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Characterization of Nano Calcium Carbonate Extracted From Eggshells

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Abstract: Organic waste, especially eggshells, represents a valuable resource for the synthesis of calcium carbonate nanoparticles, which have significant industrial and medical applications. This study describes the methodology for converting eggshells into calcium carbonate nanoparticles through heat treatment and nano milling processes. Advanced characterization techniques, including TEM, SEM, and AFM, were used to analyze the morphology and structure of the synthesized nanoparticles. The particles were found to be of nanometer dimensions, with a size of around 150 nm and a distinctive spherical shape, as shown in the TEM images. SEM images showed that the surface of calcium carbonate nanoparticles synthesized from eggshells is smooth, crystalline, and spherical or nearly spherical. FTIR analysis revealed the presence of distinct functional groups for calcium carbonate, with peaks at 713–868 cm^{-1}, consistent with previous studies. The results show that nanoparticles manufactured from calcium carbonate possess unique properties that enhance their applicability in various fields, and promote sustainability and environmental preservation.

Key points: Nano Calcium Carbonate, Nano Milling, Nano Sieves, Waste Recycling, Eggshells.

Introduction:

The new millennium has seen a continuous rise in global egg production (Shawkat et al., 2019). By 2018, the world was producing a whopping 76.7 million tons of eggs, a jump of nearly 15% over the past decade (Shahbendeh, 2020). China remains the undisputed king of egg production, holding the title for the past thirty years. Their peak production hit 31 million tons in 2016, with 26.90 million tons produced in 2018 (FAO, 2020). The United States follows closely behind as the second-largest producer, churning out 6.46 million tons annually. India takes the third spot with 5.23 million metric tons produced each year. Mexico (2.87 million metric tons), Brazil (2.66 million tons), the largest country in South America, and Japan (2.62 million tons) round out the top egg-producing countries (FAO, 2020). This global boom in egg production is driven by a corresponding rise in consumption around the world. For example, the United States has seen a significant increase of over 16% in per capita egg consumption over the past twenty years, reaching a staggering 304.3 eggs per person annually in 2030.

Eggshells constitute roughly 10% of the total weight of a chicken egg (Laca et al., 2017). Substantial quantities of eggs are produced annually, with a substantial portion (30%) undergoing industrial processing, resulting in the accumulation of significant eggshell waste (Ahmad et al., 2019). Much of this is treated as waste and directly disposed of in landfills with minimal or no prior treatment. The decomposition of eggshells is a source of environmental contamination, making the disposal of eggshell waste an undesirable practice (Tsai et al., 2008). Some efforts have been made to find beneficial uses for eggshells. However, the primary applications are in agriculture (soil pH correction), livestock feed (calcium source), and biodiesel catalyst production (Park et al., 2007). The massive surge in egg yield, such as a 27.38% increase in the last five years for India and an 8.24% rise for the United States in the same period (FAO, 2020), has led to a rise in eggshell waste generation, where eggshells account for up to 8-10% of the total egg mass. These discarded tons of eggshells contribute to food waste, causing significant environmental harm by increasing the global carbon footprint (3.3 tons of CO2 equivalent in 2007) when landfilled, one of the main greenhouse gases driving global warming (Wahid et al., 2019).

Calcium is the most plentiful mineral found within the human body. It plays a critical function in the development of bones and teeth, accounting for 99% of their composition (Fayet-Moore et al., 2019). A small portion (1%) of calcium exists outside the skeletal structure, carrying out a wide array of diverse responsibilities. Dairy products provide a sufficient calcium intake to meet the body's requirements (Fayet-Moore et al., 2019). However, people generally do not consume enough calcium according to clinical guidelines, leading to weakened bones, which is significant (Foutrerl et al., 2013).

There has been an increase in the consumption of dietary calcium supplements due to calcium deficiency in postmenopausal women and individuals with osteoporosis (Dingbrok et al., 2002). Furthermore, many people experience lactose intolerance, particularly in regions such as Asia and Africa, which also necessitates new calcium supplements in the form of fortified food products to satisfy dietary calcium needs (Flamini et al., 2016). Existing supplements made from crustacean shells in tablet form are costly and sometimes involve difficulties in the body's absorption of calcium, necessitating targeted therapies (Foutrerl et al., 2013). On the other hand, poultry waste can serve as an excellent alternative source of dietary calcium, as the primary component found in it is calcium carbonate, which has been shown to be beneficial in increasing bone mineral density. Although these applications hold economic significance, eggshells are underutilized, and further research is needed to add value to them (Neunzehn et al., 2015). The development of suitable valorization techniques remains a challenge for the food industry, which relates to environmental protection due to the large amount of waste generated and microbial proliferation (Kim et al., 2016). This research focuses on the synthesis of calcium carbonate nanoparticles from eggshells, a topic of great importance in current food science studies (Shawkat et al., 2020; ALKaisy, Q. et al., 2023). Nanoparticles are materials with dimensions in the nanometer range (1-100 nanometers) and possess distinctive physical and chemical properties due to their small size and high surface-to-volume ratio (Abbas, S.F. et al., 2023). These properties can significantly enhance the applications of calcium carbonate in the field of the food industry and food security.

Materials And Methods:

Preparation of Eggshells

Eggshells were collected from local markets in the City of Baghdad, Republic of Iraq to prepare eggshell powder. The shells were soaked for a full day and then washed with deionized water. Subsequently, they were dried in an electric oven at a temperature of 60°C. After drying, the shells were ground using an Electric Powerful, Powder, Cereal Grinder with a 400g capacity.

Synthesis of Calcium Carbonate Nanoparticles from Eggshells:

The synthesis of calcium carbonate nanoparticles was carried out according to the method used by researchers (Cree, D et, al.,2015), with some modifications. The eggshells, previously ground using the electric grinder, underwent an initial roasting process at 300°C for two hours. This thermal treatment decomposed the organic components while preserving the structure of calcium carbonate ($CaCO_3$).

Following this, the nano grinding process was conducted at the Industrial Research and Development Authority under the Ministry of Industry, Republic of Iraq. The grinding apparatus consisted of an electric motor with an elliptical steel cylinder containing numerous small iron balls. The device included a speed control tool. An eggshell powder sample was placed inside the container, and the top-down grinding process was carried out for approximately 8 hours at a constant speed., around 70% of the critical speed (Vc), determined by the following equation:

$$Vc = \sqrt{\frac{g}{R-r}\frac{1}{2\pi}}$$

where R is the radius of the cylinder, r is the radius of the balls, and g is the gravitational constant.

The grinding speed was determined based on the radius of the elliptical container and the iron balls. The container's volume was approximately 22.5 cm^3, while the diameter of the iron balls was about 6.36 mm. Therefore, the grinding speed was set using a measurement device, resulting in about 167 revolutions per minute.

A wet grinding technique was employed by adding deionized water and eggshell powder in a ratio of 3:100. Following this, the sieving process was conducted to remove large particles using a Vibratory Sieve Shaker ANALYSETTE 3 PRO with mesh sizes of 25 micrometers. The sieving process was aided by 5 mm beads for about half an hour.

Samples Preparation for FTIR Spectroscopy Analysis

The examination method by using Fourier Transform Infrared (FTIR) spectroscopy was followed the approach described by (Kumar et al. 2009). Discs were made from the samples by mixing 40 mg of the sample with 120 mg of potassium bromide, grinding well with a ceramic mortar for 10 minutes, then taking 40 mg of the mixture and pressing it with a hydraulic press specific for the FTIR device at 8 bar pressure for 60 seconds. The pressed discs were placed in a dryer inside an oven at 80°C for 16 hours before analyzing them with the FTIR device in the frequency range of 4000 – 500 cm^{-1}.

Samples Preparation for Transmission Electron Microscopy (TEM)

To prepare the sample for TEM analysis, the method described by (Nogueira et al., 2014) was followed. Initially, the sample was dispersed in deionized water, and a drop of this dispersion was placed on a carbon-coated copper grid. The grid, containing the deposited particles, was allowed to dry at room temperature in a dust-free environment. After drying, the grid was exposed to a glow discharge to render the surface hydrophilic, aiding in the uniform distribution of the synthesized particles on the grid. Finally, the prepared grid was placed in the TEM, which was operated at an accelerating voltage not exceeding 200 kV. The imaging was then conducted at various magnification levels to provide detailed visual information.

Samples Preparation for Scanning Electron Microscopy (SEM)

The calcium carbonate nanoparticle sample was examined using the method described by (Goldstein, J. et al., 2018). After dispersion in deionized water, a small portion of the sample was distributed onto a silicon wafer pre-cleaned with Piranha solution (comprising Sulfuric acid (H_2SO_4) and Hydrogen peroxide (H_2O_2). The sample was then dried at room temperature. After drying, a thin layer of carbon was deposited on the sample using a sputter coater to improve conductivity and imaging quality. The prepared sample was loaded into the SEM under high vacuum conditions. The SEM was equipped with an Energy Dispersive X-ray Spectroscopy (EDS) system to enhance the absorption of high-energy electrons by the sample, generating high-resolution images of the synthesized nanoparticles.

Sample Preparation for Atomic Force Microscopy (AFM)

The sample preparation for AFM analysis was similar to the TEM preparation method. The sample was dispersed in deionized water to create a dilute suspension. Following the method described by (Kumar, B. et al. 2015), a clean, dust-free silicon wafer was treated with Piranha solution. A few small drops of the sample suspension were placed on the silicon substrate and allowed to dry at room temperature. The prepared substrate was then transferred to the AFM, operated in tapping mode. The AFM scan was conducted in an environment free of air currents, with controlled temperature and humidity, to ensure accurate and reliable measurements.

Results and Discussion

Characterization of Calcium Carbonate Derived from Eggshells Before and After Nanosynthesis Using FTIR Spectroscopy

Figures 1 and 2 show the absorption bands of the functional groups using Fourier Transform Infrared (FTIR) spectroscopy for untreated eggshell powder at the nanoscale level and for eggshell powder exposed to 300°C for two hours,

The initial results for the untreated powder showed a prominent absorption band at 3427 cm⁻¹ and 2515 cm⁻¹, which correspond to the stretching of the alcoholic hydroxyl group (-OH) and the acidic hydrogen group (-OH), respectively. Additionally, stretching vibrations between 2980 – 2873 cm⁻¹ were observed, attributed to the C-H groups caused by the organic layers of amino acids in the eggshell. The absorption peak at 1797 cm⁻¹ corresponds to the C=O group, and the peak at 1423 cm⁻¹ is due to the stretching of carbonates. Finally, the peaks at 711 – 876 cm⁻¹ associated with the bending mode confirm the presence of calcium carbonate in the tested sample.

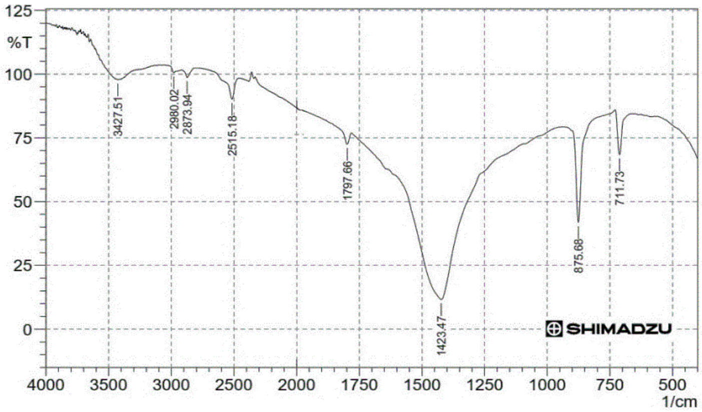

Figure 1. Shows the infrared absorption bands for untreated eggshell powder.

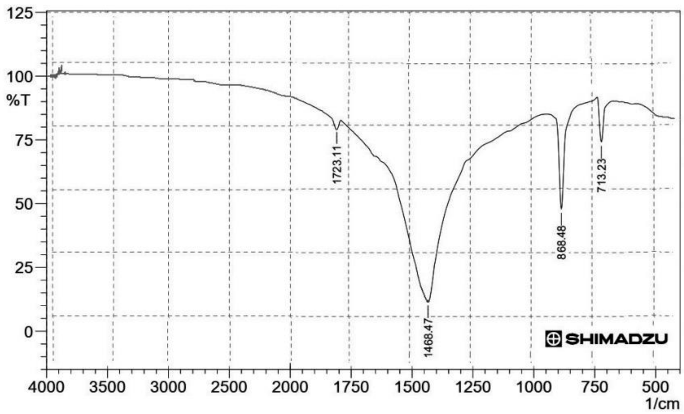

Figure 2. Shows the infrared absorption bands for nanoscale-treated eggshell powder**.**

For the FTIR absorption bands of the nanoscale-synthesized eggshell powder, different absorption bands were observed compared to the untreated powder. No peaks appeared in the absorption bands ranging from 4000 - 2000 cm⁻¹, attributed to the roasting process at 300°C, which eliminated organic groups. The absorption peak at 1723 cm⁻¹ corresponds to the C=O group, and the peak at 1468 cm⁻¹ is due to the stretching of carbonates. Finally, the peaks at 713 – 868 cm⁻¹ belong to the functional group in calcium carbonate, consistent with a previous study by (Shawkat et al., 2019)

Structural Characterization of Synthesized Nanoparticles Using TEM

The Transmission Electron Microscopy (TEM) was used to investigate the structure of calcium carbonate obtained from eggshell powder. The image below reveals that the particles are of nanometric dimensions, approximately 150 nanometers, with a distinctive spherical shape. The Selected Area Electron Diffraction (SAED) results for the nanoparticle indicate a crystalline nature with distinctive rings for calcite, a form of pure calcium carbonate. This was further confirmed by the Energy-Dispersive X-ray Spectroscopy (EDS) analysis, which showed the presence of calcium, carbon, and oxygen, with minor traces of other elements. This indicates the successful synthesis of calcite nanoparticles from local eggshells

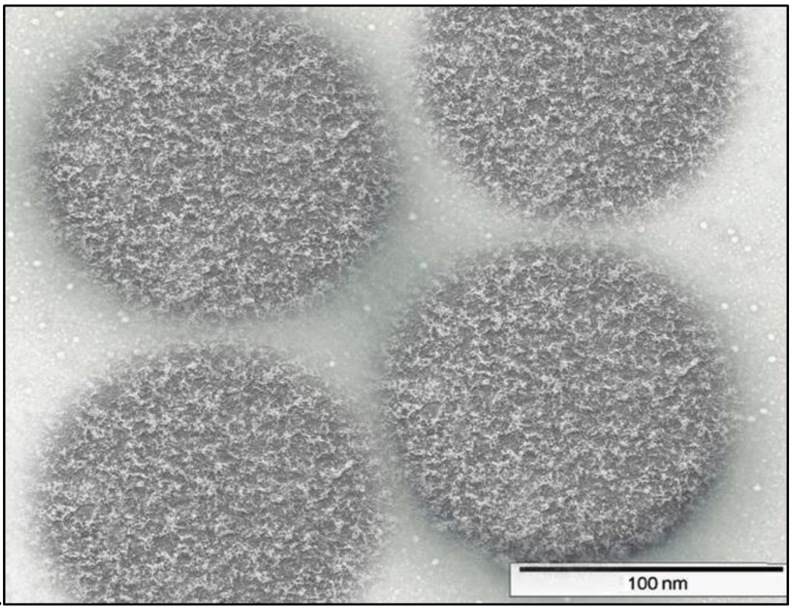

Figure 3. TEM image of calcium carbonate nanoparticles at 100 nm magnification.

Surface Characterization Using SEM

The SEM image shows that the surface of the calcium carbonate nanoparticles synthesized from eggshells is smooth, crystalline, and spherical or nearly spherical. This is consistent with the TEM image, showing good dispersion with minimal unwanted agglomerations, forming a uniform matrix. The particle dimensions ranged from 150.35 – 220.14 nanometers.

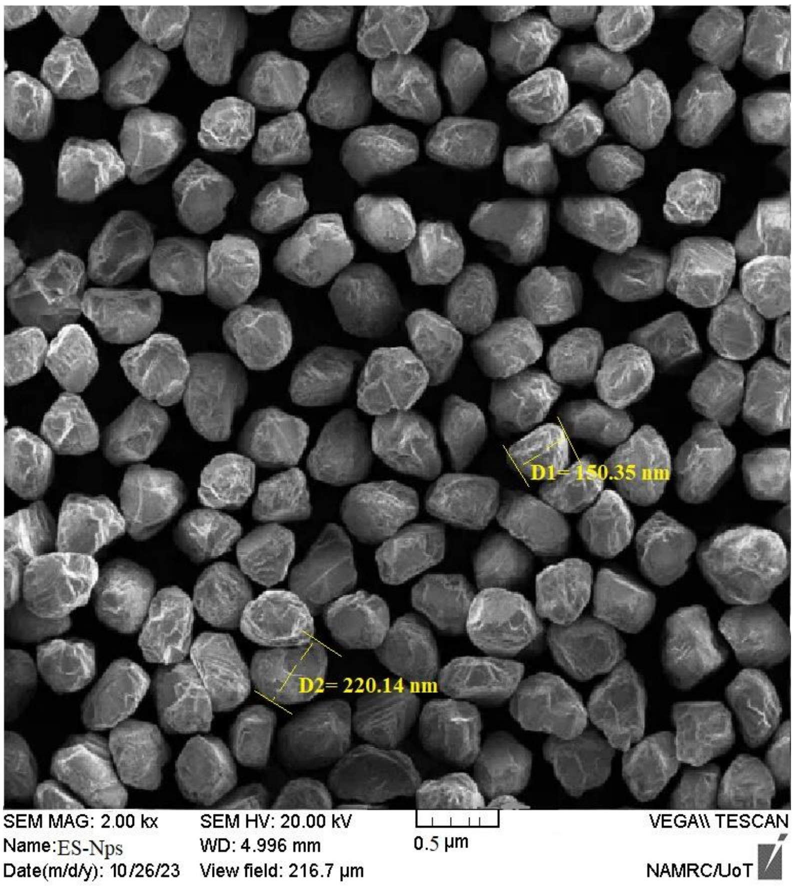

Figure 4. SEM image of calcium carbonate nanoparticles.

Nanostructural Characterization Using AFM

The Atomic Force Microscopy (AFM) scan of the calcium carbonate nanoparticles revealed that due to the interaction between the probe and the sample surface and the resulting forces, the calcium carbonate ($CaCO_3$) particles exhibited unique properties. These properties are due to their small size and high surface-to-volume ratio, giving them high surface energy and making them prone to aggregation or interaction with other materials. This characteristic helps understand their behavior and potential new applications. Additionally, it suggests the possibility of increasing the bioavailability of calcium ions (Ca^{2+}) in the medium through biocalcification, which occurs more readily in the presence of carbonate ions (- CO_3^{2}) in the compound's chemical structure. This is supported by other factors such as suitable temperature and sufficient dissolved carbon dioxide levels, as well as the active role of dietary proteins as organic molecules that enhance the formation of a crystalline network with calcium by directly binding with it, preventing complex formation with magnesium ions (Mg^{2+}) or phosphate ions (PO_4^{3-}).

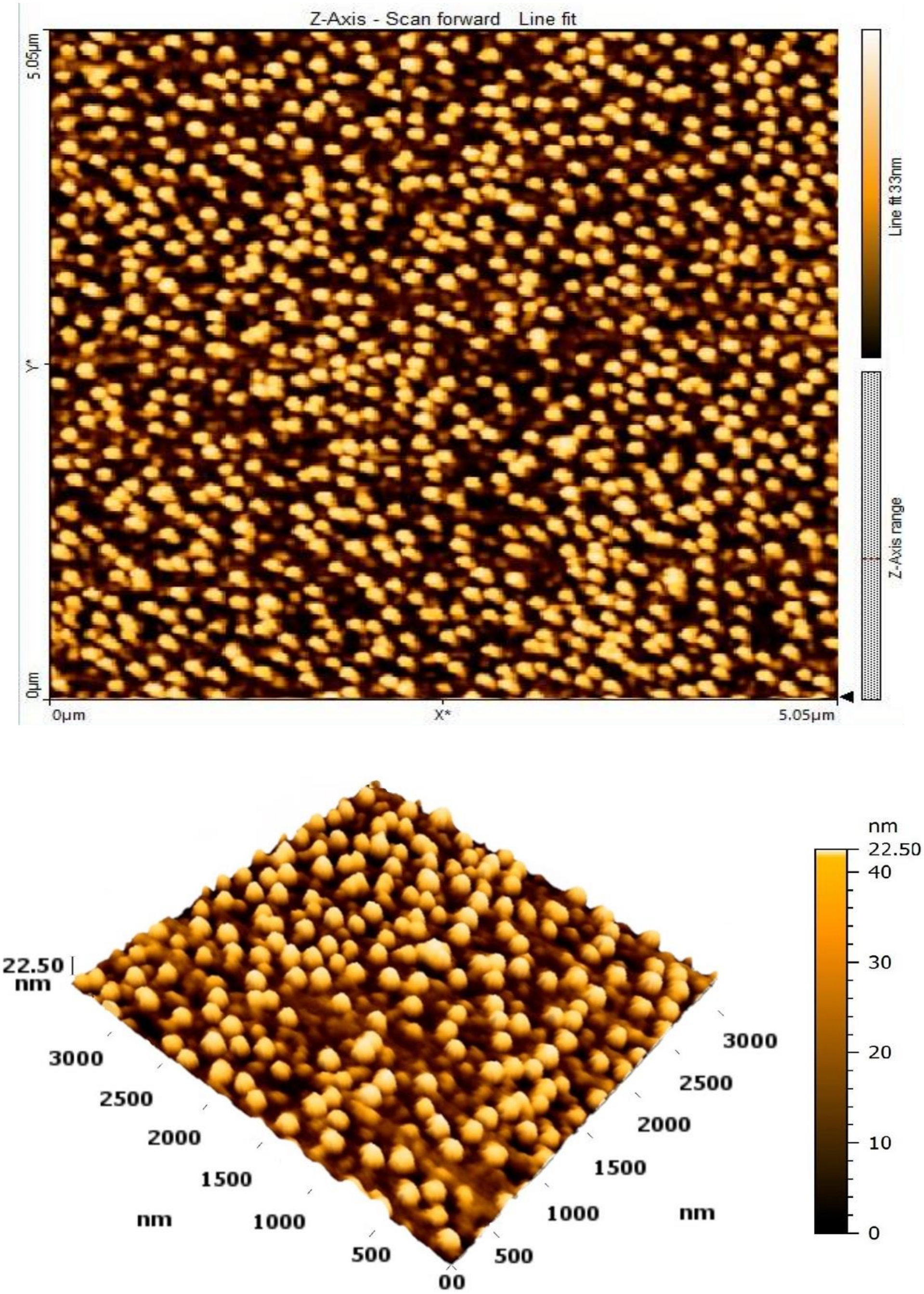

Figure 5. 2D and 3D images of calcium carbonate nanoparticles synthesized from eggshells using AFM.

Conclusions:

The synthesis of calcium carbonate nanoparticles from eggshell waste through thermal treatment and nanogrinding processes. The advanced characterization techniques used, including TEM, SEM, and AFM, confirmed the nanometric dimensions and unique properties of the synthesized nanoparticles. The FTIR analysis revealed the presence of calcium carbonate within the active groups in the chemical structure post-treatment, indicating the effective conversion of eggshells into calcium carbonate nanoparticles.

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