

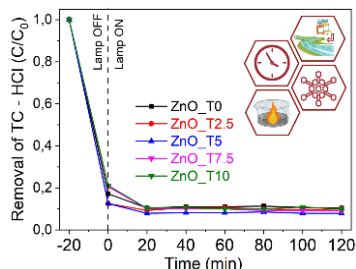
## Optimizing Photocatalytic Performance of ZnO Nanoparticles via Controlled Calcination Time for Tetracycline Removal

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This study aims to optimize the synthesis of ZnO nanophotocatalyst via calcination, striking a balance between phase purity and particle size to enhance photocatalytic performance. ZnO nanomaterials were synthesized by SCS, with calcination times varying from 0 to 10 min. Characterization techniques including XRD, SEM, and UV-visible were employed to elucidate the physicochemical properties. The photocatalytic activity was evaluated by removing tetracycline hydrochloride (TC-HCl) under simulated solar light conditions. The results show a correlation between calcination time and particle morphology, with larger particles exhibiting improved carbon removal efficiency. XRD analysis indicates a decrease in residual carbon content with increasing calcination time. Optimum removal is achieved at 5 minutes of calcination (ZnO\_T5) with a rate of 92.1% removal of TC – HCl.

### Introduction

Zinc oxide (ZnO) exhibits a wide range of physical, chemical, and optical properties, making it a versatile material used in various industrial and technological fields [1]. ZnO has excellent photocatalytic capabilities due to its band gap of about 3.3 eV. This property enables it to effectively absorb ultraviolet (UV) radiation, with a performance compared to the standard TiO<sub>2</sub> [2]. Emerging contaminants, such as the 157 compounds found in different aqueous matrices in Brazil, can be degraded on the surface of ZnO by redox processes stimulated by electronic excitation between the valence and conduction bands. ZnO can generate reactive oxygen species (ROS) when exposed to UV light or visible light when functionalized, facilitating the degradation of the pollutants and the disinfection or inhibition of microorganisms in water [3].

A versatile method for producing nanocrystalline and nanostructured zinc oxide materials is solution combustion synthesis (SCS). The combustion process is known for its rapid reaction by a self-sustaining exothermic process. It has attracted attention for its inherent ability to serve as a strategy for fine-tuning semiconductor oxide properties [4,5]. The SCS method is excellent for producing photocatalytic materials with a porous structure and large active surface area. However, due to fuel combustion during the synthesis reaction, residual carbon can remain in the material. This excess of

carbon hinders the direct contact between pollutant-photocatalyst, the light income, and absorption capability, reducing its efficiency [5]. Therefore, this study aims to develop a calcination study on the SCS method to prepare ZnO nanophotocatalyst, attempting to achieve an optimum balance between phase purity and particle size of the materials to maximize the photocatalytic performance. A correlation was carried out between the physicochemical properties at various calcination times and the removal performance of tetracycline hydrochloride (TC – HCl) as a model pollutant.

### Material and Methods

ZnO nanomaterials were prepared using 3.567 g of zinc nitrate hexahydrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) as the oxidizing agent and 1.197 g of sucrose (C<sub>12</sub>H<sub>22</sub>O<sub>12</sub>) as the fuel, which corresponded to a fuel-to-oxidizer ratio of  $\phi = 1.4$ . 3 ml of distilled water was added, and the reagents were mixed with a glass rod until the solids were completely dissolved. The mixture was then placed in a preheated muffle furnace at 500°C, where the combustion reaction occurred with varying calcination times of the process: 0 minutes (T0), 2.5 minutes (T2.5), 5 minutes (T5), 7.5 minutes (T7.5), and 10 minutes (T10). The resulting material was a fine gray-to-white powder of nano-ZnO, depending on each studied condition. Materials characterization techniques, such as XRD, SEM, and UV-vis spectral analysis, were used to

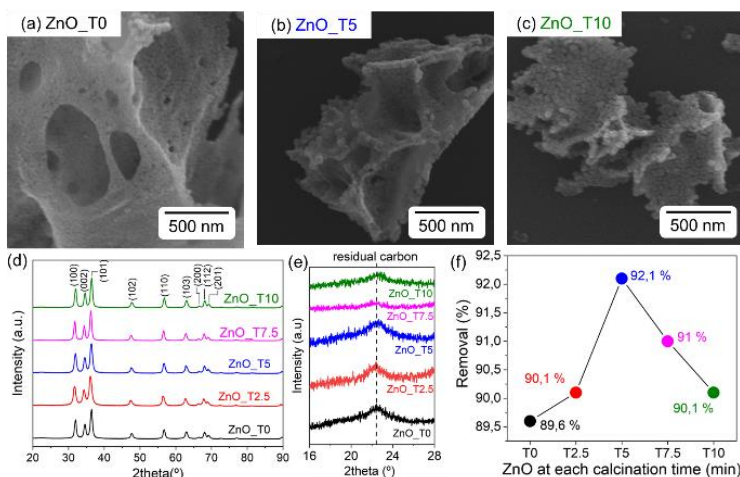
support the study. The photocatalytic performance of the materials was evaluated by photocatalytic essays using 10 ppm of TC-HCl, under simulated solar light driven (85W fluorescent lamp) with 0.5 g/L of each photocatalyst.

## Results and Discussion

Figure 1 (a) to (c) presents the morphology of the ZnO nanoparticles calcinated at T0, T5, and T10 times. There is a tendency for these particles to grow as the calcination times increase. X-ray diffraction (XRD) analysis shows the formation of the zinc oxide hexagonal crystal structure (Figure 1 (d)), for all specimens. Figure 1 (e) reveals a peak at about  $22.5^\circ$  in the calcination time T0, related to the residual carbon phase. When analyzing the other calcination times, it is possible to see a tendency for this peak to decrease, indicating the residual carbon removal as the calcination is carried out. The reflectance analysis resulted in band gap values that did not change from one calcination time to the next, remaining at around 3.29 eV.

According to the Graphical Abstract, the point of ZnO\_T5 outperformed the other points when the data from adsorption in the dark (lamp off) and degradation driven by visible light are taken as figures of merit. In the step of light on, T5 shows a photocatalytic removal rate of approximately 87.5% of TC-HCl. Furthermore, as shown by Figure 1 (f), T5 exceeded all removal rates with a percentage of about 92.1%, which is the optimum point for the total removal rate.

The specimen ZnO\_T5 presented good removal of the residual carbon and slight particle growth. However, at time T10, although the residual carbon is removed even further, the reduction of the surface area of the nanophotocatalyst due to the presence of larger particles causes a decrease in the photocatalytic performance. These results indicate that it is possible to achieve an optimal TC-HCl removal performance by choosing a calcination time that optimally balances the particle size and the amount of residual carbon.



**Figure 1.** (a) – (c) SEM micrographs of the ZnO at T0, T5, and T10; (d) – (e) XRD diffractograms at each calcination time focusing on the residual carbon, and (f) evolution of the removal performance.

## Conclusions

Optimization of calcination time, obtained in this work at 5 minutes (T5), significantly enhances the photocatalytic performance of ZnO nanomaterials synthesized via solution combustion synthesis, demonstrating superior free surface area, and achieving a total removal rate of over 92.1% for tetracycline hydrochloride under simulated solar light conditions.

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