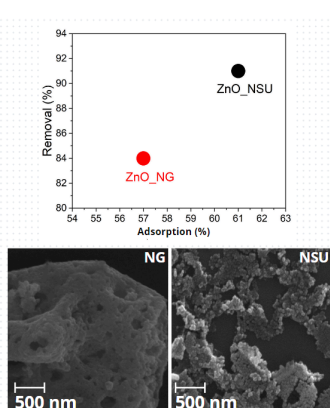


# Effect of Fuel Type in the Solution Combustion Synthesis of N-doped ZnO and its application as a Photocatalyst for Tetracycline

ORAL  
Ph.D. Student: N  
Journal: Journal of  
Environmental  
Chemical Engineering

C. Cuneo<sup>1</sup>, A. Lucena<sup>1</sup>, T. Pigosso<sup>1</sup>, L. Evangelista<sup>1</sup>, C. Binder<sup>1</sup>. (1) Universidade Federal de Santa Catarina, Florianópolis, Brazil, caio.cuneo@labmat.ufsc.br



The use of semiconductors in photocatalysis is a very efficient process for the removal and degradation of complex molecules present in aqueous media. Solution combustion synthesis (SCS) is a fast and efficient method to synthesize porous semiconductor nanoparticles, in which its properties are strongly related to the fuel used in the synthesis. This technique allows the simultaneous synthesis and nitrogen doping of nano-ZnO, through nitrogen-based fuels, such as glycine. This work proposes the use of both sucrose and urea (NSU) in the synthesis of N-doped ZnO as an alternative to glycine (NG), aiming to achieve N-doping alongside improved morphology and surface area. Despite both formulations presented a band gap energy of around 3.28 eV, photocatalysis essays showed a total removal of TC-HCl of 91% for the NSU sample and 84% for the NG sample.

## Introduction

Increasing industrialization and population growth are leading to various types of contamination of water resources by substances known as emerging contaminants, which are unregulated compounds that pose high risks to the environment. Tetracycline, one of the most widely used antibiotics in Brazil with a daily consumption of 23 kg, is an example of such contaminants [1].

Advanced oxidation processes (AOP), such as photocatalysis, are a group of processes based on the production of highly reactive free radicals that are capable of degrading complex molecules, like antibiotics. These processes are very cost-effective as they have high photocatalytic activity and no selectivity [2].

Nanostructured semiconductors are commonly used as photosensitizers in heterogeneous photocatalysis for the degradation of pharmaceutical pollutants. Zinc oxide (ZnO) has great photocatalytic activity in addition to being non-toxic and low-cost. The main limitation of ZnO as a photocatalyst is its wide band gap, which means that it requires UV light to be activated. The band gap energy can be lowered to extend the absorption to visible light by mechanisms such as doping with nitrogen.

Solution Combustion Synthesis (SCS) is a simple and versatile method to synthesize ZnO nanostructures and also to introduce defects into the lattice of the material, such as nitrogen doping. The self-propagating combustion reaction and the release of gas during the process result in a porous

powder with a high level of defects, essential properties for a good photocatalyst. The morphological and surface properties are directly related to the fuel used in the synthesis [3].

The use of glycine as fuel allows the formation of nanostructured powder. The molecule itself contains the nitrogen needed for doping, enhancing the photocatalytic activity [4].

For the same purpose, a mixture of sucrose and urea in a molar ratio of 1:1 can be used analogously to glycine. In this case, it's expected that the urea provides the N<sub>2</sub> necessary to dope the ZnO, and the sucrose acts by controlling the size and morphological parameters of the nanoparticles formed. In this context, the present work aims to compare the use of these two systems in terms of the characteristics of the synthesized powders and their photocatalytic capacity in the removal and degradation of tetracycline hydrochloride (TC-HCl).

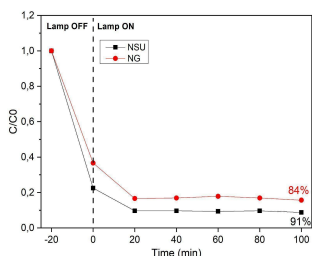
## Material and Methods

Zinc nitrate hexahydrate was used as the oxidizing agent. Glycine (NG) and the 1:1 mixture of sucrose and urea (NSU) were used as reducing agents (fuel). The reactants were mixed at a fuel-to-oxidizer ratio of 1.4 and dissolved in 3 mL of distilled water. The solution was placed in a 50 mL beaker over a ceramic vessel. Another 250 mL beaker was placed on top of the system to prevent the powder from spilling. A muffle furnace was preheated to 500°C and the mixture reacted for 10 minutes, after which the upper beaker was removed and the powder was calcined for another

20 minutes. The photocatalytic assays were performed in a solution containing 10 ppm TC-HCl and 0.5 g/L of the photocatalytic material, irradiated by an 85 W lamp simulating the solar spectrum. The total test time was 140 min, with the first 20 min in the dark.

**Results and Discussion**

The percentage removal of TC-HCl over time is shown in Figure 1. It is observed that during the dark period of the assay, the NSU sample adsorbed 77% of the contaminants, 15% more than NG. This may be due to the larger surface area of the NSU particles. After 40 minutes of reacting with light, the removal of both systems stabilized, reaching a maximum of 91% removal for NSU and 84% removal for NG.



**Figure 1.** Photocatalysis essay results of NSU and NG.

As shown in Table 1, both samples have very similar band gap energy values (Figure 2), indicating that the nitrogen doping phenomena was comparable for both systems. However, when evaluating the final TC-HCl removal results, it can be seen that the NSU NPs showed better removal properties. Since there is no difference in the band gap, we can correlate this better performance with the morphology and the size of the formed particles.

As expected for this type of synthesis, the analysis of the morphology presented in the SEM images

**Conclusions**

The ZnO nanoparticles produced with the sucrose and urea fuel system showed greater removal compared to the glycine system, which can be explained by their smaller particle size and, consequently, larger surface area. Both samples presented the same band gap value, which confirms the greater influence of nanoparticle morphology on the difference in photocatalytic potential between the samples.

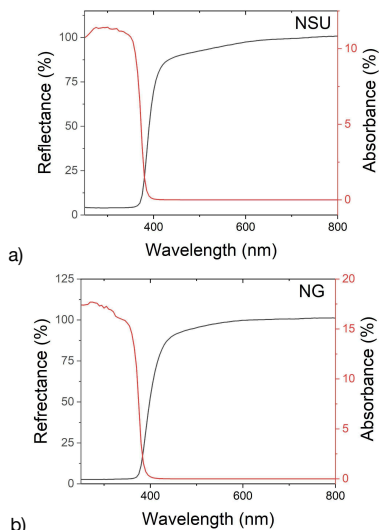
**Acknowledgments**

This work has been supported by CNPq, CAPES, FAPESC, PRH-ANP/FINEP, and EMBRAPII.

**References**

- [1] A. Fiaz, D. Zhu, J. Sun. Environmental Sciences Europe. 33 (2021) 1.
- [2] R. Dewil, D. Mantzavinos, I. Poulios, M. Rodrigo. Journal of Environmental Management, 195 (2017) 93.
- [3] F. Siddique, S. Gonzalez-cortes, A. Mirzaei, T. Xiao, M. Rafiq, X. Zhang. Nanoscale, 14 (2022) 11806.
- [4] C. Hwang, T. Wu. Journal of Materials Science, 39 (2004) 6111.

(Graphical abstract) shows that both samples have porous characteristics. The NSU NPs showed slightly smaller and more dispersed agglomerates than the NG ones, which can be explained by the flame temperature and by the gases formed during the SCS process. The presence of sucrose generates more gasses in the combustion reactions, resulting in smaller particles and more porous structures.



**Figure 2.** Reflectance and absorbance graph of NSU (a) and NG (b).

**Table 1.** Values of Band gap energy of each sample.

Sample	Band gap (eV)
NSU	3,27
NG	3,29