RESEARCH PAPER

Biowaste to Biomaterial: Synthesis and Characterization of Eggshell-Derived Hydroxyapatite Nanoparticles

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ABSTRACT

Hydroxyapatite (HAp) nanoparticles synthesized from biogenic resources have emerged as promising materials for sustainable environmental applications. In this research, eggshell waste was utilized as an alternative calcium precursor for the synthesis of hydroxyapatite nanoparticles. The biowaste was cleaned, dried and calcined to obtain calcium oxide, followed by controlled reaction with phosphate source to produce HAp nanoparticles under optimized conditions. The main objective of the research was to synthesize hydroxyapatite nanoparticles from eggshell waste using chemical precipitation method. The characterization of the HAp nanoparticles was investigated using Scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). SEM analysis revealed hydroxyapatite nanoparticles with irregular morphology and particle size in the nanometer range. EDX confirms the elemental composition of HAp nanoparticles by providing the Ca/P ratio, which was 1.31. XRD investigation revealed a distinctive apatite peak at 31.0 to 32.5 for 2θ values, indicating the formation of HAP nanoparticles. XRD patterns confirmed the crystalline nature and phase formation of hydroxyapatite nanoparticles. The FTIR spectrum's peaks show that the powder sample contains hydroxyl (OH-), phosphate (PO_4^{3-}), and carbonate (CO_3^{2-}) groups, which validates the synthesis of that HAP nanoparticles. As per the findings, eggshell waste was successfully converted into hydroxyapatite (HAp) nanoparticles, which were confirmed by characterization techniques.

Keywords: Hydroxyapatite, Eggshells, Precipitation, Characterization.

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1. Introduction

The increasing demand for sustainable and eco-friendly nanomaterials has encouraged the utilization of biowaste as a low-cost resource for nanoparticle synthesis [1,2]. Eggshells are a valuable precursor for calcium-based biomaterials since they are produced in significant quantities from the domestic and food industries and are primarily constituted of calcium carbonate [3,4]. In addition to reducing environmental impact, turning eggshell waste into valuable nanoparticles promotes waste valorization and circular economy strategies [5]. Hydroxyapatite (HAp) nanoparticles have drawn a lot of attention recently because of their special physicochemical characteristics, which include high biocompatibility, porosity, thermal stability, and adsorption potential [6-8]. Because of these qualities, HAp nanoparticles can be used in water treatment technologies and environmental remediation. Hydroxyapatite nanoparticles can be synthesized using a variety of techniques. Using natural waste-derived precursors has benefits which includes low production costs, less chemical use, and environmental sustainability [9-13]. While offering a more affordable and environmentally friendly option, eggshell-derived HAp nanoparticles share structural and compositional characteristics with synthetic hydroxyapatite. The resultant hydroxyapatite nanoparticles' shape, crystallinity, particle size, and purity are strongly influenced by the synthesis procedures, and these factors have a direct impact on their functional performance [14,15]. As a result, thorough characterization is necessary to verify that hydroxyapatite nanoparticles were successfully formed.

In this study, eggshell waste was used as a sustainable calcium source to synthesize hydroxyapatite nanoparticles. The crystalline structure, surface morphology, and elemental content of the synthesized nanoparticles were examined using scanning electron microscopy (SEM), energy dispersive X-ray (EDX) analysis, X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The findings demonstrate an environmentally benign and

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economically viable strategy for converting eggshell biowaste into functional hydroxyapatite biomaterials. This study highlights the significance of waste valorization and supports the development of sustainable biomaterials from naturally available biogenic waste resources.

2. Materials and Methods

The eggshells were collected from local egg shops and were used for the synthesis of hydroxyapatite nanoparticles. The collected eggshells were properly cleaned with distilled water in order to get rid of organic matter and clinging contaminants followed by boiling and drying in a hot air oven, as shown in Figure 1(a) and (b).



(a)



(b)

Figure 1. (a) Boiling of eggshells; (b)Drying of cleaned eggshells in hot air oven.

The method of chemical precipitation was used to synthesize hydroxyapatite (HAp) nanoparticles as shown in Figure. 2.

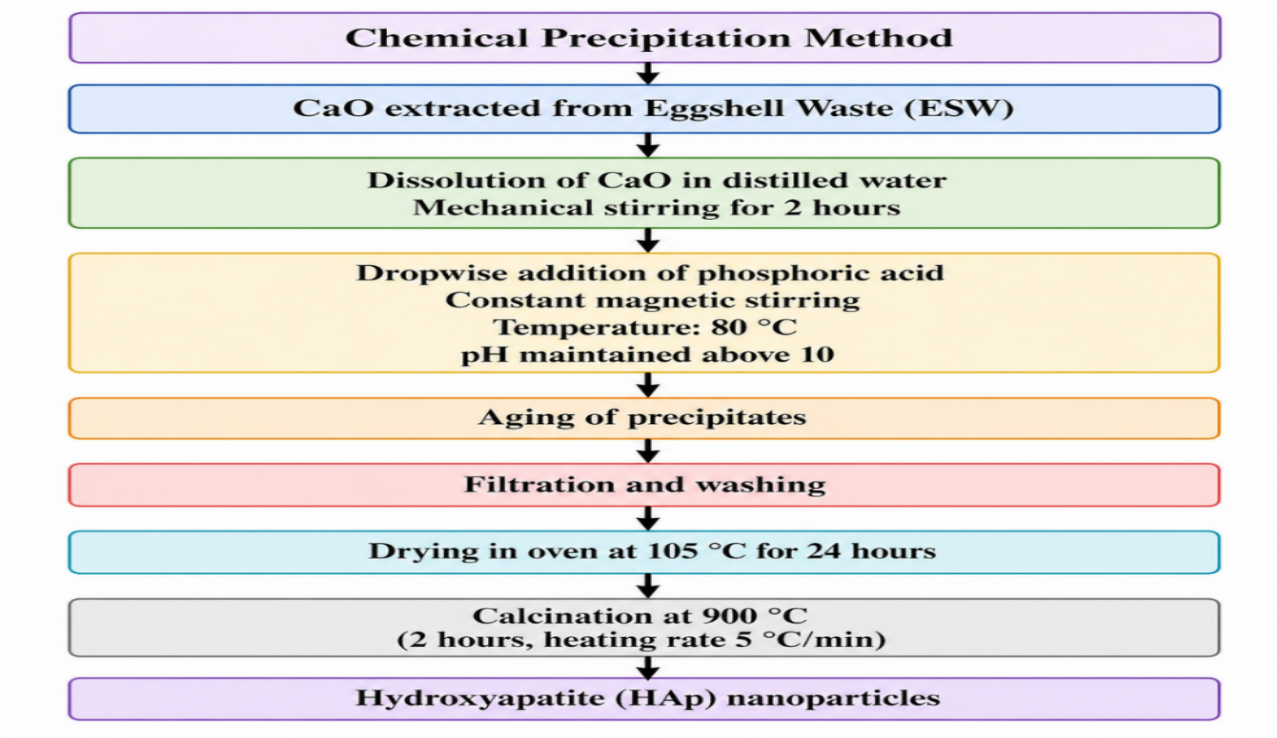


Figure.2. Stepwise synthesis route of hydroxyapatite (HAp) nanoparticles

This method involved the preparation of a calcium precursor, such as calcium hydroxide in an aqueous solution and the separate dissolution of a phosphate source, such as diammonium hydrogen phosphate. In order to promote the formation of hydroxyapatite precipitate, pH level of the reaction mixture was brought to a basic range (about 10–11) using NH_4OH.

To ensure full precipitation and formation of hydroxyapatite nanoparticles, the solution was constantly agitated. After aging, the white precipitates were left overnight to settle down and the solution was filtered. The product was repeatedly cleaned with distilled water to get rid of contaminants and unreacted ions. In order to improve crystallinity, the precipitates were dried at a moderate temperature. At the end of the process, white crystalline hydroxyapatite nanoparticles were obtained.

3. Characterization of Synthesized Hydroxyapatite Nanoparticles

The synthesized hydroxyapatite (HAp) nanoparticles were characterized using analytical techniques including Scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR). SEM micrographs demonstrated irregular and aggregated particles with porous surface features. The atomic and weight percentage of all the elements in HAp nanoparticles were computed using EDX to find the calcium to ratio of phosphate. The crystalline material's phase identification was analysed using XRD. The XRD patterns of prepared nanoparticles were recorded in the 2θ range of 15° to 80°. The FTIR range of 600 cm-1 to 4000 cm-1 was selected for the examination of HAp nanoparticles functional groups.

4. Result & Discussion

4.1 SEM analysis

The surface morphology of the manufactured hydroxyapatite (HAp) nanoparticles made from

eggshell waste was investigated using scanning electron microscopy (SEM). The production of irregular to almost spherical nanoparticles with observable agglomeration is shown in the SEM micrographs (Figure 3). The images are taken at (a) and (b) 100,000 x magnification. Due to strong interparticle interactions and high surface energy, such agglomeration is frequently seen in nanoscale materials. The comparatively tiny individual particles appear to be grouped together to create porous aggregates. The particular surface area and availability of active areas for interaction with metal ions are increased by this porous structure [17,18]. The effective production of nanoparticles using the precipitation process was confirmed by the particle size, which was less than 100 nm.

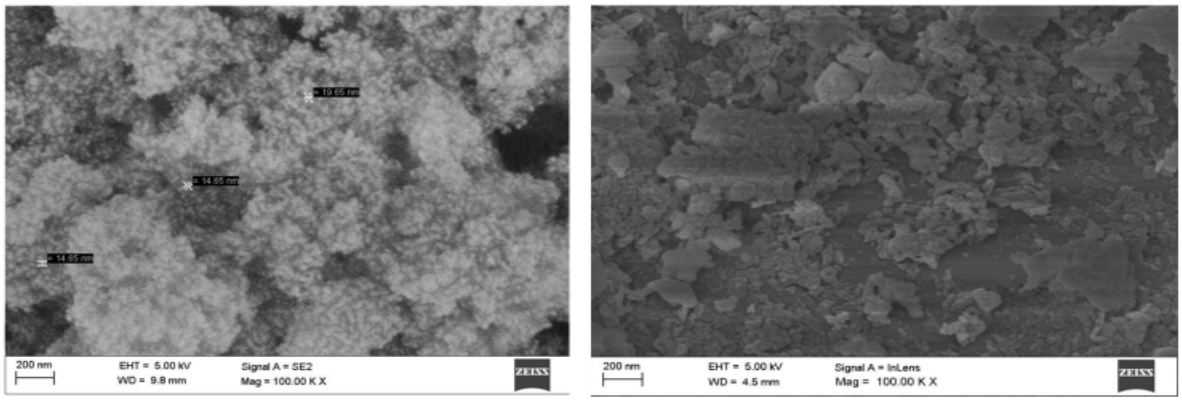
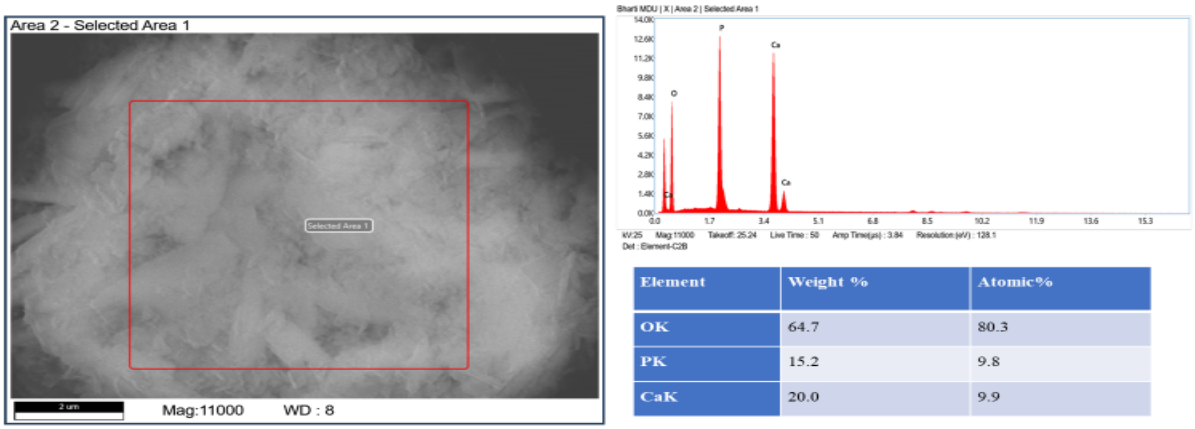


Figure. 3 SEM micrograph of HAp nanoparticles at (a) and (b) 100,000 x

4.2. EDX analysis

EDX analysis revealed the presence of calcium (Ca), phosphorus (P), and oxygen (O) with significant weight and atomic percentages, and the Ca/P ratio around 1.31 confirmed the formation of stoichiometric hydroxyapatite nanoparticles [19]. Figure 4 displays the EDX analysis of chemically synthesized HAp nanoparticles.



Element	Weight %	Atomic%
OK	64.7	80.3
PK	15.2	9.8
CaK	20.0	9.9

Figure. 4 EDX analysis of HAp nanoparticles

4.3. X-Ray Diffraction Analysis

The crystalline structure and phase composition of the produced hydroxyapatite nanoparticles were examined using X-ray diffraction (XRD) analysis. The prepared HAp nanoparticle's X-ray diffractogram is displayed in Figure 5. The 2θ scan range was chosen to be between 15 and 80 degrees. The apatite's typical peak at 31.75 of 2θ values, was clearly visible [19,20]. HAp nanoparticles were calcined at temperature around 900 degrees Celsius. The XRD diffractogram makes it evident that there is no breakdown of HAP and that the intensity of the prominent peak at 31.75, increased with temperature up to 900 degrees celsius. These findings support the formation of HAp nanoparticles which are consistent with earlier research [21,22].

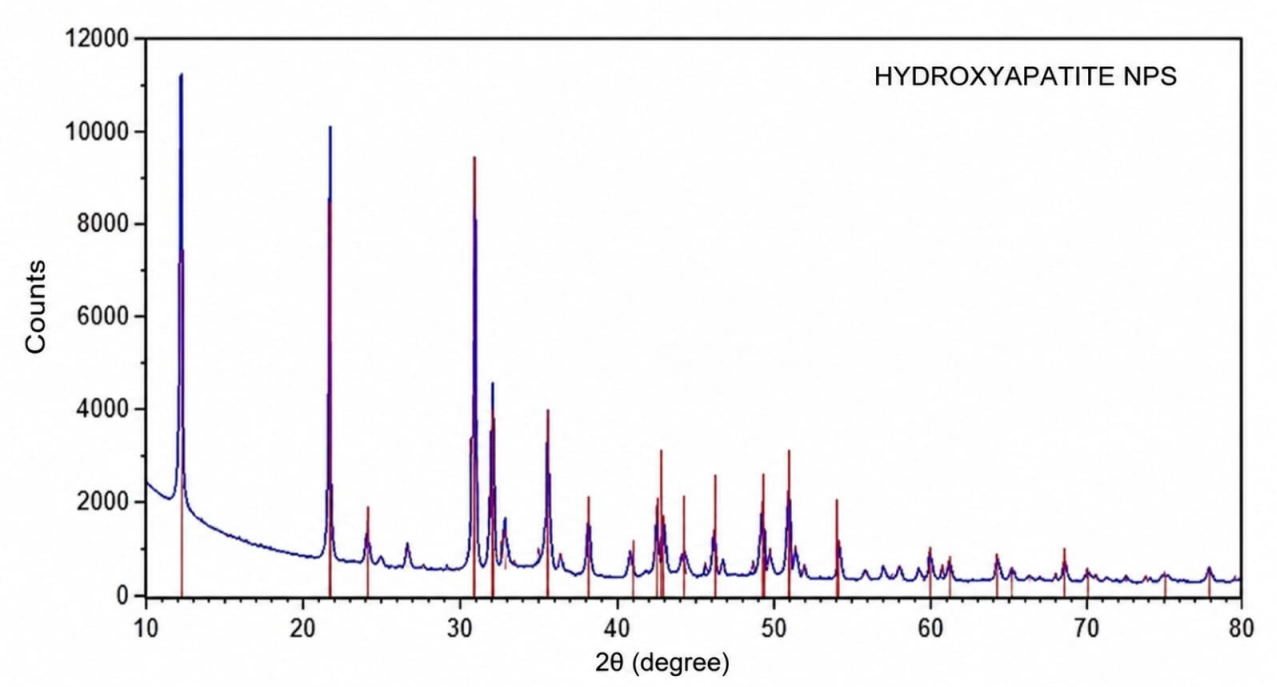


Figure.5 XRD Pattern for HAp nanoparticles

4.4 FTIR Analysis

The production of hydroxyapatite nanoparticles was confirmed and the functional groups were identified using Fourier Transform Infrared spectroscopy. Phosphate (PO_4^{3-}), hydroxyl (OH^-), and carbonate (CO_3^{2-}) groups are represented by distinct vibrational bands in the FTIR spectra of the produced HAp nanoparticles. (Figure.6).

The stretching vibration of hydroxyl (–OH) groups, a feature of hydroxyapatite, is responsible for the wide absorption band about 3620.38 cm^{-1}. Furthermore, a faint band about 650.21 cm^{-1} is associated with the bending vibration of adsorbed water molecules, suggesting the existence of surface-bound moisture, which is frequently seen in nanostructured HAp because of its large surface area. Strong absorption bands in the 1000–1150 cm^{-1} range demonstrate the existence of phosphate groups, the primary structural components of hydroxyapatite. The asymmetric stretching vibrations (ν_3) of PO_4^{3-} ions are responsible for these bands. The symmetric stretching vibration (ν_1) of phosphate groups is represented by the sharp band seen at 954.01 cm^{-1}. The vibrational modes of the carbonate ion (CO_3^{2-}) can be used to identify its distinctive bands. The ν_1 symmetric C–O stretching vibration of CO_3^{2-} is represented by a peak at around 1050–1100 cm^{-1}. The carbonate group's σ_2 out-of-plane bending vibration is responsible for the band seen between 870 and 900 cm^{-1}, while the ν_4 in-plane bending mode is responsible for the peak about 650 cm^{-1}. The existence of carbonate groups in the sample is confirmed by these peaks. The efficient formation of pure hydroxyapatite nanoparticles was confirmed by the presence of all distinctive phosphate and hydroxyl vibrational bands [20-22].

Overall, the FTIR analysis revealed the formation of hydroxyapatite nanoparticles with distinct functional groups, which makes their use in environmental remediation, and heavy metal ion adsorption.

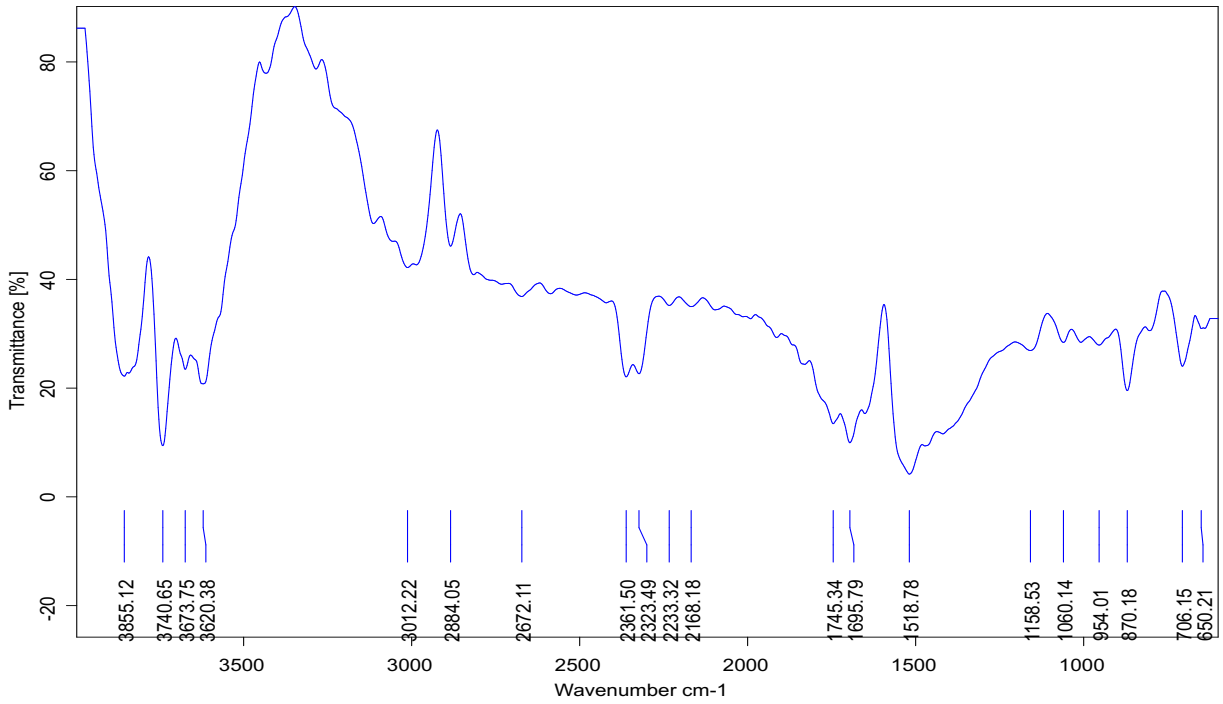


Figure. 6. FTIR Spectra of HAp nanoparticles

5. Conclusion

The present study effectively synthesized hydroxyapatite (HAp) nanoparticles from discarded chicken eggshells using a sustainable waste valorization strategy. The development of HAp nanoparticles was verified by SEM examination confirmed the synthesized material's nanoscale shape and well-defined particle structure, showing that nanoparticles were successfully formed. With a Ca/P ratio of around 1.3, which is near the stoichiometric value of hydroxyapatite and indicates the effective integration of calcium and phosphate into the apatite framework, EDX analysis verified the elemental composition of the nanoparticles. The crystalline quality of the produced HAp nanoparticles was shown by XRD data, and phase purity and successful HAp production were confirmed by FTIR spectra that confirmed the existence of distinctive phosphate and hydroxyl functional groups. Overall, the results show that leftover eggshells may be used as an effective and affordable calcium precursor for the synthesis of superior hydroxyapatite nanoparticles. This ecologically friendly method not only encourages resource recovery and sustainable waste management, but it also offers a viable path for the synthesis of value-added nanomaterials for adsorption and environmental applications.

CRediT authorship contribution statement

Bharti Singh: conceptualization, visualization, literature search, original draft, and writing—review and editing. Sandeep Kumar: investigation and writing—review and editing. Rachna Bhateria: Conceptualization, review, editing draft, and supervision. All authors read and approved the final manuscript.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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