

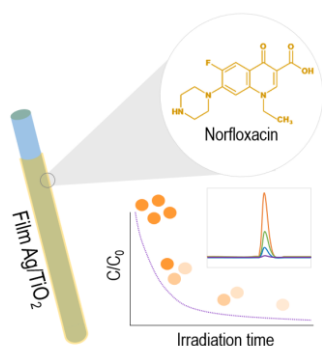
Study of the photodegradation of the antibacterial drug norfloxacin by thin films of Ag/TiO₂

ORAL/POSTER

Ph.D. Student: Y/N

Journal: NONE

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In this study, the efficiency and reusability of Ag/TiO₂ films immobilized on inert support for NRF degradation were investigated under UVA irradiation (365 nm), and samples were analyzed by HPLC/FL. In 100 µg.L⁻¹ solutions, photolysis achieved 94% degradation of NRF after 5 hours and its by-products within 24 hours. When using Ag/TiO₂ films, 93% of NRF was degraded within 1.5 hours, and by-products within 4 hours. The films proved to be efficient, stable, and easy to use, indicating potential application for environmental remediation of antibacterials in wastewater.

Introduction

Norfloxacin (NRF) is an antimicrobial from the fluoroquinolone (FQs) class that possesses a broad bactericidal spectrum often found in various environmental matrices, especially aqueous ones. The FQs, even at low concentrations, can induce bacterial resistance, affecting human and animal health [1].

Therefore, heterogeneous photocatalysis has proven to be quite effective for the removal of NRF and other FQs, especially with the use of TiO₂, typically in the form of suspensions [2]. However, the time-consuming filtration step, loss of material throughout the process, and decrease in photocatalytic efficiency during its reuse lead to a high cost of this treatment, making its large-scale implementation unfeasible [3].

Considering this, the objective of this work is to study the degradation of NRF through photolysis and photocatalysis with the reuse of Ag/TiO₂ films.

Material and Methods

The Ag/TiO₂ films were prepared by the *sol-gel* method using titanium (IV) isopropoxide, TiO₂ P25, and AgNO₃. The formed suspension (sol) of Ag/TiO₂ at 0.15% Ag (w/w) was immobilized on the external walls of Pyrex® borosilicate test tubes (2 cm x 9 cm) using the dip-coating method [4].

A beaker containing 800 mL of NRF fortified solution (pH 6.8) under agitation and atmospheric air flow (1.5 L.min⁻¹) was placed inside the photoreactor (40

cm x 35 cm x 55 cm), equipped with blacklight fluorescent lamps (28W), emitting light at 365 nm with an irradiance of 11.87 W.m⁻².

Aliquots were withdrawn at predetermined times and analyzed by high-performance liquid chromatography with fluorescence detection (HPLC/FL) [5].

Results and Discussion

NRF exhibited 71% photolysis at pH 6.8 after 2 hours of exposure to UVA irradiation (365 nm), reaching 94% after 5 hours. However, NRF and its degradation products were still detected after more than 15 hours of exposure.

During photolysis, 10 chromatographic peaks (N1 to N10) were observed, as shown in Figure 1. N1, N3, N7, N8, N9, and N10 were detected up to 12 hours, and only N7 was observed after 24 hours of UVA irradiation. N3 showed the highest analytical signal after 3 hours, and its area was reduced by half after 6 hours, no longer observed after 15 hours.

A recent study indicated that NRF produced five degradation products during photolysis, mainly involving hydroxylation and defluorination pathways, with a mineralization rate of 9.83% after 1 hour of irradiation using fortified tap water, with degradation slower than in ultrapure water [6].

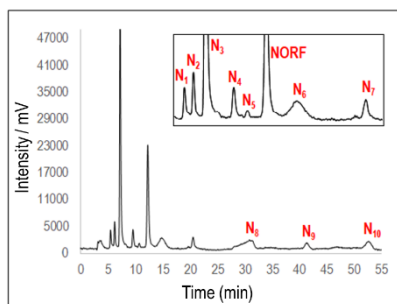


Figure 1. Chromatogram obtained by HPLC/FL from the photolysis of $100 \mu\text{g}\cdot\text{L}^{-1}$ of NRF after 2 hours of exposure to UV irradiation (365 nm) in ultrapure water, pH 6.8.

With the use of Ag/TiO_2 films in the presence of UVA light (365 nm), NRF in samples of ultrapure and tap water had 93% of its concentration eliminated after 1.5 hours, whereas in photolysis, during the same time interval, a removal percentage of 62% was achieved (Figure 2). In the photocatalysis of NRF, the formation of seven degradation products was

observed, which were not detectable after 4 hours of analysis.

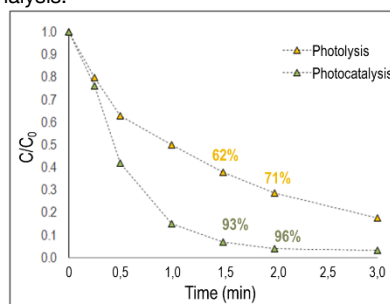


Figure 2. Degradation rates of NRF by photolysis and photocatalysis with Ag/TiO_2 film.

The Ag/TiO_2 films showed no loss in efficiency over the course of the five cycles conducted, maintaining the degradation rate over time three times more efficient, with elimination of all photoproducts observed within 4 hours in samples of ultrapure and tap water.

Conclusions

The Ag/TiO_2 films used in this research proved efficient for the degradation of the drug under study and its by-products, as these are not easily eliminated by photolysis. The photocatalysts remained stable during the tests conducted, considering that the same films were used in all photocatalysis experiments. The possible leaching of Ag from the film into the solution in the photoreactor had already been evaluated previously in the works of Araújo *et al.* (2015) [4] and Lima *et al.* (2020) [7], which demonstrated that no Ag content was lost, reinforcing the material's high stability.

Acknowledgments

The Postgraduate Program in Biodiversity and Biotechnology – Rede BIONORTE. This work was partially supported by the CNPq / Instituto Nacional de Ciência e Tecnologia de Bioanalítica [grant number 465389/2014-7]. Federal Institute of Education, Science and Technology of Maranhão (IFMA) and Federal University of Maranhão (UFMA).

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