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Evidence for hole participation during the photocatalytic oxidation of the antibiotic flumequine

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Abstract

Photocatalytic degradation of the antibiotic flumequine (FQ) was carried out on TiO_2 aqueous suspension assisted by simulated solar light. Using multivariate analysis, it was determined that the most important variable for FQ degradation is pH, where the optimal value is around 6. Hydrogen peroxide addition does not alter oxidation efficiency. Under optimised conditions, the time required to completely eliminate FQ antibiotics was 30 min. Mineralization after 60 min irradiation was around 80%. The role of hydroxyl and superoxide anion radicals was monitored by using the radical scavengers isopropanol and benzoquinone, respectively. On the other hand, the participation of oxidative holes in the reaction mechanism was evaluated by adding iodine anions (hole scavenger) to the reaction system. Isopropanol's slight influence on degradation indicated that FQ oxidation was slightly influenced by $OH^{\bullet}$ radicals. The presence of the iodide anion significantly inhibited degradation, thus suggesting that holes played a major role. Experiments carried out in acetonitrile, in absence of water, confirmed the significant role of holes in FQ oxidation. The inhibition of the reaction profile in the presence of benzoquinone confirms the participation of the superoxide anion in the FQ oxidation. The analysis of the reaction products suggests that photo-Kolbe decarboxylation mechanism and hydroxylation of aromatic ring are the reaction's primary steps. The Langmuir–Hinshelwood kinetic model was fitted for FQ photodegradation.

Keywords: Antibiotics; Flumequine; Photocatalysis; TiO_2

1. Introduction

The extraordinary growth of agribusiness and the aquaculture industry has been accompanied by some practices potentially damaging to human and animal health. In the last 20 years, industrial aquaculture has experienced four-fold growth worldwide, and in several cases has been accompanied with unrestricted antibiotic use, converting these productive activities into a public health concern [1,2]. Several authors have pointed out antibiotics' harmful environmental effects [3,1,4]. Involuntary dietary consumption of antibiotics alters the normal flora, contributing to increased susceptibility to bacterial infections. Moreover, antibiotics can also generate allergy and toxicity and favours the development of antibiotic-resistant bacteria. This resistance could be transferred to other aquatic or terrestrial bacteria as it has been demonstrated [5].

Quinolone structures are commonly found in the composition of numerous antibiotics in aquaculture cultivation. In particular, flumequine is one of the most used antibiotics in salmon farming, producing negative environmental consequences because it remains active in sediments for prolonged time periods since they are not readily biodegradable [2,6].

Advanced oxidation processes (AOPs) have been widely studied because their ability to oxidise different kind of environmentally persistent substances [7–9]. Among the most reported AOPs, semiconductor photocatalysis is considered the most versatile because it is used in environmental remediation and it can also be used for energy production and storage, chemical synthesis, sensors and in medical applications [10,11].

The photocatalytic process is initiated with the adsorption of photons with energy above the semiconductor's band gap, typically titania (3.2 eV), generating charge carriers, electron and holes (e–h), a fraction of which arrive to the TiO_2 surface. On the surface, these species can be trapped by oxygen or adsorbed by hydroxyl groups generating superoxide anion and hydroxyl radicals, respectively. Both reduced oxygen species can oxidise

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dissolved organic matter in contact with the catalyst surface [12]. On the other hand, adsorbed organic substrates can be readily and directly oxidised by superficial holes. The role that holes and reduced oxygen radicals plays in the degradation of organic substances is still controversial and depends on the substrate structure and catalyst structure. For instance, several authors suggest the formation of hydroxyl radicals on irradiated TiO_2 in experiments carried out with spin trapping and EPR [13,14]. On the other hand, other authors propose the direct participation of holes on oxidation reactions in assays done hole scavengers [15,16].

The aim of this work is to evaluate the effect of radicals and hole scavengers in order to elucidate the paths involved in the photocatalytic degradation of flumequine.

2. Experimental

2.1. Materials

Titania P-25 (surface area $52\,m^2\,g^{-1}$) was obtained from Degussa (Brazil). Flumequine (99%, $C_{14}H_{12}FNO_3$) and *p*-benzoquinone (>99%) were purchased from Sigma. The FQ structure is depicted in Fig. 1. Isopropanol (99.5%), potassium iodide, acetonitrile (HPLC grade), methanol (HPLC grade), trifluoroacetic acid, hydrogen peroxide (30%) and trifluoroacetic anhydride (99.5%) were obtained from Merck. Ethyl acetate (99.99%) was obtained from Merck (Chile). All the reagents were used as received without purification.

2.2. Photocatalytic reaction

A typical photocatalytic reaction was carried out in a 120-mL bottle stopped with a rubber seal, while allowing oxygenation and gas release through two Teflon tubes. Oxygen was continuously bubbled throughout the reactor's interior. The catalyst was used in suspension in amounts ranging from 0.5 to 1.5 g. The reaction system's pH was adjusted with NaOH or HNO_3. The FQ solution concentration was 76.5 μM. Before the light was turned on, the solution was stirred for a 30-min period in the dark. The reactor was magnetically stirred and irradiation was performed with a SUNTEST XLS+ Atlas, using $500\,W\,m^{-2}$ irradiance. Lamp emission range from 300 to 800 nm. For analysis, samples were taken at different time periods using a 10-mL plastic syringe and then filtered in a 0.20-μm Millipore disk. The effect of initial concentration was evaluated using the previously described conditions with a concentration ranging from 19.1 to 95.7 μM under illumination and dark conditions. The role of oxygen was evaluated under nitrogen bubbling.

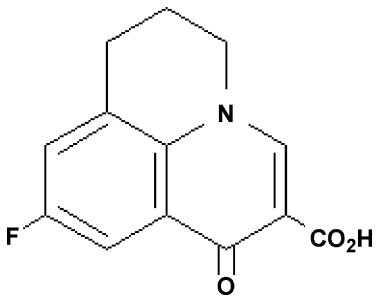

Fig. 1. Structure of the antibiotic flumequine.

2.3. Experimental design

A multivariate experimental design was performed following the methodology previously described for photocatalytic reactions [17–19]. The polynomial and contour diagrams were obtained using the software Modde 7. In the factorial design of the photocatalytic degradation of FQ, three variables were simultaneously changed: the initial pH (3–10), the amount of catalyst ($0.5–1.5\,g\,L^{-1}$), and the hydrogen peroxide concentration (0.17–0.83 mM). In all the experiments carried out for optimisation, irradiation was performed with a solarium device Philips HB 311 arranged with $6\,W \times 20\,W$ lamps ($\lambda = 300–400$ nm, $540\,W\,m^{-2}$). For n variables and two levels (low and high), the total number of experiments was 17, determined by the expression $2^n + 2n + 3$.

2.4. Analytical methods

The filtered samples obtained from the photocatalysed reactions were analysed in a Shimadzu 1603 spectrophotometer. The maximum at 331 nm was used to monitor the FQ degradation during the course of the reaction. In parallel, HPLC determinations were carried out in a Merck-Hitachi instrument equipped with a C-18 column (Merck-LicroCART 250-4/Lichrospher 100 RP-18) using a modified methodology described earlier by Pilorz and Choma [20]. Total organic carbon determinations were carried out in a Shimadzu 5000 A TOC analyser.

In order to identify the oxidation products, 1 L of concentrated FQ solution at pH 6 (0.765 mM) and TiO_2 ($0.5\,g\,L^{-1}$) were illuminated by SUNTEST for 30 min. The solution was evaporated at low temperature until 125 mL, then extracted 3 times with ethyl acetate, and finally dried with Na_2SO_4. Organic solution was concentrated to 10 mL, and separated in two vials, which were concentrated to 1 mL with nitrogen gas. One sample was directly injected into the GC (HP-5890 equipped with an HP-5872 mass selective detector) and the other one derivatised with trifluoroacetic anhydride. Fluoroacetylated compounds were also injected into the CG–MS for analysis.

2.5. Effect of radical inhibitors

In order to determine the role that radicals and holes play in the reactions, isopropanol (76.5 mM), iodide ion (0.765 mM and 7.65 mM) and benzoquinone (7.65 μM) were added to the antibiotic solutions containing FQ (76.5 μM). In a separate experiment, acetonitrile instead of water was used to evaluate water's function in OH radical formation.

2.6. Antibacterial activity of photocatalysed flumequine solutions

In order to determine the antibacterial activity of irradiated FQ samples, tripticase agar plates were seeded with a

10^5 CFU mL^{-1} suspension of *Escherichia coli* 6317. The plates were loaded, in small holes made in the agar, with 100 μL of irradiated samples and incubated for 24 h at 37 °C. The inhibition halo formed around the spot was measured in mm and compared to the calibration curve made with the pure solutions of antibiotic and the respective microorganism. The general procedure has been previously described [21].

3. Results and discussion

3.1. Factorial design

For the optimisation experiments, the assays were carried out using the Solarium device. Table 1 summarises the experiments, in real and codified values (in parenthesis), performed to optimise the photocatalytic FQ degradation. Following the factorial design, 17 experiments were performed, including three central points to mathematically validate the model. Experimental and calculated values after 15 min of irradiation are shown in the two last columns. There is a great concordance between these compared values, indicating a well-fitted model. The mathematic solution of the matrices using multiple regression in the Modde 7 software generates a polynomial (Eq. (1)). The Y_{FQ} represents the independent variable or response factor defined as the degradation percentage after 15 min irradiation of FQ.

$$Y_{FQ}(\%) = 67.66\,(\pm 1.27) - 17.78\,[\mathrm{pH}]\,(\pm 1.16) - 49.48\,[\mathrm{pH}]^2\,(\pm 1.79) \quad (1)$$

The absence of the variables TiO_2 amount and hydrogen peroxide concentration in the polynomials indicate that the relative error of these variables is larger than the correspondent coefficients. Observing the polynomial, it can be concluded that pH is the only variable that affects antibiotic degradation. The quadratic effect predicts a maximum antibiotic degradation at medium pH values. It is evident that at high and low pH values, FQ degradation decreases (see experiments 1–8) independently of the TiO_2 amount and hydrogen peroxide concentration. The contour diagrams obtained from the polynomials confirm that maximum antibiotic degradation is obtained at neutral pH, low titania load, and in absence of H_2O_2 (not shown). The results agree with the fact that the pH simultaneously modify the superficial charge of the catalyst and the extent of FQ ionisation. At very low pH the surface of the catalyst will be positive (zero charge point 6.25) and the FQ protonated (pK_a 6.35), decreasing the affinity between them. At pH over the ZCP, both species will be negatively charged provoking the repulsion. In consequence at pH close to 6, the affinity will be optimal, improving the photocatalytic process.

3.2. Photocatalytic degradation of FQ

Since the optimisation results indicate that neither the TiO_2 amount nor the hydrogen peroxide concentration affects the rate of antibiotic degradation, further experiments were carried out at pH 6, 0.5 g L^{-1} TiO_2, and without addition of H_2O_2. The irradiations were performed in the Suntest XLS+ (500 W m^{-2}). Initial concentration of the antibiotic was 76.5 μM. The spectral changes of flumequine during the irradiation in the presence of TiO_2 shows a drop in the absorption maximum (331 nm) which demonstrates that FQ is chemically modified by photocatalysis. The formation of a new chromophoric group absorbing at 270 nm is interpreted as a possible formation of phenolic moieties at the beginning of the irradiation [22].

The Langmuir adsorption constant (K_L), determined here in the dark at pH 6, was 9.2×10^3 L mol^{-1}. This value was obtained through the adsorption isotherms in dark and using the Langmuir approach. The FQ adsorption in dark, around 27%, was determined by spectrophotometric measures. After 30 min of contact in dark, no further FQ adsorption on titania was observed.

The FQ degradation profile recorded at 331 nm is shown in Fig. 2. FQ presents marked stability against light in absence of catalyst but in the presence of TiO_2, indicating a pronounced

Table 1
Experimental results from factorial design of flumequine degradation

Experiment	TiO_2 (g/L) x_1	pH x_2	H_2O_2 (mM) x_3	Y experimental FQ (%)	Y calculated FQ (%)
1	0.5 (−1)	3 (−1)	0.17 (−1)	40	36
2	1.5 (1)	3 (−1)	0.17 (−1)	37	35
3	0.5 (−1)	10 (1)	0.17 (−1)	0	1
4	1.5 (1)	10 (1)	0.17 (−1)	0	0
5	0.5 (−1)	3 (−1)	0.83 (1)	37	36
6	1.5 (1)	3 (−1)	0.83 (1)	36	35
7	0.5 (−1)	10 (1)	0.83 (1)	0	1
8	1.5 (1)	10 (1)	0.83 (1)	0	0
9	0.65 (−0.7)	6.5 (0)	0.5 (0)	69	68
10	1.35 (0.7)	6.5 (0)	0.5 (0)	67	67
11	1 (0)	4.05 (−0.7)	0.5 (0)	45	56
12	1 (0)	8.95 (0.7)	0.5 (0)	31	31
13	1 (0)	6.5 (0)	0.269 (−0.7)	70	67
14	1 (0)	6.5 (0)	0.731 (0.7)	67	67
15	1 (0)	6.5 (0)	0.5 (0)	67	67
16	1 (0)	6.5 (0)	0.5 (0)	71	67
17	1 (0)	6.5 (0)	0.5 (0)	67	67

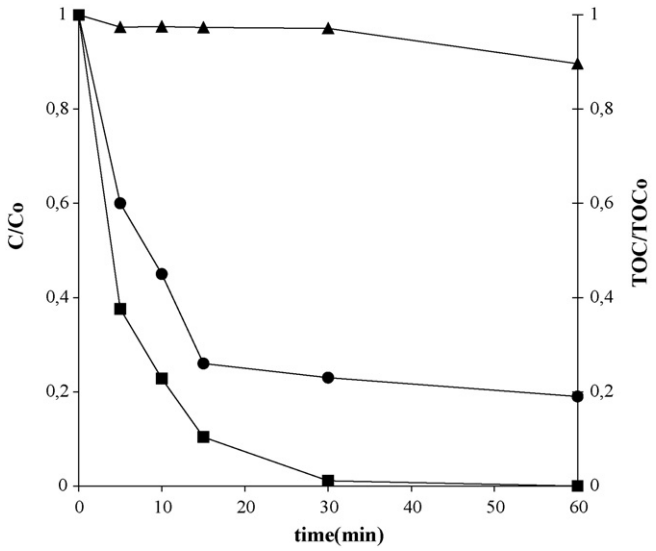

Fig. 2. Photocatalytic course of flumequine degradation in suspended solutions of TiO_2 (0.5 g L^{-1}) (■). TOC evolution during the photocatalytic process (●) and direct photolysis of FQ in absence of catalyst (▲). Initial pH 6.0 and initial antibiotic concentration 7.65×10^{-5} mol L^{-1}.

catalytic effect. Complete FQ depletion occurs at 30 min irradiation. The profiles were also monitored by HPLC analysis, giving the same results.

Since the antibiotic's complete oxidation to CO_2 is unquestionable evidence of the total destruction of the contaminant, the extent of antibiotic mineralization was also studied by TOC determinations [23]. Fig. 2 shows 74% mineralization for FQ after 15 min irradiation, a value that remains almost constant after a longer irradiation period (60 min and longer). This result is indicative of refractory intermediate formation during the beginning of the photocatalytic oxidation. Some of these intermediates were identified in 30-min irradiated solution by GC/MS analysis (Fig. 3). It can be seen that the primary event is the saturated ring opening, while the aromatic ring remains intact. Even after longer irradiation times (90 min), the structure (1) still remains in solution. Another relevant feature is that flumequine decarboxylation is one of the reaction's initial pathways. It has been proposed that the mechanism involved is a photo-Kolbe pathway with the direct participation of holes, as shown below (Eq. (2)) [24].

$$RCOO^- + h^+ \rightarrow RCOO^\bullet \rightarrow R^\bullet + CO_2 \quad (2)$$

3.3. Effect of the initial flumequine concentration in the photocatalytic reaction

The effect of initial FQ concentration in the photocatalytic process was analysed using the linearised form of the Langmuir–Hinshelwood (LH) model, shown in Eq. (3). In spite of the numerous critical studies of the LH model in terms of the veracity of all the assumptions considered, its use is recommended for its simplicity and the ability to fit well with the experimental results in heterogeneous photocatalysis [25].

$$\frac{1}{r_0} = \frac{1}{k} + \frac{1}{kK_{LH}C_0} \quad (3)$$

The values for k and K_{LH} were calculated from the graphical representation of Eq. (3) ($y = 3.7636x + 50749$; $R^2 = 0.9993$). The calculated manolayer adsorption equilibrium constant (K_{LH}) on the catalyst surface was 1.35×10^4 L mol^{-1}, and the calculated rate constant (k) was 19.7 μM min^{-1}. According to the LH model, if the photocatalytic oxidation adsorption constant (K_{LH}) reflects strictly the adsorption affinity of a substrate on the TiO_2 surface, its value should be similar to the constant in dark (K_L) [26]. Comparing the FQ values for K_L and K_{LH}, it can be seen that both values are in the same order of magnitude ($K_{LH} = 1.45K_L$). The slight increase of adsorption under illumination could be related to a change in the TiO_2 electronic properties, which have been associated to the increase of adsorption sites [27].

3.4. Effect of radical and hole inhibitors

Several substances that alter the kinetic profile of organic compound oxidation have been used to elucidate the role of the different species associated with degradation. In this work, we have used isopropanol, acetonitrile, benzoquinone and iodide anion as radical and hole inhibitors during the photocatalytic degradation of FQ. Control experiments carried out in absence of light do not alter the adsorption behaviour of FQ on the catalyst

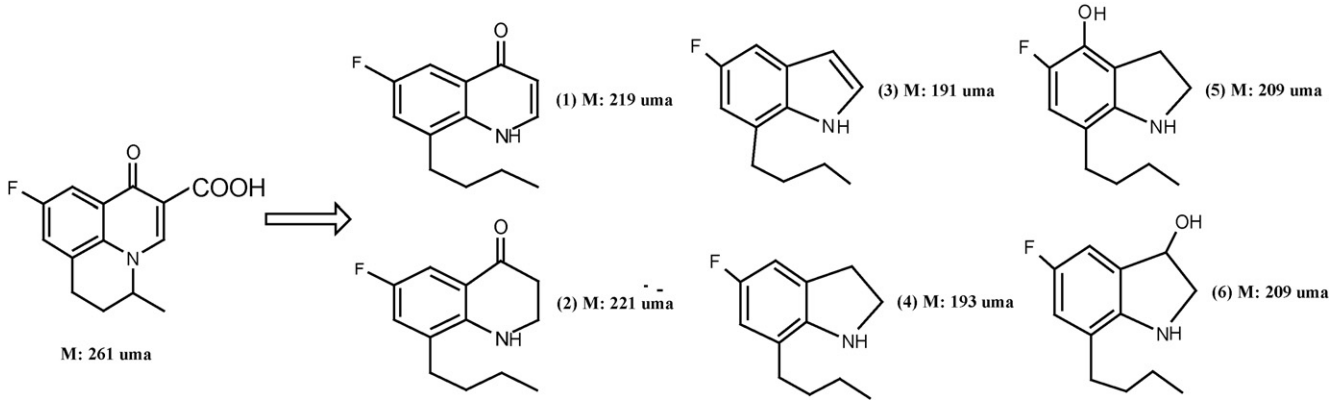

Fig. 3. Oxidation compounds identified after 30 min irradiation of flumequine solutions. Compound (3) was identified as fluoroacetic derivative.

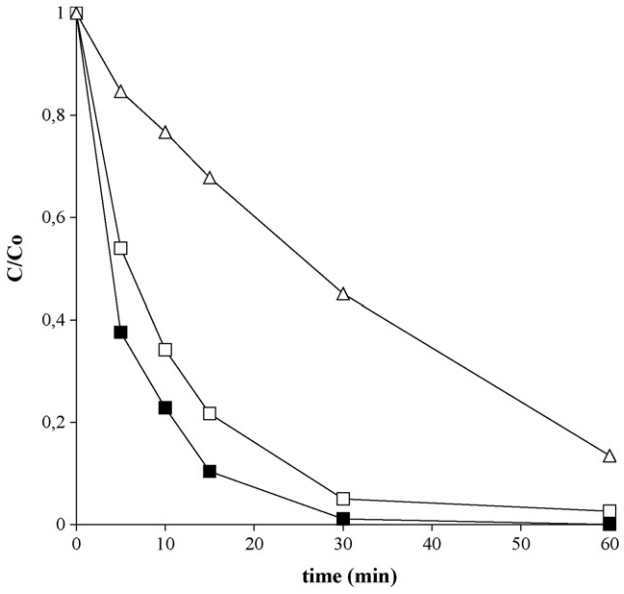

Fig. 4. Effect of the isopropanol (7.65×10^{-2} mol L^{-1}) (□) and acetonitrile as solvent (△), in comparison with the photocatalysed degradation of the antibiotic (7.65×10^{-5} mol L^{-1}) (■).

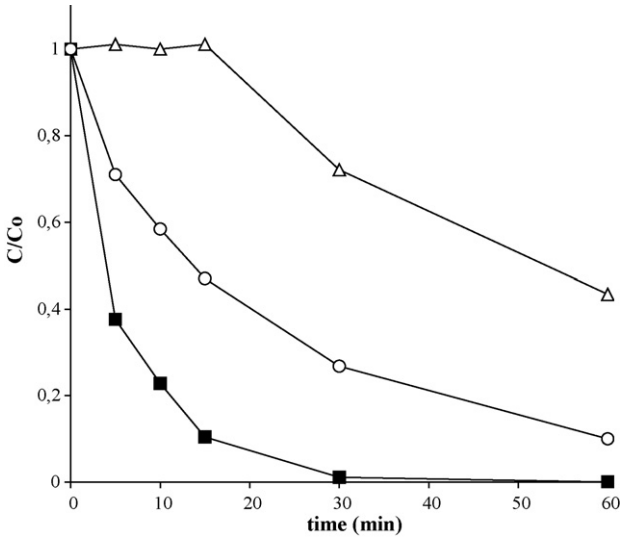

Fig. 5. Effect of the iodine addition to the reaction system at two different concentrations: 7.65×10^{-4} (◯) and 7.65×10^{-3} (△) compared to the photocatalysed degradation of the antibiotic (7.65×10^{-5} mol L^{-1}) (■).

surface. Radical and hole inhibitors are stable to irradiation and do not react directly with the antibiotic.

3.4.1. Effect of isopropanol and acetonitrile

Isopropanol has been described as the best hydroxyl radical quencher due to its high-rate constant reaction with the radical (1.9×10^9 L mol^{-1} s^{-1}) [28]. It has been widely used in photocatalysis in order to discriminate the direct oxidation of substrates by holes or by $HO^{\bullet}$ radicals [29,30]. A slight inhibitory effect was found in the FQ kinetic profile when isopropanol (76.5 mM, concentration 1000 times greater than antibiotic) was added to the solution at the beginning of the photocatalytic reaction (Fig. 4). Around 15% of inhibition was observed in FQ degradation after 15 min irradiation. In the presence of the alcohol, the complete disappearance of the antibiotic was not reached even after 60 min irradiation. Therefore, the hydroxyl radical apparently presents a moderate participation in FQ oxidation under the experimental conditions studied. Similar results have been reported for photocatalytic degradation of other aromatic organic substrates using Degussa P-25 with a weak participation of $OH^{\bullet}$ radical [15,28].

The use of a non-aqueous solution as reaction media could also help to discern the role that hydroxyl radicals play in the reaction mechanism [31]. Acetonitrile has been widely used as solvent replacing water because, as an extremely stable molecule, it can be used to distinguish the participation of holes and hydroxyl radicals in the photocatalytic reaction mechanism [28,32,33]. The photo-generated holes are strong oxidants (2.53 V versus NHE) capable of oxidising adsorbed hydroxyl groups or water molecules generating $OH^{\bullet}$ radicals [10]. Consequently, the use of a non-aqueous media could verify the role of such radicals in the reaction system.

In the FQ reaction in the photocatalytic system using only acetonitrile as solvent, a severe alteration in the kinetic profile was observed changing form a pseudo-first order to close to a zero-order reaction. The fact that complete FQ removal after long irradiation periods can be achieved is indicative that OH radicals are not the only oxidation via.

3.4.2. Effect of Iodide ion

The participation of the holes in the photocatalytic reaction can be assessed with the use of the iodide ion due to its efficient iodine formation, as in the reaction sequence shown below (Eqs. (4)–(6)) [16]. Iodide has been used to assess the role of the direct oxidation reaction in organic molecules and to determine the dynamics of hole formation in spectroscopic studies [15,28,34].

$$h^+ + I^{1-} \rightarrow I^{\bullet} \quad (4)$$

$$I^{\bullet} + I^{1-} \rightarrow I_2^{\bullet -} \quad (5)$$

$$h^+ + I_2^{\bullet -} \rightarrow I_2 \quad (6)$$

When the iodine anion was added to the FQ solution in a concentration of 7.65 mM (100 times larger than the antibiotic), an extensive inhibition in antibiotic degradation was observed (Fig. 5). While at high iodine ion concentrations, a complete inhibition of FQ degradation occurs until 15 min irradiation; at lower iodide anion concentrations (10 times larger than FQ), the same effect was observed but to a lesser extent, reaching 50% inhibition at 15 min reaction (Fig. 5). The results suggest that the holes play an essential role in the reaction mechanism of FQ oxidation, sustaining the photo-Kolbe decarboxylation mechanism [24,35].

3.4.3. Effect of benzoquinone

The superoxide anion ($O_2^{\bullet -}$) is produced by the reduction of oxygen molecules adsorbed on the catalyst surface by the photogenerated electrons. The participation of superoxide anion has been reported to be involved in several oxidation mechanisms occurring on the TiO_2 surface [36,37]. The first evidence of

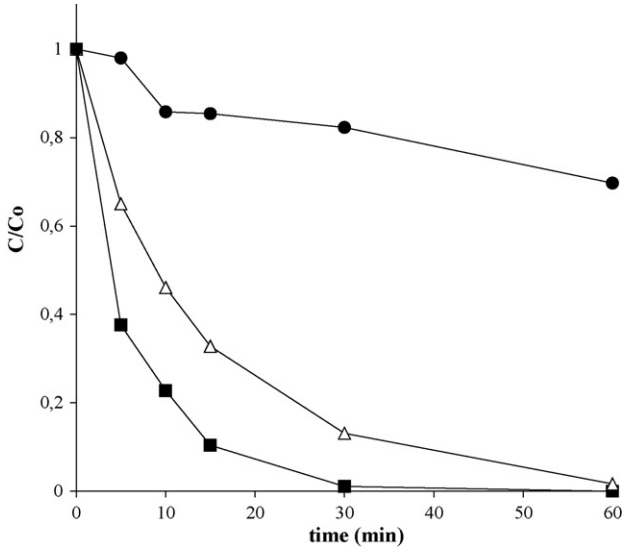

Fig. 6. Effect of the oxygen absence (●) and benzoquinone addition (7.65×10^{-6}) (△) in the photocatalysed degradation of the antibiotic (7.65×10^{-5} mol L^{-1}) (■).

the $O_2^{\bullet -}$ role was observed when the reaction was carried out in absence of oxygen because its formation requires adsorbed oxygen on the catalyst surface. Fig. 6 shows the almost total inhibition of the reaction in a solution purged with nitrogen. In order to determine the superoxide anion participation in the antibiotics oxidation, benzoquinone (BQ, 7.65 μM, 1/10 of the antibiotic concentration) was added. Benzoquinone has the ability to trap superoxide anions by a simple electron transfer mechanism (Eq. (7)).

$$BQ + O_2^{\bullet -} \rightarrow BQ^{\bullet -} + O_2 \quad (7)$$

The addition of BQ provokes partial inhibition of the FQ degradation as shown in Fig. 6. It can be concluded that the oxidation inhibition of FQ is due to the superoxide anion suppressed by the BQ addition. As mentioned in the literature, the superoxide radicals attack preferentially aromatic rings with low electronic density (as deactivated aromatic rings in FQ) [38].

In conclusion, the FQ oxidation by photocatalysis is mainly explained by the participation of holes and to a lesser extent by the contribution of hydroxyl radicals and superoxide anions.

3.4.4. Microbiologic assays on irradiated antibiotic solutions

Furthermore, to find some evidence of photocatalytic mechanistic paths of antibiotic oxidation, an additional significant goal of this study was to determine if the oxidation products of FQ still possess antibacterial activity. The susceptibility of *E. coli* (ATCC 6317) strains was used to evaluate the antibacterial activity of the oxidation products. They were chosen because of their good response at low antibiotic concentrations using the inhibition halo methodology [21]. The smaller the inhibition halo around the microdrop seeded on the agar plate inoculated with the bacteria, the less important it is in the antibacterial activity. A clear correlation between complete antibiotic depletion and total antibacterial activity inhibition was found (Fig. 7).

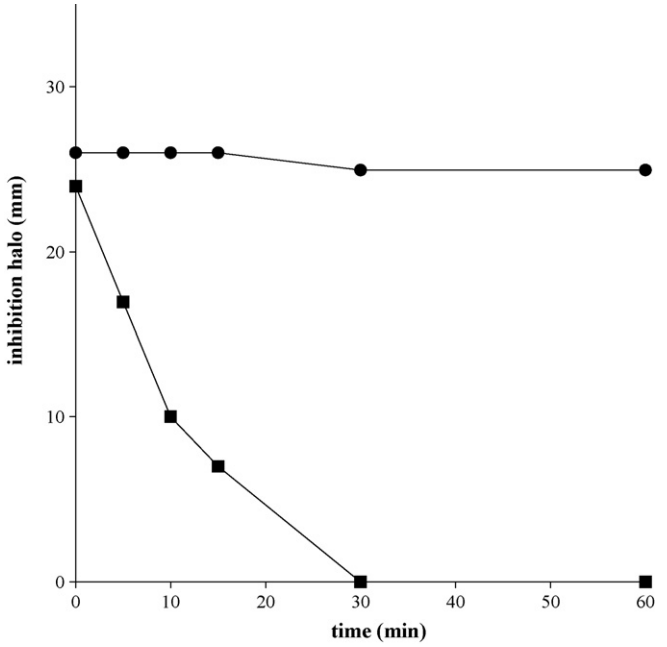

Fig. 7. Antibacterial activity of FQ photocatalysed solutions (■) and illuminate *d* solutions in absence of catalyst (●), measured as inhibition halo (mm) in agar plates inoculated with *E. coli* (ATCC 6317) strain.

The inhibition halo disappears completely after 30 min irradiation, the same time necessary to eliminate totally FQ (see Fig. 2). This result is categorical evidence that the oxidation products formed by photocatalysis of FQ are not biologically active against selected bacteria. The examination of Figs. 2 and 7 indicates that the residual antibacterial activity is completely attributed to the antibiotic that remains intact in the course of the photocatalytic reaction. On the other hand, the modification of the antibiotic structure by direct photolysis does not alter their antibiotic activity.

In consequence, photocatalysis is a valuable tool to eliminate the harmful environmental effects of this kind of substances. It has the added advantage that after short periods of photocatalytic treatment, the oxidation products could be treated by conventional biological system in an integrated photochemical–biological system as proposed for other substances [39–41].

4. Conclusions

Based on our experimental results, we summarise the most remarkable conclusions:

1. The photocatalytic FQ oxidation is mainly dependent on the pH of the solution.
2. Experimental evidence obtained with radicals and hole scavengers indicates that the holes have a preponderant participation in the oxidation mechanism of FQ oxidation. Also a slight contribution in the mechanism pathways can be attributed to hydroxyl and superoxide anions species.
3. Apparently the decarboxylation of flumequine is the primary step in the FQ oxidation by a photo-Kolbe mechanism.

4. The oxidation intermediates do not present antibacterial activity, indicating that the structural modification of the antibiotic changes drastically its biological activity.

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