

Synthesis of Calcium Phosphate from Snail Shell Waste Using the Hydrothermal Method

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Article Information	ABSTRACT
Article History Received : February 18, 2026 Revised : March 01, 2026 Published : April 02, 2026	The utilization of biowaste as an alternative raw material has attracted increasing attention in biomaterial research. Snail shell waste, which is abundant and underutilized, contains a high calcium carbonate content and offers a unique, low-cost, and sustainable precursor for calcium phosphate synthesis, particularly for bone substitute applications. This study aimed to synthesize calcium phosphate from snail shell waste using the hydrothermal method and to evaluate the effects of pH and hydrothermal time on phase formation, purity, and particle size. The shells were calcined at 800 °C for 4 hours to produce calcium oxide (CaO), then reacted with phosphoric acid at pH 8–12 under hydrothermal conditions for 25–125 minutes. The precipitates were dried and sintered at 1000 °C for 5 hours. X-ray fluorescence analysis showed a CaO content of 99.20%. X-ray diffraction revealed calcium hydrogen phosphate, hydroxyapatite, and calcium carbonate phosphate hydroxide phases. The highest hydroxyapatite content (54%) was obtained at pH 8 and 25 minutes. Higher pH and longer processing time reduced purity. Scanning electron microscopy showed granular morphology, with particle sizes decreasing from 63 nm to 28 nm as pH increased. Although promising, the hydroxyapatite content does not yet meet RSNi3 ISO 13175-3:2012 requirements.
Keywords: <i>Biomaterial; Calcium Oxide; Calcium Phosphate; Hydrothermal method; Snail Shell.</i>	

INTRODUCTION

Snail shells are commonly used as animal feed or disposed of without further processing, which creates the potential for waste generation (Septiani, 2022). Snail shells have a conical shape, are brown in color, and exhibit dark-colored spots (Leu, 2021). Snail shells have a length of 10–12 cm, a width of 4–5 cm, and a weight of 100–120 grams. The hard texture of snail shells is due to their composition, which is largely made up of calcium compounds (Damayanti, 2020). Snail shell waste can be converted into more valuable products by utilizing its main constituent. The primary component of snail shells is calcium carbonate with a calcium carbonate content of approximately 98% (Rismawati, 2020). This high calcium carbonate content makes snail shells a promising raw material for the production of biomaterials (Pangestu, 2021). Materials with high calcium carbonate content can be heated at temperatures of 600–1000 °C to obtain calcium oxide. Calcium oxide is an inexpensive source of calcium and has strong potential to be used as a raw material for the production of calcium phosphate fosfat (Sunardi, 2017).

Advancements in technology have driven increased research interest in biomaterials. The development of biomaterials continues to address challenges such as rapid degradation and

insufficient mechanical strength. Biomaterials are materials designed to replace or support the natural functions of living tissues or organs. One of the biomaterials commonly used for bone implants is calcium phosphate. Calcium phosphate is a group of minerals containing calcium ions (Ca), orthophosphate (PO_4), pyrophosphate (P_2O_7), hydrogen (H), and hydroxide (Eliaz, 2017). In general, calcium phosphate exists in crystalline form. Calcium phosphate is a naturally complex material because it occurs in various phases. The phases of calcium phosphate include dicalcium phosphate, octacalcium phosphate, tricalcium phosphate, and hydroxyapatite (Noviyanti, 2017). Calcium phosphate is suitable for bone implant applications due to its chemical and structural similarity to natural bone tissue, which enables effective bone tissue repair and regeneration (Sukmana, 2022).

Previous studies have demonstrated the potential of calcium-rich waste materials as sources for calcium phosphate synthesis. (Wadu, 2017) reported the production of 8.8–9.8 g of hydroxyapatite from 10 g of chicken eggshells at pH 10 and a sintering temperature of 1000 °C. (Rachman, 2019) obtained 467 g of hydroxyapatite powder from 1 kg of sipping clam shells at pH 8–9, a stirring speed of 700 rpm, and a calcination temperature of 800 °C. (Hutabarat, 2019) achieved a hydroxyapatite–lanthanum oxide composite yield of 90.31% using in situ and ex situ hydrothermal methods at 230 °C for 48 h. More recently, (Pratama, 2024) achieved a hydroxyapatite purity of 86.56% at 120 °C, pH 12, and a hydrothermal processing time of 25 minutes, emphasizing the critical role of process parameters in determining product quality.

Based on these studies, the hydrothermal method offers notable advantages for calcium phosphate synthesis, including environmental friendliness due to the use of water as the solvent and the formation of more uniform crystal sizes. Hydrothermal synthesis is a method for producing crystalline materials under high-pressure conditions, where the reaction temperature can exceed the boiling point of water and the pressure is generated by saturated water vapor (Amri, 2019). Snail shells are selected as a raw material because they remain underutilized and have significant potential to become waste. Therefore, this study aims to utilize snail shell waste as a calcium source for calcium phosphate synthesis via the hydrothermal method and to investigate the effects of hydrothermal processing time and pH on the resulting calcium phosphate crystal phases.

RESEARCH METHODS

Time and Location. This experimental research was conducted over two months at the Chemical Engineering Research Laboratory, Universitas Pembangunan Nasional "Veteran" Jawa Timur.

Materials. Snail Shell, H_3PO_4 2 M, NaOH 2 M, and distilled water.

Equipment. The equipment used in this research include thermometer, oven, tray and hydrothermal autoclave

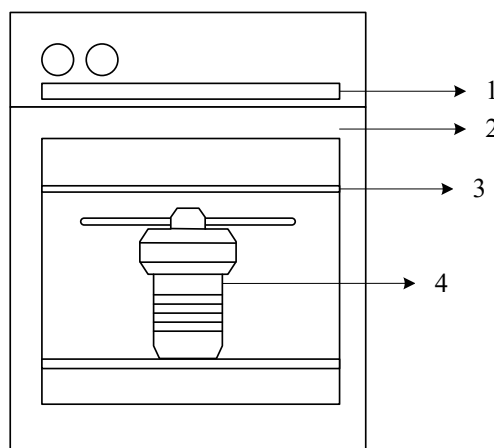


Figure. 1 Calcium Phosphate Synthesis Apparatus Setup

Raw Material Preparation. The snail shells were washed thoroughly and then dried in an oven at 100 °C for 2 hours. After drying, the shells were ground into a fine powder and sieved using a 60-mesh sieve. The powdered snail shells were subsequently calcined at 800 °C for 4 hours.

Calcium Phosphate Formation. Calcium oxide (CaO) powder was first reacted with distilled water to produce calcium hydroxide (Ca(OH)₂). The resulting calcium hydroxide was subsequently reacted with phosphoric acid (H₃PO₄), and sodium hydroxide (NaOH) was added to adjust the pH of the reaction mixture to 8, 9, 10, 11, and 12. The mixture was then transferred into an autoclave and treated for varying hydrothermal times of 25, 50, 75, 100, and 125 minutes to facilitate precipitation. After the hydrothermal process, the suspension was filtered to obtain the calcium phosphate precipitate.

The selection of pH values ranging from 8 to 12 was based on the stability region of calcium phosphate formation, where precipitation is more favorable under alkaline conditions. At this pH range, the formation of calcium phosphate phases becomes more stable and significantly influences the phase composition of the resulting product. Meanwhile, the hydrothermal treatment times of 25 to 125 minutes were selected to investigate their effect on crystal growth behavior, as longer hydrothermal durations can affect the development and size of the crystals formed.

Sintering Process. After weighing, the calcium phosphate samples were dried in an oven at 100 °C until a constant weight was achieved. The dried samples were then subjected to a sintering process in a furnace at a sintering temperature of 1000 °C for 5 hours.

Analysis Method. After raw material preparation, a portion of the calcined powder was used as a sample to determine the composition of calcium oxide (CaO) using X-Ray Fluorescence (XRF) analysis and after sintering, phase characterization and microstructural analysis were carried out using X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM).

RESULTS AND DISCUSSION

Characteristics of Raw Material Using X-Ray Fluorescence (XRF)

The CaO powder obtained from the preparation of snail shell was analyzed using X-Ray Fluorescence (XRF) to determine the composition of CaO produced from the snail shell preparation. The results of the XRF analysis of the CaO powder are presented in Table 1.

Table.1 Results of raw material preparation analysis using the XRF method

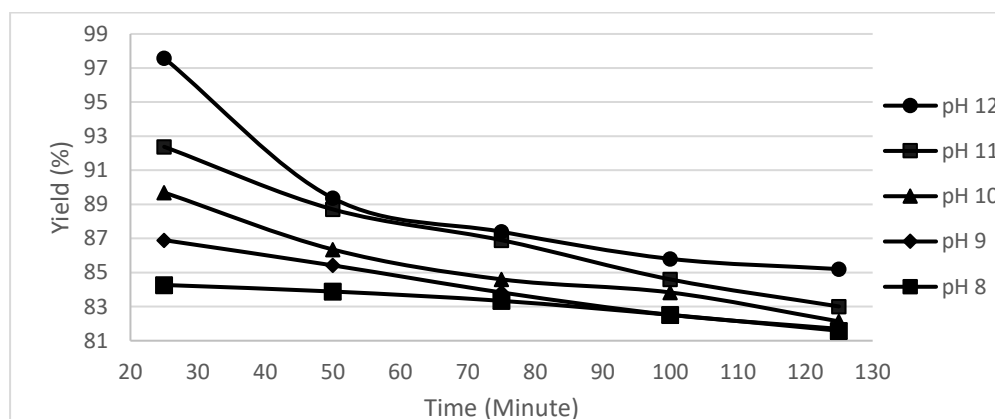
Compound	Composition (%)
CaO	99,2
Fe ₂ O ₃	0,11
CO ₃ O ₄	0,088
CuO	0,03
ZnO	0,01
SrO	0,033
Er ₂ O ₃	0,06
Lu ₂ O ₃	0,14
Re ₂ O ₇	0,04

Source : (State University of Malang Laboratory, 2025)

Based on Table 1, it can be observed that a CaO content of 99.2% was obtained, which can be used as a raw material for the synthesis of calcium phosphate.

Yield of Calcium Phosphate

Yield is calculated to determine the percentage of solid products obtained from the precipitation process relative to the initial mass of raw materials. The results of the calcium phosphate synthesis are presented in the following Figure 2.

**Figure. 2** The effect of pH and hydrothermal time on yield

Based on Figure 2, the results indicate that a higher pH leads to a higher yield. This is evidenced by the comparison at pH 12 and pH 8 with a processing time of 25 minutes, where a yield of 97.03% was obtained at pH 12, while at pH 8 the yield was 86.70%. It was also observed that a longer hydrothermal processing time tends to result in a decrease in yield. This is demonstrated at pH 11, where a yield of 90.14% was obtained at 50 minutes, where as at 100 minutes the yield decreased to 88.74%. The increase in yield is influenced by the pH condition, as under alkaline pH the concentration of phosphate ions (PO_4^{3-}) becomes more dominant, there by accelerating the precipitation process. This condition enhances the nucleation and crystal growth processes, leading to an increased amount of precipitate and a higher yield. These findings are consistent with the study by (Ebrahimi, 2021), which reported that an increase in pH significantly enhances crystal formation, resulting in a higher yield value.

X-Ray Diffraction (XRD) Analysis Result

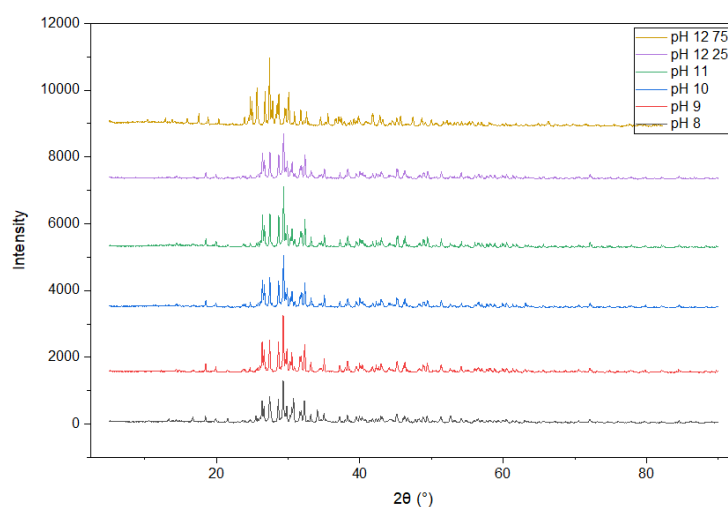


Figure. 3 XRD Analysis Result

Based on Figure 3, the XRD results of samples prepared at various pH values with hydrothermal times of 25 and 75 minutes are presented. The results obtained at pH 8, 9, 10, 11, and 12 are predominantly composed of calcium hydrogen phosphate and hydroxyapatite. Phase identification was carried out by comparing the sample data with reference data from the ICDD (International Centre for Diffraction Data). The ICDD reference data used for comparison were ICDD 04-013-6615 and ICDD 01-091-6031. According to the ICDD data, the main diffraction peaks of hydroxyapatite appear at 2θ values of $31-33^\circ$. In this study, hydroxyapatite was formed at pH 8, 9, 10, and 12, as indicated by the main peaks at 2θ values of 30.74° , 30.52° , 30.51° , and 30.58° , respectively. The presence of calcium hydrogen phosphate is indicated by the appearance of its main peaks at 2θ values of $27-29^\circ$. In this study, calcium hydrogen phosphate was formed at pH 8, 9, 10, 11, and 12, as indicated by diffraction peaks at 2θ values of 29.30° , 29.35° , 29.34° , 29.36° , and 29.36° .

Table. 2 Result Phase Composition

Time	pH	Phase	Composition (%)
25	8	Hydroxyapatite	54
		Calcium Hydrogen Phosphate	46
	9	Hydroxyapatite	15
		Calcium Hydrogen Phosphate	85
	10	Hydroxyapatite	16,8
		Calcium Hydrogen Phosphate	83,2
	11	Calcium Carbonate Phosphate Hydroxide	50
		Calcium Hydrogen Phosphate	50
	12	Hydroxyapatite	44,5
		Calcium Hydrogen Phosphate	55,5
75	12	Hydroxyapatite	28
		Calcium Hydrogen Phosphate	72

Source : (Materials and Metallurgy Laboratory ITS, 2025)

Based on XRD analysis, the synthesized calcium phosphate exhibited various phase compositions depending on pH and hydrothermal processing time. At pH 12 with hydrothermal times of 25 and 75 minutes, the calcium phosphate phases consisted of 72% calcium hydrogen phosphate and 28% hydroxyapatite, indicating a decrease in hydroxyapatite purity compared to the sample synthesized for 25 minutes, which showed a hydroxyapatite content of 44.5%. This reduction is attributed to recrystallization effects caused by prolonged hydrothermal treatment, where smaller hydroxyapatite crystals dissolve and redeposit onto larger crystals, leading to

excessive crystal growth, non-uniform crystal size, and a less ordered structure that facilitates the formation of other phases (Pratama, 2024). Variations in pH also significantly affected phase formation. At pH 8, hydroxyapatite was obtained at 54%, indicating that mildly alkaline conditions support hydroxyapatite nucleation due to sufficient availability of phosphate ions (PO_4^{3-}), consistent with the findings of (Palanivelu, 2014). However, the hydroxyapatite content decreased sharply to 15–16.8% at pH 9–10, before increasing again to 44.5% at pH 12 as highly alkaline conditions accelerated the interaction between Ca^{2+} and PO_4^{3-} ions.

Calcium hydrogen phosphate was also a dominant phase under several conditions, accounting for 46% at pH 8, with its composition generally increasing as pH increased due to incomplete binding between Ca^{2+} and PO_4^{3-} ions caused by residual water during $\text{Ca}(\text{OH})_2$ formation. At pH 12, the calcium hydrogen phosphate content decreased to 55.5% as HPO_4^{2-} ions were converted into PO_4^{3-} ions, which preferentially formed more stable calcium phosphate phases such as hydroxyapatite. At pH 11, calcium phosphate formation was dominated by calcium carbonate phosphate hydroxide (50%), resulting from interactions between Ca^{2+} and carbonate ions (CO_3^{2-}) originating from residual CaCO_3 that was not fully decomposed during calcination (Fitri, 2024). Overall, three phases were identified: calcium hydrogen phosphate, hydroxyapatite, and calcium carbonate phosphate hydroxide. Among these, hydroxyapatite is the most desirable phase for bone implant applications due to its low solubility and high stability in the human body (Redhwi, 2024). However, the highest hydroxyapatite content obtained in this study was only 54%, which does not meet the RSNI3 ISO 13175-3:2012 requirement of 95% hydroxyapatite for bone substitute materials, indicating that the synthesized material is not yet suitable for bone implant applications.

Scanning Electron Microscopy (SEM) Result

Calcium phosphate synthesis at pH 8 and pH 12 resulted in the formation of hydroxyapatite and calcium hydrogen phosphate phases, which exhibited relatively higher values compared to other pH conditions. Therefore, these two samples were selected for Scanning Electron Microscopy (SEM) analysis to determine the surface morphology and the size of the formed crystals.

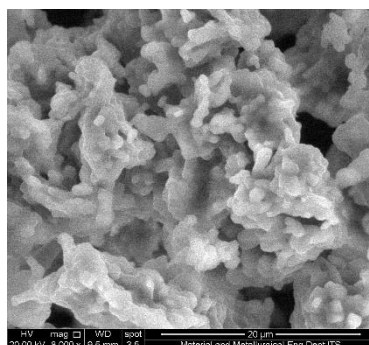


Figure. 4 Analysis SEM at pH 8

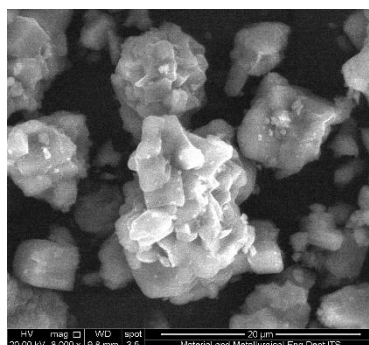


Figure. 5 Analysis SEM at pH 12

Source : (Materials and Metallurgy Laboratory ITS, 2025)

SEM characterization results revealed the structural and morphological features of calcium phosphate. The Scanning Electron Microscopy (SEM) analysis showed that calcium phosphate synthesized at pH 8 exhibited a spherical-to-granular morphology with an average particle size of 63 nm, where the particles appeared as agglomerated clusters with relatively close interparticle spacing. In comparison with Figure 5, calcium phosphate with a more uniform particle morphology was observed, exhibiting a spherical-to-granular shape with a smaller average particle size of 28 nm. These findings are consistent with the study by (Haruda, 2016), which reported that increasing pH affects the crystal size of hydroxyapatite, where crystals measuring 65.66 nm were obtained at pH 5 and decreased to 54.78 nm at pH 11. The formation of calcium phosphate structures is influenced by calcination and stirring processes, where calcination at a high temperature of 800 °C enhances crystal growth activity and promotes agglomeration (Lazar, 2006), while non-uniform stirring leads to uneven particle distribution and particle agglomeration (Putri, 2016). Based on the obtained average particle size, the synthesized calcium phosphate is not yet suitable for biomedical or biomaterial applications, as hydroxyapatite intended for bone regeneration must have a particle size in the range of 500–800 nm to support bone regeneration after 12 weeks of implantation, where as smaller hydroxyapatite particles may inhibit cell regeneration (Gani, 2022).

The XRF, XRD, and SEM results show a clear relationship between phase formation and microstructure of the synthesized calcium phosphate. XRF analysis confirmed a high CaO content of 99.2%, indicating sufficient Ca^{2+} availability during synthesis. This directly influenced the phase composition identified by XRD, where variations in pH and hydrothermal time affected the formation of hydroxyapatite and calcium hydrogen phosphate phases. The phase differences observed in XRD were consistent with the SEM results, where samples with higher hydroxyapatite content exhibited more uniform and finer particle morphology, while samples dominated by secondary phases showed greater agglomeration. These findings confirm that phase composition and particle morphology are strongly correlated with the final characteristics of the synthesized material.

CONCLUSION

Hydrothermal time affects the yield obtained. The longer the hydrothermal time, the lower the yield produced. This was demonstrated by the results at pH 12, where a hydrothermal time of 25 minutes produced a yield of 97.03%, while a hydrothermal time of 75 minutes resulted in a yield of 89.12%. Hydrothermal time also influences the purity of hydroxyapatite. As the hydrothermal process time increases, the purity of hydroxyapatite decreases. This is evidenced by the results at pH 12, where a hydrothermal time of 25 minutes produced a hydroxyapatite purity of 44.5%, whereas at 75 minutes the purity decreased to 28%. The variation of pH affects the particle size of calcium phosphate. Higher pH values result in smaller calcium phosphate crystal sizes. This is shown by the results at pH 8 with a hydrothermal time of 25 minutes, which produced an average particle size of 63 nm, while at pH 12 with the same hydrothermal time of 25 minutes, the average particle size decreased to 28 nm. The best condition for calcium phosphate synthesis was obtained at a hydrothermal time of 25 minutes and pH 8, resulting in a hydroxyapatite purity of 54%. Future research is recommended to vary the hydrothermal time around 25 minutes, such as 15, 20, 30, and 35 minutes, in order to determine a more precise optimum time for achieving the highest yield and hydroxyapatite purity.

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