



## UV-C radiation based methods for aqueous metoprolol elimination

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### ABSTRACT

The endocrine disruptor metoprolol has been oxidised in aqueous solution by means of the systems UV-C, UV-C/H<sub>2</sub>O<sub>2</sub>, UV-C/percarbonate, UV-C/monopersulfate, UV-C/TiO<sub>2</sub>, UV-C/H<sub>2</sub>O<sub>2</sub>/TiO<sub>2</sub> and photo-Fenton. From simple photolysis experiments the quantum yield of metoprolol has been calculated (roughly  $5 \times 10^{-3}$  mol Einstein<sup>-1</sup> at circumneutral pH). Addition of free radicals promoters significantly enhanced the metoprolol depletion rate. Mineralization degree was negligible when no promoter was added, while low values were achieved in the presence of either inorganic peroxides or titanium dioxide. The combination of radiation, hydrogen peroxide and TiO<sub>2</sub> increased the mineralization level up to values in the proximity of 45–50% under the best conditions investigated. The photo-Fenton process was the best system in terms of total oxidation (mineralization degree 70%) when optimum conditions were applied.

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### 1. Introduction

During the last two decades, a growing concern related to the presence of new aqueous contaminants has appeared. The so called “endocrine disruptors” capable of interfering the normal function of the endocrine system are incessantly found in surface and groundwater. The monitoring of pharmaceuticals and other endocrine disruptors in drinking water supplies has raised the public perception of health threats [1,2]. Amongst the considerable number of pharmaceuticals that can be detected in receiving effluents, metoprolol is characterised by an increasing use in recent years, and, as a consequence, an increasing presence in aqueous effluents is envisaged. This pharmaceutical is a beta-blocker used in treating hypertension, angina, arrhythmia and acute myocardial infarction. Metoprolol shows slow direct phototransformation and/or hydrolysis, although indirect photolysis and photo-induced biodegradation can be the main sources of its depletion in the environment [3]. In any case, the half life of metoprolol under sun light has been reported to be several hundreds of hours and efficient technologies for its removal from waters are required. Several treatments including UV-C radiation [4–6], Fenton’s reagent [6] or ozone [7] have previously been reported. The aim of this work was going a step further in terms of analysing the efficiency of several UV-C radiation based technologies at the time of mineralization. Thus, in this work, metoprolol has been irradiated in the presence/absence of several inorganic peroxides and/or titanium dioxide and also by

the photo-Fenton reagent. Addition of peroxides in UV-C radiation processes involves the formation of highly reactive radicals capable of unselectively attack most of organic compounds present in an aqueous sample [8]. Additionally, an attempt has been completed to calculate some important kinetic parameters typical of photolytic processes.

### 2. Experimental

Metoprolol was purchased from Aldrich and used as received (tartrate salt of 99%). Titanium dioxide (TiO<sub>2</sub>) P25 from Degussa was used as photocatalyst with no previous treatment. According to manufacturers Degussa P-25 is a non-porous solid formed by the combination of the anatase (70%) and rutile (30%) forms of titanium dioxide. The solid is characterised by the following properties: density 3.8 g cm<sup>-3</sup>, BET surface area 50 m<sup>2</sup> g<sup>-1</sup>, average primary particle 30 nm, pH in aqueous solution 3–4.

Experiments were carried out in a 1 L glass annular jacketed photochemical reactor (see Fig. 1). In control experiments, an air or oxygen stream was continuously fed through a porous plate situated at the reactor bottom. Since no differences were observed regardless of the gas used, experiments were thereafter conducted under an oxygen stream. Water pumped from a thermostatic bath circulated through the reactor jacket to ensure a constant temperature inside the reactor. The reactor walls were insulated to avoid release of radiation and/or heat outside. Prior to the photocatalytic experiments in the presence of titanium dioxide, the suspension was stirred for 60 min in the dark to achieve the adsorption equilibrium.

A 15 W HERAEUS low pressure mercury vapour lamp introduced in a quartz well was used for experiments carried out by using UV-C

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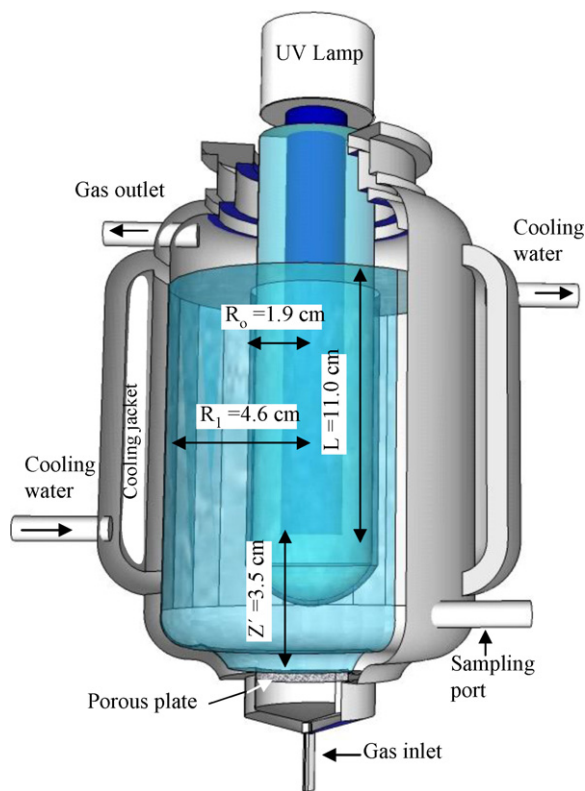
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### Nomenclature

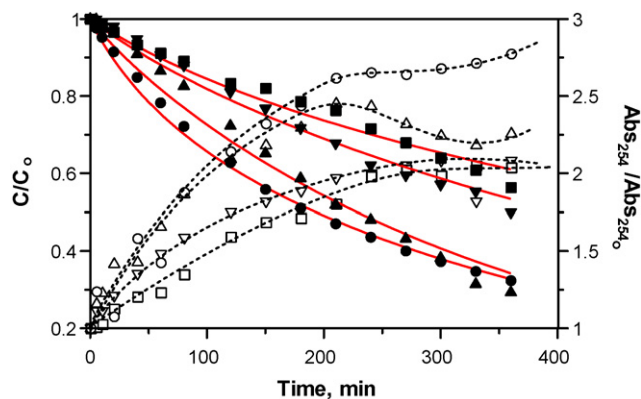
$A_{254}$	Absorbance at 254 nm
$C$	Metoprolol concentration ( $\text{mol L}^{-1}$ )
$E_0$	Radiant power ( $\text{Einstein s}^{-1}$ )
$L$	Length of immersed lamp (cm)
$q_0$	Incident radiation flux ( $\text{Einstein cm}^{-2} \text{s}^{-1}$ )
$r$	Integration variable in Eq. (2) (cm)
$R_i$	Reactor dimension according to Fig. 1 (cm)
$V$	Reaction volume (L)
TOC	total organic carbon ( $\text{mg L}^{-1}$ )
$z$	Integration variable in Eq. (2) (cm)
$z'$	Reactor dimension according to Fig. 1 (cm)
$\omega$	Parameter defined in Eq. (3)
$\varepsilon$	Molar absorption coefficient ( $\text{M}^{-1} \text{cm}^{-1}$ )
$\phi$	Metoprolol quantum yield ( $\text{mol Einstein}^{-1}$ )

radiation (254 nm). Actinometry experiments led to the determination of the incident radiation flux ( $q_0 = 2.5 \times 10^{-8} \text{ Einstein cm}^{-2} \text{ s}^{-1}$ ) and radiant power ( $E_0 = 3.3 \times 10^{-6} \text{ Einstein s}^{-1}$ ).

Total organic carbon (TOC) was determined by a Shimadzu TOC 5000A analyser by directly injecting the aqueous solution. Peroxides were monitored by iodometric titration. Metoprolol concentration was quantified by UV absorption at 275 nm. A high-performance liquid chromatograph (Agilent Technologies, series 1100) equipped with a Chromasil C-18 column was used. The analysis was performed in isocratic mode. The mobile phase used was a mixture of acetonitrile/water (70/30, v/v).



**Fig. 1.** Photolysis reactor dimensions.  $L$ : lamp length introduced into the metoprolol aqueous solution,  $R_0$ : distance from UV lamp central axis to quartz well surface,  $R_1$ : distance from UV lamp central axis to reactor wall and  $z$ : distance from reactor bottom to UV lamp end.



**Fig. 2.** Photolysis of metoprolol. Evolution of normalized metoprolol concentration (solid symbols) and normalized absorbance at 254 nm (open symbols). Experimental conditions: pH = 6.0;  $T = 295 \text{ K}$ ,  $C_0 (\times 10^4 \text{ M})$ : (▲) 1.0; (▼) 2.0; (■) 5.0; (●) 5.0 (pH = 11). Solid lines correspond to LSPP model calculations.

## 3. Results and discussion

### 3.1. Photolysis

To ascertain the photoreactivity of metoprolol, a series of experiments was conducted by simple irradiation of the pharmaceutical in the absence of any promoter/catalyst. Fig. 2 shows the results obtained after applying different operating conditions. As observed, the metoprolol phototransformation process is not fast enough to be considered as an adequate technology. The low molar absorption coefficient ( $\varepsilon$ ) of metoprolol confirms the previous experimental facts. Thus, in the pH range 2–10, the  $\varepsilon$  value calculated was  $560 \pm 12 \text{ M}^{-1} \text{ cm}^{-1}$  quite different to other lower reported values around  $235 \text{ M}^{-1} \text{ cm}^{-1}$  [4,9] or even higher values of  $950 \text{ M}^{-1} \text{ cm}^{-1}$  [6]. No clear explanation can be given for such differences. In this sense, it has to be pointed out that Sigma–Aldrich metoprolol tartrate bottle shows a molecular formula for this compound ( $\text{C}_{15}\text{H}_{25}\text{NO}_3 \cdot (1/2)\text{C}_4\text{H}_6\text{O}_6$ ) whose molecular weight is, obviously, half of the real structure [ $\text{C}_{15}\text{H}_{25}\text{NO}_3$ ] $_2\text{C}_4\text{H}_6\text{O}_6$  with MW = 684.8. This hypothesis would explain absorption coefficients in the proximity of  $250 \text{ M}^{-1} \text{ cm}^{-1}$ .

In no case, mineralization of the pharmaceutical took place, confirming the inadequacy of UV-C radiation to deal with metoprolol contaminated waters.

The quantum yield of metoprolol was calculated by considering two different approaches describing the photolytic process of a substance in a batch reactor [10,11].

The linear source with emission in parallel planes model (LSPP).

The equation describing the phototransformation of metoprolol (C) is the following:

$$-\frac{dC}{dt} = \phi \frac{q_0 2\pi R_0 L \varepsilon C}{A_{254} V} [1 - 10^{(-A_{254}(R_1 - R_0))}] \quad (1)$$

where  $\phi$  is the metoprolol quantum yield,  $q_0$  is the incident radiation flux ( $\text{Einstein cm}^{-2} \text{ s}^{-1}$ ),  $R_i$  is defined in Fig. 1,  $V$  is the reaction volume,  $\varepsilon$  the molar absorption coefficient of metoprolol and  $A_{254}$  is the absorbance of the photolysed solution.

The point source with spherical emission model (PSSE).

Now the expression used to calculate the metoprolol quantum yield is:

$$-\frac{dC}{dt} = \phi \frac{E_0 A_{254}}{V 2L} \int_0^L \int_{R_0}^{R_1} \int_{z'}^{z'+L} r \frac{e^{(-A_{254}\omega)}}{r^2 + (z - z')^2} dr dz dz' \quad (2)$$

**Table 1**  
Metoprolol UV-C photolysis. Quantum yield determination.

$C_0$ (M)	pH	$\phi$ (mol Einstein <sup>-1</sup> )	
		LSPP ( $R^2$ )	PSSE ( $R^2$ )
$1.0 \times 10^{-4}$	5.8	$6.4 \times 10^{-3}$ (0.990)	$5.5 \times 10^{-3}$ (0.980)
$2.0 \times 10^{-4}$	6.2	$4.8 \times 10^{-3}$ (0.996)	$5.5 \times 10^{-3}$ (0.991)
$5.0 \times 10^{-4}$	7.0	$5.6 \times 10^{-3}$ (0.993)	$5.9 \times 10^{-3}$ (0.979)
$5.0 \times 10^{-4}$	11.0	$18.1 \times 10^{-3}$ (0.998)	$18.0 \times 10^{-3}$ (0.983)

where  $E_0$  is the radiant power (Einstein s<sup>-1</sup>) and  $\omega$  is defined as:

$$\omega = \frac{\sqrt{r^2 + (z - z')^2}}{r} \quad (3)$$

Results of the quantum yield determination are shown in Table 1. It has to be pointed out that the LSPP model gave a better correlation between experimental and theoretical metoprolol concentrations in the whole reaction period (360 min) while the PSSE model was only applicable to the first 60–100 min depending on reaction conditions. Both models led to similar results confirming the low photoreactivity of metoprolol at circumneutral conditions.

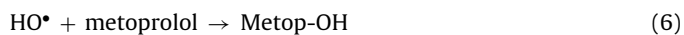
However, when pH was increased above the pK<sub>a</sub> of metoprolol (9.7) the obtained quantum yield experienced a three-fold increase up to around 0.02 mol Einstein<sup>-1</sup>.

In any case, it seems that a more effective treatment is required. As a consequence, a series of experiments was conducted by adding a free radical promoter at the beginning of the process.

### 3.2. Peroxide promoted experiments

#### 3.2.1. Hydrogen peroxide addition

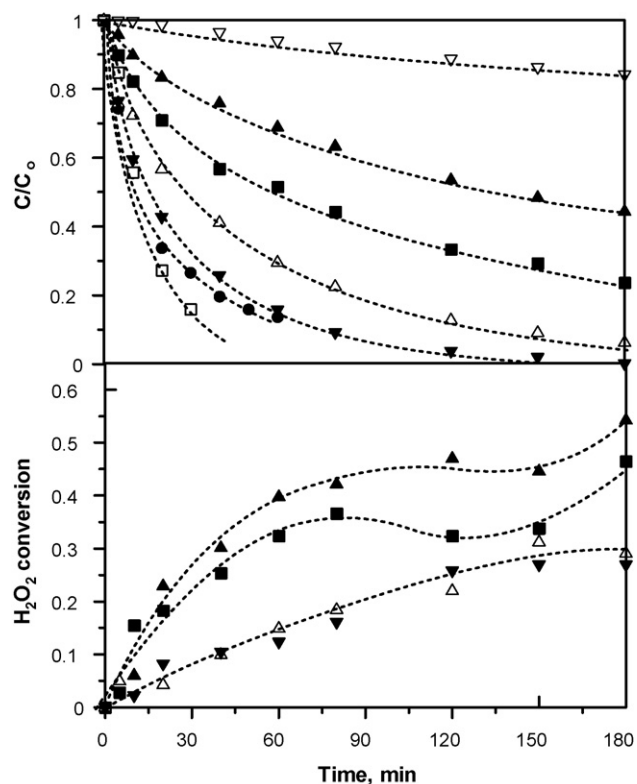
Hydrogen peroxide generates two hydroxyl radicals in the presence of UV-C radiation. Hydroxyl radicals are capable of unselectively oxidising most of organic pollutants leading to a radical mechanism which is simplified in reactions (4)–(8):



Obviously, Metop-OH is a generic nomination for a wide range of oxidation products, however to propose a detailed mechanism is out of the scope of this manuscript. A more useful and descriptive work based on metoprolol oxidation products can be found elsewhere [12].

Fig. 3 shows the effect of adding different amounts of hydrogen peroxide to metoprolol photolysis. As observed the positive effect of hydrogen peroxide addition is increased as its concentration is raised in comparison to metoprolol initial concentration. The previous results suggest that, under the operating conditions investigated, the scavenging effect of an excess of the promoter (reaction (7)) is still negligible in comparison to the increase in HO<sup>•</sup> production. Additionally, it is also observed a decrease in hydrogen peroxide conversion as the ratio metoprolol:H<sub>2</sub>O<sub>2</sub> also decreases. Mineralization levels achieved with this system were not very promising with only a 10% carbon removal as an average.

Assuming that hydroxyl radicals are predominantly scavenged by hydrogen peroxide and methanol, a first guess on the value of  $k_6$  could be carried out by solving the set of differential equations derived from the previous mechanism. The experiment with the highest H<sub>2</sub>O<sub>2</sub> concentration was used to favour the hypothesis

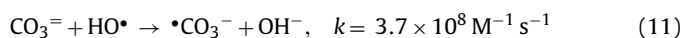
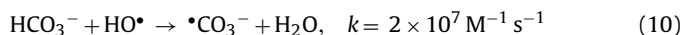
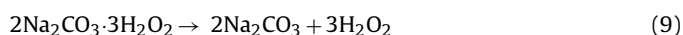


**Fig. 3.** H<sub>2</sub>O<sub>2</sub>-promoted photolysis of metoprolol. Evolution of normalized metoprolol concentration and hydrogen peroxide conversion. Experimental conditions: pH=6.0; T=295 K,  $C_0 = 5.0 \times 10^{-4}$  M,  $C_{\text{H}_2\text{O}_2}$  ( $\times 10^4$  M): ( $\nabla$ ) 0.0; ( $\blacktriangle$ ) 8.3; ( $\blacksquare$ ) 14.0; ( $\triangle$ ) 28.0; ( $\blacktriangledown$ ) 50.0; ( $\bullet$ ) 6.0 ( $C_0 = 1.0 \times 10^{-4}$  M); ( $\square$ ) 2.5 ( $C_0 = 5.0 \times 10^{-5}$  M).

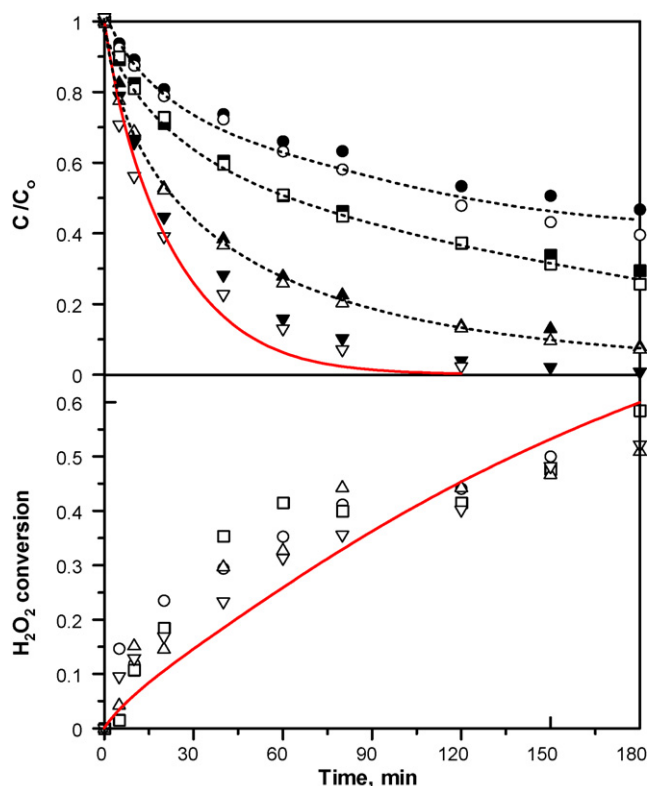
of low scavenging of radicals by intermediates. The fitting process completed to minimize the differences between metoprolol theoretical and experimental concentrations led to a rather low value of  $k_6 = 3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , one order of magnitude below the expected value [7]. Moreover, the model overestimated the hydrogen peroxide conversion rate, indicating that either the promoter phototransformation is not well modelled and/or HO<sup>•</sup> are scavenged to a significant extent by generated intermediates.

#### 3.2.2. Percarbonate addition

In order to make the process more attractive from a practical point of view, a different source of hydrogen peroxide was used. Percarbonate is a H<sub>2</sub>O<sub>2</sub> carrier in solid form (see Eq. (9)). Percarbonate should offer the same features than H<sub>2</sub>O<sub>2</sub> with a safer handling and delivery. Moreover, when applied as HO<sup>•</sup> promoter, the only potential drawback of sodium percarbonate could be the scavenging effect exerted by released carbonates according to.



In this work several runs were conducted in the presence of varying amounts of percarbonate and keeping constant the rest of operating variables. Additionally, some experiments were conducted by maintaining the ratio percarbonate:metoprolol and changing the initial concentration of the pharmaceutical. Fig. 4 shows the results obtained in the first series. By direct comparison of Figs. 3 and 4 it is inferred that percarbonate has the same oxidising power than liquid hydrogen peroxide, even in the presence of released carbonates. Also, no effect can be appreciated between runs conducted at initial basic pH or circumneutral conditions. Thus, although the



**Fig. 4.** Percarbonate promoted photolysis of metoprolol. Evolution of normalized metoprolol concentration and hydrogen peroxide conversion. Experimental conditions: pH = 6.0 (open symbols) and pH  $\approx$  10.0 (solid symbols);  $T = 295$  K,  $C_0 = 5.0 \times 10^{-4}$  M,  $\text{CH}_2\text{O}_2 \cdot (\times 10^{-4} \text{ M})$ : (●) 6.8; (■) 12.4; (▲) 33.0; (▼) 65.0 (solid lines correspond to numerical solution of Eqs. (4)–(7) and (9)–(10) at pH 10.0 with  $k_6 = 4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ).

quantum yield of metoprolol is higher at alkaline pH, bicarbonates show a lower scavenging effect than carbonates. Also some  $\text{CO}_2$  stripping at circumneutral pH cannot be discarded.

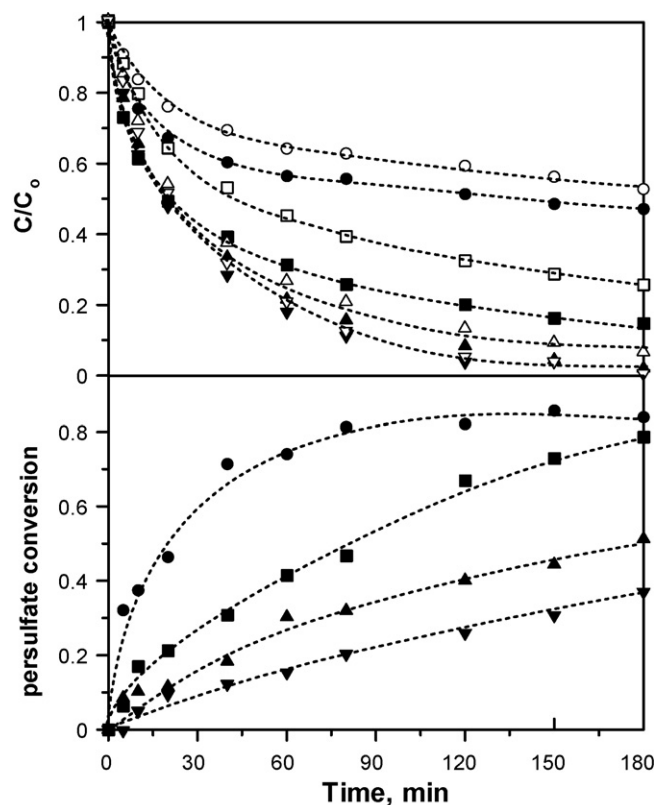
Once more, a new attempt to calculate the value of  $k_6$  was conducted. In this case, the presence of a high amount of carbonates allows for the hypothesis of  $\text{HO}^\bullet$  scavenging preferentially by metoprolol, hydrogen peroxide and carbonates. To ensure the previous hypothesis the experiments with the highest percarbonate:metoprolol ratios at pH 10 were chosen. Hence, this pH involves a higher scavenging effect of carbonates preventing the stripping of  $\text{CO}_2$  from carbonic acid equilibrium. The values of  $k_6$  that best fitted the experimental metoprolol concentrations were located in the proximity of  $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , a normal value reported for the constants of hydroxyl radicals and organic compounds.

Experiments carried out at different initial metoprolol concentration and similar ratio oxidant:pharmaceutical led to lower conversion rates for the experiments conducted with increasing concentrations of metoprolol. Nevertheless, the latter experiments showed a higher metoprolol elimination rate.

TOC conversions after 3 h reached a poor 35% when the best conditions were applied (highest percarbonate concentration). An attempt was conducted to improve this percentage by using a different source of radicals.

### 3.2.3. Monopersulfate addition

Radical promotion by the peroxymonopersulfate molecule under UV radiation proceeds by scission according to



**Fig. 5.** OXONE<sup>®</sup> promoted photolysis of metoprolol. Evolution of normalized metoprolol concentration and hydrogen peroxide conversion. Experimental conditions: pH = 6.0 (open symbols) pH  $\approx$  3.0 (solid symbols);  $T = 295$  K,  $C_0 = 5.0 \times 10^{-4}$  M,  $\text{COXONE}^\bullet (\times 10^3 \text{ M})$ : (●) 1.0; (■) 1.9; (▲) 4.7; (▼) 8.5.

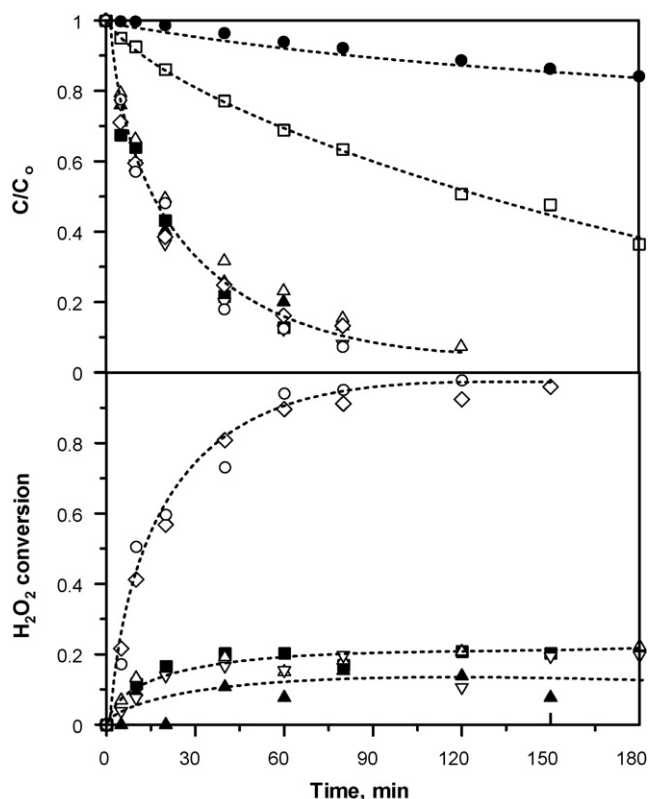
Hydroxyl and sulfate radicals are responsible of the further oxidation of organics in aqueous medium.

Fig. 5 depicts the results obtained when adding different amounts of OXONE<sup>®</sup>. Two aspects have to be highlighted. On the one hand, similarly to  $\text{H}_2\text{O}_2$  and percarbonate, a notorious enhancement of the process is experienced if compared to metoprolol conversion obtained in the absence of promoters. On the other hand, a slight positive effect is evidenced when the initial pH of the solution was acidic (low pH is due to monopersulfate addition). The latter effect is more patent when the lowest OXONE<sup>®</sup> concentrations were used.

Additionally, the inorganic peroxide conversion was also higher than in the case of the previous promoters. Unfortunately, this was not an indication of higher mineralization, TOC removal did not improve the results obtained when hydrogen peroxide or percarbonates were used. Again, with the aim of enhancing the mineralization level, it was decided to check for the efficacy of the photocatalysis in the presence of titania powder.

### 3.2.4. Promoted photocatalysis in the presence of $\text{TiO}_2$ and $\text{H}_2\text{O}_2$

To check for the potential activity of  $\text{TiO}_2$ , a control experiment was completed in the presence of  $1 \text{ g L}^{-1}$  of titanium dioxide. Results are shown in Fig. 6. As observed,  $\text{TiO}_2$  exerts a positive effect in the photolysis of metoprolol if compared to results in the absence of the photocatalyst. However, the capacity of this system to reduce the TOC content was still below the expectations for this kind of process (only a scarce 30% mineralization was achieved). Accordingly, to assess any synergistic effect, it was decided to combine the action of  $\text{TiO}_2$  and  $\text{H}_2\text{O}_2$ . Fig. 6 shows the results of experiments conducted under different concentrations of promoter and catalyst. As observed, increasing the  $\text{TiO}_2$  concentration from 0.25



**Fig. 6.**  $\text{H}_2\text{O}_2$ -promoted photocatalysis of metoprolol. Evolution of normalized metoprolol concentration and hydrogen peroxide conversion. Experimental conditions:  $\text{pH} = 6.0$ ;  $T = 295 \text{ K}$ ,  $C_0$  ( $\times 10^4 \text{ M}$ ),  $C_{\text{H}_2\text{O}_2}$  ( $\times 10^3 \text{ M}$ ),  $C_{\text{TiO}_2}$  ( $\text{g L}^{-1}$ ): (●) 5.0, 0.0, 0.0; (□) 5.0, 0.0, 1.0; (▲) 1.0, 1.0, 1.0; (■) 1.0, 1.0, 0.5; (△) 1.0, 1.0, 2.0; (∇) 1.0, 1.0, 0.25; (◇) 1.0, 0.5, 0.5; (○) 1.0, 2.0, 0.5.

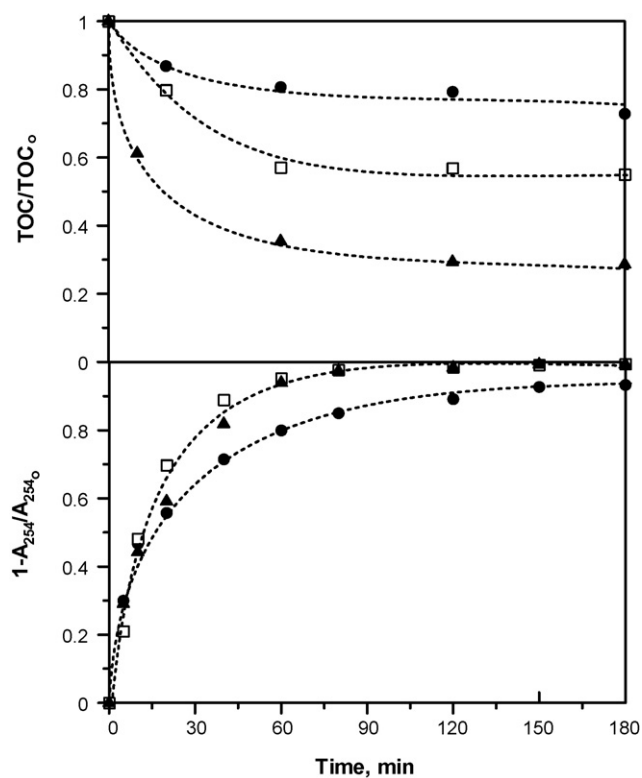
to  $2.0 \text{ g L}^{-1}$  did not affect the metoprolol reaction rate. Moreover, TOC conversion after 180 min was always similar (in the proximity of 45%) regardless of the photocatalyst concentration used. It could be hypothesised that  $\text{TiO}_2$  has no effect in the combined system, however the direct comparison for similar experiments in Figs. 5 and 6 ( $C_0 = 10^{-4} \text{ M}$  and  $\text{H}_2\text{O}_2 \approx 5 \times 10^{-4} \text{ M}$ ) revealed a higher TOC and  $\text{H}_2\text{O}_2$  conversions when the solid was present.

Also, different amounts of hydrogen peroxide did not result in appreciable variations in metoprolol depletion rate. TOC conversion was 27% for the lowest  $\text{H}_2\text{O}_2$  concentration (likely the low promoter concentration limited the efficiency of the process) and 35% when the highest  $\text{H}_2\text{O}_2$  amount was used. In the latter case, at the sight of the high promoter conversion obtained, an increase in the inefficient decomposition/scavenging effect can be considered.

### 3.2.5. Promoted photolysis in the presence of $\text{Fe}^{2+}$ and $\text{H}_2\text{O}_2$ (photo-Fenton)

In a final attempt to find a suitable oxidation system capable of removing a significant fraction of the organic carbon content the photo-Fenton system was studied. This process is characterised by a continuous regeneration of the  $\text{Fe}(\text{II})$  species so three simultaneous actions can be contemplated, direct photolysis, hydrogen peroxide photolysis and Fenton's reagent.

Fig. 7 shows the evolution of TOC profiles with time for experiments conducted in the presence of different amounts of  $\text{H}_2\text{O}_2$ . Under the operating conditions used, this system is characterised by an instantaneous metoprolol removal in less than 5 min and an increasing TOC conversion as  $\text{H}_2\text{O}_2$  initial concentration is raised. Thus, even when high hydrogen peroxide concentrations are used, it seems that the promoter is not in excess. TOC removal rate clearly



**Fig. 7.** Photo-Fenton oxidation of metoprolol. Evolution of normalized TOC concentration and absorbance ( $A_{254}$ ) conversion. Experimental conditions:  $\text{pH} = 4.3$ ;  $T = 295 \text{ K}$ ,  $C_0 = 1 \times 10^{-4} \text{ M}$ ,  $C_{\text{Fe}^{2+}} = 1 \times 10^{-4} \text{ M}$ ;  $C_{\text{H}_2\text{O}_2}$  ( $\times 10^3 \text{ M}$ ): (●) 1.0; (□) 10.0; (▲) 20.0.

shows two distinct periods. The first rapid stage proceeds when  $\text{H}_2\text{O}_2$  is present in solution, in the second stage, TOC removal comes to a halt due to  $\text{H}_2\text{O}_2$  disappearance. At the best conditions used, a significant 70% TOC elimination is achieved which is accompanied by a sharp decrease in the absorbance at 254 nm. It has to be highlighted that this is the only system capable of continuously decrease the absorbance of the solution from the beginning of the process. For the rest of systems  $A_{254}$  always increased along the reaction period. When aggressive conditions were used (UV-C/ $\text{TiO}_2$ / $\text{H}_2\text{O}_2$  system) this parameter showed a Gaussian-like shape, decreasing its value at the end of the experiments.

## 4. Conclusions

From the results obtained in this study the following conclusions can be derived:

- Metoprolol cannot be considered as a photoreactive compound under UV-C radiation. The values of the molar absorption coefficient (roughly  $560 \text{ M}^{-1} \text{ cm}^{-1}$ ) and quantum yield (roughly  $5 \times 10^{-3} \text{ mol Einstein}^{-1}$  at circumneutral pH) indicate a relative recalcitrance to photolytic processes.
- Addition of promoters/photocatalysts significantly increases its degradation rate (i.e. after 180 min,  $5 \times 10^{-3} \text{ M}$  of  $\text{H}_2\text{O}_2$  totally eliminates  $5 \times 10^{-4} \text{ M}$  of metoprolol, compared to 10–20% of conversion achieved in the absence of promoters). However, this increase is not extrapolated to TOC elimination. Mineralization degree observed is rather low in all cases and independently of the promoter used.
- If the  $\text{H}_2\text{O}_2$ -promoted photocatalytic process is applied, results in TOC conversion are notoriously improved to values in the proximity of 45% when the initial metoprolol concentration was

$10^{-4}$  M,  $\text{H}_2\text{O}_2 = 10^{-3}$  M and regardless of the catalyst dose (from 0.25 to  $2.0 \text{ g L}^{-1}$ ).

- The photo-Fenton system shows the highest capability in terms of TOC and absorbance removals. A 70% TOC elimination is achieved when  $10^{-4}$  M of metoprolol were irradiated in the presence of  $10^{-4}$  M in Fe(II) and 0.02 M in  $\text{H}_2\text{O}_2$ .

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