Ciprofloxacin oxidation by UV-C activated peroxymonosulfate in wastewater

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HIGHLIGHTS

- UV/PMS more efficient than UV/H_2O_2 for ciprofloxacin removal in wastewater.
- PMS decomposition into sulfate radical was activated by bicarbonate ions.
- CIP degradation pathways elucidation support sulfate radical attacks as a main route.
- Sulfate radical generation allows for CIP antibacterial activity elimination.

ABSTRACT

This work aimed at demonstrating the advantages to use sulfate radical anion for eliminating ciprofloxacin residues from treated domestic wastewater by comparing three UV-254 nm based advanced oxidation processes: UV/persulfate (PDS), UV/peroxymonosulfate (PMS) and UV/H_2O_2. In distilled water, the order of efficiency was UV/PDS > UV/PMS > UV/H_2O_2 while in wastewater, the most efficient process was UV/PMS followed by UV/PDS and UV/H_2O_2 mainly because PMS decomposition into sulfate radical anion was activated by bicarbonate ions. CIP was fully degraded in wastewater at pH 7 in 60 min for a [PMS]/[CIP] molar ratio of 20. Nine transformation products were identified by liquid chromatography–high resolution-mass spectrometry allowing for the establishment of degradation pathways in the UV/PMS system. Sulfate radical anion attacks prompted transformations at the piperazinyl ring through a one electron oxidation mechanism as a major pathway while hydroxyl radical attacks were mainly responsible for quinolone moiety transformations as a minor pathway. Sulfate radical anion generation has made UV/PMS a kinetically effective process in removing ciprofloxacin from wastewater with the elimination of ciprofloxacin antibacterial activity.

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1. Introduction

Due to the intensive use of pharmaceutical active compounds (PhACs), a wide variety of PhAC residues occurs in the aquatic environment. Their fate is potentially a major issue that is yet to be understood [1]. Little is known about their long term effects on ecosystems and up till now, they have escaped from regulations even though diclofenac, 17-α-ethynilestradiol and 17-β-estradiol have been proposed as priority substances in an updated version of the EU Water Framework Directive [2]. As far as wastewater reclamation and reuse is concerned, partial PhAC removal is probably necessary to reduce their impact on irrigated soil quality and to limit PhAC plant uptake. One point of concern lies in the bacterial resistant community evolution [3]. Antibiotics exert a selective pressure for resistant bacteria [4], particularly broad spectrum

antibiotics like fluoroquinolones due to their widespread usage. For instance, ciprofloxacin (CIP) has been classified as one of the prevalent antibiotics in wastewater treatment plant (WWTP) effluents [5]. Furthermore, similarly to many PhACs, CIP is poorly biodegradable and tertiary treatments might be needed for its elimination prior to its discharge into the receiving waters. Advanced oxidation processes (AOPs) relying on the generation of highly reactive hydroxyl radicals (HR) have gained a large interest for CIP degradation including, ozonolysis [6], UV/H_2O_2 [7] and TiO_2 photocatalysis [8]. However, HR based AOPs proceed through unselective multistep pathways which limit its efficiency in complex environmental matrices, dissolved organic matter (DOM), carbonate/bicarbonate anions being among the main HR scavengers in wastewater [9]. To avoid in part these limitations, sulfate radical anion ($SO_4{\cdot}^-$, SRA) has been regarded as a promising alternative to HR even though less is known about its reactivity in aqueous media. SRA has generated absolute kinetic rate constants with PhACs equivalent to those with HR but reacts more selectively than HR mainly through one electron oxidation mechanisms limiting the scavenging effect of DOM and

Table 1
Rate constants for the elementary reactions used in this study.

No eq.	Reaction	k (M^{-1} s^{-1})
1	$S_2O_8{}^{2-} + h\nu \rightarrow 2SO_4{}^{\cdot-}$	
2	$HSO_5{}^-/SO_5{}^{2-} + h\nu \rightarrow SO_4{}^{\cdot-} + HO\cdot$	
3	$SO_5{}^{2-} + H^+ \rightarrow HSO_5{}^-$	pKa = 9.4
4	$HSO_5{}^- + HO\cdot \rightarrow SO_5{}^{\cdot-} + H_2O$	1.7×10^7
5	$SO_4{}^{\cdot-} + HO^- \rightarrow HO\cdot + SO_4{}^{2-}$	6.5×10^7
6	$SO_4{}^{\cdot-} + HSO_5{}^- \rightarrow SO_5{}^{\cdot-} + HSO_4{}^-$	$< 10^4$
7	$HO\cdot + HO\cdot \rightarrow H_2O_2$	5.5×10^9
8	$SO_4{}^{\cdot-} + SO_4{}^{\cdot-} \rightarrow S_2O_8{}^{2-}$	3.1×10^8
9	$HO\cdot + SO_4{}^{\cdot-} \rightarrow HSO_5{}^-$	1.1×10^{10}
10	$Cl^- + HO\cdot \rightarrow Cl\cdot + HO^-$	4.3×10^9
11	$HCO_3{}^- + HO\cdot \rightarrow HCO_3\cdot + HO^-$	8.5×10^6
12	$DOM + HO\cdot \rightarrow Pdts + HO^-$	2.23×10^8
13	$Cl^- + SO_4{}^{\cdot-} \rightarrow Cl\cdot + SO_4{}^{2-}$	6.6×10^8
14	$HCO_3{}^- + SO_4{}^{\cdot-} \rightarrow HCO_3\cdot + SO_4{}^{2-}$	9.1×10^6
15	$DOM + SO_4{}^{\cdot-} \rightarrow Pdts + SO_4{}^{2-}$	6×10^6
16	$CPFX + HO\cdot \rightarrow Pdts$	2.15×10^9
17	$CPFX + SO_4{}^{\cdot-} \rightarrow Pdts$	1.2×10^9

inorganic ions [10]. SRA generation can be achieved through per-oxydisulfate (PDS) or peroxymonosulfate (PMS) activation by UV irradiation leading in the former case to two moles of SRA and in the latter case to one mole of HR and one mole of SRA. Table 1 reports the main chemical reactions taking place in these advanced oxidation systems. Surprisingly, CIP degradation upon SRA reactivity has not been investigated yet. Consequently, the major objectives of this work were the following: (1) to demonstrate the advantages to use SRA for CIP removal from treated domestic WWTP effluents by studying kinetic performances of the UV/PMS and UV/PDS systems and by comparing the results with those obtained with HR by taking the UV/H$_2$O$_2$ system as a reference system for HR generation; (2) to optimize CIP degradation upon UV/PMS system by varying different operating conditions; (3) to elucidate CIP transformation pathways upon UV/PMS system for a better understanding of SRA reactivity in water and for checking for the antibiotic activity elimination.

2. Experimental

2.1. Chemicals

Ciprofloxacin (>98%), hydrogen peroxide (H$_2$O$_2$, 50% v/v), sodium PDS (Na$_2$S$_2$O$_8$, 98%), sodium PMS (available as a triple potassium salt with the commercial name of Oxone, 2KHSO$_5$·KHSO$_4$·K$_2$SO$_4$), sodium bicarbonate (NaHCO$_3$, >99%) and humic acid (technical grade) used as a representative for dissolved organic matter (DOM) were purchased from Sigma Aldrich (St. Quentin-Fallavier, France). Sodium nitrite (NaNO$_2$, 99%), monosodium phosphate (NaH$_2$PO$_4$, 98%) and disodium phosphate (Na$_2$HPO$_4$, 98%) salts were purchased from VWR (Fontenay-sous-Bois, France). Methanol (LC grade) and acetonitrile (LC grade) were purchased from Merck (Darmstadt, Germany). All chemicals were used as received without further purification. All aqueous solutions were prepared with UHQ milliQ water (Millipore, Bedford, USA).

2.2. Analytical methods

CIP concentration evolution was followed by HPLC–UV (L-2200, VWR) equipped with a L-2400 UV–vis detector at $\lambda = 278$ nm. The mobile phase consisted of acidified water (pH = 4.8) with H$_3$PO$_4$ and acetonitrile (50/50, v/v). CIP was resolved on a C-18 Betabasic column (150 × 2.1 mm^2, 3 μm particle size) at a flow rate of 0.2 mL min^{-1} in the isocratic mode of elution. Total organic carbon (TOC) concentration was measured using a Shimadzu-5050A TOC analyzer. Transformation products were detected and identified by liquid chromatography–electrospray-quadrupole time of

flight mass spectrometry (LC–ESI-qTOF-MS, Agilent 6530 series) in the positive mode of ionization. Separation was done by a HPLC system (Agilent1290 LC Infinity) equipped with a Zorbax Eclipse Plus C-18 analytical column (2.1 × 100 mm^2, 1.8 μm particle size). The eluents consisted of water with 0.1% formic acid (A) and methanol (B). The LC method consisted of a linear gradient increasing from 5% to 80% B in 15 min, maintained at 80% B for 5 min and back to initial conditions in 5 min. The flow rate and injection volume were 0.2 mL min^{-1} and 5 μL, respectively. A second orthogonal sprayer was used with a reference solution as a continuous calibration following reference masses of m/z = 1,210,230 and 9,220,098. The data was obtained in the profile mode and processed with the Agilent Mass Hunter Qualitative analysis software (version B.04.00). Metal residues in wastewater samples were determined by ICP-MS in the facilities of the HydroSciences laboratory at Montpellier.

2.3. Photochemical experiments

All experiments were carried out with a 0.5 L cylindrical immersion-type photoreactor equipped with a quartz water cooling jacket with a negligible light absorption at $\lambda = 254$ nm and wrapped with an aluminum foil. The solutions temperature was set at $25 \pm 2\,^\circ$C by water cooling so that the thermal activation of PDS and PMS could be neglected. Aqueous solutions were irradiated with a nominal power 15 W low pressure mercury monochromatic lamp (LP Hg lamp) emitting at 254 nm (Heraeus Noblelight model TNN 15/32, Germany) with a 2.15 cm radiation path length inside the reactor. The photon fluence rate was determined by chemical actinometry using ferrioxalate as an actinometer and was found to be 9.3×10^{-7} E L^{-1} s^{-1}. Typical experiments consisted of preheating the lamp for approximately 10 min. 250 mL solutions were then introduced into the reactor. At specified time intervals, aliquots were sampled and quenched with methanol and sodium nitrite for HPLC–UV or MS and TOC analysis, respectively. All kinetics were in agreement with a first order kinetic model and apparent kinetic rate constant (k_{app}) together with half-life values were determined accordingly. Experiments were conducted in triplicates and results for each sampling point are reported as a mean of three values. The quantum yield Φ of CIP at $\lambda = 254$ nm was determined according to the following equation: $-d[CIP]/dt = \Phi I_0\, e^{\,(-\varepsilon l[CIP])}/V$ where I_0, ε, l and V stand for the photonic flux, the molar absorption coefficient, the optical path and the volume of the reactor, respectively. The competition kinetic studies were carried out to determine the second-order reaction rate constant of CIP with SRA using phenol with a known $k(SO_4{}^{\cdot-})$ of 8.8×10^9 M^{-1} s^{-1} [11] as the competitor. PMS was activated by Co(II) in dark conditions due to the selective SRA generation through the homolytic cleavage of the peroxide bond using this transition metal and to avoid CIP transformation by direct UV photolysis [9]. An equimolar solution of CIP and phenol (50 μM) was oxidized in phosphate buffered solutions (10 mM, pH 7). CIP has two pKa values at 6.15 and 8.6 related to the carboxylic acid function and the secondary amine of the piperazine ring, respectively. Consequently, at pH 7, CIP exists with an overall zero charge zwitterion and no ionic strength correction was applied in the determination of k($SO_4{}^{\cdot-}$). The electrical energy per order (EE/O, kWh m^{-3}/order of degradation) was used to compare the efficiency of UV-based AOPs. It is defined as the electrical energy necessary to reduce the concentration of a pollutant by one order of magnitude in 1 m^3 of wastewater and was calculated using kinetic results into the following expression: EE/O = $(38.4 \times P)/(V \times k_{app})$ where P: the lamp power (kW), V: the reactor volume (L) and k_{app}, the apparent kinetic rate constant (min^{-1}). Wastewater samples were collected from a WWTP effluent involving activated sludge. Major water quality parameters are reported in Table SM-1 of the Supplemental Material (SM).