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UV-C photolysis of endocrine disruptors. The influence of inorganic peroxides

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ABSTRACT

Norfloxacin, doxycycline and mefenamic acid have been photolysed with UV-C radiation (254 nm) in the presence and absence of inorganic peroxides (hydrogen peroxide or sodium monopersulfate). Quantum yields in the range $(1.1–4.5)\times10^{-3}$ mol Einstein^{-1} indicate the low photo-reactivity of these pharmaceuticals. Inorganic peroxides considerably enhanced the contaminants conversion, although no appreciable mineralization could be obtained. A simplistic reaction mechanism for the hydrogen peroxide promoted experiments allowed for a rough estimation of the rate constant between hydroxyl radicals and norfloxacin ($k>1\times10^{9}$ M^{-1} s^{-1}), doxycycline ($k>1.5\times10^{9}$ M^{-1} s^{-1}) and mefenamic acid ($k>11.0\times10^{9}$ M^{-1} s^{-1}).

1. Introduction

Water treatment describes those processes used to make water more acceptable for a predetermined end-use. These can include use as drinking water, industrial processes, medical and many other applications. The final goal of all water treatment processes is to remove existing contaminants in the water bulk, or reduce the concentration of such contaminants so water becomes suitable for its desired end-use. UV-C irradiation is becoming an attractive technology in water treatment facilities due to several advantages. Thus, UV is a relatively safe technology, no dangerous chemicals need to be handled or monitored, if the adequate dose is applied, disinfection is normally immediate and shows a low initial investment cost and a low operating costs [1]. However, when pollutants with low molar adsorptivity and/or quantum yield are considered, the possibility of adding free radical promoters should be contemplated [2]. Inorganic peroxides are a source of radicals when exposed to radiation of enough energy:

$$\mathrm{MOOH}\xrightarrow{h\nu}\mathrm{MO^{\bullet}}+\mathrm{HO^{\bullet}} \quad (1)$$

The radicals formed in Eq. (1) are responsible of the further oxidation of pollutants present in water.

In this work the UV-C photolysis at 254 nm of three contaminants potentially catalogued as "endocrine disruptors" has been assessed. Also, the effect of two free radical promoters, namely hydrogen peroxide and sodium monopersulfate has also been investigated.

According to EPA's working definition [3], endocrine disruptors compounds (EDCs) "interfere with the synthesis, secretion, transport, binding, action, or elimination of natural hormones in the body that are responsible for the maintenance of homeostasis (normal cell metabolism), reproduction, development, and/or behavior". Some EDCs are not completely eliminated by the conventional treatments applied in water and wastewater purification [4], as a consequence, information and investigation of alternative elimination technologies is required [5,6].

2. Experimental

Experiments were carried out in a 1 L glass annular jacketed photochemical reactor (see Fig. 1) already described elsewhere [7]. An oxygen stream was fed through a porous plate situated at the reactor bottom. Water pumped from a thermostatic bath circulated through the reactor jacket to ensure a constant temperature inside the reactor.

A 15 W HERAEUS low pressure mercury vapour lamp was used for experiments carried out by using UV-C radiation (254 nm). Actinometry experiments with hydrogen peroxide [7] allowed for the calculation of the incident radiation intensity per

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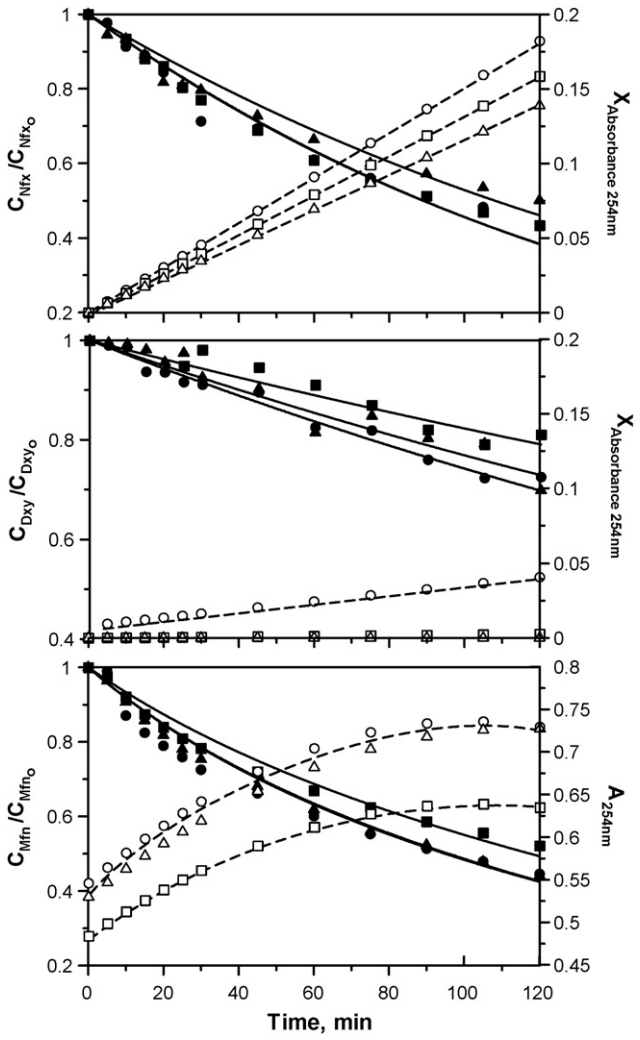

Fig. 1. UV-C (254 nm) photolysis of endocrine disruptors (experiments in triplicate). Experimental conditions: $C_o = 10.0 \times 10^{-5}$ M; pH_o 5.5 (Nfx), 3.5 (Dxy), 10.0 (Mfn), $T = 20\,^{\circ}C$. Solid lines = model calculations according to Eq. (2).

volume $I_o = 3.3 \times 10^{-6}$ E L^{-1} s^{-1} and radiation pathlength in the reactor $L = 3$ cm.

Norfloxacin (Nfx), doxycycline (Dxy) and mefenamic acid (Mfn) were purchased from Aldrich and used as received. EDC's concentrations were quantified by UV absorption at 260 nm for norfloxacin and 280 nm for doxycycline and mefenamic acid. A high-performance liquid chromatograph (Agilent Technologies, series 1100) equipped with a Kromasil 100 C-18 (15 × 0.4) column by Teknochroma was used. The analysis was performed in isocratic mode. The mobile phase used was a mixture of acetonitrile/water 85:15.

The total organic carbon content (TOC) of the samples was measured using a Shimazdu TOC-V_{CSH} analyzer. Peroxide/monopersulfate evolution was monitored by iodometric titration. The pH of the solution was measured with a Crison 507 pH-meter. Absorbance of samples at 254 nm was monitored by a Thermo Spectronic Helios α spectrophotometer.

3. Results and discussion

3.1. Photolysis of EDCs. Quantum yield determination

To assess the photo-reactivity of the studied EDCs, norfloxacin (Nfx), doxycycline (Dxy) and mefenamic acid (Mfn) were separately irradiated at 254 nm. Results are shown in Fig. 1 where the evolution of normalized disruptor concentrations, conversion of absorbance at 254 nm ($X_{\text{Absorbance 254 nm}}$) and absorbance at 254 nm ($A_{254\,\text{nm}}$) are displayed.

As illustrated in Fig. 1, none of the EDCs studied presents a high reactivity when radiation was applied. After 2 h of treatment approximately 50% of norfloxacin and mefenamic acid were removed while roughly 20% of doxycycline was eliminated.

No mineralization (results not shown) was observed in any case. Solution absorbance did not significantly change throughout the photolytic process. Thus, a slight decrease was observed when irradiating norfloxacin while no appreciable variation was experienced in the case of doxycycline. A moderate increase in absorbance was observed when photolysing mefenamic acid. An increase in the absorbance at 254 nm is due to the higher molar absorptivity of intermediates formed if compared to the photolysed parent compound.

The capacity of a substance to undergo a photolytic reaction does depend on two main factors, namely the molar absorptivity and the quantum yield. The latter parameter indicates the efficiency of absorbed photons to decompose the irradiated substance.

The quantum yield in photolytic experiments was calculated by integration of Eq. (2). This equation describes the photodecomposition of a generic compound of concentration $C_i(t)$ in a discontinuous batch reactor [8]:

$$-\frac{dC_i(t)}{dt} = \phi_i \frac{\varepsilon_i C_i(t)}{A_{254\,\text{nm}}(t)} I_o [1 - \exp(-2.303\, L\, A_{254\,\text{nm}}(t))] \quad (2)$$

where φ_i and ε_i are the quantum yield and molar absorptivity at 254 nm of compound i, respectively. $A_{254\,\text{nm}}(t)$ accounts for the absorption of UV light of all the species present in solution. The latter term was monitored along the experiments (see Fig. 1) and fitted to a mathematical expression.

Previously to the application of Eq. (2), the molar absorptivities of norfloxacin, doxycycline and mefenamic acid were determined at different pH conditions. Results are shown in Table 1. Differences found in ε_i depending on pH can be attributed to the predominance of the distinct forms of the disruptor studied (protonated, non-dissociated or dissociated). Hence, in the case of norfloxacin, the first pK_a of 6.26 explains the increase of the molar absorptivity at basic pH if compared to values found at acidic or circumneutral conditions. When doxycycline is considered, three pK_a values can be found in the literature. The first one between 2.8 and 3.3 corresponds to the hydroxyl groups, the second one in the range 7.2–7.8 corresponds to the phenolic groups while the third one in the interval 9.1–9.7 is attributable to amino groups. Values in Table 1 indicate the different absorptivity at acidic pH, neutral conditions and basic pH, similarly to the values of the different pK_as.

Now, from Eq. (2), the only adjustable/unknown parameter is φ_i. Two different approaches were used to integrate expression (2). In a first attempt, the differential equation was applied to the beginning of the process. At low reaction times, it is supposed that the following approximation $\varepsilon_i C_i(t) \approx A_{254\,\text{nm}}(t)$ can be considered, i.e., the absorption of radiation is manly due to the parent compound (intermediate light absorption can be neglected). Under these circumstances, analytical integration of the kinetic equation leads to (the subscript "o" indicates time zero):

$$C_{i_o} - C_i(t) - \frac{1}{\xi} \ln \left[\frac{1 - \exp(-\xi \times C_{i_o})}{1 - \exp(-\xi \times C_i(t))} \right] = \phi_i \times I_o \times t \quad (3)$$

where

$$\xi = 2.303 \times \varepsilon_i \times L \quad (4)$$

Eq. (3) is the base of the so-called integral method of quantum yield determination [9].

Table 1
Molar absorptivity and quantum yield determination at 254 nm of investigated EDCs.

Compound (method)	Φ, $\times 10^3$ mol E^{-1}	ε, $\times 10^{-4}$ L mol^{-1} cm^{-1}
Norfloxacin (integral) Norfloxacin (numerical)	3.4 ± 0.3 (pH 5.5) 3.2 ± 0.3 (pH 5.5)	1.03 (pH 2), 1.08 (pH 3.7), 1.60 (pH 6.0), 1.54 (pH 8.8), 1.53 (pH 10.0)
Doxycycline (integral) Doxycycline (numerical)	1.1 ± 0.2 (pH 3.5) 1.2 ± 0.3 (pH 3.5)	15.1 (pH 2), 12.2 (pH 3.7), 12.5 (pH 6.0), 12.5 (pH 8.8), 15.7 (pH 10.0)
Mefenamic acid (integral) Mefenamic acid (numerical)	4.7 ± 1.4 (pH 10.0) 4.2 ± 0.8 (pH 10.0)	0.55 (pH 12.7), 0.55 (pH 10.2)

A plot of the left member in Eq. (3) versus time should lead to a straight line of slope $\varphi_i \times I_o$, provided that the aforementioned approximation $\varepsilon_i C_i(t) \approx A_{254\,nm}(t)$ holds.

Fig. 2 depicts the different plots obtained and the time period applicable when considering the integral method of quantum yield calculation. From Fig. 2 it is observed how Eq. (3) is valid for the first 10–25 min in the case of norfloxacin and mefenamic acid while the low photoactivity of doxycycline allows for the application of expression (3) during the whole reaction period considered in this study. The average calculated values of φ_i in triplicate experiments are shown in Table 1.

A second attempt to calculate the quantum yield values was carried out by numerical integration of Eq. (2) (numerical method). Thus, $A_{254\,nm}(t)$ was fitted to a simple mathematical expression and the fourth order Runge Kutta method was thereafter applied. To initiate the mathematical algorithm, a supposed value for φ_i was assigned. Next, the Excel addin SOLVER minimized the squared differences between calculated and experimental concentrations of the considered pollutant. Table 1 shows the results obtained while Fig. 1 depicts the theoretical calculated profiles. Both methodologies (integral and numerical) lead to similar results. The relatively low values of φ_i for the three EDCs studied confirm the recalcitrant nature to photodecomposition. Accordingly, a more aggressive

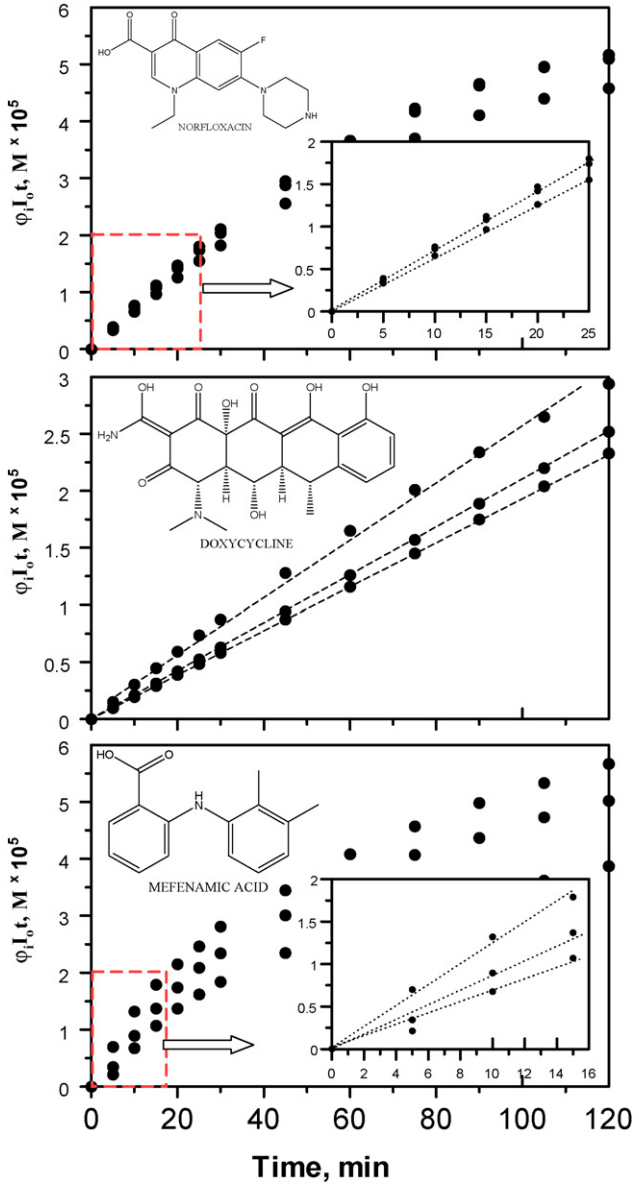

Fig. 2. UV-C (254 nm) photolysis of endocrine disruptors (experiments in triplicate). Application of Eq. (3) to experiments shown in Fig. 1.

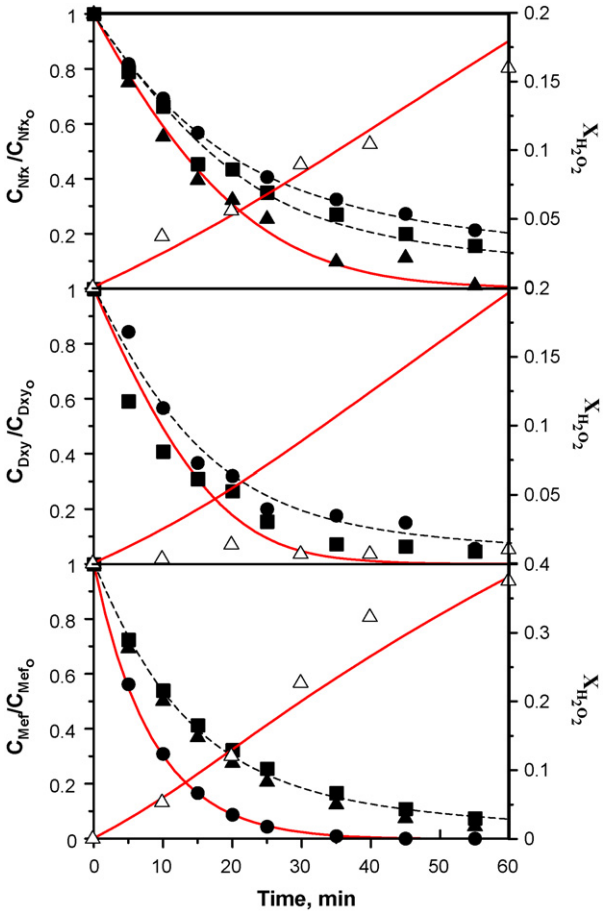

Fig. 3. Hydrogen peroxide promoted UV-C (254 nm) photolysis of endocrine disruptors. Experimental conditions: $C_o = 10.0 \times 10^{-5}$ M; pH$_o$ 7.0 (Nfx), 4.0 (Dxy), 11.0 (Mfn), $T = 20$ °C; $C_{H_2O_2\ o} = (M \times 10^3)$: ●, 1.25 (Nfx), 2.00 (Dxy), 0.59 (Mfn); ■, 1.80 (Nfx), 2.92 (Dxy), 1.35 (Mfn); ▲, 2.68 (Nfx), 2.82 (Mfn). Solid lines = model calculations according to Eqs. (12)–(14) (only runs with the highest H_2O_2 concentration are modelled).

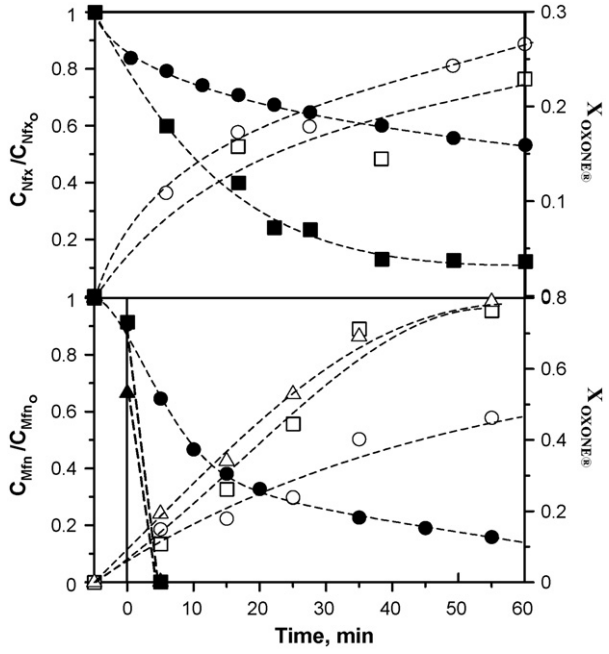

Fig. 4. OXONE® promoted UV-C (254 nm) photolysis of endocrine disruptors. Experimental conditions: $C_o = 10.0 \times 10^{-5}$ M; pH_o 8.0 (Nfx), 11.0 (Mfn), $T = 20\,^{\circ}C$; $C_{OXONE^{®}\ o} = (M \times 10^4)$: ●, 3.1 (Nfx), 1.7 (Mfn); ■, 3.7 (Nfx), 4.9 (Mfn); ▲, 7.8 (Nfx), 5.6 (Mfn).

treatment is recommended. Use of peroxides was, consequently, tested.

3.2. Peroxide promoted photolysis of EDCs

3.2.1. Use of hydrogen peroxide

Experiments conducted by using different concentrations of hydrogen peroxide were carried out in the presence of UV radiation. Fig. 3 shows the results obtained in these runs (EDCs normalized concentration and peroxide conversion). As observed, hydrogen peroxide significantly enhanced the conversion rate of the EDCs considered in this study. Hydroxyl radicals generated after H_2O_2 photodecomposition steadily react with organics leading to oxygenated species. Nevertheless, in spite of the notorious improvement in EDC's oxidation experienced, no statistically appreciable mineralization of the contaminants could be achieved. TOC values hardly decreased 2–3 ppm at the end of the process.

Under the experimental conditions used, the fraction of light absorbed by hydrogen peroxide is significantly lower than the fraction absorbed by the pharmaceutical considered, thus, for instance, in the case of norfloxacin, for an initial H_2O_2 concentration of 2.68×10^{-3} M it follows that:

$$F_{H_2O_2|t=0} = \frac{\varepsilon_{H_2O_2} \times C_{H_2O_2}}{\sum_j \varepsilon_j \times C_j} = \frac{19 \times 26.8}{19 \times 26.8 + 16,000 \times 1} \times 100 = 3.1\% \quad (5)$$

However, the phototransformation of hydrogen peroxide is much faster than that of norfloxacin, allowing for the generation of a sufficient amount of hydroxyl radicals:

$$\left.\frac{-dC_{H_2O_2}/dt}{-dC_{Nfx}/dt}\right|_{t=0} = \frac{\phi_{H_2O_2} \times \varepsilon_{H_2O_2} \times C_{H_2O_2}}{\phi_{Nfx} \times \varepsilon_{Nfx} \times C_{Nfx}} = 4.8 \quad (6)$$

As stated previously the base of the system UV/H_2O_2 is the photodecomposition of hydrogen peroxide, the rest of main reactions that can be considered in this system complete the following mechanism:

$$\text{EDC (norfloxacin, doxycycline, mefenamic acid)} \xrightarrow{h\nu} \text{Photolytic products} \quad (7)$$

$$H_2O_2/HO_2^- \xrightarrow{h\nu} 2HO^{\bullet} \quad (8)$$

$$HO^{\bullet} + EDC \rightarrow \text{Products} \quad (9)$$

$$HO^{\bullet} + H_2O_2/HO_2^- \rightarrow H_2O + HO_2^{\bullet} \quad (10)$$

$$HO^{\bullet} + \text{Products} \rightarrow \text{Endproducts} \quad (11)$$

Reactions (7)–(11) constitute an oversimplified reaction mechanism leading to the following set of differential equations:

$$-\frac{dC_{EDC}(t)}{dt} = \phi_{EDC} \frac{\varepsilon_{EDC} C_{EDC}(t)}{A_{254\,nm}(t)} I_o[1 - \exp(-2.303\, L\, A_{254\,nm}(t))] + k_9 C_{EDC}(t) C_{HO^{\bullet}}(t) \quad (12)$$

$$-\frac{dC_{H_2O_2}(t)}{dt} = \phi_{H_2O_2} \frac{\varepsilon_{H_2O_2} C_{H_2O_2}(t)}{A_{254\,nm}(t)} I_o[1 - \exp(-2.303\, L\, A_{254\,nm}(t))] + k_{10} C_{H_2O_2}(t) C_{HO^{\bullet}}(t) \quad (13)$$

$$\frac{dC_{HO^{\bullet}}(t)}{dt} = 2\phi_{H_2O_2} \frac{\varepsilon_{H_2O_2} C_{H_2O_2}(t)}{A_{254\,nm}(t)} I_o[1 - \exp(-2.303\, L\, A_{254\,nm}(t))] - k_9 C_{EDC}(t) C_{HO^{\bullet}}(t) - k_{10} C_{H_2O_2}(t) C_{HO^{\bullet}}(t) - k_{11} C_{Products}(t) C_{HO^{\bullet}}(t) \quad (14)$$

Eqs. (12)–(14) could be numerically solved to make a rough estimation of k_9. However, since the nature and amount of products competing to trap hydroxyl radicals are unknown, it was assumed that:

$$k_9 C_{EDC}(t) C_{HO^{\bullet}}(t) + k_{10} C_{H_2O_2}(t) C_{HO^{\bullet}}(t) \gg k_{11} C_{Products}(t) C_{HO^{\bullet}}(t) \quad (15)$$

To minimize the errors associated to the previous assumption, only the experiments with the highest hydrogen peroxide concentration (highest value of $k_{10} C_{H_2O_2}(t) C_{HO^{\bullet}}(t)$) were taken into consideration. Obviously, as stated previously, Eqs. (12)–(14) are oversimplified reaction mechanism and kinetic parameters derived from its application should be considered as a rough approximation of actual rate constants. Fig. 3 shows a good fitting of the calculated EDC's concentration and experimental values regardless of the contaminant considered. Additionally, hydrogen peroxide evolution is also quite well modelled with the exception of the doxycycline experiment. In the latter case, an abnormal low consumption of the peroxide was experienced, suggesting the generation of this species along the oxidation period. Fitting values for k_9 of 1.0, 1.5 and $11.0 \times 10^9\ M^{-1}\ s^{-1}$ for norfloxacin, doxycycline and mefenamic acid, respectively, indicate that the actual values of the rate constants between these EDCs and HO• should be higher than the previous figures.

3.2.2. Use of sodium monopersulfate (OXONE®)

In an attempt to improve the mineralization degree of the photolytic process, a different promoter was used, i.e. sodium monopersulfate. OXONE® shows a higher quantum yield than hydrogen peroxide, although a slightly lower molar absortivity ($12.5\ M^{-1}\ cm^{-1}$ and $2.9 \pm 0.2\ mol\ E^{-1}$ for the monopersulfate molecule). Fig. 4 displays the evolution profiles of the photolysis of norfloxacin and mefenamic acid in the presence of OXONE® and the

conversion of the latter. Doxycycline could not be monitored with this system because this pharmaceutical instantaneously decomposed in the presence of monopersulfate with no need of UV radiation. A possible explanation could be based on the direct reaction of molecular monopersulfate with doxycycline, similarly to the reaction of benzaldehyde proposed by Renganathan and Maruthamuthu [10].

As observed in Fig. 4, norfloxacin is efficiently eliminated when OXONE® concentration is at least of the order 7.8×10^{-4} M. When the promoter concentration is halved, no significant improvement in comparison to the non-promoted experiment was experienced. A similar behavior was obtained in the case of mefenamic acid, although some points should be highlighted. Hence, just a concentration of 1.7×10^{-4} M in OXONE® is enough to significantly enhance the simple photolytic process of mefenamic acid. Moreover, even in the absence of light (in 5 min), mefenamic acid is partially removed from water (i.e. when OXONE® initial concentration was set to 5.6×10^{-4} M, mefenamic acid initial concentration decreased a 34% before the UV lamp was turned on). When OXONE® concentration was sufficiently high, mefenamic acid was eliminated in less than 5 min after switching on the UV lamp. It is hypothesised that, similarly to the cobalt mediated decomposition of monopersulfate, basic pH favours the photo-excission of the monopersulfate molecule to give the corresponding radicals. Unfortunately, neither in norfloxacin nor in mefenamic acid photoprocesses, TOC conversion led to promising results (just a few ppm were eliminated).

4. Conclusions

From the previous investigation the following conclusions could be derived:

- Norfloxacin, doxycycline and mefenamic acid present low photoreactivity when UV-C radiation at 254 nm is applied.
- Addition of free radical promoters (hydrogen peroxide or OXONE®) significantly enhances the pharmaceuticals conversion.
- None of the processes tested could achieve acceptable mineralization levels.

Acknowledgments

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