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Photocatalytic oxidation of the antibiotic tetracycline on TiO_2 and ZnO suspensions

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ABSTRACT

The photocatalytic oxidation of the antibiotic tetracycline (TC) has been performed in aqueous suspension containing TiO_2 or ZnO under simulated solar light. The experimental conditions to attain the optimal degradation rate for each catalyst were determined using multivariate analysis and response surface methodology (RSM). The optimal oxidation conditions found were $1.5\ g\ L^{-1}$ and pH 8.7 for TiO_2 and $1.0\ g\ L^{-1}$ and pH 11 for ZnO. The catalytic activity of both catalysts indicates that ZnO presents a slightly higher oxidation rates than TiO_2 when both catalysts were compared under optimised conditions. Using radical scavengers, it was determined that titania TC oxidation occurs principally by direct hole oxidation with participation of hydroxyl radicals and that the oxidation on ZnO is driven mainly by hydroxyl radical. The direct photolysis at pH 8.7 degrade TC to TC-derivatives that maintain their antibiotic activity. However the irradiation in the presence of catalyst completely removes the solution's antibacterial activity (AA). The microbiologic analyses were performed on agar plates loaded with *Staphylococcus aureus*.

1. Introduction

The sustained use of antibiotics in human medicine and veterinary has provoked an alarming increase of antibiotic-resistant bacteria in the environment. This resistance can be transmitted to human beings through complex biochemical transference processes [1]. At present, wastewater treatment plants are not capable of completely eliminating these kinds of pharmaceuticals, which in turn can reach superficial waters or sediments constituting a public health concern.

Tetracycline (TC) is one of the most used antibiotics in aquaculture and veterinary medicine. It has been monitored either in superficial or in potable waters [2]. Recent publications indicate that tetracycline is completely oxidized by homogeneous [3] and heterogeneous photocatalysis in short time periods, concomitantly with the deletion of their antibacterial activity (AA) [4,5].

The photocatalytic process is initiated when a semiconductor absorb photons with an energy equal or superior to their band gap, promoting the valence band electrons to the conduction band energy level (Eq. (1)). The electrons in the conduction band (e^-_{CB}) can recombine with the photo-generated vacancies (holes, h^+_{VB}) decreasing the efficiency of the photocatalytic process (Eq. (2)). On the other hand, electrons can migrate to the surface of the catalyst particle being trapped by adsorbed oxygen molecules, thus forming the superoxide anion ($O_2{}^{-\bullet}$) increasing the efficiency of the process (Eq. (3)). In parallel, the vacancies generated in the valence band (h^+_{VB}) can be trapped on the catalyst surface promoting the splitting of adsorbed water molecules or hydroxide anions generating hydroxyl radicals ($HO^\bullet$) (Eqs. (4) and (5)). These hydroxyl radicals have been considered as the responsible for the oxidation of organic matter due to their high oxidation capability. Finally, the holes can directly oxidise the adsorbed organic matter conducting to oxidised intermediates (Eq. (6)) [6]:

$$\text{Semiconductor} + h\nu \rightarrow e^-_{CB} + h^+_{VB} \tag{1}$$

$$e^-_{CB} + h^+_{VB} \rightarrow \text{semiconductor} + \text{heat} \tag{2}$$

$$e^-_{CB} + O_{2(\text{adsorbed})} \rightarrow O_2^{-\bullet} \tag{3}$$

$$h^+_{VB} + H_2O_{(\text{adsorbed})} \rightarrow H^+ + HO^\bullet \tag{4}$$

$$h^+_{VB} + HO^-_{(\text{adsorbed})} \rightarrow HO^\bullet \tag{5}$$

$$h^+_{VB} + \text{organic matter(OM)} \rightarrow OM^{+\bullet} \rightarrow \text{oxidised products} \tag{6}$$

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Heterogeneous photocatalysis on TiO_2 suspensions have been amply described as one of the most promissory advanced oxidation technology for eliminating contaminants in low concentration using artificial or natural light [6]. Even though ZnO is less studied, it presents promissory results due to their higher photocatalytic activity in comparison with TiO_2 [7,8].

The present study evaluates TiO_2 and ZnO in the oxidation of the antibiotic tetracycline. The response surface methodology (RSM) was used to optimise the pH and amount of catalyst for each semiconductor and their efficiency to degrade tetracycline was compared. To understand better the role of the radicals and holes in the reaction, mechanism radical scavengers were used.

2. Experimental

2.1. Materials

Titania P-25 (surface area 52 $m^2\,g^{-1}$, particle size 20–30 nm) was obtained from Degussa (Brazil). ZnO (minimum purity 99%, particle size 50–70 nm, surface area 15–25 $m^2\,g^{-1}$), Tetracycline ($C_{22}H_{24}N_2O_8 \times HCl$) and p-benzoquinone were purchased from Sigma and used without further purification. Isopropanol (HPLC grade), acetonitrile (HPLC grade), potassium iodide (99.5% purity) were obtained from Merck (Chile) and used as received.

2.2. Photocatalytic reaction

The photocatalytic reactions were carried out in 100 mL of tetracycline solution (20 mg L^{-1}) in a borosilicate bottle (120 mL). The reaction was always maintained under magnetic stirring and pure oxygen bubbling. Irradiations were carried out in a SUNTEST XLS^+ (Atlas) (300–800 nm, Xe lamp, 250 W m^{-2}). The catalysts (TiO_2 or ZnO) were used in suspension. Sampling was carried out using a syringe connected to the reactor by a Teflon tube. Samples were immediately filtered in a Millipore filtration system using 0.2 μm nitrocellulose filters and sent for chemical and microbiologic analyses. Before each reaction, the system was maintained in the dark for at least 10 min in order to reach the adsorption equilibrium. In the multivariate study, the initial pH was adjusted with NaOH or HNO_3.

2.3. Response surface methodology

The Central composite circumscribed (CCC) statistic model was used in order to optimise the amount of catalyst and the pH of the reaction for each studied catalyst (TiO_2 or ZnO). Its model consists of a complete factorial design with 2^n ($n = 2$) experiments, 4 star points and 3 central points, given a total of 11 experiments. This methodology has been previously described for photocatalytic degradation of antibiotics [9]. The amount of catalyst was ranged between 0.5 g L^{-1} and 1.5 g L^{-1} for TiO_2 and between 0.2 g L^{-1} and 1.5 g L^{-1} for ZnO. The pH ranged from 3 to 10 and 6 to 11 for TiO_2 and ZnO, respectively. The response factor was defined as the extent of antibiotic degradation after 10 min and 2 min irradiation for TiO_2 or ZnO, respectively.

To obtain the associated polynomial for each reaction system and to build the response surface plot, the data was analysed using the software Modde 7.0. The model was statistically validated with the same software using ANOVA (95% confidence level).

2.4. Effect of radical inhibitors

In order to determine the role played by the hydroxyl radical, superoxide anion and holes in the photocatalytic degradation of tetracycline (7.65×10^{-5} mol L^{-1}), isopropanol (×1000, 7.65×10^{-2} mol L^{-1}), benzoquinone (×1/10, 7.65×10^{-6} mol L^{-1}) and iodide anions (×100, 7.65×10^{-3} mol L^{-1}) were added to the antibiotic solution, respectively. In a separate experiment, acetonitrile was used instead of water in order to confirm the role of hydroxyl radicals in both photocatalytic systems.

2.5. Analytical methods

After each reaction, filtered samples were analysed in a Shimadzu 1603 spectrophotometer (360 nm at neutral pH and 380 nm at alkaline pH). The methodology was previously validated by HPLC determinations, generating the same results [5]. Total organic carbon was determined in a TOC-V CPN Shimadzu analyser. The concentration of zinc ions after reactions on ZnO was determined by AAS in a Perkin Elmer equipment.

2.6. Antibacterial activity

The antibacterial activity was measured for the samples irradiated in the presence of TiO_2 and ZnO in order to evaluate if the long-term intermediates maintain the biological activity. The test was carried out as previously described [5]: 100 μL of the samples in agar plates were inoculated with *Staphylococcus aureus* ATCC 6538P. The plates were then incubated a 37 °C for 24 h, and the inhibition halo was measured. The results are presented as antibacterial activity and expressed in mm.

3. Results and discussion

3.1. Optimisation of the reaction

The optimisation procedure for photocatalytic reactions consisted of an experimental design to identify the importance of each variable involved in the reaction with a minimum set of experiments. The variables under study are codified for their higher and lower values (+1, −1), simultaneously changed in a defined range and processed with the adequate statistical software. Multivariate analysis is used to determine the weight and interaction between the variables, obtaining a polynomial and a graphical representation, or response surface, which provides the region where the optimised reaction occurs [10]. In the present study, the two catalysts evaluated, TiO_2 and ZnO, where the variables under study were the initial pH and the amount of catalyst.

3.1.1. Optimisation with TiO_2

Table 1 shows the experiments performed in the TC oxidation using TiO_2 in suspension. The amount of catalyst ranged between 0.5 g L^{-1} and 1.5 g L^{-1} and the pH between 3 and 10. These values were chosen considering the most common values reported in the literature. The figures in parenthesis represent the codified variables. The response factor (*Y*) was defined as the TC degradation percent after 10 min of irradiation under simulated solar light. In Table 1, the response factor indicates that high degradation levels, over 90%, are reached for a determined set of variables. The consistency of the statistical model is validated by the calculated values shown in the last column, where high agreement with the experimental ones is shown. The polynomial (Eq. (7)), obtained from the multivariate analysis, indicates that the pH is the main variable that affects the extent of TC degradation, showing first order and quadratic interactions. In the polynomial, the values in parenthesis represent the standard deviation for each coefficient:

$$Y_{TiO_2}(\%) = 93.7(\pm 0.6) + 1.7\,TiO_2(\pm 0.7) + 6.5\,pH(\pm 0.7) - 5.1\,pH^2(\pm 1.0) \qquad (7)$$

Table 1
Experimental results from factorial design of the tetracycline oxidation assisted by TiO_2 and simulated solar light. Codified values of the variables are in parenthesis.

Run	TiO_2 (g/L)	pH	Y^a exp. (%)	Y calc. (%)
1	0.5 (−1)	3 (−1)	79	80.4
2	1.5 (1)	3 (−1)	85.3	83.8
3	0.5 (−1)	10 (1)	93.3	93.3
4	1.5 (1)	10 (1)	96.4	96.7
5	0.65 (−0.7)	6.5 (0)	94.7	92.5
6	1.35 (0.7)	6.5 (0)	93.4	94.9
7	1 (0)	4.05 (−0.7)	86.5	86.6
8	1 (0)	8.95 (0.7)	96.4	95.7
9	1 (0)	6.5 (0)	95	93.7
10	1 (0)	6.5 (0)	93.1	93.7
11	1 (0)	6.5 (0)	92.1	93.7

[a] After 10 min irradiation.

Table 2
Experimental results from factorial design of the tetracycline oxidation assisted by ZnO and simulated solar light. Codified values of the variables are in parenthesis.

Run	ZnO (g/L)	pH	Y^a exp. (%)	Y calc. (%)
1	0.2 (−1)	6 (−1)	30.5	29.4
2	0.2 (−1)	11 (1)	70.1	66
3	1.5 (1)	6 (−1)	66.3	68.3
4	1.5 (1)	11 (1)	76.6	75.7
5	0.85 (0)	6 (−1)	57	55.6
6	0.85 (0)	11 (1)	73.1	77.6
7	0.2 (−1)	8.5 (0)	42.6	47.7
8	1.5 (1)	8.5 (0)	73.2	72
9	0.85 (0)	8.5 (0)	67.6	66.6
10	0.85 (0)	8.5 (0)	69.1	66.6
11	0.85 (0)	8.5 (0)	66.3	66.6

[a] After 2 min irradiation.

The quadratic effect of the pH indicates that at both high and low pH values, the reaction will be less efficient, where this negative effect is more pronounced in acidic conditions as shown in the 3-D representation of the polynomial (Fig. 1a). The fact that the best conditions for TC degradation are found at pH 8.7 can be explained because titania has a point of zero charge (pzc) close to the neutrality (6.25). Moreover, TC presents pK_a values at 3.3, 7.68 and 9.7 [11]. Under acidic pH (<3.3), both tetracycline and titania are positively charged provoking a repulsive effect. At pH 8.7, TC shows a negative charge increasing the repulsive effect with the titania surface, which is also partially negative charged. At higher pH (>9.7) the repulsive effect increase because TC shows a double negative charge.

In conclusion, the optimal values for TiO_2 amount and pH, determined by the Modde 7.0 software, were 1.5 g L^{-1} and 8.7, respectively.

3.1.2. Optimisation with ZnO

When the reaction was carried out in the presence of ZnO the response factor was chosen after 2 min of irradiation in the presence of the catalyst. The amount of catalyst was varied between 0.2 g L^{-1} and 1.5 g L^{-1}. Due to the fact that ZnO can suffer photo-corrosion under acidic conditions, the pH was varied in the range 6–11 [12]. Table 2 shows the 11 runs performed and the experimental and calculated percentages of TC degradation after 2 min irradiation with simulated solar light. A high coincidence is observed when comparing the two last columns, indicating a good correspondence of the statistical model. The polynomial representing the TC abatement is presented in Eq. (8), where it can be observed that the amount of catalyst and the pH plays a significant role in the TC degradation on ZnO. The maximum degradation is obtained at a high pH and a medium value of ZnO. The quadratic effect of ZnO suggests that at low and high ZnO loads, the reaction will be less efficient. The antagonism presented between the variables implies that when they simultaneously have high values, TC oxidation is minimised. This effect can be clearly seen in the 3-D representation of the polynomial shown in Fig. 1b:

$$Y_{ZnO}(\%) = 66.6(\pm 1.6) + 11.0\,pH(\pm 1.5) + 12.2\,ZnO(\pm 1.5) - 6.7\,ZnO^2(\pm 2.2) - 7.3\,pH \cdot ZnO(\pm 1.8) \quad (8)$$

The optimised reaction conditions were found at pH 11 and around 1.0 g L^{-1} of ZnO. It is important to note that the pzc of ZnO is around 8 [13]. Even though at pH 11 either the catalyst surface or the TC is negatively charged, the oxidation rate is highest. These experimental results suggest that the TC oxidation mechanism on ZnO may be different from the one obtained when the reaction was performed on TiO_2. A probable explanation for this behaviour at pH 11 is that there is a high concentration of adsorbed hydroxide anions (HO^-) that promote the formation of hydroxyl radicals, enhancing the tetracycline oxidation (Eq. (5)). The same finding has been reported for a dianionic azo dye photocatalysed on suspended ZnO [14]. In conclusion, our results indicate that ZnO presents comparable photocatalytic activity with TiO_2 when acting on tetracycline irradiated by sunlight. Additionally, earlier reports indicate that ZnO absorbs a major fraction of the solar spectrum than TiO_2 that could explain the slight efficiency of ZnO compared with TiO_2 [15].

3.2. Oxidation of tetracycline under optimised conditions

When the reactions were performed under optimised conditions, a rapid degradation of TC can be observed (1.5 g L^{-1} TiO_2 and

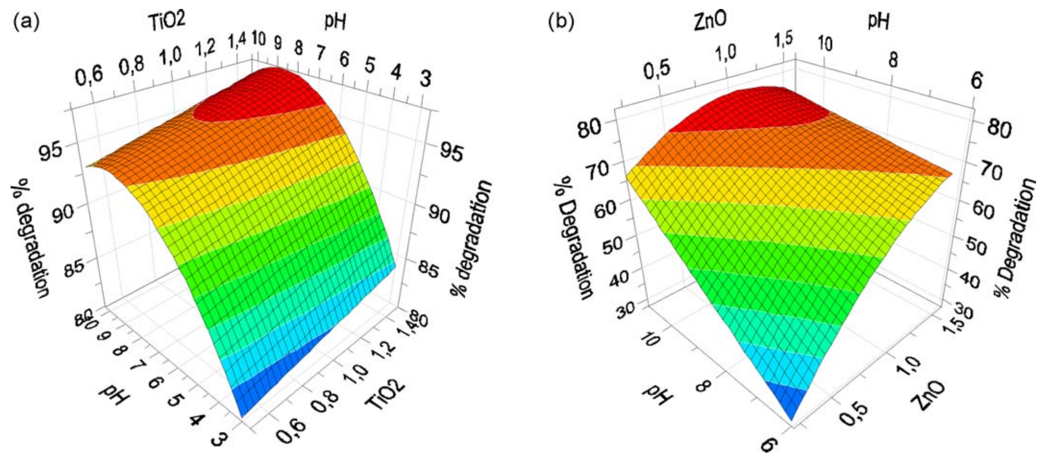

Fig. 1. Response surface showing the percentage of TC degradation using TiO_2 (a) and ZnO (b).

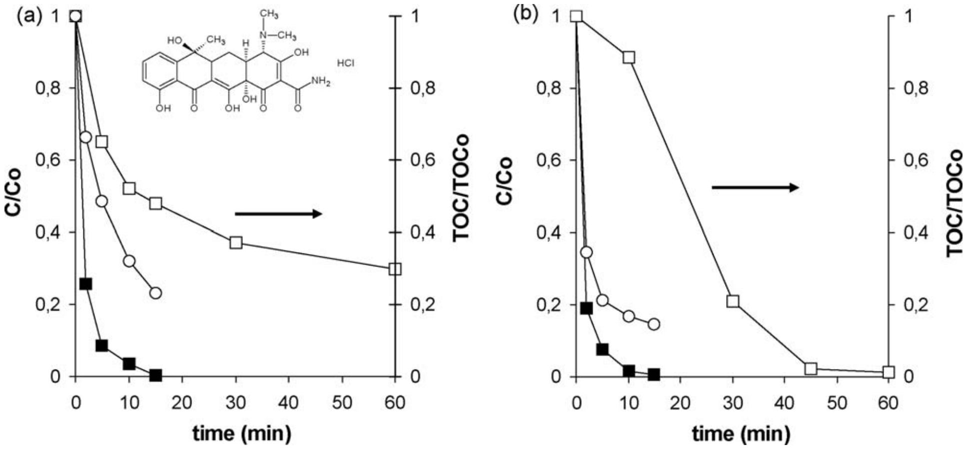

Fig. 2. Degradation profile of tetracycline under optimised conditions. (a) pH 8.7 and TiO_2 1.5 g L^{-1}; (b) pH 11 and ZnO 1.0 g L^{-1}. Normalised values for tetracycline concentration (■), TOC (□) and photolysis (○).

pH 8.7). Fig. 2a depicts the course of the antibiotic oxidation on TiO_2. After 15 min of irradiation with simulated solar light, the antibiotic was completely removed and more that 50% of the carbon content was mineralised. In addition, high TC degradation is observed due to the direct photolysis at pH 8.7. The adsorption in the dark reaches close to 65% after 10 min of contact.

On the other hand, the photolysis of TC at pH 11, in absence of catalyst, occurs at a high rate, reaching values around 80% after 10 min irradiation (Fig. 2b). The high photolysis rate of TC at alkaline conditions has been recently reported as a consequence of the participation of reduced oxygen species [11]. In the presence of ZnO, the antibiotic was completely eliminated after 10 min of irradiation accompanied with a very low mineralisation. The complete conversion of the organic matter to CO_2 was reached after 45 min irradiation. It is important to point out that the adsorption of TC in the dark at pH 11 was low (less than 10%) due to the repulsion between the negative surface of the ZnO and the double negative charged TC. In spite of the high TC photolysis at the assayed pHs, no modification of TOC was observed even at high illumination times (data not shown).

3.3. Effect of the radical and holes inhibitors

Radical scavengers have been used to assess the photocatalytic reaction mechanism of an antibiotic because they can alter the kinetic profile of the reaction, providing information about the participation of different radicals [10]. Isopropanol has been proposed in order to discern the role played by the hydroxyl radical in the oxidation mechanism [16]. In addition, acetonitrile, an extremely stable molecule, has been used replacing water as a solvent in order to discern the participation of hydroxyl radicals or holes in the photocatalytic reaction mechanism [17].

The formation of iodide from a solution containing iodide anions and a photocatalyst under irradiation ($h^+ + I^- \rightarrow\rightarrow\rightarrow I_2$) can be used to identify the involvement of holes in the direct oxidation of organic substrates [18]. On the other hand, benzoquinone can be used to detects the superoxide anion due to their ability to trap this anion radical by an electron transfer mechanism ($BQ + O_2^{-\bullet} \rightarrow BQ^{-\bullet} + O_2$) [19].

In the present work, we have used isopropanol and acetonitrile in order to evaluate the participation of hydroxyl radicals, iodine anions to demonstrate the participation of holes and benzoquinone to detect superoxide anions in the TC oxidation by TiO_2 and ZnO.

3.3.1. Effect of isopropanol and acetonitrile on TC photocatalysis

Fig. 3a shows the oxidation profile of tetracycline on TiO_2 under optimised conditions, compared with the degradation profile in the presence of isopropanol and acetonitrile. Isopropanol is a well-known hydroxyl radical scavenger due to its high-rate constant with the radical (1.9×10^9 L mol^{-1} s^{-1}) [16]. The addition of isopropanol (concentration ×1000) to the solution containing tetracycline in the presence of TiO_2 and irradiated with simulated solar light, modifies the reaction course. This result suggests the participation of hydroxyl radical in the reaction mechanism. Furthermore, when the reaction was carried out in absence of water (100% acetonitrile), the reaction is largely inhibited, confirming that $HO^{\bullet}$ play a significant role in the oxidation of tetracycline.

In the case of the reaction catalysed by ZnO, the effect of OH scavengers is also pronounced (Fig. 3b), indicating that hydroxyl radical probably plays an important role in TC oxidation. This result is concordant with the mechanism proposed by Daneshvar et al. in the degradation of a reactive dye with ZnO at high pH [12]. The most evident indication of the $HO^{\bullet}$ participation is the inhibition of the reaction in absence of water, concomitant with the decrease of the reaction rate in the presence of isopropanol.

3.3.2. Effect of benzoquinone and iodide anions on TC photocatalysis

The effect of iodide anions (×100) in the profiles of the reactions catalysed by TiO_2 and ZnO, respectively (Fig. 4a and b) is clearer in the reaction driven by titania although the effect is not completely absent in the case of ZnO. These results confirm that direct oxidation by holes is probably more important in the titania catalysis. On the other hand, hydroxyl radicals, together with a minor participation of holes, are the responsible for the TC oxidation on ZnO. This statement is valid for the reaction carried out under the optimised conditions found by factorial design. These findings agree with previous reports [9,12,16,18].

Finally, superoxide anions do not participate in the TC oxidation reaction on any of the studied catalyst. It became evident when the reaction was performed with addition of benzoquinone (×1/10).

3.4. Antibacterial activity

One of the most important aspects to be taken into account in the treatment of pharmaceuticals is the verification of the biological activity of the long-term intermediates after the treatment. In the case of toxic substances, the measure of the residual toxicity is critical; in the case of antibiotics, the antibacterial activity of the oxidation products is indispensable. The analysis of antibacterial activity must be done using selected bacteria that present a linear response with the bactericidal agent concentration [5,9,20]. For this reason, a previous screening must be done with several bacteria in order to establish microorganism

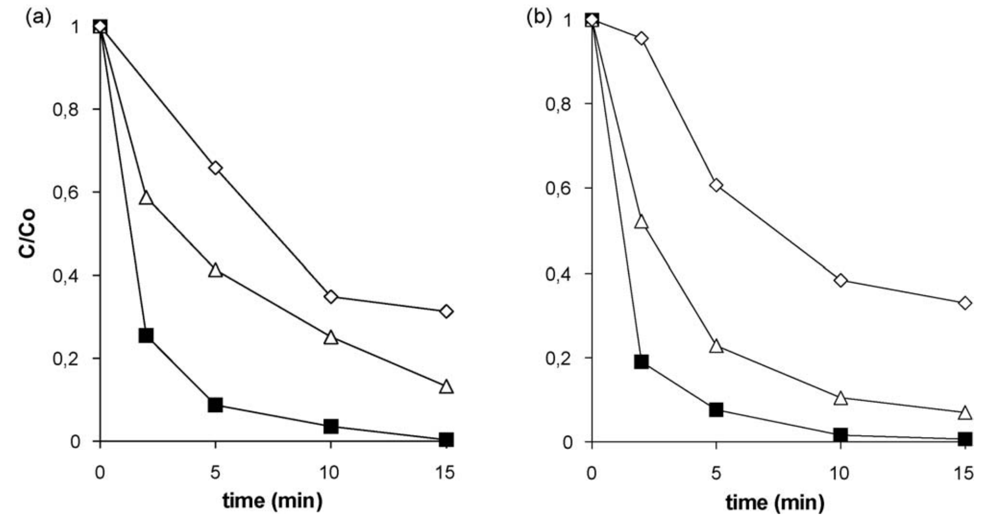

Fig. 3. Effect of isopropanol and acetonitrile on tetracycline oxidation catalysed by TiO_2 (a) and ZnO (b). Normalised TC concentration (■); TC in the presence of isopropanol (×1000) (△), and using acetonitrile as a solvent (◇).

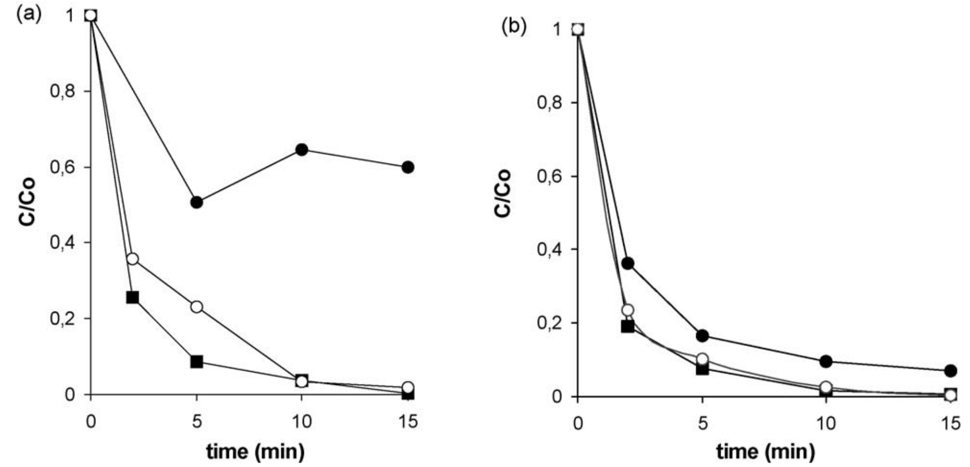

Fig. 4. Effect of iodide anions and benzoquinone on tetracycline oxidation by TiO_2 (a) and ZnO (b). Normalised tetracycline concentration (■); TC in the presence of benzoquinone (×1/10) (○); TC in the presence of iodide (×100) (●).

sensitivity to a determined antibiotic. In the case of tetracycline, *Staphylococcus aureus* ATCC 6538P was chosen because it provides the best response. In Fig. 5, it is clearly shown that the inhibition halo formed around the loaded drop of treated solution decreases rapidly reaching the complete inhibition of the bacterial activity after 30 min of reaction with TiO_2. In addition, the antibacterial activity of the photolysed sample (in absence of TiO_2) remains without significant changes indicating that direct photolysis do not alter the antibiotic's biological activity even at 15 min irradiation despite the significant reduction of the absorbance (80% after 15 min irradiation, Fig. 2a). The most plausible explanation is that due to the photolysis, tetracycline was converted into another antibiotic of the tetracycline family [4].

As pointed out earlier (Fig. 2b), the TC photocatalysis on ZnO is comparable with the reaction on TiO_2. However the photolysis of TC induced by simulated solar light is exceptionally elevated and the microbiological analysis of the products obtained at pH 11 are ambiguous. Indeed, photolysis and photocatalysis cannot be discriminated at pH 11, although they can be differentiated in some experiments performed at pH 8 (data not shown). Still, the amount of Zn^{+2} released to the solution is much higher ($5.72\ mg\ L^{-1}$) in comparison to the amount released at pH 11 ($1.81\ mg\ L^{-1}$), making inadequate to perform the reaction on ZnO at neutral or acidic pH.

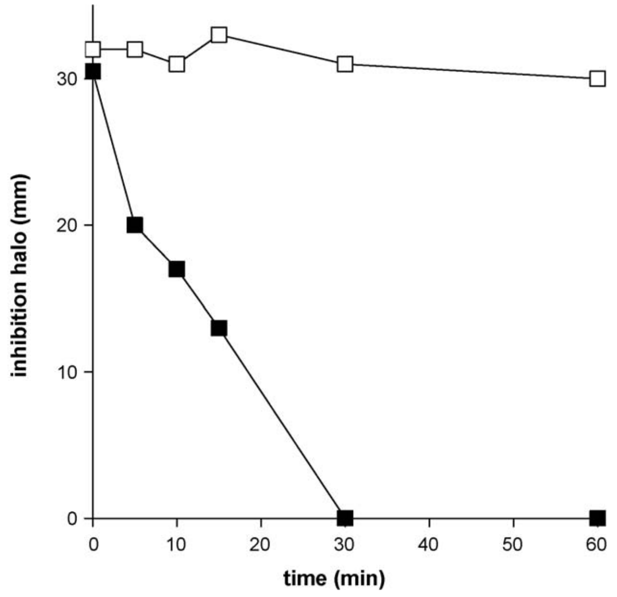

Fig. 5. Antibacterial activity evolution determined by the inhibition halo (mm) on the irradiated solutions in the presence of TiO_2. Photocatalysis (■), photolysis (□).

4. Conclusions

Based on the experimental results, the most remarkable conclusions can be summarized as follows:

1. It is possible and opportune to optimise the reaction parameters by using experimental design.
2. The photocatalytic activity of ZnO comparable to TiO_2 under simulated solar light.
3. The reaction mechanism of the photocatalytic tetracycline oxidation on TiO_2 occurs with direct participation of holes and OH radicals.
4. In the reaction on ZnO, the reaction mechanism proceeds mainly with the contribution of hydroxyl radicals and to a lesser extent by holes.
5. The degradation products obtained by direct photolysis at neutral 8.7 render new compounds with antibiotic activity similar to tetracycline. This issue confirms the need to measure antibacterial activity after some antibiotic treatment.
6. The Complete removal of the antibacterial activity was reached by using TiO_2 and simulated sunlight.

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