Synthesis of Brushite from Phosphogypsum Industrial Waste

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Abstract: Dicalcium phosphate dihydrate (DCPD) nanoparticles, also known as brushite, are considered an important bioceramic compound. In this study, brushite was prepared from Moroccan phosphogypsum (PG) using a new sol-gel method. A two-step technique undergoes the synthesis of brushite, the preparation of anhydrite from PG followed by adding phosphoric acid in the presence of sodium hydroxide. The morphology, the chemical composition, and the crystallites size were obtained using Scanning Electron Microscopy (SEM-EDAX), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR), respectively. According to the Debye-Scherrer equation, these characterization methods indicated that the synthesized brushite was highly pure according to the Ca/P ratio of 1.14 and an average crystallites size estimated at 66 nm. These results proved that the brushite was successfully synthesized from Moroccan phosphogypsum.

Keywords: brushite, phosphogypsum, nanoparticles.

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1. Introduction

Dicalcium phosphate dihydrate (DCPD), also called brushite, consists of three major elements: calcium, phosphorus, and oxygen. It is considered the main compound of the bones and teeth of vertebrates, including most human hard tissues. Some of these phosphates have cationic and/or anionic substitutions leading to many forms of structures. Due to their composition and availability, they have gained significant importance in various fields of science such as biology, chemistry, health, and medicine, including biomineralization [1–6].

The most common forms of Calcium phosphate phases studied for bio-functional applications include hydroxyapatite (HA, Ca10(PO4)6(OH)2), dicalcium phosphate anhydrous (DCPA, CaHPO4), amorphous calcium phosphate (ACP), tetra calcium phosphate (TTCP, Ca4(PO4)2O), Dicalcium phosphate dihydrate (DCPD, CaHPO4·2H2O)[7,8]. Brushite is naturally present in the pathological form of kidney stones or the form of arthritis and cavities. It is also found in guano-rich caverns and is formed by the interaction between a phosphate solution derived from guano, calcite, and clay at low pH [9,10] or by the interaction of phosphate solution and limestone rocks or blocks buried inside the guano [11]. Brushite is used for various applications, particularly in the biomedical field and the food industry [12]. DCPD phosphate can contain several other ionic elements in its structure, either by doping,
substituting calcium, or substituting phosphate groups [13–16]. Synthesis of brushite include precipitation of emulsions[17–20], crystallization of solutions[21–23], sol-gel [24], hydrothermal synthesis [25–28], microwave-assisted methods [28–30], chemical deposition [31–35], electrodeposition [36–40], and mechanic-chemical synthesis [41]. The method used in this study is a sol-gel reaction due to its simplicity, low cost, and ease of application in industrial production [42]. In this work, a new sol-gel technique was applied to synthesize the brushite from Moroccan phosphogypsum. The obtained product was dried at 105°C and was characterized.

2. Materials and Methods

2.1. Characterizations methods.

The structure was examined using an X-ray diffractometer (XRD X’Pert Pro MPD of Panalytical using Cu Kα radiation (λ=1.54 Å) at a scanning rate of 0.02°/s for a 2θ range of 5–80. Scanning Electron Microscopy was done using an SEM (FEI Quanta 200 ESEM). Infrared was performed by FTIR-8400S. Analysis ICP was performed by AESJobinYvonUltima.

2.2. Starting materials.

Sulfuric acid (H₂SO₄ 98%) and phosphoric acid (H₃PO₄ 85%) were purchased from Sigma Aldrich, and the sodium hydroxide (NaOH 99%) was obtained from Prolabo. The phosphogypsum was provided from the Moroccan phosphate industry located in El Jadida, Morocco. The collected PG was dried at 80°C, ground, and sieved through an 80 µm sieve. The chemical composition of PG was evaluated by ICP analysis; major components and traces are summarized in Table 1. According to this data, the principal components of the PG are expressed as CaO and SO₃; and the traces of P₂O₅; Al₂O₃; Fe₂O₃; K₂O, F; MgO; Na₂O, and SiO₂.

<table>
<thead>
<tr>
<th>Element</th>
<th>CaO</th>
<th>SO₃</th>
<th>P₂O₅</th>
<th>C</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>K₂O</th>
<th>F</th>
<th>MgO</th>
<th>Na₂O</th>
<th>SiO₂</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>PG</td>
<td>32.27</td>
<td>45.1</td>
<td>0.92</td>
<td>0.14</td>
<td>0.13</td>
<td>0.83</td>
<td>0.34</td>
<td>0.12</td>
<td>0.17</td>
<td>0.14</td>
<td>0.25</td>
<td>Greenish-yellow</td>
</tr>
</tbody>
</table>

2.3. Preparation of brushite powder.

The brushite was synthesized using a sol-gel method following two principal steps. The first one is preparing the anhydrate from Moroccan phosphogypsum; the phosphogypsum waste was then treated using sulfuric acid 67% to obtain an anhydrate crystal. In the second step, 0.073 moles of anhydrite were mixed with 100 mL of distilled water and 0.058 moles of H₃PO₄. The solution was stirred at a speed of 500 rpm for 48H, and the pH was adjusted in a range of 6-7 by NaOH. Brushite formation can be expressed by the following reaction (1):

\[
10\text{CaSO}_4 + 10\text{H}_3\text{PO}_4 + 20\text{NaOH} \rightarrow 10\text{CaHPO}_4\cdot2\text{H}_2\text{O} + 10\text{Na}_2\text{SO}_4 \quad (1)
\]

The resulting white suspension was then separated from the solution and washed with acetone. The resulting stoichiometric brushite was dried at 105°C for 24 hours. The schema of the preparation of brushite powder is presented in Figure 1.
3. Results and Discussion


Table 2 shows the chemical compositions of anhydrite and brushite performed by ICP. The main components of anhydrite are CaO and SO$_3$ with 40.28% and 57.5%, respectively, the P$_2$O$_5$, M.O, Al$_2$O$_3$, Fe$_2$O$_3$, and SiO$_2$ present in the form of impurities with pH 4.23. On the other hand, brushite is rich in CaO and P$_2$O$_5$ and poor in SO$_3$, Al$_2$O$_3$, Fe$_2$O$_3$, and SiO$_2$ with pH 7. The ratio of Ca/P for brushite was 1.14 [15, 43–46].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CaO</th>
<th>SO$_3$</th>
<th>P$_2$O$_5$</th>
<th>M.O</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>MgO</th>
<th>SiO$_2$</th>
<th>pH</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anhydrite</td>
<td>40.28</td>
<td>57.50</td>
<td>0.20</td>
<td>0.0096</td>
<td>0.01</td>
<td>0.04</td>
<td>0.09</td>
<td>0.72</td>
<td>4.23</td>
<td>White</td>
</tr>
<tr>
<td>Brushite</td>
<td>36.4</td>
<td>1.25</td>
<td>38.94</td>
<td>-</td>
<td>0.01</td>
<td>0.02</td>
<td>0.05</td>
<td>0.68</td>
<td>7</td>
<td>White</td>
</tr>
</tbody>
</table>

3.1.2. XRD analysis of brushite.

Figure 2 shows the XRD patterns of brushite particles dried at 105°C. The spectrum confirmed that the obtained product had higher crystallinity and was mainly composed of brushite. The results are in good agreement with the JCPDS file 009-0077 in peak position and peak intensity. The maximum peaks intensities were located at 2θ equal to 12°, 21°, and 29° these peaks were attributed to the Miller indices of (020), (021), and (111) [15,47]. The observed diffraction peaks were related to DCPD, and no impurity phases were found. The particle size was calculated by the Scherer equation [45–47]:

\[ D = K \beta^{1/2}/\cos \lambda \theta \]  

(2)

D is particle size (Å), K is 0.9, λ is the wavelength of X-rays against 1.54056 Å, λ is Bragg angle of the peak from diffraction, and β$^{1/2}$ is in terms of radians.
\[ \beta_{1/2} = (\beta_m^2 - \beta_s^2) \]  

(3)

Based on equations (2) and (3), the particle size of brushite was 66 nm.

![Figure 2. XRD spectra of brushite dried at 105°.](image)

3.1.3. FTIR of brushite.

Figure 3 shows the infrared absorption spectra of brushite treatment at 105°C. Bands located between 4000 and 1600 cm\(^{-1}\), 4 bands characteristics of the vibrations of two types of water molecules (3537, 3484, 3292, and 3166 cm\(^{-1}\)) were observed. The band at 2931 cm\(^{-1}\) corresponds to the O-H elongation vibration of the P-(OH) entities. This allocation of tapes is in perfect agreement with the structural data previously reported. The band packet at about 2373 cm\(^{-1}\) is assigned to combination vibrations. The high band at 1648 cm\(^{-1}\) corresponds to the modes of deformation of water molecules. Bands between 1600 and 400 cm\(^{-1}\) grouped all the modes of vibrational elongations (11245, 1062, 988 cm\(^{-1}\)) and deformations (576, 526, and 410 cm\(^{-1}\)) of the P-O bonds.

The band observed at 870 cm\(^{-1}\) corresponds to the elongation vibration of the P-(OH) bond. The other bands were assimilated to the shaking modes of the water molecules (657 cm\(^{-1}\)) and the in-plane and out-of-plane deformation of the O-H bonding of the (HPO\(_4\))\(^{2-}\) (1213 cm\(^{-1}\) and 790 cm\(^{-1}\)) groups. This agrees well with FT-IR data of calcium hydrogen phosphate reported in the literature [15,16,48,49].

![Figure 3. FTIR spectra of brushite dried at 105°.](image)

The micrographs in Figure 4 show our synthetized brushite dried at 105°C in different magnifications (20000X and 5000X). The results show that the particles are shaped like small plates based on the layered structure of brushite. The layers grow faster in two directions so that plates are formed. The edge lengths of these plates were determined to be between 60 nm and 66 nm [50].

![Figure 4. SEM images of brushite powder dried at 105°C.](image)

3.1.5. Energy dispersive X-ray of brushite.

The EDAX spectrum (Figure 5) confirms the presence of calcium (Ca), phosphorus (P), oxygen (O), and a trace of Na in the stochiometric brushite sample. Chemical analysis of brushite shows the Ca/P ratio is 1.14 [15].

![Figure 5. EDAX of brushite powder dried at 105°C.](image)

4. Conclusions

The brushite was synthesized by mixing anhydrite prepared from PG with phosphoric acid in the presence of Hydroxide sodium at room temperature. This DCPD was characterized by X-ray diffraction (XRD), Fourier transforms infrared spectroscopy (FTIR), Scanning Electron Microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDAX).

The XRD and FTIR spectrum showed that the prepared DCPD was pure, and the size of the crystallites was estimated at 66 nm. The EDAX spectrum of DCPD showed the existence of Ca, P, and O elements and the Ca/P ratio value of 1.14, which confirmed the formation of...
brushite. The EDAX and ICP result also established that the brushite crystals had a near theoretical chemical composition.

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**Conflicts of Interest**

The authors declare no conflict of interest.

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