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Influence of the concentration of phosphoric acid (H_3PO_4) on the Ca/P ratio in obtaining hydroxyapatite (HAp) from eggshell

Influencia de la concentración de ácido fosfórico (H_3PO_4) en la relación Ca/P en la obtención de hidroxiapatita (HAp) a partir de cascaron de huevo

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Abstract

The objective of this research was to evaluate the influence of the concentration of phosphoric acid in the impregnation to obtain hydroxyapatite (HAp) from the recycling of the eggshell reduce the residues formed in conventional synthesis; in addition to evaluating the Ca/P ratio in the type of HAp obtained, in order to test the material in the removal of dyes. The material obtained was characterized by Scanning Electron Microscopy, Energy Dispersive Spectroscopy (EDS) to obtainmorphology and elmental composition, Fourier Transform Infrared and Raman Spectroscopy, to determine functional groups and crystalline phases respectively. A carbonated HAp was obtained, increasing the concentration of phosphoric acid (0.5M, 1M, 1.5M, 2M and 2.5M) increases the presence of the phosphate group in the material; therefore, the presence of carbonates decreases. It is important to highlight that by Raman it was not possible to find the presence of phosphates, it is necessary to analyze the material by other characterization techniques. Although, with the other techniques used, it was possible to determine the presence of this in the material.

Green chemistry, Hydroxyapatite, Impregnation

Resumen

El objetivo de esta investigación fue evaluar la influencia de la concentración del ácido fosfórico en la impregnación para obtener hidroxiapatita (HAp) a partir del reciclaje del cascarón de huevo, con la finalidad de reducir los residuos formados en las síntesis convencionales; además de evaluar la relación Ca/P en el tipo de HAp obtenida, con la finalidad de probar el material en la remoción de colorantes. El material obtenido se caracterizó por microscopia electrónica de barrido (MEB) para conocer la morfología del material, Espectroscopia de Energía Dispersiva (EDS) para obtener la composición elemental, Espectroscopia de Infrarrojo con Transformada de Fourier y microRaman, para conocer los grupos funcionales y las fases cristalinas respectivamente. Se obtuvo una HAp carbonatada, al aumentar la concentración del ácido fosfórico (0.5M, 1M, 1.5M, 2M y 2.5M) incrementa la presencia del grupo fosfato en el material; por ende, disminuye la presencia de carbonatos. Es importante destacar que por Raman no fue posible encontrar la presencia de los fosfatos, es necesario analizar el material por otras técnicas de caracterización. Aunque, con las otras técnicas usadas si se pudo determinar la presencia de este en el material.

Química verde, Hidroxiapatita, Impregnación

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1. Introduction

The alternative chemical routes for the synthesis of materials, is an option to develop synthetic methodologies that reduce or eliminate the residues that are formed. They use environmentally friendly processes, which can be used in different areas, for example in photocatalysis (Marinas A., 2007) (Doria S., 2009) (Hernández L. & Prierto S., 2017).

One of the materials that has aroused interest due to its physical and chemical properties is hydroxyapatite (HAp); it used in bone implants, drug delivery, dental treatment, pollutant absorption (Nayak & Bhushan, 2021) and in the conservation of different materials (Martínez P., Álvarez G., & Cervantes J., 2021), With chemical formula $Ca_{10}(PO_4)_6(OH)_2$, there are three types of HAp:

1. Carbonated HAp (A and B type).
2. Stoichiometric HAp.
3. Calcium deficient HAp

The difference between these lies in the atomic relationship between calcium and phosphate. When the value is greater than 1.67 it indicates that it is carbonated; where the carbonate ion (CO_3^{2-}) can substitute by physicochemical means, the hydroxyl sites (OH-) or phosphate (PO_4^{3-}), which are present in the structure of the HAp (see figure 1) (Botero, 2017).

In Carbonated HAp type B the ions CO_3^{2-} replace groups PO_4^{3-}. While, in A, the CO_3^{2-} replace the group OH^- (Ochoa, López, & Copete, 2021).

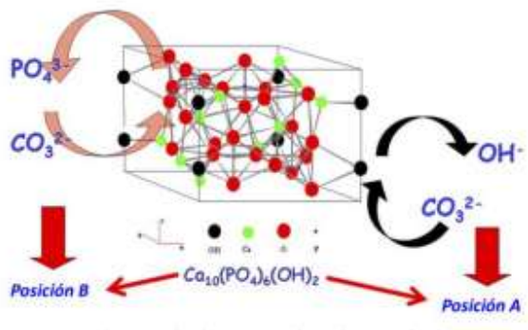

Figure 1 Types of carbonated HAp
Source: (Ochoa, López, & Copete, 2021)

When the ratio is 1.67, it is known as stoichiometric HAp, it crystallizes in the hexagonal system, it has low reabsorption kinetics and low solubility; for values lower tan 1.67, it is deficient in calcium (Londoño, Echavarría, & De La Calle, 2006).

Due to the diversity of HAp type, interest has grown to improve the synthesis method (Mohd P., y otros, 2020).

HAp can be synthesized using chemical precursors, especially calcium and phosphorus, by dry, wet, thermal methods or a combination of these (Sawada, Sridhar, Kanda, & Yamanaka, 2021), solid, state sol-gel, electrochemical, etc. (Sultana, y otros, 2021).

Also, it can be extracted from natural sources such as eggshells, bones or scales of animals that are rich in calcium (Khoo, Nor, Ardhyananta, & Kurniawan, 2015)(Agbabiaka, y otros, 2020).

Recent research has determined the absorption efficiency of HAp from natural sources over textile dyes (Vinoth K., Jani S., Ahila, Ravindran, & Chang, 2021).

For this reason, in this work the influence of the concentration of phosphoric acid during impregnation on the type of HAp is evaluated.

2. Methodology

2.1 Reactant

Hydrogen peroxide (90%), phosphoric acid (85%) purchased from Sigma-Aldrich and distilled water.

2.2 Hydroxyapatite synthesis (HAp)

For the synthesis, the methodology proposed by Enríquez *et al* (Enríquez P., Castrejon S., Rosales D., & Diaz C., 2020) was followed.

HAp source is obtained by recycling the eggshell, it is first washed with 30% H_2O_2 to remove impurities; then it was dried at 80°C for 48 h.

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Subsequently, the material is divided into five parts; Table 1 shows the impregnation conditions with H_3PO_4. It was left to settle for 24 h, to promote the interaction between the material and the solution. Subsequently, washings are carried out with distilled water until a neutral pH is reached. The material is calcined at 800°C for 2 h.

Concentration H_3PO_4 (M)
0.5
1
1.5
2.0
2.5

Table 1 Concentration of H_3PO_4
Source: Own Elaboration

2.3 Characterization of HAp

2.3.1 Scanning Electron Microscopy

To know the morphology of the material, a Scanning Electron Microscopye (Jeol IT-100) coupled to an X-ray microprobe (EDX) was used for elemental analysis.

For the elemental analysis, it was carried out on the surface of the sample in three different zones, the average was taken, to obtain the Ca/P ratio.

2.3.2 FTIR spectroscopy

To know the functional groups in HAp, a Perkin-Elmer FT model 2000 spectrophotometer was used in ATR mode, with an acquisition interval of 4000 to 500 cm^{-1}, the analysis was performed directly on the sample.

2.3.3 μ-Raman spectroscopy

To determine the crystalline phases of the samples, a μRaman equipment model XploraPlus Jobin Yvon Horiba was used, a solid state laser (λ=532 nm) was used, the maximum power is 25 mW, a 50 X lens was used to focus and collect scattered light. The power on the surface of the sample is 10% of the nominal power, diffraction grating of 1200 lines per millimeter was employed, 100 acquisitions of 1 s each were averaged.

3. Results and discusión

To study the effect of the H_3PO_4 concentration on Ca/P ratio, all samples were heat treated at 800ºC for 2 hours.

3.1 Scanning Electron Microscopy

Figure 2 shows the micrographs of the HAp, it is observed that all the samples present particles with an irregular shape and size.

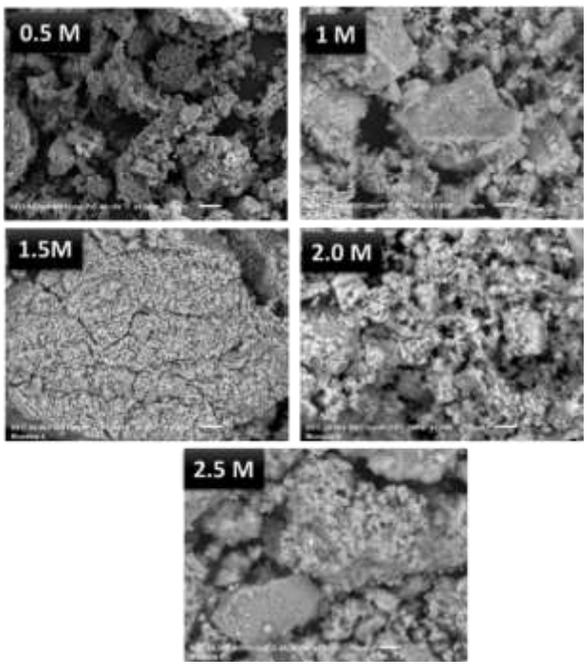

Figure 2 HAp micrographs
Source: Own Elaboration

At a molar concentration of 0.5, agglomerates are observed that are heterogeneously distributed on the surface of the material, with a porous morphology. Likewise, by increasing the concentration of phosphoric acid, the agglomerates and the presence of irregular pores are preserved.

The presence of empty spaces is since there is not a homogeneous distribution of the material. In addition, the presence of pores will facilitate contact with any liquid substance, promoting a greater exchange of ions (Fragoso A., y otros, 2018); therefore, the material has a potential use as a photocatalyst for the degradation of pollutants.

3.1.1 Elemental analysis

Table 2 shows the averages obtained from the atomic ratio, including the Ca/P ratio of the sample.

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[M]	C	O	Mg	Ca	P	Ca/P
0.5	14.6	49.7	0.55	40.6	2.1	19.33
1	6.42	57	0.41	31.5	2.4	13.30
1.5	6.36	59.5	0.39	29.1	4.3	6.90
2.0	13.5	57	0.00	24.4	5.1	4.75
2.5	5.55	61.9	0.26	25.3	6.6	3.84

Table 2. Atomic ratio vs concentration of H_3P0_4.
Source: Own elaboration

The influence of the concentration on the atomic relation Ca/P, is shown in Figure 3, as the concentration increases, the relation decreases; it indicates, at a concentration of 0.5 M there are approximately 19 calcium atoms for a phosphorus, while at 2.5 M it is reduced to 4 calcium atoms for a phosphorus.

The values obtained indicate the presence of a carbonated HAp, as reported in the literature (Rivera J.A, Fetter G., Bosch P., 2011).

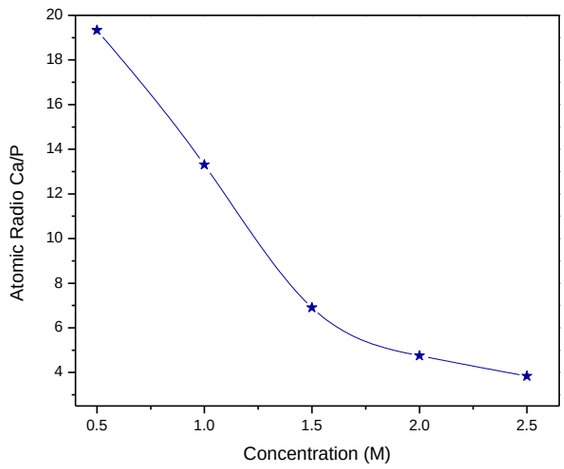

Figure 3 Ca/P atomic ratio vs H_3PO_4 concentration
Source: Own Elaboration

3.2 FTIR spectroscopy

Figure 4 presents the infrared spectra of the HAp samples as a function of the H_3PO_4 concentration (0.5 M, 1M, 1.5 M, 2.0M and 2.5M). The spectra show the characteristic bands of phosphate at 1026 cm^{-1} (1082 cm^{-1}) and hydrated phosphate at 2909 cm^{-1} (2900 cm^{-1}) (Díaz, 1974), of carbonate at 1453, 14010, 980 y 872 cm^{-1} (Pleshko N., Boskey A. and Mendelsohn R., 1991), cyclic carbonate a 2988 cm^{-1}(2990 cm^{-1}) (Velázquez López E., Gutiérrez Arzaluz M., Aguilar Pliego J., Múgica Álvarez V., Torres Rodríguez M., 2015), the OH group is observed at 3638 cm^{-1} (Rivera J.A, Fetter G., Bosch P., 2011).

When the material is impregnated with different concentrations of H_3PO_4, it is observed that the 1026 cm^{-1} band grows as the acid concentration increases, this confirms that changing the concentration of phosphoric acid increases the presence of phosphates in the material.

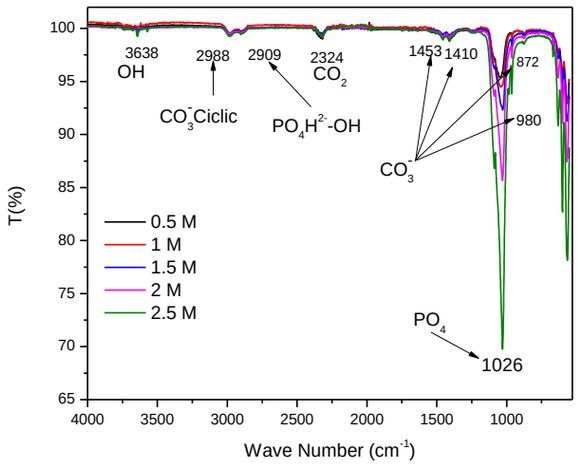

Figure 4 HAp espectra, with 0.5 M, 1M, 1.5 M, 2.0M and 2.5M
Source: Own Elaboration

3.3 MicroRaman spectroscopy

In Figure 5, it is possible to observe the normalized Raman spectra of all synthesized samples corresponding to the different concentrations of H_3PO_4. Signs were found in 150, 277, 707 y 1083 cm^{-1}.

The indicated signals all correspond to calcium carbonate and come from vibrations of the CO_3^{2-} group of vibrational modes of the lattice (Harris, Mey, Hajir, Mondeshkic, & Wolf, 2015), (Bai, Guo, Li, & Huang, 2017), (de Paula, Huila, Araki, & Toma, 2010).

In the Raman spectra, no signals corresponding to the PO_4^{3-} group corresponding to the HAp were found. In a previous report (Contreras C., Garcia G., Enriquez P., & Castrejon S., 2022) it was possible to appreciate that there were very weak signals for the internal vibrations corresponding to phosphate groups. The intention was to monitor if the signals associated with groups PO_4^{3-} suffered an affectation in their intensity as a result of the treatment with H_3PO_4. We believe that the laser used does not allow efficient Raman scattering, therefore very little signal is generated, but these groups are present in the FTIR spectra and in the EDX analysis.

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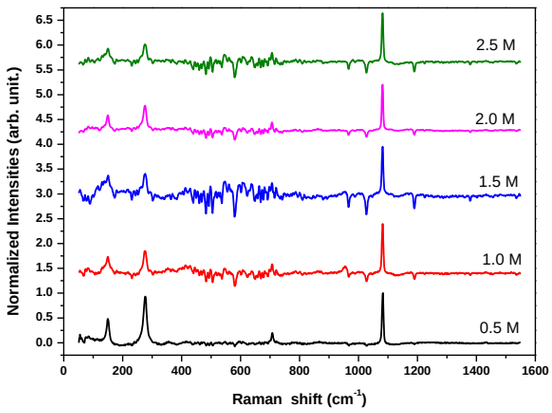

Figure 5. Normalized Raman spectra of HAp
Source: Own Elaboration

On the other hand, it was observed that the intensities of the signals located at 150 and 277 cm^{-1} in the Raman spectra are sensitive to the molar concentration of the H_3PO_4 solutions. It was noted that the intensity of these signals decreased as the concentration of H_3PO_4 increased. The following relationships were calculated:

$$I_{r1} = \frac{I_{150}}{I_{1080}} \quad (1)$$

$$I_{r2} = \frac{I_{277}}{I_{1080}} \quad (2)$$

Where I_{r1} is the ratio of intensities between the peak located at 150 cm^{-1} (I_{150}) and the one located at 1080 cm^{-1} (I_{1080}); in the case of I_{r2}, it is the ratio of intensities I_{277} corresponding to the signal located at 277 cm^{-1} and I_{1080}, which is the same as in the previous case.

Subsequently, I_{r1} and I_{r2} were plotted as a function of the molar concentration of H_3PO_4 as shown in Figure 6. The tendency of the relative intensities I_{r1} and I_{r2} to decrease as the molar concentration of H_3PO_4 increases can be clearly seen. This coincides with the tendency of the Ca/P ratio to decrease as a function of increasing H_3PO_4 concentration.

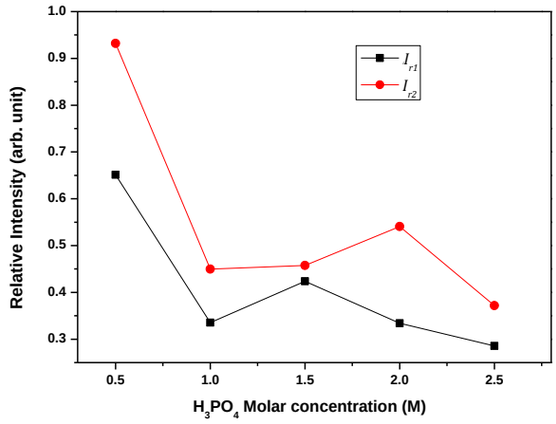

Figure 6 Relative intensity variatios as a funtion of H_3PO_4
Source: Own Elaboration

Conclusions

In the results obtained from the characterization techniques, the characteristic groups of the HAp were found; therefore, it is possible to synthesize the material using the eggshell as a precursor. With this technique it is possible to reduce the amount of waste, with water being the only by-product, which favors the environment.

A Ca/P ratio greater than 1.67 was obtained, resulting in a B type carbonated HAp. By increasing the H_3PO_4 concentration, the atomic content of phosphorus increase and carbonates decrease, as could be verified both in EDS, FTIR and micro-Raman. Additionally, photocatalytic test of all prepares HAp, Will be carried out in order stablish a relation ship between Ca/P ratio and photocatalytic performance.

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