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# Ozonation and $H_2O_2$/UV treatment of clofibric acid in water: a kinetic investigation

Roberto Andreozzi*, Vincenzo Caprio, Raffaele Marotta, Anita Radovnikovic

*Dipartimento di Ingegneria Chimica, Facoltà di Ingegneria, Università degli Studi di Napoli "Federico II", Piazzale V. Tecchio 80, 80125 Naples, Italy*

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**Abstract**

The presence of pharmaceuticals or their active metabolites in surface and ground waters has been recently reported as mainly due to an incomplete removal of these pollutants in sewage treatment plants (STP). Advanced oxidation processes may represent a suitable tool to reduce environmental release of these species by enhancing the global efficiency of reduction of pharmaceuticals in the municipal sewage plant effluents. The present work aims at assessing the kinetics of abatement from aqueous solutions of clofibric acid (a metabolite of the blood lipid regulator clofibrate) which has been found in surface, ground and drinking waters. Ozonation and hydrogen peroxide photolysis are capable of fast removal of this species in aqueous solution, with an almost complete conversion of the organic chlorine content into chloride ions for the investigated reaction conditions. A validation of assessed kinetics at clofibric acid concentrations as low as those found in STP effluents is presented for both systems.


*Keywords:* Clofibric acid; Drugs; Ozonation; Hydrogen peroxide photolysis; AOP processes; Kinetics

## 1. Introduction

Following the first studies in the 1980s [1–3], a recent increasing interest in the presence of pharmaceuticals or their active metabolites in the aquatic environment is documented [4–10]. A fairly high number of drugs belonging to different pharmaceutical classes has been detected in surface and ground waters at concentration ranging from nanograms to micrograms per liter. Previous investigations generally conclude that the main source of these environmental pollutants are the effluents of the sewage treatment plants (STP). In fact,

* Corresponding author. Tel.: +39-081-7682251; fax: +39-081-5936936.
*E-mail address:* roberto.andreozzi@unina.it (R. Andreozzi).

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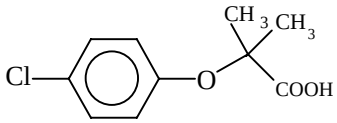



Fig. 1. Chemical structure of clofibric acid. CAS number: 882-09-7.

after their use such substances are often excreted unmetabolised, directly into the sewage system as parent compounds. Many of these pharmaceuticals have been reported to be only partially removed in STP and are thus discharged in surface waters. Additional sources are manure, through which veterinary drugs are introduced in the environment [4,11], and incorrect disposal of personal care products and unused pharmaceuticals in domestic refuse. Most scientific papers dealing with this topic outline the need to assess potential risks of pharmaceuticals for human and environmental health since the concentrations at which they are found are orders of magnitude lower than those causing acute toxic effects on aquatic organisms [12]. The impact on sexual differentiation in fish of contraceptive steroid 17α-ethyniloestradiol, which has been demonstrated at concentration of nanograms per liter is reported to support this view [13].

Recently, adverse effects on rainbow trout (*Oncorhynchus mykiss*) exposed to diclofenac, an anti-inflammatory drug, at a concentration of $1\,\mu g\,l^{-1}$ have been documented [14]. Moreover data on invertebrates gave LOEC for carbamazepine at concentrations of about $20\,\mu g\,l^{-1}$ (J. Garric, unpublished data).

Clearly, even in cases in which adverse effects are proved for some pharmaceuticals, their use cannot be abandoned, and some measures devoted to reduce the environmental risk have to be adopted. Therefore, wastewater treatment by means of advanced technologies capable of ensuring an enhanced removal of these species with respect to that achieved in conventional biological processes have thus to be considered. Among existing treatment strategies, ozonation and hydrogen peroxide photolysis have already achieved a high level of development, which makes their adoption at an industrial scale quite flexible. Following this point of view, a recent work studied the removal of carbamazepine through the use of ozonation process [15]. The oxidative degradation in aqueous solution of paracetamol by means of ozonation and $H_2O_2$/UV photolysis was also investigated by the authors [16].

The present work evaluates the removal of clofibric acid (Fig. 1), a human metabolite of clofibrate (its ethyl ester form), used as a blood lipid regulator, from aqueous solutions by means of both ozonation and hydrogen peroxide photolysis. The presence of this compound, which has been reported to be highly persistent once introduced in the surface waters [20], has been documented in STP effluents [10,17], rivers [18,19], lakes [20], ground and drinking waters [21]. Previous studies [22,34] report that ozonation effectively removes clofibric acid from drinking water but only scant indications on reaction kinetics were given.

## 2. Materials and methods

Ozonation was tested in a semicontinuous stirred tank Pyrex glass reactor (1.090 l), with constant temperature $T = 298\,K$, operated in the batch mode with respect to liquid

phase. The apparatus used for the studies was similar to that previously described [23]. The initial clofibric acid concentrations were in the range $1.0 \times 10^{-3}$ to $1.5 \times 10^{-3}$ M. An ozonized oxygen stream of 2 vol.%, generated by an ozone-generator (Fischer 502) was fed at a flow rate of $36\,l\,h^{-1}$ to the reactor containing the aqueous solution.

The ozone concentration in the outlet gaseous stream ($O_{3,freeboard}$) was evaluated by continuous UV monitoring at 253 nm ($\varepsilon_{O_3} = 3200\,M^{-1}\,cm^{-1}$) using of a Varian UV spectrophotometer equipped with a quartz cell (optical length $= 2.0 \times 10^{-2}$ dm).

Clofibric acid solutions were buffered at desired pHs by adding of $H_3PO_4$, $KH_2PO_4$ and $Na_2HPO_4$ salts. The ionic strength was adjusted at a constant value of 0.1 M with addition of NaCl salt.

Batch ozonation experiments were performed at low clofibric acid concentrations ($5.0 \times 10^{-8}$ M). For these low concentration experiments a 0.8 l aqueous solution at pH = 5.0 was previously saturated with ozone by bubbling an ozonized gaseous stream (ozone concentration in the liquid bulk was $1.0 \times 10^{-5}$ M).

Once saturation was attained, gaseous feeding was stopped and the substrate charged in the reactor by rapidly injecting 0.8 $cm^3$ of a concentrated clofibric acid aqueous solution ($5.0 \times 10^{-5}$ M). The reaction was quenched at the desired time by sparging the aqueous solution with stream of nitrogen. After quenching, the solution was recovered and 0.3 l were concentrated to a final volume of 2.0 ml for analysis.

The UV/$H_2O_2$ experiments were carried out at 298 K in a batch cylindrical glass jacketed reactor with an outer diameter of 9.5 cm and a height of 28 cm wrapped with an aluminium foil. At the top, the reactor had inlets for feeding reactants and an outlet for withdrawing samples. The reactor was equipped with a 17 W (power input) low-pressure lamp (by Helios Italquartz) with a monochromatic wavelength emission at 254 nm [24] enclosed in a quartz sleeve, which was immersed in the solution in the centre of the reactor. The radiation power ($2.7 \times 10^{-6}\,E\,s^{-1}$) was measured by means of $H_2O_2$ actinometric measurements [25]. The reactor was open to air, and mixed with a magnetic stirrer placed at the bottom.

Clofibric acid solutions were adjusted to the desired pH value with dilute $HClO_4$ and NaOH mixtures. Samples were taken at fixed reaction times and analysed. For photolytic experiments at low concentrations of clofibric acid ($5.0 \times 10^{-8}$ M), the reaction was stopped by switching off the lamp, and the solutions were recovered and concentrated by evaporation for the analyses similar to the ozonation experiments.

The substrate was analysed by Hewlett-Packard HPLC (HP 1100 L) equipped with a diode array detector and a Synergi C12 4u MAX-RP column using a 40:60 buffered aqueous solution: acetonitrile as mobile phase flowing at $1.0\,ml\,min^{-1}$. The buffered aqueous solution was prepared with 4 ml $H_3PO_4$ (85 wt.%), 50 ml methanol in 1 l HPLC water.

An Orion 96-17B combination electrode was used to detect the free chloride produced during the ozonation and UV/$H_2O_2$ processes. The total organic carbon (TOC) was monitored by means TOC analyzer (Shimadzu 5000 A).

The pH of the aqueous solutions was determined using an Orion 960 pH meter with a glass pH electrode. All of the reagents except hydrogen peroxide (Fluka, 30 wt.% not stabilized) were purchased from Sigma–Aldrich.

## 3. Results and discussion

Preliminary experiments were carried out to assess the capability of two chosen systems to remove clofibric acid. Fig. 2 reports the results obtained during 1 h of an ozonation experiment with an aqueous solution of clofibric acid at initial concentration of $1.5 \times 10^{-3}$ M. Complete clofibric acid disappearance was observed after 20 min of ozonation with a mineralization degree equal to 34.0%. It is noteworthy to observe that at the same reaction time, the initial chlorine content in the substrate was released as chloride ions, thus indicating that no hazardous chlorinated intermediates were formed. Moreover, prolonged ozonation treatment up to 60 min allowed the achievement of a mineralization degree of 49.1%. The results obtained in a photolytic runs with $[H_2O_2]_0 = 1.0$ M and $[S]_0 = 1.0 \times 10^{-3}$ M are shown in Fig. 3. An almost complete removal of clofibric acid was achieved in 60 min of treatment with a satisfactory efficiency of chlorine release as chloride although the degree of mineralization recorded at this reaction time was poor.

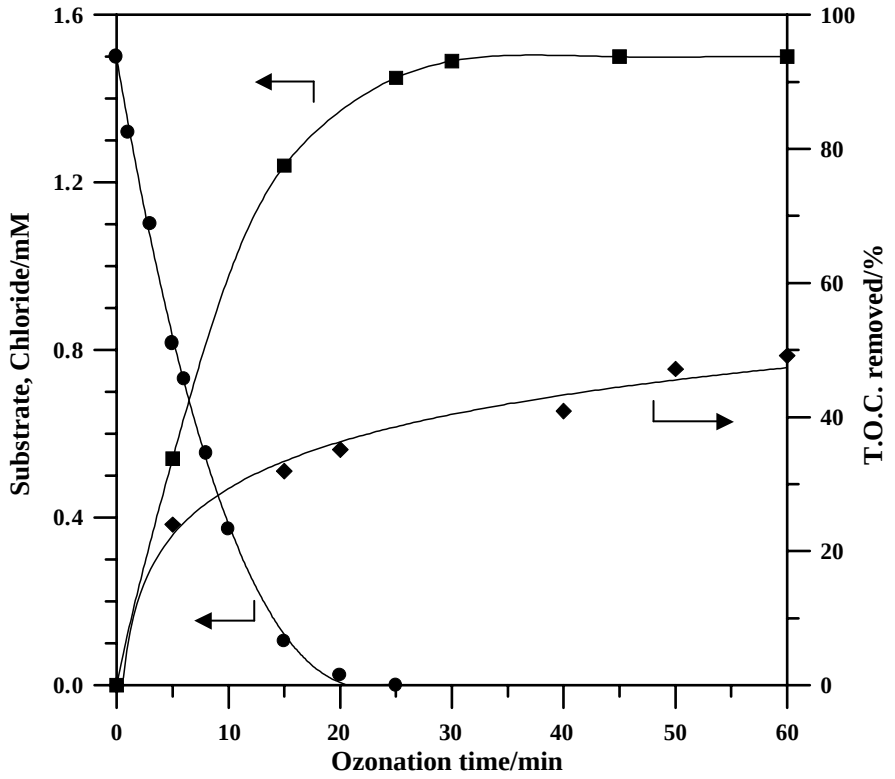



Fig. 2. Ozonation of clofibric acid at pH = 5.0, $T = 298$ K, $[TOC]_0 = 180\,mg\,l^{-1}$, $[S]_0 = 1.5 \times 10^{-3}$ M: (●) substrate; (■) chloride; (◆) TOC removed.

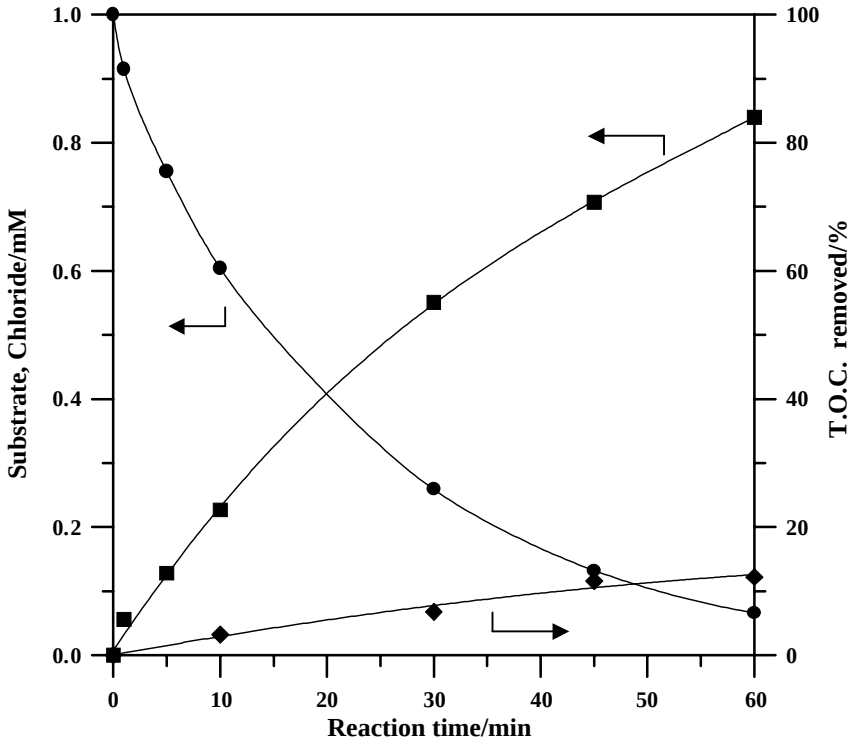



Fig. 3. UV/$H_2O_2$ oxidation of clofibric acid at pH = 5.0, $T = 298$ K, $[TOC]_0 = 120\,mg\,l^{-1}$, $[S]_0 = 1.0 \times 10^{-3}$ M, $[H_2O_2]_0 = 1.0$ M: (●) substrate; (■) chloride; (◆) TOC removed.

## 4. Reaction kinetics

### 4.1. Ozonation

In a gas–liquid reactor the oxidation process develops according to different regimes of absorption with reaction. The reactor used in the present investigation was previously characterized by determining the mass transfer coefficient $k_L^0$ ($4.26 \times 10^{-3}$ cm s$^{-1}$) and the volumetric mass transfer coefficient (in the absence of chemical reaction) $k_L^0 a$ (0.045 s$^{-1}$) at the adopted stirrer speed (380 rpm) and ionic strength (0.1 M). It has been demonstrated in previous papers [27,36] that in this reactor ozonation processes of organic species develop under (slow/fast) kinetic regimes for Hatta number $\{[D_{O_3} z k_{O_3} [S]_0]^{0.5} (k_L^0)^{-1}\} < 2.0$ and under a quasi-diffusional regime for *Ha* number values up to 25. For higher values a diffusional regime establishes.

A careful choice of clofibric acid starting concentration was thus necessary to perform kinetic experiments. In fact, for low values a complete oxidation of the substrate is achieved in a too short time scales thus hindering the collection of a significant number of experimental samples during a single run. For high values of the starting concentration, the diffusional

Table 1
Kinetic parameters for ozonation of clofibric acid, calculated for different pH values

| pH | $[S]_0$ (mM) | $k_{O_3}$ ($M^{-1}\,s^{-1}$) | $z$ | $\sigma_s$ (%) | $s_{O_3}$ (%) | Regime |
|---|---|---|---|---|---|---|
| 2.0 | 0.85 | $29.8 \pm 1.52$ | 2.00 | 3.27 | 3.66 | Kinetic regime "slow" |
| 2.5 | 0.92 | $39.7 \pm 2.30$ | 2.00 | 2.63 | 3.03 | Kinetic regime "slow" |
| 3.0 | 0.86 | $103.5 \pm 5.6$ | 2.00 | 4.32 | 3.41 | Kinetic regime "slow" |
| 3.0 | 0.86 | $91.3 \pm 4.82$ | 2.00 | 4.20 | 3.89 | Kinetic regime "fast" |
| 3.5 | 0.88 | $164.5 \pm 22$ | 2.00 | 4.66 | 6.75 | Kinetic regime "fast" |
| 4.0 | 0.90 | $155.8 \pm 12.2$ | 2.00 | 3.26 | 4.04 | Kinetic regime "fast" |
| 4.5 | 1.03 | $311.5 \pm 29.7$ | 2.00 | 5.13 | 2.44 | Kinetic regime "fast" |
| 5.0 | 1.16 | $842.1 \pm 79.2$ | $2.00 \pm 0.04$ | 3.73 | 3.93 | "Quasi-diffusive" regime |
| 5.5 | 0.90 | $1580 \pm 105.7$ | $2.11 \pm 0.03$ | 2.34 | 3.10 | "Quasi-diffusive" regime |
| 6.0 | 0.98 | $1041.1 \pm 109.3$ | $2.02 \pm 0.04$ | 3.84 | 2.64 | "Quasi-diffusive" regime |
| 6.5 | 0.88 | $2550 \pm 251$ | $z = a + bt$; $a = 2.00$; $b = 0.28 \pm 0.03$ | 5.22 | 6.83 | "Quasi-diffusive" regime |

regime of absorption with reaction could establish and render all of the collected data useless for the determination of reaction kinetics. The concentrations adopted were around $1.0 \times 10^{-3}$ M and resulted, for most cases, in the achievement of a kinetic regime of absorption with reaction (slow or fast) [26], sometimes in a quasi-diffusional one [27]. In these conditions, a fluidynamic submodel published elsewhere [27] was coupled with an overall ozonation reaction:

$$\text{Clofibric acid} + z\text{O}_3 \xrightarrow{k_{O_3}} \text{products} \qquad (r_1)$$

and used for analysis of the collected data.

The values of the parameters $k_{O_3}$ and $z$ shown in Table 1 were estimated as those which minimize for each run the sum of the squares of the differences between experimental and calculated data. Fig. 4a and b shows various examples of the agreement between experimental data and those calculated by the model (solid lines) when the best values of the parameters $k_{O_3}$ and $z$ are used. It is noteworthy to observe that the percentage standard deviations (Table 1) for the substrate concentration in the liquid bulk and ozone in the freeboard, which give a measure of the model adequacy, are as low as those found in the analytical determination of these species. At pH = 3.0, both of the models obtained by assuming a process development under a "slow" and "fast" kinetic regime of absorption with reaction gave satisfactorily results with very similar values of $\sigma$'s. In this case, the most appropriate regime was not singled out. At pH = 6.5 poor results were found by using a stoichiometric coefficient $z = a = 2.00$ ($\sigma_s = 16.6\%$, $\sigma_{O_3} = 14.8\%$). On the other hand, lower percentage standard deviations were calculated by adopting an overall stoichiometric coefficient as a linear function of the reaction time ($z = a + bt$) with $a = 2.00$. In this case, the best value of the parameter $b$ was estimated along with $k_{O_3}$ by means of the optimization procedure described earlier.

It can be easily verified that for the values of $k_{O_3}$ and $z$ estimated with this model and using an ozone diffusivity ($D_{O_3}$) of $1.77 \times 10^{-5}\,cm^2\,s^{-1}$ [37], Hatta numbers lower than 2.1 are found.

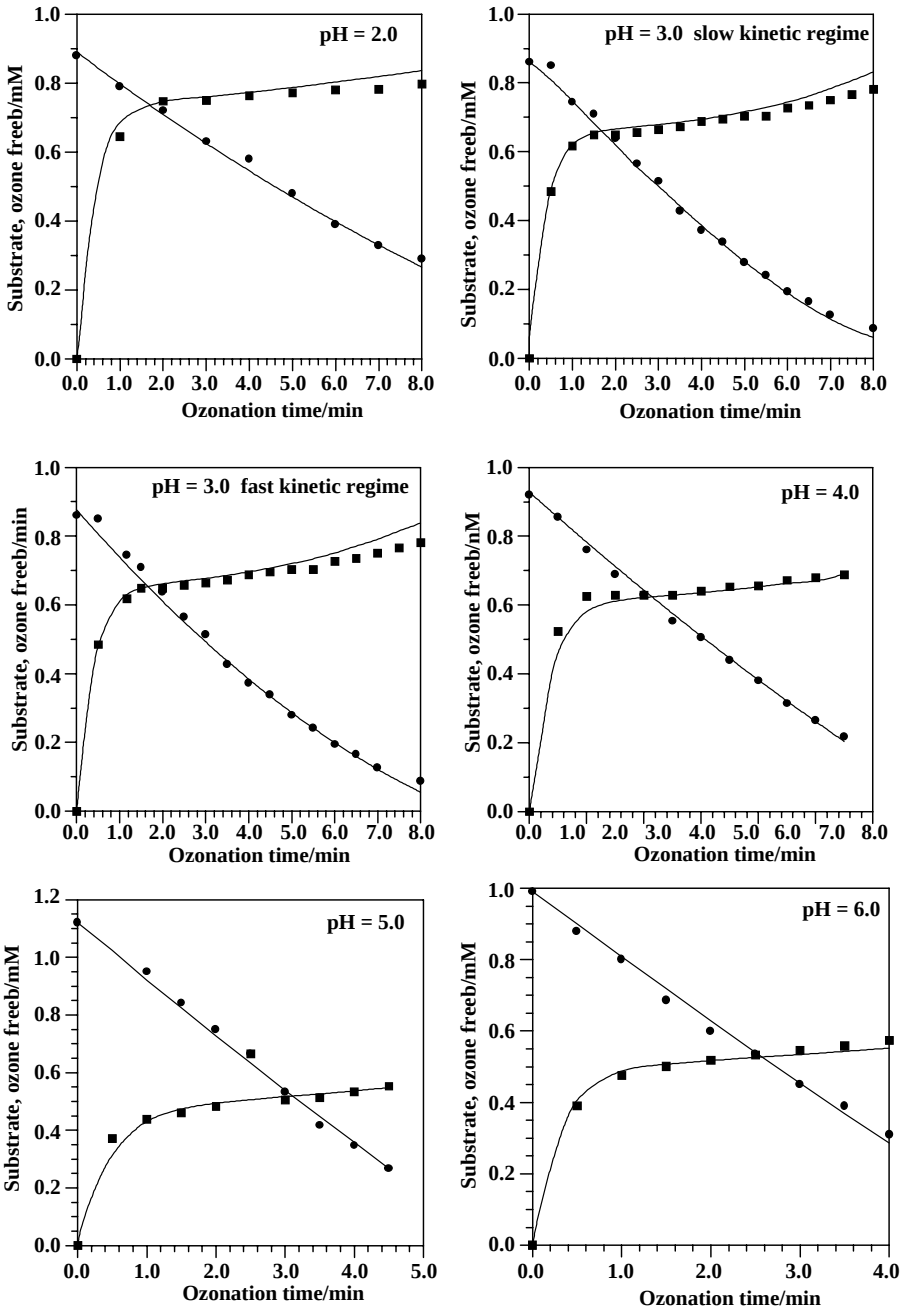
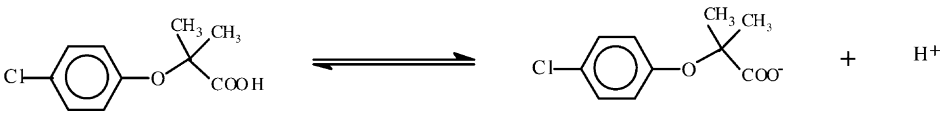



Fig. 4. Comparison between experimental (full symbols) and calculated data (solid lines) for ozonation of clofibric acid at different pH: $T = 298$ K; (●) substrate; (■) ozone in the freeboard phase.

Moreover the data in Table 1 indicate that the system reactivity increases with increasing the pH of the solution. This result can be explained by taking into account that the substrate dissociates in aqueous solution:




where the unprotonated form is more reactive than the protonated one, although the activation of radical mechanisms of oxidation at highest investigated pH values could not be completely ruled out.

### 4.2. UV/$H_2O_2$ system

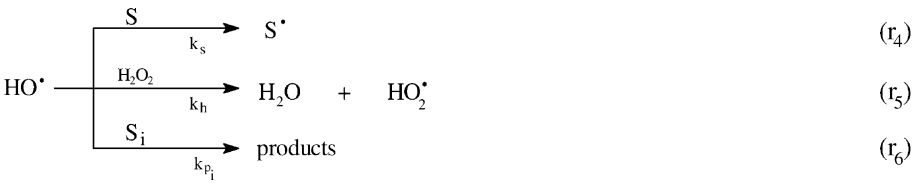
A simplified kinetic model has been developed to describe the oxidation of clofibric acid in aqueous solutions irradiated by means of a lamp emitting at 254 nm and in the presence of hydrogen peroxide. The model considers the photolysis of the substrate ($r_2$):

$$\text{Clofibric acid} \xrightarrow[\lambda=254\,\text{nm}]{h\nu} \text{photolytic products} \qquad (r_2)$$

and that of hydrogen peroxide which gives rise of formation of HO radicals:

$$H_2O_2 \xrightarrow{h\nu} 2HO^{\bullet} \qquad (r_3)$$

The $HO^{\bullet}$ attack the substrate species ($r_4$), hydrogen peroxide ($r_5$) and all the intermediates and reaction products present in the solution ($r_6$):




($r_4$)

($r_5$)

($r_6$)

with $k_h = 2.7 \times 10^7\ M^{-1}\ s^{-1}$ [28].

The hydroperoxyl radicals undergo a radical termination reaction to generate hydrogen peroxide:

$$2HO_2^{\bullet} \xrightarrow{k_t} H_2O_2 + O_2 \qquad (r_7)$$

with $k_t = 8.3 \times 10^5\ M^{-1}\ s^{-1}$ [29].

Therefore, by assuming that the presence in the aqueous solution of by-products can be neglected, the substrate and hydrogen peroxide degradation rates can be written as

$$\frac{d[S]}{dt} = -\frac{\phi_s}{V_{sol}} I_0[1 - \exp(2.3l(\varepsilon_s[S] + \varepsilon_{H_2O_2}[H_2O_2]))]f_s - k_s[HO^{\bullet}][S] \qquad (1)$$

$$\frac{d[H_2O_2]}{dt} = -\frac{\phi H_2O_2}{V_{sol}} I_0[1 - \exp(2.3l(\varepsilon_s[S] + \varepsilon_{H_2O_2}[H_2O_2]))] f_{H_2O_2} + -k_h[HO^\bullet][H_2O_2] + k_t[HO_2^\bullet]^2 \quad (2)$$

where $\phi_s$ and $\phi_{H_2O_2}$ are the primary quantum yields of the direct photolysis at 254 nm of clofibric acid and hydrogen peroxide ($\phi_{H_2O_2} = 0.5\,mol\,E^{-1}$ [30,31]), $V_{sol}$ the volume of the aqueous solution (0.42 l), $I_0$ the measured lamp UV-light intensity at 254 nm ($2.7 \times 10^{-6}\,E\,s^{-1}$), $l$ the optical pathlength (0.201 dm) of the reactor, $\varepsilon_s$, $\varepsilon_{H_2O_2}$ and $k_s$ are, respectively, the molar extinction coefficients at 254 nm for the substrate ($380\,M^{-1}\,cm^{-1}$), hydrogen peroxide ($18.6\,M^{-1}\,cm^{-1}$) and reaction products, $f_s$ and $f_{H_2O_2}$ represent the UV fraction absorbed by the substrate and hydrogen peroxide.

The mass balances on HO and $HO_2$ radical species are

$$\frac{d[HO^\bullet]}{dt} = 2\phi_{H_2O_2}\frac{W_{abs}}{V_{sol}} - k_h[HO^\bullet][H_2O_2] - k_s[HO^\bullet][S] \quad (3)$$

$$\frac{d[HO_2^\bullet]}{dt} = k_h[HO^\bullet][H_2O_2] - 2k_t[HO_2^\bullet]^2 \quad (4)$$

where $W_{abs}$ is the radiation power absorbed by the solution. $W_{abs}$ can be expressed as:

$$W_{abs} = I_0 \left\lfloor 1 - \exp(-2.3l(\varepsilon_s[S] + \varepsilon_{H_2O_2}[H_2O_2])) \right\rfloor f_{H_2O_2} \quad (5)$$

By assuming the "steady-state" hypothesis for radical species [35], the stationary $HO^\bullet$ and $HO_2^\bullet$ concentrations can be expressed as

$$[HO]_{SS} = \frac{2\phi_{H_2O_2}}{V_{sol}} \frac{I_0[1 - \exp(-2.3l(\varepsilon_{H_2O_2}[H_2O_2] + \varepsilon_s[S]))]}{k_h[H_2O_2] + k_s[S]} f_{H_2O_2} \quad (6)$$

$$[HO_2]^2_{SS} = \frac{k_h}{k_t}\frac{\phi_{H_2O_2}}{V_{sol}} \frac{I_0[1 - \exp(-2.3l(\varepsilon_{H_2O_2}[H_2O_2] + \varepsilon_s[S]))][H_2O_2]}{k_h[H_2O_2] + k_s[S]} f_{H_2O_2} \quad (7)$$

and substituting in Eqs. (1) and (2) gives

$$\frac{d[S]}{dt} = -\frac{\phi_s}{V_{sol}} I_0[1 - \exp(-2.3l(\varepsilon_{H_2O_2}[H_2O_2] + \varepsilon_s[S]))] f_s + -k_s\frac{2\phi_{H_2O_2}}{V_{sol}} \frac{I_0[1 - \exp(-2.3l(\varepsilon_{H_2O_2}[H_2O_2] + \varepsilon_s[S]))][S]}{k_h[H_2O_2] + k_s[S]} f_{H_2O_2} \quad (8)$$

$$\frac{d[H_2O_2]}{dt} = -\frac{\phi_{H_2O_2}}{V_{sol}} I_0[1 - \exp(-2.3l(\varepsilon_{H_2O_2}[H_2O_2] + \varepsilon_s[S]))] f_{H_2O_2} + -k_h\frac{\phi_{H_2O_2}}{V_{sol}} \frac{I_0[1 - \exp(-2.3l(\varepsilon_{H_2O_2}[H_2O_2] + \varepsilon_s[S]))][H_2O_2]}{k_h[H_2O_2] + k_s[S]} f_{H_2O_2} \quad (9)$$

Preliminary photolytic runs without hydrogen peroxide addition allowed the determination of quantum yield of the direct photolysis of clofibric acid at 254 nm at pH = 5.5 ($\phi_s = 1.08 \times 10^{-2} \pm 2.37 \times 10^{-4}\,mol\,E^{-1}$). Once the value of the parameter $k_s$ is known, Eqs. (8) and (9) can be integrated with the initial conditions: $t = 0$, $[S] = [S]_0$ and $[H_2O_2] =$

$[H_2O_2]_0$ and the concentrations of the substrate and hydrogen peroxide calculated at varying reaction time. Unfortunately $k_s$ was not known "a priori" and its value was estimated through the adoption of an optimization procedure [32] by using the experimental data collected in the runs at different hydrogen peroxide starting concentrations (1, 10, 20 and 30 mM) for the same initial concentration of substrate ($2.0 \times 10^{-5}$ M). A mean value for $k_s$ equal to $(2.38 \pm 0.18) \times 10^9\ M^{-1}\ s^{-1}$ was thus estimated. A comparison between experimental and calculated data for the oxidation of clofibric acid by UV/$H_2O_2$ at pH = 5.5 is shown for different initial concentrations of hydrogen peroxide in Fig. 5.

It is noteworthy to stress that a failure of the model could be expected both when $H_2O_2$ levels decrease with respect to those adopted in this investigation (keeping constant the substrate concentrations) or when the substrate concentration increases (working at the same $H_2O_2$ levels as in the present experiments). In these conditions, the consumption of OH radicals by the oxidation by-products and their light absorption cannot be neglected

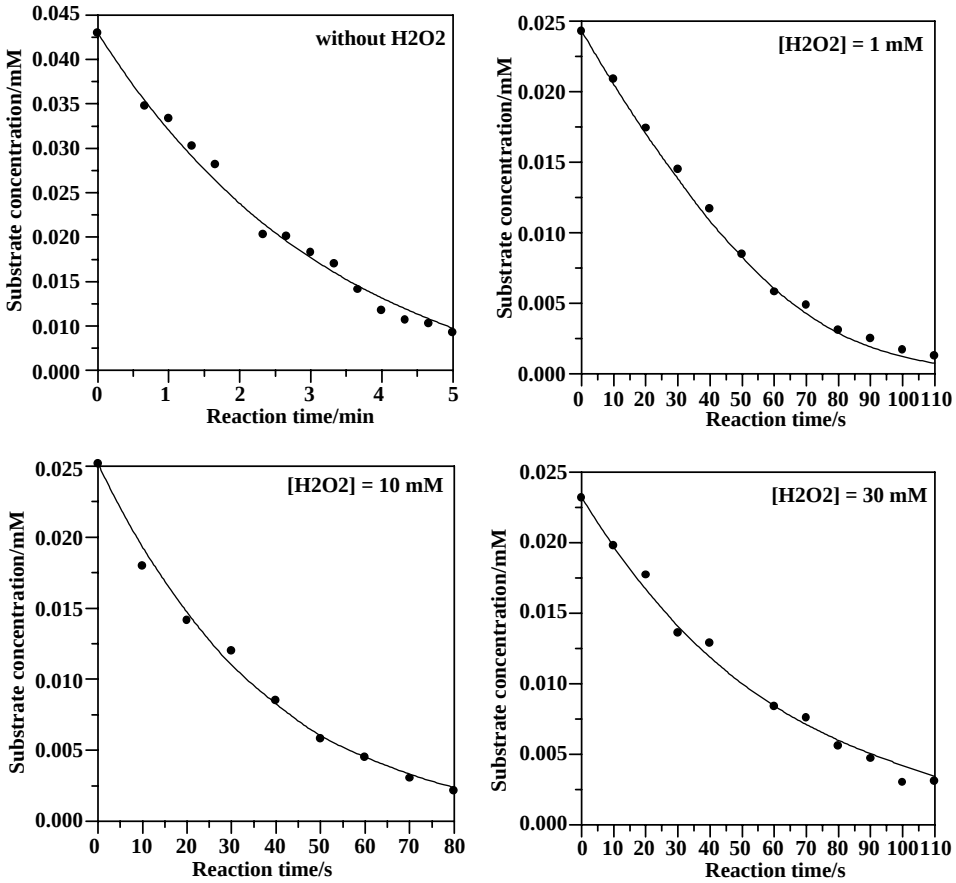



Fig. 5. Comparison between experimental (full symbols) and calculated data (solid lines) for UV/$H_2O_2$ oxidation of clofibric acid at pH = 5.5 with different $H_2O_2$ concentrations: $T = 298$ K.

as assumed for the development of the above-reported model. No effect of the pH on the kinetic constant $k_s$ was observed in the range 4.0–7.0.

## 5. Kinetic model validation at low concentration

Relevant concentrations of pharmaceuticals in the environment are on the order of few micrograms per liter [10]. It is time consuming to use diluted aqueous solutions for kinetic investigations since each sample needs to be concentrated for the analysis by means of common equipments such as HPLC and GC–MS.

For this reasons a clofibric acid starting concentration in the range $1.0 \times 10^{-3}$ to $1.5 \times 10^{-3}$ M was employed for both of the systems aqueous solutions in the first part of the present work. However, to demonstrate that kinetic constants estimated in these runs can be conveniently used in process design for the treatment of real effluents, an attempt was done to model the behaviour of both systems by reducing the starting concentration equal to the maximum value at which clofibric acid has been found in real STP effluents ($5.0 \times 10^{-8}$ M) [33].

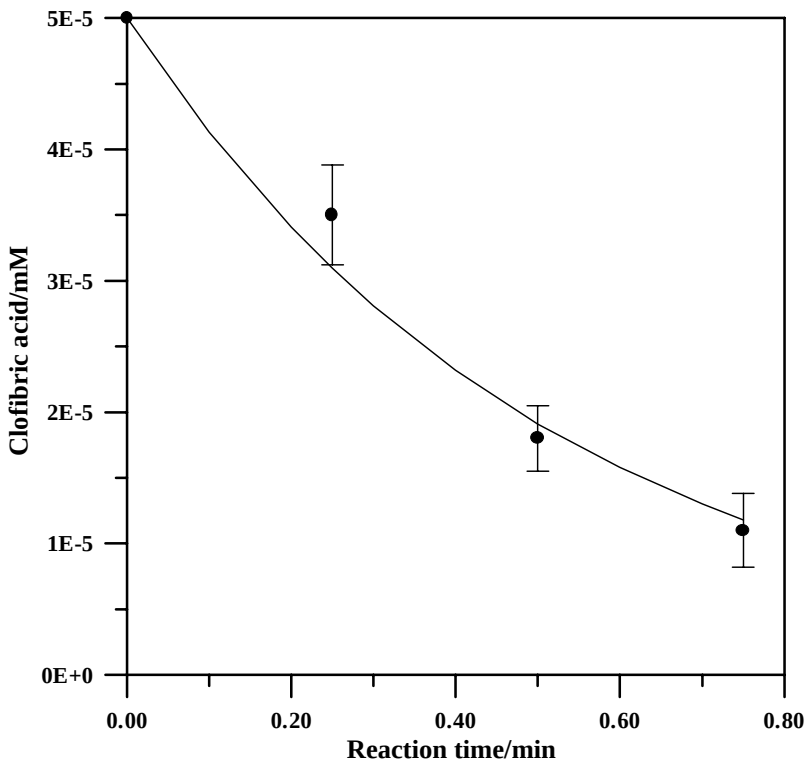



Fig. 6. Comparison between experimental (full symbols) and calculated data (solid line) for oxidation of clofibric acid with UV/$H_2O_2$ at pH = 5.5 with $[H_2O_2]_0 = 1.0 \times 10^{-2}$ M: $T = 298$ K.

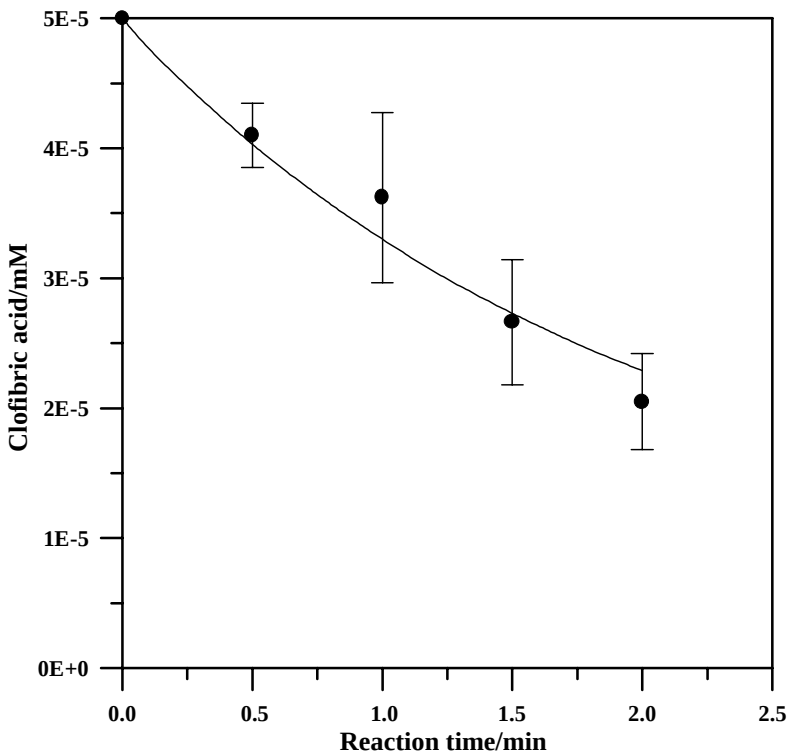



Fig. 7. Comparison between experimental (full symbols) and calculated data (solid lines) for ozonation of clofibric acid at pH = 5.0: $[\text{dissolved ozone}]_0 = 1.0 \times 10^{-5}$ M; $T = 298$ K.

Fig. 6 shows the results obtained by submitting to a photolytic run an aqueous solution containing 10 $\mu$g l$^{-1}$ of clofibric acid with an initial hydrogen peroxide of $1.0 \times 10^{-2}$ M in the experimental apparatus previously described (full circles) along with those predicted by the model (continuous line) by using a value for $k_s$ equal to $2.38 \times 10^9$ M$^{-1}$ s$^{-1}$.

Similar results have been found for the ozonation experiments. Fig. 7 shows experimental data (full circles) compared with concentrations predicted by using the mean value of the kinetic constants at pH = 5.0 ($k_{O_3} = 842.1$ M$^{-1}$ s$^{-1}$) found during the ozonation runs at higher starting concentrations (continuous line). Although standard deviations up to 18.0% were associated to clofibric acid determination, the comparison between experimental data and those predicted by the models developed in the first part of the paper are encouraging. However, an improvement in the analytical determination is required for a definitive validation of the assessed kinetics.

## 6. Conclusions

The removal of acid clofibric from aqueous solutions has been studied using ozonation and $H_2O_2$/UV systems. Both these systems are able to quickly remove this pharmaceutical

compound with an almost complete conversion of the initial chlorine content into chloride ions. Reaction kinetics have been evaluated in experimental runs with the initial substrate concentration in the range $1.5\times10^{-3}$ to $2.0\times10^{-5}$ M. A dependence of the ozonation kinetic constants upon the pH has been recorded, in agreement with the capability of the studied species to dissociate in aqueous solution into the more reactive clofibrate ion ($29.8\,M^{-1}\,s^{-1}$ at pH = 2.0 and $2550\,M^{-1}\,s^{-1}$ at pH = 6.5). No influence of the pH of the solution on the kinetic constant of OH radical attack on the substrate has been observed during $H_2O_2$ photolytic experiments ($2.38\times10^{9}\,M^{-1}\,s^{-1}$). An attempt to validate the assessed reaction kinetics at low environmentally relevant clofibric acid concentrations has been successfully performed.

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