Influence of oxygen and free radicals promoters on the UV-254 nm photolysis of diclofenac

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ABSTRACT

Diclofenac has been irradiated under UV-C light at 254 nm. The effect of some operating variables has been investigated. The kinetics of the process has been analysed by means of the corresponding quantum yield. The presence of free radical promoters has also been considered.

Diclofenac initial concentration plays an important role in its conversion profile. First order kinetics is ruled out under the applied experimental conditions. The process efficiency is significantly enhanced if oxygen is bubbled instead of air. Diclofenac quantum yield values in the range ≈ 0.1–0.3 mol Einstein^{-1} were obtained depending on the operating conditions used (air or oxygen) and the kinetic methodology followed. The mineralization level achieved also increased from 30 to 80% when oxygen was sparged instead of air. The presence of free radicals promoters did not improve the diclofenac removal efficiency.

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1. Introduction

The use of ultraviolet light radiation is a well established technology in drinking water facilities. UV-C radiation is an effective technology in drinking water treatment, achieving high cleaning levels at low UV fluence dosages [1]. Additionally, in some cases, this process can also be contemplated as a suitable route of pollutants elimination. Amongst other premises, photolytic processes can be considered when contaminants absorb radiation and their quantum yields are acceptably high. If this is not the case, UV radiation can be combined with some substances to enhance the efficiency of the overall process. Sensitizers are substances capable of absorbing light leading to excited states. Excited molecules can react thereafter with target compounds to initiate the photolytic process. Similarly to sensitizers, other species (i.e. peroxides) can undergo photolysis to generate free radicals in solution. Free radicals are powerful oxidants able to non-selectively react with a wide range of contaminants, regardless of the photolytic properties of target pollutants or the transparency of the aqueous matrix. Inorganic peroxides have extensively been used/tested when dealing with alternative water treatment technologies. Hence, hydrogen peroxide in combination with UV-C radiation leads to formation of two hydroxyl radicals [2] according to:

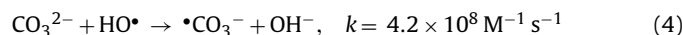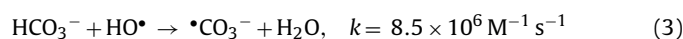$$H_2O_2 \xrightarrow{h\upsilon} 2\,HO^\bullet \tag{1}$$

Other peroxides that can also be used in a similar way are percarbonate and monopersulfate. These peroxides have not normally been used in water treatment technologies, although some recent works have used their potential oxidising power [3–6]. OXONE® is the commercialized form of potassium monopersulfate. OXONE® is a triple potassium salt whose active ingredient is the peroxymonosulfate, commonly known as monopersulfate. Activation of the peroxymonopersulfate molecule under UV radiation or temperature proceeds by scission of the peroxy bond according to [7]:

$$HOOSO_3^- \xrightarrow{\text{Temperature, } h\upsilon} HO^\bullet + SO_4^{-\bullet} \tag{2}$$
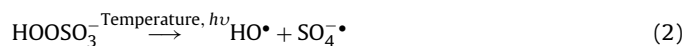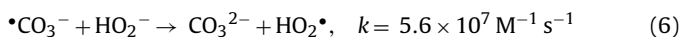
Both hydroxyl and sulfate radicals are powerful oxidants capable of destroying organic and inorganic compounds [8].

Percarbonate is a carbonate perhydrate: $2Na_2CO_3 \cdot 3H_2O_2$. Sodium percarbonate is a source of highly concentrated hydrogen peroxide with the advantage of stability and easiness of transportation if compared to solutions of concentrated H_2O_2. In aqueous systems, the combination UV-C/Percarbonate is expected to show a similar behaviour as the combination UV-C/H_2O_2 with some differences. For instance, use of percarbonate involves the presence of carbonates in the reaction media. Carbonates react with hydroxyl radicals to form carbonate radicals according to:

$$HCO_3^- + HO^\bullet \rightarrow {}^\bullet CO_3^- + H_2O, \quad k = 8.5 \times 10^6\,M^{-1}\,s^{-1} \tag{3}$$

$$CO_3^{2-} + HO^\bullet \rightarrow {}^\bullet CO_3^- + OH^-, \quad k = 4.2 \times 10^8\,M^{-1}\,s^{-1} \tag{4}$$

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Carbonate radicals can also attack hydrogen peroxide:

$$\bullet CO_3^- + H_2O_2 \rightarrow HCO_3^- + HO_2\bullet, \quad k = 4.3 \times 10^5\,M^{-1}\,s^{-1} \tag{5}$$

$$\bullet CO_3^- + HO_2^- \rightarrow CO_3^{2-} + HO_2\bullet, \quad k = 5.6 \times 10^7\,M^{-1}\,s^{-1} \tag{6}$$

The hydroperoxyl radical, $HO_2\bullet$, is more selective than $HO\bullet$, presenting, therefore, a lower reactivity. In this case carbonates are considered as scavengers of hydroxyl radicals. Alternatively, carbonate radicals might react with organic pollutants [9] contributing to the efficiency of water treatment. The use of low pH (i.e. acidic wastewaters) could be a solution of carbonate scavenging effect because of the formation and stripping of carbon dioxide.

Additionally, a slight change in reactivity in aqueous solution might be observed and attributed to the formation of *true* percarbonates according to:

$$HCO_3^- + H_2O_2 \rightarrow H_2O + HCO_4^- \tag{7}$$

Percarbonate behaves as an electrophile moiety, however, it is supposed that this molecule immediately decomposes under UV radiation to give the corresponding radicals:

$$HCO_4^- \xrightarrow{h\upsilon} \bullet CO_3^- + HO\bullet \tag{8}$$

In recent years, an increasing concern about the presence of pharmaceuticals in different types of waters is emerging. Special alarm is raised when dealing with sources of drinking water. Commonly, conventional treatments used in drinking water facilities are not efficient in pharmaceutical compounds removal. As a consequence, undesirable effects can appear even when these substances are present at trace levels [10]. Amongst the variety of pharmaceuticals, diclofenac has been considered in this study. This substance is a non-steroidal anti-inflammatory drug meant to reduce inflammation. Diclofenac is also used as analgesic. Its presence in surface waters has been previously reported [11,12]. UV-254 nm photolysis of diclofenac has also been reported by Canonica et al. [1] and Vogna et al. [10]. In the first work some kinetic aspects related to the process and the influence of water matrix nature was assessed, mineralization level was not monitored. In the second work, total organic carbon evolution was reported to be negligible in the photolytic process. Additionally, the system UV/H_2O_2 was also considered, although only one run was carried out. In the latter case, however, a 40% of mineralization was experienced.

This work is intended to analyse the diclofenac photolysis in terms of diclofenac removal and also in terms of TOC removal. The kinetics of the process has been studied by considering the absorbance evolution of the aqueous matrix at 254 nm. Quite often, in photolytic processes, the 254 nm absorbance of the water bulk is only considered at the beginning of the process and assumed to decrease with time. Additionally, the system UV/peroxide is also considered in greater depth.

2. Experimental

Experiments were carried out in a 1 L glass annular jacketed photochemical reactor (see Fig. 1) already described elsewhere [13]. An air or oxygen stream was continuously 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 using UV-C radiation (254 nm).

Diclofenac and the rest of organics used in this work (Aldrich) were quantified at room temperature by UV absorption at 275 nm for diclofenac and 254 nm for the rest. A high-performance liquid chromatograph (Agilent Technologies, series 1100) equipped with a Chromasil C-18 column was used. The analysis was performed
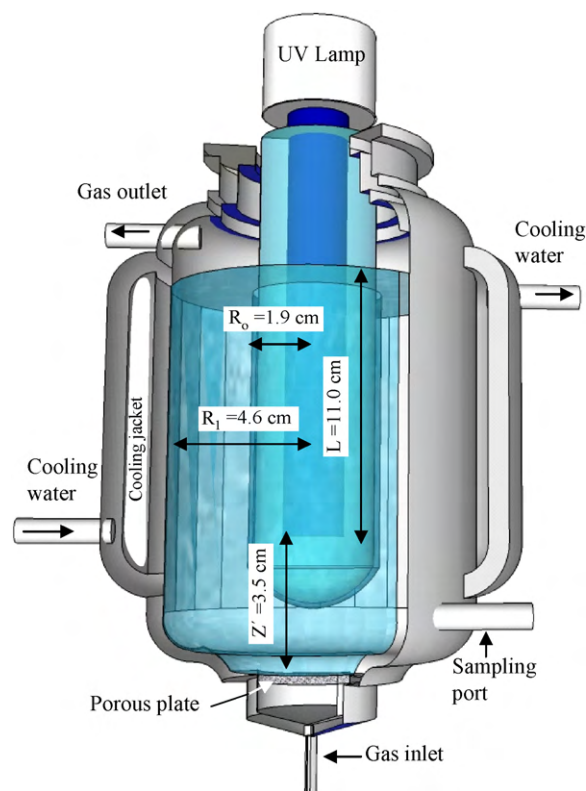

Fig. 1. Photoreactor scheme.

in an isocratic mode (flow rate = 1.0 mL min^{-1}). The mobile phase used was a mixture of acetonitrile/water (70/30, v/v).

The total organic carbon content (TOC) of the samples was measured using a Shimazdu TOC-V$_{CSH}$ analyser. Peroxides were iodometrically analysed. 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. Preliminary experiments. Determination of apparent radiation photon flux and optical pathlength

The first step taken in this work was the calculation of the main parameters of the photolytic equipment used. Hydrogen peroxide actinometry experiments were carried out both at high and at low concentrations [13]. From the simultaneous application of Lambert–Beer equation and mass balance to a perfectly mixed batch reactor, it follows that:

$$-\frac{dC_{H_2O_2}}{dt} = \varphi_{H_2O_2} I_0 [1 - \exp(-2.303 L \varepsilon_{H_2O_2} C_{H_2O_2})] \tag{9}$$

where $\varphi_{H_2O_2} = 1.0$, is the hydrogen peroxide quantum yield at 254 nm, $\varepsilon_{H_2O_2}$, is the hydrogen peroxide molar absorption coefficient (19 M^{-1} cm^{-1} at the circumneutral pH conditions used [13]), I_0 is the incident UV radiation photon flux per volume unit, L is the radiation path and $C_{H_2O_2}$ is the hydrogen peroxide concentration at time t. From (9) the following simplifications can be obtained:

If: $2.303 L \varepsilon_{H_2O_2} C_{H_2O_2} > 4.6$, then Eq. (9) simplifies to (after integration):

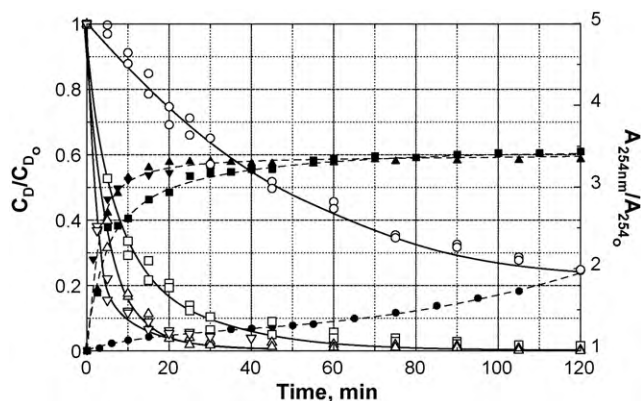$$C_{H_2O_2}|_{t=t} - C_{H_2O_2}|_{t=0} = \varphi_{H_2O_2} I_0 t \tag{10}$$

Fig. 2. UV-C photolysis of diclofenac. Influence of initial diclofenac concentration (C_{D_0}). Experimental conditions: $pH_0 = 5.2$; $T = 20\,^\circ C$; $V = 0.8$ L; Inlet gas = air. Initial diclofenac concentration ($C_{D_0} =$ mM): $\bigcirc$, 0.63; $\square$, 0.10; $\triangle$, 0.05; $\triangledown$, 0.01 (solid symbols correspond to normalized absorbance evolution).

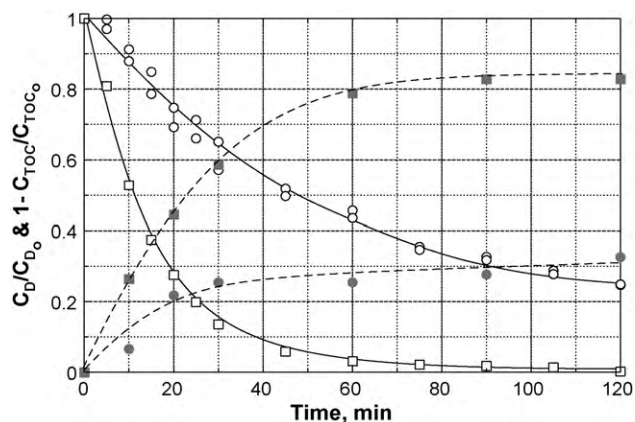**Fig. 3.** UV-C photolysis of diclofenac. Influence of inlet gas nature. Experimental conditions: $pH_0 = 5.2$; $T = 20\,^\circ C$; $V = 0.8$ L; $C_{D_0} = 0.63$ mM. $\bigcirc$, air; $\square$, oxygen (solid symbols correspond to TOC conversion).

If: $2.303L\varepsilon_{H_2O_2}C_{H_2O_2} < 0.1$, then Eq. (9) simplifies to (after integration):

$$\ln\frac{C_{H_2O_2}|_{t=0}}{C_{H_2O_2}|_{t=t}} = 2.303L\varepsilon_{H_2O_2}\varphi_{H_2O_2}I_0t \tag{11}$$

Experiments conducted in triplicate (two in air saturated solutions and the third in an oxygen saturated solution) in the presence of 5.5×10^{-2} M of initial H_2O_2 concentration allowed for the application of Eq. (10). A plot of hydrogen peroxide concentration versus time led to a straight line ($R^2 > 0.99$) with slope $\varphi_{H_2O_2}I_0$. The photon flux value obtained from the slope was $3.27 \pm 0.35 \times 10^{-6}$ Einstein L^{-1} s^{-1}. Additionally, three more experiments (two in air saturated solutions and the third in an oxygen saturated solution) were carried out in the presence of 1.0×10^{-3} M of initial H_2O_2 concentration. A plot of the natural logarithm of H_2O_2 concentration versus time led to a straight line ($R^2 > 0.99$). From the slope of the straight line and the value of I_0 previously obtained, L was calculated as 3.2 ± 0.5 cm.

At this point it should be stated that light photon flux and pathlength can be influenced by the presence of air/oxygen bubbles, however, since the actinometry experiments have been carried out under similar conditions as diclofenac photolysis, the values obtained for I_0 and L can be applied to diclofenac phototransformation, even in the case that calculated I_0 and L are not the true values.

3.2. Diclofenac photolysis

3.2.1. Influence of initial diclofenac concentration

The photolysis of diclofenac was firstly carried out in air saturated solutions by modifying the initial concentration of the parent compound. Fig. 2 shows the normalized evolution of the pharmaceutical compound as a function of time. From this figure it is observed that the photolysis of diclofenac does not obey a first order kinetic law because: (1) Conversion–time curves do depend on initial diclofenac concentration and (2) a plot of the natural logarithm for the normalized diclofenac concentration (not shown) does not strictly follow a straight line. A deeper analysis of the curves reveals that the initial diclofenac removal rate is independent of the initial concentration of the parent compound (initial rate values are calculated after differentiating a mathematical expression which is obtained from the fitting of the experimental points). Hence, values of 9.5, 10.9, 10.7, 9.13, 9.0 and 9.79×10^{-6} M min^{-1} have been obtained for experiments conducted in the diclofenac concentration interval 6.3×10^{-4} to 5.0×10^{-5} M. By considering that the molar absorption coefficient of diclofenac (ε_D) at 254 nm

is 4972 ± 243 M^{-1} cm^{-1} (similar to 4260 ± 130 given by Canonica et al. [1]), it follows that the term $2.303L\varepsilon_D C_D$ is relatively high for the diclofenac concentration interval given above. Accordingly, a zero order equation similar to (10) applies for the initial photolysis of diclofenac. However, the experiment conducted with $C_{D_0} = 1 \times 10^{-5}$ M leads to a value of $2.303L\varepsilon_D C_D = 0.36$, i.e. zero order kinetics cannot be assumed. At these conditions the initial diclofenac removal rate differs by a factor of twofold decrease from the values given previously for runs conducted with diclofenac initial concentration above 5.0×10^{-5} M.

3.2.2. Influence of oxygen

Photolysis experiments of diclofenac aqueous solutions were conducted under an oxygen stream of 40 L h^{-1}. The results are displayed in Fig. 3. From this figure it is observed the significant effect that oxygen exerts on the process efficiency. Accordingly, diclofenac half-life is reduced from 45 min in the presence of air to roughly 10 min when the solution is bubbled with oxygen. Moreover, the mineralization level obtained is also considerably improved. In this case, bubbling oxygen increases the total oxidation of diclofenac from a scarce 30% (in air saturated solutions) up to a value >80%. The beneficial effect of oxygen has also been reported previously by other authors [14]. The influence of oxygen in photolytic processes can be attributed to different routes [15]. For instance, the excited triplet state of diclofenac can transfer its energy to oxygen or alternatively an electron leading to the formation of the superoxide radical and the radical cation of diclofenac. Photosensitization of oxygen by diclofenac has been reported in the literature previously [16].

3.2.3. Quantum yield determination

3.2.3.1. Air saturated solutions. The diclofenac quantum yield in photolytic experiments was calculated by numerical integration of Eq. (12):

$$-\frac{dC_D}{dt} = \varphi_D \frac{\varepsilon_D C_D}{\sum_i \varepsilon_i C_i}I_0\left[1 - \exp\left(-2.303L\sum_i \varepsilon_i C_i\right)\right] \tag{12}$$

where φ_D is the diclofenac quantum yield at 254 nm, ε_D is the diclofenac molar absorption coefficient and $\sum_i \varepsilon_i C_i$ accounts for the absorption of UV light of all the species present in solution. The latter term was monitored along the experiments (see Fig. 2) and fitted to a mathematical expression $A_{254}(t)$.

From (12), the only adjustable parameter was φ_D. Error values estimated as the squared differences between experimental

Table 1
Diclofenac quantum yield determination by numerical integration of Eq. (12).

Inlet gas	C_{D_0} (mM)	φ_D (mol Einstein^{-1})	[a]R^2
Air	0.01	0.081	0.98
Air	0.01	0.075	0.99
Air	0.05	0.098	0.97
Air	0.05	0.095	0.97
Air	0.10	0.089	0.98
Air	0.10	0.102	0.98
Air	0.63	0.047	0.99
Air	0.63	0.066	0.99
Air	0.63	0.052	0.99
Oxygen	0.20	0.172	0.99
Oxygen	0.20	0.151	0.98
Oxygen	0.20	0.165	0.99

[a] Correlation coefficient from the plot $C_{D_{exp}}$ vs. $C_{D_{model}}$.

Table 2
Diclofenac quantum yield determination by competitive runs Eq. (14).

Inlet gas	Reference	φ_D (mol Einstein^{-1})	[a]R^2
Air	Phenol	0.114	0.96
Air	Acenaphthene	0.080	0.91
Air	Pyruvic	0.100	0.93
Air	Atrazine	0.095	0.95
Oxygen	Phenol	0.15–0.260	0.95
Oxygen	Atrazine	0.304–0.332	0.94

[a] Correlation coefficient from the plot of Eq. (14).

diclofenac concentration and model calculations

$$\text{Error} = \sum (C_{D_{exp}} - C_{D_{model}})^2 \qquad (13)$$

were minimized using the EXCEL add-in Solver. Fitted φ_D values are shown in Table 1.

From Table 1 it is noticed an acceptable concordance in values for experiments conducted in the initial diclofenac interval $1–10 \times 10^{-5}$ M. However, experiments conducted with the highest diclofenac concentration led to φ_D values significantly lower (twofold decrease). The reason for the latter anomalous result relies on the deviation of the Lambert–Beer law of the diclofenac solution, i.e. the initial absorbance of the solution was around 3 units cm^{-1} well above the recommended values of linear relationship between absorbance and concentration for the used apparatus. By only considering the first 6 runs in Table 1, the value of φ_D is 0.088 ± 0.010 mol Einstein^{-1}. Comparison to φ_D values given in the literature [1] (of the order of 0.27 mol Einstein^{-1}) results in considerable lower quantum yields obtained in this work. The photoreactor used in Ref. [1] was quite different to the experimental setup used in this work, as a consequence, direct comparison of values should be taken with caution.

In any case, it is worth to highlight that in this investigation absorbance increases as the reaction progresses. For instance, as an average, A_{254} raises up to 3.3 times from its initial value. As a consequence, the hypothesis of low optical density used in many photolysis related works may not be fulfilled along the whole reaction period and, as a consequence, the simplification considered (similar to Eq. (11) in this study) cannot be applied. As inferred from Fig. 2, first order kinetics does not apply in diclofenac concentration so apparent pseudo first order rate does not seem to be a suitable option to calculate the quantum yield.

In an attempt to confirm the previous results, a second endeavour to calculate φ_D was carried out using competitive photolysis experiments. Therefore, when two substances are present in solution it follows that:

$$\frac{dC_D}{dC_{Ref}} = \frac{\varphi_D}{\varphi_{Ref}}\frac{\varepsilon_D C_D}{\varepsilon_{Ref} C_{Ref}} \Rightarrow \ln\frac{C_D}{C_{D_0}} = \frac{\varphi_D \varepsilon_D}{\varphi_{Ref}\varepsilon_{Ref}}\ln\frac{C_{Ref}}{C_{Ref_0}} \qquad (14)$$

where the subindex "Ref" stands for a reference compound.

Phenol, acenaphthene, pyruvic acid and atrazine were used as reference substances. Obviously, calculated φ_D values were dependent on the accuracy of photolytic parameters considered for the reference compounds. For instance, different values can be found for phenol quantum yield [17,18]. Additionally, in some cases (i.e. pyruvic acid) differences in photolytic reactivity between reference substance and diclofenac led to a high uncertainty in the calculated quantum yield.

From competitive experiments with phenol [17] ($\varphi_{Ph} = 0.05$ mol Einstein^{-1}, $\varepsilon_{Ph} = 516$ M^{-1} cm^{-1}), acenaphthene [13]

($\varphi_{Ac} = 0.0055$ mol Einstein^{-1}, $\varepsilon_{Ac} = 1333$ M^{-1} cm^{-1}), pyruvic [19] ($\varphi_{Py} = 0.038$ mol Einstein^{-1}, $\varepsilon_{Py} = 87$ M^{-1} cm^{-1}) and atrazine [20] ($\varphi_{At} = 0.05$ mol Einstein^{-1}, $\varepsilon_{At} = 2486$ M^{-1} cm^{-1}) the following φ_D values were obtained 0.114, 0.080, 0.100 and 0.090 mol Einstein^{-1}, respectively (Table 2). No error is given for the previous values since errors associated to reference parameters are not reported.

3.2.3.2. Oxygen saturated solutions. Eq. (12) was used to calculate the diclofenac quantum yield in the presence of oxygen. Experiments were carried out in triplicate (initial diclofenac concentration 2×10^{-4} M) and the results are shown in Table 1.

φ_D values in the range 0.15–0.17 mol Einstein^{-1} were obtained. Additionally, some competitive experiments were also conducted using phenol or atrazine (in triplicate) (Table 2). Values obtained by this method differed by a factor of two if compared to results obtained when diclofenac was photolysed in the absence of reference substances. In this way, the run completed in the presence of phenol gave a diclofenac quantum yield of 0.26 mol Einstein^{-1}. Runs completed in the presence of atrazine (varying the initial ratio diclofenac/atrazine) led to φ_D values of 0.304, 0.315 and 0.332 mol Einstein^{-1}. Differences in quantum yield values obtained by these two different approaches are difficult to explain. In these competitive experiments, if Eq. (12) is applied to diclofenac removal, calculated φ_D values are in the proximity of 0.15–0.16, confirming the values obtained in the absence of reference compounds. A plausible explanation could be the inhibiting effect of oxygen in the phototransformation of phenol and atrazine. As a consequence, the quantum yield of these two reference compounds should be lower than the values used in experiments conducted in air. However, some data from literature contradicts this hypothesis. In this sense, Alapi and Dombi [21] report a higher phenol photoreactivity in oxygen saturated solutions than in oxygen free solutions. Quenching of excited states of the reference compounds by the simultaneous presence of diclofenac and oxygen could also account for the observed effect, however, the latter hypothesis has not been tested.

3.3. Diclofenac photolysis in the presence of free radical promoters

3.3.1. Experiments with OXONE® as promoter

To assess the possibility of improving the photolytic process, a series of experiments were conducted by adding different amounts of potassium monopersulfate. Fig. 4 shows the results obtained. From Fig. 4 it is observed a general trend of no influence of monopersulfate addition regardless of the gas introduced to the reactor (air or oxygen). The effect is the consequence of the low absorption capacity of the monopersulfate molecule. Accordingly, although the calculated *apparent* quantum yield of HSO$_5^-$ is relatively high, i.e. 2.88 mol Einstein^{-1} (standard deviation 0.23), under the conditions used in this investigation, the absorption capacity of HSO$_5^-$ at the highest concentration was only 0.08 units cm^{-1} ($\varepsilon_{HSO_5^-} = 12.5 \pm 0.12$) compared to A_{254} for diclofenac above 3 units cm^{-1}. It has to be pointed out that a quantum yield above one is not accept-
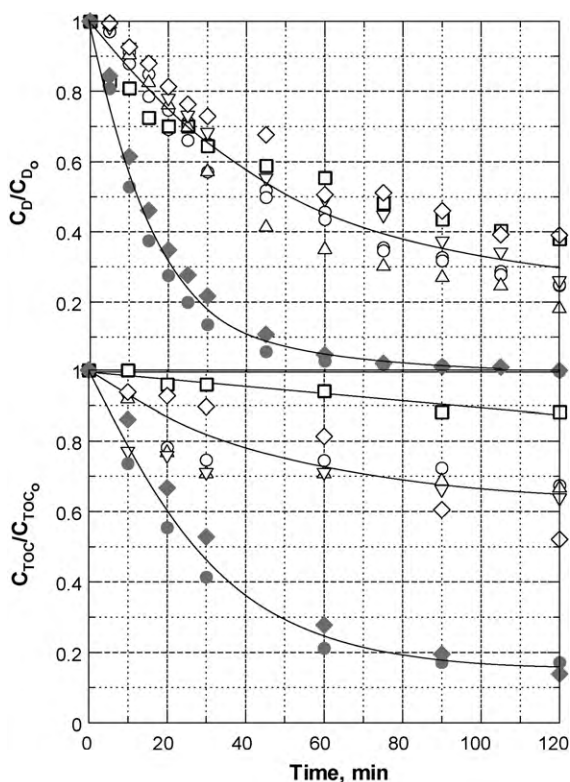
Fig. 4. OXONE® promoted UV-C photolysis of diclofenac in air (unless stated). Experimental conditions: $T = 20\,°C$; $V = 0.8\,L$; $C_{D_0} = 0.63\,mM$. $C_{OXONE^®_0}$ (mM): ○, 0.0; □, 0.16; △, 0.32; ▽, 0.63; ◇, 3.15 (solid symbols in the presence of oxygen).

Fig. 5. Percarbonate promoted UV-C photolysis of diclofenac in air (unless stated). Experimental conditions: $T = 20\,°C$; $V = 0.8\,L$; $C_{D_0} = 0.63\,mM$. $C_{H_2O_{2_0}}$ from percarbonate (mM): ○, 0.0; □, 0.63; △, 1.26; ▽, 6.3 (solid symbols in the presence of oxygen).

able from a theoretical point of view (i.e. a chain reaction must proceed) that is why the terminology "*apparent* quantum yield" is used.

3.3.2. Experiments with percarbonate and hydrogen peroxide as promoters

The use of hydrogen peroxide at concentrations of the same order to the one considered in the case of OXONE® would theoretically lead to similar results, i.e. an initial H_2O_2 concentration of $10^{-3}\,M$ would give an absorbance of roughly 0.02 units cm^{-1}, again unfavourably compared to diclofenac absorption. However, based on the results reported by Vogna et al. [10] who claimed a significant positive effect of H_2O_2 in the UV-C photolysis of diclofenac, it was decided to conduct an experimental series by replacing the aqueous solution of H_2O_2 by percarbonate. In Fig. 5 it is revealed how the presence of percarbonate negatively affects the diclofenac removal rate, moreover, it exerts a patent negative effect on TOC elimination. Considering that percarbonate dissolution is just an alternative form for H_2O_2 addition, the results obtained in this study manifestly are in opposition to those reported by Vogna et al. [10]. Nevertheless, it could be argued that percarbonate is not only a source of hydrogen peroxide but also a source of carbonates acting as scavengers through reactions (3) and (4). The scavenging nature of carbonates could be demonstrated by calculating quantum yield for the hydrogen peroxide photolysis when percarbonate was the source of H_2O_2. The value obtained was $\varphi_{H_2O_2(from\,percarbonate)} = 0.47 + 0.09\,mol\,Einstein^{-1}$, i.e. as expected, half of H_2O_2 in pure water. Furthermore, addition of percarbonate shifted the initial pH of the aqueous solution to values close to 10–11, so direct comparison to non-promoted experiments could not be accomplished. Additionally, Vogna et al. [10] used an initial concentration ratio H_2O_2/diclofenac of 5, much higher than the ratio used in this work (maximum value 1.6).
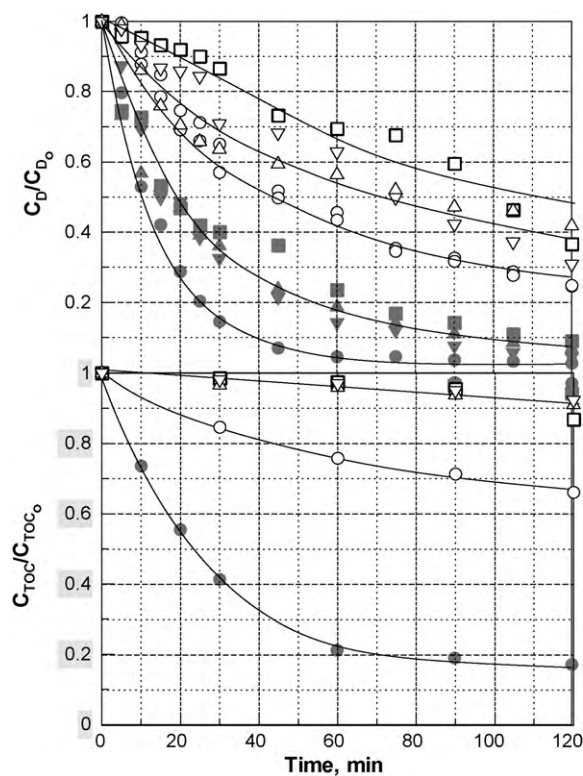

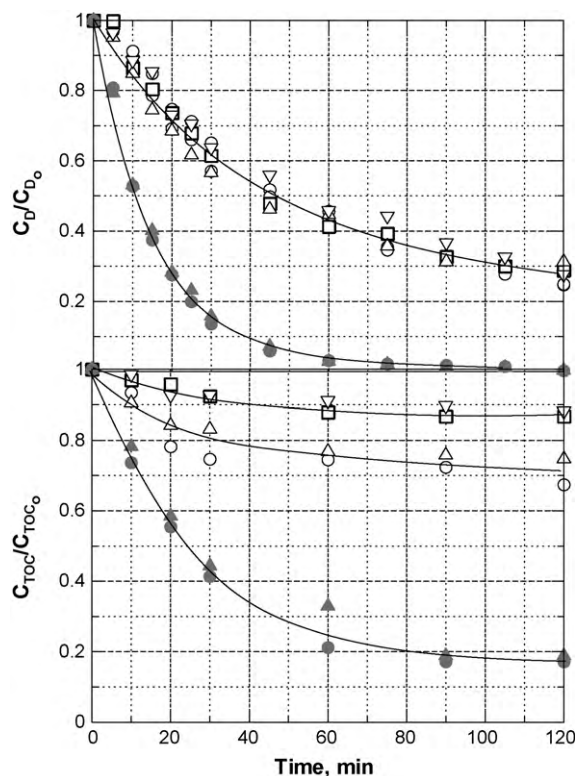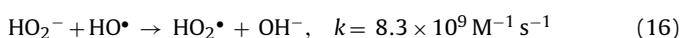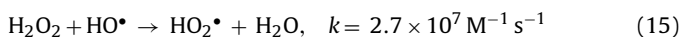**Fig. 6.** Hydrogen peroxide promoted UV-C photolysis of diclofenac in air (unless stated). Experimental conditions: $T = 20\,°C$; $V = 0.8\,L$; $C_{D_0} = 0.63\,mM$. $C_{H_2O_{2_0}}$ (mM): ○, 0.0; □, 0.4; △, 0.7; ▽, 1.0 (solid symbols in the presence of oxygen).

In any case, considering the precedent discussion, in a final attempt to improve the photolytic process, hydrogen peroxide was directly used in the absence of scavengers. Fig. 6 once again showed the negligible influence of the radical promoter, even for a H_2O_2/diclofenac ratio of 5.0 used in Ref. [10] (the latter results not shown). The reason seems to be the negligible absorption of light by hydrogen peroxide ($A_{254} = 5.7 \times 10^{-2}$ units cm^{-1} when $C_{H_2O_{20}} = 3 \times 10^{-3}$ M). A similar effect has been reported for the sunlight photolysis of diclofenac in the presence of organic matter from the Mississipi River. In this case, organic matter does not affect the process because of the domination of light screening by diclofenac [22].

Increasing the absorption of UV light by H_2O_2 would involve the increase in its initial concentration, however this is not recommended because of the high operating costs associated to the use of high hydrogen peroxide concentrations and because of the potential appearance of the scavenging nature of H_2O_2 when used in excess:

$$H_2O_2 + HO^\bullet \rightarrow HO_2^\bullet + H_2O, \quad k = 2.7 \times 10^7\,M^{-1}\,s^{-1} \tag{15}$$

$$HO_2^- + HO^\bullet \rightarrow HO_2^\bullet + OH^-, \quad k = 8.3 \times 10^9\,M^{-1}\,s^{-1} \tag{16}$$

4. Conclusions

The most important conclusions derived from this work are:

- Photolytic process kinetics is dependent on the medium absorbance evolution. From a modelling point of view, simplifications assumed at the beginning of the process may not hold true for the whole reaction period. Additionally, the approach used in kinetics determinations should also be specified; hence, different methodologies that apparently are valid can lead to different parameters determination.
- Given the significant influence of oxygen presence, its concentration should also be considered when analysing the diclofenac phototransformation.
- In this work, UV-C radiation at 254 nm achieves high levels of TOC removal, especially when oxygen is sparged into the diclofenac aqueous solution.
- As a rule of thumb, it can be suggested that addition of free radical promoters does not enhance the efficiency of the process when irradiating substances with relatively high values of quantum yield and molar absorption coefficient; moreover, a negative effect can be experienced. Actually, concentration, quantum yield and molar absorption coefficient should be simultaneously considered.

Acknowledgments

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