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Synthesis of Calcium Oxide Nanoparticles from Waste Eggshell by Thermal Decomposition and their Applications

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Abstract

This study used the physical method to synthesize calcium oxide nanoparticles (CaO NPs) from eggshell. The method provided a new and improved approach with the advantage of being low cost as it uses eggshell waste as a synthesis precursor. Calcium oxide is an important inorganic compound with many biomedical applications because of its anti-microbial activities against gram negative *Escherichia coli* and the gram positive *Staphylococcus aureus*. Results showed that the mean inhibition increased with increased concentration of calcium oxide particles (70, 140, 280, and 560) µg/ml. The obtained particles were characterised by scanning electron microscopy, energy dispersive X-ray spectroscopy, and X-ray diffraction. The images showed that the calcium oxide NPs were nearly spherical granules. The annotated SEM images that produced the CaO NPs had a mean size of 20-70 nm.

Keyword: Calcium oxide, Nanoparticles, Thermal decomposition , *Staphylococcus aureus, Escherichia coli*

1. Introduction

Scientists confirm that nanotechnology has revolutionized science in recent years .this development is clearly due to the unique general properties of nanoparticles (NPs) in terms of surface area (increased surface to volume ratio), particle size, charge, shape, and magnetic properties compared with its bulk counterparts which give nanomaterials improved and unique properties that enable their wide-ranging applications, such as in space, electronics, and energy (Kanude and Jain, 2017; Sorbiun et al.,2018) where NPs are more effective chemically and feasible at low temperatures (Bundschuh et al.,2018). The nanotechnology field has achieved extensive progress (Bano and Pillai, 2020). Thus, they are included in optical applications and catalysis applications (Zhang and Wang, 2017).

The importance of metal oxide NPs is attributed to their numerous applications, including medical ones such as drug delivery (Anderson et al., 2019), bio-imaging (McNamara et al., 2020), biosensors (Fathi et al., 2019), hyperthermia (Salem et al., 2020), gene mapping, and gene delivery (Zhang et al., 2015). Apart from their biological importance owing to their low toxicity, chemical stability, and biocompatibility (Karimi et al., 2013), metal oxide nanoparticles are also involved in catalysis applications (Yang et al., 2017) and environmental treatment (Zhang et al., 2017).

Calcium oxide (CaO) is an alkali-earth metal oxide considered as a promising oxide because of its many applications. One of the most important advantages of CaO NPs is its easy and low-cost production (Bano and Pillai, 2020). CaO has been used as a catalyst in many reactions (Kumar et al., 2016). The reaction of CaO with CO_2, SO_2, and NO_X may increase the use of calcium oxide as an excellent absorbent (Bharathiraja et al., 2018). It is also considered a narcotic to modify the optical properties (Mirghiasi et al., 2014), for the purification of vehicle exhaust gas (Habte et al., 2019), removal of sulfur from flue gas, and control of pollutant emissions (Liu et al., 2010), and it can serve as a treatment agent for toxic waste (Safaei-Ghomi et al., 2013) and an additive in refractory materials (Mirghiasi et al., 2014). In the medical field, a CaO NPs have applications in drug delivery (Butt et al., 2015), where the above research mentioned studied the toxicity of CaO nanoparticles in rats using manual hematoxylin and eosin staining protocols and acute tubular and hepatic degenerations were observed in the kidneys and liver respectively. CaO NPs are used as a synaptic factor of chemotherapeutic agents, and in phototherapy (Aseel et al., 2018). Calcium oxide and calcium hydroxide $Ca(OH)_2$ NPs have proven efficacy in human root dentin by the elimination of Enterococcus faecalis (Louwakul et al., 2017).

The synthesis processes for calcium oxide NPs vary and always preferred the process which gives the best performance in terms of surface area (Habte et al., 2019). Synthesis methods are generally divided into physical, chemical, and Biological. Physical methods include thermal decomposition (Sadeghi and Husseini, 2013), sono-chemical method (Amin and Morsali, 2010), and microwave processing (Roy et al., 2013), whereas chemical ones include co-precipitation (Ghiasi and Malekzadeh, 2012) and sol-gel method (Darcanova et al., 2015). Biological or green methods may include the use of

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some plant extracts such as Mentha piperita (Ijaz et al., 2017), benign papaya leaf extract and green tea extract (Anantharaman et al., 2016), and rhododendron arboretum extracts (Ramola et al., 2019). These plant extracts contain many bioactive compounds such as antioxidants, phenolic, enzymes, amino acids, and sterols that act as a reducing agent (Aljabali et al., 2018; Vani et al., 2017; Some et al., 2018).

Eggshells contain about 85-95 % of calcium carbonate (Awogbemi et al., 2020), and the rest consists of protein and minerals (Mustapha et al., 2020). Each gram of eggshell contains 381-401 mg of calcium (Brun et al., 2013). In the industry, eggshells have many applications (Cree and Rutter, 2015). Eggshells contain large amounts of calcite or calcium carbonate ($CaCO_3$), which are the basic material for the manufacture of limestone and lime. The limestone produced by eggshells is characterized by its purity, unlike the quarried limestone, which contains minerals, clay, and sand. Limestone is used as a filler in plastics, cement, and rubber. calcium carbonate can be transformed into calcium oxide by heating. CaO is known as lime or quicklime, which used to remove the acidity of agricultural soils and gardens. Lime is considered an ingredient in Portland cement. The overall calcination reaction of the eggshell powder is the conversion of $CaCO_3$ to CaO and CO_2, as follows (Nuryantini et al., 2019).

$$\mathbf{CaCO_3\ (s) \rightarrow CaO\ (s) + CO_2\ (g)}$$

Researchers have demonstrated the importance of the particulate size of metal oxides in anti-microorganism activity as it is characterised by high bacterial resistance and great thermal stability (Nirmala et al., 2013). In addition to the histocompatibility of calcium oxide and its anti-microbial potential (Mohammadi and Dummer, 2011), CaO NPs also have a strong anti-bacterial activity related to active oxygen species and alkalinity owing to increased pH by hydrating CaO with water and the superoxide generated on its surface, Figure 1 shows characterization of CaO NPs as anti-microbial agent (Yamamoto et al., 2010).

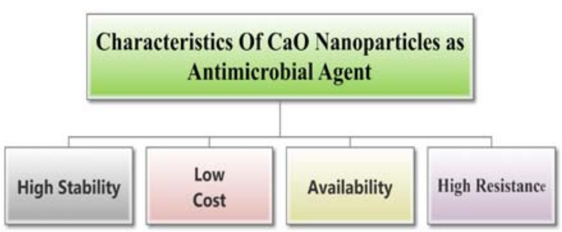


Figure1. Characteristics of calcium oxide as anti-Microbial agent.

Staphylococcus aureus is one of the most common microorganisms that cause human and animal infections alike (Foster and Geoghegan, 2015). The risk of infection increases in cases of immune deficiency. It is treated with penicillin anti-biotics, but the process became difficult owing to the development of resistance against most common anti-biotics because it carries multiple resistance to wide ranging antibiotics bearing the beta-lactam ring (Lee et al., 2018).

Escherichia coli is a Gram negative bacillus that is widespread in nature and lives in the intestines of humans and mammals. It is found in soil and surface waters contaminated with human and animal feces. Most of its types are not pathogenic, but they do become pathogenic after acquiring virulence factors (Roth et al., 2019).

The present study aimed to examine the synthesis of calcium oxide NPs through calcination of eggshells after grinding and burning them at 900 °C. The calcium oxide NPs formed were analysed by scanning electron microscopy (SEM), X-ray diffraction (XRD), and energy-dispersive X-ray spectroscopy (EDX) techniques. The effects of these particles on inhibiting the growth of *S. aureus* and *E. coli* bacteria were also investigated. It can be concluded from this study that the preparation of calcium oxide NPs gave good and encouraging preliminary results for future work as an anti-microbial agent.

2. Materials and methods

2.1. Materials

Local waste eggshell. Muller-Hinton (M-H) agar from Hi-Media (India), and ‘‘Riedel-de Haen” (Germany), Deionized water (H_2O) from Chem-Lab (Belgium).

2.2. Preparation of CaO NPs

Eggshells were collected from some houses after using the eggs. The shells were washed, and the internal membranes attached onto the eggshell were removed. The shells were dried at room temperature after breaking them into small pieces. The dried shells were ground using an electrical milling machine for 5 min, after which the fine powder was calcined at 900 °C for 1 h, as shown in Figure 2. The resulting nano-calcium oxide was characterised by SEM, XRD, and EDX techniques.

Figure 2. Diagram of preparation and applications of CaO NPs

2.3. Characterization of CaO NPs

Calcium oxide NPs size was measured by SEM to identify morphology. The content of all materials present in the composite CaO was determined by EDX. The crystalline size and structure of NPs were determined by XRD using an automated diffractometer (Shimadzu 6000 XRD) with Cu-Kα radiation (λ = 1.5418 Å).

2.4. Anti-bacterial activity of CaO NPs

The anti-bacterial activity of the CaO NPs was tested against the Gram negative *E. coli* and the Gram positive *S. aureus* through an agar-well diffusion technique (Kadhim et al., 2019). After culturing the organisms into the bored wells, different concentrations of CaO NPs (70, 140, 280, and 560) µg/ml were used. CaO NPs and the test organisms in cultured plates were incubated for 24 hours at 37 °C. Afterwards, the average diameter of the generated zones of bacterial inhibition by the respective CaO NPs concentrations was measured and recorded. The experiments were performed in triplicate (Mohammed et al., 2020).

2.5. Statistical analysis

The obtained data were statically analyzed using an unpaired t-test. (Ali et al., 2018). The values are presented as the mean ± SD of triplicate measurements (Younus et al., 2019).

3. Result and discussion

3.1. SEM

Figure 3 shows the morphology and size of spherical calcium oxide NPs prepared by the thermal decomposition of waste eggshell at 900 °C with a scanning electron microscope. The images showed particle diameters ranging from (20-70) nm as demonstrated in the SEM images.

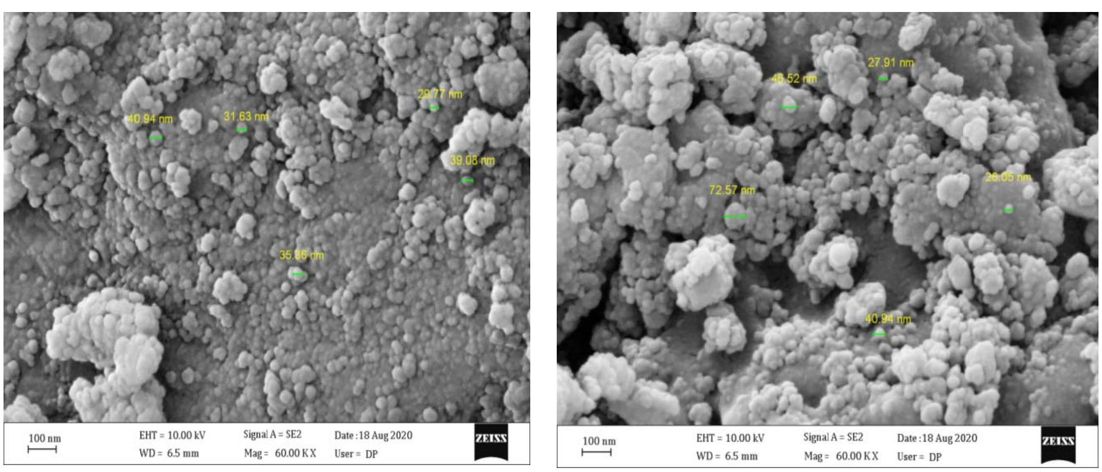


Figure 3: SEM micrograph of CaO NPs

3.2. XRD analysis

Figure 4 shows the XRD patterns of CaO NPs prepared by thermal decomposition compared with those of ICDD card No. 00-004-0784, which is the standard reference for CaO NPs. The diffraction peaks indexed to (111), (200), (220), (311), and (222) corresponded to the peaks at 2θ = 38.12°, 44.28°, 64.47°, 77.73°, and 80.10°, respectively, all these peaks confirmed the face-centered cubic structure of CaO as indicated in ICDD card No. JCPDS No. 00-033-0664.

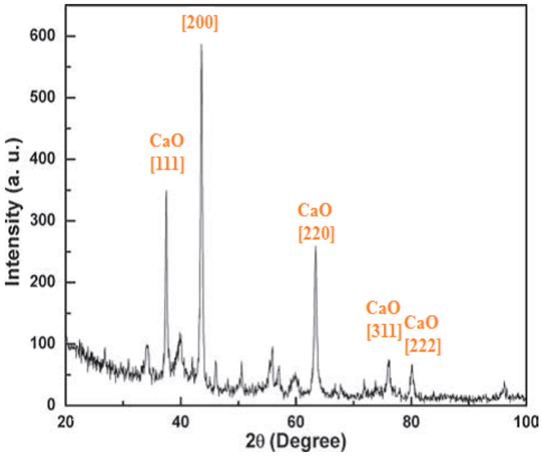


Figure 4: X-ray diffractions of CaO NPs powders after calcination at 900 °C temperatures

3.3. EDX analysis

To emphasize the presence and formation of Cao NPs, EDX analysis was performed with focus on different regions. Identical peaks are shown in Fig. 5. CaO NPs can be seen in the composite nanostructure in the EDX spectrum. As shown in the bottom spectrum, the weight percentages of Ca and O were 71.4% and 28.6% respectively, and σ was 0.9 for both. Energy-dispersive X-ray analysis showed the main peaks of calcium and oxygen. No other peaks related to impurities have been assigned in the spectra which confirm the purity of the CaO NPs.

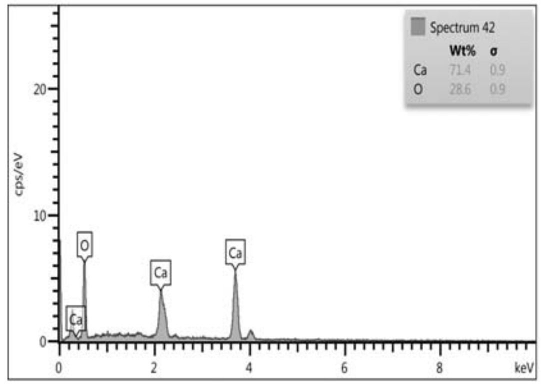
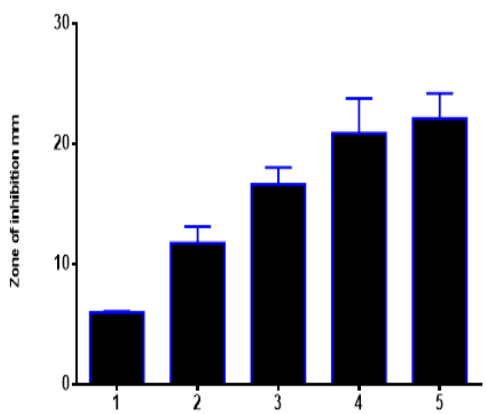


Figure 5: Energy dispersive X-ray analysis of CaO NPs powders after calcination at 900 °C temperature

3.4. Anti-microbial activity

Owing to the large surface area and small particle size of CaO NPs, they exhibited good anti-bacterial reactivity. Conversely, owing to the small size of the particles, they can easily enter the bacterial cells, and inhibition occurred inside the bacterial cells. CaO NPs destroyed and distorted the cell membrane, leading to bacterial cell death (Ramola et al., 2019). Figures 6 and 7 show the mean diameter of inhibition of calcium oxide NPs against *E. coli* and *S. aureus*. With increased concentration of calcium oxide NPs, the mean diameters of inhibition increased. The effect of inhibition appeared from the concentration 70 µg/ml, and it increased directly with increased concentration. The highest mean diameter of inhibition appeared at a concentration of 560 µg/ml against *E. coli* and *S. aureus*. These results were consistent with previous studies (Jeong et al., 2007; Anantharaman et al., 2016) in terms of the effectiveness of calcium oxide against *E. coli* and *S. aureus*. The effects of concentration and pH, considered as the main factors affecting anti-microbial activity, also agreed with previous results (Yamamoto et al., 2010).



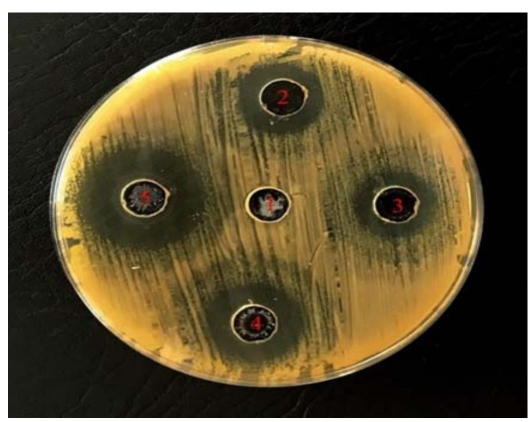


Figure 6: Anti-bacterial activity of CaO NPs against *Staphylococcus aureus*. **1**. Represented control untreated bacterial strain. **2**. Bacterial strain treated with CaO NPs at concentration 70 µg/ml **3**. Bacterial strain treated with CaO NPs at concentration 140 µg/ml **4**. Bacterial strain treated with CaO NPs at concentration 280 µg/ml **5**. Bacterial strain treated with CaO NPs at concentration 560 µg/ml

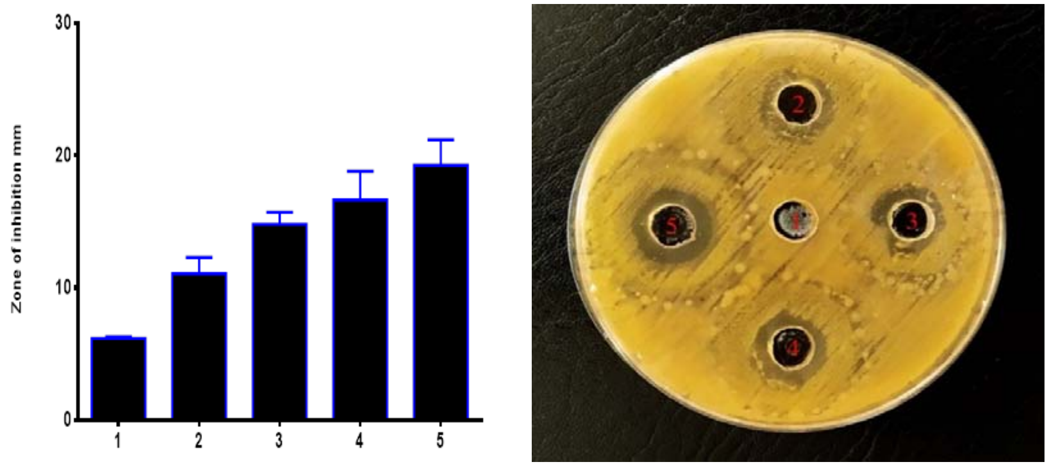


Figure 7: Anti-bacterial activity of CaO NPs against *Escherichia coli* ,**1**. Represented control untreated bacterial strain **2**. Bacterial strain treated with CaO NPs at concentration 70 µg/ml **3**. Bacterial strain treated with CaO NPs at concentration 140 µg/ml **4**. Bacterial strain treated with CaO NPs at concentration 280 µg/ml **5**. Bacterial strain treated with CaO NPs at concentration 560 µg/ml

4. Conclusion

We proposed a method that was economical, simple, and did not require expensive equipment to synthesize calcium oxide particles from eggshells containing a high percentage of calcium carbonate. The NPs formed were characterised by SEM, EDX, and XRD analyses. SEM images showed the formation of spherical granules with sizes ranging from (20 – 70) nm. Studies on the synthesis of calcium oxide particles confirmed the effectiveness of these particles against the Gram negative *E. coli* and the Gram positive *S. aureus*. Furthermore, increased concentration was found to directly affect the mean diameters of inhibition.

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