MALAYSIAN JOURNAL OF MICROSCOPY

Journal homepage: https://malaysianjournalofmicroscopy.org

RESEARCH ARTICLE

VARIATION IN CALCINATION TEMPERATURE OF COCKLE SHELL-DERIVED CALCIUM OXIDE FOR BIOMEDICAL APPLICATIONS

Nursyazwani Zulkefli[1,*], Eliza M. Yusup[1], Zulkefli Daud[2], Muhd Syahmie Sufi Abd Shukor[1]

[1]Faculty of Mechanical and Manufacturing Engineering, Universiti Tun Hussein Onn Malaysia, 86400 Parit Raja, Johor, Malaysia.
[2]Institut Pendidikan Guru Kampus Temenggong Ibrahim, 80350 Johor Bahru, Johor, Malaysia.

Abstract. Cockle shells are abundantly thrown alongside the beach, contaminating the environment with their smelly surroundings. The waste is collected and chemically derived into a material that could be useful for biomedical applications. Cockle shells contained 95-99 % by weight of $CaCO_3$, which enables the $CaCO_3$ to serve as a precursor to produce calcium oxide (CaO), primarily intended for biomedical applications. The $CaCO_3$ powder was subjected to the calcination process at temperatures of 800 °C, 850 °C and 900 °C, resulting in the conversion to CaO. The choice of these calcination temperatures was determined to be suitable for producing CaO powder for biomedical use. A notable correlation was noted between the structural characteristics of calcined CaO and the calcination temperatures. The scanning electron microscope (SEM) analysis shows that all calcined cockle shells have smooth surfaces and irregular shape particles. Fourier transform infrared spectroscopy (FTIR) analysis verifies the appearance of absorption band at a wavenumber of 711 cm^{-1} indicating the presence of CaO. Energy dispersive x-ray (EDX) spectroscopy result showed the compositional outcome are Ca and O at all temperatures after calcination. Specifically, cockle shells calcined at 900 ˚C exhibited a greater quantity of CaO compared to those calcined at 800 ˚C and 850 ˚C. Hence, 900 ˚C appears to represent the optimal calcination temperature for cockle shells. This study will not only contribute to the effective utilization of a valuable waste resource of cockle shells that can be found in Malaysia but also offer insights into the suitability of the chosen calcination temperatures for the intended biomedical applications.

Keywords: Cockle shells, calcium carbonate, calcium oxide, biomedical.

Article Info

Received 10 January 2024
Accepted 16 November 2024
Published 6 December 2024

***Corresponding author: syazazulkefli29@gmail.com**

ISSN: 1823-7010, eISSN: 2600-7444

1. INTRODUCTION

Recent advances in material science have focused on utilizing biomaterials to design tissue-engineered materials that can aid in restoring damaged tissues. Various studies have been conducted in the field of bone tissue engineering to formulate bone grafts, pastes, and scaffolds to promote bone regeneration [1]. For optimal regeneration, a biomaterial used in bone tissue engineering should possess a degradation rate that is similar to the regeneration rate of the bone. This is important to ensure that the biomaterial is not degraded too quickly, which can compromise the structural integrity of the scaffold, or too slowly, which can impede the regeneration process [2].

Calcium carbonate ($CaCO_3$) has gained popularity as a potential biomaterial for bone tissue regeneration only in recent years. Despite its abundance in nature and potential biocompatibility, the use of $CaCO_3$ in bone tissue engineering is still relatively new and requires further investigation to fully understand its properties and potential applications [3]. With the current focus of interest in nanotechnology, $CaCO_3$ can be easily converted into nanoparticles that have been observed to be biocompatible for use in medicine, pharmaceutical industries, and drug delivery systems. The unique properties of $CaCO_3$ nanoparticles, including their high surface area-to-volume ratio and biodegradability, make them ideal candidates for a range of biomedical applications [4].

Calcium oxide (CaO), a compound of paramount importance in various industries, is traditionally derived from limestone. However, a groundbreaking and sustainable approach has emerged, exploring the extraction of CaO from an unexpected source - cockle shells [5]. Recent years have seen extensive studies on the thermal decomposition of $CaCO_3$. Given that cockle shells are easily available in Malaysia, there exists great potential to exploit them as raw materials in CaO production. This innovative method not only taps into the rich $CaCO_3$ content of these marine mollusks exoskeleton but also holds promising implications for biomedical applications [6].

Research by Li et al. [7] highlights the superior CaO content in seashells compared to the limestone used in their study. Cockles, a class of bivalve molluscs, are valued at over 32 million USD and are often considered waste [8]. Furthermore, Malaysia adheres to Mazhab Shafi'i which emphasizes that impurities present in non-halal products, even if they are for medical applications, are persistent [9]. This includes animals that are permissible for consumption, such as bovine, if they are not slaughtered following Islamic law, there is a compulsory requirement regarding the issue of halal products to cater for the needs of Muslims around the world [9], which the main concern of this research.

Cockle shells have a high percentage of $CaCO_3$, ranging from 95-99 % by weight which makes it useful for various purposes [6]. The process of thermal decomposition, also known as calcination, can convert $CaCO_3$ into CaO which is widely used in industries and daily practices, including sewage treatment and wastewater, construction material, glass production, agriculture, and more [10]. Moreover, CaO is widely used as a base material for absorbing carbon dioxide (CO_2). While existing technologies for CO_2 adsorbents such as amine-based adsorbents, activated carbon, and molecular sieves can only withstand low-temperature processes (40 °C - 160 °C), limestone and dolomite can resist high-temperature processes (500 °C – 1000 °C) and can be regenerated and sustained for several CO_2 adsorption and calcination cycles [11].

Calcination is a process that involves three complicated factors. These factors are the concentration of CO_2, sizes of the particle, and impurities. The process of calcination is known to favour high temperature as it is an endothermic reaction and requires a low decomposition pressure of $CaCO_3$ to drive the equilibrium reaction forward, as mentioned by the authors [11].

According to previous studies, atmospheric pressure can be achieved when the calcination temperature reaches 800 °C to 900 °C [11]. Previous researcher also suggested that particle size resistance can be avoided by using sample sizes in the millimeter or micrometer range [11]. It is important to note that the extent of the particle size effect is uncertain and also depends on the calcination conditions such as temperature, calcination atmosphere and flow rate [12]. The objective of this study is to effectively utilize cockle shells, a valuable waste resource prevalent in Malaysia, by using the calcination process to produce high-quality calcium oxide for biomedical applications. This research not only addresses environmental concerns related to waste disposal but also provides insights into the suitability of selected calcination temperatures for enhancing the potential of CaO in biomedical applications.

2. MATERIALS AND METHODS

2.1 Materials

Cockle shells were obtained from local seafood restaurants near Pantai Sungai Lurus located at Senggarang, Batu Pahat, Johor, Malaysia.

2.2 Production of $CaCO_3$ to CaO

The work began with the extraction of $CaCO_3$ from the cockle shells. Cockle shells were cleaned, rinsed and left to dry overnight at room temperature. Dried cockle shells were crushed using a crushing machine until chip form was obtained. Chipped shells were loaded into a planetary ball mill to produce a fine powder of $CaCO_3$ at 300 rpm [13]. $CaCO_3$ powder was sieved at 100 µm as shown in Figure 1.

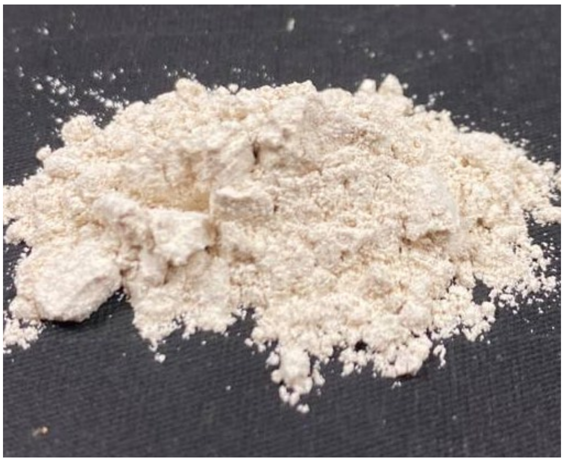

Figure 1: $CaCO_3$ fine powder 100 µm as sieved

$CaCO_3$ powder was calcined at a temperature of 800 °C, 850 °C and 900 °C with a heating rate of 10 °C min^{-1} for 120 minutes before it was cooled using the furnace natural cooling rate to produce calcium oxide (CaO) as shown in Figure 2.

Figure 2: Calcined powder of CaO

2.3 Characterizations

2.3.1 Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray (EDX) Analysis

SEM analysis is a technique used to examine the surface morphology and composition of materials at high magnifications and resolutions. The surface morphology of the cockle shells was visualized using SEM. Before the analysis, samples were coated with gold using a sputter coater JOEL JFC-1600 from Japan to obtain good-quality SEM images. The surface morphology of the powder sample was observed on SEM operated under a low vacuum at an accelerating voltage of 15 kV. The SEM equipment used was JEOL JSM-7600F from Japan and equipped with an energy dispersive X-ray (EDX). EDX analysis provides valuable information about the chemical composition, distribution, and sometimes the concentration of elements within the sample.

2.3.2 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

FTIR analysis is an analytical technique for identifying organic, polymeric, and inorganic materials. Chemical analyses were carried out using a Fourier transform infrared (FTIR) spectrophotometer (Model 100 series, Perkin Elmer) in the range of 400 – 4000 cm^{-1}. To analyse CaO powder derived from cockle shells calcined at different temperatures, first ensure the sample area is cleaned with distilled water to prevent data contamination. Next, prepare the samples and configure the scanning apparatus. During the scanning process, apply controlled pressure to enhance the frequency response. This equipment will facilitate the identification of chemical bond vibrations and generate distinct frequency patterns in the resulting graph.

3. RESULTS AND DISCUSSION

The microstructure analysis of material imposed on $CaCO_3$ and CaO was implemented based on the reason that the microstructure of an element can strongly influence the material's physical properties in terms of its strength, toughness, hardness, and other properties [14]. The calcination process involves the thermal decomposition of $CaCO_3$, resulting in the release of carbon dioxide (CO_2) and the transformation of $CaCO_3$ into CaO. The purity of the produced CaO is influenced by the calcination temperature. Higher temperatures may contribute to the removal of impurities and enhance the reactivity of the resulting CaO, impacting its suitability for specific applications.

3.1 Microstructural Analysis of the Sample

The cockle shell $CaCO_3$ powder is non-conductive, so SEM images were captured in low vacuum mode to achieve sharp resolution. Figure 3(a) illustrates the morphology of $CaCO_3$ extracted from cockle shells, while Figure 3(b) depicts the $CaCO_3$ extracted from cockle shells by Hoque et al. [6]. In both figures, blue arrows indicate the presence of cube-like crystals, which are characteristic of calcite. These cube-like crystals are also a feature associated with aragonite found in the extracted $CaCO_3$. The crystalline forms of $CaCO_3$ generally include calcite, aragonite, and vaterite.

Both calcite and aragonite have distinct crystal development processes and crystal shapes. Analysing the crystal structure reveals that the nucleation process for calcite is more difficult than aragonite [15]. It is also worth noting that cube-like crystals are fundamentally more stable than rod-like crystals. Because of their greater stability, cube-like crystals were chosen especially for bone regeneration applications [16]. Cockle shells are naturally purified source of aragonite polymorphs of $CaCO_3$. However, by applying high temperatures, the most aragonite polymorph converts to calcite, which is thermodynamically most stable [17]. The morphology of calcined CaO powder from cockle shells at three different temperatures of 800 °C, 850 °C and 900 °C was examined by SEM as shown in Figure 4, which illustrates the surface characteristics of the calcined CaO, revealing smooth surfaces with an irregular appearance. Some particles were found to agglomerate, forming larger aggregates.

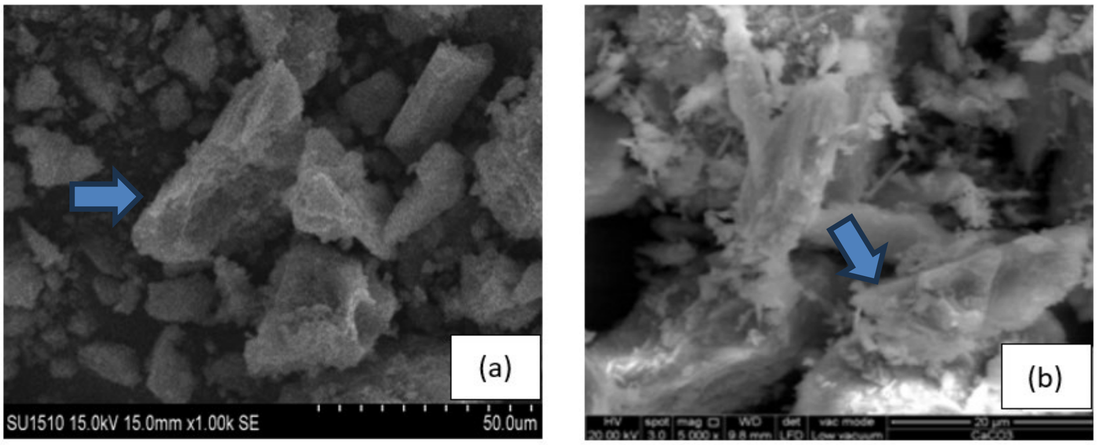

Figure 3: SEM analysis of (a) extracted cockle shells $CaCO_3$ and (b) $CaCO_3$ powder by Hoque et al. [6]

Upon comparing our findings with prior research [18], it becomes evident that the morphological characteristics of the CaO powder derived from cockle shells exhibit similarities to natural shell structure of cockle shell which is characterised by a typical layered architecture. However, when the calcination temperature is raised within the range of 800 ℃ to 900 ℃, there is a marked transformation in the microstructure of the cockle shell, transitioning from a layered architecture to a porous structure [19]. The resulting calcined cockle shells exhibited irregular shapes, with some particles formed into aggregates. At a higher calcination temperature of 900 ˚C, the surface showed smoother and more uniform surfaces confirming the thermal decomposition process in alignment with the observations made by Nordin et al, [18].

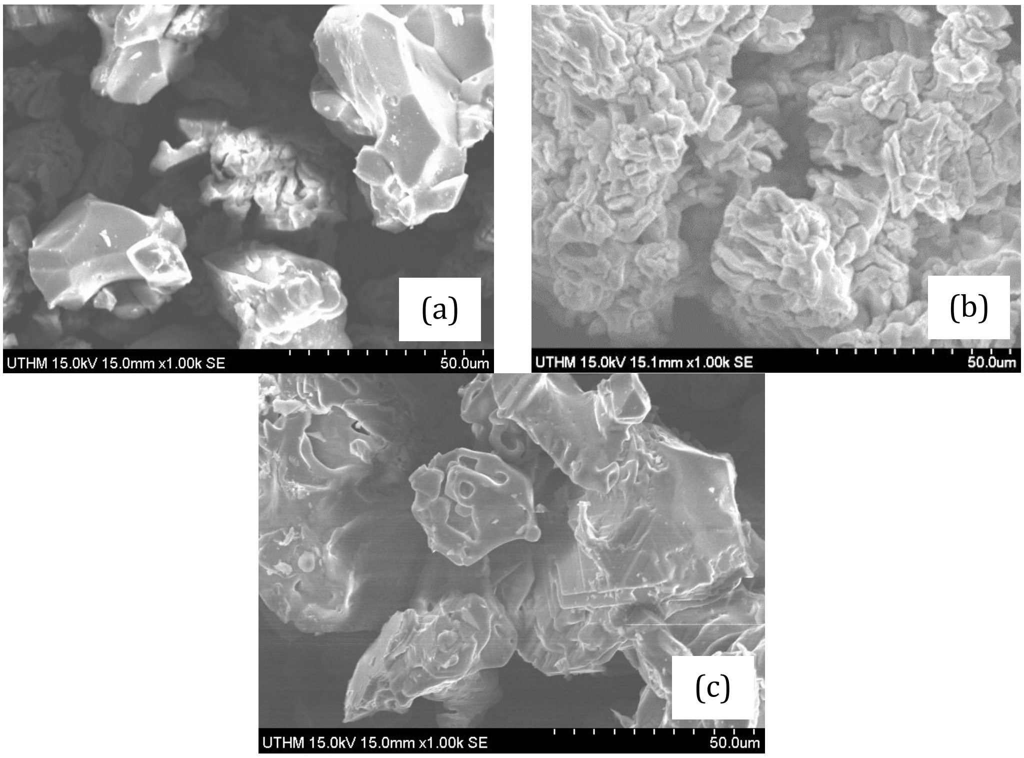

Figure 4: Calcined CaO powder at temperatures of (a) 800, (b) 850 and (b) 900 °C

3.2 Elemental Properties of $CaCO_3$ and CaO

The EDX spectrum obtained from the analysis of test samples of $CaCO_3$, as depicted in Figure 5(a), revealed the presence of calcium (Ca) as the highest peak, followed by carbon (C) and oxygen (O) in the atomic weight. This finding is consistent with the previous research conducted by Hoque et al. [6], where $CaCO_3$ powder contains Ca content, as shown in Figure 5(b). The elemental content of both Ca and O indicates that the sample is a compound of $CaCO_3$ aragonite, a biogenic polymorph of $CaCO_3$ naturally found in cockle shells [13].

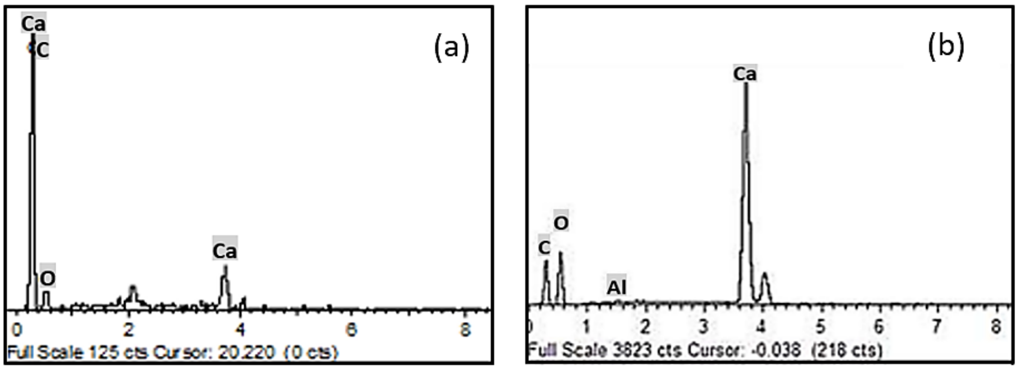

Figure 5: EDX of $CaCO_3$ (a) extracted cockle shells, (b) $CaCO_3$ of previous research [6]

Table 1 shows the weight percentages of the elemental contents of cockle shell $CaCO_3$ powder. The table was tabulated from the results determined by EDX, which shows the weight percentages of the elemental contents of $CaCO_3$ powder compared with previous research work [6]. It can be deduced that the cockle shell $CaCO_3$ powder has a higher percentage of Ca (26.09 wt.%) as compared to the $CaCO_3$ powder by Hoque et al. [6] (18.63 %). The weight percentage of C and O calculated in the cockle shells $CaCO_3$ powder was 20.68 % and 53.23 % respectively, whereas in previous study, the percentage of C and O was 26.84 % and 54.36 %.

Table 1: EDX results for weight percentage of cockle shells $CaCO_3$ powder compared with previous study [20]

Powder	Carbon, C (%)	Oxygen, O (%)	Calcium, Ca (%)	Aluminium, Al (%)	Total (%)
Extracted cockle shells $CaCO_3$ powder	20.68	53.23	26.09	-	100
Previous research [20]	26.84	54.36	18.63	0.17	100

EDX results indicated the presence of $CaCO_3$, but its proportion changed following calcination. The calcination process was maintained for 2 hours at each temperature level to ensure complete decomposition. As a result of calcination, the amount of Ca increased, while the weight percent of C decreased. Figure 6 shows that the CaO powder contains a high content of Ca and O at different calcination temperatures of a) 800 °C, (b) 850 °C and (c) 900 °C.

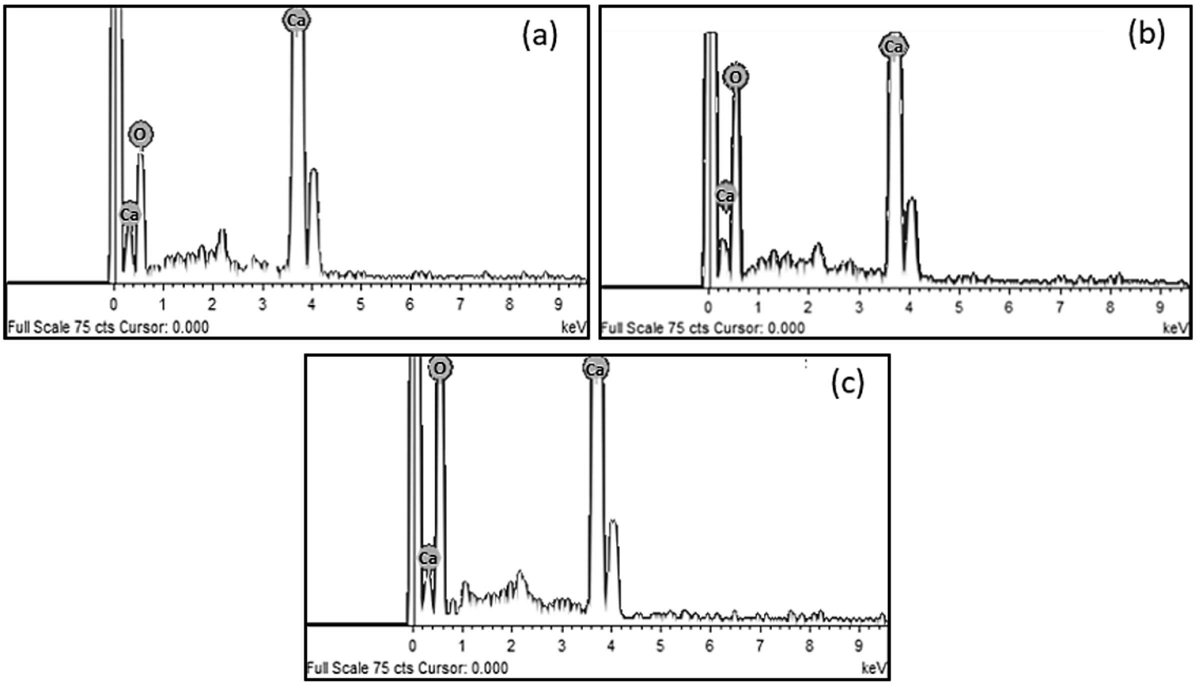

Figure 6: EDX analysis for CaO at temperature; (a) 800 °C, (b) 850 °C and (c) 900 °C

Table 2 shows the weight percentages of the elemental contents of CaO powder. The table was tabulated from the results determined by EDX, which shows the weight percentages of the elemental contents of CaO powder of different calcination temperatures. It can be deduced that the CaO powder calcined at 900 °C has a highest percentage of Ca (61.80 %) as compared to CaO powder calcined at 850 °C (54.43 %) and 800 °C (48.42 %). The weight percentage of O in the CaO powder calcined at 800 °C has a highest percentage of O (51.58 %) as compared to CaO powder calcined at 850 °C (45.57 %) and 900 °C (38.20 %).

Table 2: EDX results for weight percentage of CaO powder after different calcination temperatures

Calcination Temperature (°C)	Oxygen, O (%)	Calcium, Ca (%)	Total (%)
800°C	51.58	48.42	100
850°C	45.57	54.43	100
900°C	38.20	61.80	100

Based on Table 2, higher calcination temperature promotes higher calcination rate as this will increase the particles kinetic energy and consequently, accelerates decomposition of $CaCO_3$ to CaO. However, a very high calcination temperature may lead to sintering and attrition effects [21]. Therefore, 900 ˚C seems to be an optimum temperature for the calcination of cockle shells as it is shown to have the highest value of Ca content compared to the other temperatures.

3.3 Functional Group of $CaCO_3$ and CaO

Based on the FTIR analysis depicted in Figure 7, the spectrum showed the wave number of 1448 cm^{-1}, which can be attributed to O-H group characteristics, and wave number 858 cm^{-1} belongs to the C-O vibration in the carbonate functional group of $CaCO_3$. Additionally, the wave number 712 cm^{-1} shows the presence of Ca-O band in the powder. These findings provide valuable insight into the composition of the extracted cockle shells $CaCO_3$ powder.

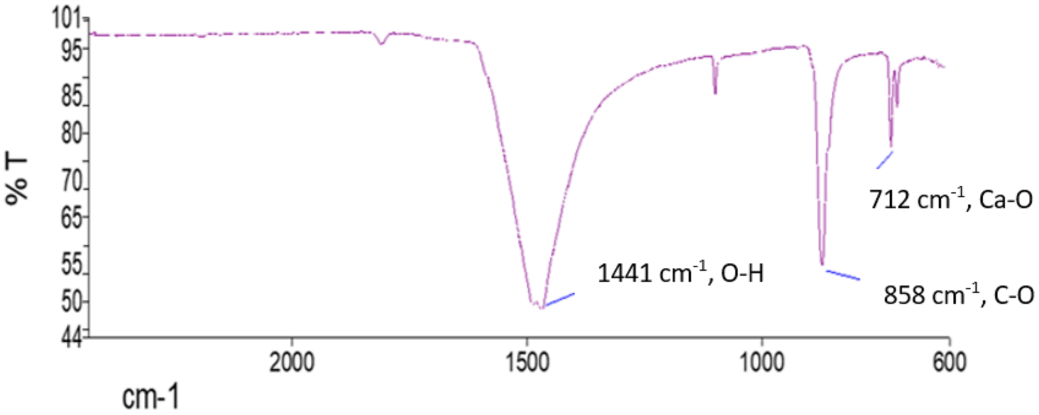

Figure 7: FTIR analysis spectrum of extracted cockle shells $CaCO_3$ powder

The IR spectrum of extracted cockle shells show the absorption band change and sharp peak appearing. In contrast, the peaks are widened after calcination. The temperature variation was sufficient to affect the IR spectrum results, shown by the widening of the spectrum peaks by the increasing of the calcination temperature [10]. This indication is pointing that $CaCO_3$ has changed into CaO due to the heating process.

Figure 8 displays the peaks observed in the FTIR spectrum of CaO at different calcination temperatures. Samples calcined at 800 °C and 850 °C exhibit a peak at a wavenumber of 1404 cm^{-1}, while the sample calcined at 900 °C shows a peak at 1405 cm^{-1}, indicating the presence of the O-H group absorption band. The detection of CaO is confirmed by the appearance of a peak at a wavenumber of 711 cm^{-1} for the samples at 800 °C and 850 °C, whereas the sample at 900 °C presents a wavenumber of 712 cm^{-1}. Additionally, absorption peaks between 871 cm^{-1} and 873 cm^{-1} are observed for all samples calcined at 800 °C, 850 °C, and 900 °C, indicating the presence of a C-O band from calcite following the calcination process. The FTIR results suggest that increasing the calcination temperature results in only minor changes to the IR spectrum values.

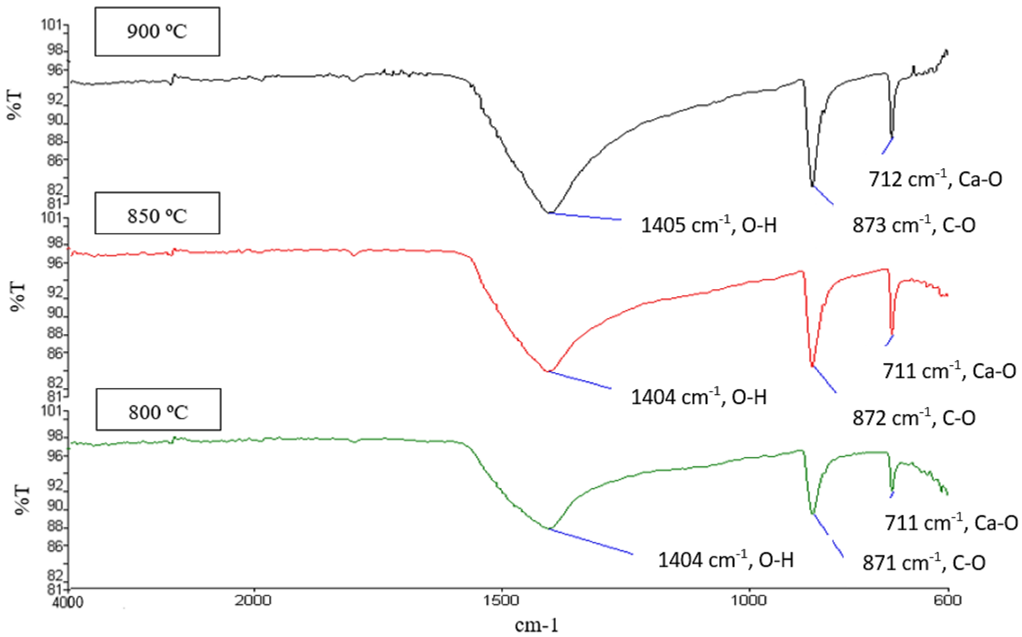

Figure 8: FTIR analysis for CaO at temperature; (a) 800 °C (b) 850 °C and (c) 900 °C

4. CONCLUSIONS

The calcination of CaO from cockle shells with variations of temperature (800 ℃, 850 ℃ and 900 ℃) was effectively carried out and subsequently characterized using SEM, EDX and FTIR analyses. SEM analysis revealed the presence of irregular particles after calcination process and EDX analysis indicated a high Ca content in the calcined cockle shells as compared to previous research. Cockle shells subjected to calcination at 900 ˚C yielded a higher Ca content in CaO powder compared to those at 800 ˚C and 850 ˚C. Therefore, 900 ˚C appears to represent the suitable temperature for CaO formation during cockle shell calcination to produce a CaO. The FTIR analysis verified the presence of characteristic bands required for the carbonate group in the calcined cockle shells powder. The absorption band at a wavenumber of 711 cm^{-1} indicating the presence of CaO bonds. High temperature exerts a significant influence on the calcination process of cockle shells. In summary, the calcination process of $CaCO_3$ to CaO at temperatures ranging from 800 ℃ to 900 ℃ is a complex transformation that offers opportunities for optimizing the characteristics of the resulting CaO for various industrial purposes. Thus, CaO calcined from Malaysian cockle shells shows great promise for applications in biomedical applications.

Acknowledgements

The authors would like to thank Dr. Zulkefli Daud and Universiti Tun Hussein Onn Malaysia (UTHM) for the financial support through Geran Penyelidikan Pascasiswazah (GPPS) no. H662.

Author Contributions

All authors contributed toward data analysis, drafting and critically revising the paper and agree to be accountable for all aspects of the work.

Disclosure of Conflict of Interest

The authors have no disclosures to declare.

Compliance with Ethical Standards

The work is compliant with ethical standards.

References

[1] Lee, S. S., Du, X., Kim, I. & Ferguson, S. J. (2022). Scaffolds for bone-tissue engineering. *Journal of Matter*, 5(9), 2722–2759.

[2] Tang, G. (2021). Recent trends in the development of bone regenerative biomaterials. *Frontiers in Cell and Developmental Biology Journal*, 9, 665813.

[3] George, P., Hamid, Z. A., Zakaria, M. Z. A. B., Perimal, E. K. & Bharatham, H. (2019). A short review on cockle shells as biomaterials in the context of bone scaffold fabrication. *Sains Malaysiana*, 48(7), 1539–1545.

[4] Shafiu Kamba, A., Ismail, M., Tengku Ibrahim, T. A. & Zakaria, Z. A. B. (2013). A pH-sensitive, biobased calcium carbonate aragonite nanocrystal as a novel anticancer delivery system. *Journal BioMed Research International*, 2013, 1-10.

[5] Cho, J., Kim, S., Park, K., Rhee, C., Hai Woong, P. & Jung, J. (2023). Eco-friendly CaO-based catalysts derived from waste oyster shells for the oxidative coupling of methane. *Journal of Material Cycles and Waste Management,* 25(1), 3355–3366.

[6] Hoque, M. E., Shehryar, M., Md, K. & Islam, N. (2013). Processing and characterization of cockle shell calcium carbonate ($CaCO_3$) bioceramic for potential application in bone tissue engineering. *Journal of Material Sciences & Engineering*, 2(2), 1-5.

[7] Li, Y. J., Zhao, C. S., Chen, H. C., Duan, L. B. & Chen, X. P. (2009). CO_2 capture behavior of shell during calcination/carbonation cycles. *Chemical Engineering & Technology*, 32(8), 1176–1182.

[8] Carss, D. N. (2020). Ecosystem services provided by a non-cultured shellfish species: The common cockle Cerastoderma edule. *Marine Environmental Research*, 158, 104931.

[9] Ab Halim, M. A. B., Kashim, M. I. A. B. M., Salleh, M. M. M., Nordin, N. B. & Husni, A. B. M. (2015). Halal pharmaceuticals. *Social Sciences (Pakistan)*, 10(4). 490–498.

[10] Dampang, S., Purwanti, E., Destyorini, F., Kurniawan, S. B., Abdullah, S. & Imron, M. (2021). Analysis of optimum temperature and calcination time in the production of CaO using seashells waste as CaCO3 source. *Journal of Ecological Engineering*, 22, 221–228.

[11] Mohamed, M., Yousuf, S. & Maitra, S. (2012). Decomposition study of calcium carbonate in cockle shell. *Journal of Engineering Science and Technology*, 7, 1–10.

[12] Rashidi, N. A., Mohamed, M. & Yusup, S. (2011). A Study of calcination and carbonation of cockle shell. *World Academy of Science, Engineering and Technology*, 60, 818–823.

[13] Zulkefli, N., Ahmad, M. D., Mahzan, S. & Yusup, E. M. (2023). The Development of Temporary Bone Scaffolds from High Density Polyethylene (HDPE) and Calcium Carbonate ($CaCO_3$) for Biomedical Application. In *Structural Integrity and Monitoring for Composite Materials*, vol. 1. (Springer Nature, Singapore), pp. 243–259.

[14] Zhipeng, Pan., Yixuan, F. & Liang, S. Y. (2017). Material microstructure affected machining: a review. *Manufacturing Review*, 4, 5.

[15] Hussein, A. I., Ab-Ghani, Z., Che Mat, A. N., Ab Ghani, N. A., Husein, A. & Ab. Rahman, I. (2020). Synthesis and characterization of spherical calcium carbonate nanoparticles derived from cockle shells. *Applied Sciences*, 10(20), 7170.

[16] Zulkefli, N., Yusup, E. M. & Othman, M. H. (2023). A review: Calcium carbonate ($CaCO_3$) extract from natural ceramics for thin film application. *Materials International,* 5(2).

[17] Widyastuti, S. & I. P. (2017). Synthesis and characterization of $CaCO_3$ (calcite) nano particles from cockle shells (Anadara granosa Linn) by precipitation method. In Proceedings of the 3rd International Conference on Engineering, Technology, and Industrial Application (ICETIA 2016), Indonesia, 7–8 December 2016.

[18] Nordin, N., Hamzah, Z., Hashim, O., Kasim, F. H. & Abdullah, R. (2015). Effect of temperature in calcination process of seashells. *Malaysian Journal of Analytical Sciences*, 19(1), 65–70.

[19] Hu, S., Wang, Y. & Han, H. (2011). Utilization of waste freshwater mussel shell as an economic catalyst for biodiesel production. *Biomass and Bioenergy*, 35(8), 3627–3635.

[20] Islam, K. N., Bakar, M. Z. B. A., Noordin, M. M., Hussein, M. Z., Rahman, N. S. B. A. & Ali M. E. (2011). Characterisation of calcium carbonate and its polymorphs from cockle shells (Anadara granosa). *Journal of Powder Technol*ogy, 213(1), 188–191.

[21] Bilton, M., Brown, A. & Milne, S. (2012). Investigating the optimum conditions for the formation of calcium oxide, used for CO_2 sequestration, by thermal decomposition of calcium acetate. *Journal of Physics: Conference Series,* 371, 12075.