APPLICATION OF $Ca(Zn(OH)_3)_2 \cdot 2H_2O$ (CZ) AND MgO NANOPARTICLES FOR CONSOLIDATION STONES

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The limestones were important materials for pre-Hispanic civilizations; they were used to construct significant buildings and structures that played a crucial role in their culture. However, environmental factors have contributed to their deterioration, leading to their loss. Therefore, it is essential to conduct multidisciplinary research to develop new conservation treatments compatible with these materials.
This research evaluated the behavior of $Ca(Zn(OH)_3)_2 \cdot 2H_2O$ $(CZ)_y$ MgO nanoparticles applied on stones samples. Firstly, the nanoparticles were synthesized using the sol-gel method and subsequently characterized by X ray diffraction (XRD) and scanning electron microscope (SEM). Therefore, it was applicated by dropwise on stones samples. Their effects were evaluated using non-destructive techniques, specifically velocity of ultrasound propagation (Vp) and contact angle measurements. The results showed that both treatments had a consolidated effect on the stones, with a significant increase on Vp recorded after the application. Additionally, variations in the contact angle were observed in the stones treated with CZ and MgO. Specifically, Stones treated with MgO reported lower contact angles values. This increased hygroscopicity behavior to suggest an enhances their water absorption capacity.

Key words: limestone, environmental, nanoparticles, sol-gel method, absorption

Introduction. Stones are materials widely used in building construction, not only for their strength and durability but also for their symbolic and aesthetic value, even becoming part of the cultural expression of certain pre-Hispanic civilizations. In the Mesoamerican context, pre-Hispanic civilizations such as the Maya and Mexica used stone not only as a structural element in the construction of ceremonial centers and temples, but also as a medium to depict their worldview, religious beliefs, and cultural expressions through sculptures, reliefs, and monuments [1,2]. However, their structural and aesthetic integrity can be compromised by environmental factors such as solar radiation, humidity, and temperature, together with biotic factors like the growth of microorganisms and intrusion by animals, which accelerate degradation processes, affecting both their functionality and the loss of their historical and cultural value [3].

The nanotechnology has become a reliable and innovative alternative for the conservation and restoration of cultural heritage. On this point, it has been reported the use of Ca $(OH)_2$ nanoparticles (NPs) as an effective solution for the preservation of cultural materials [4]. This NPs has demonstrated their ability to consolidate stone, enhancing its mechanical properties while preserving its aesthetics [5]. For this reason, the nanotechnology continues to advance in the research for new materials that not only improve the mechanical properties of stone but also provide additional benefits, such as resistance to moisture, pollutants, or biological growth.

In this regard, Zn and MgO based compounds are being widely used for the conservation of stone heritage due to their antimicrobial and antifungal properties. However, research evaluating their behavior on stone heritage is very limited [6, 7]. For this reason, the aim of this work is to synthesize and characterize $Ca(Zn(OH)_3)_2 \cdot 2H_2O$ (CZ) and MgO nanoparticles, as well as their subsequent application to stone material, assessing their mechanical properties using non-destructive techniques.

Synthesis of Ca (Zn (OH)$_3$)$_2 \cdot$2H$_2$O nanoparticles. The CZ NPs were synthesized by sol-gel method according to the methodology proposed by Soria Castro et al., 2019, with slight modifications [7], by combining two separate solutions in deionized water. The first solution contained 80 mM of $CaCl_2 \cdot 2H_2O$ and 10 mM of ZnO previously synthesized following the method reported by Gómez-Ortiz et al., 2013 [8]. The second solution contained 8 mM of NaOH. Both solutions were mixed and heated at 90 °C for 5 hours. Finally, the product was washed three times with deionized water and the product was dried at 65 °C for 5 hours.

Synthesis of MgO nanoparticles. The MgO NPs were synthesized by sol-gel method following the methodology reported by Sierra Fernández et al., 2017 with slight modifications [6]. The process involved preparing a 0.5 M solution of $C_4H_{10}MgO_2$ in ethanol, which was stirred for 2 hours at room temperature. Subsequently, a 0.2 M NaOH solution was added dropwise until the pH reached 12.8. The mixture was then vigorously stirred for 14 hours. Afterward, it was washed with deionized water and ethanol. Finally, the product was dried at 75 °C for 7 hours and calcined at 650 °C for 3 hours.

Characterization of the nanoparticles. The composition of the nanoparticles was analyzed by X-ray diffraction (XRD, Siemens D-5000), using Bragg-Brentano geometry and Cu-Kα radiation ($\lambda = 1.5418$ Å), with a step size of 0.02° and a counting time of 5 s. The crystalline phases were identified by comparing the data with the Joint Committee on Powder Diffraction Standards (JCPDS) database. The crystallite size, D, was calculated using the Scherrer equation. To confirm the formation of nanoparticles, their size and morphology were evaluated using a scanning electron microscope (SEM, JEOL JSM-7600F).

Evaluation of the efficacy of the NPs on stone. To evaluate the effectiveness of the nanoparticles on stone, the stone samples were cut into cubes measuring 5 cm on each side. The nanoparticles were applied by dropwise addition at a concentration of 1 g/L, and the consolidation of the stone was carried out over a period of 30 days.

The velocity of ultrasound propagation (Vp) was measured by PUNDIT PL 200 (PROCEQ) equipment to evaluate the mechanical proprieties, using dry contact transducers operating at 54 kHz. The measurement was performed in direct transmission mode.

The contact angle was measured using a digital portable microscope. A 20 μL drop of deionized water was placed on the surface of the sample, and the angle was analyzed using ImageJ free access software.

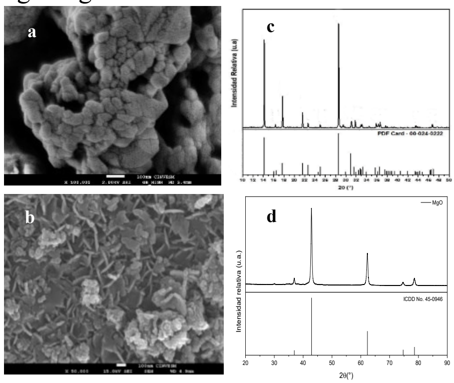

Fig. 1. Micrographs of the nanoparticles: a) CZ at 100,000× and b) MgO at 50,000×. X-ray diffraction patterns obtained from the synthesis of c) CZ (qatranaite) and d) MgO (periclase).

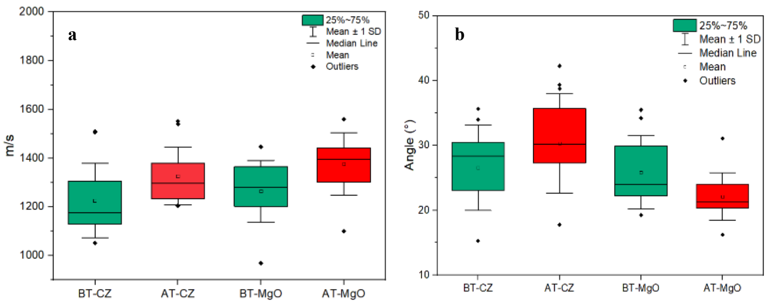

Fig 2. Descriptive Statistics: a) Ultrasound propagation velocity and b) Contact angle, before the application of treatments (BT-CZ and BT-MgO) and after the application of treatments (AT-CZ and AT-MgO).

Conclusions. CZ and MgO were successfully synthesized. The theorical crystal size was calculated with crystallography data obtained by XRD, the results were 72 and 17 nm, respectively. Comparing these values with measures obtained by SEM, an average particle size of 62.5 nm was observed for CZ nanoparticles and 36.1 nm for MgO nanoparticles. In both cases, these values fall within the nanomaterial size range. After the application of CZ and MgO nanoparticle treatments on the limestone material, the Vp values showed a statistically significant increase. Additionally, CZ contributed to an increase in the contact angle of the stone, unlike what was observed with MgO nanoparticles, who's higher hygroscopicity enhances their water absorption capacity.

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