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INVESTIGATION OF METHODS FOR EXTRACTING CALCIUM CARBONATE FROM WASTE EGGSHELLS

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Abstract: *Waste eggshells, a significant by-product of the food industry, contain a high percentage of calcium carbonate ($CaCO_3$), ranging from 94% to 97%, which has various applications in industries such as agriculture, pharmaceuticals, and construction. Utilizing eggshells as an alternative calcium carbonate supply is crucial for sustainable development and waste reduction due to their abundance, low cost, and potential to reduce environmental impact. This study investigates different methods for extracting pure calcium carbonate from waste eggshells with ethanol and sodium hypochlorite as reagents. Their effectiveness in removing organic matter and contaminants from eggshells without altering the main phase, calcium carbonate, during the extraction process was determined. X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), and scanning electron microscopy (SEM) were used to study the eggshell powders that were obtained.*

Keywords: *Waste eggshells, Calcium carbonate, Methods, Ethanol, Sodium hypochlorite.*

INTRODUCTION

Waste eggshells, often overlooked in the context of sustainable waste management, represent an important biological resource. Composed primarily of calcium carbonate, which accounts for approximately 95% of their composition (Kolekar, S., Deshmukh, S., Hiwale, V., & Dutta, A., 2020), they are a potential source of valuable minerals (Faridi, H., & Arabhosseini, A., 2018). The extraction of calcium carbonate from waste shells not only reduces biological waste but also promotes environmentally sustainable practices by recovering valuable resources and reducing production's carbon footprint, making it an eco-friendly and cost-effective recycling method (Waheed, M., Yousaf, M., Shehzad, A., Inam-Ur-Raheem, M., Khan, M., Khan, M., Ahmad, N., Abdullah, & Aadil, R., 2020; Ngayakamo, B., & Onwualu, A., 2022). It also has enormous potential for application in various industries (Baláž, M., Boldyreva, E., Rybin, D., Pavlović, S., Rodríguez-Padrón, D., Mudrinić, T., & Luque, R., 2021), such as the production of nutritional supplements (Siemiradzka, W., Dolinska, B., & Ryszka, F., 2018), construction materials (Sathiparan, N., 2021; Chong, B., Othman, R., Ramadhansyah, P., Doh, S., & Li, X., 2020; Safiki, A., Joseph, T., Thomas, O., & Annette, B., 2021), and pharmaceuticals (Rasheed, S., Shivashankar, M., Dev, S., & Azeem, A., 2019; Singh, A., Kelkar, N., Natarajan, K., & Selvaraj, S., 2021) etc.

The extraction of calcium carbonate ($CaCO_3$) from eggshells employs various chemical and physical techniques, as highlighted in recent literature (Diningsih, C., & Rohmawati, L., 2022; Kolekar, S., Deshmukh, S., Hiwale, V., & Dutta, A., 2020). Common methods include mechanical grinding (Insani, S., & Rahmatsyah, R., 2021), acid dissolution (using hydrochloric or acetic acid) (Rosnah, R., Taslim, N., Aman, A., Idris, I., As'ad, S., Bukhari, A., & Wahyudin, E., 2021; Kolekar, S., Deshmukh, S., Hiwale, V., & Dutta, A., 2020), and heat treatment through calcination

(Al-Azzawi, M., & Al-Kalifawi, E., 2023). Acidic methods yield soluble calcium salts that necessitate further processing (Szeleszczuk, U., Pisklak, D., Kuras, M., & Wawer, I., 2015), while heat treatment involves high-temperature processing to produce calcium oxide (CaO), which can then be hydrated and carbonated to obtain pure $CaCO_3$. Although heat treatment ensures high purity by eliminating organic impurities, it is energy-intensive and requires specialized equipment. Conversely, mechanical extraction focuses on grinding and crushing eggshells to isolate $CaCO_3$ with minimal chemical intervention, allowing for better control over particle size but failing to remove organic contaminants (Insani, S., & Rahmatsyah, R., 2021).

This paper investigates two methods for extracting calcium carbonate from eggshells, specifically comparing ethanol and sodium hypochlorite as chemical reagents. Ethanol is highlighted as a more environmentally friendly option, presenting fewer risks compared to strong acids or thermal calcination. In contrast, sodium hypochlorite offers strong oxidizing properties that can decompose organic impurities and sterilize the material, making it advantageous for biomedical or pharmaceutical applications.

EXPOSITION

Extraction of CaCO3 from waste eggshells

The collected waste eggshells are washed with hot water without removing the membrane from them and left in the air for 24 hours. Then, they undergo further drying at 105°C until they reach a constant weight. The dried eggshells underwent mechanical processing in a ball mill and fractionation of the resulting powders. For the purposes of the experiment, a fraction with a particle size of 0.5 μm was selected. Two chemical extraction methods were employed: the first involved mixing 20 g of eggshell powder with sodium hypochlorite (NaOCl) for 12 hours, followed by washing and drying. The second method utilized ethyl alcohol (C_2H_6O) at 25°C for 4 hours with magnetic stirring. After chemical treatment, obtained powders were heated at 300°C for 2 hours.

Characterization

The resulting powders were subjected to various characterization methods. X-ray diffraction (XRD) was employed to identify the crystal structure of calcium carbonate, while Fourier-transform infrared spectroscopy (FTIR) was utilized to analyse the chemical composition. Scanning electron microscopy (SEM) was used to determine the morphology, particle size, and surface structure of the obtained samples.

XRD (X-Ray Diffraction) characterization was carried out on a powder diffractometer Bruker 2D Phaser. The samples were irradiated with CuKα radiation (λ = 1.54060 Å) and analyzed between 2-90° (2 theta).

Fourier transform infrared spectroscopy (FTIR) is a tool for identifying the types of chemical bonds in organic and inorganic molecules. Analysis is performed by using the spectrophotometer Nicolet iS 50 FT-IR Thermo Scientific in the interval 4000–400 cm^{-1}.

Scanning electron microscopy was performed on a JSM 6390 electron microscope (Japan) in conjunction with energy dispersive X-ray spectroscopy (EDS, Oxford INCA Energy 350) equipped with an ultrahigh resolution scanning system (ASID-3D) in regimes of secondary electron image and back scattered electron image.

RESULTS AND DISCUSSION

X-ray diffraction (XRD) analysis was conducted to identify crystalline phases and assess the efficiency of reagents used for extracting calcium carbonate from eggshells. The analysis revealed that the crystalline phase of the extracted carbonate powders was calcite (PDF#83-0577), in accordance with reports by (Lu, J., Lu, Z., Li, X., Xu, H., & Li, X., 2015). Fig. 1 shows the XRD intensities of the starting eggshells and the extracted carbonate powders labeled with the reagent used, respectively. The x-axis presents the main diffraction angles (2θ) for the calcite phase, while the y-axis reports the peak intensities. Analysis showed that sodium hypochlorite treatment resulted in higher intensities of characteristic calcite peaks compared to ethanol treatment. This suggests that sodium hypochlorite is more effective in extracting calcium carbonate. Sodium hypochlorite's strong oxidizing properties help break down organic materials like proteins and lipids (Lu, J., Lu, Z., Li, X., Xu, H., & Li, X., 2015). It also keeps the purity of calcium carbonate ($CaCO_3$) and reduces the need for extra heat treatment. After heating to 300°C, sodium hypochlorite-treated shells show minimal residual organic material and maintain a stable $CaCO_3$ crystal structure.

In contrast, ethanol only partially solubilizes organic components, mainly lipids, and fails to efficiently degrade proteins, resulting in lower calcium carbonate extraction efficiency. Therefore, ethanol-treated shells require longer and more intense heating to achieve a relatively pure $CaCO_3$ product.

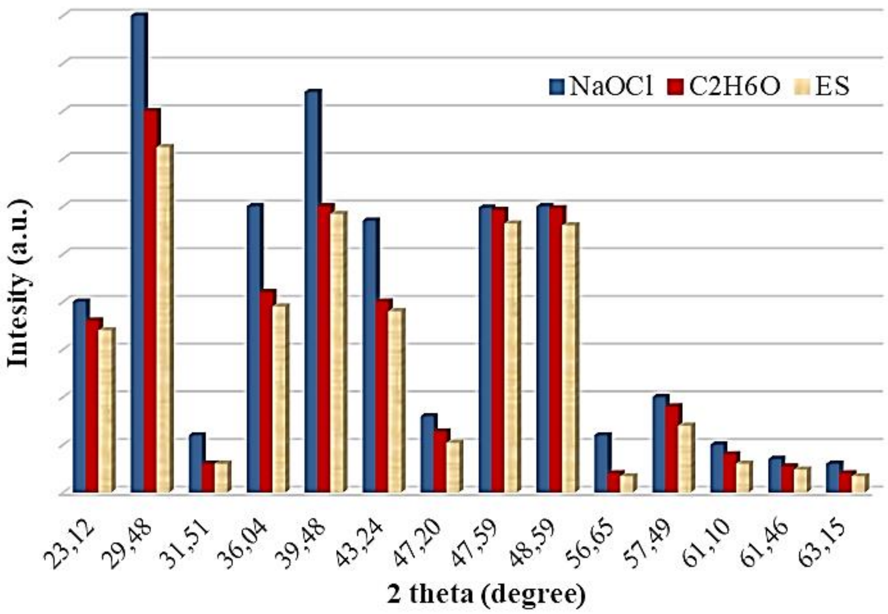

Fig. 1. XRD intensities of eggshells and $CaCO_3$ powders

The results of this research demonstrated that the extraction of $CaCO_3$ from waste eggshells at a temperature of 300 °C for 2 hours resulted in a 100% calcite phase of $CaCO_3$. In contrast to the study conducted (Mawadara, P., Mozartha, M., & Trisnawaty, K., 2016), which produced $CaCO_3$ from chicken eggshells at a high temperature of 1000 °C, the resultant material included impurities in the form of CaO. Similarly, in study Noviyanti, N., Jasruddin, J., & Sujiono, E., 2015), the application of temperatures of 550°C, 650°C, and 750°C for 4 hours yielded calcite ($CaCO_3$) percentages of 98.8%, 92.2%, and 84.0%, respectively.

Fig. 2 presents the FT-IR analysis of the resulting carbonate powders. We compared the spectra of waste eggshells, ethanol-extracted, and sodium hypochlorite-extracted carbonate powders to identify the main functional groups and analyze the efficiency of organic matter removal. The FT-IR spectrum of raw eggshells reveals the presence of various organic components, including proteins and lipids. Key findings include a strong broad peak around 3300 cm^{-1}, indicative of -OH groups, likely from residual moisture or hydroxyl groups. The C-H stretching band between 2900-2950 cm^{-1} suggests lipid content, while the amide I and II bands between 1650-1550 cm^{-1} confirm the presence of proteins (Lu, J., Lu, Z., Li, X., Xu, H., & Li, X., 2015). Additionally, band at 1400-1470 cm^{-1} and 870 cm^{-1} indicate calcium carbonate (Kiryakova, D., & Kolchakova, G., 2023), although their intensities are diminished due to the abundance of organic materials.

The FT-IR spectrum analysis of eggshells treated with sodium hypochlorite demonstrates the effective removal of organic components (proteins and lipids), evidenced by the significant reduction or absence of peaks around 3300 cm^{-1} and 2900 cm^{-1}. The calcium carbonate ($CaCO_3$) peaks at 1400 cm^{-3} and 870 cm^{-3}, on the other hand, are much clearer and stronger, which means that the treatment was able to separate pure calcium carbonate proteins (Lu, J., Lu, Z., Li, X., Xu, H., & Li, X., 2015). These sharp peaks are indicative of well-crystallized calcite.

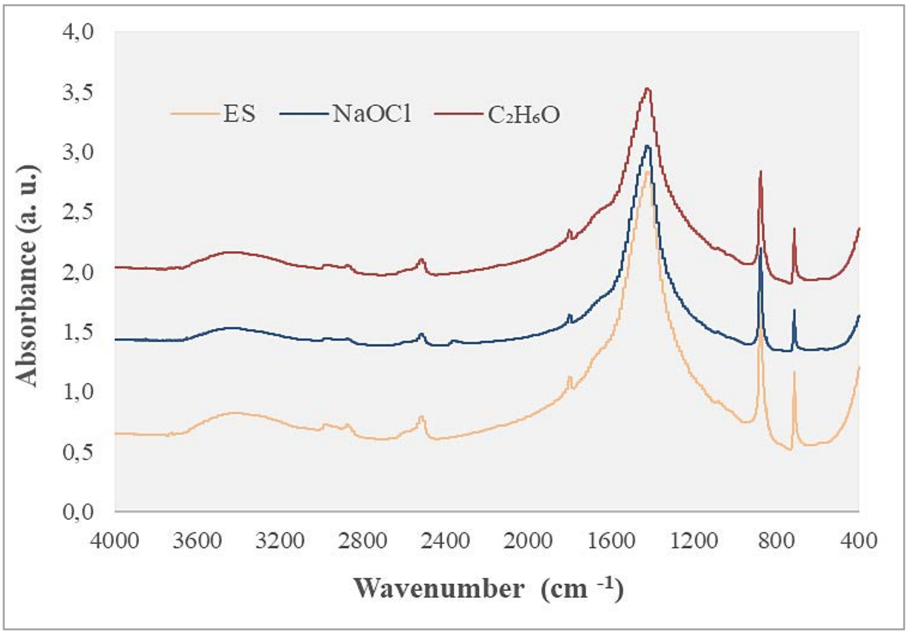

Fig. 2. FT-IR of eggshells and extracted $CaCO_3$ powders

The FT-IR spectral analysis of ethanol-treated shells indicates significant changes in the organic composition. There is a notable reduction in the intensity of lipid-related peaks around 2900 cm^{-1}, indicating that ethanol effectively solubilizes some lipids, although these peaks do not completely vanish. In contrast, amide peaks associated with proteins (1650-1550 cm^{-1}) remain present but show slightly reduced intensity, as ethanol does not solubilize proteins. Additionally, the peaks corresponding to calcium carbonate (1400 cm^{-1} and 870 cm^{-1}) become slightly more distinct compared to untreated shells, suggesting some concentration of calcium carbonate, though organic residues still interfere with the overall spectrum.

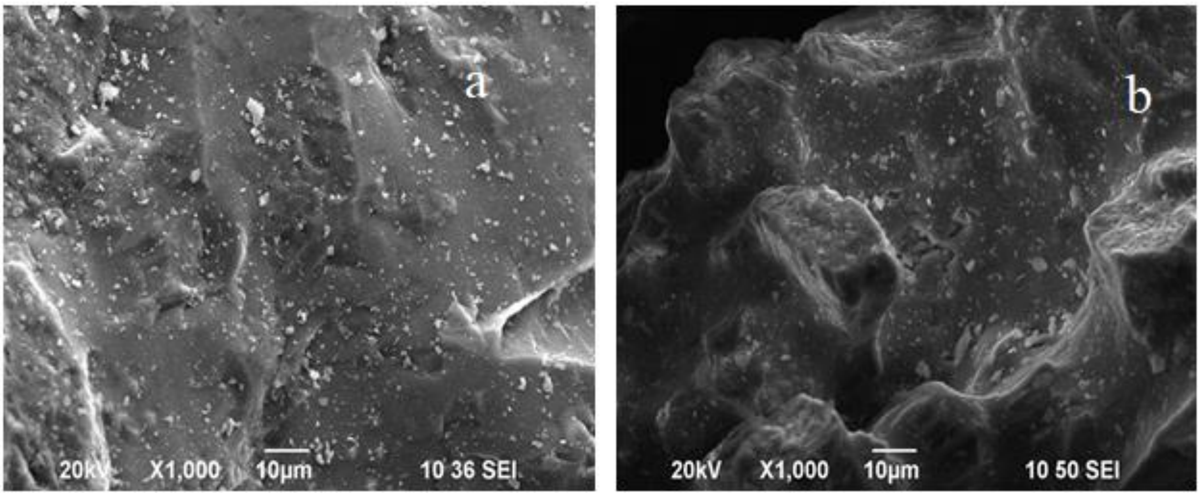

Fig. 3. SEM images for extracted $CaCO_3$ powders by: a) NaOCl; b) C_2H_6O

Fig. 3 shows SEM images of calcium carbonate that was extracted using ethanol and sodium hypochlorite. The pictures clearly show that the particles' shape and surface structure are very different. Upon treatment with sodium hypochlorite, we observed particles with a more heterogeneous morphology and smaller sizes, ranging from 1-3 μm (Fig. 3a). The aggressive action of sodium hypochlorite degrades the organic components in the eggshells while also changing the surface structure of the crystals, giving them a rough and porous appearance. On the other hand, ethanol treatment results in calcium carbonate particles with a smooth surface and the typical rhombohedral shape characteristic of calcite crystals (Fig. 3b). Ethanol effectively removes organic impurities while keeping the particle structure intact, which gives the surface a denser and more uniform texture. The shape difference shows how the different chemicals affect the calcium carbonate's surface and size. Sodium hypochlorite makes the particles more porous and textured, while ethanol keeps the crystals dense and smooth.

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CONCLUSION

The results show that both methods lead to the extraction of calcium carbonate but differ significantly in terms of the purity of the final product. Extraction with sodium hypochlorite demonstrated a higher degree of calcium carbonate purity and a shorter processing time compared to ethanol. Furthermore, XRD analysis shows that the calcite form of calcium carbonate has more intense and clear peaks. This implies higher crystallinity and purity in the product. Calcium carbonate obtained with ethanol has a lower peak intensity, which is the result of incomplete purification of organic impurities. FT-IR spectroscopy confirmed the structural differences between the two extracts. The product that was extracted with NaOCl shows the characteristic calcium carbonate peaks, especially those around 874 cm^{-1} and 1400 cm^{-1}, which are caused by the carbonate group's vibrational modes. However, the ethanol-treated sample showed additional peaks around 3400 cm^{-1}, indicating the presence of organic compounds. SEM images of calcium carbonate extracted using ethanol and sodium hypochlorite reveal distinct shapes and surface structures. Sodium hypochlorite causes porous, textured particles with smaller sizes (1-3µm), while ethanol maintains a smooth, rhombohedral shape.

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