Evaluation of tray drying on the particle size in the synthesis of three phases apatites
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Abstract. Ceramics, such as calcium phosphates are employed in bone regeneration procedures, due to their interesting properties. The objective of this research was to evaluate the influence of tray drying on particle size for each of the apatite phases obtained in the synthesis. Several apatite synthesis methodologies are reported in the literature. One of the methodologies of apatite synthesis is the wet synthesis. Three phases of apatite were synthesized according to the described methodology. In this procedure, a product suspended in aqueous medium was obtained. One part was separated by evaporation process to remove water and the other part was tray dried at 80 °C for 24 hours. The obtained samples were characterized by X-ray Powder Diffraction, FTIR spectroscopy and Scanning Electron Microscopy. Particle size was determined by scanning electron microscopy. Both drying processes were compared. These comparative analysis showed that there were no differences in X-ray and IR results, but it was observed differences in particle size. It can be concluded that the particle size in the samples dried in trays was smaller in each of the apatite phases.

Keywords: Apatite, Tray Drying, Biomaterials, Particle size, Ceramics.

INTRODUCTION

Ceramics, glass and glass ceramics are part of the class of biomaterials used in the repair or replacement of hard connective tissues. The reabsorbable ceramics, such as calcium phosphates and some bioactive glasses (particulated or in porous form) are used for bone regeneration procedures. Currently, synthetic calcium phosphates are the principal compounds studied and used as biomaterials in the replacement and regeneration of bone tissue (Guastaldi et al, 2010; Dorozhkin, 2007, 2009, 2010a, 2010b, 2010c; Raynaud et al, 2001).

One of the methodologies of apatite synthesis is the wet synthesis. In this process, a suspended product in aqueous medium was obtained. An evaporation process to separate the sample was carried out. This process has the advantage of that the generated waste is water, so it is a methodology with a low possibility of contamination (Jarchon et al, 1976). However, it presents the difficulty of forming agglomerates during the separation process, affecting the particle size of the sample. Within the used operations in the chemical and pharmaceutical industry, drying represents one of the most important operation because of it depends on, many occasions, of the physical and chemical properties of the product as well as the quality of it. Drying is defined as the removal process of volatile substances present in a solid product by means of steam and does not include the evaporation process.
One of the drying variants used in the industry is the tray drying. It consists of placing the material on a tray inside a drying oven by recirculating air at a temperature for a time to achieve that the moisture content of the sample is within the established ranges (Rigo et al, 2007; Saeri et al, 2003; Koutsopoulos, 2002). Highlighting the importance of the influence of drying on the particle size, the objective of this work was to evaluate the influence of tray drying for each of the apatite phases obtained by synthesis.

MATERIALS AND METHODS

Synthesis of apatites
In the synthesis of the three different phases of the apatite, the wet method was used. This method consists in developing the direct reaction between solutions containing PO$_4^{3-}$ ions and solutions containing Ca$^{2+}$ ions (calcium hydroxide or calcium carbonate) (Rodriguez-Chanfrau, 2015, Ishihara et al, 2009). The phases of amorphous calcium phosphate (ACP) were synthesized using the methodology reported by Rigo et al, 2007. While the synthesis of octacalcium phosphate phase (OCP) was performed according to the methodology described by Komev, 2010. In both synthesis after completion of the reaction, the suspension obtained was divided into two parts. One part was maintained according to the initial methodology (evaporation process), and the other part was placed in the oven at 80°C for tray drying until they become completely dry. To obtain tricalcium phosphate (TCP) a sample of each of the dried parts (evaporation and tray drying) of the ACP batch were used. Fractions at 600 ºC for 3 hours were dried.

X-ray powder diffraction studies
The XRD spectra were recorded at room temperature (25 ºC) with a SIEMENS D5000, DIFFRAC PLUS XRD diffractometer (Germany) with BRAGG-Brentano geometry, Cu Kα radiation ($\lambda=0.154$ nm), Flicker detector and graphite monochromator. The scattering angle range from 4º to 80º with 20 step intervals of 0.02º was used. Apatites samples were cut into small pieces and laid on the glass sample holder, analyzed under plateau conditions. An operating voltage of 40 kV and current of 30 mA were used and the intensity was measured in the range of 5º < 2θ< 30º. Peak separations were carried out using Gaussian deconvolution. The d-spacings were calculated using the Bragg equation. Crystallographic search match software was used to identify the crystal structure of samples.

FTIR spectroscopy
FTIR spectra of the samples were measured on a FTIR-VERTEX 70, BRUKER spectrometer (Germany). 64 cumulative scans were taken, with a resolution of 4 cm$^{-1}$, in the frequency range of 4000 to 400 cm$^{-1}$, in transmission mode.

Scanning Electron Microscopy
Scanning electron microscopy (SEM) imaging of ACP was carried out using a FEGMEV; JEOL 7500F scanning electron microscope (Germany). The equipment was operated at an acceleration voltage of 2 kV. The samples were coated by carbon evaporation (Baltec SCD 050 Spputer Coater, USA). Particle size by scanning electron microscopy was determined. Five SEM images at magnifications X 2000 were evaluated. In each images, five random measurements of the particle size were performed. With the obtained data, the mean particle size was determined.
Statistical analysis.
The comparison of means by analyzing samples paired t test was performed. The results were considered significant at p <0.05.

RESULTS AND DISCUSSION

Samples from each of the syntheses were characterized. Figure 1 shows the X-ray spectrum. In each of the phases characteristic peaks were observed. In the ACP sample (Figure 1a) representative peaks of hydroxyapatite (2θ = 25.5, 34.1, 39.6, 50.6), octacalcium phosphate (2θ = 35.5, 49.2), amorphous calcium phosphate (2θ = 20.9; 29.2; 45.2) and monohydrogen phosphate phosphate of calcium (DCPD) (2θ = 11.5) were observed. In the case of the OCP sample (Figure 1b), the presence of octacalcium phosphate (2θ = 16.2, 25.3, 30.6, 46.7, 50.1) and DCPD (2θ = 29.1, 54, 6) were observed. While in the diffractogram deTCP (Figure 1c) the presence of characteristic peaks calcium triphosphate (2θ = 17.1, 26.6, 30.5, 33.4, 37.6, 46.6) and hydroxyapatite (2θ = 18.9, 29.2, 48.2, 51.4) were observed. These results are similar to those reported in the literature and no differences were observed between the drying fractions and the tray-drying fraction (RodriguezChanfrau, 2015; Veranes-Pantoja, 2012; Perez Pavinato, 2012; Aparecida, 2006; Morejon et al, 2007; Downs et al, 2003).

Figure 1. X-ray diffraction spectrum of the synthesized samples. A: ACP sample; B: OCP sample and C: TCP sample.

Figure 2 shows the results of the infrared spectrum. In all cases, bands in the region between 1200 and 900 cm⁻¹ indicative of the presence of phosphate groups were observed. The spectrum of the ACP sample (Figure 2a) shows that the bands between 3700 and 3000 cm⁻¹, characteristic of the presence of OH groups, appear with greater intensity in the sample dried in tray. Likewise occurs with the band at 1640 cm⁻¹ and 1342 cm⁻¹ the latter related to the possible presence of carbonated hydroxyapatite. Figure 2b corresponds to the spectrum of the OCP sample. A similarity was observed in the bands, being more intense in the bands corresponding to the sample dried in tray.
Something similar was observed in the sample corresponding to the TCP phase (Figure 2c). In all cases the characteristical bands of the presence of phosphate groups were observed. These results coincide with those reported by other authors in the literature (Veranes-Pantoja, 2012; Perez Pavinato, 2012; Aparecida, 2006; Stoch et al, 2000; Silverstein, 2000).

Figure 2. Infrared spectrum of the synthesized samples. A: ACP sample; B: OCP sample and C: TCP sample.

Figure 3 shows the results of the analysis by scanning electron microscopy. A morphological difference between the samples dried by evaporation (Figure 3a, 3b and 3c) and the samples dried in tray (Figure 3d, 3e and 3f) were observed. The sample dried by evaporation presents thicker and agglomerated particles. The results of the analysis to determine the particle size are shown in Figure 4. In general, the tendency is to obtain smaller particle sizes in the samples dried in trays. This may be due to the formation of agglomerates that occurs during the process of elimination of water by evaporation.

Statistical analysis using the paired samples t test ($\alpha = 0.05$) showed that for the ACP and TCP samples there were no significant differences between the mean particle size values ($p = 0.1372$ and $p = 0.1971$ for ACP and TCP, respectively), whereas, in the OCP sample, significant differences ($p = 0.0236$) were observed between mean values of particle size. This result suggests that the characteristics of the starting material to perform the synthesis also influence the particle size of the final sample.
Figure 3. Scanning electron microscopy images. A: evaporation-dried ACP sample; B: evaporation-dried OCP sample; C: evaporation-dried TCP sample; D: tray-dried ACP sample; E: tray-dried OCP sample and F: tray-dried TCP sample.

Figure 4. Results of the evaluation of particle sizes in the phases studied for each drying method.

In general, the drying treatment does not influence the physical and chemical characteristics of the apatite obtained phases. In all cases, the results of X-ray analysis and infrared spectroscopy show that the samples are similar. In the case of analysis by electron microscopy, the results show a slight morphological modification in the batches dried by evaporation which appeared to have a thicker appearance and agglomeration. In the case of samples dried in a tray this thick structure is smaller.
Technologically, evaporation drying presents greater difficulty in being employed on an industrial scale, hence the importance of demonstrating the effectiveness of tray drying to dry the different phases of synthesized apatites. On the other hand, guaranteeing smaller particle sizes improves the quality of the synthesized material and its use as a ceramic in bone regeneration.

CONCLUSIONS

The study showed that the drying in tray has influence on the size of particles, avoiding the formation of agglomerates during the process. This influence was only statistically significant in the case of the synthesis of octacalcium phosphate phase, where the results suggested that besides drying, the starting material for the synthesis played an important role in the whole experimental results.

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