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EFFECT OF DIGESTION TIME ON THE SYNTHESIS OF HYDROXYAPATITE CERAMIC POWDER

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Resumen

Este trabajo tiene como objetivo la preparación e investigación de la hidroxiapatita (HAP) en polvo de cerámica con la fórmula química Ca\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}(OH)\textsubscript{2} a través de vía húmeda precipitación química mediante la adición gradual de 0,1 N de nitrato cálcico tetrahidratado (Ca(NO\textsubscript{3})\textsubscript{2}.4H\textsubscript{2}O) para 0,06N de fosfato dihidrógeno de amonio (NH\textsubscript{4}H\textsubscript{2}PO\textsubscript{4}) a un pH de más de 11, con la digestión (agitación) en diferentes momentos, 18, 20, 22, 28 y 36 horas, y la cocción durante 90 minutos a 1 050 °C. El polvo obtenido se investigó utilizando el transmisor de infrarrojos análisis espectroscópico de Fourier (FT-IR), el análisis de difracción de rayos X (DRX) y calorimetría diferencial de barrido (DSC). El tamaño de las partículas de la mezcla preparada se calcula a partir de patrones de difracción de rayos X mediante la ecuación de Scherrer. Los espectros IR muestran las bandas de absorción que caracteriza al grupo fosfato (PO\textsubscript{4})\textsuperscript{3-}, además de las bandas de absorción que caracteriza estiramiento del grupo hidroxilo (OH). De todos los patrones de difracción de rayos X de los picos principales que caracterizan a la hidroxiapatita se pudo detectar, en algunas muestras de algunos picos que caracterizan a un fosfato de calcio también pueden ser detectados. DSC muestran un pico pronunciado caracterizando la pérdida del grupo hidroxilox. La combinación de la IR, los resultados de difracción de rayos X y DSC confirmar la formación de compuestos de hidroxiapatita. Todos los pawder hidroxiapatita cerámica preparados tienen un tamaño de partícula inferior a 100 nm, por lo que considera como prometió materiales en el campo de la nanotecnología. Las 20 horas de tiempo de digestión se consideró como la condición óptima para la preparación del contenido relativamente alto de polvo de hidroxiapatita de cerámica pura.

Palabras clave: hidroxiapatita, polvo de cerámica.

Abstract

This work aims at preparation and investigation of hydroxyapatite (HAP) ceramic powder with the chemical formula Ca\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}(OH)\textsubscript{2} via wet chemical precipitation method through stepwise addition of 0.1N calcium nitrate tetrahydrate (Ca(NO\textsubscript{3})\textsubscript{2}.4H\textsubscript{2}O) to 0,06N of dihydrogen ammonium phosphate (NH\textsubscript{4}H\textsubscript{2}PO\textsubscript{4}) at pH over 11, with digestion (stirring) at different times ; 18, 20, 22, 28 and 36 hours, and firing for 90 minutes at 1 050 °C. The obtained powder was investigated using Fourier transmitter infrared spectroscopic analysis (FT-IR), X-ray diffraction analysis (XRD) and Scanning differential calorimetry (DSC). The particle size of the prepared mixes was calculated from x-ray diffraction patterns using Scherrer’s equation. The IR spectra show the absorption bands characterizing the phosphate group (PO\textsubscript{4})\textsuperscript{3-} in addition to the absorption bands characterizing streching hydroxyl group (OH). From XRD patterns all of the main peaks characterizing hydroxyapatite could be detected, In some samples some peaks characterizing á-calcium phosphate could also be detected. DSC show a pronounced peak characterizing the loss of the hydyroxyl group. The combination of the IR, XRD and DSC results confirm the formation of hydroxyapatite compound. All the prepared hydroxyapatite ceramic pawder have particle size less than 100 nm, so they considered as promised materials in the field of nanotechnology. The 20 hrs of digestion time was considered as the optimum condition for preparation of relatively higher content of pure hydroxyapatite ceramic powder.

Key words: hydroxyapatite, ceramic powder.
Introduction

Hydroxyapatite (HAP) is an inorganic compound with the chemical formula of $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. It has been recognized as a substitute material for bone and teeth in orthopaedic and dentistry fields due to their chemical and biological similarity to human hard tissue /1-3/. In addition, HAP has a wide scope of applications in different fields such as chromatography, solid-state ionic catalysts as well as fuel cells /4, 5/. It also has a promising application as a chemical gas sensor due to its high ion exchange ability.

The HAP bioceramic materials have been prepared with different approaches like solid state, hydrothermal, sol-gel, microwave, chemical wet precipitation, ultrasonic spray pyrolysis, emulsion system and soft chemical system techniques /6, 7/.

This work aims to reach the optimum digestion time for obtaining HAP through the chemical wet precipitation method.

Materials and experimental

Materials

Calcium nitrate tetrahydrate (Ca(NO$_3$)$_2$.4H$_2$O; riedle-de doyen; assay: 99% and dihydrogen ammonium phosphate (NH$_4$H$_2$PO$_4$); T-baker lab chemicals, India; assay: 98-100% were used as calcium and phosphate precursors, respectively. In addition, ammonia solution was used to adjust the pH during the precipitation process.

Preparation of HAP

HAP was prepared using the wet conventional precipitation method. The precipitation was performed through stepwise addition of dihydrogen ammonium phosphate solution (0.06N) to calcium nitrate tetrahydrate solution (0.1N) with continuous and gentle stirring. As a result of the reaction, a slurry and somewhat milky precipitate was obtained, which was continuously stirred at 55 °C for different times; 18, 20, 25, 28, and 36 hrs (table 1) using a magnetic stirrer. Afterwards the precipitate was kept away for 48 hrs for coagulation, then collected through centrifuging and separated through decantation. The resulting white precipitate was oven-dried at 90 °C for 26 hrs, and then fired in a porcelain dish at 1 050 °C for 90 minutes.

Characterization

The HAP ceramic powders prepared at different digestion times were investigated by Fourier Transform infrared spectroscopy (FT-IR; FT-IR-3600 type A, light source: standard, detector: TGS, resolution: 4cm$^{-1}$). The composition of the prepared powders was investigated using x-ray diffraction technique (a Philips 1730 diffractometer with Ni filtered Cu Kα radiation at a scan speed of 120 min$^{-1}$ was used). The particle size of the prepared mixes was calculated from x-ray diffraction patterns using Scherrer’s equation as follow /1/.

$$D = \frac{k\lambda}{\beta \cos \theta}$$

where $\beta$ is the full width at half maxima of the powder diffraction peak in radians, $\theta$ the reflection angle of the peak, $k$ a constant nearly equal 0.9, and $\lambda$ the wavelength of the x-ray radiation. The prime reflections with considerable intensities such as (201), (210), (211), (300), (212), (203) and (320) are employed for calculation of Scherrers broadening.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|}
\hline
Digiele time (hrs) & Sample no. \\
\hline
18 & 1 \\
20 & 2 \\
25 & 3 \\
28 & 4 \\
36 & 5 \\
\hline
\end{tabular}
\caption{The Prepared Sample and The Digestion Time}
\end{table}
The thermal behavior was also followed using differential scanning calorimetry technique (DSC; setaram labsys™ TG-DSC using argon atmosphere).

- **Results and discussion**

  **Fourier transmitter infrared spectroscopic analysis (FT-IR)**

  Figures 1(a-e) show IR spectra of the hydroxyapatite ceramic powders prepared using different digestion times (18, 20, 25, 28 and 36 hrs). The figures shows the following absorption bands /8-11/:

1. Two absorption bands at 601 cm⁻¹ and 750 cm⁻¹ which correspond to the \( \nu_4 \) fundamental bending mode of phosphates (PO₄)⁻³ functional group.

2. The hydroxyl liberation mode is found to be present at 633 cm⁻¹.

3. The strong absorption bands in the range (1039-1089 cm⁻¹) are due to the \( \nu_3 \) vibration of phosphates (PO₄)⁻³.

4. The absorption band at 1995 cm⁻¹ confirms the presence of stretching hydroxyl group (OH)⁺.

5. The absorption band at 3572 cm⁻¹ confirms the presence of stretching mode of hydroxyl group.

6. The absorption band at 1388 cm⁻¹ corresponds to the carbonate group (CO₃)²⁻ resulting of the carbonated HAP.

![Fig. (1a) Infrared absorption spectra Mix 1.](image1)

![Fig. (1b) Infrared absorption spectra of Mix 2.](image2)

![Fig. (1c) Infrared absorption spectra of Mix 3.](image3)
By comparing the FT-IR spectra of the powders prepared at different time of digestion, it is obvious that the optimum conditions are reached with 18 hr of stirring (figures 1b) which shows strong triplet with well resolved band at 1 096, 1 085 and 1 056 cm^{-1} identical to phosphate band in addition to the triply degenerate bending vibration of the (PO_4)^{3-} ions at 570, 602 and 632 cm^{-1} which indicate the presence of hydroxyapatite phase. This is confirmed also by the more intense stretching and vibration bands of (OH)^{-1} group and the less intense (CO_3)^{2-} band.

Fig. (1d) Infrared absorption spectra of Mix 4.

Fig. (1e) Infrared absorption spectra of Mix 5.

**X-ray diffraction analysis (XRD)**

Figures 2 (a-e) display the x-ray diffraction patterns of the prepared ceramic materials at different times of stirring. The figures show the following /12/:

1. All of the main peaks characterizing hydroxyapatite could be detected at 2\theta; 31.7°; 32.9° and 32.1°, however the highest peaks intensity are observed in sample prepared with 20 hr stirring (figures 2b).

2. In some samples some peaks characterizing ã-calcium phosphate at 2\theta; 31.064°, 20; 27.828°, 20; 34.387° could be observed in samples prepared after 15, 28 and 36 hrs as shown in Figures 2a, 2d and 2e, respectively.

3. No peaks characterizing any other phases could be detected.
Fig. (2a) XRD pattern of Mix 1.

Fig. (2b) XRD pattern of Mix 2.
So, XRD results confirm the IR spectra that the optimum soaking time of stirring (digestion) during the preparation of hydroxyapatite ceramic powder is 20 hrs.
Scanning differential calorimetry (DSC)

DSC test was carried for one selected sample with 20 hr digestion time. Figures 3 shows the thermal behavior of the prepared sample. The figure shows a pronounced sharp exothermic peak at $\approx 300 ^\circ C$ which corresponds to the liberation of tow hydroxyl groups that confirms their presence along with calcium phosphate in the form of hydroxyapatite.

Fig. (2e) XRD pattern of Mix 5.

Fig (3) DSC thermo diagram of mix 2.
Grain Size

Table 2 summarizes the grain size results of different mixes of the prepared HP powder. The table indicated that the particles of all the studied mixes are located in the class of nanoparticles (less than 100 nm). The table indicates also that mixes 1 and 2 (prepared at 18 and 20 hrs of digestion time) possess the lowest particle size (43 and 47 nm, respectively), with further digestion time the particle size increases because the relatively longer digestion time allows a relatively bigger chance for grain growth.

<table>
<thead>
<tr>
<th>Grain size (nm)</th>
<th>Mix no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>43</td>
<td>1</td>
</tr>
<tr>
<td>47</td>
<td>2</td>
</tr>
<tr>
<td>51</td>
<td>3</td>
</tr>
<tr>
<td>54</td>
<td>4</td>
</tr>
<tr>
<td>71</td>
<td>5</td>
</tr>
</tbody>
</table>

Summary and conclusions

Hydroxyapatite bioceramic powder could be prepared via conventional wet precipitation method using the stepwise addition of 0.1N Ca(NO₃)₂·4H₂O to 0.06N of NH₄H₂PO₄ using ammonia solution to adjust the PH over 11.

According to the FT-IR, XRD and DSC investigation, 20 hrs of digestion time is considered as the optimum condition at which relatively high content of pure hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂) could be obtained.

Bibliography