramic applications.

**Keywords:** clay, organic matter, composting, ceramic characterization.

## INTRODUCTION

The ceramic industry is a major consumer of industrial minerals around the world. Every year, millions of tons of raw materials are used in several segments to produce the most diverse ceramic products [1]. The clays are in the group of raw materials most suitable for use in ceramic processes, where many intrinsic properties of their genesis guarantee suitable characteristics to various applications. One of the unwanted items is the presence of organic matter in large quantities (the percentage considered high varies according to the product manufactured). A significant amount of organic matter in the clay can cause undesired changes in its properties, which can change the coloring, reduce mechanical strength, increase fire loss (due to its volatility) causing material losses, and increase the firing costs, among other unwanted problems in ceramic manufacturing [2].

The region of Poços de Caldas, MG, stands out in the mining sector due to the formation of several mineral deposits throughout its history. Some potassic rocks of the region are in stages of more accentuated change, thus generating deposits of clay, explored by local industries. Characterization of raw materials of the region shows considerable amounts of organic matter, making the processing of this clay of little economic viability, leading to low use of them in the industrial sector [3-6]. The organic material present in this raw material is called peat. Peat is an organic mineral compound, a product of incomplete decomposition of plants in excessively humid environments, such as river meadows, coastal plains, and lacustrine regions. Because of chemical and microbiological transformations, peat is mostly formed on the ground up to 0.5 m depth, where there are significant activities of aerobic bacteria and fungi. Below this depth

other microorganisms, now anaerobic, come into action, ceasing their activities in depths below 10 m, where only chemical transformations occur. In the studied region, large deposits of clay are found in these soil profiles, leading to undesired mixing [7, 8].

As a processing route for these clays, current studies look to ensure that in the ore the presence of organic matter has its content decreased before being processed. For this, the composting method is suggested in this study, in which the material goes through stages of degradation of the organic matter. Composting is a process responsible for recycling nutrients or accelerating the decomposition of organic matter through aerobic microorganisms, initially occurring biochemical reactions and later occurring a humidification process, also called maturation phase. The composting process in a solid material can be done by manual stirring, also called windrow process, where the material is manually rotated at certain times for oxygenation, or in static aerated piles, where fans are used to force the insertion of oxygen into the material [9, 10]. Based on this, this work aimed to apply the composting method on a sample of clay with high organic matter content, from the region of Poços de Caldas, MG, to analyze the efficiency of the method and the possibility of using the obtained product in the ceramic industry. The possibility of implementing a new beneficiation route for the raw material under study can be considered as an innovation, since it can supply solutions, still non-existent, in the ceramic and mining industries. Products from the process in question may also be considered innovations when judged from the technical-scientific point of view.

## EXPERIMENTAL

The samples used in the process, called peat clays, came from a company found in Poços de Caldas, MG, in the Marco Divisório neighborhood, at Chapadão Farm. Initially,

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the chemical analysis was performed by X-ray fluorescence technique (Philips, 1000) using pressing and semi-quantitative screening method for determination of major elements. Then, the samples to be characterized were divided into three piles: the first pile was formed only by turfous clay; the second cell was formed by peat clay with a mixture of 5 wt% ammonium sulfate (AdvanSix, 21% concentration of ammoniacal nitrogen + 24% of sulfur sulfate), as a source of nitrogen, considered macronutrient for the microorganisms possibly presenting in the peat clay, in order to create a favorable environment for their development; the third pile was formed by peat clay and 25 wt% of bovine wastes were added, a known source of microorganisms in composting processes, aiming to increase the amount of microorganisms present in the cell environment, in order to potentiate the process. In all three piles, the treatment by manual composting (windrow) was applied [11, 12].

The cells were stored in three PVC boxes with dimensions of 370x300x140 mm, each filled with 9 kg of material, where the parameter of storage volume per box was the determining factor for this value. For the storage of the bovine waste used in three stacks, a PVC pipe apparatus was developed, with four 90° knee connections of PVC and three 90° PVC 'T' fittings, all with a diameter of 40 mm and without thread. After being placed in a rectangular position, the apparatus was completely perforated in the form of a regular mesh, seeking the transfer of microorganisms to the pile without direct contact with the waste, thus avoiding any type of contamination in the treated raw material. To perform the perforations, a common drill equipped with a 3 mm drill bit was used. In this apparatus, 2.25 kg of bovine waste was stored. The PVC boxes and PVC pipe apparatus used are shown in Fig. 1.

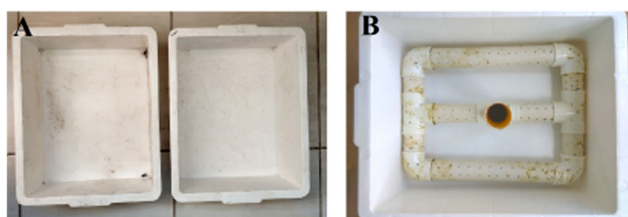


Figure 1: Images of PVC boxes used for composting (A), and PVC device used to store bovine waste (B).

After the development of the piles, the composting process was started, which lasted over 6 months. In this period the humidity control was performed visually and through the touch, adding 5% of water to the mass of the pile (450 mL) whenever the humidity of the pile was low. The value of 5% was fixed, trying not to form a pulp in the pile and, at the same time, avoiding that the pile reached a low humidity. Aeration was also carried out with manual shovels. The aeration process was performed every two days. Also, at the end of each month, the modified Walkley-Black assay for organic matter (OM) determination and monitoring of the results was performed [13, 14]. At the end of 6 months, the ceramic characterization of the raw materials was carried out. Formulations were prepared from untreated peat clay and compost-treated material. A reference ceramic raw material with acceptable characteristics by the industry was also added. This formulation was used as the reference sample for comparison with peat and was not used in the composting process due to its acceptable amounts of OM. Table I shows the analyzed samples.

For the analysis, about 1 kg of each raw material was collected, and this mass was subjected to grinding, reaching a grain size of 100 mesh. After milling, the formulations were produced, and all raw materials were taken to an oven for 48 h at 100 °C to remove moisture from the material. After drying, 10 wt% water (100 mL) was added to each sample, thus controlling the moisture content in the material. With the raw material prepared, 25 specimens with a mass of 18 g, of each formulation, were pressed into a rectangular-shaped mold of average dimensions of 70x20 mm. The pieces were formed in uniaxial pressing (10 tons hydraulic press, P10 ST, Bonevau), with an applied load of 1.5 ton for the relief of the material and 3 ton for 5 s for the pressing process. After pressing, dimensions and weight of each sample were measured in the green state. Sintering of the specimens was carried out at 1000, 1050, 1100 and 1160 °C: a heating rate of 7 °C/min was used, holding for 30 min at 1000 °C; for the other sintering temperatures, a heating rate of 30 °C/min was used with a holding time of 5 min. This change occurred because muffle used in the first firing (1000 °C) damaged, not allowing the other firing in the same condition. As a positive aspect, it was possible to evaluate the behavior of the materials in relation to the

Table I - Description and nomenclature of the samples.

| Description   | Sample |
|---|--------|
| Reference refractory clay   | S      |
| Untreated turfous clay  | T      |
| Treated turfous clay  | TP     |
| Treated turfous clay with the addition of biomass                                   | TB     |
| Treated turfous clay with the addition of ammonium sulfate                          | TN     |
| Clay formulation: 50/50 untreated turfous clay/reference refractory clay            | T-S    |
| Clay formulation: 50/50 treated turfous clay/reference refractory clay              | TP-S   |
| Clay formulation: 50/50 treated turfous clay with biomass/reference refractory clay | TB-S   |

heating rate. The firing at 1000 °C was carried out using a Teklabor muffle (FSM200) and the other firings were done in an industrial electric furnace (INTI, FSQQW999). Later, the water absorption, apparent density, apparent porosity, and linear shrinkage were analyzed according to NBR 13818 and NBR 6220 standards [15].

## RESULTS AND DISCUSSION

Table II shows the results of chemical analysis of the samples studied. The clay deposits of the alkaline complex of Poços de Caldas were formed due to the recent evolution of the relief associated with weathering, soil mobilization, and erosion that gave rise to a large part of the basins, then filled by the sedimentary residues of the rocks present there. Due to this fact, its formation has a considerable variety of chemical elements from these rocks, some of them with elevated levels, such as aluminum oxide ( $\text{Al}_2\text{O}_3$ ) with contents up to 56% and silicon oxide ( $\text{SiO}_2$ ) with contents up to about 52%, as well as lower amounts of alkalis. Another fact related to the formation of these deposits is the constant water circulation in these regions, in some cases with the presence of supernatant vegetation in decomposition, raising organic matter contents [3-5, 16]. The reference clay presented a high amount of  $\text{Al}_2\text{O}_3$  (51.78%) and low alkali content, characteristics of refractory raw material found in the region. In addition, this material had a loss on ignition of 26.56%, showing the presence of organic matter, which decomposes at elevated temperatures, altering its properties. On the other hand, the turfous clay presented higher loss on ignition (44.73%), showing higher volatility, and so, greater alterations in the final product are expected in relation to the reference sample. The peat material presented lower  $\text{Al}_2\text{O}_3$  content (26.77%), indicating material with reduced refractory properties compared to the reference sample [6, 17]. In this context, the decrease of organic matter (OM) of this turfous raw material could be an alternative for this to present features close to the reference. The composting method is currently used efficiently in the decomposition of organic matter present in agricultural residues (straw, bagasse and vegetable waste), livestock (animal manure), and urban waste. The quantification of degraded OM depends on the way the process is performed, and the raw material used. However, even with variations, studies show the efficient reduction of tons of OM to humus in all processes hitherto applied, which can be returned to the environment in the form of natural fertilizer. No citations were found about the use of composting in the processing of mineral raw materials, making this pioneering work in this type of application [18-21].

The composting biomineralization process was carried out for 6 months, and samples were collected every 2 months of the process, obtaining three groups of results over this time for each pile proposed with its proper characteristics (Table I). At the end of each 2 months of the process, the titrations were carried out by the modified Walkley-Black method and then the organic carbon (OC) was calculated, obtaining the variation of organic matter values. The results are shown in Fig. 2. It can be seen that organic matter (OM) values decreased in all raw materials with treatment over 6 months. The reference sample (T) showed an average of  $26.1\% \pm 0.8\%$  OM, which was analyzed at the beginning of the process as a comparison for the samples after treatment. The pure sample (TP) reached averages of  $25.6\% \pm 2.1\%$ ,  $15.1\% \pm 1.1\%$  and  $13.7\% \pm 1.3\%$  of OM at 2, 4 and 6 months, respectively. The sample with ammonium sulphate (TN) showed an average of  $19.5\% \pm 2.1\%$  of OM at 2 months,  $15.4\% \pm 1.6\%$  at 4 months and  $12.8\% \pm 0.9\%$  MO at 6 months. Finally, the sample with the addition of bovine manure (TB) reached  $20.7\% \pm 3.9\%$  of OM at 2 months,  $13.5\% \pm 1.5\%$  of OM at 4 months and after 6 months the average of  $11.6\% \pm 1.2\%$  MO. Based on the

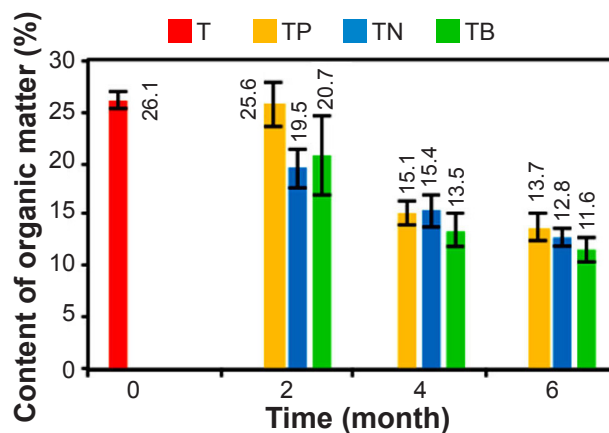


Figure 2: Content of organic matter in the samples over 6 months.

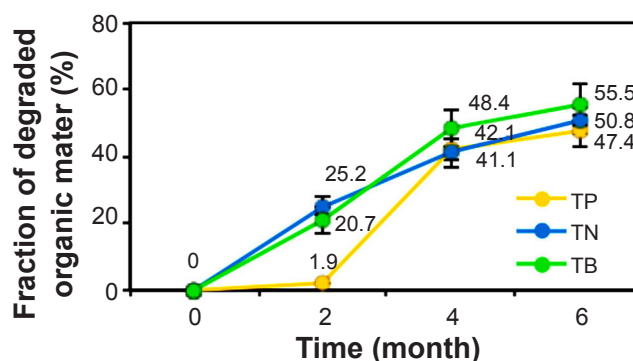


Figure 3: Fraction of organic matter degraded over 6 months.

Table II: Chemical composition (wt%) of the samples.

| Sample                    | SiO <sub>2</sub> | TiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | MnO  | MgO  | CaO  | Na <sub>2</sub> O | K <sub>2</sub> O | P <sub>2</sub> O <sub>5</sub> | LOI   |
|---------------------------|------------------|------------------|--------------------------------|--------------------------------|------|------|------|-------------------|------------------|-------------------------------|-------|
| Turfous clay              | 23.72            | 1.27             | 26.77                          | 1.76                           | 0.03 | 0.26 | 0.38 | 0.03              | 0.82             | 0.24                          | 44.73 |
| Reference refractory clay | 14.80            | 5.10             | 51.78                          | 1.41                           | nd   | 0.05 | 0.05 | 0.06              | nd               | 0.02                          | 26.56 |



results of MO throughout the process, it is best to observe the occurrence of degradation of organic matter through the graph of Fig. 3.

From the results shown in Fig. 3, all the samples started from time zero with no occurrence of degradation, being estimated in the values of organic carbon and organic matter of the standard peat without treatment (T). Analyzing the degradation graph, it was seen that the pure sample (TP) achieved a degradation of  $1.9\% \pm 0.2\%$  OM with 2 months of process,  $42.1\% \pm 3.3\%$  of MO at 4 months and  $47.4\% \pm 4.6\%$  of OM at 6 months. The sample with ammonium sulphate (TN) showed degradation of  $25.2\% \pm 2.6\%$ ,  $41.1\% \pm 4.4\%$  and  $50.8\% \pm 3.8\%$  of OM with 2, 4 and 6 months of process, respectively. Finally, the sample with the addition of bovine manure (TB) showed degradation of  $20.7\% \pm 4.0\%$  of OM with 2 months of process,  $48.4\% \pm 5.8\%$  of OM at 4 months and  $55.5\% \pm 6.1\%$  of OM at 6 months. Analyzing the results, there was degradation of OM throughout the full process in the three samples analyzed, proving the efficiency of composting for the degradation of organic matter in ceramic raw material, as seen in other sources of OM. As shown by composting studies, the maturation time of the organic matter extends for about 120 days, when the degradation stabilized, and the process became slower and with less efficiency compared to the first phase. During the process, it was also possible to analyze that even with different routes, at the end of the process the decomposition of all materials had approximate the same results, being understood that when different substrates are involved, different organisms are stimulated and can develop in different forms and concentrations. Thus, an organism with faster kinetics can compete with another organism of slower kinetics, even in smaller quantity, thus obtaining equivalent results at the end of the process [18-21].

At the end of the composting stage, the ceramic test bodies were prepared with the raw materials based on the formulations S, T, TP, TN, TB, TS, TP-S and TB-S, described in Table I. The TN samples were excluded from the analysis, because after the sintering extremely fragile bodies with an exceptionally low mechanical strength were obtained, making it impossible to continue the ceramic analysis proposed in these samples, as can be seen in Fig. 4. The remaining samples of each formulation were sintered at 1000, 1050, 1100 and 1160 °C. For the other formulations, the bodies kept a light coloration, but with a certain darkening according to the increase of sintering temperature. The reference clay showed no significant cracks on its surface. It is worth mentioning that this clay is considered with the minimum acceptable characteristics for use in the local industry. For the formulations with turfous clay, a greater deformation and increase of number of cracks was seen, according to the increase of the temperature. In all formulations, with the difference in the firing heating rate, the higher temperature gradient used in the firing at 1050, 1100 and 1160 °C caused some bodies to span with a higher linear shrinkage. Another crucial factor was the appearance of 'black heart' in the pieces with the increase in

the temperature gradient. This fact was related to the lower permanence of the bodies between 200 and 500 °C, which is the temperature range where the oxidation of organic matter occurs during sintering [22].



Figure 4: Image of TN samples after sintering.

After the first visual analysis, the properties of apparent density, apparent porosity, water absorption and linear shrinkage were analyzed according to NBR 13818 and NBR 6220 standards [15]. The results of apparent density are shown in Fig. 5. When analyzing the green density of the samples, it was noted that the reference clay (S) presented the highest density, around 1.6 g/cm<sup>3</sup>, while the peaty samples presented lower densities, around 1.4 g/cm<sup>3</sup>. For the mixtures containing reference clay and peat clays, the density became higher than the peat samples, around 1.5 g/cm<sup>3</sup>. The values found were consistent with the literature showing higher densities for clays (0.9 to 1.7 g/cm<sup>3</sup>), lower for organic matter (0.9 to 1.3 g/cm<sup>3</sup>) and average when mixing both [23, 24]. All samples showed a green density  $\leq 1.6$  g/cm<sup>3</sup>, indicating low plasticity [6, 25]. After the first

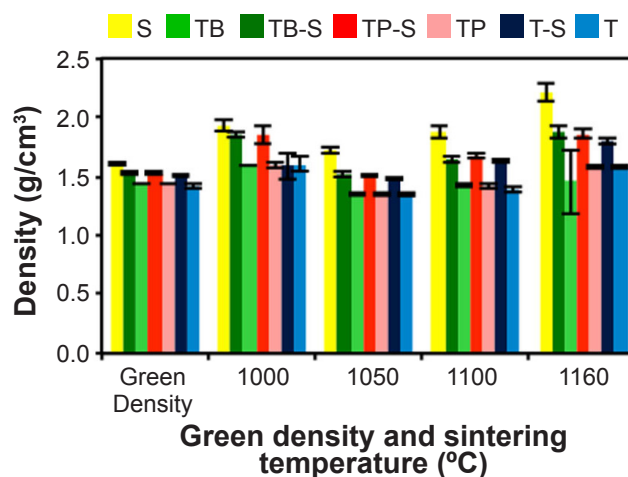


Figure 5: Green density and density of the samples after sintering at different temperatures.

firing at 1000 °C, all densities of the pieces increased, and the mixed formulations presented a significant difference compared to the pure samples. In the other firings, due to the change in the furnace (change in the heating rate), it was noted that the densities of all formulations with 100% peat material decreased in relation to the first firing (1000 °C). This fact may have occurred due to the higher temperature variation and so the alteration of the organic matter present there. For the 50/50 samples, with the increase in firing temperature, the densities also presented higher values, as the reference formulation (S), which had a higher density, and the mixtures had an average density when compared to the two extremes [26].

The results of apparent porosity are shown in Fig. 6a. The firing temperatures which resulted in the lowest porosities in all samples were 1000 and 1160 °C. However, it was noted that the reference formulation (S) had the lowest apparent porosity, while the 100% peat formulations had the highest values. This fact was justified by the influence of organic matter in increasing the porosity of ceramic raw materials due to their shape and arrangement in the structure of the same. As noted, the 50/50 mixtures showed a decrease in porosity compared to those 100% peat formulations [23, 27]. The results of water absorption are shown in Fig. 6b. As the water absorption was influenced by the porosity and cracks in the samples, it was expected to show the same tendencies of porosity. Then, again the temperatures that resulted in the lowest water absorptions were 1000 and 1160 °C in all samples. Following the earlier reasoning, the standard formulation (S) had the lowest water absorption because it had lower porosity and cracks, while the 100% peat formulations had the highest values because they had higher porosities and cracks. The 50/50 mixtures showed an improvement in the decrease in porosity and cracking relative to those 100% peat formulations, therefore, they had lower values for water absorption [23]. The results of linear shrinkage are shown in Fig. 6c. It can be seen that at 1000 °C the formulations 50/50 reached values higher than the reference formulation (S), except for the T-S that presented the lowest value among all, including its sample with 100% peat material. This may have occurred because the specimens were deformed, which would also be the reason for the standard deviation of the sample being greater than those found in the others. In the other firings, there was a tendency for the shrinkage to increase according to the sintering temperature. The reference formulation (S) had the highest linear shrinkage, while the 100% peat formulations had the lowest values. The 50/50 mixtures showed an increase over those 100% peat formulations, approaching the values found for the reference sample, reaffirming that the change in furnace and heating rate affected the ceramic results, including linear shrinkage [26].

Based on all the results, it can be said that the peat samples that passed through the composting treatment presented, for the analyzed properties, results close to the peat sample without treatment. However, with the mixtures with the reference clay, a significant variation in the results was seen,

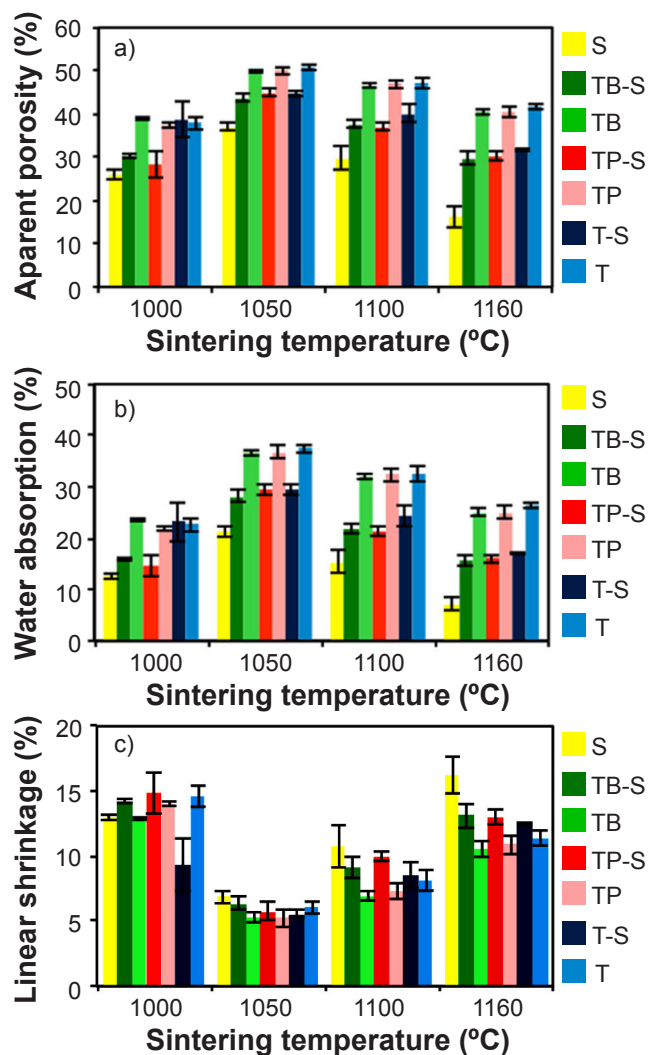


Figure 6: Apparent porosity (a), water absorption (b), and linear shrinkage (c) of the samples after sintering at different temperatures.

approaching the values found for reference formulation. The change of furnace, and so the change in the firing temperature gradient, proved to change the results as well. For the firings above 1000 °C, all the samples presented a greater occurrence of cracks, even breaking some specimens. This fact may have occurred due to the faster heating and lower level of organic burn out. In this context, the appearance of cracks impaired the quantification of the properties and made it impossible to measure the mechanical strength of the pieces.

## CONCLUSIONS

The composting biomineralization method was efficient in the reduction of organic matter in the analyzed samples. During the two stages of composting, it was possible to prove that the proposed method is efficient in the reduction of organic matter in the ceramic raw material. For this reason, the proposed method is the beginning for a new beneficiation route never studied before. The study also showed that the addition of bovine manure in the composting

process of peat clay accelerated the degradation of organic matter in relation to the same compost without the substrate, increasing its efficiency. With the ceramic analysis, it was possible to conclude that even the peat samples that presented degradation of organic matter did not have characteristics that allowed them to be used alone. The appearance of cracks and the fragility of these materials constituted a barrier to ceramic applications. However, the results showed that the formulation having this type of material and a second clay, with acceptable characteristics, improve their properties, thus allowing applications. Considering the firing results, it was concluded that the ceramic materials produced with this type of raw material should be subjected to slow heating so that the gases released by the organic matter remaining from the composting process can be removed avoiding the formation of 'black heart' and improving the characteristics of the same, since the firing carried out under this condition, at 1000 °C, achieved satisfactory results, in relation to the higher firing temperatures with higher heating rate. It was noted that the temperature gradient also interfered the sample's cracking. With a ramp of 30 °C/min, in the second heating condition, the appearance of cracks increased, while with the heating rate of 7 °C/min, cracks were not formed in most samples.

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