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Photolytic and photocatalytic degradation of fluoroquinolones in untreated river water under natural sunlight

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ABSTRACT

The photodegradation of some among the most frequently prescribed fluoroquinolone antibacterials (FQs) was investigated in untreated river water under solar light as well as under the same conditions in the presence of suspended TiO_2. The drugs considered included ciprofloxacin (CIP), danofloxacin (DAN), enrofloxacin (ENR), levofloxacin (LEV), marbofloxacin (MAR) and moxifloxacin (MOX), the last two belonging to the most recent FQ generation. The experiments were carried out in lab-scale batch reactor at concentrations (20–50 $\mu g\,L^{-1}$) comparable to those actually measured in surface waters, and the course of the reaction was monitored by high pressure liquid chromatography (HPLC) with fluorescence detector (FD). A first order kinetics was obeyed upon both direct photolysis and TiO_2 heterogeneous photocatalysis. The photoproduced intermediates were identified by HPLC with electrospray ionization tandem mass spectrometry (ESI-MS/MS) and the degradation paths were identified. It was concluded that direct irradiation caused fluorine substitution and reductive elimination, while photocatalysis caused oxidative degradation of the amine side-chain (most efficient with tertiary amines and five-membered cyclic amines). The latter one was a minor process upon direct photolysis and involved hydrogen abstraction by excited states or photoproduced radicals. Photocatalytic decomposition occurred at a rate from two to five times faster than direct photolysis for all of the drugs, except for CIP, that is roughly proportional to the amine oxidation potential. The kinetic constants ranged from 0.061 to 0.66 min^{-1} in direct photolysis, from 0.22 to 2.78 min^{-1} in the presence of TiO_2. In the latter process, a 90% abatement of the concentration of these otherwise highly persistent drugs was obtained in ca. 15 min. This supports the contention that TiO_2 photocatalysis under solar light is a convenient and efficient method for the remediation of pollutants at the $\mu g\,L^{-1}$ levels despite the presence of other non-target matrix constituents. Noteworthy, TiO_2 side-chain photo-oxidation was equally effective in the further degradation of the primary intermediates at a rate comparable to that of the parent compounds. The degradation proceeded further so that it could be expected that the antimicrobial activity, related to the FQ quinolone core more than to the substituent pattern, could be effectively eliminated.

1. Introduction

The persistence of drugs in the environment and their fate are the matter of increasing concern in recent years [1,2]. As an example, the widespread diffusion of fluoroquinolone antibiotics (FQs) in different ecosystems has been well documented [3–5]. These antibacterial agents are largely prescribed both in human and veterinary medicine and are only partially metabolized in the body. Thus, a significant fraction is excreted as such, or to a lesser degree, as metabolites conserving the quinolone structure deriving from the addition of reactive functional groups or via covalent conjugation to polar molecules [6,7].

Furthermore, heterocycles such as FQs are only partially removed by wastewater treatment plants [7]. Such broad-spectrum antibiotics are thus present in the environment and can have a selective effect on microbial communities, thus stimulating bacterial resistance, even at very low concentrations [8,9]. Furthermore, the co-occurrence of multiple FQs must be taken into account in order to properly evaluate the total biologically effective levels [10].

Advanced oxidation processes (AOPs), such as ozonation [11,12], sonolysis [13], photolysis [1,14–16] and titanium dioxide

Abbreviations: AOP, advanced oxidation process; ACN, acetonitrile; CIP, ciprofloxacin; DAN, danofloxacin; DOM, dissolved organic matter; ENR, enrofloxacin; ESI-MS/MS, electrospray ionization tandem mass spectrometry; FD, fluorescence detector; FQs, fluoroquinolones; HPLC, high pressure liquid chromatography; LEV, levofloxacin; MAR, marbofloxacin; MOX, moxifloxacin.

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(TiO_2) photocatalytic degradation [10,17–21] have been recently applied for the remediation of FQs. Using TiO_2, an inexpensive and safe semiconductor as photo-oxidant, is an appealing possibility in the perspective of green chemistry, because it is active under natural sunlight [19]. TiO_2 has been extensively employed for the remediation of pollutants, such as herbicides [22,23], polycyclic aromatic hydrocarbons [24,25], chlorophenols [26–28] and many others [29–38].

Photoexcitation of TiO_2 causes the promotion of electrons from a filled valence band to an empty conduction band, giving rise to electron–hole pairs. The valence band holes migrate to the particle surface and react with adsorbed water to produce hydroxyl radicals •OH or 'trapped holes'($\equiv Ti^{IV}O^{\bullet}$) generated by the combination of the holes photogenerated in TiO_2 valence band with water and dissolved molecular oxygen, whereas the conduction band electron reacts with adsorbed electron acceptors [17]. It has been demonstrated that direct UV–visible (UV-A/B) irradiation causes the decomposition of FQs in water and the main paths are defluorination and amine side-chain oxidation [1,14–16]. As for TiO_2 photocatalysis, this has been explored only for a few FQs, with scarce attention to the products structure. The available studies have been carried out in ultrapure (double-distilled or deionized) water at the ppm levels [17,19–21,39] and have assessed the effect of pH [21] and of the nature of free radicals [20] on the reaction kinetics.

The overall picture is further complicated by the fact that TiO_2 and FQs absorb light in the same wavelength region (300–370 nm) and thus the two processes may occur competitively and also the matrix constituents under environmental conditions, such as dissolved organic matter (DOM) or other xenobiotics [17], may have a role.

In view of the above, we embarked in exploring both direct photolysis and TiO_2 photocatalytic decomposition of six FQs, chosen among those most largely used for both human and veterinary purposes, *under actual environmental conditions*. Thus, the study was carried out at concentrations actually determined in surface waters, viz. at the $\mu g\,L^{-1}$ level [40–43], by sunlight irradiation of raw river water samples. The drugs were ciprofloxacin (CIP), danofloxacin (DAN), enrofloxacin (ENR), levofloxacin (LEV), marbofloxacin (MAR) and moxifloxacin (MOX), the last one belonging to the rapidly expanding "new generation" of FQs [21]. Quantitative analyses were performed by high pressure liquid chromatography (HPLC) with fluorescence detector (FD).

Structure attribution to byproducts was based on HPLC measurements with electrospray ionization tandem mass spectrometry (ESI-MS/MS). For these experiments more concentrated solutions (at $mg\,L^{-1}$ levels) were purposely irradiated. Results from photolysis and from photocatalysis have been compared in terms of conversion yields and byproducts structures.

2. Experimental

2.1. Chemicals and materials

All the chemicals employed were reagent grade or higher in quality and were used without any further purification. FQs standards and reagent grade HCOOH (>95%, w/w) were supplied by Fluka (Sigma–Aldrich, Milan, Italy), HPLC gradient grade acetonitrile (ACN) by VWR (Milan, Italy), H_3PO_4 (85%, w/w), HCl (37%, w/w) and NaOH anhydrous pellets (97%, w/w) by Carlo Erba (Milan, Italy). Ultrapure water (resistivity 18.2 $M\Omega\,cm^{-1}$ at 25 °C) was produced in laboratory by means of a Millipore (Milan, Italy) Milli-Q system. FQs stock solutions of 300 $mg\,L^{-1}$ were prepared in methanol (0.1%, v/v 1 M NaOH) and stored in the dark at 4 °C for a maximum of three months. Working solutions of 6 $mg\,L^{-1}$ in 25 mM H_3PO_4 were renewed weekly. Degussa P25 titanium dioxide (Degussa AG, Frankfurt, Germany), a known mixture of 80% anatase and 20% rutile with an average particle size of 30 nm and a reactive surface area of $50 \pm 15\,m^2\,g^{-1}$, was used for the photocatalytic experiments. IC Acrodisc® 13 mm syringe filter with 0.2 μm Supor® (PES) membrane (Pall Corporation, Milan, Italy) were used before HPLC injection.

2.2. Analytical determination

The HPLC system consists of a pump Series 200 (Perkin Elmer) equipped with vacuum degasser and a programmable FD. The fluorescence excitation/emission wavelengths selected were 280/500 for LEV, 297/507 nm for MAR, 290–500 for MOX and 280/450 nm for the other analytes. After an equilibration period of 10 min, 50 μL of each sample were injected into a 250 × 4.6 mm, 5 μm Ascentis RP-Amide (Supelco) coupled with a similar guard-column. The mobile phase was 25 mM H_3PO_4–ACN (85:15), except for MOX (80:20), for 30 min, followed by a 1 min-linear gradient to 100% ACN. After washing for 5 min, the initial conditions were re-established by a 1 min-linear gradient, at a flow rate of 1 $mL\,min^{-1}$.

The HPLC–ESI-MS/MS was performed by using an Agilent 1100 HPLC with a Luna C18 (150 × 4.6 mm, 5 μm) column, maintained at 30 °C. The mobile phase was HCOOH 0.5%, v/v in ultrapure water–ACN (85:15) for MOX and (90:10) for the other analytes. The flow rate was 1.2 $mL\,min^{-1}$ and the injection volume was 5 μL. The MS/MS-system consisted of a linear trap Thermo LXQ. ESI experiments were carried out in positive-ion mode under the following constant instrumental conditions: source voltage of 4.5 kV, capillary voltage of 20 V, capillary temperature of 275 °C and normalized-collision energy 35.

The HPLC-UV system consists of a PU-1580 pump (JASCO) equipped with a programmable UV-1575 UV–vis detector (JASCO). The analysis wavelength selected for all FQs was 275 nm. 20 μL of each sample were injected into a 150 × 4.6 mm, 5 μm Symmetry Column (Waters) coupled with a similar guard-column. The mobile phase was water (pH adjusted to 2.5 with 37% HCl)–ACN (90:10) except for MOX (85:15) for 30 min, at a flow rate of 1.2 $mL\,min^{-1}$.

2.3. Kinetic experiments

Irradiation was carried out in Pavia (45°11′N, 9°09′E, July 2011, 10.00 a.m.–4.00 p.m., 27–30 °C) under natural sunlight. The incident power was measured by means of a HD 9221 (Delta OHM) (450–950 nm) and a Multimeter (CO.FO.ME.GRA) (295–400 nm) pyranometers and resulted to be in the range 290–470 $W\,m^{-2}$ (Vis) and 20–31 $W\,m^{-2}$ (UV). Batch experiments were typically performed in a 500 mL open glass container (20 mm depth, exposed surface 280 × 200 mm) under magnetic stirring on the window ledge.

2.4. Sample preparation

With the target of assessing the efficiency of the photo(cata)lytic process for FQs remediation in a actual matrix, all the experiments were carried out on raw surface water samples (pH 7.7 ± 0.1, conductivity 232 $\mu S\,cm^{-1}$, DOC 0.97 $mg\,L^{-1}$, calcium 25 $mg\,L^{-1}$, magnesium 5 $mg\,L^{-1}$, iron 82 $\mu g\,L^{-1}$, manganese 10 $\mu g\,L^{-1}$, chloride 9 $mg\,L^{-1}$, nitrate 6.5 $mg\,L^{-1}$, sulfate 29.3 $mg\,L^{-1}$) collected in the Ticino river (0–30 cm depth) in Pavia. In order *not* to remove suspended particles and DOM, which may affect the photodecomposition kinetics (see Section 3), filtration was omitted. The amount of native FQs was negligible, being below the instrumental detection limits (IDLs). Before irradiation, samples were individually fortified with 20 $\mu g\,L^{-1}$ of DAN, which is indeed the most FD-sensitive FQ [44], and 50 $\mu g\,L^{-1}$ of the other FQs.