

Utilization of Waste From Shells *Placuna Placenta* For The Production of Hydroxyapatite Using The Precipitation Method

Khusnul Mubarak*, Muhammad Gary Raditya, Ketut Sumada

Chemical Engineering Department, Universitas Pembangunan Nasional "Veteran" Jawa Timur, Surabaya

*Corresponding author: rumokta@gmail.com

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Abstract

The problem in Indonesia of *Placuna Placenta* clam shell waste encouraged the development of this research. The aim was to determine the ratio of calcium (Ca) content to phosphorus (P) content in scallop shell waste using the H₃PO₄ addition precipitation method. The Ca content of scallop shell waste was 98.71%, still within the set quality standard of 95-98%. The international standard for Hydroxyapatite is the Ca/P atomic ratio of 1.61-1.76 mol/mol. Characterization included hydroxyapatite test, Scanning Electron Microscope-Energy Dispersive X-ray (SEM-EDX). The results showed that the volume of H₃PO₄ that approached the results of Hydroxyapatite was 2 ml at a stirring speed of 200 RPM with a pH of 12, resulting in a Ca/P ratio of 1.79 mol/mol with a final Ca content of 1.105 mol and a final P content of 0.617 mol. However, the addition of 10 ml of H₃PO₄ volume, Ca/P ratio of 1.60 mol/mol with a final Ca content of 0.985 mol and a final P content of 0.615 mol, resulted in the formation of hydroxide complexes such as [Ca₁₀(PO₄)₆(OH)₂]⁻ soluble in water, causing the weight of the precipitate to decrease even though the Ca content in the filtrate decreased. This study also found a relatively optimal precipitation time at a stirrer rotation speed of 300 RPM ensuring constant results. The resulting Ca₁₀(PO₄)₆(OH)₂ precipitate has the potential to be further utilized in various applications, such as bone formation, bone and dental implants, in the pharmaceutical field.

Keywords: shell waste *placuna placenta*, hydroxyapatite, natrium fosfat, sem-edx

Abstrak

Permasalahan limbah cangkang kerang (*Placuna Placenta*) di Indonesia mendorong pengembangan untuk penelitian ini. Bertujuan mengetahui rasio kadar kalsium (Ca) per kadar fosfor (P) dalam limbah cangkang kerang simping dengan metode presipitasi penambahan H₃PO₄. Limbah cangkang kerang simping kadar Ca sebesar 98,71 %, masih standar baku mutu yang ditetapkan sebesar 95-98 %. standar internasional Hydroxyapatite rasio atom Ca/P sebesar 1,61-1,76 mol/mol. Karakterisasi mencakup uji hydroxyapatite, *Scanning Electron Microscope-Energy Dispersive X-ray* (SEM-EDX). Hasil penelitian menunjukkan volume H₃PO₄ yang mendekati hasil dari Hydroxyapatite adalah pada 2 ml pada kecepatan putaran pengaduk 200 RPM dengan pH 12, menghasilkan rasio Ca/P sebesar 1,79 mol/mol dengan kadar Ca akhir sebesar 1,105 mol dan kadar P akhir sebesar 0,617 mol. Namun, penambahan volume H₃PO₄ 10 ml, rasio Ca/P sebesar 1,60 mol/mol dengan kadar Ca akhir sebesar 0,985 mol dan kadar P akhir sebesar 0,615 mol, terjadi pembentukan kompleks hidroksida seperti [Ca₁₀(PO₄)₆(OH)₂] larut dalam air, menyebabkan berat endapan berkurang meskipun kadar Ca dalam filtrat menurun. Penelitian ini juga menemukan waktu pengendapan relatif optimal pada kecepatan putaran pengaduk 300 RPM memastikan hasil yang konstan. Endapan Ca₁₀(PO₄)₆(OH)₂ dihasilkan memiliki potensi untuk dimanfaatkan lebih lanjut dalam berbagai aplikasi, seperti pembentukan tulang, implan tulang dan gigi, dalam bidang farmasi.

Kata Kunci: limbah cangkang kerang *placuna placenta*, hydroxyapatite, natrium fosfat, sem-edx

1. Introduction

Hydroxyapatite (HAp) is a synthetic material synthesized for bone and tooth repair purposes, especially in the pharmaceutical industry. HAp is a derivative of CaCO₃ and Ca₃PO₄ through a synthesis process producing a new structure [Ca₁₀(PO₄)₆(OH)₂]. In Indonesia, materials for dental and bone care, including HAp, still use imported materials from abroad, but Indonesia still has many materials that can be synthesized to produce Hap [1]. In a study [2] in 2023, the results of Hydroxyapatite calcium phosphate bioceramics with a stoichiometric ratio of Ca²⁺/PO₄ of 3-1.67, from the research, it was found that the peak temperature in HAp synthesis ranged from 30°C to 35°C indicating the presence of PO₄, OH, CO₃, and HPO₄ groups which are characteristic of HAp. Hydroxyapatite has high biocompatibility, bioactivity, non-toxicity, and is also able to improve the mechanical properties of scaffolds. In Sari's research [5] in 2022,

Hydroxyapatite results were obtained with Ca and P content of 59.09% and 40.91% with a Ca/P ratio of 1.44. Forming HAp is indicated by the observation of functional groups PO_4 , OH, CO_3 , and HPO_4 which are characteristic of HAp. Formed at peak temperatures of HAp synthesis ranging from 25° to 40° . In research [2] in 2023, different methods of adding phosphate during HAp synthesis obtained different final pHs. This is also influenced by the low rate of reaction equilibrium during synthesis. The solution was stirred at 250 RPM at 60°C for 1 hour. Stirring at 250 RPM was performed to produce polycrystalline HAp with uniform (homogeneous) ion mixing, to avoid the formation of monocrystalline HAp, which can affect the mechanical properties (compressive strength) of HAp.

The reason for choosing scallop shells as the material is easily available and relatively inexpensive, and contains a high calcium content for making Hydroxyapatite. The precipitation method is the process of converting a solution into a solid form by converting the substance into an insoluble form or making the solution saturated. Precipitation is the reaction between an acid and a base with a crystalline solid to form salt and water. This involves adding chemicals and then separating the precipitate from the solution [4].

In this study, it was found that several factors were influenced by several factors, including the addition of phosphoric acid volume and the influence of the stirring rate, which can affect the quality of Hydroxyapatite. Therefore, an experiment was conducted to synthesize Hydroxyapatite from scallop shell waste to understand the concept and its application in industry.

2. Research Methods

Preparation of Research Materials

The materials used in this study were 100 mesh scallop shell powder, distilled water, and phosphoric acid. Several other tools were used for observation, namely a thermometer and pH paper/pH meter. Other tools used in the study were a magnetic stirrer, 500 ml beaker glass, and aluminum foil as a cover.

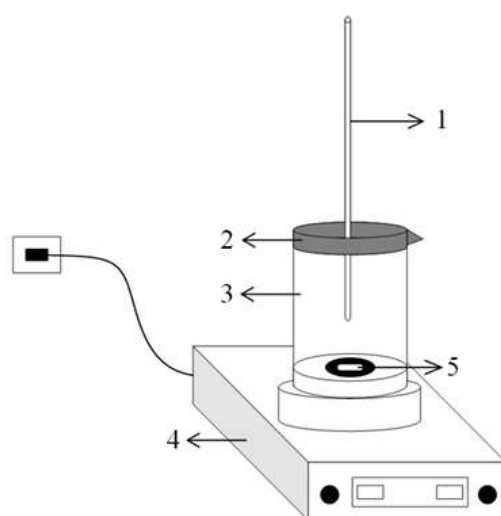


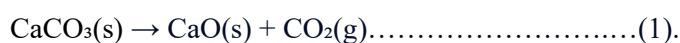
Figure 1. Research Tools Series

Description of the tool series: (1) Thermometer, (2) Aluminum Foil, (3) Beaker Glass, (4) Stirrer, (5) Magnetic. The size of the Beaker Glass is 500 ml.

Precipitation Process

Research Material Preparation 10 grams of HAp powder was transferred into a beaker and dissolved in 50 ml of distilled water. Then, the mixture was placed on a magnetic stirrer at the appropriate RPM and the addition of H_3PO_4 solvent at room temperature of 30°C for 30 minutes. After the mixture was allowed to stand, the sample was filtered and washed until the pH was 8-12. Afterward, it was dried in an oven at 100°C . After the oven, it was left overnight and then placed in a furnace at 850°C for 2 hours.

1. reactions in the calcination process



The calcium carbonate contained in the scallop shell is calcined to form calcium oxide and carbon dioxide [5].

2. Dissolution reaction with water



Calcium oxide from the calcination results is dissolved with water to control the pH, it will form calcium hydroxide [2].

3. Reaction in the synthesis of Hydroxyapatite by precipitation method



Calcium hydroxide dissolved with phosphoric acid will form Hydroxyapatite with water as a byproduct [9].

Analysis Method

First, the calcium (Ca) content of the Placuna placenta shells was analyzed using X-Ray Fluorescence (XRF) to meet HAP standards. Furthermore, a (SEM-EDX) test was conducted to determine the Ca/P content. This analysis was conducted to evaluate the effectiveness of the formation process and to determine any impact on product quality and quantity.

3. Results And Discussion

Initial HAP Composition

The research was conducted using scallop shell waste (Placuna Placenta) as raw material. The raw material of scallop shell waste (Placuna Placenta) was tested for calcium (Ca), copper (Cu), nickel (Ni), lead (Pb), silica (Si), and tin (Sn) content using the X-Ray Fluorescence (XRF) method. Based on the tests carried out, the results obtained are summarized in **Table 1**.

Table 1. Results of preliminary analysis of the content of raw materials

Compound	Level (%)
Ca	98,71
S	0,28
Fe	0,099
Cu	0,034
Sr	0,66
Lu	0,22

Source: Laboratorium Mineral dan Material Maju Universitas Negeri Malang (2025).

Based on **Table 1**, the results of the XRF test of raw materials that have been carried out, several levels were found in the scallop shell waste (Placuna Placenta) with Ca/P levels that are still below the Hydroxyapatite quality standard. Therefore, the Ca content in the scallop shell waste (Placuna Placenta) needs to be synthesized to obtain P levels using the precipitation method until it meets the Ca/P ratio standard for Hydroxyapatite, namely 1.67 [3].

The Effect of H₃PO₄ Volume and Stirring Speed on Product Weight

The effect of H₃PO₄ volume on product weight with variable Stirring Speed (200, 300, and 400 RPM). It is known that the highest average product weight at each sedimentation time is obtained on average of 10 grams. This shows that to achieve a good quality level of Hydroxyapatite, the resulting product weight is ±10 grams.

Table 2. Results and calculations of H₃PO₄ Volume and Stirring Rotation Speed Against Product Weight

Volume H ₃ PO ₄ (ml)	Stirring Speed (RPM)	Product Weight (gram)
2	200	10,2
	300	12,9
	400	10,4
4	200	11,6
	300	13,5
	400	10,3
6	200	10,8
	300	12,1
	400	10,7
8	200	10,8

Volume H ₃ PO ₄ (ml)	Stirring Speed (RPM)	Product Weight (gram)
10	300	11
	400	10,4
	200	7,8
	300	11,2
	400	9,2
	200	13,5

The largest result was obtained by adding 4 ml of H₃PO₄ volume with a stirring speed of 300 RPM of 13.5 grams. This shows that the effect of product weight on the Ca/P content ratio is not significant in **Table 2**, which shows the table of Ca/P content ratio. The addition of H₃PO₄ volume also affects the weight of the product obtained. This is in accordance with research conducted by [8].

There is a phenomenon that occurs in the process of adding the volume of H₃PO₄ which affects the weight of the resulting product. It is known that the average weight of the product at a volume of 2 ml of H₃PO₄ with a solution pH of 12 is lower than that of 4 ml of H₃PO₄ with a solution pH of 10. This can occur because at a pH above 10, Ca²⁺ ions will dissolve back into the solution due to unsuitable solution conditions [7]. This condition occurs because when too much base compound is added, a complex hydroxide compound will form. This compound is easily soluble in water, which ultimately increases the total solubility [8], so that the filterable precipitate will be reduced and the weight of the product obtained will be lower. With these results, it can be seen that the addition of an excessive volume of H₃PO₄ does not produce maximum precipitate.

The phenomenon that occurs during the stirring speed process affects the weight of the resulting product. For example, in a volume of 4 ml of H₃PO₄, the product weight at a stirring speed of 400 RPM was lower than at a stirring speed of 200 RPM. This can occur when HAp precipitates are formed, this compound is not completely stable. The precipitate is continuously in dynamic equilibrium with its ions. Ca²⁺ and PO₄⁻ ions on the surface of the precipitate can diffuse into the solution if their concentration in the solution is lower than on the surface of the precipitate. This process occurs slowly, because the HAp compound that has formed has exceeded the solubility limit so that by increasing the stirring speed, the originally formed compound can be re-dissolved. Another factor that can occur is the ineffective filtration process due to the limitations of the equipment used, so the filtration process takes a long time which causes the stirring speed so that the HAp precipitate dissolves again. This is also supported by the implementation of pre-laboratory, where a stirring speed of 300 RPM produces constant precipitate results. This indicates that the relatively optimal stirring speed occurs at 300 RPM.

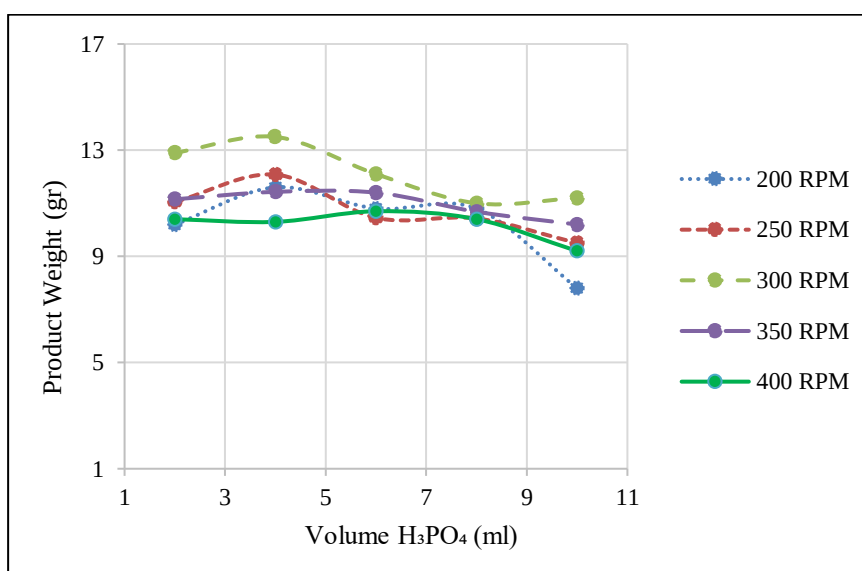


Figure 2. Relationship between H₃PO₄ Volume and Stirring Rotation Speed Against Product Weight

The Effect of H₃PO₄ Volume and Stirring Speed on the pH Conditions of the Solution Process

The effect of H₃PO₄ volume on the pH of the solution (2, 4, 6, 8, and 10 ml). Several variations in the pH of the Hydroxyapatite product solution are known. Based on the image above, the pH of the solution is 12, 10, 8, 6, and 4, respectively.

Table 3. Results and calculations of H_3PO_4 volume and stirring speed against pH conditions of the solution process

Volume H_3PO_4 (ml)	Stirring Speed (RPM)	pH of Solution
2	200	12
	300	
	400	
4	200	10
	300	
	400	
6	200	8
	300	
	400	
8	200	6
	300	
	400	
10	200	4
	300	
	400	

The addition of H_3PO_4 volume affects the weight of the product obtained and the pH changes that occur in the solution. It can be seen that the effect of H_3PO_4 volume on the pH of the solution is inversely proportional. The more volume of H_3PO_4 mixed, the smaller or acidic the pH will be. However, if it is too acidic, the product obtained will dissolve again so that the Hydroxyapatite precipitate product that will be obtained decreases as the pH of the solution decreases. According to [6], Hydroxyapatite compounds have an optimal pH for Ca precipitation between pH 9 and pH 10. This is in accordance with research conducted by [20] that most hydroxyapatite after reaching pH 10 forms a stable phase.

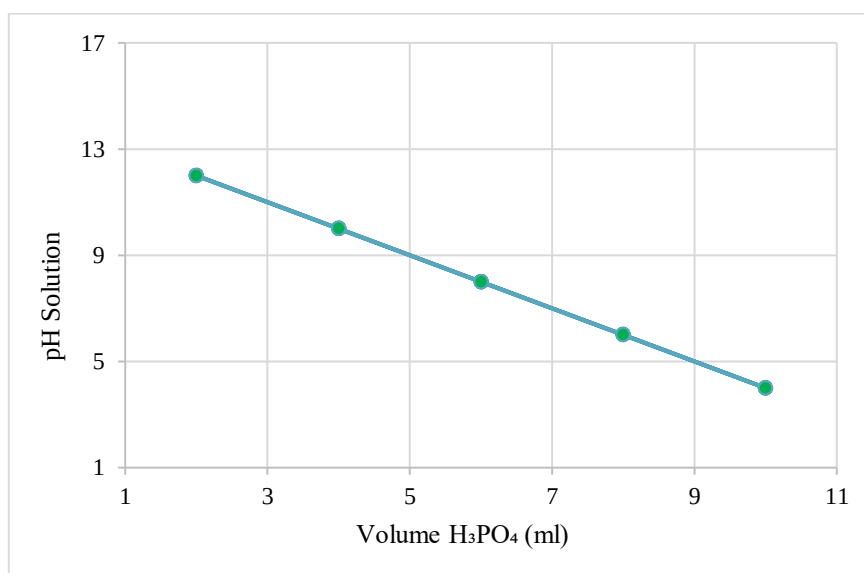


Figure 3. Relationship between H_3PO_4 Volume and Solution pH

Analysis of Filtrate Weight Percentage of Ca and P Content in Variables Using SEM-EDX Test

The results of the chemical composition levels of each Ca and P element were obtained with the stirring rotation speed (200, 300, and 400 RPM) at each additional volume of H_3PO_4 . Based on the image above, the relationship between stirring speed and the chemical composition of Ca and P elements at each additional volume of H_3PO_4 can be seen. The relationship between stirring rotation speed and the composition of Ca elements can be seen.

Table 4. Results of Filtrate Analysis of Percent Weight of Ca and P Content in Each Variable Using SEM-EDX

Volume H ₃ PO ₄ (ml)	Stirring Speed (RPM)	Level (%)	
		Ca	P
2	200	44,23	19,14
	300	47,25	10,64
	400	50,28	2,14
4	200	46,12	10,82
	300	49,55	5,85
	400	48,14	2,07
6	200	48	2,5
	300	51,85	1,06
	400	46	2
8	200	46,72	6,82
	300	47,12	8,75
	400	44,28	11,87
10	200	47,94	11,13
	300	42,26	16,43
	400	36,57	21,73

The faster the stirring rotation is carried out, the greater the composition of the Ca element that will be produced, however, at the stirring rotation point of 300 RPM the Ca element is obtained decreasing. A relationship was also obtained between the stirring rotation speed and the composition of the P element. The faster the stirring rotation is carried out, the smaller the composition of the P element that will be produced, however, at the stirring rotation point of 300 RPM the P element is obtained increasing.

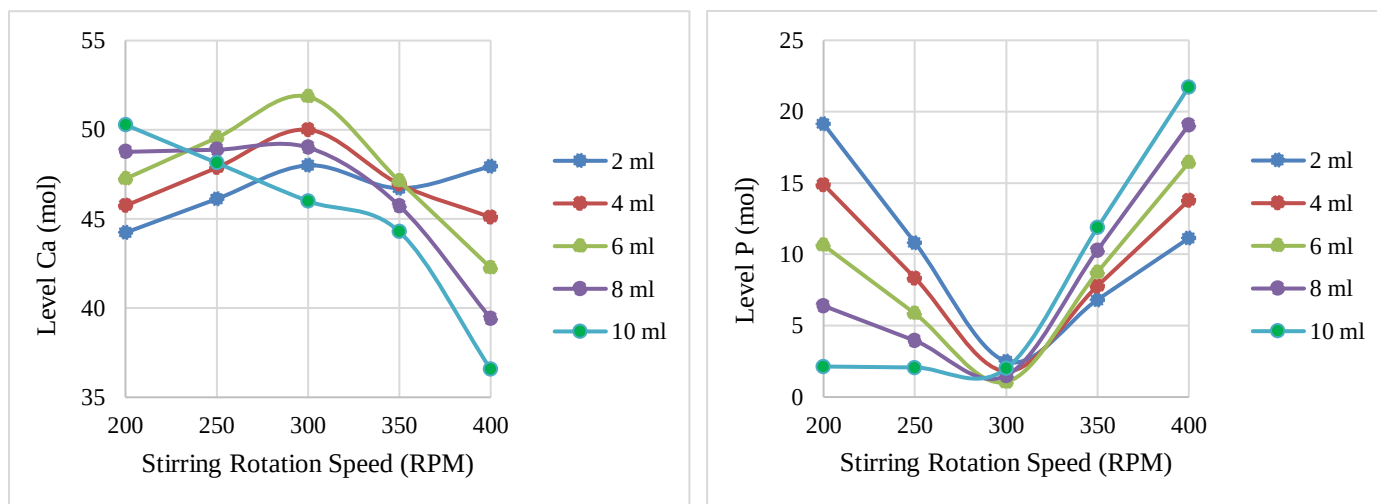


Figure 4. Relationship Between Stirring Speed and Chemical Composition of Ca and P

Results of the analysis of the calculation of Ca/P content in variables using the SEM-EDX test

The results of the Ca/P content obtained at the stirring rotation speed (200, 300, and 400 RPM) for each additional volume of H₃PO₄. Based on the table below, the Ca/P levels at 200 RPM were respectively 1.79 mol/mol; 3.3 mol/mol; 14.88 mol/mol; 5.3 mol/mol; and 3.33 mol/mol. at 300 RPM respectively 3.44 mol/mol; 6.56 mol/mol; 37.9 mol/mol; 4.17 mol/mol; and 1.99 mol/mol. at 400 RPM respectively 18.2 mol/mol; 18.02 mol/mol; 17.82 mol/mol; 2.89 mol/mol; and 1.3 mol/mol.

Table 5. Results of Filtrate Analysis Comparison of Ca/P Content Ratio in Each Variable Using SEM-EDX

Volume H ₃ PO ₄ (ml)	Stirring Speed (RPM)	Level Ratio Ca/P (mol/mol)
2	200	1,79
	300	3,44
	400	18,2
4	200	3,3
	300	6,56
	400	18,02
6	200	14,88
	300	37,9
	400	17,82
8	200	5,3
	300	4,17
	400	2,89
10	200	3,33
	300	1,99
	400	1,3

In the image below, it can be seen that the effect of the stirring rotation speed on the Ca/P content ratio is up and down. The faster the stirring rotation produced, the greater the Ca/P content obtained, however, at the 300 RPM stirring rotation point the Ca/P content ratio obtained decreases. After SEM-EDX analysis testing was carried out, the best, middle, and final products were obtained. The best product that approaches the Ca/P content ratio of Hydroxyapatite itself which is around 1.67 is at the 200 RPM point with the addition of 2 ml of H₃PO₄ volume. The middle product is at the 300 RPM point with the addition of 6 ml of H₃PO₄ volume. Meanwhile, the final product is at the 400 RPM point with the addition of 10 ml of H₃PO₄ volume. The following is the composition of the structure of the best, middle, and final products.

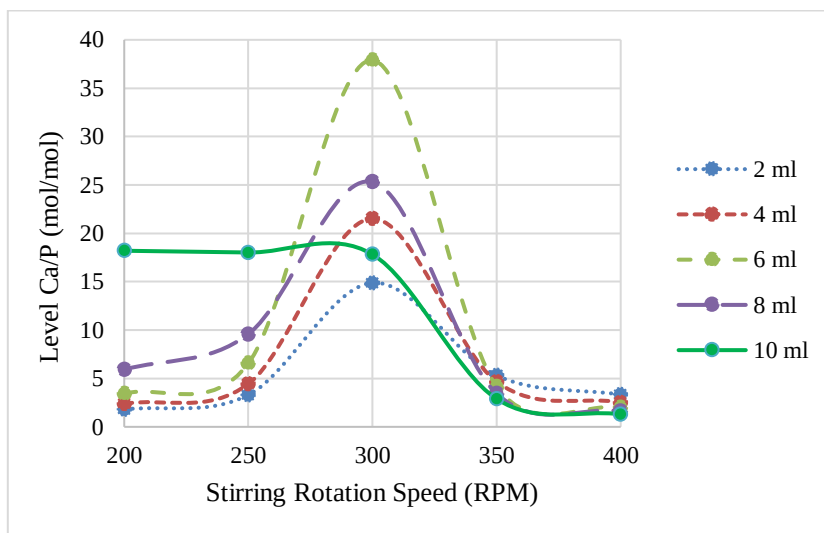


Figure 5. The Effect of H₃PO₄ Volume and Stirring Speed on Ca/P Content

Table 5. Elemental composition obtained from SEM-EDX analysis.

Element	Weight %	Atomic %	Error %
O K	36.62	57.07	10.26
P K	19.14	15.41	3.99
CaK	44.23	27.52	4.32

Source: Laboratorium Mineral dan Material Maju Universitas Pembangunan Nasional (2025)

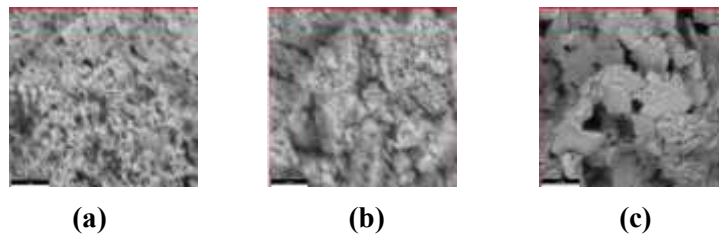


Figure 6. The results of the SEM morphological analysis are presented in Figure 4. Scanning Electron Microscopy (SEM) images of the hydroxyapatite at 3000x (a), 200 RPM & 2 ml (b) 300 RPM & 6 ml (c) 400 RPM & 10 ml

Based on the image above, it can be seen that the structure of each Hydroxyapatite point, as described, the powder is used for SEM characteristic testing, consists of small particles formed irregularly, some of which are bound together like aggregates. The higher the sintering temperature used, the larger and more fused the particles become. This is consistent with the study conducted by [6], which states that the SEM method is used to observe the surface details of cells or the microscopic structure of Hydroxyapatite and has the capability to render the observation of objects in 3D. Viewed from SEM, it shows small, fine, grain-shaped crystals approximately 0.6 μm in size, with a pore spacing of around 1 μm .

4. Conclusion

The average weight of the hydroxyapatite product obtained with varying volumes of phosphoric acid: 2, 4, 6, 8, and 10 ml and stirring speeds of 200, 300, and 400 rpm was 10 grams, using 10 grams of clam shell powder as the raw material. This indicates that clam shells are capable of producing good-quality hydroxyapatite, with a product weight of approximately 10 grams.

The more phosphoric acid added, the lower the pH of the solution. The initial pH of the clam shell $\text{Ca}(\text{OH})_2$ solution was 14 and decreased with the addition of phosphoric acid in volumes of 2, 4, 6, 8, and 10 ml. Experiments showed that the precipitated product began to thicken at a solution pH of 8-10. If the product is too acidic, it will dissolve again, thereby reducing the yield of the hydroxyapatite precipitate obtained. The Ca/P ratio (mol/mol) ranged from 1.3 to 37.9, and the results of the study showed that the most optimal conditions for production close to Hydroxyapatite, a Ca/P ratio of 1.79 mol/mol was obtained at a stirring speed of 200 RPM and a volume of phosphoric acid addition of 2 ml.

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