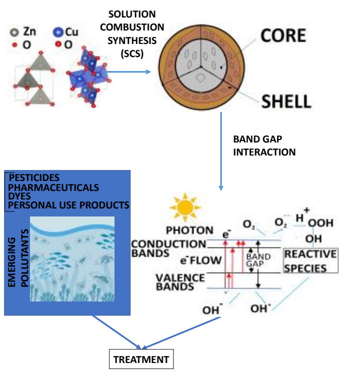
The photocatalytic potential of the ZnO/CuO heterojunction in the abatement of tetracycline hydrochloride

ORAL
Ph.D. Student: N
Journal: JECE

B. Melo[1], *T. Pigosso*[1], *L.L. Evangelista*[1], *C. Binder*[1]. *(1) Federal University of Santa Catarina (UFSC), Eng. Agronômico Andrei Cristian Ferreira Street, s/n, Florianópolis, Brazil, byron.melo@labmat.ufsc.br*.



Emerging pollutants are a new class of contaminants originating in high-complexity industries affecting both water life and humans. In this problem, there are a lot of promising technologies, such as photocatalysis/adsorption techniques. In this work, we evaluated the feasibility of producing ZnO/CuO heterojunctions by solution combustion synthesis (SCS) for the photocatalytic abatement of tetracycline hydrochloride (TC – HCl), as a model pollutant. In the optimal ratio between zinc nitrate hexahydrate, copper nitrate, and sucrose as the starting reactants, we obtained ZnO/CuO materials with a photocatalytic removal of 85% after 60 minutes of essay, due to the phases obtained and their high crystallinity, their core/shell morphology which translated in a band gap reduction and the size of the powders obtained increasing contact area with the pollutant. These experiments show the versatility and efficiency of SCS, a rapid route for synthesis towards the treatment of complex molecules by adsorption/photocatalysis mechanisms.

Introduction

Technology serves us all. Whether it is on a personal level used for connecting with the world and its many different cultures or as a society making more efficient technology to facilitate the transit of information, capital, and people. But that came with a great cost to the environment, the greenhouse effect getting worse caused by an increase in pollution-affected climate, air, and water source quality. And now, emerging pollutants are a reality. This new class of pollutants originates from high-complexity industries such as pesticides, pharmaceuticals, personal care products, and dyes, which have a higher impact on water sources [1].

There's been an increase in the search for solutions to this problem. Filtering, disinfection, adsorption, and photocatalysis, or the simultaneous application of multiple methods. Using adsorption and photocatalysis can highlight the strengths of both techniques, developing integrated photocatalysts-adsorbents.

This could lead to several benefits such as the adsorbent assisting in concentrating the pollutant near the vicinity of the photocatalyst to improve the removal efficiency [2]. Solution combustion synthesis (SCS) is a relatively novel and versatile technique to produce nanometric and porous semiconductor materials to act as photocatalysts, such as ZnO, TiO_2, CuO, and heterojunctions of multiple oxides [2]. The combustion process is a fast self-sustained exothermic reaction between an oxidizer and fuel, which makes the method energy-saving and cost-effective without hazardous reactants. Herein, this work proposes to produce ZnO/CuO heterojunctions by simply tailoring the reactants based on the fuel-to-oxidizer ratio, resulting in different physicochemical features that influence the application of the photocatalytic removal of TC – HCl.

Material and Methods

For the making of ZnO/CuO heterojunctions, the following reagents were used: trihydrate copper nitrate, hexahydrate zinc nitrate, sucrose, and distilled water. Maintaining the fuel-to-oxidizer ratio (ϕ = 1.4), which is important definitive in the final properties of the powders synthetized by this method. Everything is added to a crucible and stirred until it is homogenous and the reaction starts by inserting it in a 500 ºC Muffle furnace, and then a self-sustainable reaction starts until a porous material composed of nanocrystals of the metal oxides is obtained. It set for 10 minutes for synthesis and then the porous structure was broken down and added again to the furnace for 20 minutes to remove residual carbon. We proposed five formulations with 5 different molar ratios of Zn and Cu ranging from 100% to 0% of Zn as an oxidant agent (ZnO/CuO 100:0; ZnO/CuO 75:25; ZnO/CuO 50:50; ZnO/CuO 25:75; and, ZnO/CuO 0:100).

The powders obtained were evaluated by XRD, SEM, FTIR, UV-Vis, particle size by hydrodynamic radius, and photocatalytic efficiency essays to degrade tetracycline hydrochloride, lasting 60 minutes with 20 minutes for equilibrium under the radiation of low-pressure mercury lamp (85 W,430 < λ < 750 nm).

Results and Discussion

To evaluate the phases formed during the SCS method, XRD diffractograms (Figure 1) of the ZnO/CuO materials were obtained. For the pure oxides, we had the zinc oxide phase in the hexagonal wurtzite structure, as validated by the CIF card nº 2300112. As for the pure copper precursor, the CuO monoclinic phase (CIF card nº 1100028) was observed. Besides, the cubic phases of both

Cu_2O and metallic copper, according to CIF card nº 1000063 and CIF card nº 4105681 were identified.

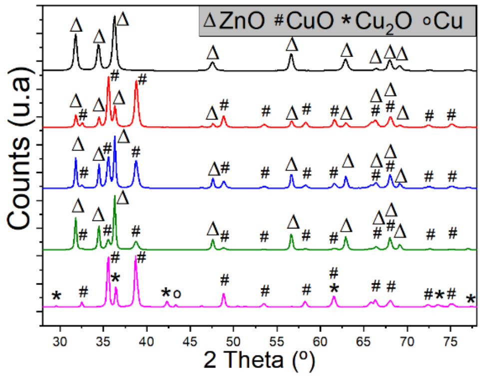


Figure 1. XRD patterns for ZnO/CuO formulations.

With SEM and dynamic light particle size measurements, the work achieved core/shell configurations and segregated phases for the heterojunctions with sizes ranging to 60 nm to over the micrometric phases. The UV-Vis analysis pointed out that the heterojunction formulations were excited by visible radiation and by calculating their respective band gaps with the Kubelka Munk function, resulting in band gaps corresponding to the metal oxides ZnO, CuO, and Cu_2O in the acceptable range (3.1; 1.8 and 2.5 eV), and for the heterojunctions 1.7 eV. All three specimens presented a band gap low enough for visible light applications, and also literature reported that the presence of copper phases in the 400 nm range was correlated to better efficiency in ZnO/CuO heterojunctions[3].

Functional groups investigated by FTIR also corroborated metal oxide formation and gave interesting information, a hydroxide layer on the surface or remaining of the fuel, which should be investigated specially for incorporation on a matrix and adsorption mechanisms.

The evaluation of photocatalytic performance is shown in Figure 2.

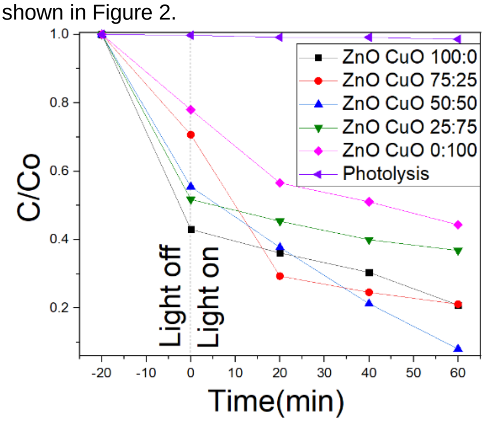


Figure 2. Photocatalytic efficiency of ZnO/CuO formulations in the treatment of Tetracycline HCl (0.5 mg/L photocatalyst, 10 ppm concentration of pollutant)

The powders obtained showed great adsorption capability by getting as much as 55% of the pollutant before the light turned on and after the 60 minutes of essay, the sample ZnO/CuO 50:50 showed the best photocatalytic activity, achieving as much as 85%, which is double the efficiency of the pure oxides.

Conclusions

The powders obtained are made up of phases intended, ZnO and CuO, except for the pure copper that showed the Cu_2O and Cu. On top of that, the investigation of morphology and size showed core/shell and segregated phases of the nanometric scale with ranges of 60 nm until the micrometric phase. FTIR analysis also checked the interaction of the material with the mean and the functional groups associated. UV-Vis is pointed for both UV and Visible light activity, and that agrees with the band gap calculation obtained via the Kubelka Munk function. The powders submitted to photocatalytic essays showed a great adsorption capability and after the lights were turned on, they had a photocatalytic efficiency as high as 85% with a first order kinetics coefficient of 1,7. This shows that materials obtained are a promise in the treatment of emerging pollutants like Tetracycline HCl. This shows SCS is an efficient method to obtain metal oxide nanocrystals with tailorable characteristics by changing fuel, coefficient, and synthesis temperature, achieving a high photocatalytic efficiency for treating complex molecules such as Tetracycline-HCl.

Acknowledgments

I would like to thank the fomenting organizations, CAPES, CNPq, FAPESC, and Embrapii for the funding of the research presented. Also, acknowledge my research group in LabMat for the help and hard work towards this research. Last but not least, my university UFSC for providing the installations and energy needed.

References

[1] S.R. Mishra, M. Ahmaruzzaman, CuO and CuO-based nanocomposites: Synthesis and applications in environment and energy, Sustain. Mater. Technol. (2022) e00463. https://doi.org/10.1016/j.susmat.2022.e00463.

[2] T. Pigosso, B.A.A. Melo, L.L. Evangelista, S.Y. Gómez González, C. Binder, Rapid synthesis of in situ nitrogen-doped ZnO nanoparticles for visible-light-driven photocatalytic removal of emerging contaminants, Mater. Today Chem. 33 (2023) 101753. https://doi.org/10.1016/J.MTCHEM.2023.101753.

[3] T. Chang, Z. Li, G. Yun, Y. Jia, H. Yang, Enhanced photocatalytic activity of ZnO/CuO nanocomposites synthesized by hydrothermal method, Nano-Micro Lett. 5 (2013) 163–168. https://doi.org/10.5101/nml.v5i3.p163-168.