Samarra J. Engineering Sci. and Res. , 2024; 2 (2): 12-19

IRAQI Academic Scientific Journals

SAMARRA JOURNAL OF ENGINEERING SCIENCE AND RESEARCH

S.J.E.S.R

Preparation of hydroxyapatite from eggshell chicken waste by calcination process

Sura Saleem Hasan[1*]

1- Department of Civil Engineering, College of Engineering, University of Wasit, Iraq

Article Information

Received: 21/02/2024

Accepted: 20/04/2024

Keywords:

Hydroxyapatite, bio-waste materials, chicken eggshells, calcination temperature, and heating rate.

Corresponding Author

E-mail: s.hasan@uowasit.edu.iq

Mobile: 07808383884

Abstract

Hydroxyapatite is stable, has biological activity and is biocompatible; it is also one of the bioactive materials that are commonly utilized in biomedical fields. The objective of this research was to create HAp from the chicken eggshell's waste by utilizing the calcination method. The powder was heated in a furnace to different temperatures of 900 to 1050 °C, and the difference between the temperature and the other was 50 °C for 2 hours at a heating rate of 10 °C/min, then the powder was slowly cooled. After the process of calcination is over. The results demonstrated the creation of a portion of HAp via the presence of peaks that corresponded to a strong band (OH) at 3643 cm-1, 3435 cm-1 (OH-) that refers to the hydroxyl group, and phosphate groups (PO43) appeared at 960 cm-1 in the Fourier transform infrared spectrum.. In calcined sample hydroxyapatite found at an angle of 32° with an angle of 29.3 in the waste sample in X-ray diffraction. Scanning electron microscopy showed that the formation of pores and smooth surface appeared, and the EDX analysis showed the existence the oxygen and calcium only, this indicates that the decarbonation reaction occurred, and at 1000°C the results shown that, the existence of phosphorus, oxygen, and calcium and this refers the formation of hydroxyapatite. In general, the results observed that the calcination process is not enough to prepare pure hydroxyapatite from chicken eggshells.

Introduction:

The increasing demand for ceramic materials in the medical field, especially in dentistry, causes new discoveries to be made as an alternative to the utilization of new materials because denture materials are imported and have a high cost. Bioceramic is a popular material for use in repairs, substitutes, bone and teeth [1].

Hydroxyapatite is an inorganic natural material that utilized by human for a long time which has 3.14~3.16 cm^2 density, good stability, biocompatibility, and biological activity, no irritation and rejection reaction in vivo, bone formation ability, and bio decomposition, also has good bone conduction, and has hexagonal crystal system. In 1970, after the successful preparation of hydroxyapatite, (AP) apatite began to be studied and utilized as an artificial synthetic material [2]. HAp is composed of 70% bone, while collagen is composed of 20% and water is composed of 10%. HAp's chemical composition is Ca10(PO4)6(OH)2. HAp is producible using different methods that are high temperature, wet, or dry. The high temperature method involves the pyrolysis and combustion of biomass, the wet method is divided into hydrothermal, chemical precipitation, and hydrolysis methods, and this method is concerned with the utilization of water-based solutions, the dry method is divided into mechanical and solid state methods. [3]. All of the aforementioned methods are typically synthetic, but there are also non-synthetic methods that are relatively inexpensive, simple, and contain no dangerous chemicals, metabolic activity, or dynamic response to the environment. Some of the methods are based on natural sources, such as the shells of fish, eggshells, plants, seashells, cow's bones, and snail's shells. These natural resources are categorized into four primary groups: animal-based sources, aquatic-based sources, plant-based sources, and the benefits of HAp derived from animal-based sources are significant, including its stability, lack of organic components, and significant crystallinity, all of which make it appropriate for biomedical applications [4,5]. Eggshells have been comprehensively studied, it was discovered that eggshells that are confined by their shells have a composition of 95% inorganic minerals, 3.3 to 3.5% organic material, and 1.6% water [6]. It's made up of 11% of the total weight of the egg, this percentage is composed of magnesium carbonate, 1%, calcium phosphate, 1%, organic matter, 4%, and calcium carbonate, 94%. The eggshells are environmentally friendly and cost-effective for the production of hydroxyapatite, and they have a three-layered structure, which includes the lamellar layer, the spongeous layer, and the cuticle layer. The outer layer is called the cuticle, and it consists of multiple proteins, including the lamellar and spongeous layers, these layers form a matrix that is composed of protein fibers that are bonded to calcium-based crystals [7]. While synthetic process has many problems such as adding chemicals materials to develop mechanical strength and increased structural stability, but on the other hand, the chemical material is fixed in the human body and It causes many symptoms [5].

The applications of hydroxyapatite is used in the bone graft because of stoichiometrically similar Ca/P ratio, and it is similar to the composition of the native hard tissue. Moreover, it has good bioactivity, biocompatibility, and osteoconductivity [8] and can be used to fill the voids or bone defects because it is can take shape in many forms such as hybrid composites, porous blocks, and powders. Further, it can be used especially when a big portion of bones is taken away and in dental applications [9]. In the current synthesis procedure, an attempt has been made to create a biocompatible HAp powder by means of calcination using a natural source of chicken eggshell as the calcium component.

Methodology

Powder preparation and calcination process

Bio-waste material chicken eggshells were collected from incubation. After that, the chicken eggshells were cleaned under water to remove the internal layers, then washed in distilled water. Then it was dried for three days, was crushed in a simple grinding and then grinded in ball milling (SFM-1(QM-3SP2)), which is provided with balls made from alumina at various sized without use of any lubricants at 4000 rpm for four hours. After that, there was fire and thermal dry furnace (Naberthem GmbH, German made) to conduct calcination process at 900 °C, 950 °C, 1000 °C and 1050 °C at a heating rate 10°C/min for 2 hours in each temperature and then cooled slowly to room temperature. Finally, the chicken eggshells waste powder and calcined powders were characterized by XRD, SEM with EDS, and FTIR.

Characterization Tests

Fourier Transform Infrared (FTIR)

FTIR (SHIMADSO, Japan created) is a beneficial instrument that identifies the types of chemical bonds and active substances by creating an infrared spectrum of absorption. 200 mg of potassium bromide powder combined with 1-2 mg of hydroxyapatite powder samples were used. Moreover, 20 scans and a spectral resolution of 4 cm-1, the spectra from the 400 to 4000 cm-1 range were recorded.

X-Ray Diffraction (XRD)

X-Ray diffraction (SHIMADZU Lab XRD-6000, Japan x-ray) can be used to determine the phase composition and the crystalline structure of the powders, the data were collected over 2Θ from 10º to 50º, using Voltage = 40 KV, Current = 30 mA and CuKα radiation (λ = 0.154056 nm).

Scanning Electron Microscopy with Energy Dispersive Spectroscopy

The SEM-FEI Quanta model, which is manufactured by Holland, has a speed of 12.5 kV, and is used to observe the microstructure and appearance of the powders. The EDS is incorporated into the model as an extra tool, and is used to analyse the specific chemical composition of the samples around the circumference of the device.

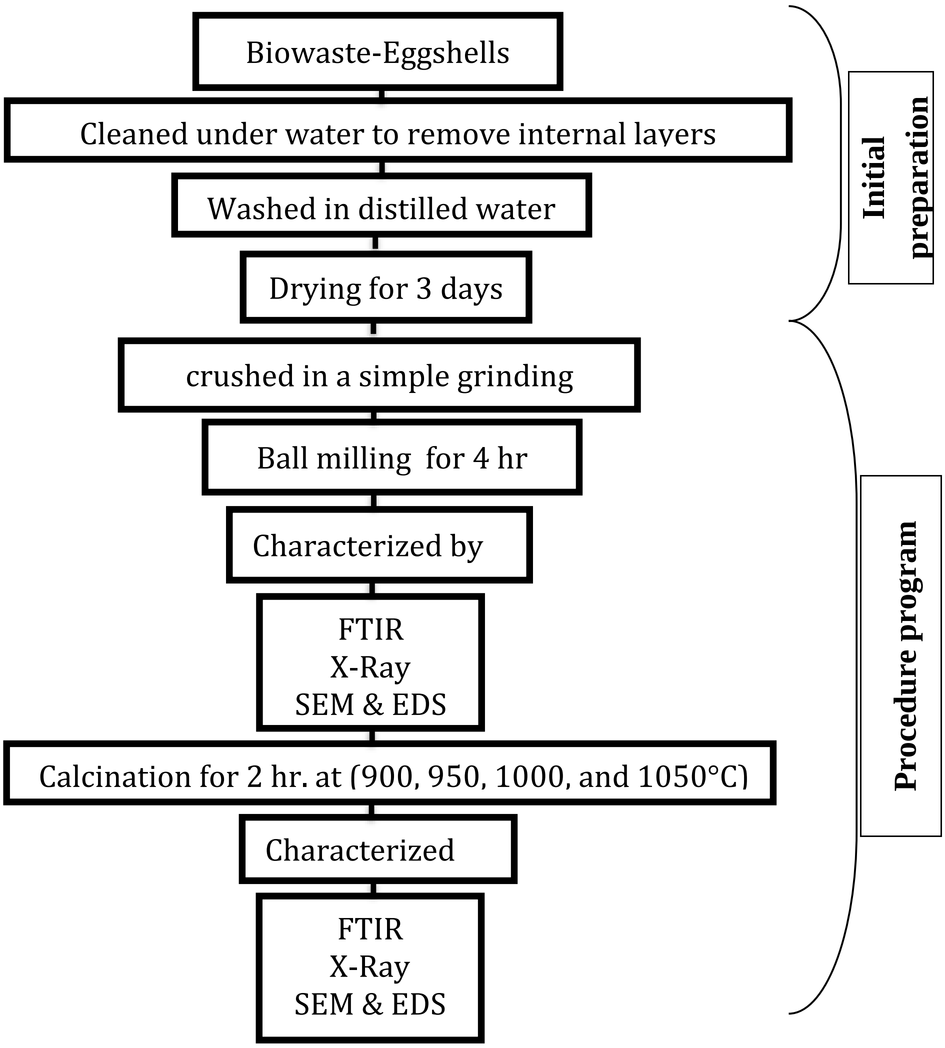

Fig. 1 ***Flow chart of Research Experimental Program***

Results and discussion

Fourier Transform Infrared

The FT-IR spectrum of the chicken eggshells raw powder and powder produced by calcination method at 900 °C, 950 °C, 1000 °C and 1050 °C shown in '**Fig. 2**'. In the raw waste powder, the carbonate group exist at bands 875 cm^{-1}, 1423 cm^{-1} and 1794 cm^{-1} [10,11] and the $CaCO_3$ at 2515 cm^{-1} and 870 cm^{-1}. In the calcined powder at 900 °C for two hours, the $CaCO_3$ transformed into CaO. So these bands appeared at 1415 cm^{-1} and 886 cm^{-1} refer to the substitutional group (C-O) and OH^- groups respectively [10], and the traces of water correspond in the range 3000–3400 cm^{-1} broad band of low intensity combined with the structure. However, there is a very weak broad band bending mode of H-O-H around 1640 cm^{-1}[9]. After 900 °C to 1050 °C, the results showed a strong band (OH) at 3643 cm^{-1}, 3435 cm^{-1} (OH^-) referring to the hydroxyl group [1], and phosphate groups ($PO^4{}_3$) appeared at 960 cm^{-1}.

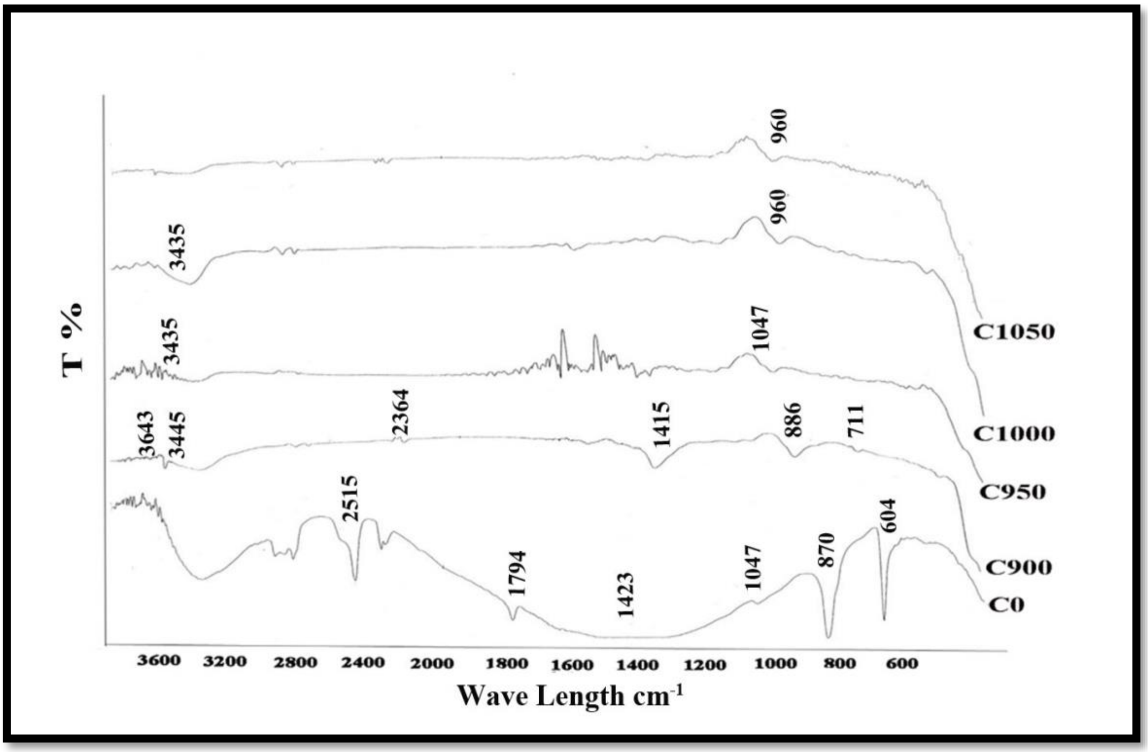

Fig. 2 ***Fourier transform infrared spectroscopy of raw chicken eggshells C0 and calcined at various temperatures (C900-900 °C, C950-950 °C, C1000-1000 °C and C1050-1050 °C).***

X-Ray Diffraction analysis

The X-ray diffraction patterns before and after calcination method from 900 °C to 1050 °C of the chicken eggshells powders are presented in **'Fig. 3'**. The results of the diffraction patterns of the chicken eggshells waste powder indicated to presence of the calcite $CaCO_3$ at 39.5°, 48°, and 36° as a mineral phase in the collected chicken eggshells powder. However, the calcined chicken eggshells powder hydroxyapatite ($Ca_4O_{14}P_3$) found at an angle of 32° with an angle of 29.3 in the waste sample [1].

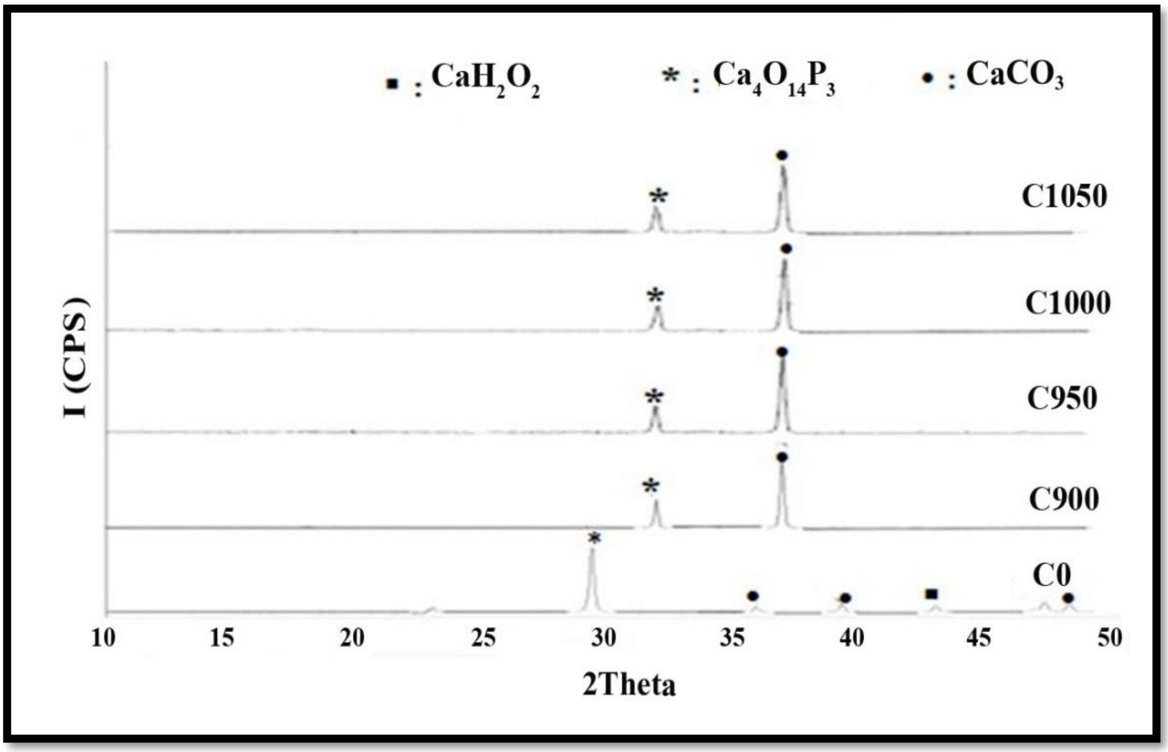

Fig. 3 ***XRD patterns for raw chicken eggshells C0 and calcined chicken eggshells powder (C900-900 °C, C950-950 °C, C1000-1000 °C and C1050-1050 °C).***

Scanning Electron Microscopy with Energy Dispersive Spectroscopy

Scanning Electron Microscopy (SEM)

Figure 4 shows a surface morphology for raw and calcined chicken eggshells at different calcination temperatures. In the raw chicken eggshells, samples can illustrate the individual fine particles as heterogeneous in size and shape as semi-spherical shapes, spherical, and oval shapes [10]. Whereas the calcined chicken eggshells powders, the formation of pores is useful and allows the circulation of body fluid therefore it can be used in the applications of coating. Homogeneous size distribution and small particles size micrographs may be obtained with coagulated samples and smooth surface appear after calcination process [9].

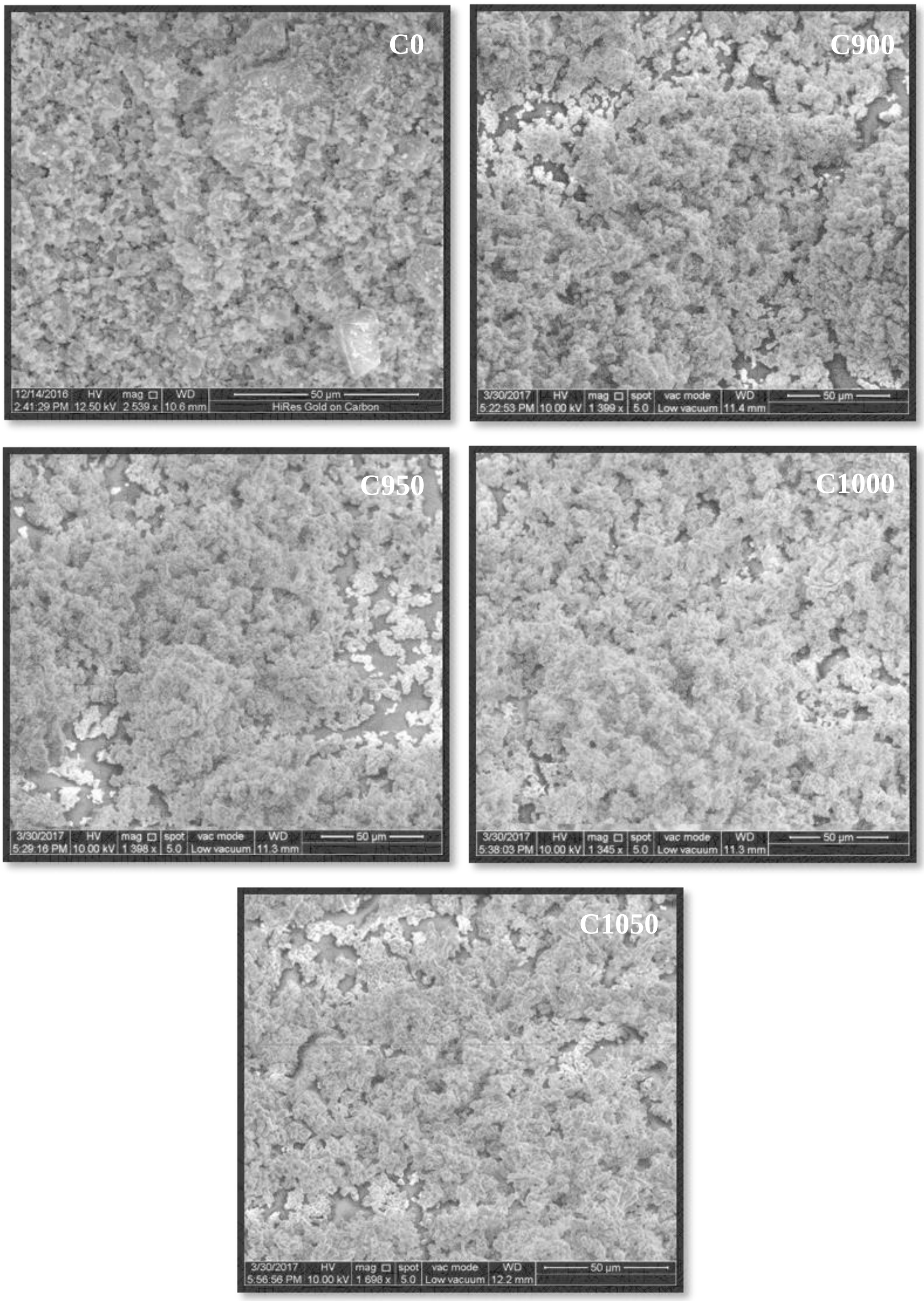

Fig. 4 ***Scanning electron microscopy for the raw chicken eggshells powder C0 and calcined chicken eggshells (C900-900 °C, C950-950 °C, C1000-1000 °C and C1050-1050 °C).***

Energy Dispersive Spectroscopy Analysis

The EDX analysis for the chicken eggshells before and after calcination method at various temperatures from 900 °C to 1050 °C shown in **'Fig. 5'**. The chemical composition of chicken eggshells indicates a large amount of calcium and oxygen in the raw powder (C0) before calcination process. In addition, the spectrum contained phosphorus, and after the calcination process at 900 °C and 950 °C, the EDX analysis showed existence of oxygen and calcium only. This indicates that the decarbonation reaction occurred, and at 1000°C, the results show that the existence of phosphorus, oxygen, and calcium. As a result, this refers the formation of hydroxyapatite.

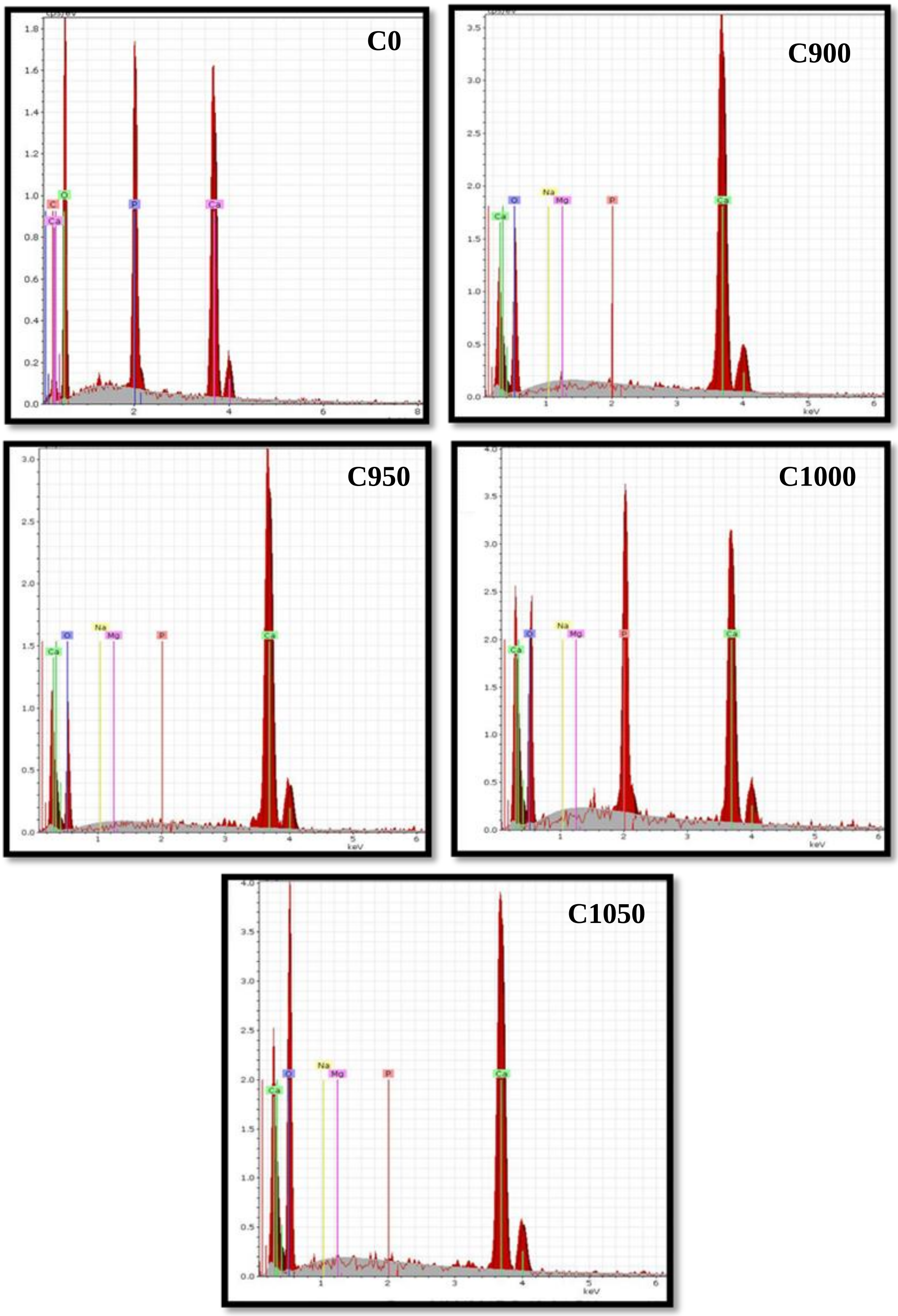

Fig. 5 ***Energy dispersive spectroscopy analysis for raw chicken eggshells C0 and calcined chicken eggshells powder (C900-900 °C, C950-950 °C, C1000-1000 °C and C1050-1050 °C).***

Conclusions

This research uses calcination process to synthesize hydroxyapatite from bio-waste material chicken eggshells. The major results showed that, biogenic sources are a source without any kind of contamination, which allow hydroxyapatite to be environmentally friendly. The chicken eggshells are a suitable source of calcium, and the calcination process is a smart and economical method due to low cost and uncomplicated method. As revealed by FTIR, XRD and EDS analyses, the formation of CaO from CaCO3 is faster when the calcination temperature is higher, but the calcination process is not enough to obtain pure hydroxyapatite from chicken eggshells, so we must use another method such as the precipitation method.

References

1. Sabir, A., Abbas, H., Aminy, A. Y., & Asmal, S., 2022, (Analysis of duck eggshells as hydroxyapatite with heat treatment method) EUREKA: Physics and Engineering, (16-24.). https://doi.org/10.21303/2461-4262.2022.002017

2. Ma, G., 2019, (Three common preparation methods of hydroxyapatite), In IOP conference series: materials science and engineering, (033057). https://doi.org/10.1088/1757-899X/688/3/033057

3. Pu'ad, N. M., Haq, R. A., Noh, H. M., Abdullah, H. Z., Idris, M. I., & Lee, T. C., 2020, (Synthesis method of hydroxyapatite: A review), Materials Today: Proceedings, (233-239). https://doi.org/10.1016/j.matpr.2020.05.536

4. Agbeboh, N. I., Oladele, I. O., Daramola, O. O., Adediran, A. A., Olasukanmi, O. O., & Tanimola, M. O., 2020, (Environmentally sustainable processes for the synthesis of hydroxyapatite), Heliyon. https://doi.org/10.1016/j.heliyon.2020.e03765

5. Mustafa, N., Ibrahim, M. H. I., Asmawi, R., & Amin, A. M., 2015, (Hydroxyapatite extracted from waste fish bones and scales via calcination method), Applied mechanics and materials, (287-290). https://doi.org/10.4028/www.scientific.net/AMM.773-774.287

6. Gautron, J., Stapane, L., Le Roy, N., Nys, Y., Rodriguez-Navarro, A. B., & Hincke, M. T., 2021, (Avian eggshell biomineralization: an update on its structure, mineralogy and protein tool kit), BMC Molecular and Cell Biology, (1-17). https://doi.org/10.1186/s12860-021-00350-0

7. Thakur, V. K., & Kessler, M. R., 2016, (Green biorenewable biocomposites: from knowledge to industrial applications), CRC press. https://doi.org/10.1201/b18092

8. Radulescu, D. E., Vasile, O. R., Andronescu, E., & Ficai, A., 2023, (Latest Research of Doped Hydroxyapatite for Bone Tissue Engineering), International Journal of Molecular Sciences, (13157). https://doi.org/10.3390/ijms241713157

9. Gergely, G., Wéber, F., Lukács, I., Tóth, A. L., Horváth, Z. E., Mihály, J., & Balázsi, C., 2010, (Preparation and characterization of hydroxyapatite from eggshell), Ceramics International, (803-806). https://doi.org/10.1016/j.ceramint.2009.09.020

10. Tlili, S., Bouyegh, S., Labiod, K., Traiaia, N., Hassani, M., & Ariche, B, 2021, (Synthesis and characterization of hydroxyapatite powder derived of eggshell by precipitation method), In Proceedings of the international conference on industrial engineering and operations management monterrey (1550-1557). http://ieomsociety.org/proceedings/2021monterrey/258.pdf