

Article

Upcycling of Eggshell Waste into Calcium Phosphates for Use in Sustainable Biomedical Engineering Applications

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Abstract: Eggshells are an inorganic waste, and their accumulation rate is increasing globally, complicating waste management. However, the European Union defines eggshells as low-risk material that can be recycled and reused safely in other applications. Their chemical composition renders them an attractive precursor of calcium phosphate materials (CaPs). Because of their remarkable biocompatibility and capacity for natural degradation, CaPs are frequently employed in biomedical engineering applications. In this research, the wet precipitation method was employed for fabricating CaP powder. Initially, the eggshells were processed into CaCO_3 powder and then reacted with HCl to obtain CaCl_2 (aq). This reacted with Na_2HPO_4 to obtain a precipitate that was filtered and dried. The precipitate in powder form underwent X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) analysis to evaluate its microstructure, and elemental and phase composition. The results indicated that the recovered powder was brushite.

Keywords: eggshells; recycling/upcycling; calcium phosphates; wet precipitation; biomaterials; biomedical; sustainability



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1. Introduction

Egg production increased massively through the years all over the world and it is estimated that in the future egg production will sustain its increasing rate, reaching 90 million tons by 2030 [1,2]. Eggshell represents 9–12 percent of the egg's weight [1,3], reaching about 10 million tons. Until now, eggshell waste management included its deposition to landfills leading to environmental degradation [1–3]. Eggshells consist of 98 percent dry matter, while the rest is water [1,4,5]. The dry matter is mainly composed of eggshell ash [4] and its predominant element is CaCO_3 [6], while a small fraction of crude protein also exists [1,4]. Among the elements observed in smaller fractions is sulfur, emitted in the form of H_2S during the decomposition of sulfide proteins, causing odor [7]. In addition to odor, microbial growth is also observed [1–3,7], and apart from its environmental impact, eggshell waste management becomes cost-effective due to the necessity of transporting the waste away from inhabited regions [7].

The European Union has classified animal wastes into three categories, depending on the risk potential of public health, starting with category 1, which represents animal by-products of high public health risk, and going up to category 3, which stands for waste of low risk [8]. Eggshells belong to the latter category, which means that this waste can be reused after processing [8].

Calcium phosphate (CaP) materials belong to the added value materials that can be derived from eggshells [9–11]. CaP materials are monetite (CaHPO_4), brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$), a-tricalcium phosphate ($\text{a-Ca}_3\text{PO}_4$), b-tricalcium phosphate ($\text{b-Ca}_3\text{PO}_4$), monocalcium phosphate ($\text{Ca}(\text{H}_2\text{PO}_4)_2$), oxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6\text{O}$), octacalcium phosphate $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$, tetracalcium phosphate $\text{Ca}_4(\text{PO}_4)_2\text{O}$, and calcium pyrophosphate ($\text{Ca}_2\text{P}_2\text{O}_7$), and the most important is hydroxyapatite. $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$'s properties are the most desirable ones [11–13]. All of the aforementioned CaPs are distinguished from each other by the molar ratio of calcium to phosphate, whose range is between 0.5 and 2 [14]. In general, calcium phosphates are applied in many fields. One of the most important sectors is biomedicine, as calcium phosphate-based biomaterials.

Biomaterials are commonly used in the medical field [15]. Their purpose is to integrate into the human body to support proper tissue function, with this integration being either permanent or temporary, depending on the specific medical application [16]. Biomaterials have been developed over the years. Right now, we are going through the third generation of biomaterials. In this generation, the goal is to develop materials that interact effectively with the tissue systems in the body where they are implanted, promoting tissue restoration and optimization [16]. There are another two generations of biomaterials: the first and the second. The first generation dates back to the 1940s. The materials used during this time were primarily metallic alloys and polyester polymers. While these materials were biocompatible, they did not bond with tissues and were mainly used to meet mechanical needs. Lastly, the second biomaterials' generation dates between the 1960s and the 1990s. In this generation, the materials could be accepted by the human body [17]. Also, the materials were called bioactive and their aim was to restore, for example, bone restoration [18]. Nonetheless, in this generation, despite any improvements compared to the first generation, the biomaterial could not attach to the tissue [2]. Biomaterials are categorized in two categories: biological biomaterials and artificial biomaterials. Biological biomaterials are organic as they are derived from biological systems. Artificial biomaterials, on the other hand, are synthetically produced [15].

Calcium phosphates and other calcium-based biomaterials are commonly used in the medical industry due to their exceptional biocompatibility and ability to break down naturally. Different biomaterials with unique physicochemical characteristics have been thoroughly studied and advanced in medical and public health sectors, such as disease detection, medication distribution, and organ regeneration. From this perspective, biomaterials are growing in significance in the medical field, and their effective utilization will significantly enhance the quality of life for countless individuals globally. In addition, due to the fast advancements in various functional biomaterials and assisted reproductive technologies, there is a growing tendency among clinicians and researchers to utilize these biomaterials in reproductive biology, leading to significant advancements [19]. Recently, calcium-based biomaterials have been combined with imaging contrast agents and therapeutic agents for different molecular imaging techniques, and for various therapeutic methods. Compared to other biomaterials, calcium-based biomaterials have the ability to dissolve into harmless ions and are able to be involved in the natural metabolism of living organisms. Therefore, they provide more secure clinical options for disease theragnostics [20]. Calcium phosphate nanoparticles do not possess any intrinsic toxicity, but they can result in a rise in the intracellular calcium concentration following their uptake into endosomes and degradation in lysosomes [21]. In their research in 2024, Fan et al. [22] investigated how CaP-based biomaterials could affect cell metabolism. They concluded that CaP ceramic surfaces create a less oxidative environment for cells by absorbing oxidized metabolites, leading to increased cell viability and reduced oxidative stress due to their unique physicochemical properties.

All hard tissues of the human body, like bones and teeth, consist of calcium phosphates [14,23]. For example, hydroxyapatite (HAp) is the most important mineral within bones consisting of 70 percent of it [24]. Another CaP is tricalcium (TCP) which is also utilized in bone regeneration applications [25,26]. Tlmacheva al. [27] investigated the uses

of 3D-printed scaffolds made with calcium phosphates, and explored why some types of calcium phosphates are more common than others in the scientific community. Moreover, monetite gained attention over orthopedic applications and in many cases seems to be preferred over traditional CaPs like HAp and TCP [25]. Another applied field is wastewater treatment [25]. Materials that have shown efficiency in adsorbing heavy metals are monetite, HAp, and brushite [28–31].

Additionally, CaPs participate in catalytic reactions both as a catalyst and inorganic support [32]. The most used CaP in this category is HAp, while many studies have been conducted, proving that HAp catalytic systems are promising [32–34]. In addition to HAp, TCP showed great catalytic behavior and reusability of about five times more [35,36]. Lastly, CaPs are applied also to agriculture [16], where HAp nanoparticles are applied [37,38]. To acquire CaP material from eggshells, the chemical wet precipitation method was employed [9,13]. The eggshells were converted into CaCO_3 powder and calcined to CaO through high-temperature exposure. In this way, it was ensured that the existing carbon dioxide was removed from the powder. Then, the powder was dissolved into chemical reagents under stirring at a constant temperature. After stirring, a solid matter was created and it was acquired through filtration. Then, the residue was dried and finally, it was sintered to the desired temperature.

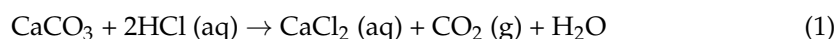
Eggshells constitute a highly used precursor for calcium phosphate synthesis due to their abundance in calcium. Alternative precursor materials include animal bones, corals, and synthetic sources. Corals provide a natural structure similar to bone but require extensive processing to remove organic components. Bones, on the other hand, contain natural hydroxyapatite but carry contamination risks. Synthetic sources, such as lime sludge, are increasingly being explored, but they have major setbacks such as their impurity content, variability in composition, and the environmental harm their processing offers [39].

In this research, we focused on recovering calcium and turning it into CaP starting from eggshell waste using the wet precipitation technique. The eggshells were processed into powder form and, after two chemical reactions, the initial powder was turned into a CaP sediment. For this purpose, experimental details from other relevant studies were critically reviewed and an innovative approach was adopted therein, to transform/upcycle this secondary resource (eggshell waste) via the wet precipitation method into a high-value-added CaP powdery product, for the first time brushite, with significant applications in the field of biomedicine, offering potential advancements in various medical and healthcare technologies.

2. Materials and Methods

For the recovery of the CaP powder, 70 white-celled chicken eggshells were used, due to their high calcium content. After removing the interior (yolk), the eggshells were rinsed with distilled water to remove the inner membrane layer. Then, to obtain the desired form (powder) they were dried at 110 °C, crushed, and sieved using a 100 m mesh sieve [9,13,40].

The powder that was obtained (64.88 g) required the removal of any impurities, so it was subjected to 15 min of boiling [41] and then washing with 70% alcohol using a Whatman-type filter no. 1 (Sigma-Aldrich, St. Louis, MO, USA and Burlington, MA, USA). Finally, it was dried at 45 °C for 24 h. An X-ray diffraction (XRD) using Bruker D8 advance (Bruker, Billerica, MA, USA), in addition to an energy dispersive X-ray spectroscopy (EDS) analysis (Jeol Ltd, Tokyo, Japan), took place to determine the chemical composition and structure of the powder [40]. At this point of the study, after the eggshell powder was cleaned of impurities and other substances, we began the wet precipitation process to obtain the desired CaP form. The wet precipitation method was performed based on Equation (1), as follows:



26.8 g of the eggshell powder was added into 500 mL of HCl (aq) (Supelco, Bellefonte, PA, USA) under low pace constant stirring for 2 h to avoid undesirable effects during the removal of CO₂. Then, 21.3 g of Na₂HPO₄ (Sigma-Aldrich, St. Louis, MO, USA and Burlington, MA, USA) was added into the obtained solution under constant stirring at 50 °C for 1 h Equation (2).



To retrieve the precipitate, the solution was vacuum filtered using Whatman filter no.1. The obtained powder was then dried at 100 °C for 24 h (ThermConcept, Bremen, Germany) and measured at 14.96 g. Finally, calcination of the powder at 900 °C for 2 h at a rate of 2 °C/min, took place. Also, the final form of the powder underwent scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) (SEM/EDS) and XRD analysis to determine the achieved result [40].

3. Results and Discussion

The results of the XRD analysis on the eggshell powder showed similarities with those in the literature [40]. Specifically, the chemical structure of the eggshells consisted mostly of CaCO₃ and other trace elements in lower content. In Figure 1, the corresponding peak plot is also depicted. The aforementioned analysis was proven by the EDS analysis, which showed a strong presence of calcium and carbon, and secondarily iridium and magnesium. The EDS analysis of the eggshells is depicted in Figures 2 and 3 depicts the microstructure of the initial material.

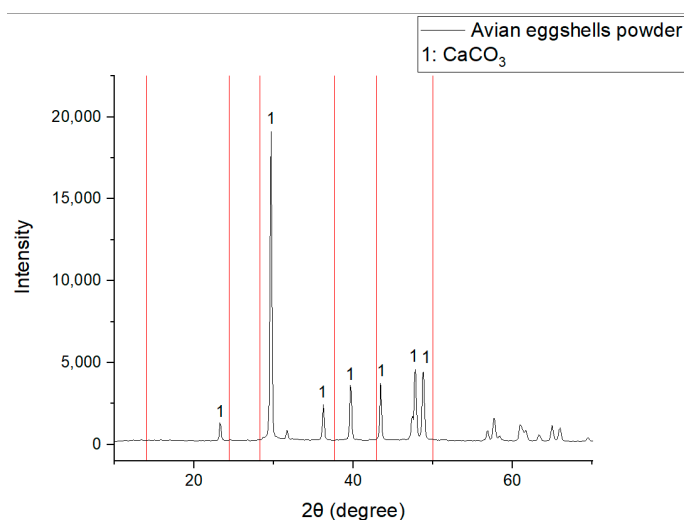


Figure 1. XRD analysis of the eggshells, demonstrating the chemical structure of the eggshells consisted mostly of CaCO₃ and other trace elements in lower content. The red lines represent the fitting of the instrument, incorporating the theoretical peaks of CaCO₃.

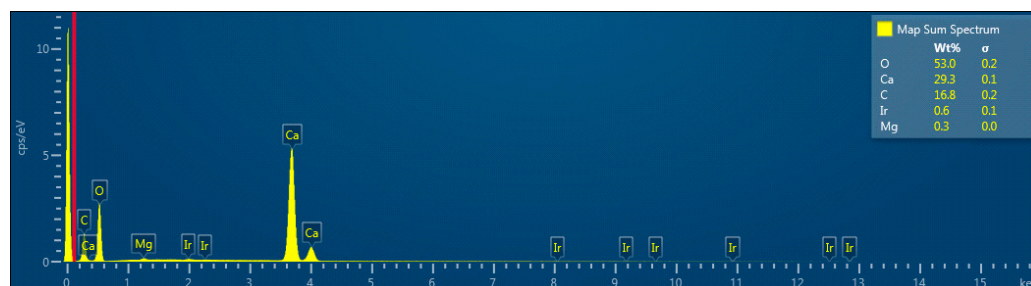


Figure 2. EDS results for the eggshells, confirming the XRD analysis results, proving the strong existence of CaCO₃ and some other trace elements.

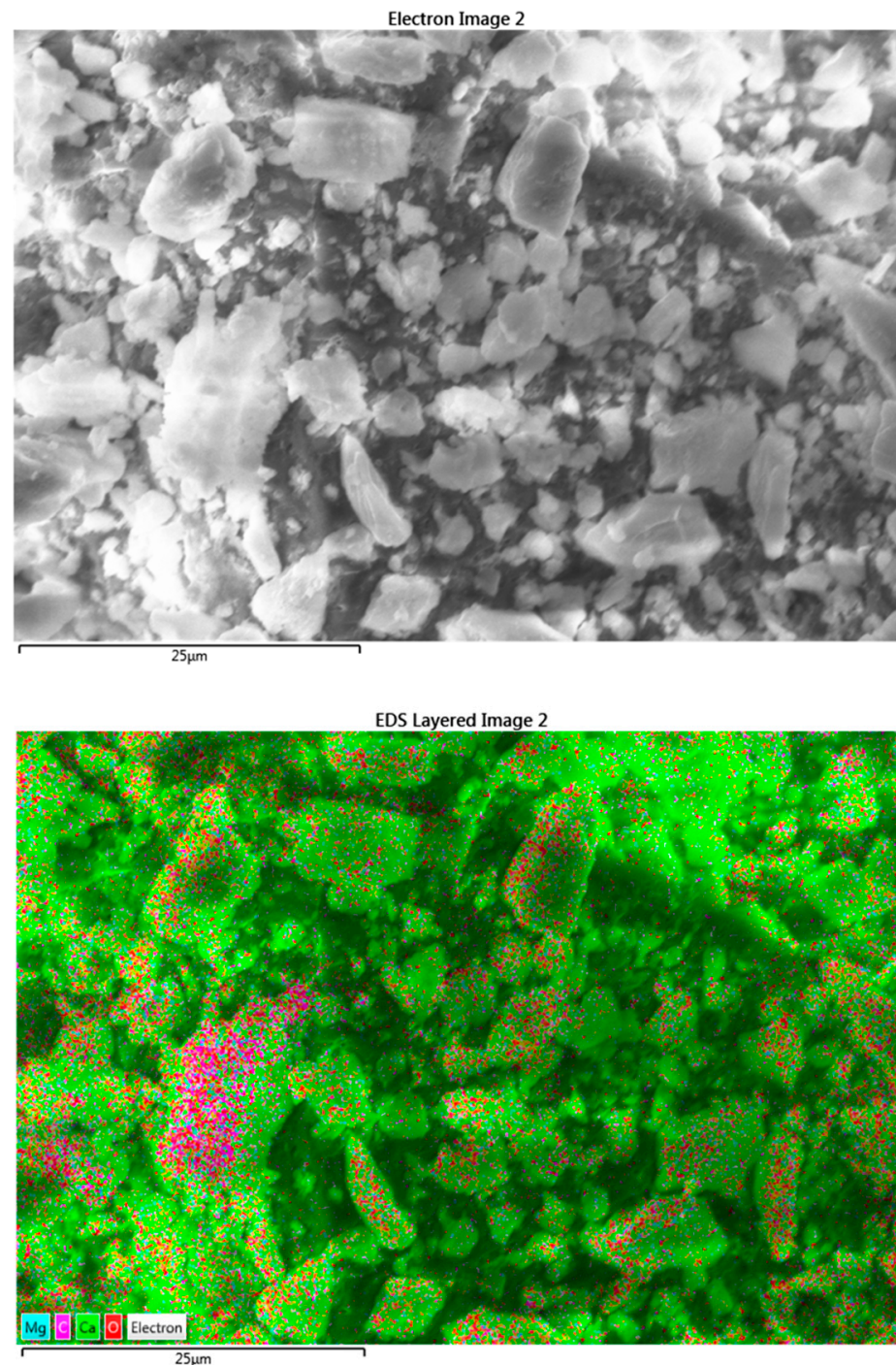


Figure 3. SEM analysis for initial material with elemental mapping.

Regarding the CaP powder that was obtained after the precipitation, XRD analysis (Figure 4) showed the transformation of the initial structure of the eggshell powder (CaCO_3) to a different one, which highly resembled the one of brushite. The EDS analysis (Figure 5) of this specimen also demonstrates brushite formation. Specifically, the % wt composition of the elements was close to the theoretical ones for brushite, with low deviation.

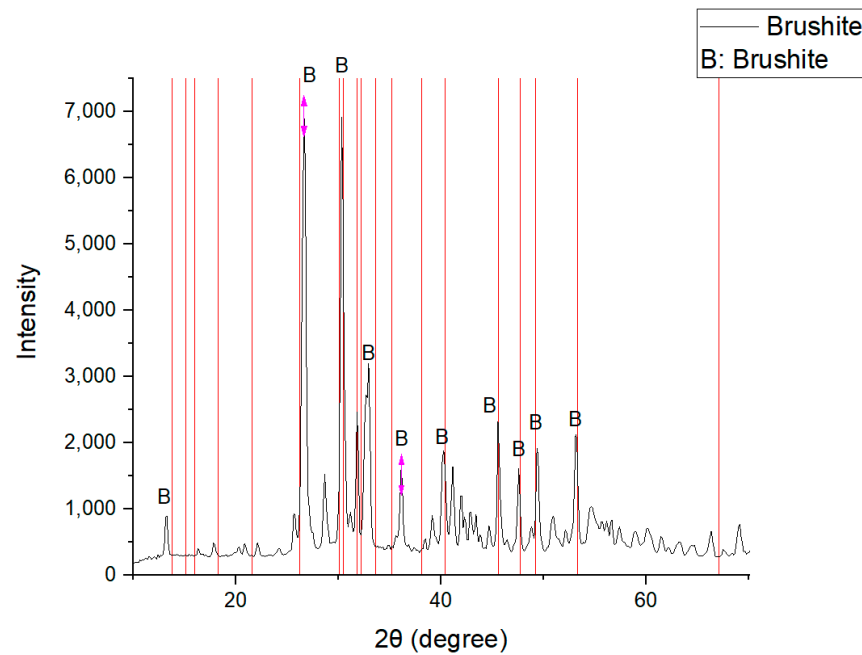


Figure 4. XRD analysis of the powder produced, verifying the transformation of the initial eggshell structure into CaP powder corresponding to brushite. The red lines represent the fitting of the instrument, incorporating the theoretical peaks of brushite.

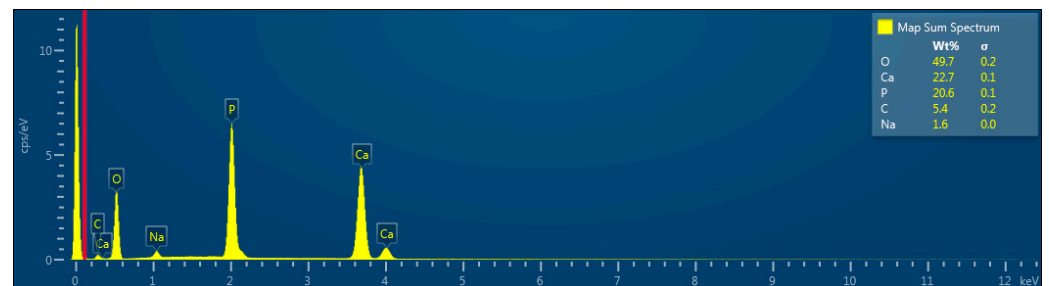


Figure 5. EDS results for CaP material, whose % wt elements' ratio resembles brushite's.

Figures 6 and 7 depict the microstructure of CaP powder. Conversely, there does not seem to be any significant porosity in the powder, as the pores presented are a small percentage [42]. Additionally, as depicted in Figure 4, CaP comes with a high carbon content. Analyzing the precipitation step, HCl was chosen as the reagent as it provides ease of use, low risk, and cost. Its use had a dual significance: it helped to remove CO₂ as well as to produce the CaCl₂ salt that is important for the subsequent transformation to CaP. At the beginning of the process, with the addition of the first few quantities of HCL into the solution, intense foaming started to appear due to the high concentration of CO₂ in the solution. The more HCl was added, under constant stirring, the more the foaming phenomenon subsided. The intensity of the phenomenon subsided after approximately 30 min, while after 2 h of constant stirring, no visual signs of CO₂ inside the solution existed. It is possible that a longer exposure to constant stirring would have lowered the amounts of carbon inside the final powder.

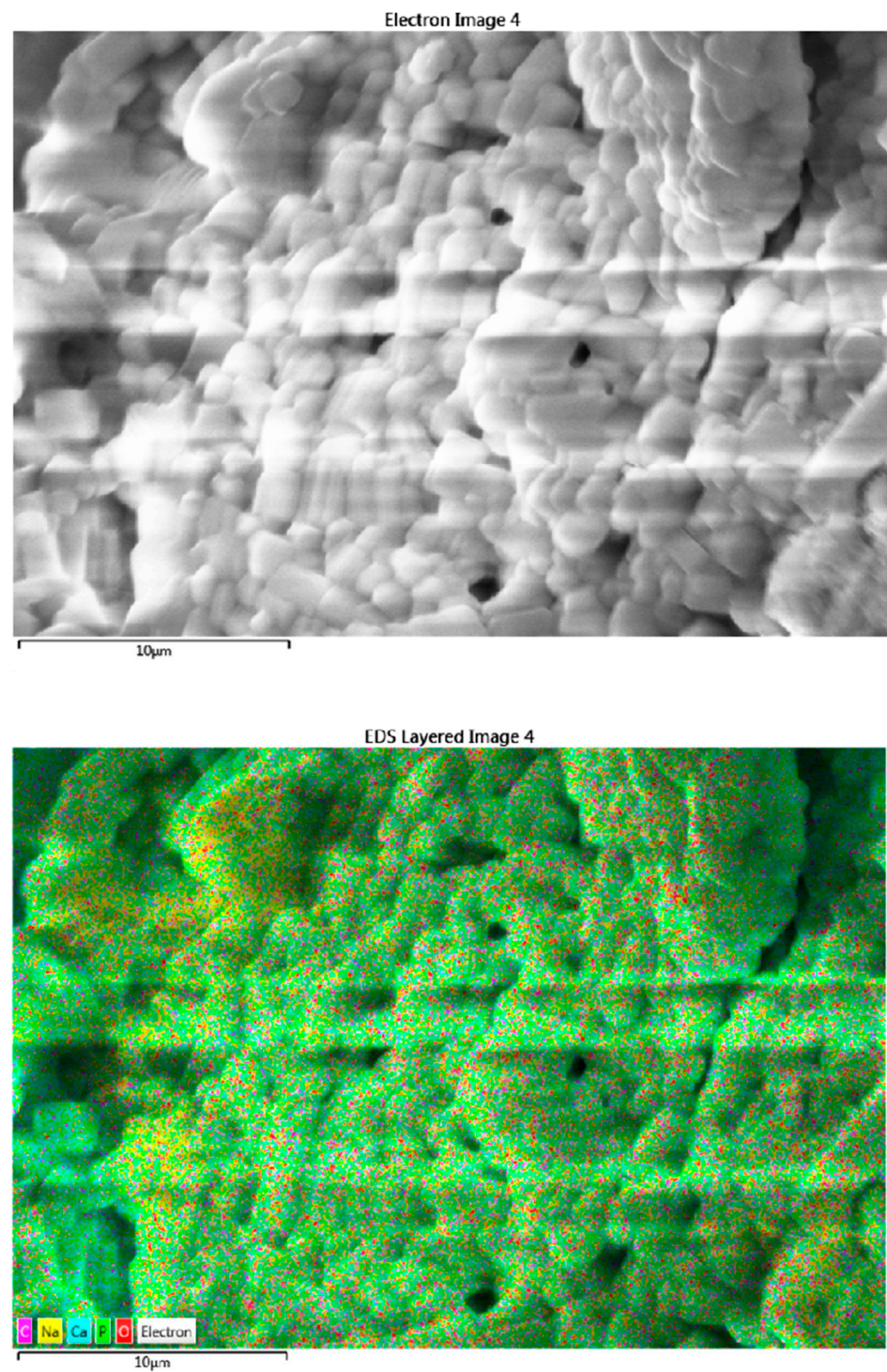


Figure 6. SEM analysis of CaP powder with elemental mapping.

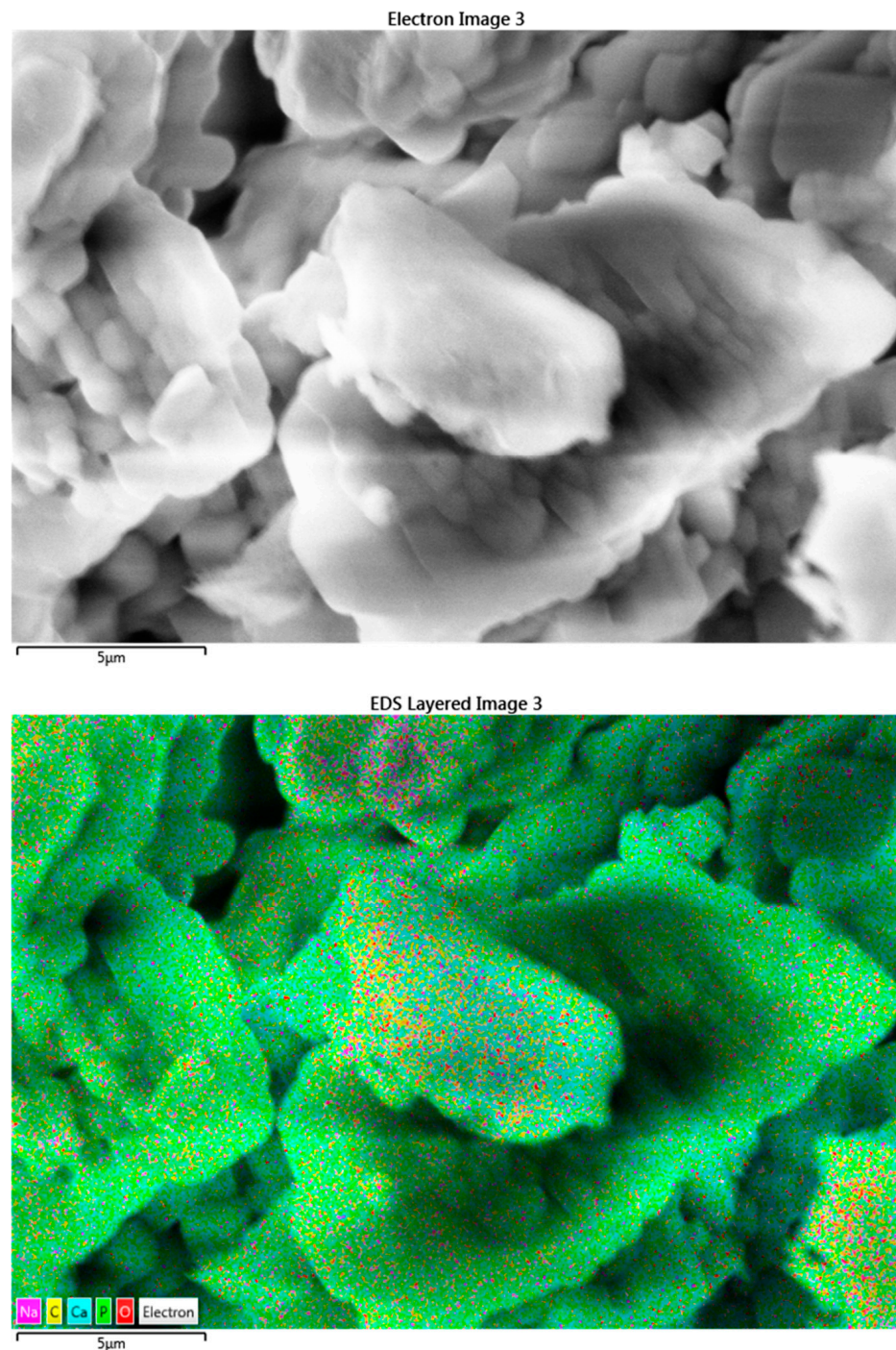


Figure 7. SEM analysis for initial final product with elemental mapping.

According to our analysis from EDS and XRD, we finally determined that the acquired material is brushite, especially in XRD analysis, where the diagram fits perfectly with brushite ones. EDS analysis also indicates brushite formation.

The wet precipitation method yielded a calcium phosphate (CaP) material. EDS analysis indicated brushite formation and it strongly aligned with the XRD analysis, which also indicated the brushite's formation. Brushite application in biomedical engineering is mainly in the human skeletal system, due to its resemblance to bones' structure and capability to regenerate them [43], while further research is conducted to evaluate the brushite's involvement in drug delivery systems [44,45]. The current studies in biomedicine are focusing on metal-doped brushite. The incorporation of metal ions can enhance the

mechanical and biological properties of the material, rendering it more suitable for bone treatment applications [43]. The wet precipitation method yielded CaP material as expected, which was cost-effective, with low energy requirements, and easy to operate [46]. It also has an environmental benefit, as the only emission is CO₂ which is emitted according to Equation (1).

4. Conclusions

The increased production of eggshell waste and its high composition in CaCO₃ makes it an ideal precursor of CaP materials. In fact, in this research, the fabrication of CaP powder was successfully attained via wet precipitation. The final powder form obtained was brushite, which is justified by the XRD and EDS analysis results. Further research is underway to assess the potential of the CaPs obtained for use in biomaterial development for biomedicine applications. Altering wet precipitation variables can be useful, in view of future optimization research for modeling this process. Thoroughly studying and appropriately adjusting the system parameters may lead to the production of different CaP phases and also affect their morphology. An increase in stirring time can be applied to evaluate its role in CO₂ removal mechanism. Also, experimentation with reaction conditions, such as temperature, reagent concentration, and pH may be conducted to assess their impact on the phase of the final CaP product, its properties and its potential application in biomedical engineering applications.

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Conflicts of Interest: The authors declare no conflicts of interest.

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