CIPROFLOXACIN IN CONVENTIONALLY TREATED URBAN WASTEWATER: OXIDATION BY UV/H_2O_2 TREATMENT AND TOXICITY ASSESSMENT

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ABSTRACT

This study aimed at evaluating the degradation of the antibiotic ciprofloxacin (CIP) in urban wastewater effluents, using UV-C-driven oxidation processes with H_2O_2 as oxidant. Various concentrations of H_2O_2 were examined for the process optimization. The complete degradation of CIP was achieved within 15 min of treatment under the optimum concentration of H_2O_2 which it was found to be 10 mg L^{-1}. The phytotoxicity and ecotoxicity of the treated samples was investigated against one plant species and a crustacean, respectively. At the end of the process the phytotoxic effect was eliminated. In addition, this study demonstrated the ability of the UV-C process to reduce the toxicity towards *D. magna* since the immobilization of the organisms was significantly reduced comparatively to the untreated wastewater. The antibacterial activity of the treated samples was investigated and a total inactivation of CIP-resistant *Escherichia coli* within 2 min of treatment was recorded.

Keywords: *antibiotics, ciprofloxacin, UV-C/H_2O_2, toxicity, antibiotic resistance.*

NOMENCLATURE

CIP	ciprofloxacin
CAS	conventional activated sludge.
UWTPs	urban wastewater treatment plants.
dE_fOM	dissolved effluent organic matter.
$HO^{\bullet}$	hydroxyl radicals.
H_2O_2	hydrogen peroxide.
TBX	Tryptone Bile X-Glucuronide medium agar.
E. coli	Escherichia coli.
D. magna	Daphnia magna.

1. INTRODUCTION

Several studies have reported the presence of a variety of pharmaceuticals in the environment such as antibiotics, anti-inflammatories, antidepressants, analgesics, natural and synthetic hormones [1-3]. Antibiotics are among the pharmaceuticals most commonly detected in the aquatic environment [4], since they are not completely removed during the conventional activated sludge (CAS) process applied in urban wastewater treatment plants (UWTPs) [5-7], so, their presence became a major concern due to their continuous input and persistence in the aquatic ecosystems [8, 9]. Ciprofloxacin (CIP) is one of the most prescribed antibiotics worldwide for the treatment of urinary and respiratory tract infections, among others [10, 11]. CIP is poorly biodegradable since it consists of a

recalcitrant quinolone structure and a piperazine moiety, therefore tertiary treatment is needed for its elimination prior to its discharge into the environment.
The aim of this study was to assess the efficiency of a UV-C driven chemical oxidation process in the presence of H_2O_2, in degrading CIP at environmentally relevant concentration level in urban wastewater effluents. The effect of the H_2O_2 concentration and the degradation kinetics of the process were investigated. The treatment efficiency through the evaluation of phyto- and eco-toxicity effects, towards *Sinapis alba* and *Daphnia magna*, respectively, was evaluated. Additionally, the study investigated the removal of *Escherichia coli* harbouring resistance to CIP during UV-C irradiation.

2. EXPERIMENTAL PART

All experiments were run in a photochemical apparatus consisting of an immersion well, batch type bench-scale cylindrical reaction vessel. The CIP-spiked wastewater solution was introduced into the reaction vessel, and the UV-C lamp with its quartz glass sleeve was immersed inside the solution. The exterior of the reactor was completely covered by a black cloth, in order to prevent external light penetration during the experimental duration.

CIP was spiked into the secondary treated wastewater effluents from a prepared stock solution to achieve an initial concentration of 100 μg L^{-1}. Then, the appropriate amount of H_2O_2 was added to achieve the desired oxidant concentration. At specific time intervals, samples were withdrawn from the reactor, transferred into vials previously filled with the appropriate reagents' volume to quench further reactions.

Toxicity tests were carried out in samples taken prior to and after the UV-C oxidation treatment performed at the optimum experimental conditions. The phytotoxicity and ecotoxicity of the treated samples was evaluated towards *Sinapis alba* and towards the crustacean *Daphnia magna*.

The prevalence of total cultivable and CIP-resistant *E. coli* prior to and after the UV-C oxidation treatment was evaluated. *E. coli* were enumerated on TBX agar or on this medium supplemented with CIP.

3. RESULTATS

The degradation of CIP during the UV-C/H_2O_2 process, was investigated under various H_2O_2 concentrations, in order to determine the optimum oxidant concentration (Fig. 1).

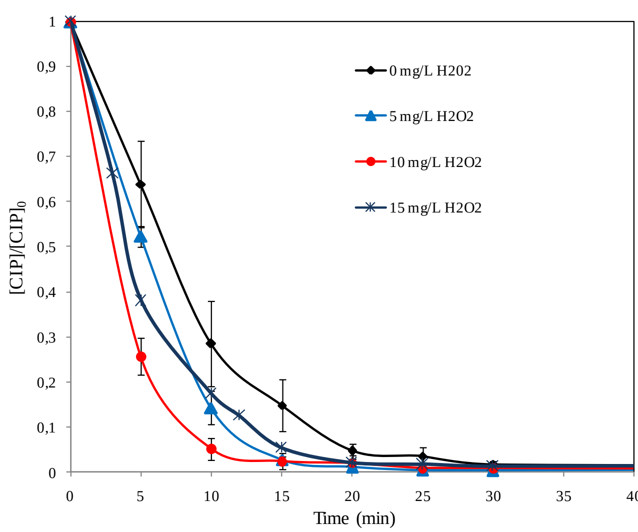

FIGURE 1. Effect of H_2O_2 concentration on the degradation of CIP-spiked wastewater solutions under UV-C irradiation.

The results demonstrated that the photolytic experiments yielded approximately complete degradation of CIP after 30 min of treatment. The degradation rate was rapidly increased by increasing the concentration of H_2O_2 until 10 mg L^{-1}, attributed to the generation of highly reactive $HO^{\bullet}$, that enhance the rate of CIP degradation. Beyond of $[H_2O_2]$=10 mg L^{-1}, a decrease in the degradation rate of CIP was observed resulting in longer photooxidation time for the complete removal of the substrate. The degradation of CIP during the oxidation process followed pseudo-first-order kinetics between CIP and $HO^{\bullet}$, and this was confirmed by the linear behaviour of $-\ln([CIP]/[CIP]_0)$ against time (where $[CIP]_0$ and [CIP] refer to the concentrations of the antibiotic at times 0 and t (min)).

As shown in Fig. 2, the untreated wastewater resulted in a complete immobilization (100%) of *D. magna* after 24 h exposure time, indicating the toxic effects of dE_fOM originally present in the matrix. At 0 min (collection of sample after the addition of the oxidant and CIP), the toxicity decreased until 55% after 24 h exposure, indicating that the oxidant resulted in the formation of less toxic compounds.

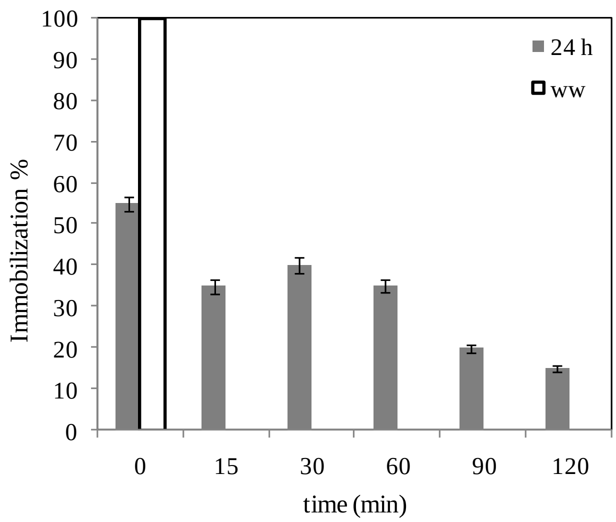

FIGURE 2. Evolution of toxicity to *D. magna* at 24 exposure times during UV-C/H_2O_2. Experimental conditions: $[CIP]_0$ =100 µg L^{-1}, $[H_2O_2]_0$=10 mg L^{-1}, pH = 7.8

This behavior may be attributed to the formation of new intermediates less toxic. From that time onwards, the immobilization decreased and reached 15% after 24 h exposure time.

4. CONCLUSIONS

Urban wastewater treatment plants effluents are among the possible sources of antibiotics spread into the environment. In this study, advanced oxidation process (UV-C/H_2O_2) was successfully investigated to remove ciprofloxacin in urban wastewater at concentration, especially after optimization of H_2O_2 concentration (10 mg L^{-1}), reaching a complete degradation of CIP within a short duration.

Excess H_2O_2 (>10 mg L^{-1}), would scavenge hydroxyl radical and decrease the oxidation efficiency of CIP. Pseudo first-order kinetics was observed for the degradation of CIP under the UV-C/H_2O_2 treatment.
The phytoxicity and ecotoxicity were reduced at the end of treatment.
A complete and very fast removal of CIP-resistant bacteria was obtained.

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