FLUOROQUINOLONES IN WATER: REMOVAL ATTEMPS BY INNOVATIVE AOPs

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INTRODUCTION

Water pollution is becoming dramatic because of increasingly invasive and deleterious anthropic activities.
A significant number of contaminants called "Emerging Pollutants" (EPs) resulting from point and diffuse pollution are present in the aquatic environment.
These compounds, belonging to pharmaceuticals, industrial chemicals, surfactants, personal care products, analgesics, antibiotics, hormones and a whole range of other pharmaceutical compounds including anti-inflammatory, anti- diabetic, and antiepileptic drugs, are not commonly monitored but have the potential to enter the environment and cause adverse ecological and human health effects (1).
The threat lies in the fact that the environmental and human toxinology of most of these compounds has not been well addressed yet and many of these compounds are not removed by the conventional WasteWater Treatment Plants (WWTPs). Moreover, when these contaminants pass through the drinking water treatment systems undergo trasformations that generate derivative substances whose chemical properties remain undetermined. For this reason, it is necessary to try to find low-cost and easy-to-handle alternative methods to solve this vast problem.
Fluoroquinolones, which are powerful antibiotics used in human and veterinary medicine for the treatment of diseases and infections are among the drugs most frequently found in environmental waters along with sulfonamides, tetracyclines and macrolides. The synergistic action of these drugs can cause what is known as "bacterial resistance", which is the cause of 700,000 annually people death in worldwide due to resistant infections according to Joint Research Center (JRC) 2018 report.. This means that if no action is taken the estimated annual deaths attributable to bacterial resistance will be 10 million by 2050.
Adsorption by using porous materials (like activated carbon, polymeric resins, natural clay and organoclay complex adsorbents) was found to be one of the most simple, efficient, cost-effective, flexible methods to remove fluoroquinolonesin the wastewater treatment process. However, this technique does not lead to the complete removal of parent chemicals and their degradation products and, consequently, other treatments are needed for their mineralization.
Advanced Oxidation Processes (AOPs) can be a good choice because, basically, involve the generation of highly reactive free radicals, which convert the organic contaminants into final non-toxic by-products.
Among the various semiconductors employed, TiO_2 is the most preferable material for the photo-catalytic process (high photosensitivity, non-toxic nature, large band gap, chemical stability and low cost).
In this research the photocatalytic activity of this semiconductor immobilized onto the surface of glass borosilicate tubes was evaluated on levofloxacin (trade name Levaquin and other), which is an antibiotic used to treat a number of bacterial infections including acute bacterial sinusitis, pneumonia, urinary tract infections, chronic prostatitis, and some types of gastroenteritis. Kinetics of photoreactions were determined in ultrapure and ground water samples spiked with levofloxacin and photoproducts where identified by liquid chromatography coupled with micrOTOF-Q-II-Mass Spectrometer (LC-MS, Bruker Daltonik GmbH, Bremen).

MATERIAL AND METHODS

Levofloxacin (MW, 361,37 g mol^{-1}) pure standard (purity, 98%) was purchased from HPC (High Purity Compounds, Cunnersdorf, Germany), all solvent for HPLC analysis grade were purchased from Sigma Aldrich (Munich, Germany).
All the solutions were daily prepared and to avoid microbial contamination, all glass apparatus were heat sterilized by autoclaving for 60 minutes at 121°C before use. Aseptic handling materials and laboratory facilities were used throughout the study to maintain sterility.
The groundwater was characterized according to standard methods (APHA, 2005).
The solar experiments were performed using a solar simulator device Heraeus Suntest CPS+ (Atlas, Chicago, USA), equipped with a 1,500 W xenon arc lamp protected with a quartz filter (total passing wavelength: 280 nm < λ < 800 nm). The irradiation chamber was maintained at 20°C by both circulating water from a thermostatic bath and through a conditioned airflow.
The irradiation system was dynamic: the solutions of levofloxacin (dissolved in ultrapure water or groundwater) was passed through the borosilicate tube, coated with TiO_2 on the internal and external surfaces, closed into the photoreactor and irradiated with the xenon arc (Fig. 1) (2). At predetermined

times aliquots of solution were collected for the subsequent analytical determinations. The behaviour of this pharmaceutical in the dark was tested too.

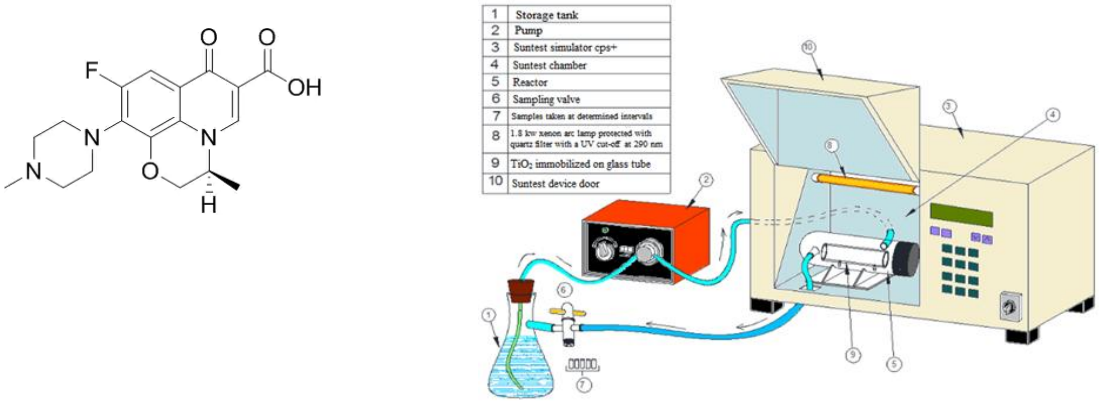


Figure 1. Levofloxacin structure and dynamic system of irradiation.

Levofloxacin concentrations were monitored using High Performance Liquid Chromatography (HPLC) (1200 series, Agilent Technologies, USA) equipped with a C-18 column (SUPELCOSIL Discovery 5 micron-C18, 250 x 4.6 mm) and a diode array detector (DAD); λ, 295 nm.
The isocratic mobile phase was 75% formic acid (0.05%) and 25% methanol . The flow rate was 1.0 mL min^{-1}.
The identification of photoproducts was performed using micrOTOF-Q-II-Mass Spectrometer (LC-MS, Bruker Daltonik GmbH, Bremen). Mass spectrometric conditions were optimized by direct infusion of standard solutions. The instrument was tuned to facilitate the ionization process and to achieve the highest sensitivity.

RESULTS AND DISCUSSION

The chemical characteristics of the groundwater used in the experiments are reported in table 1.

Table 1. Chemical and microbiological characteristics of ground Water samples used for the photodegradation assays

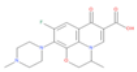
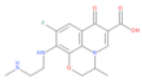
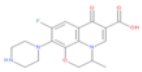
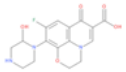
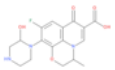
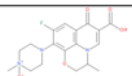
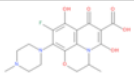
Parameters	Units	data
pH	pH unit	7,98
Conductivity	µS/cm a 20°C	332
Alkalinity	mg L^{-1}CaCO3	187
Bicarbonate	mg L^{-1}	207
Ca	mg L^{-1}	61
Residual Chlorine	mg L^{-1}	0,20
Chloride	mg L^{-1}	7,98
Na	mg L^{-1}	8,55
Settable solids (180°C)	mg L^{-1}	264
Fecal streptococci	CFU/100 ml	<1
Escherichia Coli	CFU /100 ml	<1
Pseudomonas Aeruginosa	CFU /250 ml	0
Total microbial loads at 22°C	CFU /1 ml a 22°C	1
Total microbial loads at 37°C	CFU /1 ml a 37°C	1

Kinetic data calculated considering three replicates for each experiment are summarized in table 2.

Table 2. Kinetic parameters of Levofloxacin degradation: n, reaction order; $t_{1/2}$, half-life; k, kinetic constant; R^2, determination coefficient of the linearized kinetic equation. Values were obtained on the basis of three replicate experiments

Samples	Method of degradation	Apparent kinetic order	k ($L\ mol^{-1}\ min^{-1}$)	$t_{1/2}$ (min)	R^2
Levofloxacin in distilled water	Xenon lamp + TiO_2-coated borosilicate tube	Second order $C_t = C_0\ t_{1/2}/(t+t_{1/2})$	0.06119	272	0.9954
Levofloxacin in ground water			0.10978	152	0.9985

Table 3 . Structure and molecular formula of photo products obtained and identified during the photodegradation assays.

Structure	Molecular formula $[M+H]^+$	Accurate m/z $[M+H]^+$	Error (ppm)	Sunligth + Tube	Sunlight + Tube (G.W.)
	$C_{18}H_{21}FN_3O_4^+$	362.1511	-3.4	x	x
	$C_{16}H_{19}FN_3O_4^+$	336.1354	-4.3	x	
	$C_{17}H_{19}FN_3O_4^+$	348.1354	-7.9	x	x
	$C_{16}H_{17}FN_3O_5^+$	350.1147	-4.9	x	x
	$C_{17}H_{19}FN_3O_5^+$	364.1303	-9.4	x	x
	$C_{18}H_{21}FN_3O_5^+$	378.1460	-9.7	x	x
	$C_{18}H_{21}FN_3O_6^+$	394.1409	-13.1	x	x

The levofloxacin fates in ultrapure and in groundwater seem to follow the same kinetic behaviour and the same photo-intermediates were detected and identified until the complete mineralization of the parent compound. During the photoreactions samples were collected to test the remaining toxicity of the solution by using official environmental assays (*Daphnia magna and Vibrio fischeri*) and phytotoxicity assays as seed germination (SG) and radical elongation (RE) of *Solanum lycopersicum* L. (tomato) and *Lepidium sativum* L. (garden cress).The toxicological data shows that the products of intermediate degradation are more toxic than the parent compound. Therefore, it is necessary to complete the reaction up to the mineralisation of the contaminant and its derivatives to avoid the diffusion of more toxic products to the environment. In any case, the developed photocatalysis system solves two fundamental problems:

1) eliminates the contaminant that with the filtration and adsorption systems would only be moved from one environment to another;

2) eliminates the need to recover titanium dioxide powder once the process is complete

References

1. E. Zuccato, S. Castiglioni, R. Fanelli, 2005 *"Identification of the pharmaceuticals for human use contaminating the Italian aquatic environment"*, J Hazard Mater, 15;122(3):205-9

2. S.Khalaf, Jawad H. Shoqeir, L. Scrano, R. Karaman & S. A. Bufo (2019) *Photodegradation using TiO2-activated borosilicate tubes*. Environmental Science and Pollution Research, 26, 19: 19025 – 19034