Indonesian Physical Review
Volume 08 Issue 03, September 2025
P-ISSN: 2615-1278, E-ISSN: 2614-7904

Synthesis of Single-Phase Hydroxyapatite Powder from Eggshell Waste via Co-precipitation Method and Its Structural Characterization

Musyarofah[1*], Adinda Kholif Mahera[1], Gusti Umindya Nur Tajalla[3], Azmia Rizka Nafisah[4], Budi Prayitno[5*], Siti Norhidayah[5], Siska Ayu Kartika[5]

[1] *Department of Physics, Institut Teknologi Kalimantan, Indonesia*
[2] *Research Center of Biomaterial, Institut Teknologi Kalimantan, Indonesia*
[3] *Department of Material and Metallurgy Engineering, Institut Teknologi Kalimantan, Indonesia*
[4] *Department of Chemistry Engineering, Institut Teknologi Kalimantan, Indonesia*
[5] *Department of Mechanical Engineering, Universitas Balikpapan, Indonesia*

Corresponding Authors E-mail: musyarofah@lecturer.itk.ac.id, budi.prayitno@uniba-bpn.ac.id

Article Info

Article info:
Received: 18-12-2024
Revised: 16-05-2025
Accepted: 17-06-2025

Keywords:
Hydroxyapatite; Calcination; Biowaste; Structural property; Single-phase

How To Cite:
Musyarofah, A. K. Mahera, G. U. N. Tajalla, A. R. Nafisah, B. Prayitno, S. Norhidayah, S. A. Kartika, "Synthesis of single-phase hydroxyapatite powder from eggshell waste via co-precipitation method and its structural characterization", Indonesian Physical Review, vol. 8, no. 3, p 660-674, 2025.

DOI:
https://doi.org/10.29303/ipr.v8i3.451.

Abstract

This study aims to synthesize a single-phase hydroxyapatite powder using waste chicken eggshells as a calcium source via the co-precipitation method. The process focuses on optimizing calcination time and temperature to achieve high-purity hydroxyapatite. The co-precipitation procedure involved controlled pH adjustment and aging time, contributing to the formation of homogeneous particles. Chicken eggshells, predominantly composed of calcium carbonate ($CaCO_3$), were calcined at 1000°C for 15 hours to produce calcium oxide (CaO). The resulting CaO was then reacted with phosphate ions in an aqueous solution, followed by a calcination at 900°C for varying holding times of 5 and 10 hours. X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), and Brunauer-Emmett-Teller (BET) analysis were conducted to evaluate phase composition, crystal size, and texture properties. The optimum condition was found at 900 °C for 10 h calcination, resulting in single-phase hydroxyapatite, a crystallite size of 220 nm, an average pore radius of 6.78 nm, a total pore volume of 0.02 cc/g, a surface area of 6.38 m^2/g, and an average particle radius of 213.89 nm. These findings highlight the potential of this method for producing bioceramics with desirable properties for use in bone grafts and other biomedical materials.

Introduction

Hydroxyapatite ($Ca_5(PO_4)_3OH$) is a calcium phosphate compound known for its excellent biocompatibility and chemical similarity to the mineral component of bone and teeth. It has a wide range of applications in the biomedical field, including bone grafts, dental implants, and tissue engineering scaffolds [1], [2], [3]. Traditional methods for synthesizing hydroxyapatite often rely on high-purity chemical reagents, which can be costly and environmentally unfriendly. Recently, the use of biowaste materials, such as chicken eggshells, as a source of calcium for hydroxyapatite synthesis has gained attention due to its potential for cost reduction and environmental sustainability.

The global demand for eggs has shown a consistent upward trend, with consumption over 8 billion dozen eggs in 2020 [4]. In every egg production of around 78 million metric tons will produce around 8.58 million metric tons of egg shells as a by-product. These eggshells are commonly disposed of in landfills, posing potential environmental challenges and underscoring the importance of exploring sustainable strategies for such biowaste. Chicken eggshells, as a commonly discarded biowaste, hold significant potential for sustainable applications due to their high calcium carbonate ($CaCO_3$) content, which constitutes approximately 95% of their composition [5]. The utilization of eggshell waste as a calcium precursor offers a sustainable alternative to conventional chemical sources, thereby reducing reliance on synthetic reagents. Moreover, this approach aligns with circular economy principles by transforming readily available biowaste into value-added materials, while simultaneously addressing environmental concerns related to landfill overaccumulation and waste management. The process of transforming eggshell-derived calcium carbonate into calcium oxide (CaO) through calcination—a thermal decomposition reaction—enables its subsequent conversion into hydroxyapatite, a biomaterial widely recognized for its applications. Despite the demonstrated feasibility of synthesizing hydroxyapatite from eggshells, achieving a reproducible method for producing high-purity, well-crystallized hydroxyapatite remains a significant challenge, necessitating further exploration into process optimization.

Current research has highlighted the potential of eggshell-derived hydroxyapatite, yet notable gaps persist, particularly concerning the impact of calcination parameters on the structural and functional properties of the final product. Parameters such as calcination temperature, heating rate, and holding time critically influence the decomposition of calcium carbonate and the formation of calcium oxide, which subsequently affects the quality of hydroxyapatite produced during synthesis [6], [7]. For example, insufficient calcination temperatures may leave unreacted calcium carbonate, while excessively high temperatures can lead to unwanted secondary phases or agglomeration of particles. Additionally, the duration of the calcination process influences the degree of crystallinity and homogeneity in the resultant hydroxyapatite. Despite some studies exploring these variables [8], [9], [10] a comprehensive understanding of the interplay between calcination conditions and the structural characteristics of hydroxyapatite—such as phase purity, crystallinity, and particle morphology—is still lacking. Addressing these knowledge gaps is crucial for advancing the scalability and application potential of eggshell-derived hydroxyapatite.

Research on obtaining single-phase or pure hydroxyapatite from chicken eggshell waste remains significantly underexplored. Most existing studies focus on the initial transformation of calcium carbonate ($CaCO_3$) in eggshells into calcium oxide (CaO) through calcination, followed by the synthesis of hydroxyapatite using methods such as chemical precipitation or co-precipitation. One of the key challenges in synthesizing single-phase hydroxyapatite is the tendency for secondary phases—such as tricalcium phosphate (TCP), octacalcium phosphate (OCP), and monetite—to form, especially under non-optimized calcination conditions [7], [8], [9], [10]. These impurities affect the purity, bioactivity, and mechanical properties of the material. This study introduces a novel approach to systematically investigate and optimize the synthesis of hydroxyapatite powders from chicken eggshell-derived calcium oxide, focusing on the effects of calcination temperature and holding time on structural characteristics. The co-precipitation method was selected for its operational simplicity, economic feasibility, and superior control over key synthesis parameters such as stoichiometry and pH, which are essential for obtaining uniform particle morphology and high phase purity. As a widely adopted approach in the synthesis of inorganic powders with tailored composition and microstructure, the co-precipitation technique in this study was combined with controlled calcination to further improve the crystallinity of the resulting hydroxyapatite powder. By analyzing critical parameters such as phase composition, crystal size, and lattice integrity through advanced characterization techniques—such as X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM)—this study aims to establish a direct correlation between calcination conditions and material properties. It is hypothesized that controlling calcination temperature and holding time will influence the phase purity and surface morphology of hydroxyapatite powder. The insights gained will contribute to developing a robust and reproducible protocol for producing high-quality hydroxyapatite, paving the way for its broader utilization in biomedical and industrial applications, including its potential use in bone grafts, orthopedic implant coatings, and drug delivery systems, owing to its high phase purity.

Experimental Method

The primary raw material utilized in this study was chicken eggshells, which were sourced from domestic household waste to ensure the sustainability and low-cost nature of the process. Initially, the eggshells were thoroughly cleaned using deionized water to remove organic residues. The shells were rinsed thoroughly with deionized water five cycles until the rinsing water appeared clear and free from visible organic matter. Fresh deionized water was used in each cycle to minimize the risk of recontamination. The cleaned samples were subsequently dried in an oven at 100°C for 24 hours to eliminate residual moisture. Following the drying process, the eggshells were mechanically milled into a fine powder using a grinder. The resulting powder was then sieved through a 200-mesh screen, corresponding to particle sizes smaller than 75 µm, to achieve a uniform particle size distribution suitable for subsequent synthesis steps. The prepared eggshell powder was subjected to calcination in a muffle furnace at 1000°C for 15 hours [11]. This calcination step aimed to thermally decompose calcium carbonate ($CaCO_3$) in the eggshells into calcium oxide. The calcined powder served as the precursor for hydroxyapatite synthesis.

Hydroxyapatite ($Ca_5(PO_4)_3OH$) was synthesized via the coprecipitation method. In this process, the calcined calcium oxide powder was reacted with phosphoric acid (H_3PO_4, ≥99% purity) was purchased from Merck. The reaction was carried out by gradually adding phosphoric acid to a calcium oxide suspension under controlled conditions to form hydroxyapatite precipitates. The Ca/P molar ratio was maintained at 1.67 to match the stoichiometry of hydroxyapatite. The co-precipitation procedure involved controlled pH adjustment of 10 and aging time of 24 hours, contributing to the formation of homogeneous particles. The resulting precipitate was filtered, washed with deionized water to remove impurities, and dried. Subsequently, the dried material underwent a secondary calcination at 900°C, with varied holding times of 5 hours and 10 hours. A duration of 5 hours was chosen to represent a moderate holding time commonly used in similar synthesis studies [8], [9], [10], while 10 hours was selected to evaluate the effect of prolonged heat treatment on phase purity. This comparison was intended to assess the time-dependent structural properties of hydroxyapatite under identical temperature conditions. The reaction durations of 5 and 10 hours were chosen based on preliminary experiments and supported by previous studies indicating that longer reaction times can enhance the crystallinity [8], [9], [10].

The sample was analyzed using the Horiba X-Ray Fluorescence (XRF) Mesa-50V3 Benchtop & Portable instrument to determine the presence and concentration of elements in the sample. The phase composition and crystal lattice parameters of the powders were analyzed through X-ray diffraction (XRD) using a Bruker D8 Advanced diffractometer, with Cu-Kα radiation ($\lambda = 1.5406$ Å), scanning from 5° to 120° in 2θ with a step size of 0.02° per second. The XRD data were refined using the Rietveld method with the *Match!* and *Rietica* software to extract phase and lattice parameter details. A correction was applied to account for instrument peak broadening in the estimation of phase composition and crystallite size [12], [13]. FTIR measurements at room temperature under ambient atmospheric conditions were performed using a Bruker Vertex7.0v FTIR spectrometer, covering a wavenumber range of 500 to 4000 cm^{-1}, to analyze the interatomic bonding states based on the vibrational spectra. To assess the textural properties of the calcined powders, a BET Surface Area & Pore Size Analyzer (NOVATouch LX4) was used. Samples were degassed at 300°C for 3 hours before analysis to eliminate adsorbed moisture and gases. Nitrogen adsorption-desorption isotherms were measured at 77 K, and the surface area was determined using the Brunauer-Emmett-Teller (BET) method. The pore size was calculated from the adsorption branch of the isotherm using the Barrett-Joyner-Halenda (BJH) method.

Result and Discussion

The X-ray fluorescence (XRF) analysis of the eggshell powder revealed its elemental composition, confirming the presence of calcium (Ca) as the predominant element, alongside trace amounts of iron (Fe), copper (Cu), and cobalt (Co). The high calcium content is consistent with the well-documented composition of chicken eggshells, which are primarily composed of calcium carbonate ($CaCO_3$), typically accounting for over 94% of their weight [14]. This finding aligns with recent studies that emphasize the role of calcium carbonate in eggshells as a critical component for structural integrity and biological functions in avian species [5]. The detection of trace elements such as Fe, Cu, and Co indicates the presence of minor impurities or naturally occurring trace minerals.

Table 1. Elemental content (wt%) of dried chicken eggshell powder

Sample	Element (wt%)			
	Ca	Fe	Cu	Co
Eggshell powder	99.973	0.022	0.005	-

The X-ray diffraction (XRD) analysis provided further insights into the crystalline phases present in the eggshell powder. The XRD pattern (Figure 1) indicated a single presence of the calcium carbonate (calcite, $CaCO_3$). The distinct peaks corresponding to calcium carbonate were clearly identifiable, underscoring its crystalline nature with COD No. 9016706, trigonal crystal form (hexagonal axes), space group *R-3c* (167), and has lattice parameters $a = b = 4.9844$ Å and $c = 17.0376$ Å. This phase analysis is crucial, as it establishes the baseline composition before any thermal treatment, such as calcination, which transforms calcium carbonate into calcium oxide.

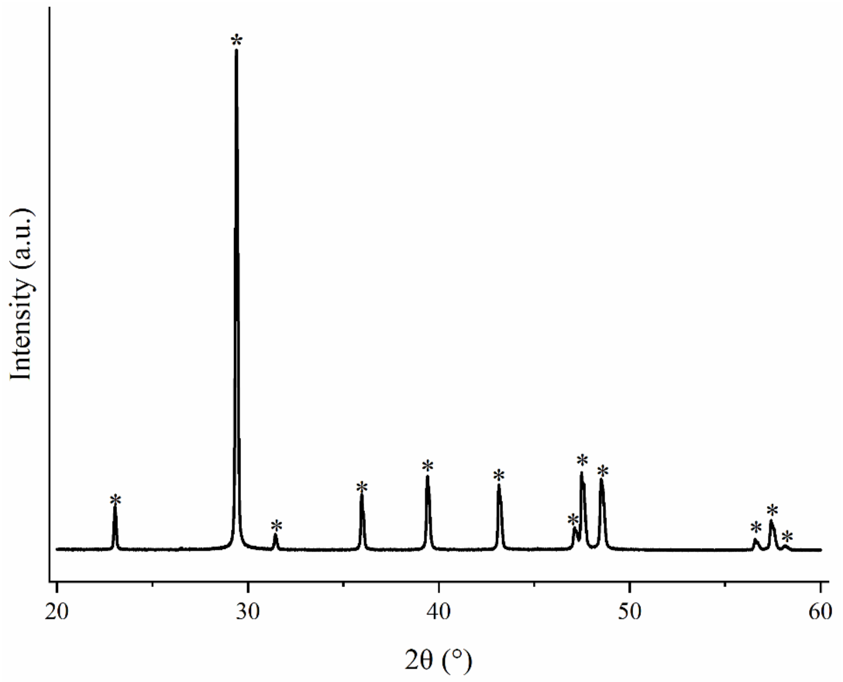

Figure 1. X-ray diffraction patten (Cu-Kα) of dried eggshell powder

These comparative studies highlight the significance of XRD in determining the crystalline phases of various biogenic materials. In the case of eggshells, understanding the crystalline phase content before any treatment provides a foundational understanding for subsequent processes such as calcination. For example, the transformation of calcium carbonate to calcium oxide during calcination is reported [15], [16], [17], and having precise initial phase data ensures the efficiency and predictability of this conversion. This detailed phase analysis supports the broader application of eggshell-derived materials in fields ranging from bioceramics to environmental remediation.

From the IR spectrum (Figure 2), it can be seen that the chicken eggshell powder has a functional group of carbonate minerals at a wave number of 2600 cm^{-1} indicating the presence of a C–H vibration functional group, this indicates the presence of an organic layer, formed from amino acids, in the chicken eggshell [18]. At wave numbers 1422.07 cm^{-1} and 1665.63 cm^{-1} which are shown with strong and wide peaks. This indicates the presence of a carboxyl group (C=O) which is identified as carbonate (CO_3) for bending vibration and asymmetric stretching in $CaCO_3$ [19]. Then at wave numbers 700.72 cm^{-1} (*υ4* on the plane bend) and 872.44 cm^{-1} (*υ2* outside the plane bend) the presence of $CaCO_3$ is seen, namely the C─O functional group [20]. Eggshells are primarily composed of calcium carbonate, but the presence of organic components such as proteins and glycoproteins contribute to their overall structure. Studies have shown that the organic matrix in eggshells, composed mainly of proteins like collagen, provides the scaffold for mineral deposition [5].

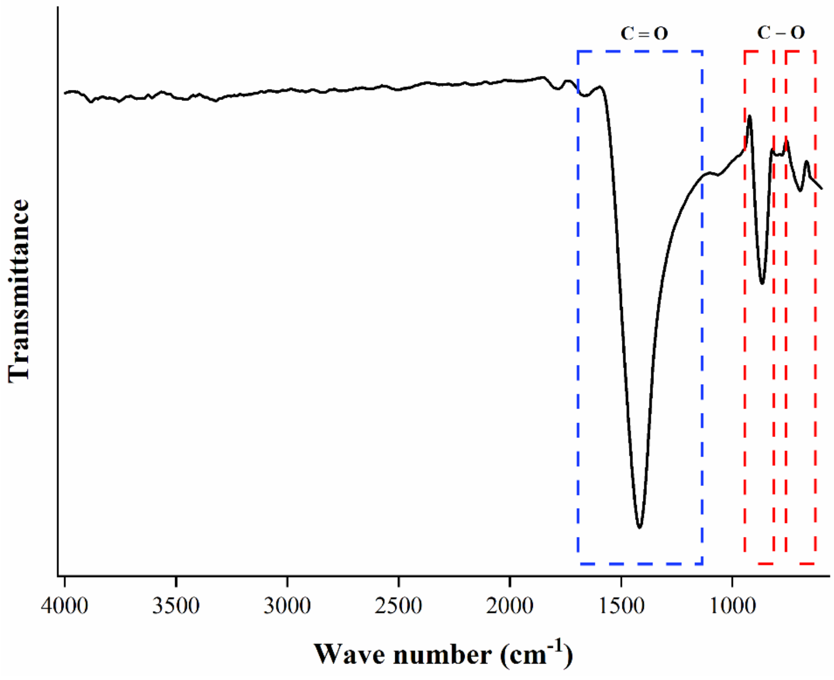

Figure 2. FTIR spectrum of dried eggshell powder

The eggshell powder, primarily composed of calcium carbonate, was subjected to a calcination process at a temperature of 1000°C for 15 hours. This thermal treatment aimed to decompose the calcium carbonate into calcium oxide, a process critical for producing high-purity calcium oxide powder. The choice of 1000°C as the calcination temperature and a prolonged duration of 15 hours was based on optimizing the transformation efficiency and ensuring the complete conversion of calcium carbonate. The decomposition of calcium carbonate ($CaCO_3$) into calcium oxide (CaO) occurs through a thermal decomposition reaction, which is an endothermic process requiring significant energy to break the bonds in the calcium carbonate structure [21]. At 1000°C, the thermal energy provided is sufficient to drive the decomposition reaction to completion, ensuring that most of the calcium carbonate is converted into calcium oxide.

The results of the XRD analysis post-calcination revealed significant changes in the phase composition of the powder, see Figure 3. The XRD pattern indicated the presence of two main phases: calcium oxide (CaO) and calcium hydroxide ($Ca(OH)_2$). The peaks corresponding to CaO and $Ca(OH)_2$ were identified and matched with the Crystallography Open Database (COD) entries No. 100044 and No. 100045, respectively. Calcium oxide (CaO) exhibits a cubic crystal system with a space group of *Fm-3m*. The most prominent diffraction peaks for CaO are located at 2θ angles of 37° and 53°. In contrast, calcium hydroxide ($Ca(OH)_2$) displays a trigonal crystal system with a space group of *P-3m1*. The characteristic diffraction peaks of

$Ca(OH)_2$ appear at 2θ angles of 18° and 34°. Quantitative phase analysis showed that the calcined powder consisted of 93.75 mol% calcium oxide and 6.25 mol% calcium hydroxide. The high percentage of calcium oxide confirms the successful decomposition of the calcium carbonate during the calcination process following Equation (1).

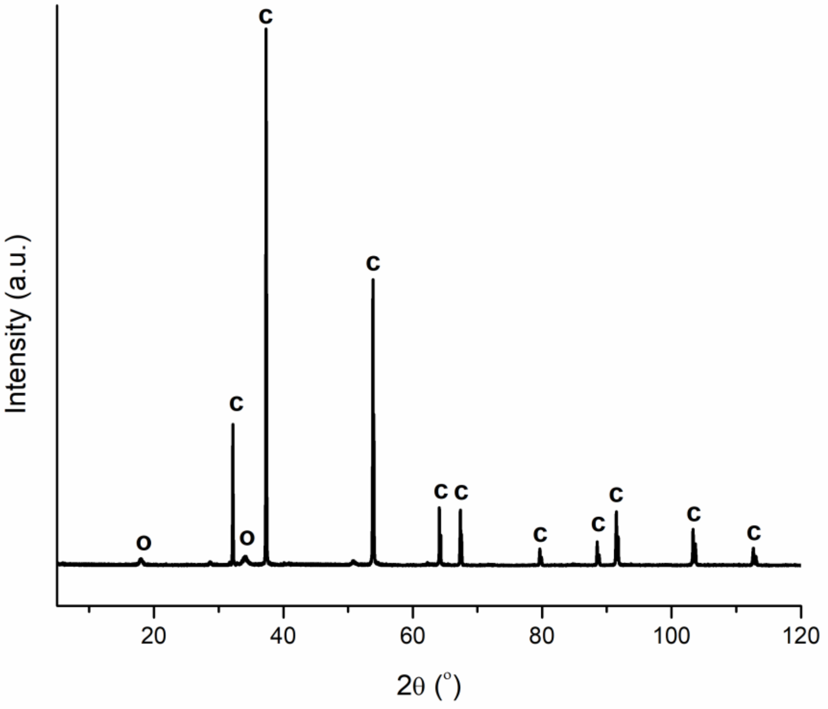

Figure 3. X-ray diffraction patten (Cu-Kα) of calcia powder calcined at 1000 °C for 15 hours, symbol **c** for calcium oxide (CaO) and **o** for calcium hydroxide ($Ca(OH)_2$)

The presence of calcium hydroxide as a secondary phase, albeit in a smaller proportion, can be attributed to the rehydration of calcium oxide when exposed to atmospheric moisture post-calcination following Equation (2). Calcium oxide is highly hygroscopic and readily reacts with water vapor in the air to form calcium hydroxide. This minor phase indicates a slight degree of interaction with environmental humidity, which is common in calcined products stored in ambient conditions.

$$CaCO_3 \rightarrow CaO + CO_2 \qquad (1)$$

$$CaO + H_2O + Ca(OH)_2 \qquad (2)$$

The calcination temperature and holding time are crucial for achieving the desired phase transformation. Khalid et at [22] and Suwannasingha et al [23] reported that $CaCO_3$ began to convert to calcium oxide at 900 °C. A temperature of 1000°C is sufficiently high to ensure the complete decomposition of calcium carbonate into calcium oxide. However, if the temperature were lower, the decomposition might be incomplete, resulting in a mixture of calcium carbonate and calcium oxide. On the other hand, excessively high temperatures could lead to sintering or melting of the calcium oxide, adversely affecting its reactivity and purity. The prolonged duration of 15 hours ensures that the heat penetrates thoroughly throughout the material, allowing for uniform decomposition. Shorter holding times might not provide enough energy for the complete conversion, especially in larger samples or those with lower thermal conductivity.

Previous research has explored various temperatures and durations for the calcination of eggshells and other calcium carbonate sources. For instance, Tangboriboon et al [24] reported that calcination at 700°C for 3 hours resulted in partial decomposition of calcium carbonate, with residual amounts of $CaCO_3$ detected in the XRD analysis. In contrast, another study by Borgwardt [25] found that calcination at above 1000°C led to nearly complete conversion but also indicated the potential for over-heating, which could reduce the material's surface area and reactivity. In this study, the combination of 1000°C and 15 hours was found to be optimal, balancing the need for complete decomposition with the risk of over-processing. The results align well with previous findings, confirming that both temperature and duration are key parameters in achieving high-purity calcium oxide from eggshells.

The calcium oxide powder produced through the calcination of eggshell powder was further synthesized into hydroxyapatite ($Ca_5(PO_4)_3OH$) using the coprecipitation method. Due to its hygroscopic nature, calcium oxide powder can readily react with atmospheric moisture, forming $Ca(OH)_2$, which may influence the reproducibility of the synthesis process. To mitigate this, the powder was promptly stored in a sealed desiccator and used within 24 hours. These precautions are essential for researchers aiming to replicate the synthesis with consistent results. This synthesis process involved reacting the calcium oxide powder with a phosphate source in an aqueous solution to form hydroxyapatite following Equation (3). The resulting precipitate was then subjected to a secondary calcination at 900°C with varying holding times of 5 and 10 hours to enhance the crystallinity and phase purity of the hydroxyapatite. XRD analysis of the synthesized powders indicated the successful formation of the hydroxyapatite phase in both samples, as shown in Figure 4. The XRD patterns displayed characteristic peaks corresponding to hydroxyapatite (COD No. 9011093), confirming the effective transformation of the precursor materials through the coprecipitation and calcination processes.

$$5Ca(OH)_2 + 3H_3PO_4 \rightarrow Ca_5(PO_4)_3OH + 9H_2O \tag{3}$$

The formation mechanism of hydroxyapatite involves the reaction between calcium ions (Ca^{2+}) from calcium oxide powder and phosphate ions (PO_4^{3-}) in the aqueous solution. The coprecipitation method facilitates the nucleation and growth of hydroxyapatite crystals by providing a controlled environment for the ions to combine and form the desired crystalline phase. During the subsequent calcination at 900°C, the thermal energy promotes the crystallization and stabilization of hydroxyapatite, enhancing its structural integrity. Javadinejad et al [26] in their work, thermal and kinetic study of hydroxyapatite formation, reported that the activation energy values for the transformation were found to vary between about 100–139kJ/mol.

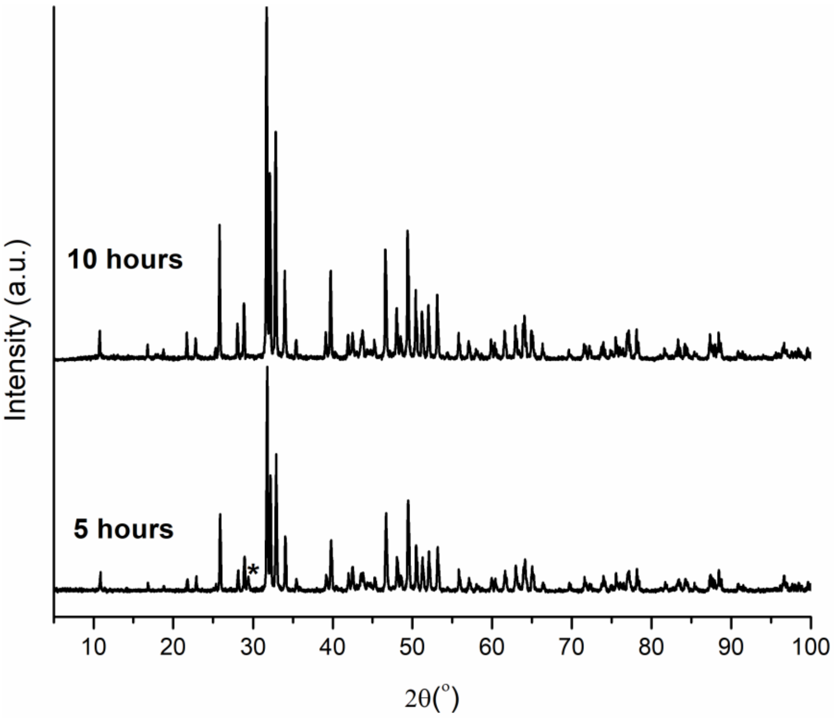

Figure 4. X-ray diffraction pattens (Cu-Kα) of hydroxyapatite powders calcined at 900 °C for 5 and 10 hours

In the sample subjected to 5 hours of calcination, XRD analysis at 2*θ* 29,42° revealed the presence of a secondary phase of calcium carbonate ($CaCO_3$, No. 1547350) alongside hydroxyapatite. This secondary phase likely results from the interaction of the sample with atmospheric CO_2 during the synthesis process. The shorter holding time may have been insufficient to fully convert all precursor materials into hydroxyapatite, leaving residual calcium carbonate in the sample.

The qualitative analysis of XRD data showed that the powder from coprecipitation synthesis and calcination at 900°C for 5 and 10 hours exhibits the presence of the hydroxyapatite phase as shown by Figure 5. At the temperature calcined for 5 hours, a secondary phase of calcium carbonate was also detected. The qualitative analysis of XRD peaks, particularly the peak height and width, is associated with the phase composition and crystal size. Sharp and well-defined peaks indicate larger and more crystalline grains, whereas broader peaks suggest smaller and less ordered crystals.

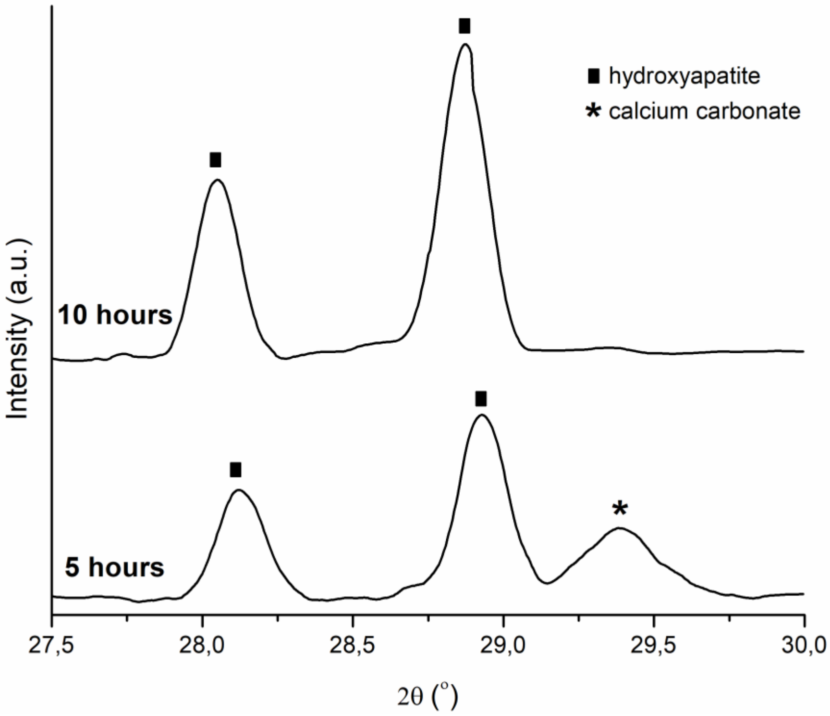

Figure 5. XRD peak broadening details of hydroxyapatite powder calcined at 900 °C for 5 and 10 hours

Quantitative analysis of the XRD data, as shown in the Table 2, reveals the effect of calcination holding time on the phase composition and crystal size of hydroxyapatite. The sample calcined for 5 hours had a noticeable amount of calcium carbonate, indicating incomplete conversion. In contrast, the sample calcined for 10 hours showed a purer hydroxyapatite phase with no detectable secondary phases. This extended calcination time allowed for a more complete conversion of the precursors and better elimination of residual carbonates, resulting in a higher phase purity of hydroxyapatite.

Table 2. Results of quantitative analysis of the XRD patterns hydroxyapatite powder calcined at 900 °C for 5 and 10 hours using *Rietica* and *MAUD* software with Rietveld method. Numbers in the parentheses represent the estimated standard deviations of the associated average values at their least significant level.

Holding time (hours)	Phase Composition (wt%)		Crystallite size of hydroxyapatite (nm)
	Hydroxyapatite	Calcium carbonate	
5	99.13 (9)	0.67 (3)	179 (1)
10	100.00 (0)	-	220 (2)

The effect of calcination holding time on the phase composition and crystal size of hydroxyapatite can be explained by the crystal grain growth mechanism. During calcination, the thermal energy provides the necessary activation energy for atoms to migrate and rearrange into a more stable crystalline structure. As the holding time increases, these processes are allowed to continue, leading to the growth of larger and more well-defined crystals. This is evidenced by the sharper and more intense XRD peaks observed in the sample calcined for 10 hours compared to the one calcined for 5 hours.

Previous studies have also investigated the effects of calcination temperature and duration on the formation of hydroxyapatite. For example, Fitriyana et al [27] reported that hydroxyapatite synthesized at lower temperatures or shorter holding times often contains secondary phases such as calcium carbonate due to incomplete conversion. The current study's use of 900°C for 10 hours optimized the phase purity and crystallinity, demonstrating the critical balance between temperature and duration in achieving high-quality hydroxyapatite.

The BET (Brunauer–Emmett–Teller) analysis provided insights into the pore structure and surface characteristics of the synthesized hydroxyapatite powders, with specific attention to the effects of calcination holding time. The measured parameters included average pore radius, total pore volume, BET surface area, and average particle size, as summarized in Table 3. The average pore radius of the sample calcined for 5 hours was 7.4556 nm, which decreased to 6.7822 nm for the sample calcined for 10 hours. This reduction in pore size with extended calcination time suggests that prolonged thermal treatment promotes the densification of the material. The reduction in average pore radius can be attributed to the grain growth and pore closure mechanisms that occur during prolonged calcination [28], [29]. As the calcination time increases, the particles have more time to rearrange and densify, leading to smaller pore sizes.

Table 3. Average pore size, total pore volume, surface area, and average particle size summary using BET-Multi-point method

Holding time (hours)	Average Pore Radius (nm)	Total Pore Volume (cc/g)	BET Surface Area (m^2/g)	Average Particle Radius (nm)
5	7.4556	0.038679	10.3758	131.42
10	6.7822	0.021619	6.37535	213.89

The total pore volume also showed a significant decrease with increased calcination time, from 0.038679 cc/g for the 5-hour sample to 0.021619 cc/g for the 10-hour sample. This reduction indicates that the material undergoes significant structural changes, becoming denser and less porous as calcination time increases. The total pore volume is closely linked to the average pore radius, and the decrease in both parameters suggests that the extended holding time facilitates the reduction of pore spaces within the material. BET surface area measurements revealed that the sample calcined for 5 hours had a surface area of 10.3758 m^2/g, which decreased to 6.37535 m^2/g for the sample calcined for 10 hours. This reduction in surface area is consistent with the observed decrease in pore volume and radius, indicating that the material becomes more compact and less porous with longer calcination times. The reduction in surface area can be explained by the sintering and grain growth processes, which lead to the merging of smaller particles into larger grains, thereby reducing the overall surface area available for adsorption. The average particle size increased significantly with extended calcination time, from 131.42 nm for the 5-hour sample to 213.89 nm for the 10-hour sample. This increase in particle size aligns with the grain growth mechanism, where longer calcination times allow for more extensive diffusion of atoms, leading to the coalescence of smaller particles into larger crystals. The increase in particle size is a common outcome of prolonged thermal treatment and is indicative of the enhanced crystallinity and structural integrity of the material.

The calcination holding time has a profound impact on the physical properties of the hydroxyapatite powders. Shorter calcination times (5 hours) result in higher surface areas, larger pore volumes, and smaller particle sizes, which are beneficial for applications requiring high surface reactivity and porosity. However, these characteristics also imply lower structural stability and potential for residual phases such as calcium carbonate. In contrast, longer calcination times (10 hours) lead to less porous materials with larger particle sizes and lower surface areas. These changes enhance the structural integrity and phase purity of the hydroxyapatite, making it more suitable for applications requiring high mechanical strength and stability. Currently, hydroxyapatite is extensively applied across various medical disciplines, including otolaryngology, cranial and maxillofacial reconstruction, spinal procedures, orthopedic interventions, fracture treatment, bone-related diseases, percutaneous implants, and dental or periodontal surgeries [30]. The performance of hydroxyapatite in these applications is significantly affected by multiple factors, such as porosity—which enhances solubility and promotes interaction with cells and biomolecules—as well as its phase composition, crystallinity level, and specific surface area [31].

The decrease in pore size and volume, along with the increase in particle size, indicates a transition towards a more consolidated material structure, which is desirable for certain biomedical and industrial applications. Studies by Nurlaila et al [32] and Alhalili et al [33] have similarly reported that extended calcination times improve phase purity and crystallinity but reduce porosity and surface area. These findings align with the current study, demonstrating the critical balance between achieving high structural integrity and maintaining desirable surface characteristics for specific applications.

Conclusion

This study successfully synthesized single-phase hydroxyapatite (HAp) powder from chicken eggshells using a co-precipitation method. The results demonstrated that calcination parameters, specifically temperature and holding time, significantly influenced the structural and functional properties of the synthesized hydroxyapatite. At 1000°C for 15 hours, calcium carbonate in the eggshells was decomposed into 93.75 mol% calcium oxide and 6.25 mol% calcium hydroxide, which served as a precursor for hydroxyapatite synthesis. Subsequent calcination of the hydroxyapatite at 900°C with a holding time of 10 hours yielded a product with 100% phase purity, a crystallite size of 220 nm, an average pore radius of 6.78 nm, a total pore volume of 0.02 cc/g, a surface area of 6.38 m2/g, and an average particle radius of 213.89 nm. These findings affirm the potential of biowaste-derived materials as viable, cost-effective raw sources for producing high-quality hydroxyapatite, supporting sustainable material synthesis practices. The improvement in crystallinity with prolonged calcination is particularly relevant for biomedical applications that require enhanced structural characteristics, such as bone grafts and implant coatings. Although this work focused on evaluating the effect of calcination time, future research may extend toward in vitro testing, scaling-up processes, and exploring other biowaste precursors. Overall, this study provides valuable insight into synthesis optimization and contributes to the advancement of hydroxyapatite materials in both biomedical and industrial domains.

Acknowledgment

This research was financially supported by the Ministry of Research, Technology, and Higher Education of the Republic of Indonesia and the Institute for Research and Community Services ITK, which was awarded to the corresponding author.

References

[1] A. Singh, K. Kumari, and P. P. Kundu, “Synthesis of Biomimetic Hydroxyapatite from Natural Sources for Bone Tissue Engineering,” in *Encyclopedia of Green Materials*, C. Baskar, S. Ramakrishna, and A. Daniela La Rosa, Eds., Singapore: Springer Nature, 2022, pp. 1–14.

[2] Y. Oshida and T. Miyazaki, *Bone-Grafting Biomaterials: Autografts, Hydroxyapatite, Calcium-Phosphates, and Biocomposites*. Walter de Gruyter GmbH & Co KG, 2024.

[3] D. G. Filip, V.-A. Surdu, A. V. Paduraru, and E. Andronescu, “Current Development in Biomaterials—Hydroxyapatite and Bioglass for Applications in Biomedical Field: A Review,” *J. Funct. Biomater.*, vol. 13, no. 4, Art. no. 4, Dec. 2022.

[4] M. Waheed, M. Yousaf, A. Shehzad, M. I. U. Raheem, M.K. I. K. Khan, M. R. Khan , N. Ahmad, Abdullah, and R. M. Aadil, “Channelling eggshell waste to valuable and utilizable products: A comprehensive review,” *Trends in Food Science & Technology*, vol. 106, pp. 78–90, Dec. 2020.

[5] Y. Zhang, H. M. Pham, and S. D. Tran, “The Chicken Egg: An Advanced Material for Tissue Engineering,” *Biomolecules*, vol. 14, no. 4, Art. no. 4, Apr. 2024.

[6] A. Szcześ, L. Hołysz, and E. Chibowski, “Synthesis of hydroxyapatite for biomedical applications,” *Adv. Colloid Interface Sci.*, vol. 249, pp. 321–330, Nov. 2017.

[7] N. A. S. Mohd Pu’ad, R. H. Abdul Haq, H. Mohd Noh, H. Z. Abdullah, M. I. Idris, and T. C. Lee, “Synthesis method of hydroxyapatite: A review,” *Mater. Today Proc.*, vol. 29, pp. 233–239, Jan. 2020.

[8] P. Arokiasamy, M. M. A. B. Abdullah, S. Z. A. Rahim S. Luhar, A. V. Sandu, N. H. Jamil, and M. Nabiałek, “Synthesis methods of hydroxyapatite from natural sources: A review,” *Ceramics International*, vol. 48, no. 11, pp. 14959–14979, Jun. 2022.

[9] V. G. DileepKumar, M. S. Sridhar, P. Aramwit, V. K. Krut'ko, O. N. Musskaya, I. E. Glazov, and N. Reddy, “A review on the synthesis and properties of hydroxyapatite for biomedical applications,” *Journal of Biomaterials Science, Polymer Edition*, vol. 33, no. 2, pp. 229–261, Jan. 2022.

[10] P. O. Etinosa, O. A. Osuchukwu, E. O. Anisiji, M. Y. Lawal, S. A. Mohammed, O. I. Ibitoye, P. G Oni, V. D. Aderibigbe, T. Aina, D. Oyebode, and S. C. Nwigbo, “In-depth review of synthesis of hydroxyapatite biomaterials from natural resources and chemical regents for biomedical applications,” *Arabian Journal of Chemistry*, vol. 17, no. 12, p. 106010, Dec. 2024.

[11] B. Prayitno, M. Musyarofah, G. U. N. Tajalla, A. R. Nafisah, S. Norhidayah, and S. A. Kartika, “The effect of calcination temperature and holding time on structural properties of calcia powders derived from eggshell wastE,” *Indonesian Physical Review*, vol. 8, no. 1, pp. 281–299, Jan. 2025.

[12] M. Musyarofah, Y. P. Sari, A. R. Hilmi, M. Z. Asrori, Triwikantoro, M. Zainuri, B. N. Kim and S. Pratapa, “Ultra-dense (Bi, V, B)-oxide-added zircon ceramics fabricated by liquid-

phase assisted spark plasma sintering (SPS)," *Mater. Res. Express*, vol. 10, no. 5, p. 055002, May 2023.

[13] Musyarofah, E. F. Damanik, A. R. Septiana, D. M. Shoodiqin, Husain, and G. Yudoyono, "Phase study of Mg1-xZnxTiO3 powders prepared by dissolved metals mixing method," *AIP Conf. Proc.*, vol. 2652, no. 1, p. 050013, Nov. 2022.

[14] H. Faridi and A. Arabhosseini, "Application of eggshell wastes as valuable and utilizable products: A review," *Res. Agric. Eng.*, vol. 64, no. 2, pp. 104–114, Jun. 2018.

[15] J. M. Valverde, P. E. Sanchez-Jimenez, and L. A. Perez-Maqueda, "Limestone Calcination Nearby Equilibrium: Kinetics, CaO Crystal Structure, Sintering and Reactivity," *J. Phys. Chem. C*, vol. 119, no. 4, pp. 1623–1641, Jan. 2015.

[16] Z. Li, X. Guo, X. Xue, X. Xu, and B. Wang, "Investigations on Kinetics and Mechanisms of CaCO3 Calcination in Calcium Looping," *Ind. Eng. Chem. Res.*, vol. 62, no. 12, pp. 4851–4863, Mar. 2023.

[17] M. Silakhori, M. Jafarian, A. Chinnici, W. Saw, M. Venkataraman, W. Lipiński, and G. J. Nathan, "Effects of steam on the kinetics of calcium carbonate calcination," *Chem. Eng. Sci.*, vol. 246, p. 116987, Dec. 2021.

[18] B. C. Smith, *Infrared Spectral Interpretation: A Systematic Approach*. Boca Raton: CRC Press, 2018.

[19] A. Mittal, M. Teotia, R. K. Soni, and J. Mittal, "Applications of egg shell and egg shell membrane as adsorbents: A review," *J. Mol. Liq.*, vol. 223, pp. 376–387, Nov. 2016.

[20] M. S. Hossain, M. A. A. Shaikh, and S. Ahmed, "Synthesis of gypsum fertilizer from waste eggshells for a sustainable environment," *Mater. Adv.*, vol. 4, no. 1, pp. 240–247, Jan. 2023.

[21] R. Sumang and P. Panpho, "Investigating the potential of waste oyster shell as a sustainable bio-mordant in natural dyeing," *Sci. Rep.*, vol. 14, no. 1, p. 25509, Oct. 2024.

[22] M. Khalid, S. S. Jikan, S. Adzila, Z. M. Yunus, and N. A. Badarulzaman, "Characterizations of Calcium Oxide from Calcined Eggshell Waste," *Key Eng. Mater.*, vol. 908, pp. 130–134, 2022.

[23] N. Suwannasingha, A. Kantavong, S. Tunkijjanukij, C. Aenglong, H.-B. Liu, and W. Klaypradit, "Effect of calcination temperature on structure and characteristics of calcium oxide powder derived from marine shell waste," *J. Saudi Chem. Soc.*, vol. 26, no. 2, p. 101441, Mar. 2022.

[24] N. Tangboriboon, R. Kunanuruksapong, and A. Sirivat, "Preparation and properties of calcium oxide from eggshells via calcination," *Mater. Sci.-Pol.*, vol. 30, no. 4, pp. 313–322, Dec. 2012.

[25] R. H. Borgwardt, "Sintering of nascent calcium oxide," *Chem. Eng. Sci.*, vol. 44, no. 1, pp. 53–60, Jan. 1989.

[26] H. R. Javadinejad and R. E. Kahrizsangi, "Thermal and kinetic study of hydroxyapatite formation by solid-state reaction," *International Journal of Chemical Kinetics*, vol. 53, no. 5, pp. 583–595, May 2021.

[27] D. Fitriyana, R. Ismail, A. Bayuseno, J. Siregar, and T. Cionita, "Characterization of Hydroxyapatite Extracted from Crab Shell Using the Hydrothermal Method with Varying Holding Times," *J. Renew. Mater.*, vol. 12, no. 6, pp. 1145–1163, 2024.

[28] J. Zhao and M. P. Harmer, "Effect of Pore Distribution on Microstructure Development: II, First- and Second-Generation Pores," *J. Am. Ceram. Soc.*, vol. 71, no. 7, pp. 530–539, 1988.

[29] S. Jaenicke, G. K. Chuah, V. Raju, and Y. T. Nie, “Structural and Morphological Control in the Preparation of High Surface Area Zirconia,” *Catal. Surv. Asia*, vol. 12, no. 3, pp. 153–169, Sep. 2008.

[30] J. Jeong, J. H. Kim, J. H. Shim, N. S. Hwang, and C. Y. Heo, “Bioactive calcium phosphate materials and applications in bone regeneration,” *Biomater Res*, vol. 23, p. 4, 2019.

[31] E. Fiume, G. Magnaterra, A. Rahdar, E. Verné, and F. Baino, “Hydroxyapatite for Biomedical Applications: A Short Overview,” *Ceramics*, vol. 4, no. 4, Art. no. 4, Dec. 2021.

[32] R. Nurlaila, Musyarofah, N. F. Muwwaqor, Triwikantoro, A. Kuswoyo, and S. Pratapa, “Phase analysis of ZrO2-SiO2 systems synthesized through Ball milling mechanical activations,” *AIP Conf. Proc.*, vol. 1788, no. 1, p. 030122, Jan. 2017.

[33] Z. Alhalili and M. Smiri, “The Influence of the Calcination Time on Synthesis of Nanomaterials with Small Size, High Crystalline Nature and Photocatalytic Activity in the TiO2 Nanoparticles Calcined at 500 °C,” *Crystals*, vol. 12, no. 11, Art. no. 11, Nov. 2022.