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RESEARCH ARTICLE

EFFECT OF DIFFERENT CALCINATION TEMPERATURES ON SYNTHESIZED HYDROXYAPATITES FROM WASTE EGGSHELL

Nur BAYRAM [1], Sedef DİKMEN [2,*], Semra MALKOÇ [3]

[1] Department of Advanced Technologies, Graduate School of Sciences, Eskişehir Technical University, Eskişehir, Türkiye
nurbayram96@hotmail.com- 0000-0003-4431-387X

[2] Department of Physics, Science Faculty, Eskişehir Technical University, Eskişehir, Türkiye
sdikmen@eskisehir.edu.tr - 0000-0002-6164-4710

[3] Department of Environmental Engineering, Faculty of Engineering, Eskişehir Technical University, Eskişehir, Turkiye
satik@eskisehir.edu.tr- 0000-0002-8092-411X

Abstract

ABSTRACT

About 94% of waste eggshells are composed of calcium carbonate ($CaCO_3$), which allows for the generation of calcium oxide (CaO), which can be utilized to synthesize hydroxyapatite (HAp). This study uses chemical precipitation and calcination methods to synthesize natural HAp from eggshell waste. In the first stage, the powdered eggshell was calcined at 900 °C to convert the calcium carbonate ($CaCO_3$) in the eggshell into calcium oxide (CaO), the precursor particles of HAp, before being subjected to chemical precipitation. To obtain HAp, the calcined eggshell powder was mixed with deionized water, and the suspension, whose pH was adjusted to 8.5 using phosphoric acid, was allowed to age. The precipitates obtained in the second stage were calcined at various temperatures (500 °C, 700 °C, 900 °C, 1000 °C, and 1100 °C) to produce hydroxyapatite (HAp) with the highest purity. The HAp samples synthesized at these calcination temperatures were characterized using several techniques: phase analysis through X-Ray Diffraction (XRD), chemical analysis via X-Ray Fluorescence (XRF) and microscopy, and thermal analysis using differential thermal analysis and thermogravimetric analysis (DTA-TG). XRD patterns show that the most suitable calcination temperature for HAp is 900 °C, and samples calcined at 900 °C, 1000 °C and 1100 °C contain peaks belonging to biphasic HAp and β-tricalcium phosphate (β-TCP) phase. The chemical analysis results show that HAp samples are mostly composed of Ca, P and O elements. The calculated Ca/P ratio for HAp samples recalcined at 900 °C is 1.73, which is close to the expected stoichiometric ratio of 1.67. HAp recalcined at 900 °C exhibited characteristic peaks at 571, 632, 962, 1046 and 1090 cm^{-1}. The intensities of most of the bands belonging to phosphate vibrations of HAp increased at calcination temperatures of 900 °C and above. As a result, the study showed that HAp can be synthesized from eggshell waste by using the precipitation and calcination methods together.

Keywords

Calcination,
Characterization,
Chemical precipitation,
Hydroxyapatite,
Waste eggshell

Time Scale of Article

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1. INTRODUCTION

Hydroxyapatite (HAp) is a calcium phosphate compound with the chemical formula $Ca_{10}(PO_4)_6(OH)_2$. It belongs to the apatite family, similar to the mineral structure of bones and teeth. Due to this similarity, it is highly biocompatible. HAp can bond with hard tissues, accelerating bone formation in diseased or damaged areas and preventing adverse effects caused by the immune system. Because of this, hydroxyapatite is used in various applications such as orthopedics, dental implants, and controlled drug

*Corresponding Author: sdikmen@eskisehir.edu.tr

release systems [1]. It can be obtained from natural sources as well as synthesized chemically. Natural hydroxyapatite is derived from animal scales, bones, minerals, and shells [2]. The molar ratio of calcium and phosphate in hydroxyapatite (HAp) is 1.67. However, natural HAp is not stoichiometric and can have varying calcium and phosphorus content. There are several methods to obtain HAp, including chemical precipitation [3], sol-gel [4], hydrothermal synthesis [5], and mechano-chemical methods [6]. Currently, the most preferred method is chemical precipitation due to its low processing temperature, simplicity, high yield, and product quality [7, 8]. Panda et al. produced hydroxyapatite (HAp) from fish scales using calcination and alkaline heat treatment [9]. Janus et al. and Haberko et al. used pig bone for HAp synthesis and combined calcination with alkaline heat treatment in the synthesis process [10, 11]. Jaber et al. synthesized HAp from natural camel bone using the calcination method [12]. Pal et al. synthesized HAp from late calcarifer fish bone using the calcination method [13]. The use of seashells such as cockles [14], clams [13], and mussels [15] for processing HAp has shown promising results, with successful synthesis of HAp reported. Santhosh and Prabu synthesized HAp from seashells using chemical precipitation [16]. In addition to seashells, eggshells containing calcium carbonate ($CaCO_3$) have also been used as a calcium precursor for HAp synthesis. Goloshchapov et al. synthesized HAp using eggshells through calcination and chemical precipitation [17], while Okur and Koyuncu, and Patel et al. used eggshells for HAp synthesis through the precipitation method [18, 19].

Approximately 94% of the eggshell comprises calcium carbonate ($CaCO_3$), which makes it a valuable source for hydroxyapatite synthesis. The remaining percentage contains trace amounts of elements such as magnesium, sulphur, potassium, and sodium [18-20]. HAp obtained from eggshells has environmental, industrial, and biomedical applications and can be used as an adsorbent in cosmetics and water treatment systems [21].

Chicken eggshells, which are widely used in the food industry and by consumers every day, are often discarded as waste. With the global egg production totalling 70 million tons, and roughly 11% of the egg's weight being shell, approximately 8 million tons of eggshells are wasted each year [22].

This research uses chemical precipitation and calcination methods to obtain hydroxyapatite from waste eggshells, which helps reduce the environmental impacts of improper waste disposal. In the initial stage, calcium carbonate ($CaCO_3$) in eggshells was converted to calcium oxide (CaO) at 900 °C, creating the precursor particles of hydroxyapatite (HAp). During the synthesis stage, CaO combined with deionized water to form $Ca(OH)_2$. Finally, hydroxyapatite synthesis was completed by adding H_3PO_4 to the medium. The synthesized hydroxyapatite was subjected to different calcination temperatures (500 °C, 700 °C, 900 °C, 1000 °C, and 1100 °C) to determine the effect of temperature on HAp formation. For the purpose of characterizing the HAp samples synthesized from eggshells at these calcination temperatures, various analysis and imaging techniques were used. These included phase analysis (XRD; X-Ray Diffraction), chemical analysis (XRF; X-Ray Fluorescence), molecular structure analysis (FTIR; Fourier Transform Infrared Spectroscopy), imaging of the components in the structure (SEM; scanning electron microscope), and thermal analysis (TGA).

2. EXPERIMENTAL SECTION

2.1 Materials

A local company provided the eggshells for the experiments. The eggshells were washed with tap water, rinsed with deionized water, and left to air dry in the laboratory for one day. Afterwards, they were placed in an oven (Nuve FN 500) at 80 °C for 2 hours to remove any remaining moisture. The dried eggshells were then crushed using a Retsch mortar mill and sieved through a 250-micron sieve to prepare them for hydroxyapatite synthesis.

Orthophosphoric acid (H_3PO_4; Tekkim, 85%) was used as the phosphate source for the hydroxyapatite synthesis. During all experimental procedures, ultrapure water was utilized. A high-temperature furnace (Carbolite RHF 1400) was utilized for the calcination processes.

2.2. Synthesis of HAp

The synthesis of hydroxyapatite involved the use of a precipitation method with calcined eggshells [2]. The eggshells in powder form, with a particle size below 250 microns, were heated to 900°C in a high-temperature furnace at a heating rate of 20 °C/min and calcined for 1 hour at this temperature. During this process, CaO formed due to CO_2 being released from the $CaCO_3$ in the eggshell powder (Eq. 1). In the synthesis process, 2.8 g of calcined eggshell was initially added to 50 mL of deionized water. This caused the formation of $Ca(OH)_2$ as described in Eq. 2. Then, a 0.6 M H_3PO_4 solution was added until the pH value of the suspension reached 8.5. The suspension was then left to age for 24 hours. After 24 hours, it was stirred for 30 minutes with a magnetic stirrer and left to age again for another 24 hours. This ageing process resulted in the formation of $Ca_{10}(PO_4)_6(OH)_2$, as shown in Eq. 3. At the end of the ageing period, the calcined eggshells aged with phosphoric acid in the solution were washed with ultrapure water for 2 hours and then dried in an oven at 80°C for one day. Dried hydroxyapatite in powder form was subjected to recalcination at temperatures of 500 °C, 700 °C, 900 °C, 1000 °C, and 1100 °C for two hours to investigate the impact of temperature on various properties.

$$CaCO_3 \rightarrow CaO + CO_2 \quad (1)$$

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad (2)$$

$$10Ca(OH)_2 + 6H_3PO_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 18H_2 \quad (3)$$

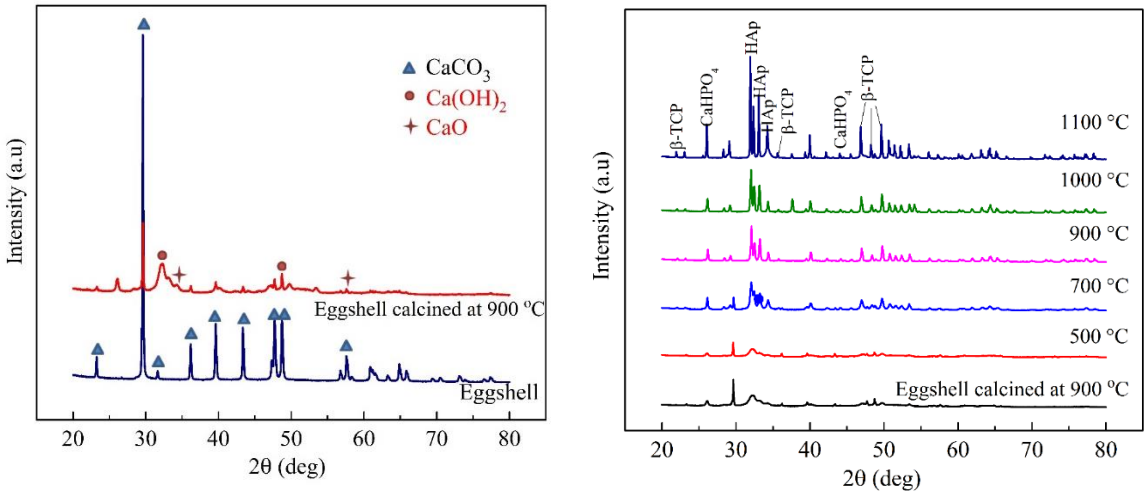
2.3. Characterization of HAps

Hydroxyapatite phases were determined using X-ray diffraction (XRD). A Bruker Advance D8 diffractometer with 45 kV anode voltage and 40 mA filament current settings was used. The instrument emitted nickel-filtered Cu Kα radiation at a wavelength of 0.154 nm. The goniometer of the diffractometer scanned the range 20°- 80° at a rate of 0.1°/s with a step size of 0.01°. Chemical analysis and to estimate the Ca/P ratio were performed using XRF (Bruker Tiger S8). Zeiss Ultra Plus FE-SEM instrument was used to visually confirm the synthesis of hydroxyapatite, the system operates in an acceleration voltage range of 5 kV, with the samples previously metalized with a gold layer and fixed on a carbon support. Molecular structure analysis of FT-IR spectra was obtained using Perkin Elmer Spectrum 100. Mass loss of the samples in nitrogen (N_2) environment was also measured using TGA (Netzsch STA 449 F3).

3. RESULTS

3.1. XRD Analysis of HAps

Figure 1(a) shows the XRD analysis of eggshell in powder form and calcined eggshell subjected to calcination process at 900 ℃ for 1 hour. Figure 1(b) shows the XRD patterns of the samples synthesized at 500 ℃, 700 ℃, 900 ℃, 1000 ℃ and 1100 ℃ for 2 hours after reacting with H_3PO_4.



(a) **(b)**

Figure 1. **(a)** Eggshell and eggshell calcined at 900 ℃ for 1 hour; **(b)** XRD patterns of hydroxyapatite samples sintered at different temperatures (500 °C, 700 °C, 900 °C, 1000 °C and 1100 °C) after synthesis with H_3PO_4.

The XRD patterns of the eggshell reveal that all peaks indicate the presence of calcium carbonate ($CaCO_3$). The highest peak for $CaCO_3$ is observed at an angle of 29.6°. After 1 hour of calcination, it is observed that some of the peaks for $CaCO_3$ have completely disappeared, while some remain in small amounts. The calcination process transforms the $CaCO_3$ in the eggshell to CaO, which is the precursor for HAp synthesis [23]. According to a study by Kamalanathan et al., the characteristic peak in the XRD results of $CaCO_3$ occurs at approximately 2θ=29° [24].

After blending the calcined eggshell powder with H_3PO_4, the material was subjected to calcination at various temperatures. At a calcination temperature of 900 ℃, it was observed that the peak intensity increased. The peaks obtained at this temperature completely overlapped with the peaks at 28.9°, 32.0°, 32.9°, and 34.3° according to card number ICDD 00-003-0747. XRD analysis shows that the optimal calcination temperature for HAp is 900 °C. HAp samples calcined at 900, 1000, and 1100°C exhibit peaks corresponding to biphasic HAp and β-tricalcium phosphate (β-TCP) phase. The peak generated at 900℃ and higher calcination temperatures were even more intense and well-defined. It can be concluded that the material's crystallinity increases with higher calcination temperatures [23]. In a study conducted by Patel et al., clean and dry eggshells were taken and dried at 100°C for two days. Later, the eggshells were calcined at different temperatures (600°C, 800°C, 1000°C, and 1200°C) for three hours. The calcination process degraded $CaCO_3$ to yield CaO, producing $Ca(OH)_2$ with excess water. Afterwards, the $Ca(OH)_2$ reacted with phosphoric acid to yield TCP, which then reacted with CaO in a closed container at 1050°C for three hours, producing highly crystalline HAp powders [18]. In addition to the hydroxyapatite peaks, weak peaks are occurred at 25.8°, 34.5°, and 44.1° at 1100°C. These peaks are attributed to monetite ($CaHPO_4$) phase. The dominance of hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) is not observed in the HAp recalcined at 1100°C. Similar results were obtained by Agbaika et al. [25].

Ramirez-Gutierrez et al. indicated that the hydroxyapatite (HAp) obtained from pig bone exhibited intense peaks at high temperatures [26]. At high temperatures, HAp starts to decompose, leading to the formation of β-TCP as a new substance. Weak peaks are observed at 2θ angles of 21.9°, 35.4°, 44.1°, 46.8°, and 48.4° beginning at 900℃, corresponding to the presence of β-TCP [27]. Sun et al. and Hosseinzadeh et al. reported that the formation of β-TCP occurred at calcination temperatures of 750℃ and 850℃ for HAp, respectively [28, 29].

3.2. XRF Analyses of HAps

Chemical analysis determined the weight percentages of the elements in the eggshell and hydroxyapatite samples that were heated at different temperatures. The value presented in Table 1 indicates the transformation of the eggshell, which has a $CaCO_3$ structure after the calcination process, into CaO due to the loss of CO_2. Additionally, the weight percentages of CaO and P_2O_5 obtained from the recalcination of hydroxyapatite samples—produced by treating the calcined eggshell with H_3PO_4 at different temperatures, provide characteristic data [25]. The Ca/P ratio calculated from XRF results equals 1.73 for HAp recalcined at 900 °C, the closest value to 1.67. From XRF analysis, this ratio increases at calcination temperatures above 900 °C. At temperatures higher than 900 °C, other phases (such as monetite) affect the amount of hydroxyapatite, thus increasing the expected stoichiometry ratio. The main difference between synthetically produced HAp and natural HAp produced from animal-derived materials is that natural HAps have a higher Ca/P ratio than synthetic HAps. The stoichiometric ratio of synthetic HAps is closer to 1.67. Additionally, other researchers have noted Ca/P ratios that exceed the stoichiometric value [2, 25].

Table 1 Chemical composition of samples includes eggshell, eggshell calcined at 900°C for 1 h, and HAps heated at different temperatures.

Chemical composition	**Eggshell (wt. %)**	**Eggshell calcined at 900 ºC (wt. %)**	**HAp samples heated at different temperatures (wt.%)**				
			500 ºC	**700 ºC**	**900 ºC**	**1000 ºC**	**1100 ºC**
CaO	90.75	96.81	64.01	63.52	62.25	64.09	66.17
P_2O_5	2.45	0.60	33.90	34.37	35.89	34.01	31.71
MgO	0.84	0.69	0.65	0.66	0.56	0.47	0.72
Na_2O	0.21	0.17	0.07	0.09	0	0	0
SO_3	4.11	0.55	0.30	0.28	0.20	0.37	0.28
K_2O	0.32	0.09	0	0.01	-	-	-
SrO	0.13	0.05	0.03	0.03	0.03	0.03	0.03
SiO_2	0.09	-	0.04	-	-	0	0.05
Fe_2O_3	0.02	-	0.01	0,01	-	0.01	0.04
Cl^-	0.72	0.04	-	-	-	0.02	0.02
Total	**99.64**	**99.00**	**99.01**	**98.97**	**99.00**	**99.00**	**99.02**

3.3. FTIR Analysis of HAps

The FT-IR analysis of the eggshell and the eggshell subjected to calcination at 900 ℃ for 1 hour is given in Figure 2 (a), and the FT-IR analysis of the samples obtained by the reaction of calcined eggshells with H_3PO_4 after being calcined at the different temperatures for two hours is given in Figure 2 (b).

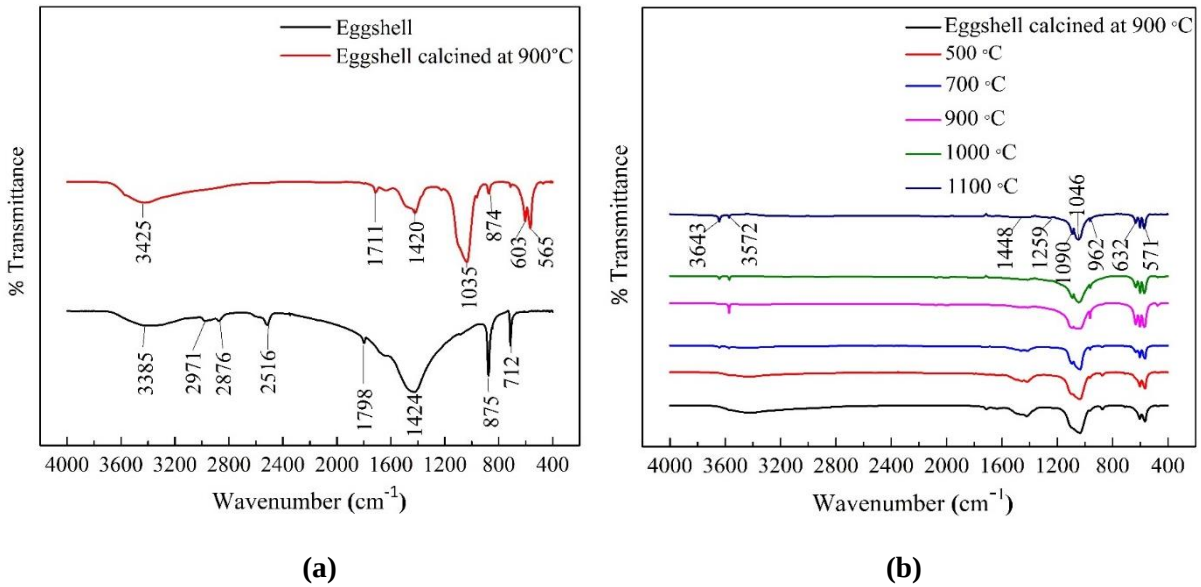


Figure 2. FT-IR analysis of **(a)** eggshell and calcined eggshell at 900 ℃ for 1 hour; **(b)** HAp samples heated at different temperatures (500 °C, 700 °C, 900 °C, 1000 °C and 1100 °C)

As seen in Figure 2 (a), the bands formed by the eggshell in the presence of the characteristic bands of CO_3^{-2} ion at 1424 and 874 cm^{-1} are occurred to be intense, while the intensity of these characteristic bands decreases as a result of calcination of the eggshell for one-hour [30]. This result also confirms the findings from the X-ray diffraction (XRD) analysis. The characteristic absorption peaks of hydroxyapatite (HAp) observed at 571, 632, 962, 1046, and 1090 cm^{-1} is present in samples that were calcined at temperatures of 700 °C and above. Among these peaks, the absorption peaks at 571 and 632 cm^{-1} are attributed to the ν_3 and ν_4 bending modes, respectively. The peak at 962 cm^{-1} corresponds to the ν_1 symmetric stretching mode, while the absorption bands at 1046 and 1090 cm^{-1} are associated with ν_3 asymmetric stretching. For the OH^- group in the crystal structure of HAp, characteristic adsorption bands are observed at 3572 and 3643 cm^{-1} [12, 30].

3.4. SEM Images of HAps

Figure 4 displays SEM images of the eggshell calcined at 900°C for 1 hour and the HAp samples calcined at 500°C, 700°C, 900°C, 1000°C, and 1100°C for 2 hours, respectively. Upon examining the SEM images of the samples, it is evident that the eggshell calcined at 900°C for 1 hour exhibits a more homogeneous structure compared to the original eggshell. In other words, calcination resulted in a microstructure comprising dispersed grains. Following chemical precipitation and a second calcination, an interesting process unfolds. The particles appear to agglomerate, resulting in the formation of larger particles of varying sizes. These spherical agglomerates, predominantly small, occasionally manifest as larger entities, particularly noticeable at 1000 °C. However, upon comparison of images at 900°C, small-sized agglomerates were observed in eggshells, while large agglomerates were observed due to HAp synthesis. Furthermore, HAp exhibited agglomeration, leading to the formation of pores. Exposure of HAp samples to high temperatures is a factor that causes the skeletal structure to bond together [32, 33]. Other research has also found a similarly irregular particle structure of HAp derived from eggshells [17, 34]. Puad et al. also reported that increasing temperature causes particles to agglomerate, thus increasing the particle size. These findings are consistent with the results obtained from XRD and FTIR analyses of the microstructures formed as HAp begins to decompose [2].

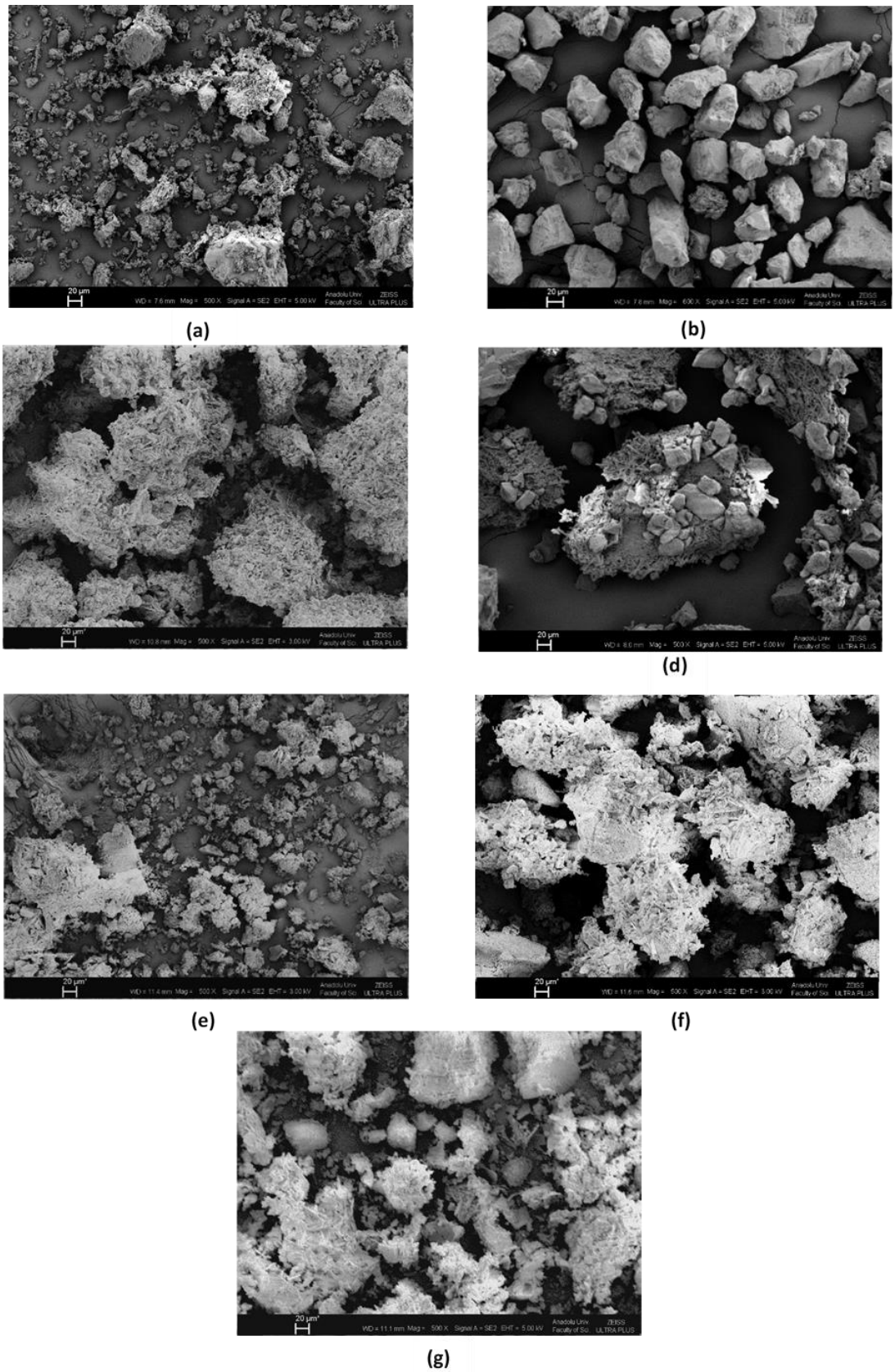


Figure 4. SEM images of **(a)** eggshell, **(b)** eggshell calcined at 900 ℃ for 1 hour, HAps calcined at **(c)** 500 ℃, **(d)** 700 ℃, **(e)** 900 ℃, **(f)** 1000 ℃ and **(g)** 1100 ℃

3.5. Thermal Analysis of Eggshell

In Figure 5, the DTA-TG curves for eggshells are presented. In the DTA curve, there is an endothermic peak at 115 ℃, indicating a sudden mass loss, which can be attributed to the removal of water from the eggshell. The TGA curve shows a 3.25% mass loss between 400 and 470 ℃, caused by the desorption of water and other particles from the eggshell. Another strong endothermic peak is observed in the DTA curve at 463 ℃. Starting at 600 ℃, the mass of $CaCO_3$ rapidly decreases, with a continuous loss up to 850 ℃. The wider endothermic curve between 600 and 854 ℃ shows a 16.82% mass loss, which indicates the conversion of calcium carbonate to calcium oxide with the release of carbon dioxide. Beyond 850 ℃, no further mass loss occurs, and the sample stabilizes. Haberko et al. state that the low endothermic effect should plausibly be attributed to the evaporation of water adsorbed on the high surface area of the material, and at higher temperatures, two exothermic effects occurred [11]. Khandelwal and Prakash stated from DTA-TG analysis that a weight loss of about 2% up to 600˚C due to evaporation of absorbed water [33].

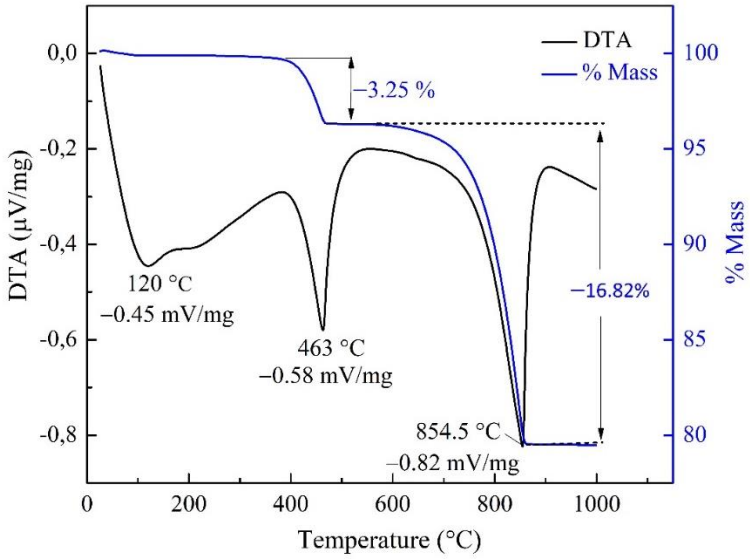


Figure 5. DTA-TG curve of eggshell

4. DISCUSSION AND CONCLUSION

In this study, HAp was synthesized from waste eggshells using chemical precipitation and calcination method and the effect of varying calcination temperatures (500 °C, 700 °C, 900 °C, 1000 °C, and 1100 °C) on the quality of HAp produced was investigated. The analyses were used to characterize the HAp samples synthesized from eggshells at these calcination temperatures. These included phase analysis (XRD), chemical analysis (XRF), molecular structure analysis (FT-IR), changes in the microstructure (SEM). Accordingly, the results can be explained as follows:

I) The XRD patterns for HAp samples with calcination temperatures of 900°C and above show a well-defined intense peak for the hydroxyapatite phase. XRD results show that the most suitable calcination temperature for HAp is 900 °C, and HAp samples calcined at 900, 1000 and 1100 °C contain peaks belonging to biphasic HAp and β-tricalcium phosphate (β-TCP) phase. In addition to the hydroxyapatite peaks at the highest temperature, weak peaks appeared at 25.8°, 34.5° and 44.1° attributed to monetite ($CaHPO_4$). If the calcination temperature is increased beyond 1100°C, we can expect the monetite phase to completely transform into hydroxyapatite.

II) The XRF results indicate that the HAp samples mainly consist of the elements Ca, P, and O. The calculated Ca/P ratio for the HAp samples recalcined at 900 °C is 1.73, which is close to the expected stoichiometric ratio of 1.67. Based on the XRF analysis, it can be inferred that the sample recalcined at 900 °C approaches the hydroxyapatite phase. However, the presence of the monetite phase, as revealed by the XRD results, also explains why the Ca/P ratio is not exactly equal to 1.67.

III) FT-IR results show that the characteristic bands of calcium carbonate (eggshell) are observed at 1424 and 875cm $^{-1}$. After heating at 900°C for 1 h to form CaO, the precursor of HAp, a decrease in the intensity of these characteristic bands is observed in the FT-IR spectra. When the FTIR spectrum of HAp was examined, the characteristic asymmetric P−O stretching band belonging to PO_4^{-3}in its structure was observed at 1086 cm^{-1} and 1024 cm^{-1}. The symmetric P−O stretching band was determined at 962 cm^{-1}. HAp, obtained in its purest form at 900°C, exhibited characteristic peaks at 571, 632, 962, 1046, and 1090 cm^{-1}. The intensities of most of the bands belonging to the phosphate vibrations of HAp increased at calcination temperatures of 700 °C and above.

IV) In the SEM images, we noticed small clusters in eggshells and larger clusters resulting from the synthesis of HAp. Following chemical precipitation and a second calcination process, the particles formed larger particles of different sizes. These spherical clusters were evident as larger agglomerates at 1000°C. As the HAp samples were subjected to higher temperatures, the skeletal structure became more tightly bonded.

V) The research shows that eggshells can be used as recycling material to produce HAp powder, help with waste management, and keep the environment clean. Further research is expected to be conducted using other waste materials such as seashells (cockles, clams and mussels), fish bones, cattle, chicken bones to synthesize larger amounts of purer hydroxyapatite. Specifically, researchers should investigate different calcination temperatures to determine the optimal temperature for producing the purest hydroxyapatite phase.

VI) Consequently, eggshells could be further synthesized and transformed into valuable Ca-based compounds such as hydroxyapatite (HAp), tri-calcium phosphate (β-TCP), calcite ($CaCO_3$), and calcium hydroxide $Ca(OH)_2$.

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CONFLICT OF INTEREST

The authors stated that there are no conflicts of interest regarding the publication of this article.

CRediT AUTHOR STATEMENT

Nur Bayram: Investigation, Writing – original draft, Visualization. **Sedef Dikmen:** Resources, Validation, Formal analysis. **Semra Malkoç:** Conceptualization, Methodology, Project administration, Resources, Funding acquisition.

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