Jurnal Polimesin
Department of Mechanical Engineering
State Polytechnic of Lhokseumawe
http://e-jurnal.pnl.ac.id/polimesin
e-ISSN : 2549-1999 No. : 2 Month : April
p-ISSN : 1693-5462 Volume : 24 Year : 2026

Processing dates: received on 2026-1-11, reviewed on 2026-02-09, accepted on 2026-02-25 and online availability on 2026-04-25

Green synthesis of hydroxyapatite from eggshells using orange peel (*Citrus sinensis*) as a template for bioceramic

Manty Aldilani Ikaningsih[1,*], Wahyu Hidayat[2], Wirawan Piseno[2], Lulu Nurdini[3], Besse Titing Karmiati[2], Arif Rahman[1], Ba'adilla Akhista Gamara[1]

[1]Metallurgical Engineering Department, Jenderal Achmad Yani University, Cimahi 40531, Indonesia
[2]Mechanical Engineering Department, Jenderal Achmad Yani University, Cimahi 40531, Indonesia
[3]Chemical Engineering Department, Jenderal Achmad Yani University, Cimahi 40531, Indonesia
*Corresponding author: manty.aldilani@lecture.unjani.ac.id

Abstract

This study addresses the environmental challenge posed by chicken eggshell and orange peel waste by developing a sustainable green synthesis route for hydroxyapatite (HAp). This work aimed to synthesize hydroxyapatite from eggshell-derived calcium using orange peel (*Citrus sinensis* L.) extract as a natural template and to evaluate the effect of extract concentration on the structural and morphological characteristics of the resulting material. Hydroxyapatite was synthesized via a wet-chemical precipitation method under alkaline conditions using orange peel extract at concentrations of 0%, 10%, 20%, and 30%. X-ray diffraction analysis confirmed hydroxyapatite as the dominant crystalline phase in all samples, with crystallinity values of 100%, 99.55%, 95.6%, and 95.2% for extract concentrations of 0%, 10%, 20%, and 30%, respectively, indicating controlled reduction in crystallite size with increasing extract concentration. Scanning electron microscopy revealed a progressive reduction in particle size, decreased agglomeration, and enhanced surface porosity, while energy-dispersive X-ray spectroscopy confirmed consistent elemental composition and high purity. Among the investigated conditions, the use of 30% orange peel extract produced the most favorable overall characteristics, combining refined microstructure and controlled crystallinity.

Keywords:
Eggshell, green synthesis, hydroxyapatite, orange peel extract, wet precipitation.

1 Introduction

Hydroxyapatite (HAp) is one of the most extensively investigated bioceramic materials due to its chemical composition and crystal structure, which closely resemble those of the mineral phases of human bone and teeth. Its excellent biocompatibility, bioactivity, and osteoconductivity make HAp a suitable material for bone implants, bone graft substitutes, and tissue engineering scaffolds [1,2]. Despite these advantages, conventional hydroxyapatite synthesis routes typically rely on synthetic chemical precursors, elevated processing temperatures, and environmentally hazardous reagents, raising significant concerns about sustainability and environmental impact [3].

In response to these challenges, green synthesis has emerged as a sustainable paradigm in bioceramic material development, emphasizing the utilization of natural raw materials, reduced energy consumption, and environmentally benign reaction conditions [4]. Within the context of hydroxyapatite synthesis, green synthesis should not be viewed merely as an alternative processing route, but rather as a strategic approach that integrates environmental responsibility with advanced material engineering. Several studies have reported that hydroxyapatite produced via green synthesis exhibits physicochemical properties comparable to, or even superior to, those obtained through conventional synthesis methods [5]. Nevertheless, major challenges persist, particularly in achieving precise control over particle morphology, particle size, and crystallinity, especially when waste-derived precursors are employed [6].

Among various sustainable calcium sources, eggshell waste has attracted increasing attention due to its abundance and high calcium content. Eggshell waste is generated in large quantities from household and food industry activities, contributing substantially to solid waste accumulation. Statistical data on chicken egg production in Indonesia indicate a high annual output, which directly correlates with the growing volume of eggshell waste [7]. Chemically, eggshells consist predominantly of calcium carbonate, rendering them a highly promising natural calcium precursor for hydroxyapatite synthesis. Numerous studies have demonstrated that eggshell-derived calcium can be effectively converted into hydroxyapatite with structural and compositional characteristics closely resembling those of natural bone mineral [8,9].

Beyond waste reduction, the utilization of eggshells offers significant added value by transforming low-cost waste into high-value bioceramic materials. Previous investigations have shown that eggshell-derived hydroxyapatite exhibits physicochemical properties comparable to those synthesized from commercial calcium sources, along with favorable biocompatibility and strong structural similarity to biological apatite [10]. Comparative studies further indicate that eggshell-derived hydroxyapatite often displays more uniform particle morphology and better-controlled particle size, which positively influence mechanical performance and biological interactions. Despite these advantages, effective microstructural control remains a key challenge in waste-based green synthesis systems.

Microstructural characteristics, including particle size, morphology, porosity, and crystallinity, play a crucial role in determining the performance of hydroxyapatite in bioceramic applications. Nanoscale and submicron hydroxyapatite particles are known to exhibit enhanced surface reactivity and improved interaction with biological environments, while porous structures facilitate nutrient diffusion, vascularization, and cell migration during bone regeneration. Consequently, strategies that enable controlled microstructural engineering are essential for optimizing hydroxyapatite performance.

To address these limitations, the use of natural templates or biotemplates has been widely explored as an effective strategy for directing nucleation and crystal growth during hydroxyapatite formation. Organic compounds such as polysaccharides and organic acids can interact with calcium and phosphate ions, thereby regulating supersaturation levels and influencing crystal growth orientation [11,12]. Various plant extracts have been successfully applied as green templates, leading to the formation of nanostructured and porous hydroxyapatite materials suitable for biomedical applications [13,14].

Agricultural and fruit wastes represent particularly attractive sources of natural templates due to their rich organic composition and widespread availability. Orange peel (*Citrus sinensis*), for instance, contains abundant pectin, citric acid, flavonoids, and phenolic compounds that can function as chelating agents and crystal growth modifiers during hydroxyapatite synthesis. However, studies systematically integrating eggshell-derived calcium with orange peel extract as a green template remain scarce, and the synergistic effects of these two waste resources on the hydroxyapatite microstructure are not yet fully understood.

From an application perspective, hydroxyapatite synthesized via green routes exhibits substantial potential in bioceramic material

engineering. Hydroxyapatite with small particle size and well-controlled porous structures has been shown to enhance cell adhesion and proliferation, thereby accelerating bone tissue regeneration [15]. In addition, hydroxyapatite crystallinity strongly influences mechanical stability and degradation behavior in physiological environments [1], highlighting the importance of controlled synthesis.

Therefore, the present study aims to synthesize hydroxyapatite from eggshell waste using orange peel extract as a green template and to systematically investigate the effects of orange peel addition on the crystal structure, morphology, and particle characteristics of the resulting hydroxyapatite for bioceramic material engineering. Unlike previous studies that utilized either eggshell-derived calcium or plant-based templates independently, this work integrates both waste resources within a single green synthesis framework, offering a more sustainable and microstructurally tunable approach to hydroxyapatite production.

2 Research methodology

2.1 Preparation of eggshells as a calcium source

Chicken eggshells were utilized as the primary source of calcium ions (Ca^{2+}) for hydroxyapatite synthesis. The preparation process began with physical and chemical cleaning to remove residual proteins and the inner membrane, which could interfere with the purity of the resulting calcium oxide (CaO). The eggshells were thoroughly washed with running water, dried at 100°C for 2 h, and subsequently ground into a fine powder. The powder was then sieved through a 100-mesh sieve to obtain a uniform particle size distribution. The main stages of eggshell preparation are illustrated in Fig. 1.

(a) (b) (c)

Fig. 1. (a) Raw eggshells, (b) ground eggshell powder, and (c) eggshell powder sieved to 100 mesh.

The dried eggshell powder was calcined at 800°C for 3 h to convert calcium carbonate ($CaCO_3$) into CaO through thermal decomposition, as described by the reaction Eq. (1).

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

This calcination step was essential to obtain highly reactive and relatively pure CaO, which subsequently served as the calcium precursor in the hydroxyapatite precipitation process.

The preparation of eggshells as a calcium source followed previously reported and widely adopted procedures for eggshell-derived hydroxyapatite synthesis, including washing, drying, grinding, sieving, and calcination, with minor modifications [8,10,18].

2.2 Preparation of orange peel extract as a green template

Orange peel (*Citrus sinensis* (L.)) was selected as a green template due to its high content of organic compounds, such as pectin, flavonoids, tannins, and essential oils, which are known to function as crystal growth modifiers and natural pore-forming agents [4]. The orange peel extract was prepared by thoroughly washing fresh orange peels to remove surface impurities, cutting them into small pieces, and extracting them using boiling distilled water. The resulting suspension was filtered, and the obtained filtrate was used as the orange peel extract. The prepared orange peel extract was used directly as a green template during hydroxyapatite synthesis, as shown in Fig. 2.

(a) (b)

Fig. 2. (a) Orange peel and (b) orange peel extract.

The extract contains functional groups such as –COOH and –OH from pectin, as well as aromatic groups from flavonoids, which can interact with Ca^{2+} ions during hydroxyapatite formation and influence crystal nucleation and growth. Similar biomass-based templates have been reported to effectively regulate crystal growth and reduce particle size in hydroxyapatite synthesis [10]. Therefore, the use of orange peel extract is expected to promote microstructural refinement and the formation of porous structures by thermal decomposition of organic components during calcination.

2.3 Synthesis of hydroxyapatite via wet chemical precipitation

Hydroxyapatite synthesis was carried out using a wet chemical precipitation method with a fixed calcium-to-phosphorus (Ca/P) molar ratio of 1.67, corresponding to the stoichiometric composition of hydroxyapatite. The synthesis was performed in an aqueous medium under alkaline conditions, adjusted with ammonium hydroxide (NH_4OH).

Initially, a phosphate precursor solution was prepared by dissolving diammonium hydrogen phosphate ($(NH_4)_2HPO_4$) in distilled water under continuous stirring until a homogeneous solution was obtained. Separately, calcium oxide (CaO) derived from eggshell calcination was slowly added to distilled water under constant stirring to form a calcium hydroxide slurry, according to the exothermic reaction Eq. (2).

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad (2)$$

Subsequently, the phosphate solution was added dropwise to the $Ca(OH)_2$ slurry over 30 min while maintaining the reaction mixture pH between 9 and 10 with NH_4OH. The reaction Eq. (3) can describe the formation of hydroxyapatite.

$$10Ca(OH)_2 + 6(NH_4)_2HPO_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 12NH_3 + 18H_2O \quad (3)$$

Orange peel extract was then added at the designated concentration levels to serve as a green template. The organic compounds present in the extract interacted with Ca^{2+} ions, thereby influencing crystal growth, particle size, and morphology. The reaction mixture was stirred for 1 h and subsequently aged for 24 h to promote crystal growth and improve structural ordering.

After aging, the precipitate was filtered and washed repeatedly with distilled water until the pH was neutral. The washed precipitate was then dried, followed by calcination at 800°C for 6 h to remove residual organic components from the orange peel extract and to enhance the porosity and crystallinity of the synthesized hydroxyapatite. The appearance of the synthesized hydroxyapatite powder obtained via green synthesis is shown in Fig. 3.

Fig. 3. Synthesized hydroxyapatite powder obtained via green synthesis.

Structural, morphological, and elemental characterizations of the synthesized hydroxyapatite were subsequently performed using X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Energy-dispersive X-Ray Spectroscopy (EDS), respectively. The overall synthesis procedure of hydroxyapatite is summarized in the flowchart shown in Fig. 4.

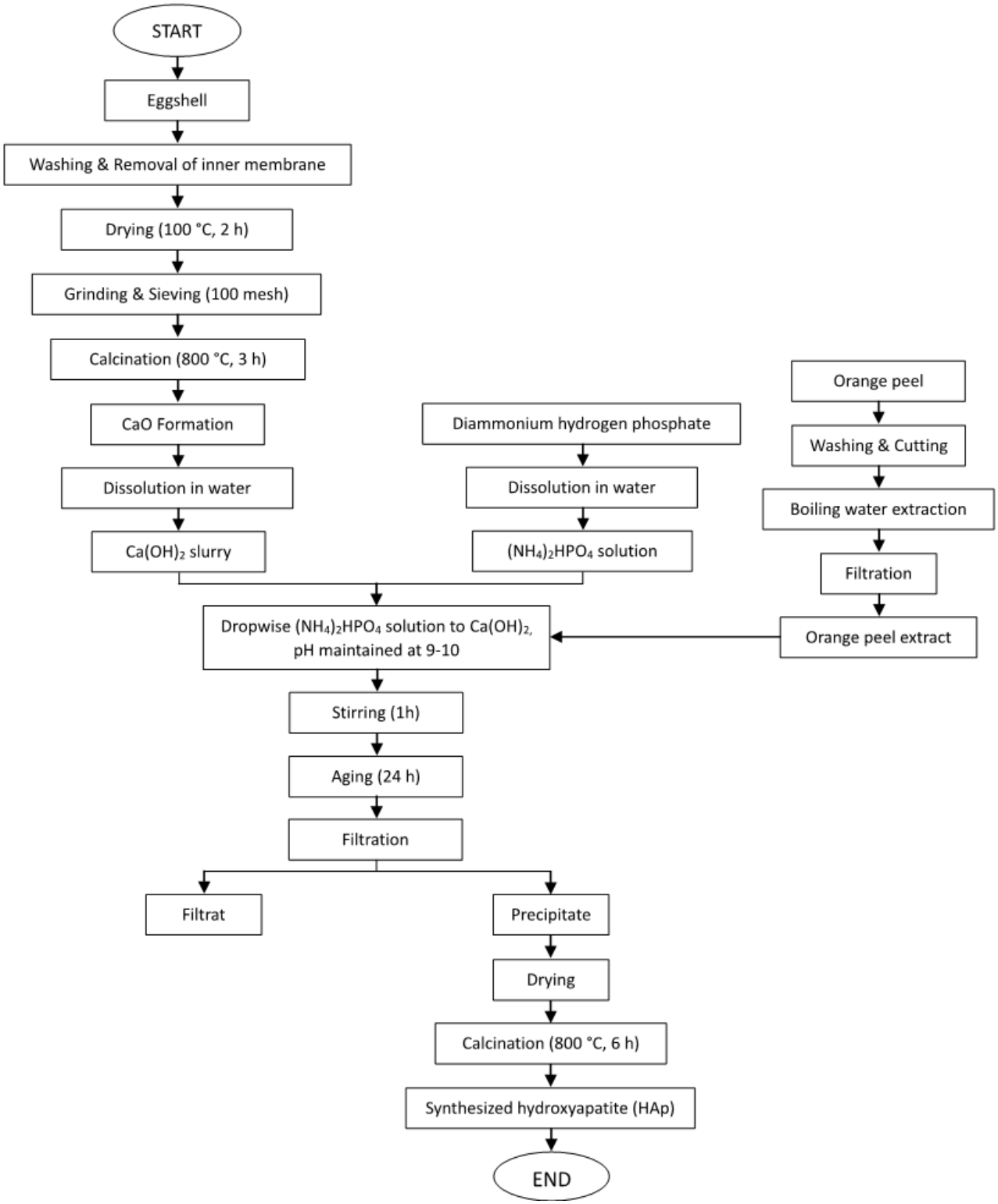


Fig. 4. Flowchart of green synthesis of hydroxyapatite from eggshells using orange peel (*Citrus sinensis*) extract as a template.

3 Results and discussion

3.1 Results

This study investigates the green synthesis of HAp from chicken eggshell waste using orange peel (*Citrus sinensis*) extract as a natural template. The synthesis was carried out via a wet chemical precipitation method, which is commonly employed for hydroxyapatite preparation due to its simplicity and controllability [8,10]. Hydroxyapatite was synthesized from eggshell-derived CaO using a wet precipitation method, as described in Section 2. Orange peel extract, rich in naturally occurring organic compounds, was prepared using distilled water and employed as a green template during the precipitation process, consistent with plant-mediated green synthesis strategies [4,16].

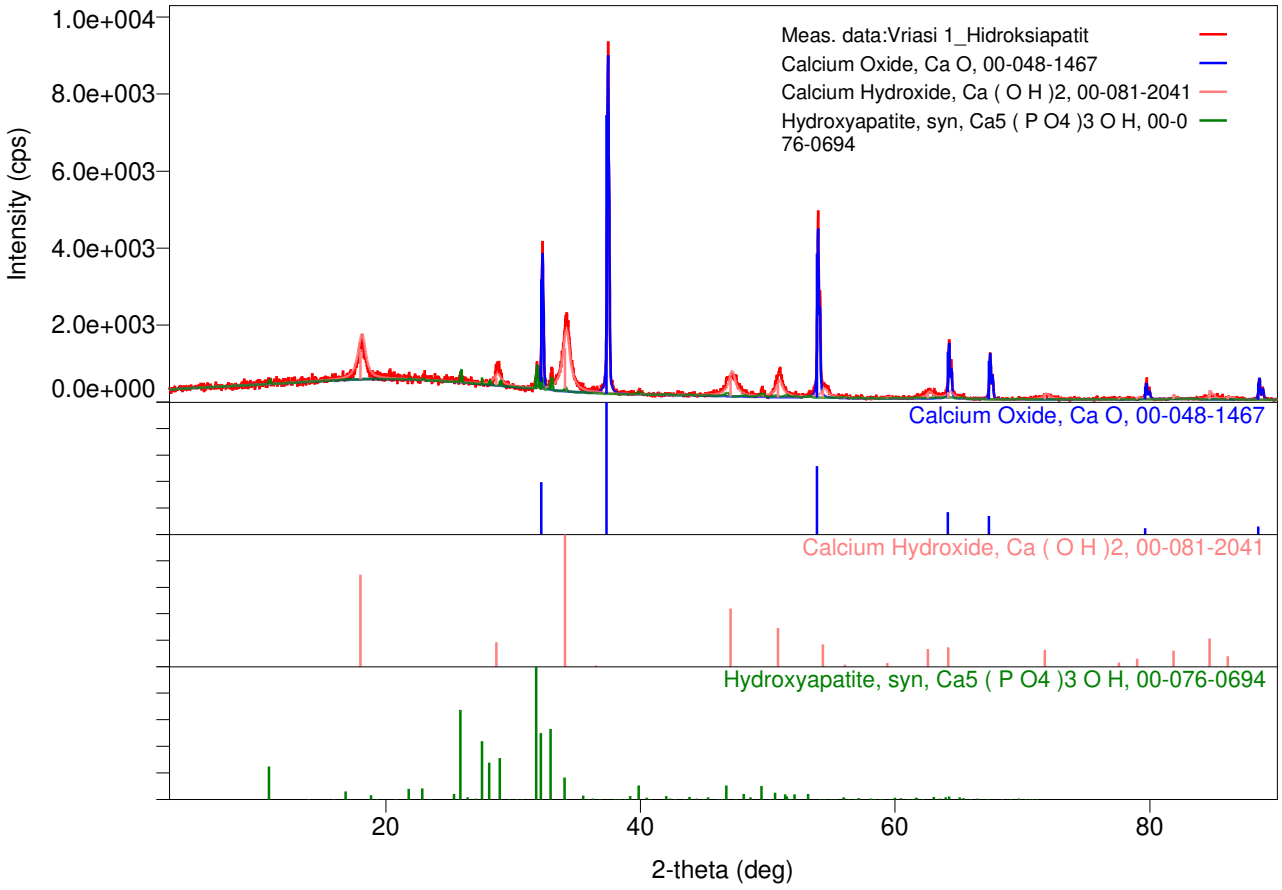
Hydroxyapatite samples were synthesized at four orange peel extract concentrations (0%, 10%, 20%, and 30%), with the sample without extract (0%) serving as the control. These variations were designed to systematically evaluate the influence of template concentration on the structural and morphological characteristics of the synthesized hydroxyapatite. All samples were prepared using a fixed Ca/P molar ratio of 1.67, corresponding to the stoichiometric ratio of hydroxyapatite [1], and the reaction pH was maintained at alkaline levels.

3.1.1 X-Ray Diffraction (XRD)

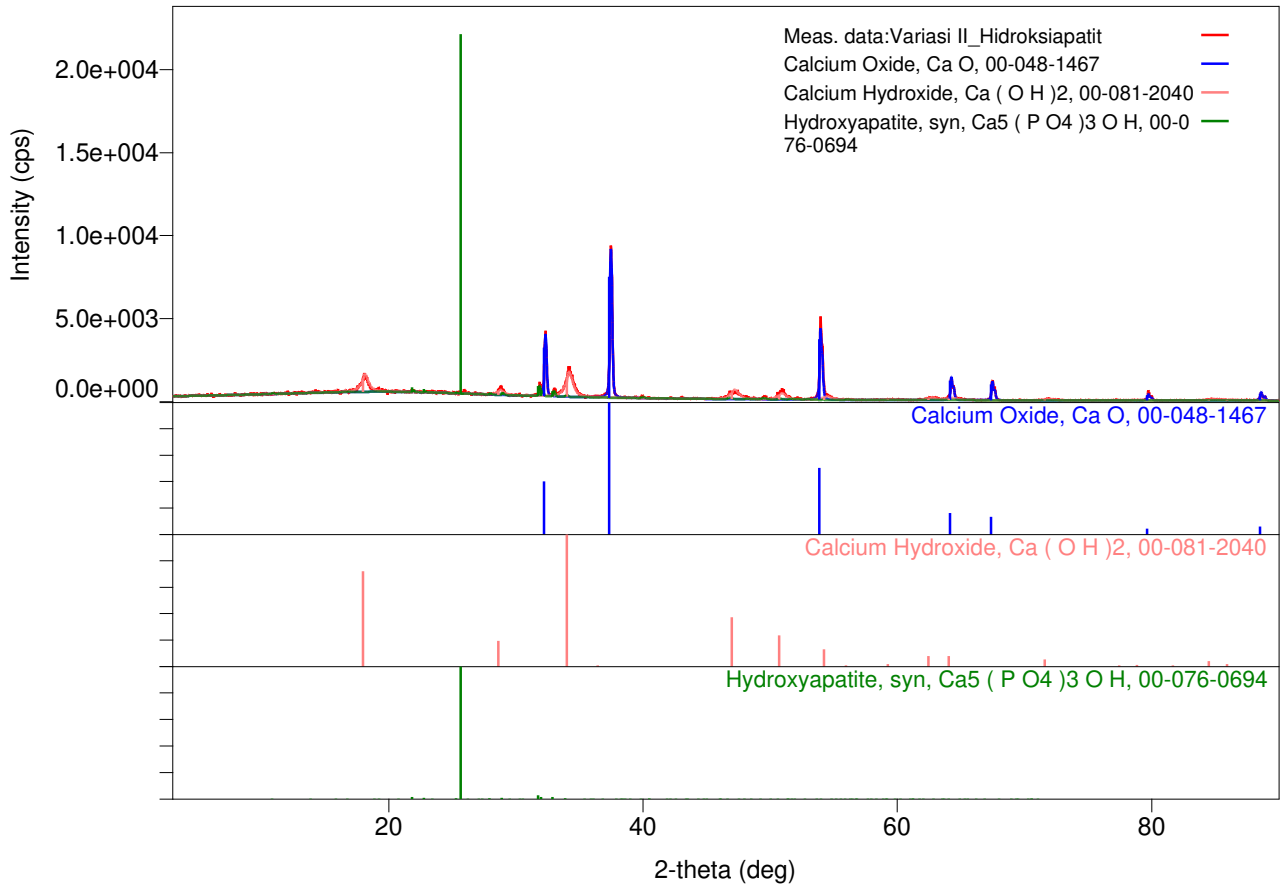
XRD analysis was performed to identify the crystalline phases formed in the synthesized HAp and to evaluate changes in

diffraction characteristics resulting from variations in orange peel extract concentration. XRD measurements were conducted on all samples containing 0%, 10%, 20%, and 30% orange peel extract, which is commonly applied for phase identification in calcium phosphate–based materials [1,11].

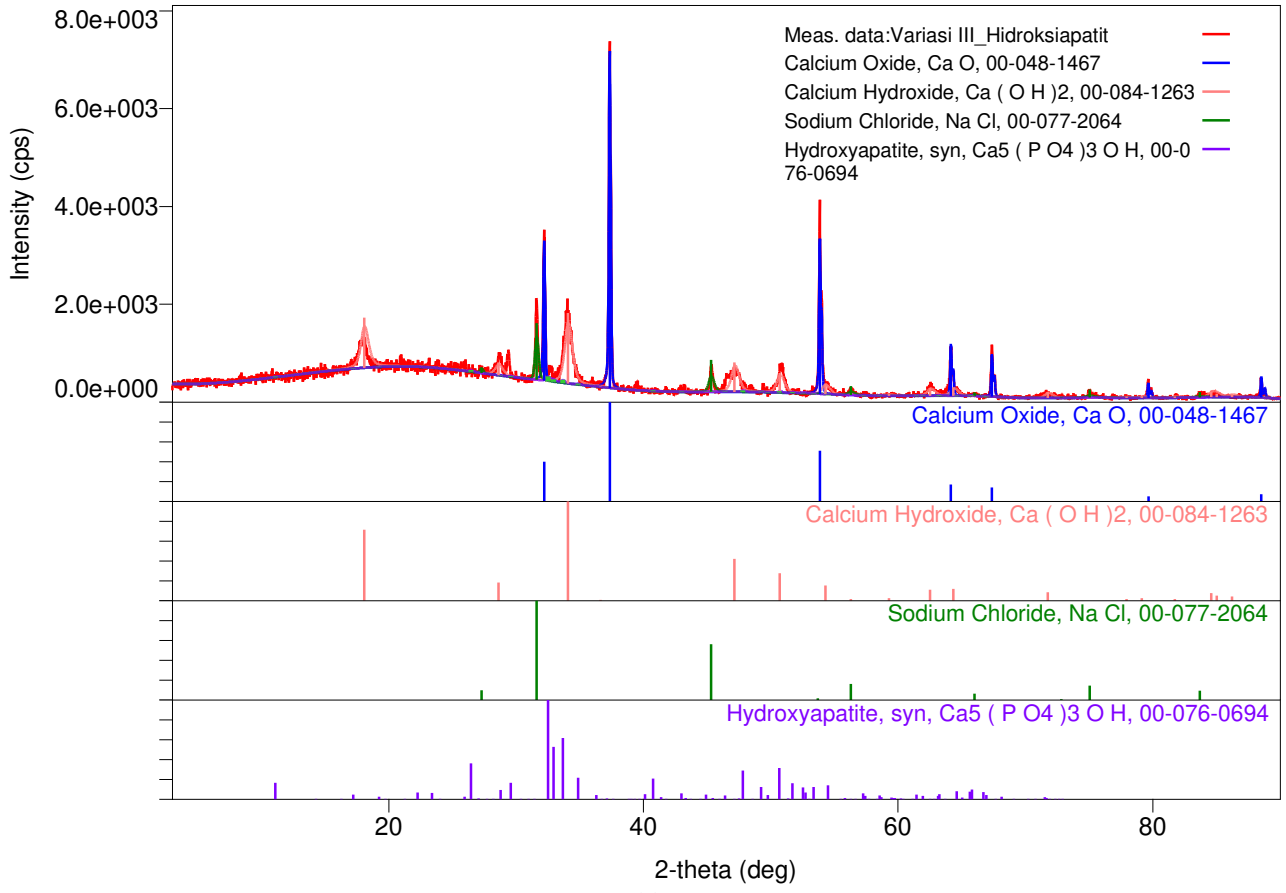
As shown in Fig. 5, all diffraction patterns consistently exhibited characteristic peaks corresponding to the hexagonal crystal structure of hydroxyapatite. The main diffraction peaks were observed at 2θ values of 25.9°, 31.9°, 32.3°, 34.2°, 39.9°, 47.1°, and 49.5°, confirming that hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] was the dominant crystalline phase in all synthesized samples. These diffraction features are in good agreement with hydroxyapatite synthesized via green routes reported in previous studies [5,12,13,16,17].



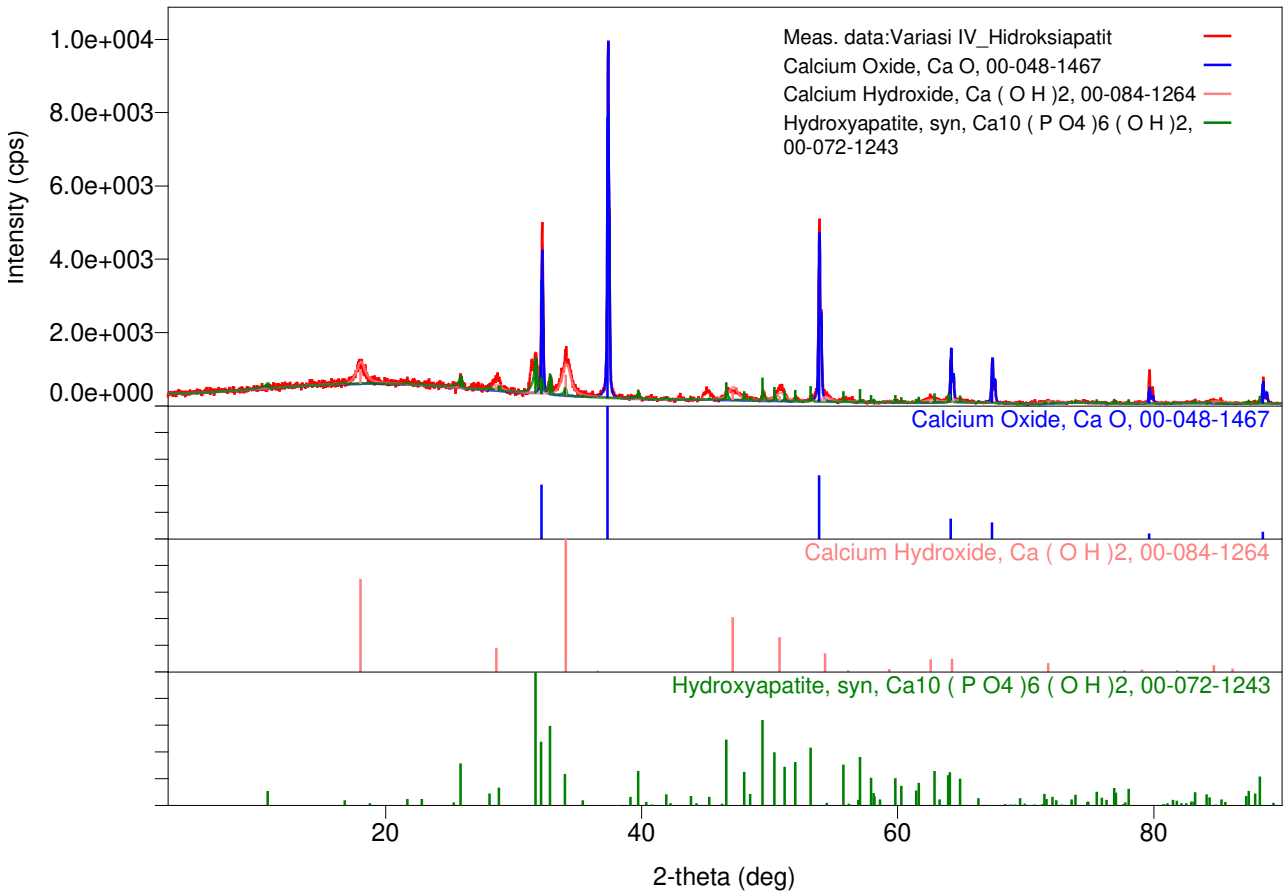
(a)



(b)



(c)



(d)

Fig. 5. XRD pattern of hydroxyapatite synthesized with different orange peel extract concentrations: (a) 0%, (b) 10%, (c) 20%, and (d) 30%.

In addition to the dominant hydroxyapatite phase, minor secondary phases were detected in several samples. A diffraction peak at approximately $2\theta \approx 37.46°$ was attributed to residual calcium oxide (CaO), indicating incomplete phase transformation during synthesis. Furthermore, a weak peak observed around $2\theta \approx 28.7°$ was assigned to calcium carbonate ($CaCO_3$), which may originate from partial carbonation of CaO by atmospheric CO_2 or from incomplete decomposition of $CaCO_3$ during calcination, as commonly reported in eggshell-based hydroxyapatite synthesis [18].

With increasing orange peel extract concentration, a slight broadening of hydroxyapatite diffraction peaks was observed. This peak broadening indicates a reduction in crystallite size and a marginal decrease in crystallinity. Similar behavior has been reported in template-assisted green synthesis systems, where organic compounds derived from plant extracts act as crystal growth–controlling agents, limiting excessive crystallite growth [5,12]. The reduced crystallite size implied by peak broadening is often associated with increased surface reactivity, which is advantageous for subsequent bioceramic applications.

Quantitative analysis of crystallinity further supports the observed XRD trends. The hydroxyapatite sample synthesized without orange peel extract (0%) exhibited the highest crystallinity, reaching 100%, indicating unrestricted crystal growth under conventional precipitation conditions. Upon the addition of orange peel extract, a gradual decrease in crystallinity was observed. The crystallinity values decreased to 99.55% for the 10% extract sample, 95.6% for the 20% extract sample, and 95.2% for the 30% extract sample.

The reduction in crystallinity with increasing extract concentration is attributed to the interaction between organic functional groups in the orange peel extract and calcium ions, which hinder excessive crystal growth and promote controlled nucleation. Although a slight decrease in crystallinity occurred, the values remained relatively high (>95%), indicating that the hydroxyapatite phase was well preserved. This controlled reduction in crystallinity is consistent with the observed refinement in particle size and enhanced porosity, as confirmed by SEM analysis, and is considered beneficial for applications requiring higher surface reactivity.

3.1.2 Scanning Electron Microscopy (SEM)

SEM was employed to examine the surface morphology, particle size tendencies, and degree of particle agglomeration of the synthesized hydroxyapatite samples. SEM observations were conducted for all samples containing 0%, 10%, 20%, and 30% orange peel extract, following standard morphological characterization practices for bioceramic materials [13].

Fig. 6 presents SEM micrographs of hydroxyapatite synthesized with different orange peel extract concentrations. The control sample without orange peel extract (0%) exhibited large, dense agglomerates with irregular morphology. The particle surfaces appeared rough, and individual particles were strongly bonded, resulting in a non-uniform particle size distribution and extensive agglomeration. This morphology is characteristic of hydroxyapatite synthesized via conventional wet precipitation in the absence of organic growth-controlling agents, where rapid nucleation and unrestricted crystal growth promote particle coalescence [18,19].

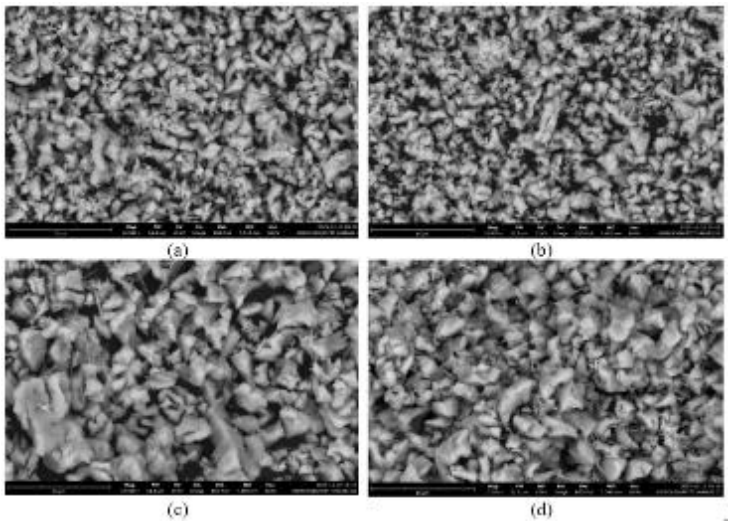


Fig. 6. SEM micrograph of hydroxyapatite synthesized with different orange peel extract concentrations: (a) 0%, (b) 10%, (c) 20%, and (d) 30%.

In the sample containing 10% orange peel extract, noticeable morphological changes were observed. The hydroxyapatite particles appeared smaller and more uniformly distributed than in the control sample, although partial aggregation remainedevident. The smoother particle surfaces suggest that organic compounds in the orange peel extract began to adsorb onto the particles, partially suppressing excessive crystal growth and agglomeration. Similar morphological refinement at low template concentrations has been reported in plant-mediated green synthesis systems [14].

Further morphological evolution was observed in the sample synthesized with 20% orange peel extract. The hydroxyapatite particles appeared finer and more dispersed, accompanied by a clear reduction in agglomeration. In addition, surface features indicative of pore formation became more apparent. These observations suggest that a higher concentration of organic molecules provided more effective surface coverage during nucleation and crystal growth, resulting in improved particle dispersion and the development of porous microstructures.

At an orange peel extract concentration of 30%, the most pronounced morphological modification was observed. The hydroxyapatite particles appeared to be the finest and smallest among all sample variations, with minimal agglomeration and a more open, porous structure. The high porosity observed at this concentration indicates that the organic constituents of the orange peel extract acted not only as growth inhibitors but also as pore-forming agents. Comparable morphological trends have been reported in studies using plant-derived biotemplates, in which increasing template concentration led to enhanced porosity and reduced particle size [13].

Overall, the SEM results demonstrate that the incorporation of orange peel extract significantly influences the morphology of eggshell-derived hydroxyapatite. Increasing the extract concentration led in a progressive reduction in particle size, decreased agglomeration, and enhanced porosity, indicating effective microstructural control via the green template approach. These morphological characteristics are particularly advantageous for applications requiring high surface area, such as bone tissue engineering scaffolds and adsorption-based systems. The SEM observations further corroborate the XRD results, confirming that orange peel extract acts as an effective structure-directing agent in the green synthesis of hydroxyapatite from eggshell waste.

3.1.3 Energy-Dispersive X-Ray Spectroscopy (EDS)

EDS analysis was employed to evaluate the elemental composition and purity of the synthesized hydroxyapatite samples and to assess the influence of orange peel extract addition on elemental distribution. As shown in Fig. 7, the EDS spectra of all samples consistently revealed calcium (Ca), phosphorus (P), and oxygen (O) as the predominant elements, irrespective of the orange peel extract concentration. This elemental composition is characteristic of calcium phosphate–based materials and confirms the successful formation of hydroxyapatite, in agreement with previous reports on eggshell-derived hydroxyapatite synthesized via green routes [1,15].

The consistent presence of Ca and P across all samples indicates that the incorporation of orange peel extract did not alter the fundamental chemical composition of the hydroxyapatite phase. This observation is important, as the introduction of natural templates in green synthesis routes may potentially lead to compositional variability if not properly controlled. Similar findings have been reported in plant-mediated hydroxyapatite synthesis, where organic additives primarily influenced particle morphology and microstructure without disrupting the Ca–P framework [5,14].

Carbon (C) was detected in samples synthesized with orange peel extract (10%, 20%, and 30%), whereas it was absent or negligible in the control sample without extract. The presence of carbon is attributed to residual organic species originating from the orange peel extract, such as pectin and flavonoids, which may not

be completely eliminated during calcination. Comparable carbon signals have been reported in other studies employing plant extracts as green templates and are commonly associated with partial decomposition of organic components during thermal treatment [5,15].

Importantly, the detection of carbon did not coincide with the appearance of undesired calcium phosphate phases, as confirmed by XRD analysis, indicating that residual carbon species did not interfere with hydroxyapatite phase formation. In fact, several studies suggest that trace amounts of carbon or carbonate substitution in hydroxyapatite can enhance biological performance by mimicking the composition of natural bone mineral, which inherently contains carbonate ions [1].

Element Symbol	Element Name	Atomic Conc.	Weight Conc.
C	Carbon	20.229	12.136
O	Oxygen	59.609	47.643
P	Phosphorus	0.324	0.502
Ca	Calcium	19.838	39.719

(a)

Element Symbol	Element Name	Atomic Conc.	Weight Conc.
C	Carbon	29.128	18.581
O	Oxygen	54.191	46.054
P	Phosphorus	0.304	0.500
Ca	Calcium	16.377	34.865

(b)

Element Symbol	Element Name	Atomic Conc.	Weight Conc.
C	Carbon	5.598	2.903
O	Oxygen	63.318	43.744
P	Phosphorus	1.122	1.502
Ca	Calcium	29.962	51.852

(c)

Element Symbol	Element Name	Atomic Conc.	Weight Conc.
C	Carbon	4.638	2.400
O	Oxygen	64.260	44.300
P	Phosphorus	1.049	1.400
Ca	Calcium	30.053	51.900

(d)

Fig. 7. EDS elemental composition of hydroxyapatite samples synthesized under various experimental conditions: (a) 0%, (b) 10%, (c) 20%, dan (d) 30% adding orange peel.

No heavy metals or foreign elements were detected at significant levels in any of the samples, demonstrating a high degree of elemental purity. This is particularly important for biomedical applications, where contamination with toxic elements can compromise biocompatibility and safety. Previous studies have emphasized that hydroxyapatite intended for bone-related applications must exhibit chemical purity and be free of harmful trace elements [2].

Overall, the EDS results support the effectiveness of the green synthesis approach employed in this study. The integration of eggshell waste as a calcium source and orange peel extract as a natural template successfully produced hydroxyapatite with appropriate elemental composition and high purity, while enabling microstructural modification without introducing undesirable contaminants.

3.2 Discussion

The results of this study demonstrate that the green synthesis approach employing chicken eggshell waste as a calcium source and orange peel extract as a natural template is effective in producing HAp with controlled structural and microstructural characteristics. Across all synthesis conditions, hydroxyapatite was confirmed as the dominant crystalline phase, indicating that the incorporation of a plant-based template did not hinder the fundamental Ca–P reaction pathway required for HAp formation. This finding is consistent with previous studies reporting the feasibility of eggshell-derived calcium precursors in environmentally benign synthesis routes for bioceramic materials [9,10,12].

The presence of minor secondary phases, such as CaO and $CaCO_3$, observed in several samples is commonly reported in eggshell-based hydroxyapatite synthesis. These phases are typically attributed to incomplete phase transformation during calcination or partial carbonation of CaO by atmospheric CO_2 [18]. Importantly, the persistence of hydroxyapatite as the dominant phase across all orange peel extract concentrations indicates that the green template did not disrupt phase formation, but rather influenced crystal growth behavior. This observation aligns with earlier reports that phase purity in green synthesis systems is often determined by calcination conditions rather than by organic templates alone.

A notable effect of orange peel extract addition was observed in the broadening of XRD diffraction peaks with increasing extract concentration. Peak broadening is generally associated with reduced crystallite size and a slight decrease in crystallinity. In plant-mediated green synthesis systems, this phenomenon is widely attributed to the interaction between organic biomolecules and Ca^{2+} ions during nucleation and crystal growth. Compounds such as pectin, flavonoids, and organic acids present in orange peel extract can act as chelating agents, temporarily binding calcium ions and limiting excessive crystal growth [4,16,20]. As a result, smaller crystallites with higher surface area are formed, which is advantageous for bioactive and adsorption-related applications.

The SEM observations strongly support the XRD findings by providing direct visual evidence of microstructural modification induced by the orange peel extract. The control sample synthesized without extract exhibited large, densely agglomerated particles with irregular morphology, a characteristic feature of hydroxyapatite synthesized via conventional wet precipitation without structure-directing agents [18,19]. As the concentration of orange peel extract increased, the hydroxyapatite particles became progressively finer, more uniformly distributed, and less agglomerated, with enhanced surface porosity. This trend clearly demonstrates the role of orange peel extract as an effective green template in regulating particle growth and aggregation.

The reduction in agglomeration and the emergence of porous structures can be attributed to the adsorption of organic molecules from the extract onto the surface of newly formed hydroxyapatite nuclei. These molecules act as steric barriers, preventing particle coalescence and promoting more homogeneous growth [13,14]. Similar morphological evolution has been reported in studies employing other plant-derived templates, such as banana peel, neem leaf, and citrus extracts, in which biomolecules function as stabilizing and structure-directing agents during synthesis [12].

The strong correlation between SEM and XRD results indicates that the observed reduction in crystallite size is directly linked to the refined particle morphology. Smaller crystallites and higher porosity are often associated with broader diffraction peaks, as reported in template-assisted green synthesis of hydroxyapatite [5]. This correlation confirms that orange peel extract influences not only surface morphology but also crystal growth kinetics at the microscopic scale.

EDS analysis further confirmed that the integration of orange peel extract did not compromise the elemental composition or purity of the synthesized hydroxyapatite. Calcium, phosphorus, and oxygen remained the dominant elements in all samples, confirming the preservation of the Ca–P framework characteristic of hydroxyapatite [1,15]. The detection of carbon in extract-containing samples is attributed to residual organic species

originating from the plant-based template, a common feature in green synthesis systems [4,15]. Importantly, the absence of heavy metals and other foreign elements underscores the suitability of the synthesized material for biomedical and environmental applications.

From an application perspective, the microstructural characteristics achieved in this study are highly desirable for bioceramic materials. Hydroxyapatite with reduced particle size, enhanced porosity, and high surface area has been shown to promote osteoblast adhesion and proliferation, thereby improving osteoconductive behavior in bone tissue engineering applications [1,2]. Furthermore, porous hydroxyapatite structures are advantageous for non-biomedical applications, such as the adsorption of dyes and heavy metal ions, where surface area and accessibility of active sites are critical [19].

Overall, this study demonstrates that the combined use of eggshell waste and orange peel extract offers a sustainable and effective strategy for producing hydroxyapatite with tunable structural and microstructural properties. The findings contribute to the growing body of literature on waste-derived and plant-mediated green synthesis of bioceramics, highlighting the potential of agricultural and food industry by-products as valuable resources for advanced material development.

4 Conclusions

This study demonstrated a sustainable green synthesis route for HAp using chicken eggshell waste as a calcium source and orange peel (*Citrus sinensis* L.) extract as a natural template via a wet-chemical precipitation method. In terms of crystal structure, XRD analysis confirmed hydroxyapatite as the dominant hexagonal phase under all synthesis conditions, while the addition of orange peel extract led to controlled peak broadening and a gradual decrease in crystallinity from 100% (0%) to 99.55% (10%), 95.6% (20%), and 95.2% (30%), indicating reduced crystallite size without phase degradation.

Regarding particle morphology, SEM observations revealed that increasing extract concentration resulted in finer particle size, reduced agglomeration, and enhanced surface porosity, with the most pronounced microstructural refinement observed at 30% extract concentration. Concerning material characteristics, EDS analysis confirmed consistent elemental composition and the absence of harmful contaminants, demonstrating that the incorporation of orange peel extract effectively modified microstructural features without disrupting the fundamental hydroxyapatite framework.

Among the investigated conditions, 30% orange peel extract was identified as the most preferable concentration, providing the best balance between crystal growth control, morphological refinement, and structural stability. Overall, integrating eggshell waste and orange peel extract offers an environmentally friendly and cost-effective approach for producing hydroxyapatite with tunable properties, highlighting the potential of waste-derived green synthesis strategies for sustainable bioceramic material development.

References

[1] LeGeros RZ, LeGeros JP. Calcium Phosphate Bioceramics: Past, Present and Future. Key Eng Mater. 2003;240–242:3–10.

[2] Marcacci M, Kon E, Moukhachev V, Lavroukov A, Kutepov S, Quarto R, et al. Stem cells associated with macroporous bioceramics for long bone repair: 6- To 7-year outcome of a pilot clinical study. Tissue Eng. 2007;13(5):947–55.

[3] Eliaz N, Metoki N. Calcium Phosphate Bioceramics: A Review of Their History, Structure, Properties, Coating Technologies and Biomedical Applications. Mater 2017, Vol 10, Page 334 [Internet]. 2017 Mar 24 [cited 2026 Jan 10];10(4):334. Available from: https://www.mdpi.com/1996-1944/10/4/334/htm

[4] Prakash M, Rajan HK, Chandraprabha MN, Shetty S, Mukherjee T, Girish Kumar S. Recent developments in green synthesis of hydroxyapatite nanocomposites: relevance to biomedical and environmental applications. Green Chem Lett Rev [Internet]. 2024 [cited 2025 Apr 12];17(1). Available from: https://www.tandfonline.com/action/journalInformation?journalCode=tgcl20

[5] Alorku K, Manoj M, Yuan A. A plant-mediated synthesis of nanostructured hydroxyapatite for biomedical applications: A review. RSC Adv. 2020;10(67):40923–39.

[6] Pal K, Chakroborty S, Nath N. Limitations of nanomaterials insights in green chemistry sustainable route: Review on novel applications. Green Process Synth. 2022;11(1):951–64.

[7] BPS. Produksi Telur Ayam Petelur menurut Provinsi - Tabel Statistik - Badan Pusat Statistik Indonesia [Internet]. 2024 [cited 2025 Apr 12]. Available from: https://www.bps.go.id/id/statistics-table/2/NDkxIzI=/produksi-telur-ayam-petelur-menurut-provinsi.html

[8] Khandelwal H, Prakash S. Synthesis and Characterization of Hydroxyapatite Powder by Eggshell. J Miner Mater Charact Eng. 2016;04(02):119–26.

[9] Gowri A, Kala K. Evaluating synthesis of Novel Hydroxyapatite from Egg Shell Compared with Chemically Synthesized HAP for Orthopedic application. J Pharm Negat Results. 2022;13(4).

[10] Irwansyah FS, Amal AI, Hadisantoso EP, Noviyanti AR, Eddy DR, Risdiana R, et al. How to Make and Characterize Hydroxyapatite from Eggshell Using the Hydrothermal Method: Potential Insights for Drug Delivery System. Indones J Sci Technol. 2023;8(3):469–86.

[11] Studart AR, Gonzenbach UT, Tervoort E, Gauckler LJ. Processing routes to macroporous ceramics: A review. J Am Ceram Soc. 2006 Jun;89(6):1771–89.

[12] Gopi D, Kanimozhi K, Bhuvaneshwari N, Indira J, Kavitha L. Novel banana peel pectin mediated green route for the synthesis of hydroxyapatite nanoparticles and their spectral characterization. Spectrochim Acta Part A Mol Biomol Spectrosc [Internet]. 2014 Jan 24 [cited 2025 Dec 27];118:589–97. Available from: https://www.sciencedirect.com/science/article/abs/pii/S1386142513010041X

[13] Kalaiselvi V, Mathammal R, Vijayakumar S, Vaseeharan B. Microwave assisted green synthesis of Hydroxyapatite nanorods using Moringa oleifera flower extract and its antimicrobial applications. Int J Vet Sci Med [Internet]. 2018 Dec 1 [cited 2025 Dec 27];6(2):286–95. Available from: /doi/pdf/10.1016/j.ijvsm.2018.08.003?download=true

[14] Ragunath C, Kousalya L, Venkatachalam R, Anitha S. Green Synthesis of Hydroxyapatite Nanoparticles from Wrightia tinctoria and Its Antibacterial Activity. Bionanoscience. 2022;12(3):723–30.

[15] Baladi M, Amiri M, Mohammadi P, Salih Mahdi K, Golshani Z, Razavi R, et al. Green sol–gel synthesis of hydroxyapatite nanoparticles using lemon extract as capping agent and investigation of its anticancer activity against human cancer cell lines (T98, and SHSY5). Arab J Chem [Internet]. 2023;16(4):104646. Available from: https://doi.org/10.1016/j.arabjc.2023.104646

[16] Manoj M, Subbiah R, Meena P, Mangalaraj D, Ponpandian N, Viswanathan C, et al. Green Synthesis and Characterization of Bioceramic Hydroxyapatite (HAp) Nanosheets and Its Cellular Study. Adv Sci Eng Med. 2016 Mar 30;8(3):216–21.

[17] Gopi D, Bhuvaneshwari N, Kavitha L, Ramya S. Novel malic acid mediated green route for the synthesis of hydroxyapatite particles and their spectral characterization. Ceram Int [Internet]. 2015 Mar 1 [cited 2025 Dec 27];41(2):3116–27. Available from:

https://www.sciencedirect.com/science/article/abs/pii/S0272884214017088
[18] Wardani SC, Rujati B, Nuraprilla E, Salsabila H, Wibowo MA, Rahmatina SP, et al. Sintesis Nanohidroksiapatit Turunan Cangkang Telur sebagai Pengganti Cangkok untuk Regenerasi Tulang dalam Kedokteran Gigi: Studi Literatur. E-Prodenta J Dent. 2024;8(1):109–22.
[19] Setiawan H, Anindi UF, Pulungan DY, Akbar N, Noviyanti AR, Solihudin S. Biocomposite of Hydroxyapatite from Chicken Egg Shells and Biochar from Rice Husk As an Adsorbent for Copper Ion and Methylene Blue. J Keramik dan Gelas Indones. 2020;29(1):1.
[20] Upadhyay P, Ullah A. Facile synthesis of hydroxyapatite nanoparticles from eggshell biowaste using Azadirachta indica extract as a green template. New J Chem [Internet]. 2024 Jan 15 [cited 2025 Dec 12];48(3):1424–35. Available from: https://pubs.rsc.org/en/content/articlehtml/2024/nj/d3nj01715j