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 $(1.1–4.5) \times 10^{-3}$ 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 ($k > 1 \times 10^9$ M^{-1} s^{-1}), doxycycline ($k > 1.5 \times 10^9$ M^{-1} s^{-1}) and mefenamic acid ($k > 11.0 \times 10^9$ 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:

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

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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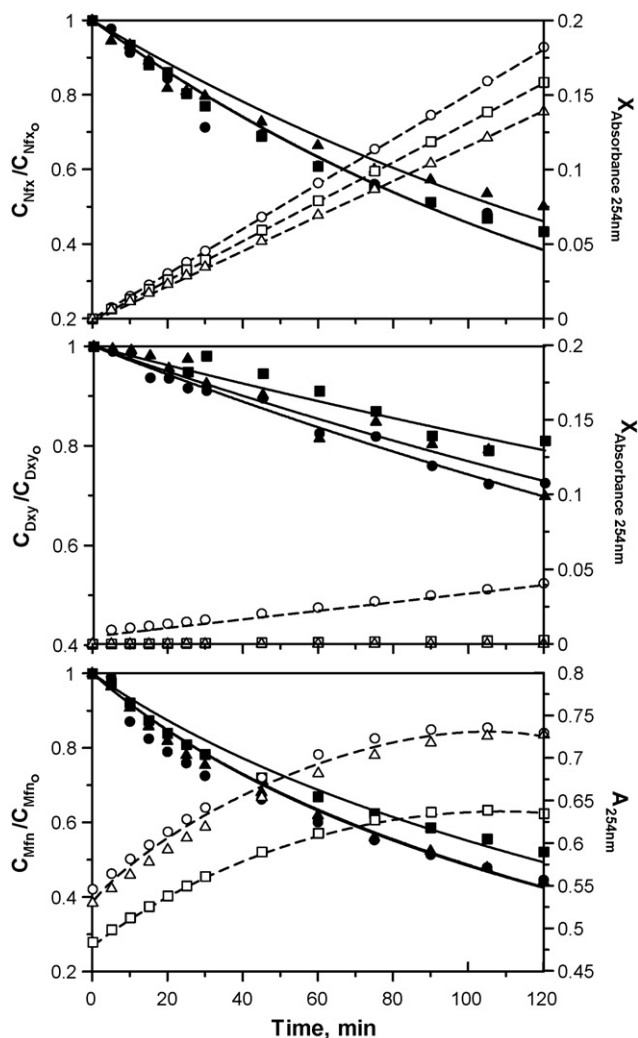*E-mail address:* fjrivas@unex.es (J. Rivas).

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 sepa-

rately 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]:

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

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):

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

where

$$\xi = 2.303 \times \varepsilon_i \times L \tag{4}$$

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