DOI: http://doi.org/10.21698/simi.2022.ab04

IDENTIFICATION OF TRANSFORMATION PRODUCTS AND POSSIBLE DEGRADATION PATHWAYS OF CIPROFLOXACIN FROM AQUEOUS SYSTEMS VIA UV/VIS/TiO_2

Lucian Alexandru Constantin[1], Florentina Laura Chiriac[1], Mirela Alina Constantin[1]

[1]National Research and Development Institute for Industrial Ecology – ECOIND Bucharest, 57-73 Drumul Podu Dambovitei, 060652, Bucharest, lucian.constantin@incdecoind.ro, Romania

Keywords*: ciprofloxacin, degradation pathways, photo catalyse, transformation products*

Introduction

One of the most commonly used antibiotic worldwide, ciprofloxacin (CIP) is leading to the development of bacteria resistance in aqueous systems. Similar with other pharmaceutical compounds, CIP is not adequately removed from water via conventional treatment process, and therefore asks for more advanced treatment methods such as advanced oxidation processes (AOPs). Among AOPs, photo catalyse proved to be a promising method for advanced degradation of emerging pollutants such as CIP. Even if CIP degradation via AOPs was thoroughly investigated in the last period, the literature information on active species roles within CIP photocatalytic degradation are controversial, some researchers attributing the major role on hydroxyl radicals and holes since others are considering superoxide radical as the major active specie involved in CIP degradation. Therefore, there is a need for more experimental investigations on CIP photocatalytic degradation mechanism.

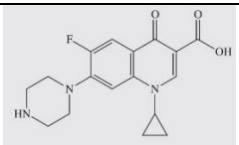
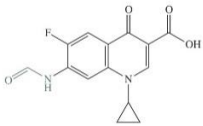
Materials and methods

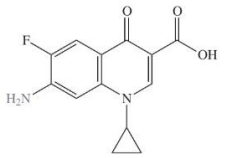
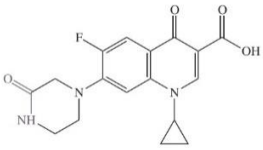
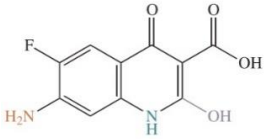
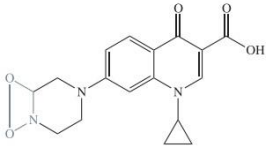
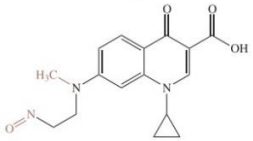
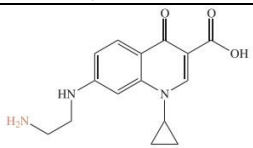
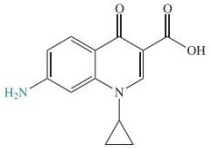
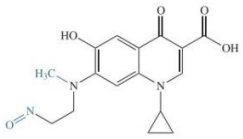
Photo degradation experiments were performed using an UV-VIS Heraeus reactor with a TQ150-Z3 lamp emitting in the domain 320-550 nm. CIP solution was prepared using 99% purity CIP, purchased from Sigma Aldrich and ultrapure water generated by a Milli-Q equipment. TiO_2 used as photo catalyst was purchased from Merck. CIP and transformation products determination was performed by High Performance Liquid Chromatography on a Agilent 1200 equipment.

Results and conclusions

Nine transformation products were identified:

Table 1. Identified CIP transformation products (TPs)

 CIP, m/z = 332	 TP1, m/z = 291

 TP2, m/z = 263	 TP3, m/z = 346
 TP4, m/z=238	 TP5, m/z = 344
 TP6, m/z = 316	 TP7, m/z=288
 TP8, m/z = 245	 TP9, m/z = 332

Based on identified TPs and on information already available within the literature, three main degradation routes were identified:

1. Attack of photo generated holes upon piperazine ring with formation of TP1, TP2 and TP3
2. Successive oxidation of cyclopropyl group of quinolone structure with formation of TP4
3. Superoxide radical attack with defluorination of CIP and its intermediates with formation of TP5, TP6, TP7, TP8 and TP9.

From the proposed degradation pathways presented within the literature, only three were identified in the tested experimental conditions. The hydroxil radicals involvement in CIP degradation in tested experimental conditions is rather low, the identified degradation routes suggesting that photo generated holes and superoxide radicals are the main active species in this particular conditions.

Acknowledgement. The work was funded by Ministry of Research, Innovation and Digitalization of Romania through Programme Nucleu through contract 20N/2019, Project PN 19 04 03 01.