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Synthesis of Biomaterial-Grade Whitlockite from Crab Shell Waste: An Eco-friendly Approach

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Abstract

Crab shells, rich in calcium carbonate ($CaCO_3$), provide a sustainable source of calcium oxide (CaO) for synthesizing Whitlockite (WH, $Ca_9(MgFe)(PO_4)_6PO_3H$), a potential biomaterial for bone replacement. This study addresses prior research gaps by exploring synthesis temperature variations from 700℃ to 1000℃ and employing acid precipitation to yield high-purity WH. Characterization was performed using Fourier Transform Infrared (FT-IR), X-ray Diffraction (XRD), X-ray fluorescence (XRF), Scanning Electron Microscopy (SEM), and Brunauer Emmet-Teller (BET) analysis. Results indicate that the crab shell powder contains 99.0944%wt. The XRD results show that optimal crystallinity and purity of WH were achieved at a calcination temperature of 900℃. The FTIR test results show that the functional groups of WH at calcination temperatures of 700℃, 800℃, 900℃, and 1000℃ for 5 hours are detected in specific wave ranges, namely PO_4^{3-} (673-671 cm^{-1}), and OH^- (3340-3198 cm^{-1}), which contribute to the bone formation process. SEM tests revealed that changes in calcination temperature affected the morphology of WH, with the optimal temperature producing a smaller size, minimal agglomeration, and a more uniform size distribution. BET analysis showed that 900℃ gave the highest adsorption capacity and good stability, indicating a more significant potential for interaction with body cells. These findings confirm the ability of WH to be a promising biomaterial for bone replacement applications.

Introduction

Crab, known by the scientific name *Scylla olivacea* herbst, is a source of animal protein full of essential nutrients such as vitamins, minerals, and healthy fats. The benefits of crab after consumption include maintaining bone health, heart health and increasing immunity [1]. The

Ministry of Maritime Affairs and Fisheries (KKP) noted that crab production in Indonesia reached 58,106.54 tons in 2021, of which 4849.88 tons of crabs were produced in East Kalimantan [2]. Crab is a typical commodity of Balikpapan City, which is the center of business and industry, so crab is one of the foods that attract tourists. Crab consumption positively impacts health, but inadequate management of crab shell waste may lead to harmful environmental consequences. Crab shell waste management can reduce the potential for environmental pollution and can increase its added value. Along with the increase in crab shell waste, there is a need for innovations in its processing. Crab shells can usually be processed into a mixture of animal feed, water purification, and essential ingredients for cosmetics. Crab contains 32.95% protein, 10.89% crude fiber, 22.93% calcium, and 0.78% phosphorus [3]. Crab shells are rich in calcium carbonate ($CaCO_3$). The $CaCO_3$ content in crab shells reaches 40–70% [4]. Due to the presence of $CaCO_3$, crab shells are utilized as a source of whitlockite (WH, $Ca_9(MgFe)(PO_4)_6PO_3H$). Whitlockite in crabs is an interesting material for further development because it is a source of calcium and phosphate. During calcination, the high $CaCO_3$ content can be converted into CaO, which can be further used to synthesize Whitlockite (WH). This enables the utilization of crab shells into WH as an alternative biomaterial to bone substitute.

Calcium carbonate, with the molecular formula $CaCO_3$, is the simplest mineral containing no silicon and one of the primary sources of commercial calcium compounds [5]. Meanwhile, Whitlockite (WH) is a calcium phosphate mineral represented by the chemical formula $Ca_9(MgFe)(PO_4)_6PO_3H$). Whitlockite is often found in lunar samples and meteorites but is also present in terrestrial environments, especially in igneous and metamorphic rocks. Due to its bioactive properties, this mineral has been widely studied in materials science and biomedical applications, particularly in bone tissue engineering [2]. The performance of Whitlockite (WH) in bone engineering demonstrates significant advantages over traditional materials such as hydroxyapatite (HAp) and β-tricalcium phosphate (β-TCP). Whitlockite's unique properties, including its magnesium content and mechanical strength, enhance its osteoconductivity and biocompatibility. Magnesium ions significantly affect the crystallization process, with varying Mg^{2+} concentrations influencing the structural properties of Whitlockite [6]. This is also mentioned in the research [7] WH showed superior compressive strength compared to HAp and β-TCP, with research showing that WH maintains higher volumetric stability and mechanical integrity than in research [8-9] it is known that Whitlockite promotes osteoblast differentiation and mineralization more effectively than HAp and β-TCP, as evidenced by increased alkaline phosphatase activity in cell studies.

Whitlockite (WH), a biomineral that self-assembles hierarchically, is the second most abundant biomineral found in the natural bone at the nanoscale. Its size and shape primarily influence its properties at this scale. However, achieving a single-phase synthesis of WH is a complex process, as it is sensitive to variations in pH and temperature. Research has demonstrated that new bone regenerative minerals, including whitlockite, can be formed with different shapes and sizes using a single-solvent approach [10]. Based on the above explanation, research will be conducted on synthesizing and characterizing Whitlockite (WH) in crab shells using the acid precipitation method. The source of calcium used in this research is calcium found in crab shells.

The calcination process is essential in this research, where the object is heated to a high temperature but still below the melting point to remove volatile components [11]. The calcination process produces nanoparticles, which can be characterized through several methods, such as X-ray diffractometer (XRD) and Scanning Electron Microscopy (SEM). This

study used several characterization techniques to analyze the resulting material. Fourier Transformed Infrared (FTIR) serves to detect functional groups and identify compounds, while X-ray diffraction (XRD) helps identify the crystalline phase and particle size of nanocrystals [12]. Scanning Electron Microscope (SEM) is used to observe the surface of solids with magnification up to 12,000 times. In addition, the Brunauer-Emmett-Teller (BET) technique is also applied to determine the specific surface area of porous substances (Irwansyah et al.). Previous research by Adinda Kholif Mahera explored calcination temperatures of 800℃, 900℃, and 1000℃ [13]. Another study examined calcination temperatures of 700℃, 800℃, and 900℃ [14], while this study used temperatures of 700℃ to 1000℃ for 5 hours each. In this research, the temperature of 700℃ to 1000℃ for 5 hours each is used because the research is expected to make a significant contribution to the understanding of calcination and the properties of the material produced; the use of temperature variations can also provide comparative data that is useful for understanding trends and changes that occur at lower and higher temperatures.

Using crab shell waste as a whitlockite (WH) source represents an innovative and sustainable approach for high-value applications, particularly as a promising biomaterial for bone tissue engineering. Crab shells, 40-70% calcium carbonate ($CaCO_3$), can be converted to calcium oxide (CaO) during calcination and serve as an essential precursor for WH synthesis. Replacement of iron (Fe) and magnesium (Mg) in its structure improves its mechanical properties and biocompatibility compared to hydroxyapatite (HAp), which makes it beneficial for bone regeneration applications. This study examines a controlled calcination process at temperatures ranging from 700°C to 1000°C for 5 hours, providing deeper insight into the material's properties and allowing comparative analysis across temperature variations. Advanced characterization techniques such as XRD, SEM, FTIR, and BET are employed to analyze the material's structural, morphological, and surface properties to ensure comprehensive understanding. Additionally, using an acid precipitation method for synthesizing Whitlockite demonstrates a scalable and efficient approach to producing high-quality WH nanoparticles. These findings highlight the bioactive properties of Whitlockite, positioning it as a valuable alternative biomaterial for bone substitute applications while simultaneously addressing environmental concerns by converting crab shell waste into a resource of high scientific and industrial relevance.

Experimental Method

The wet precipitation method is a commonly used technique for the synthesis of whitlockite by mixing a solution of calcium and phosphate ions under certain pH conditions, followed by calcination at 700−1000°C to maximize crystal growth and phase stability. The temperature range is 700−1000°C was chosen because, below 800°C, the crystallization is imperfect, so the amorphous phase or hydroxyapatite is dominant. While above 900°C, the thermal stability of whitlockite is disrupted, and the tricalcium phosphate (TCP) phase may develop [15]. In this synthesis, 4.6731 g of CaO was used for each sample calcined at different temperatures and then tested by XRD to analyze the crystal structure, XRF for chemical composition, FTIR for functional group identification, BET to measure the specific surface area, and SEM to study the morphology and particle size, ensuring the optimization of high-grade whitlockite synthesis.

The experimental approach employed in this research is presented in diagram form in Figure 1:

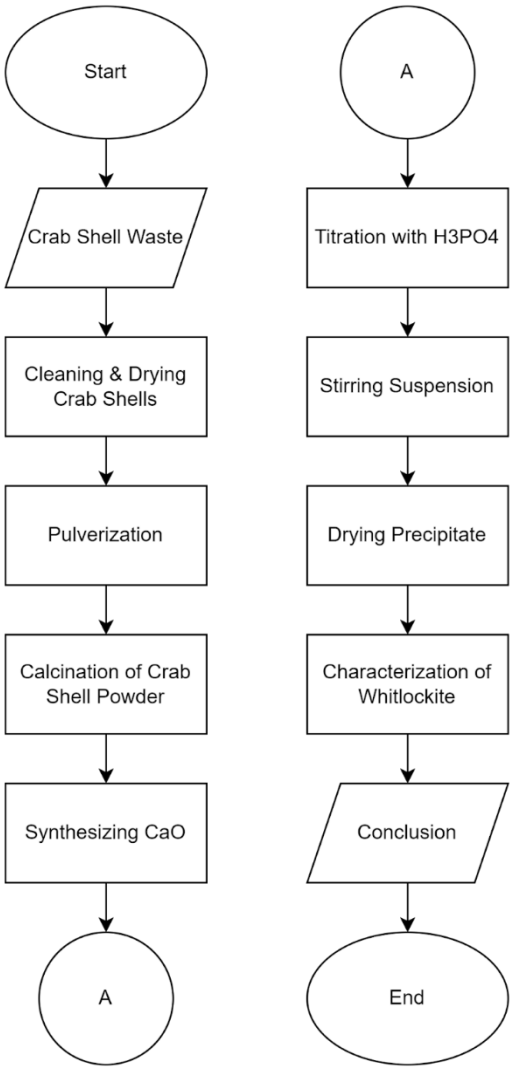

Figure 1. Diagram Experimental Method

In this study, crab shells were washed with water and brushed thoroughly, then dried in the sun until dry. After drying, the crab shells were pulverized using a mortar and pestle blender and sieved using a 200-mesh sieve. The crab shell powder weighed as much as 15 grams and was calcined in a furnace at 1000°C for 15 hours. The calcination temperature of 1000°C is considered optimal for manufacturing Whitlockite due to its influence on phase stability and structural integrity. Research indicates that at this temperature, the formation of β-$Ca_3(PO_4)_2$ is maximized, significantly substituting magnesium for calcium, enhancing the material's properties. The calcined powder was transferred to a desiccator and weighed for constant mass.

Whitlockite (WH) synthesis was done by dissolving 4.6731 grams of CaO powder in 50 ml of distilled water at 90°C for 1 hour with a stirring speed of 250 rpm. H_3PO_4 0.05 M solution of 100 ml was titrated at a rate of 4 ml/min at 80°C, and the reaction process was kept constant

during stirring. Then, the suspension was stirred for 24 hours at 100°C with a stirring speed of 500 rpm, forming a white precipitate. Next, the precipitate was dried using a dehydrator at 80°C for 10 hours.

After hydroxyapatite was formed, the samples were characterized using four instruments, namely Fourier Transform Infrared (FTIR), X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Brunauer Emmet-Teller (BET).

The data were collected at the Integrated Laboratory of the Kalimantan Institute of Technology. XRD data was collected using a Bruker D8 Advance X-Ray Diffraction instrument with a diffraction angle (2θ) of 5° - 120°, step size 0.020/s, and operating conditions of 40 kV and 30 mA using a monochromatic CuKα radiation source (λ = 1.54056Å). The test data was analyzed qualitatively and quantitatively. Qualitative analysis was carried out using the Match! application to identify the angles on the diffraction peaks and the size of the crystal plane. Quantitative analysis using Rietica software using the Rietveld method. The Rietveld method is a refinement method for material characterization that provides information on various aspects of the crystal in the sample. The method aims to determine the lattice parameters and phase composition by matching the diffractogram with the database. In addition, MAUD analysis was carried out to obtain the sample crystal size. SEM data was collected using a Phenom ProX Desktop Scanning Electron Microscope instrument. However, the sample will be coated before being inserted into the SEM tool. The purpose of coating the sample is to increase the electrical conductivity sample. SEM utilizes high-energy electrons; therefore, non-conductive samples such as HAp will cause electrons to gather on the surface and create image distortion; coatings will increase the resolution of the resulting image. BET characterization aims to determine the specific surface area and porosity through gas adsorption, such as nitrogen. BET data was collected using the NOVAtouch LX2 instrument. The characterization process was carried out by degassing the sample at 100°C for 1 hour. After degassing, the tube was transferred to the analysis port on the SEM instrument. The characterization data was analyzed quantitatively using Micromeritics Software to generate surface area and pore size parameters. After that, the OriginPro application was also used to produce BET data visualization. FTIR data were collected for the 500 to 4000 cm-1 wavenumbers using Bruker Vertex7.0v FTIR spectrometer to characterize the interatomic bonding states through the vibration spectra. In situ, measurements were performed in the air to analyze the phase evolution of the 400 °C pre-calcined sample by raising the temperature by 10 °C/min up to 700 °C. The temperature was kept constant for 1 s during the XAS measurement. XRF data was collected using a Horiba X-ray fluorescence (XRF) instrument with operating specifications with a maximum voltage of 50 kV and a maximum current of 0.2 mA. In addition, the filter diameters of 1.2 mm, 3 mm, and 7 mm increase the analysis's flexibility and accuracy.

Results and Discussion

The content of $CaCO_3$ compounds owned by crab shells is very high. Figure 1 shows the data obtained from qualitative analysis using Match!4 software, finding peaks that indicate the presence of $CaCO_3$ in crab shells. The highest peak analysis result of $CaCO_3$ is at an angle of 2θ 29.65°, which has an h k l (1 0 4) plane structure. This diffraction peak refers to COD No. 4502443. Compounds that have crab shells contain a single phase of $CaCO_3$ as much as 100%. $CaCO_3$ is formed as a calcite phase, with trigonal crystal shape (hexagonal axes), space group R-3 c (167), and has lattice parameters a = 4.97577 Å and c = 16.99207 Å.

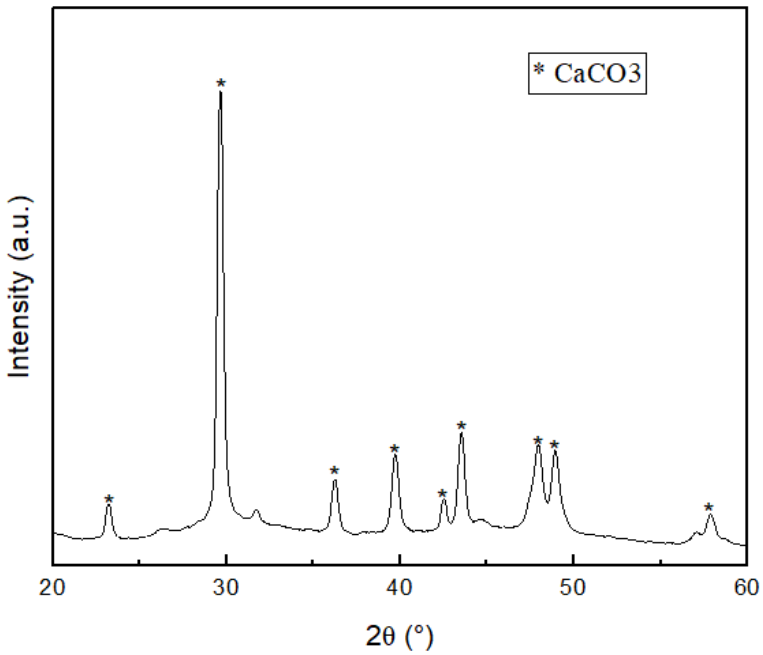

Figure 2. X-ray Diffraction Pattern of Crab Shell Powder

The XRD results in this study showed a typical diffraction pattern of $CaCO_3$, with high-intensity peaks at 2θ angles of about 29.65°, which were confirmed as calcite phase. These peaks indicate that the sample has a predominantly stable crystal structure. Compared to the XRD graph of $CaCO_3$ from the study [13] using eggshells as a calcium source for the preparation of Hydroxyapatite (HAp), there is a difference in the relative intensity of the main peak, where this study shows a lower intensity at 29.44°. This difference may be due to the difference in raw materials and Mn impurities in the crab shell powder with a concentration of 0.3%, as shown by the following XRF characterization data. Table 1 shows the results of quantitative XRF characterization by showing the values contained in the crab shell powder.

Table 1. Elemental Composition of Crab Shell Powder

No	Elements	Concentrate (wt%)
1	Ca	99.0944
2	Mn	0.3365
3	etc.	0.5746

The results showed that the Ca content in crab shell powder has the highest concentration of 99.0944 wt% compared to other elements. The presence of manganese (Mn) as an impurity in calcium carbonate ($CaCO_3$) can significantly influence the formation and properties of whitlockite. Studies show that varying manganese content changes calcium phosphate's phase composition and structural characteristics, including whitlockite. A study by [16] states that manganese content affects whitlockite formation in calcium phosphate. At 0.15 wt% of manganese, whitlockite was 90 wt%, but at 1.49 wt%, it decreased to 70 wt%, showing the significant impact of manganese. In this study, crab shells were used as a source of calcium

WH by utilizing the $CaCO_3$ phase. The $CaCO_3$ phase can be further processed into WH through the calcination process to convert it into the CaO phase.

WH synthesis requires CaO compound powder as a calcium precursor. The following equation can represent the decomposition of CaCO3 into CaO:

$$CaCO_3(s)\ CaO(s) + CO_2(g)$$

XRD analysis was employed to determine the crystalline phases present in the CaO powder. This is important to ensure that the samples used conform to the desired specifications and to understand the material's crystalline composition. The XRD pattern of CaO synthesis from crab shells with calcination temperature treatment of 1000°C for 15 hours is shown in Figure 3. The peaks on the graph show a very high level of CaO purity. The analysis results of the highest peak of CaO is at an angle of 2θ 37.35 °, which has an hkl (2 0 0) plane structure.

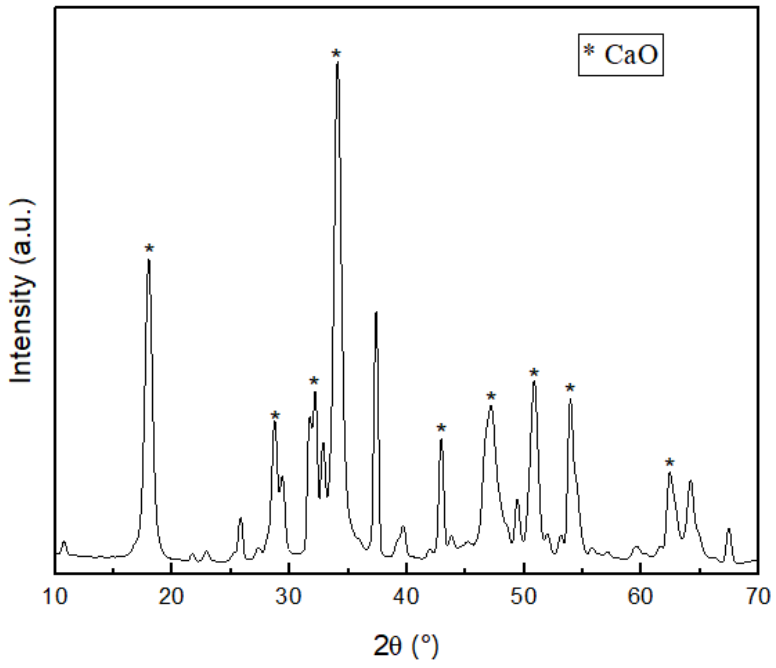

Figure 3. XRD Graph of CaO Powder

This diffraction peak refers to COD No. 1011095. The compound with crab shells contains a single phase of CaO as much as 100%. CaO formed in the form of lime phase, with cubic crystal form, space group F m -3 m (225), and has a lattice parameter a = 4.80500

In this study, the method used for the synthesis is the precipitation method or wet deposition, which is an acid and base reaction that produces crystalline precipitates and water. The powder produced from the procedure was calcined with four different temperature variations, 700°C, 800°C, 900°C, and 1000°C, each for a duration of 5 hours

The results of XRD analysis of samples that have been calcined with temperature variations show a hexagonal crystal structure that is very similar to Hydroxyapatite (HAp), which is distorted due to the presence of magnesium (Mg) and iron (Fe).

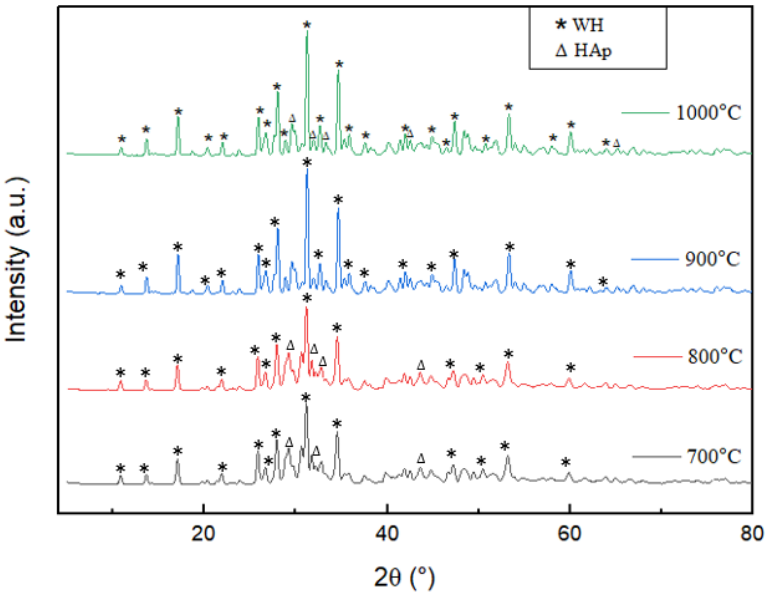

Figure 4. Graphics XRD WH

Figure 4 shows the X-ray diffraction pattern at 700−1000 ℃ for 5 hours. The WH phase is seen to fill the peaks in the sample. The highest peaks are at 2θ angle 31.14 (700℃), 31.16 (800℃), 31.24 (900℃), and 31.2 (1000℃) which has an h k l (1 0 1) plane structure, which were confirmed as WH phase. The crystal compound was identified as Whitlockite (WH) in this case. Based on [10], a group of researchers studied how pH levels impact the stability of ceramic particles and noted that the zeta potential of Whitlockite is highest at low pH values. So, the XRD analysis results for WH powder are compared with the WH COD (Crystallography Open Database) database No. 9012136. Figure 4 illustrates the X-ray diffraction patterns of WH powder calcined at temperatures of 700°C, 800°C, 900°C, and 1000°C for a period of 5 hours. Table 2 below displays the phase composition of all samples.

Table 2. Phase Composition of WH Powder at Temperature

Calcination 700°C, 800°C, 900°C and 1000°C for 5 hours

Sample	Phase Composition (%wt)	
	WH	Other Mixed Phases
WH5-700	92.7	7.3
WH5-800	93.2	6.8
WH5-900	100	-
WH5-1000	97.3	2.7

Whitlockite has a chemical composition that can be written as $Ca_9(MgFe)(PO_4)_6PO_3OH$. From the calculation results, it can be concluded that the quantity and ratio of magnesium (Mg) and calcium (Ca) ions significantly affect the stability and characteristics of this phase. The synthesis of pure whitlockite is challenging, requiring precise control of parameters like pH, temperature, and precursor ratios [10, 17]. Whitlockite is often found at high temperatures or under certain pH conditions, and its composition shows relatively high thermodynamic stability.

The phase composition results above show that the WH compound formed is very dominating. At 900° C, the purity level of the WH sample reaches the maximum level. From X-ray diffraction (XRD) calculations or chemical composition analysis, if the Whitlockite phase dominates, this suggests that synthesis parameters, including temperature and pressure, promote the development of this crystal structure. In biomaterial research, the presence of Whitlockite is often desirable due to its properties that favor integration with biological tissues. This shows that calcination temperature is vital in the formation of WH.

Residual phases usually consist of hydroxyapatite ($Ca_5(PO_4)_3OH$), amorphous calcium phosphate, or even other phases such as tricalcium phosphate (TCP). These phases often appear due to synthesis conditions that do not fully favor the formation of pure Whitlockite or as intermediate products before transformation into Whitlockite.

From the compositional calculations, the dominance of the Whitlockite phase indicates success in achieving conditions that favor the formation of thermodynamically stable materials. However, residual phases, especially hydroxyapatite and amorphous phases, need further attention, depending on the final application of the material. Modifying factors like temperature, reaction time, or the composition of the precursors can further achieve optimization.

Examination of the functional groups in Whitlockite (WH) powder was performed using the FTIR test with a wavelength of 3500 cm^{-1}–500 cm^{-1} against powder WH. FTIR characterization identifies WH powder with calcination temperature variation treatment 700℃, 800℃, 900℃, and 1000℃ for 5 hours. Table 3 shows the presence of functional groups in all samples. The functional groups identified in WH powder, namely OH^-, PO_4^{3-}, CO_3^{2-}.

Table 3. WH Functional Groups at Calcination Temperature 700℃, 800℃, 900℃, 1000℃ for 5 hours

Function Group	Wave Numbers (cm^{-1})
PO_4^{3-}	671-669
OH^-	3340-3198

The functional groups observed in the WH sample are the groups of OH^- at wave numbers around 3340 cm^{-1}– 3198 cm^{-1} [18]. The presence of OH^- indicates the presence of adsorbed water [19]. Based on the FTIR data, it can be seen that the main functional groups possessed

by WH come from their phosphate structure. The FTIR absorption pattern of the WH sample can be seen in Figure 5.

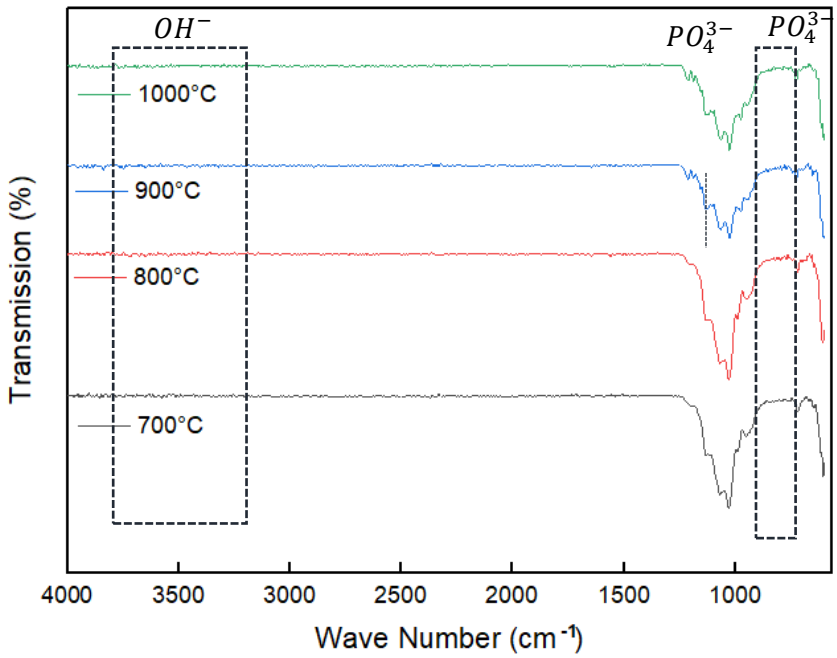

Figure 5. FTIR Absorption Pattern

BET test is an adsorbent characterization test that aims to determine the size of the adsorbent surface area and its pores. The BET analysis results for all WH samples are presented in Figures 6–9 below. Table 4 displays the surface area, pore volume, and diameter values from the nitrogen adsorption-desorption isotherms. WH samples calcined with a temperature of 700°C have a surface area of 8.09101 m^2/g, and at temperatures 800°C and 900°C decreased in the area to 6.58737 m^2/g and 0.828934 m^2/g, it shows a significant decrease in area, but after passing the temperature where the purity level of WH reaches 100% which is 900°C, the area increases again to 1.26043 m^2/g. This happens because increasing the calcination temperature causes a reduction in the number of pores due to the closure of open pores, which results in closed pores [20]. This proves that the size of pores, the surface area, and the volume of the pores can be regulated by modifying the calcination temperature.

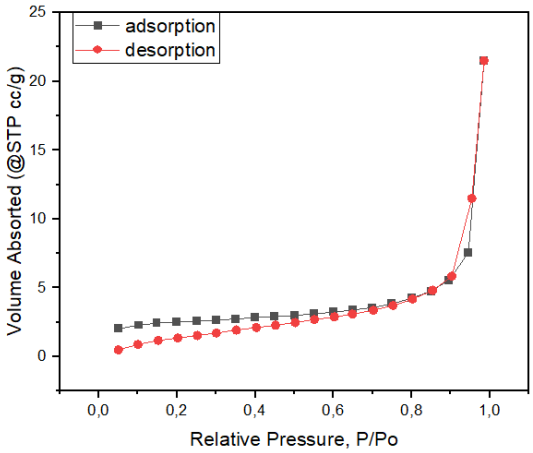

Figure 6 Analysis BET WH for calcination temperature 700℃

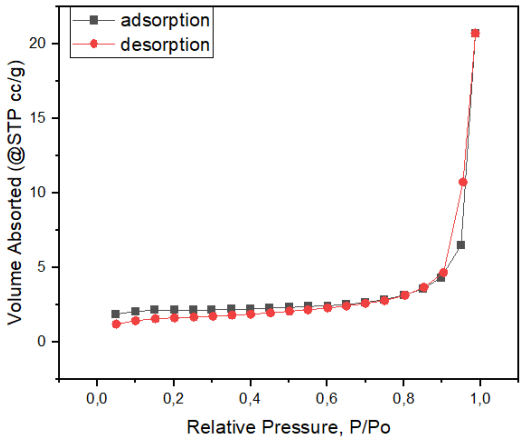

Figure 7 Analysis BET WH for calcination temperature 800℃

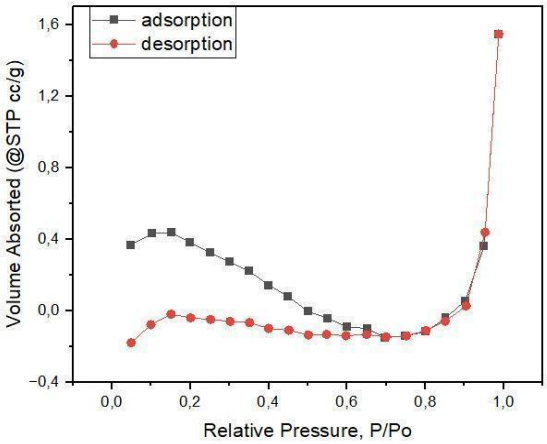

Figure 8 Analysis BET WH for calcination temperature 900℃

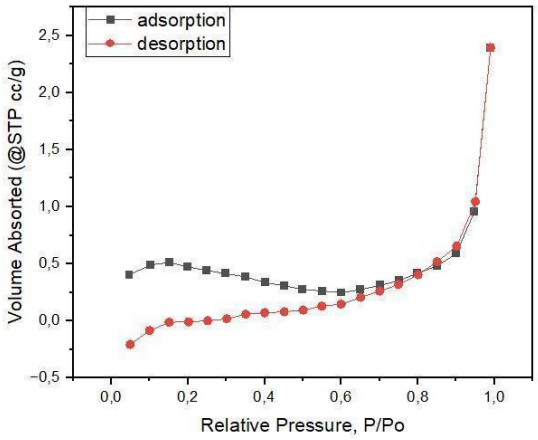

Figure 9 Analysis BET WH for calcination temperature 1000℃

Table 4. Results of Surface Structure Characterization

Sample	Surface Area (m^2/g)	Pore Volume (cc/g)	Pore Diameter (nm)
WH-700	8.09101	$3.3366e^{-2}$	8.2477
WH-800	6.58737	$3.2151e^{-2}$	9.7615
WH-900	0.82893	$2.3994e^{-3}$	5.7892
WH-1000	1.26043	$3.7141e^{-3}$	5.8934

According to the characteristics of adsorption isotherms, the International Union of Pure and Applied Chemistry (IUPAC) categorizes eight distinct types of adsorptions [21]. The isotherm curve from sample testing shows a type IVa isotherm in the BET classification attributed to mesoporous solids (2–50 nm). The IUPAC classification for type IVa isotherm curves is characterized by a sharp increase indicating capillary condensation at high P/P0, usually accompanied by a hysteresis circle characteristic of mesopores. The pore diameter size indicates this at WH 700°C of 8.2477 nm, WH 800°C of 9.7615 nm while at WH 900°C of 5.7892 nm, and WH 1000°C samples obtained 5.8934 nm. The pore diameter value possessed by all samples corresponds to the average pore diameter, which is in the range of mesoporous materials (2-50 nm) [22]. These data show that the high-purity WH often forms larger, well-crystallized particles, which may reduce surface area and pore volume.

BET analysis is used to characterize the surface area and porosity of biomaterials. Whitlockite is one of the calcium phosphate minerals frequently found in the human body, particularly in bones and teeth. This makes it very attractive for biomedical applications, especially in biomaterials for bone regeneration, implants, and tissue engineering. The results of the BET analysis of Whitlockite can provide important information that affects the material's properties and performance in biomedical applications. To improve the quality, material durability, and osseointegration function of implants, the design focuses not only on the type of material used but also on the structure of the implant surface [23]. In biomedical applications, the larger the surface area, the greater the area available for interaction with cells, proteins, or ions in the biological environment. In bone implant materials, a large surface area allows for better cell attachment and accelerates osseointegration (bonding between bone and implant). Mesoporous materials have also attracted considerable interest in biomedical applications because of their distinctive properties. These materials offer high surface area, porosity, and controllable pore sizes, making them excellent candidates for drug delivery systems [24, 25]. The study by [26, 27] mentioned that a high surface area in bioceramics increased osteoconductivity, facilitating faster bone growth. In contrast, decreased pore surface area of bioceramics may limit cell and tissue growth, potentially reducing the effectiveness of the scaffold in promoting bone regeneration. However, narrower pores may prevent soft tissue calcification, making the scaffolds more suitable for biomedical applications. Not only that, Whitlockite, with its high porosity and good pore distribution, is ideal for nutrient exchange, cell penetration, and accelerated bone regeneration, making it suitable as a bone graft or scaffold material. BET analysis measures the adsorption ability of gases, which can be linked to the material's ability to bind essential ions in biomedical applications. BET helps understand the capacity of Whitlockite surfaces to bind and release ions in a targeted manner within the body, which can control the growth of new bone and avoid too rapid degradation of the material. These studies demonstrate the importance of BET analysis in optimizing biomaterial properties for specific biomedical applications.

As outlined below, SEM analysis was performed to examine the material's surface morphology and microstructure.

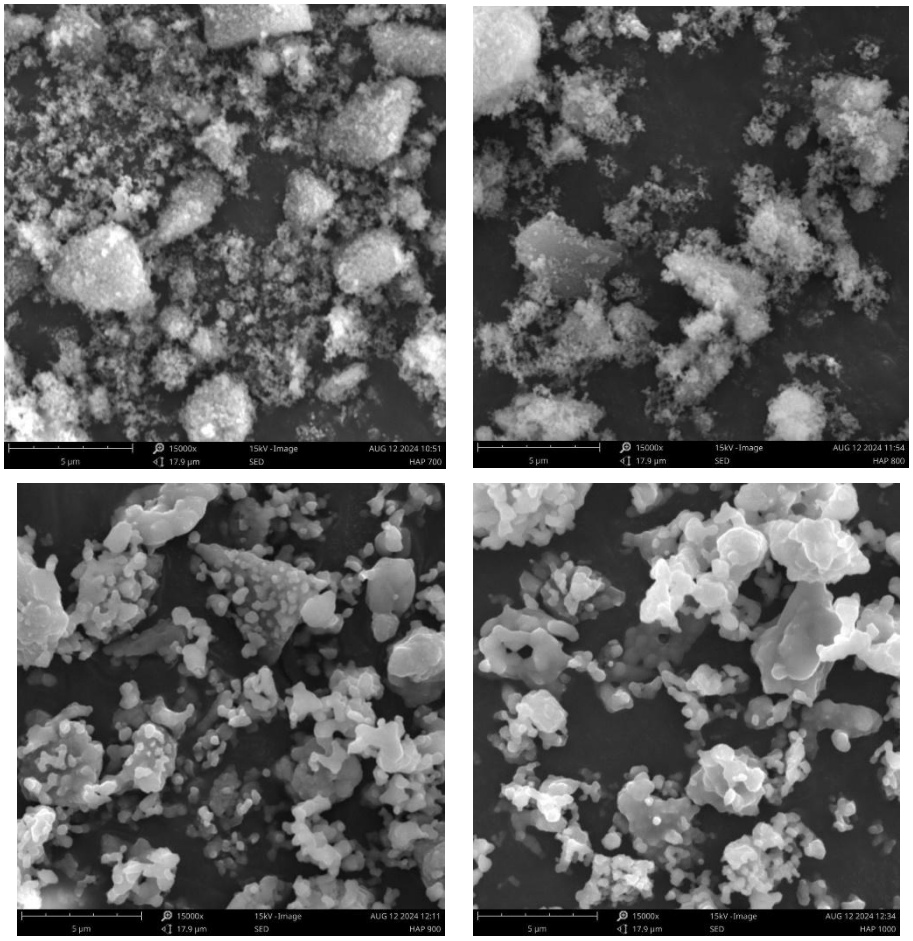

Figure 10. SEM test results on Whitlockite samples at temperatures of 700°C – 1000°C with magnification 15000 times.

The results of Scanning Electron Microscopy (SEM) characterization of Whitlockite samples calcined at temperature variations of 700°C, 800°C, 900°C, and 1000°C show significant morphological changes. At a calcination temperature of 700°C, Whitlockite particles appear to have an irregular shape with a relatively small size and rough surface. When the temperature increases to 800°C, there is a reduction in particle size. At 900°C and 1000°C, the Whitlockite particles show a more regular shape with smoother edges, larger size, minimal agglomeration, and a more uniform size distribution. These morphological changes indicate that increasing the calcination temperature affects the Whitlockite samples' recrystallization process and grain growth.

Maintaining a constant temperature during calcination can be challenging and crucial for successfully synthesizing Whitlockite (WH). Variability in temperature can arise from factors such as non-uniform heat distribution in the furnace, fluctuations in power supply, or inaccuracies in temperature control systems. These variations may lead to uneven heating of the sample, causing partial decomposition or incomplete phase transitions, which can affect the purity and crystallinity of the WH. For instance, temperatures below the optimal range may result in residual precursor materials or secondary phases like hydroxyapatite or

tricalcium phosphate. Conversely, exceeding the target temperature can promote grain growth, reduce surface area, and potentially introduce structural defects. Such inconsistencies can impact WH's reproducibility and desired properties, including its biocompatibility and mechanical strength. Addressing these challenges requires precise temperature monitoring, ensuring proper insulation and calibration of the furnace, and using a controlled heating rate to achieve uniform thermal conditions throughout the sample.

This research can contribute to biomedical development and sustainable utilization of bio-waste. Some previous studies discussing the utilization of biological waste, especially in coastal areas, were conducted by [28, 29], who utilized Sargassum sp. and Kappaphycopsis cottonii, which are usually rejected by industry into bio-oil through the pyrolysis process. Research on bio-oil production from Sargassum sp. and Kappaphycopsis cottonii and whitlockite synthesis from crab shell waste have in common the utilization of biological resources and organic waste to produce value-added products. In bio-oil research, macroalgae biomass is processed through pyrolysis to produce renewable liquid fuel, providing a solution to fossil energy dependence while reducing algae waste accumulation in coastal environments. Meanwhile, whitlockite synthesis utilizes calcium carbonate-rich crab shell waste to produce calcium phosphate materials with high potential as bone implants in biomedical applications.

Both studies demonstrate the importance of a sustainability-based approach in managing waste and natural resources. The technologies used in converting biomass to bioenergy and transforming fishery waste into functional materials illustrate the integration of chemistry, biology, and materials technology. With a focus on environmental solutions and innovative product development, both studies contribute to sustainable energy, health, and environmentally friendly materials development.

Conclusion

Whitlockite (WH) can be synthesized from calcium precursors derived from crab shells and phosphoric acid under acidic conditions, with the optimal calcination temperature for high-purity WH determined to be 900°C based on XRD characterization. This temperature yields WH with excellent crystallinity, smaller particle sizes, minimal agglomeration, and uniform distribution, as confirmed by SEM and BET analyses, indicating superior adsorption capacity and stability, enhancing its potential for bone replacement applications. Functional groups essential for bone formation, such as PO_4^{3-} and OH^-, were identified via FTIR, while XRF confirmed the calcium content of the crab shell powder. Despite its promise, challenges include potential ectopic ossification, energy-intensive synthesis, and biocompatibility testing, such as cytotoxicity, osteointegration, and in-vivo studies, to ensure clinical safety and effectiveness. Scalability from abundant natural sources like crab shells offers industrial promise, but cost-efficient optimization of the calcination process remains crucial.

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