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PRELIMINARY EXPERIMENTS ON CIPROFLOXACIN DEGRADATION VIA TiO₂ ASSISTED PHOTO CATALYSE

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Introduction

Ciprofloxacin (CIP) is an intensively used antibiotic, which led to the development of bacterial resistance in water. Therefore, both ciprofloxacin and ciprofloxacin resistant bacteria are emerging concerns that can threaten human health.

CIP photo catalyse was studied in the last period for various newly synthesized catalysts and experimental results proved that CIP photocatalytic degradation represents a promising method for CIP removal from aqueous systems.

The results on role of various active species for photocatalytic degradation of CIP are contradictory. Some researchers are stating that hydroxyl radicals and holes play the major role and others are attributing the major role to superoxide radicals formed by electrons and oxygen. Therefore, there is need for more investigations on CIP photocatalytic degradation.

Materials and methods

UV/TiO₂ system was tested for CIP degradation from mono component synthetic solutions. The influence of photo catalyst dose (TiO₂ purchased from Merck) was investigated. Photocatalytic experiments were carried out using a UV-VIS Heraeus type reactor equipped with a TQ150-Z3 lamp which emits in the domain $\lambda = 320 - 550$ nm.

High purity standard (99.0%) of Ciprofloxacin was purchased from Sigma-Aldrich (Germany).

Ciprofloxacin assay in samples coming from UV/TiO₂ degradation experiments was performed by HPLC on an Agilent 1200 series HPLC system (Agilent Scientific).

F⁻ mineralization was monitored using ion chromatography.

Results and conclusions

In order to establish optimum photo catalyst dose, degradation experiments were performed using a solution with initial CIP concentration $[CIP]_0 = 22.13$ mg/L = 6.68×10^{-5} M and TiO₂ doses varying within the domain 100-400 mg/L.

Table 1. CIP degradation via UV/TiO₂ system, [CIP]₀=22.13 mg/L, irradiation time 30 minutes

<i>TiO₂</i> <i>mg/L</i>	<i>[CIP],</i> <i>mg/L</i>	<i>Efficiency</i> <i>CIP, %</i>	<i>F</i> <i>mg/L</i>	<i>Efficiency</i> <i>F, %</i>	<i>k_{CIP} x</i> <i>10³, s⁻¹</i>	<i>k_F x 10³,</i> <i>s⁻¹</i>
100	0.87	96.07	1.07	82.66	1.798	0.973
200	0.24	98.92	1.12	86.59	2.513	1.116
300	0.13	99.41	1.18	91.32	2.854	1.357
400	0.02	99.91	1.23	95.25	3.894	1.693

As it was expected, the increase of initial photocatalyst dose up to amount of 400 mg/L led to the improvement of CIP degradation efficiency due to the increased number of active sites.

A further increase above this concentration is not necessary since CIP degradation efficiency is reaching more than 99.9% after 30 minutes of irradiation. Moreover, residual target compound concentration is of 0.02 mg/L.

Process efficiency is demonstrated also by organic F mineralization, which reached values of more than 95% in the same operating conditions. Mineralization efficiencies permanently lower than CIP degradation efficiency demonstrated the formation of organic intermediary compounds that contains F.

Summarising, CIP degradation via UV/TiO₂ system proved to be a promising method for CIP removal from aqueous systems at least in the following working conditions:

- Initial target compound concentration [CIP]₀ = 22.13 mg/L = 6.68 x 10⁻⁵ M
- Photo catalyst dose [TiO₂] = 400 mg/L
- Irradiation time = 30 minutes
- Degradation rate constant k_{CIP} = 3.894 x 10⁻³ s⁻¹
- CIP degradation efficiency = 99.91%
- Organic F mineralization rate constant k_F = 1.693 x 10⁻³ s⁻¹
- Organic F mineralization efficiency = 95.25%

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