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COMPARISON OF AIR CONTACT AND DISTILLED WATER DISTRIBUTION METHOD IN THE CONVERSION OF Cao TO $Ca(OH)_2$ AS A PRECURSOR HYDROXYAPATITE SYNTHESIS

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ABSTRACT

Eggshells containing $CaCO_3$ have potential as bioceramics for several tissue engineering applications. The content of $CaCO_3$ converted into $Ca(OH)_2$ can be used as a precursor to implant material. The purpose of the study was to compare two methods of converting CaO into $Ca(OH)_2$ as the primary material for making hydroxyapatite. The method used is direct contact with air and dissolution with water. Hydroxyapatite synthesis using $Ca(OH)_2$ is calcined from $CaCO_3$ with *a sintering* temperature of 900 °C. The result of calcination is in the form of CaO. The stages of obtaining $Ca(OH)_2$ by converting CaO using two methods, namely direct contact with air and dissolution with water. The XRD characterization results obtained that $Ca(OH)_2$ results from direct contact with air show the formation of phase (*portlandite*), which is characterized by its presence at the highest typical 2θ angles = 18.18°, 28.68°, 34.30°, 47.40°, 50.92°, 54.16°, and 62.62°. The XRD $Ca(OH)_2$ pattern with the distilled water distribution process shows the formation of a phase (*portlandite*) characterized by its presence at angles of 2θ = 18.18°, 28.68°, 34.30°, 47.40°, 50.92°, 54.16°, and 62.62 °. The results of FTIR $Ca(OH)_2$ characterization of air contact and water dissolution showed strong O-H functional groups at wave numbers 3643 cm^{-1} and 3642 cm^{-1}, C-O groups at 1487 cm^{-1} and 1483 cm^{-1}. This suggests that both methods can convert CaO to $Ca(OH)_2$, which synthesizes hydroxyapatite. The hydroxyapatite characterization results obtained have met the standard.

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INTRODUCTION

Biomaterials, encompassing synthetic and natural substances, are increasingly being developed for various applications, including bone substitutes for implants, injectable solutions, absorbents, and more. These materials are designed to replace or support tissues or structures within the human body. A plethora of biomaterials are derived from raw materials found in nature. Hydroxyapatite stands out due to its versatility and can be synthesized from various natural sources including fish scales, animal bone bio-waste, natural gypsum, and calcite [1].

Hydroxyapatite (HA), chemically denoted as $Ca_{10}(PO_4)_6(OH)_2$, is a key component of enamel, dentin, and bone. It is renowned for its biomimetic properties and chemical stability, making it a preferred alternative in medical applications. HA's applications are diverse, ranging from bone grafting and restorative materials to usage in root canal sealers and dentifrices. As a member of the apatite mineral group, HA comprises calcium and phosphorus, closely resembling the mineral component of bone [2]. This chemical similarity to bone minerals significantly enhances the demand for HA in various biomedical applications. Hydroxyapatite (HAp) is suitable for bone replacement due to its compatibility with biological systems. Biomaterials, in a broader sense, refer to synthetic substances that can be implanted into living systems to replicate the functions of living tissues or organs [3]. The synthesis and application of HAp epitomize the advancements in biomaterials, emphasizing the importance of materials science in healthcare and medical technologies.

The potential of eggshell waste as a resource for biomaterials like hydroxyapatite is considerable, given the widespread consumption of eggs as a protein source. Eggshells, predominantly composed of calcium carbonate ($CaCO_3$), are not extensively utilized due to limited exploration into effective methods of converting CaO to $Ca(OH)_2$ from unconventional sources like eggshells. However, with the growing demand for effective and efficient biomaterials, eggshells present a sustainable and environmentally friendly option. Chicken eggshells, containing about 94% $CaCO_3$, are a promising starting material for the synthesis of hydroxyapatite, offering a significant supply of calcium [4].

Purebred chicken (Gallus gallus) eggshells are a potential source of hydroxyapatite, with a composition that includes 94% calcium carbonate ($CaCO_3$), 1% magnesium carbonate, 1% calcium phosphate, and 4% organic matter. The high level of $CaCO_3$ in eggshells makes them suitable for hydroxyapatite synthesis. The choice of chicken eggshells is driven by their availability and the fact that chicken eggs are a commonly consumed source of animal protein, leading to significant waste accumulation [5]. Hydroxyapatite derived from purebred chicken eggshells has potential applications in the medical field, such as bone grafts or dental implants. However, certain conditions, including biocompatibility, must be met for these applications. Biocompatibility ensures the material can interact with a living system without causing adverse effects [6]. This attribute is crucial to prevent implant rejection by the host.

New biomaterials, including those derived from eggshells, must also pass biological assessments, such as cytotoxicity tests. Cytotoxicity testing often employs periodontal ligament fibroblast cells, key in regenerating dental support tissue. These cells play an essential role in facilitating the reattachment of teeth to the alveolar bone [7]. The development and utilization of eggshell-based hydroxyapatite in healthcare and medical technologies underscore the importance of sustainable practices in biomaterials research and application.

The synthesis of hydroxyapatite using synthetic materials often involves using calcium oxide (CaO), which is derived from calcium carbonate ($CaCO_3$) calcination. CaO is produced free of organic compounds that might impede hydroxyapatite synthesis during calcination. One key aspect of this process is the influence of calcination temperature on the yield of CaO. Higher calcination temperatures lead to greater CO_2 release, thereby accelerating the decomposition of $CaCO_3$ into CaO [8]. Moreover, an increase in combustion temperature can enhance the crystallinity of the produced hydroxyapatite. Higher degrees of crystallinity imply a more orderly arrangement of the constituent atoms of hydroxyapatite. Consequently, higher combustion temperatures are associated with increased crystallinity and, hence, smaller sizes [9].

In the synthesis process, the precursor CaO is transformed into calcium hydroxide ($Ca(OH)_2$), the primary material for hydroxyapatite production. The conversion of CaO to $Ca(OH)_2$ can be achieved through different methods, each offering an alternative approach to procuring the primary material needed for high-quality hydroxyapatite synthesis. These methods are considered efficient and effective due to their simplicity and the relatively short duration of the process.

This study compares two distinct methods of converting CaO to $Ca(OH)_2$ from eggshells to synthesize hydroxyapatite. The comparison aims to identify the most efficient and effective technique for advancing biomaterials production. By exploring alternative methods for hydroxyapatite synthesis, this research endeavors to enhance the quality and efficiency of biomaterials, potentially benefiting various applications in healthcare and medical technologies.

METHODS

1. Material and Instrument

The synthesis process of hydroxyapatite involves several stages, each requiring specific equipment and materials. Initially, for the calcining of chicken eggshells, 1 kg of eggshells is cleaned using running water to remove any mucous membranes and dirt. These eggshells are then dried in an oven at 110-115 °C for 2 hours to evaporate moisture and ground into a powder at 900 °C for 5 hours in a furnace to yield calcium oxide (CaO).

Two methods convert CaO to calcium hydroxide ($Ca(OH)_2$). The first method involves exposing CaO to air at room temperature for 24 hours, with the material being analyzed using X-ray diffraction (XRD). The second method involves mixing CaO with distilled water, drying the mixture to form a powder, and then characterizing it using XRD. The calcium (Ca) levels in the calcined eggshell powder are measured using an atomic absorption spectrometer (AAS). The sample preparation involves mixing 0.1 grams of the powder with 5 mL of 37% HCl, which is then transferred into a 100 mL measuring flask. A separate 1 mL sample solution is prepared in another 100 mL flask using a blank of 5 mL HCl 37% and aquades. The measurement is conducted at a wavelength of 422.5 nm using an ethylene flame. The synthesis of hydroxyapatite, prepared $Ca(OH)_2$ and diammonium hydrogen phosphate ($(NH_4)_2HPO_4$) are used in a Ca/P ratio of 1.67:1. The solutions of these two compounds are gradually mixed, stirred to ensure homogeneity, and then left to stand overnight. The resulting soft powder precipitate is filtered, washed, and dried at 100 °C for 3 hours. This precipitate is then calcined at 900 °C for 5 hours, ground into a fine powder, and stored in a desiccator. The synthesized material is further characterized using FTIR and XRD.

2. Calcining of chicken eggshells

The process begins by thoroughly cleaning 1 kg of chicken eggshells under running water to eliminate mucous membranes and dirt. Subsequently, the eggshells are rinsed with clean water. The cleaned eggshells are then dried in an oven at a temperature range of 110-115 °C for 2 hours to remove residual moisture. After drying, the eggshells are ground into a fine powder at a temperature of 900 °C for 5 hours in a furnace, transforming them into calcium oxide (CaO) and eliminating organic compounds [10].

3. Convert of CaO to $Ca(OH)_2$ by air contact.

The conversion of calcium oxide (CaO) to calcium hydroxide ($Ca(OH)_2$) in the synthesis process includes two distinct approaches. In the first method, the air contact method, CaO derived from the calcination of eggshells is exposed to the ambient air at room temperature for 24 hours. This exposure facilitates the natural transformation of CaO into $Ca(OH)_2$. Once this conversion is complete, the resultant material is analyzed using X-ray Diffraction (XRD). This analytical technique helps assess the chemical composition and structural properties of the newly formed $Ca(OH)_2$.

4. Convert CaO to $Ca(OH)_2$ with distilled water.

The second approach involves a direct interaction with distilled water. In this method, the calcined CaO is thoroughly mixed with distilled water. After mixing, the resultant slurry is dried until it forms a dry powder. This powder, presumed to be $Ca(OH)_2$, is also analyzed using XRD. This analysis aims to confirm the successful conversion of CaO to $Ca(OH)_2$. Both methods aim to provide a reliable and efficient route for producing $Ca(OH)_2$, a crucial precursor in the synthesis of hydroxyapatite for various biomedical applications.

5. Measurement of Calcium (Ca) Levels

Atomic absorption spectroscopy (AAS) is employed to determine the calcium content. A sample of 0.1 grams of the calcined eggshell powder is mixed with 5 mL of 37% HCl and diluted in a 100 mL flask. A separate aliquot of this solution is prepared for measurement. The calcium levels are analyzed at a wavelength of 422.5 nm using an ethylene flame, and the samples are further characterized using FTIR and XRD to understand their composition and structure.

6. Hydroxyapatite Synthesis

The synthesis involves preparing a mixture of $Ca(OH)_2$ and diammonium hydrogen phosphate ($(NH_4)_2HPO_4$) in a Ca/P ratio of 1.67:1. $Ca(OH)_2$ is dissolved in water to form the first solution, and $(NH_4)_2HPO_4$ is dissolved separately to form the second solution. The second solution is gradually added to the first, maintaining a controlled flow rate, and the mixture is stirred to ensure homogeneity. After an overnight rest, the soft powder precipitate is filtered, washed, and dried. This precipitate is then calcined, ground into a fine powder, and stored for further use. The synthesized hydroxyapatite is characterized using FTIR and XRD [11], ensuring its suitability for applications in biomaterials.

RESULTS AND DISCUSSION

In Figure 1, the eggshells represent waste from egg consumption, a byproduct currently lacking commercial utilization.

Unmanaged accumulation of such eggshell waste can lead to environmental issues, including air pollution characterized by unpleasant odors. The structure of chicken eggshells comprises several layers: a cuticle, a crystalline layer, a spongy calcareous layer with pores, a nucleus, and a mammillary layer. Typically, high-quality eggshells are distinguished by their bright color and smooth texture, devoid of any blemishes

Figure 1 Eggshell.

The inner shell membrane consists of two distinct layers of fibrous material, called the inner and outer skin membranes. These membranes have been identified as potential adsorbents capable of removing reactive dyes from colored wastewater and heavy metal ions, thus contributing to water purification efforts [12]. Compositionally, chicken eggshells predominantly contain calcium carbonate (98.4%), alongside minor constituents like magnesium carbonate (0.8%) and tricalcium phosphate (0.8%) [13]. The high calcium carbonate content in purebred chicken eggshells presents a valuable opportunity for the synthesis of hydroxyapatite, a material with significant applications in the field of biomaterials. This approach not only offers a sustainable solution for waste management but also contributes to the development of valuable materials for various industrial and medical applications.

The Tutut shell powder, primarily composed of calcium carbonate ($CaCO_3$), is subjected to a calcination process at a temperature of 900 °C for 5 hours. Calcining at lower temperatures might lead to the reversion of the resultant calcium oxide (CaO) back to $CaCO_3$, accompanied by a relatively low decomposition rate of CO_2. At 900°C, the precursor compounds react, forming the hydroxyapatite phase. The purpose of this calcination process is to transform $CaCO_3$ into CaO. During this process, all organic components within the Tutut shell are eliminated, resulting in the emission of CO_2 and H_2O [14].

Calcination also plays a crucial role in removing organic compounds and impurities that may hinder the formation of hydroxyapatite (HAp) [15]. Consequently, after the calcination process, the eggshell is expected to be converted into CaO, reducing the sample's mass [16]. The removal of organic compounds is beneficial as it can enhance the yield of hydroxyapatite.

The chemical reaction involved in this process is as follows:

$$CaCO_{3(s)} \xrightarrow{\Delta} CaO_{(s)} + CO_{2(g)} \quad \textbf{....(1)}$$

Calcium carbonate ($CaCO_3$) is the primary constituent of eggshells, and its transformation into calcium oxide (CaO) is efficiently achieved through calcination at high temperatures. This decomposition of $CaCO_3$ into CaO is critically facilitated by applying elevated temperatures during the calcination process. Empirical studies and systematic observations have determined that the optimal temperature for the calcination of eggshell powder, leading to the formation of CaO, is 900 °C [17]. This optimal calcination temperature is essential for ensuring the complete decomposition of $CaCO_3$ while preventing its reformation.

The relevance of this process lies in the generation of CaO, a key precursor essential in the synthesis of hydroxyapatite. Hydroxyapatite synthesized from such procedures is extensively utilized across various domains, notably in developing and manufacturing biomaterials. The conversion of eggshell waste, an abundant and sustainable resource, into a valuable entity like CaO highlights the significance of this research in advancing sustainable practices within the field of material science and technology. This approach addresses waste management concerns and contributes to the broader goal of sustainable resource utilization in scientific and industrial applications.

1. Conversion of CaO to $Ca(OH)_2$ using two methods

The conversion of calcium oxide (CaO) to calcium hydroxide ($Ca(OH)_2$) is conducted using two distinct methods: direct air contact and dispersion in distilled water. This process aims to hydrate CaO into $Ca(OH)_2$, following the reaction equation:

$$2CaO\ (s) + 2H_2O\ (g) \rightarrow 2Ca(OH)_2\ (s).\ \textbf{(2)}$$

These methods offer alternative approaches to convert CaO to $Ca(OH)_2$, serving as the primary precursor for hydroxyapatite (HAp) synthesis. X-ray diffraction (XRD) analysis of $Ca(OH)_2$ obtained through direct air contact indicates the formation of the portlandite phase. This is evidenced by characteristic peaks at angles of 2θ = 18.18°, 28.74°, 34.06°, 47.18°, 50.94°, 54.56°, 57.38, 59.48, 62.48°, 64.50°, 67.46°, as per JCPDS No. 44-1481 data (Figure 2). Similarly, the XRD pattern of $Ca(OH)_2$ produced by the distilled water dispersion process also displays the portlandite phase, characterized by peaks at 2θ = 18.18°, 28.74°, 34.20°, 47.26°, 50.92°, 54.56°, 57.56, 59.48, 62.20, and 64.34 (Figure 3), according to the same JCPDS data. Both methods are efficient in cost and duration, as they do not require specialized chemicals and are relatively quick and straightforward to apply.

The XRD and Fourier Transform Infrared Spectroscopy (FTIR) results confirm that both methods' Ca(OH)2 exhibit typical compound characteristics. The X-ray diffraction pattern of $Ca(OH)_2$ derived from eggshells indicates the production of the $Ca(OH)_2$ compound. CaO's highly hygroscopic nature leads to a rapid reaction with water vapor in the air, forming $Ca(OH)_2$. The alkaline surface of CaO, enriched with oxide anions, facilitates this reaction. The XRD patterns align with the portlandite phase's expected $Ca(OH)_2$ [18].

Additionally, XRD analysis provides insights into the average crystal size influenced by the calcination process. The temperature and duration of heating play pivotal roles in crystal growth. Inappropriate calcination conditions can lead to increased crystal sizes, while optimal heating processes result in regular crystal shapes, maintaining the phase and alleviating internal stress [19]. These findings underscore the importance of precise control over the calcination process to achieve desirable properties in the synthesized hydroxyapatite.

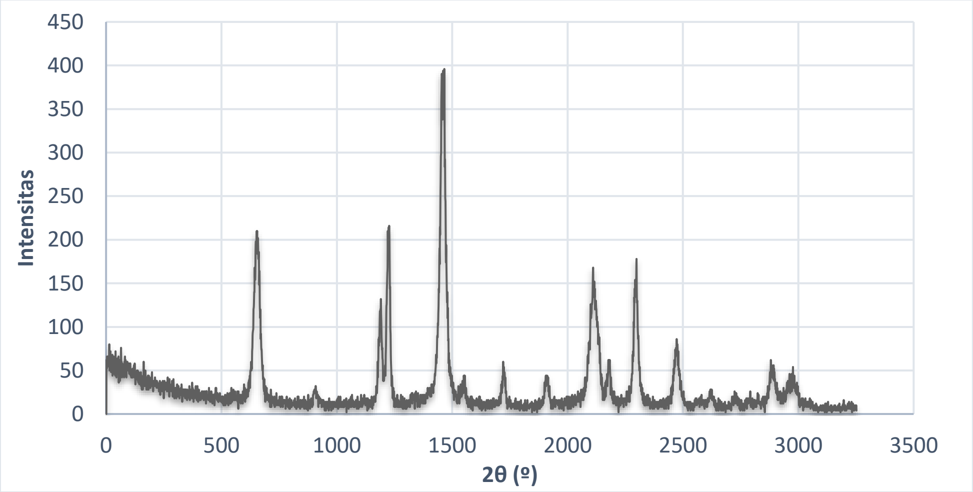


Figure 2 XRD Diffractogram of $Ca(OH)_2$ with Air Contact

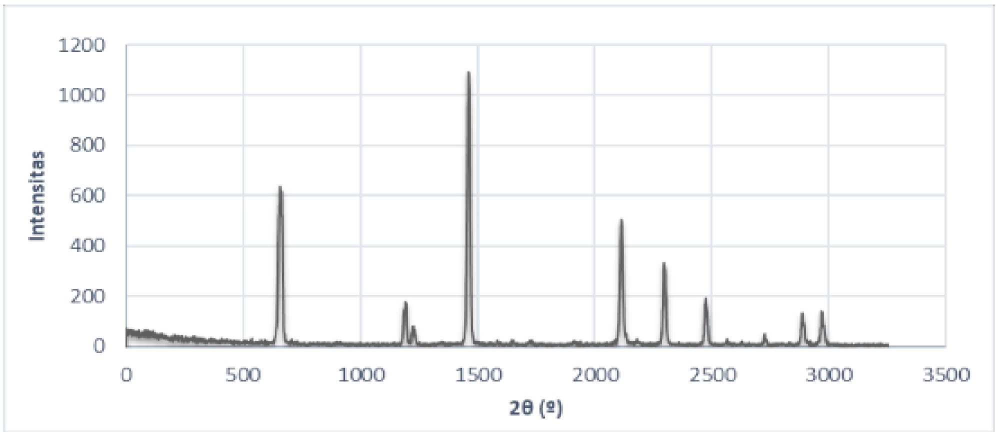


Figure 3 XRD Diffractogram of $Ca(OH)_2$ with distilled water

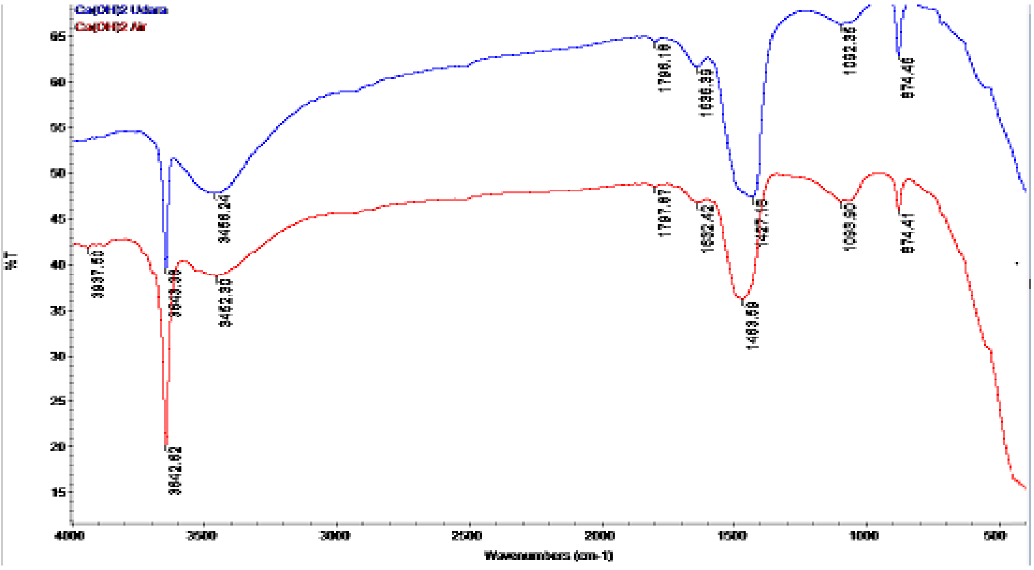


Figure 4 FTIR spectrum $Ca(OH)_2$ with air contact process (blue) and distilled water distribution process (red)

The $Ca(OH)_2$ compound obtained is the *starting material* used in the HAp synthesis stage. Data from XRD analysis of eggshell powder after calcination can be seen in Appendix 2b and $Ca(OH)_2$ phase standards. $Ca(OH)_2$ powder produced by air conversion and distilled water dispersion showed XRD results according to JCPDS and is suitable as Ca precursor material Hap

The Fourier Transform Infrared Spectroscopy (FTIR) characterization results for calcium hydroxide ($Ca(OH)_2$) obtained through both air contact and water dissolution methods revealed prominent absorption bands indicative of specific functional groups. A strong absorption band corresponding to the O-H functional group was observed at wavenumbers 3643 cm^{-1} and 3642 cm^{-1} for the samples obtained through air contact and water dissolution methods, respectively. Additionally, the absorption bands for the C-O group were identified at 1487 cm^{-1} for the air contact method and 1483 cm^{-1} for the water dissolution method.

The presence of these distinct absorption bands at these wavenumbers strongly indicates the successful conversion of calcium oxide (CaO) to calcium hydroxide ($Ca(OH)_2$) in both methods. The characteristic O-H stretching vibrations at around 3642-3643 cm^{-1} are typical for the hydroxyl groups in $Ca(OH)_2$, confirming the formation of the hydroxide phase. Similarly, the absorption bands for the C-O group further corroborate the chemical structure of the synthesized $Ca(OH)_2$.

These FTIR results are significant as they demonstrate that the air contact and water dissolution methods effectively convert CaO to $Ca(OH)_2$. This is crucial in synthesizing hydroxyapatite, where $Ca(OH)_2$ is a vital precursor. The ability to successfully convert CaO to $Ca(OH)_2$ using these methods lays the groundwork for the subsequent synthesis of hydroxyapatite, a material widely used in various biomedical applications such as bone replacement and dental implants.

2. Eggshell Ca Content

The analysis conducted on the calcium content of calcined tutut shells revealed a notable presence of calcium, quantified at approximately 68%. This high percentage of calcium in the shells positions them as an ideal primary material for synthesizing hydroxyapatite (HAp). The significant calcium content in these shells highlights their potential as a calcium precursor in HAp synthesis.

This finding is particularly relevant in producing hydroxyapatite from purebred chicken eggshells for medical applications. Hydroxyapatite synthesized from such sources is anticipated to be used in various biomedical applications, where its biocompatibility is a critical factor. Biocompatibility ensures that the material, when introduced into the human body, does not elicit any adverse reactions and integrates well with the surrounding biological tissues. This attribute is crucial for materials like hydroxyapatite, often used in bone grafts, dental implants, and other applications where direct interaction with body tissues is inevitable. The high calcium content in tutu shells not only paves the way for the efficient synthesis of biocompatible hydroxyapatite but also promotes the utilization of a natural and sustainable resource in the medical field, aligning with the principles of environmental sustainability and cost-effectiveness.

3. Hydroxyapatite Synthesis

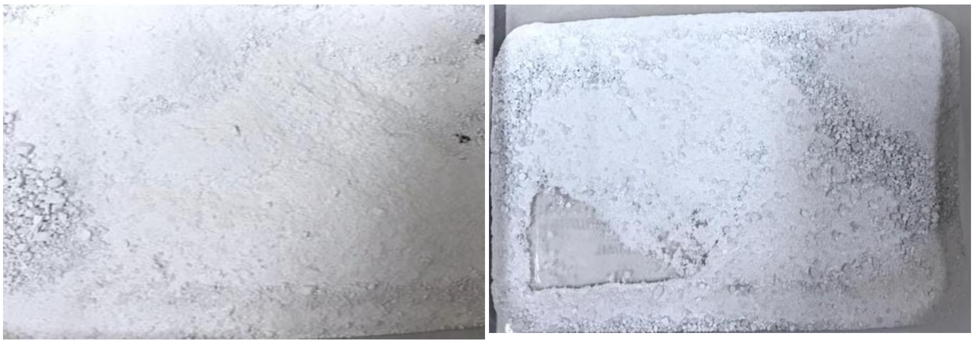
Hydroxyapatite (HA) is recognized as a bioactive biomaterial suitable for bone applications [20]. Biomaterials, defined as synthetic substances that can be implanted into living systems to replace or support the functions of living tissues or organs, play a crucial role in medical applications [21]. Eggshells have been identified as a recommended source for HAp synthesis [22]. Hydroxyapatite with an appropriate carbonate content exhibits compositional similarities to natural bone minerals, enhancing its bioactivity and biodegradability [23].

Hydroxyapatite can be synthesized from natural sources, particularly those of animal origin, such as crab shells, fish bones, and eggshells [24]. The synthesis process typically involves the precipitation method, which offers advantages in controlling hydroxyapatite's composition and physical properties. This method is environmentally friendly, as its by-product is primarily water, resulting in minimal contamination during synthesis and high purity levels in the hydroxyapatite particles [20].

The chemical reaction for HAp synthesis through precipitation involves combining $Ca(OH)_2$ derived from eggshells with diammonium hydrogen phosphate. The reaction proceeds as follows:

$$10Ca(OH)_2 + 6(NH_4)_2HPO_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 6H_2O + 12NH_4OH \text{ ………….} \textbf{(3)}$$

The resulting Particle HAp has high purity in a fast synthesis time (Figure 5).



Contact with air　　　　distribution of distilled water

Figure 5 Hydroxyapatite process of contact with air and distribution of distilled water

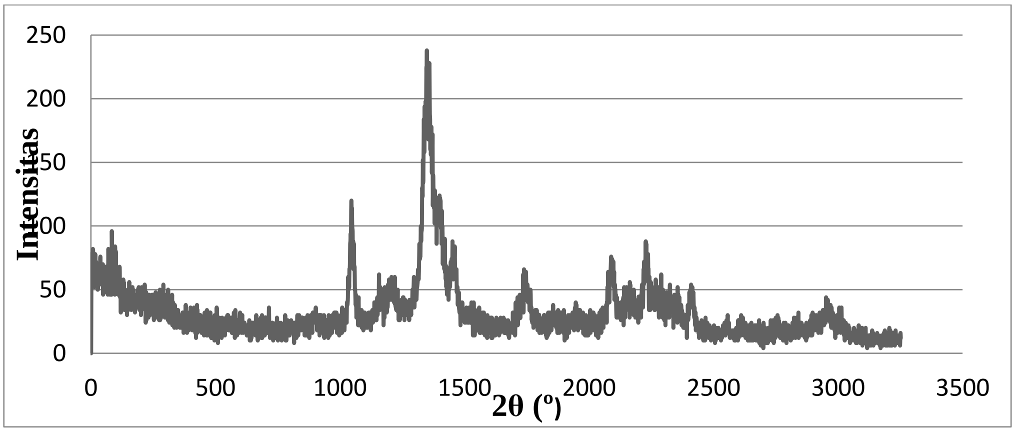


Figure 6 XRD Diffractogram of hydroxyapatite with Air Contact

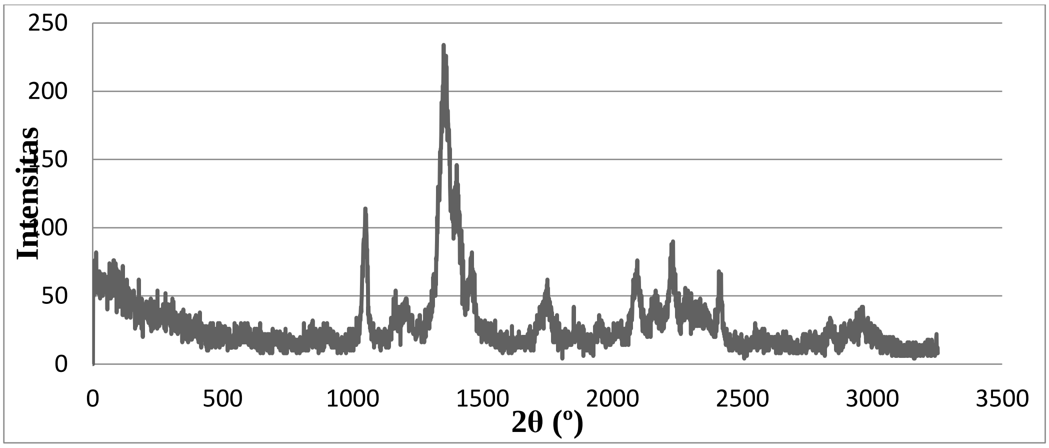


Figure 7 XRD Diffractogram of hydroxyapatite with distilled water

The X-ray diffraction (XRD) analysis of hydroxyapatite synthesized from the eggshells of purebred chickens, using calcium hydroxide ($Ca(OH)_2$) precursors derived from both air contact and distilled water dispersion methods, reveals significant findings (as depicted in Figures 6 and 7). Utilizing the precipitation method for synthesis, the XRD diffractogram exhibits distinct peaks at 2θ angles of 25.88°, 31.94°, 32.96°, 34.04°, 39.88°, 46.88°, and 49.54°.

The characterization results confirm that these peaks correspond to the hydroxyapatite phase, per the standards set by the Joint Committee on Powder Diffraction Standards (JCPDS No. 09-432). According to this standard, hydroxyapatite typically exhibits main peaks at 2θ angles of 25.89°, 31.73°, 32.96°, 34.048°, 39.88°, 46.9°, and 49.54° [16]. Notably, the diffractogram of the hydroxyapatite derived from chicken eggshells demonstrates that the most pronounced peak occurs at a 2θ angle of 31.94°, with a high peak intensity. This observation confirms the specificity of the hydroxyapatite phase in the synthesized sample. The XRD results are crucial in verifying the phase purity and crystallinity of the synthesized hydroxyapatite. The alignment of the observed peaks with the standard hydroxyapatite peaks signifies the hydroxyapatite's successful synthesis and crystalline quality, which is essential for its application in various biomedical fields.

CONCLUSION

The calcination process employed in this study has successfully facilitated the transformation of calcium carbonate ($CaCO_3$) from eggshell powder into calcium oxide (CaO), followed by the conversion of CaO to calcium hydroxide ($Ca(OH)_2$). The effectiveness of this transformation was assessed using two distinct methods: direct air contact and dispersion in distilled water. The effectiveness of both methods in achieving the conversion from CaO to $Ca(OH)_2$ has been substantiated through X-ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) analyses. These analytical techniques have confirmed the presence of characteristic OH functional groups, indicating Ca(OH)2 formation. The successful implementation of these conversion methods underscores their practicality and relevance in producing precursors for hydroxyapatite synthesis. The outcomes of this study bear significant implications for the field of biomaterials. Specifically, they demonstrate the feasibility of using eggshell-derived $Ca(OH)_2$ as a viable raw material in the synthesis of hydroxyapatite. This approach offers an efficient and sustainable pathway for utilizing eggshell waste and contributes to developing advanced biomaterials for various applications, particularly in the medical and dental fields. The study thus provides a valuable foundation for future research and development in the sustainable synthesis of biomaterials.

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