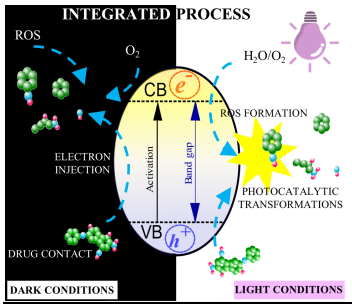
Perovskite and Graphitic Carbon Nitride Hybrid as Bifunctional Dark(photo)catalyst for Tetracycline Fast Abatement

POSTER
Ph.D. Student: Y
Journal: CEJ

A. H. Da Silva Júnior[1], *C. R. S. De Oliveira*[1], *S. V. M. Lima*[1], *S. L. De Carvalho Neto*[1], *A. A. U. De Souza*[1], *S. M. A. G. U. De Souza*[1], *L. Da Silva*[2], *A. Da Silva*[1]. *(1) Federal University of Santa Catarina, 88040-900, Florianópolis, Brazil, afonso.ufsc@gmail.com. (2) Centro de Investigación en Química Aplicada, 25294, Saltillo, Mexico.*



This study introduces a novel bifunctional hybrid catalyst comprising perovskite oxide and graphitic carbon nitride for the fast abatement of tetracycline (TC) in both dark and light environments. Employing an experimental design methodology, the degradation parameters were optimized under dark ambient conditions (99%). Moreover, the catalyst's potential in a UVC light-assisted process was explored, leading to complete antibiotic removal within 30 minutes. This investigation not only elucidates on the mechanisms underlying antibiotic degradation in low-light settings but also unveils innovative applications for water treatment in contaminated environments.

Introduction

Antibiotics have received significant attention due to their potential effects on the environment and public health, *e.g.*, bacterial resistance. Several chemical treatment processes have been applied to reverse water contamination, emphasizing advanced oxidation processes (AOPs) [1]. A promising method within AOPs is photocatalysis, which involves the activation of catalysts using light to promote oxidation reactions. In addition, an innovative approach in water treatment is dark catalysis, which aims to harness the catalytic activity of materials even in the absence of light. This strategy may significantly reduce the energy costs associated with the effluent treatment process.

Catalysts play a crucial role in the effectiveness of catalytic processes [2]. Recent trends have pointed to using catalysts based on perovskite oxides and carbon, such as graphitic carbon nitride (*g*-CN). These materials have unique properties that make them highly efficient in promoting contaminant degradation reactions.

A significant study by Luo and coworkers has demonstrated the effectiveness of direct heterogeneous catalysis in decontaminating water polluted by doxycycline (DXC) [3]. They synthesized perovskite-type materials ($La_xSr_{(1-x)}CoO_3$) through a green mechanical milling method and applied them in the efficient catalytic DXC degradation without the addition of chemical reagents or illumination (89.64%).

Composites based on perovskite and *g*-CN hold great promise in enhancing the efficiency of water treatment processes. Therefore, we produced a hybrid of *g*-CN and perovskite oxide based on strontium, copper, and iron and applied it to the TC degradation in a dark environment. Also, we studied the photocatalysis in the TC degradation using hybrid.

Material and Methods

Firstly, *g*-CN and $SrCu_{0.5}Fe_{0.5}O_3$ (SCF) powders were previously synthesized [3,4]. The hybrid's production was based on the methodology reported in the literature from pure materials with alcohol in appropriate proportions [4]. Thus, the mixture was sonicated, dried, and calcined. Finally, the powder obtained (SCF/*g*-CN) was applied in the catalysis. In a typical experiment, 100 mL of pollutant solution and a catalyst dose were added to a 250 mL beaker. The degradations were carried out in a batch reactor in dark conditions at 25°C. Experiments were executed following a Box-Behnken-type experimental design to optimize parameters such as pollutant concentration (10, 20, and 30 $mg{\cdot}L^{-1}$), pH (3, 5, and 7), and catalyst dosage (0.5, 1.0, and 1.5 $g{\cdot}L^{-1}$) (Statistica® 10). In the optimized dark catalysis condition, it was tested with UVC light (8 W). Contaminant concentration was analyzed by measuring the absorbance (356 nm).

Results and Discussion

The hybrid material was successfully synthesized. Through TEM, SEM, and XRD characterizations, it was possible to verify that the heterojunction had formed. Figures 1(A-C) illustrate the TEM images of SCF, *g*-CN, and SCF/*g*-CN. It is possible to observe the SCF reveals that the primary particles, approximately 200 nm, exhibit notable aggregation and high densification. TEM image of the *g*-CN revealed random particle shapes ranging from nanometers to micrometers. Darker parts in the TEM image may be attributed to the stacking of *g*-CN layers. Regarding the TEM image of SCF/*g*-CN, it is possible to observe the characteristics of both pure materials, demonstrating the effectiveness of the synthesis.

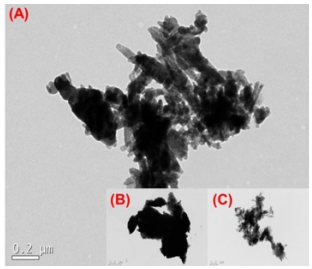


Figure 1. TEM. (A) SCF/*g*-CN; (B) SCF; (C) *g*-CN.

Figures 2(A-C) present the SEM images of SCF, *g*-CN, and SCF/*g*-CN. The SCF image shows particles of varied sizes and configurations, indicating distinct growth behaviors during the catalyst preparation phase. The *g*-CN structure presented composed of rough, micrometer-sized particles with multiple stacked layers. The synthesized hybrid, with a rough surface and dense material, presents characteristics of both pure materials.

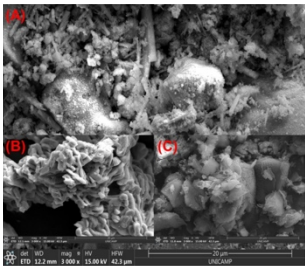


Figure 2. SEM. (A) SCF/*g*-CN; (B) SCF; (C) *g*-CN.

Figure 3 details the XRD pattern of the materials. The SCF exhibits a prominent crystalline characteristic, with a pure cubic structure associated with the $PM\bar{3}M$ space group (JCPDS 40-0905) [4]. The *g*-CN phase of the (0 0 2) plane is evident in the peak around 26°. The heterojunction, with peaks from both materials, demonstrates the successful formation of the composite.

The hybrid's application to TC degradation obtained excellent results in a dark environment. The best removal result (99%) through experimental design was with pollutant concentration, pH, and catalyst dose of 10 ppm, 7, and 1 $g.L^{-1}$, respectively. In order to optimize the process, surface curve was analyzed, and it was found that at a catalyst dose of 0.5 $g.L^{-1}$, pH 6, and pollutant concentration of 10 ppm, degradation also was close to 100% (Figure 4), reducing costs with pH correction as it is natural and has a smaller amount of catalyst.

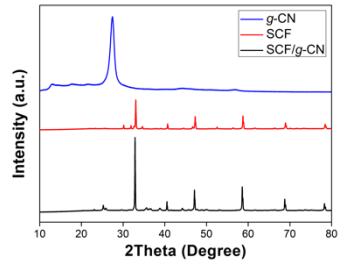


Figure 3. XRD.

In this sense, a new experiment was carried out with light to verify the potential of the hybrid in UVC and propose a combined process of catalysis in the dark and photocatalysis. Thus, complete removal of the antibiotic was achieved, however, in less time (30 min) compared to the dark (60 min). Experiments with only UVC light without the catalyst were also carried out and there was no significance in the antibiotic's reduction.

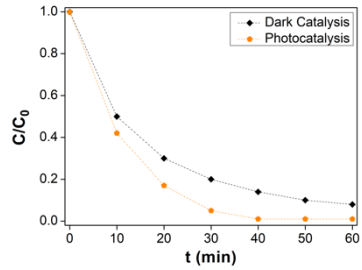


Figure 4. Degradation kinetics.

Conclusions

Therefore, the hybrid catalyst exhibited catalytic efficacy in both dark conditions and under UVC irradiation for the TC degradation. Consequently, this study offers novel insights and represents a pioneering contribution to the understanding and exploration of antibiotic degradation mechanisms in low-light environments.

Acknowledgments

The authors acknowledge the CNPq, LabMASSA/UFSC, LCME/UFSC, LRAC/UNICAMP, and LINDEN/UFSC.

References

[1] F. Ali, J. Khan, N. Shah, M. Sayed, H. Khan, *Process Safety and Environmental Protection*, 117 (2018) 307.
[2] K. Hu, R. Li, C. Ye, A. Wang, W. Wei, D. Hu, R. Qiu, K, Yan, *Journal of Cleaner Production*, 253 (2020) 120055.
[3] X. Luo, C. Su, Z. Chen, L. Xu, L. Zhao, J. Zhao, R. Qiu, Z. Huang, *Separation and Purification Technology*, 300 (2022) 121891.
[4] S. Hu, J. Yuan, S. Tang, D. Luo, Q. Shen, Y. Qin, J. Zhou, Q. Tang, S. Chen, X. Luo, D. Xu, *Optical Materials*, 132 (2022) 112760.