Photocatalytic and photoelectrocatalytic degradation of the antibacterial agent ciprofloxacin

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Abstract

Photocatalytic and photoelectrocatalytic degradation of the antibacterial fluoroquinolone drug, Ciprofloxacin, has been studied in the presence of nanocrystalline titania films supported on glass slides or transparent electrodes. Degradation has been examined either in pure water or in the presence of NaOH or NaCl. Titania films can photocatalytically or photoelectrocatalytically degrade Ciprofloxacin. In the presence of NaOH, the degradation rate was smaller than in pure water and this is explained by the fact that at high pH values attraction of Ciprofloxacin to the titania surface is discouraged. In the presence of NaCl, the degradation rate was the largest, thanks to Cl-based radicals, which can be photocatalytically created by interacting with photogenerated holes. Application of a forward (anodic) bias increased photodegradation rate in the presence of both electrolytes while a reverse (cathodic) bias decreased photodegradation rate. Electrocatalytic effects, i.e. degradation of Ciprofloxacin in the dark or in the absence of photocatalyst under applied bias of up to ±1.0 V vs. Ag/AgCl, were not detected in the case of NaOH and were of limited importance in the case of NaCl.

Introduction

Photocatalytic degradation of organic pollutants using nanocrystalline titania (nc-TiO_2) photocatalyst has been acknowledged as a promising technology for removing pollutants from water, especially, organic substances that resist other oxidation processes. Photocatalytic degradation can be accelerated in a photoelectrochemical cell by applying an electric bias. A photoelectrochemical cell comprises a photoanode electrode, for example a FTO (Fluorine doped Tin Oxide) glass, which usually carries a nc-TiO_2 film, a counter electrode, a reference electrode and an electrolyte, where the target substance is dissolved. Excitation of the photocatalyst generates electron-hole pairs. Holes are consumed by oxidizing the organic target, either directly or by the intermediate of active radicals[1]. Electrons move through an external circuit to the counter electrode where they participate in reduction reactions, for example, water or oxygen reduction[2]. Application of an electric bias may facilitate photogenerated electron-hole separation and may additionally facilitate formation of oxidative radicals. This is particularly true in the case of NaCl, where direct anodic oxidation of chloride ions leads to the formation of free chlorine and/or chlorine-oxygen species that can oxidize organic pollutants[1,3,4].

In the present work, we have undertaken the study of photocatalytic and photoelectrocatalytic degradation of an antibacterial fluoroquinolone drug, Ciprofloxacin (CIP), in order to assess the importance of the photoelectrocatalytic vs. photocatalytic process and also assess the

importance of the choice of supporting electrolyte. The chemical structure of CIP is given in Fig.1a. CIP is used both in Human and Veterinary medicine and because it is not completely metabolized it is carried into surface water and soil[5-7]. The presence of an antibacterial drug in natural waters may have serious consequences to the aquatic life. It is then necessary to develop effective procedures for its removal. We have examined two possible supporting electrolytes for running photoelectrocatalytic degradation of CIP: NaOH, an alkaline electrolyte that may facilitate degradation by providing $OH^\bullet$ radicals and NaCl, a natural product, which can provide, as already said, chlorine-based radicals[1,8]. The degradation of CIP has been easily monitored by absorption spectrophotometry using its UV absorbance, as seen in Fig.1b. Of course, decrease of the characteristic absorbance does

not necessarily mean mineralization. However, the scope of the present work was not to develop a mechanistic model for Ciprofloxacin mineralization but to compare the photoelectrocatalytic vs. photocatalytic capacity of nanostructured films made of commercial titania towards a real water pollutant and to assess the applicability of supporting electrolyte. In this respect the present work highlights the superiority of photocatalytic and photoelectrocatalytic degradation in the presence of NaCl. It is then realistic to look forward to the construction of a system that utilizes a renewable source of electricity, solar radiation and a natural salt for effective water cleaning[9]. Information on CIP photocatalytic mineralization route is provided in literature and it seems that a possible first step may involve removal of fluorine and breakage of the side amine group [7,10].
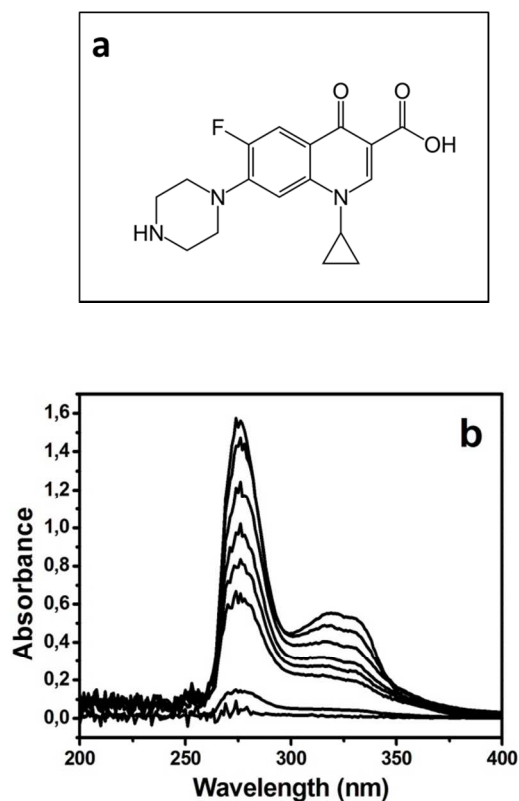

Experimental

Materials. Reagents were obtained from Aldrich and were used as received. Ciprofloxacin was a Fluka product. Commercial nanocrystalline titania Degussa P25 was used in all reactor constructions and Millipore water was used in all experiments. SnO_2:F transparent electrodes (FTO, Resistance 8 Ω/square) were purchased from Pilkington.

Description of the reactor. We used a batch reactor, which was made of a pyrex cylinder that could accept 100 ml of aqueous solution of the photodegradable substance. Nanocrystalline titania (nc-TiO_2) photocatalyst was deposited on four microscope slides, only on one side of the slide, covering an area of 2.5 cm x 6.5 cm. The four slides were introduced into the reactor at an upright position. In turn, the reactor was introduced into a home-made cylindrical construction carrying 4 Black Light tubes giving radiation peaking in the UVA, ideal for titania excitation[11]. The tubes were placed at four symmetrical positions around the reactor and were covered by a metallic reflecting

Figure 1. _Chemical structure (a) and absorption spectrum of 9.1 x 10^{-5} mol.L^{-1} aqueous solution of Ciprofloxacin before and during photocatalytic degradation_

cylinder[11]. The intensity of radiation at the position of the sample was approximately 1.5 mW.cm^{-2}. Cooling of the reactor was assured by means of air flow using an incorporated fan. The concentration of the photodegradable substance was monitored by absorption spectrophotometry using 2 ml aliquots, which were returned to the reactor.

Photoelectrocatalytic measurements were made in the same reactor but using only one FTO electrode covered on the conductive side by nc-TiO$_2$ over the same area, i.e. 2.5 cm x 6.5 cm. Both counter electrode (Pt foil 2.5 cm x 2.5 cm) and Ag/AgCl reference electrode were accommodated within the same reactor. In all cases the reactor was exposed to the ambient atmosphere. The electrolyte concentration was always 0.25 mol.L^{-1}.

Deposition of the phototocatalyst as film. The following procedures, were undertaken in order to deposit photocatalyst on microscope slides or FTO electrodes. nc-TiO$_2$ film was deposited in two layers, a bottom compact layer and a top open structure[12]. The bottom layer was synthesized by the sol-gel method while the top layer was deposited by using a paste made of Degussa P25 nanoparticles. Deposition of a compact bottom layer is a common practice in making titania photoanodes since it facilitates upper layer attachment and increases electrical contact with FTO electrode. The same was practiced also with the microscope glass slides for reasons of uniformity. The bottom dense layer was deposited by the following procedure. 3.5 g of the non-ionic surfactant Triton X-100 was mixed with 19 ml ethanol. Then 3.4 ml glacial acetic acid and 1.8 ml of titanium tetraisopropoxide were added under vigorous stirring. After a few minutes stirring, the film was deposited by casting a thin layer of the sol and then it was left to dry in air for a few minutes. Finally, it was calcined at 550°C. The temperature ramp was 20 degrees/min up to 550°C and the sample was left for about 10 min at that temperature. The final compact film, was about 300-350 nm thick. On the top of this compact nanostructured layer, commercial Degussa P25 was deposited. For this purpose, we used a paste, which was applied by screen printing. It was finally calcined again at 550°C. This last sequence was repeated in order to obtain a top layer of about 10 μm thick. The thickness of the films was measured by their SEM profiles. The geometrical area of the film was, as already said, 2.5 x 6.5=16,25 cm^2 and the quantity of photocatalyst in each film was approximately 35 mg.

Methods. Absorption measurements were made with a Cary 1E spectrophotometer. Percent degradation was calculated relative to the initial absorbance (C/C$_0$) of the untreated sample. Pseudo-first-order decay rate k was calculated by fitting a straight line to the equation ln(C/C$_0$)=-kt. Linear voltametry curves were traced with an Autolab potentiostat PGSTAT128N and the same was used for applying bias. All current-voltage curves were traced at 5 mV.s^{-1}.

Results and Discussion

The chemical structure of Ciprofloxacin (CIP) is presented in Fig.1a while Fig.1b shows its absorption spectrum. It consists of one major peak at 276 nm and a second band peaking at 321 and 335 nm. Since it is possible that these two major spectral contributions may come from a different moiety, which may degrade at a different rate, the degradation of CIP has been monitored by the variation of absorbance at both 276 and 321 nm. The absorption spectra have been first monitored in the absence of photocatalyst, in the dark and under illumination using 100 ml aqueous solutions of 9.1 x 10^{-5} mol.L^{-1} CIP. This quantity corresponds to about 30 mg.L^{-1}, a quantity, which is much higher than the usual quantities of CIP detected in surface water[5-7]. Higher concentrations were chosen in order to test the photocatalytic capacity under elevated pollution levels and to facilitate monitoring by absorption spectrophotometry. CIP was practically unaffected even after 20 h of irradiation by

Black Light of approximately 1.5 mW.cm^{-2} (see Experimental Section). CIP aqueous solution was then irradiated in the presence of 4 titania films deposited on microscope glass slides (total of 140 mg of photocatalyst). The four films were placed at four diametric positions in front of the four Black-light tubes used for excitation (see Experimental Section). Titania did act as an effective photocatalyst, as can be seen by the data of Fig.1b and Fig.2. Figure 2 records the decay of the relative concentration C/C_0 of CIP by making the reasonable
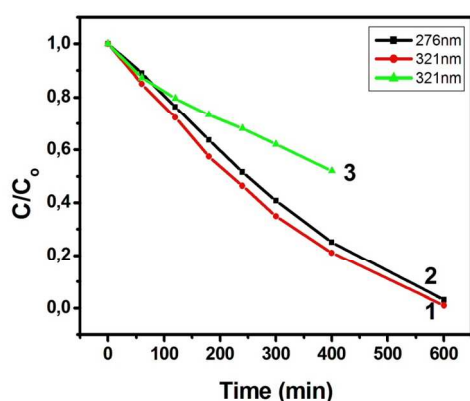

Figure 2. *Variation of the relative absorbance of 9.1 x 10^{-5} mol.L^{-1} CIP (30 mg.L^{-1}) at two different wavelengths during photocatalytic degradation in the presence of nc-TiO$_2$ photocatalyst deposited in the form of thin films on glass slides: (1,2) 4 slides; and (3) 1 slide.*

assumption that absorbance and concentration of intact CIP are proportional. The absorbance of CIP was practically zero after 10 h of irradiation. Interestingly, the two major parts of

the spectrum decayed at a similar rate. This is also roughly indicated by the spectra of Fig.1b. Therefore, the rest of the data were reported only for the variation of absorbance at 321 nm. Photocatalytic degradation was also carried out by using only one nc-TiO$_2$ film. The results are shown also in Fig.2. As expected, the decay was then slower, obviously because of the smaller quantity of photocatalyst (only 35 mg). The corresponding pseudo-first order rate constants are given in Table 1. They were 3.9 x 10^{-3} min^{-1}, in the case of 4 photocatalyst films and 1.5 x10^{-3} min^{-1}, in the case of 1 film.

Photocatalytic degradation of CIP has been previously reported[10,13-15]. An interesting approach is introduced by two recent works[10,13] where titania photocatalyst was synthesized by molecular imprinting using CIP as template. It has been shown that the ensuing selective photodegradation accelerated photocatalytic mineralization of CIP. For the sake of comparison, the present work essentially used 1.4 g.L^{-1} photocatalyst deposited as thin film and degraded 70% of 30 mg.L^{-1} CIP in a time of 5 hours. This corresponds to 3 mg of degraded CIP per gram of catalyst per liter of solution per hour. In Ref.10, 2 g.L^{-1} molecular imprinted photocatalyst was employed in powder form and degraded 70% of 10 mg.L^{-1} CIP in a time of 1 hour. This corresponds to 3.5 mg of degraded CIP per gram of catalyst per liter of solution per hour. The two rates are then comparable. Of course, such comparison is mostly qualitative since it does not take into

Table 1. List of the pseudo first order decay constants extracted from the decay curves of Figs.2,4 and 5. Degradation of 9.1 x 10^{-5} mol.L^{-1} CIP was monitored at 321nm.

Salt	Bias (Volts vs. Ag/AgCl)	k (10^{-3}min^{-1})
No salt (4 films)	No bias	3.9
No salt (1 film)	No bias	1.5
NaOH	No bias	0.8
NaOH	+1	0.9
NaOH	-1	0.6
NaCl	No bias	4.8
NaCl	+1	6.8
NaCl	-1	3.9

account other factors, for example the intensity of incident radiation or the configuration of the reactor used in each case, but it helps getting an idea of how efficient the studied system is. Photocatalyst supported as thin film is less effective than photocatalyst in powder form[14], due to smaller interface with the liquid phase, but is more practical since it can be easily recuperated. Of course, in the present case, deposition of photocatalyst as thin film was necessary in order to carry out photoelectrochemical treatment.

The present work searches, as already said, for ways to enhance photocatalytic degradation rates by applying photoelectrocatalytic conditions. For this reason, CIP was also subjected to photoelectrocatalytic degradation. Since it was then necessary to introduce an electrolyte, photoelectrocatalytic decay of CIP was first examined in the presence of NaOH. The increase of the number of OH^- ions in the presence of an alkaline electrolyte provides an effective means for oxidative radical formation. The possible effect of NaOH on CIP in the absence of photocatalyst or electric bias was first examined. Again it was found that CIP was very resistant to the presence of NaOH, both under illumination or in the dark and practically suffered no changes. However, in the presence of titania and by applying an electric bias, photoelectrocatalytic conditions did affect photodegradation rate. Figure 3 shows IV curves obtained in the presence and in the absence of CIP in a photoelectrochemical cell containing an alkaline electrolyte. The presence of the organic substance resulted in substantially increasing anodic photocurrent, indicating that an important interaction took place between the photoanode and the photodegradable target. Obviously, CIP was oxidized by consuming photogenerated holes thus liberating electrons and causing a current increase. As a consequence, the decay curves of Fig.4 differentiated themselves according to the applied static bias. Curve 2 of Fig.4 presents the decay of CIP in the absence of any bias. In fact in that case, the electrode was not connected to any device or circuit. The data of Curve 2 correspond to 1 photocatalyst- bearing slide. Interestingly, the decay rate was 0.8×10^{-3} min^{-1}, i.e. lower than in pure water $(1.5 \times 10^{-3}$ min$^{-1})$. Contrary to the expectation that the presence of OH^- might enhance photodegradation rate by offering an increased number of $OH^\bullet$ radicals, the presence of the
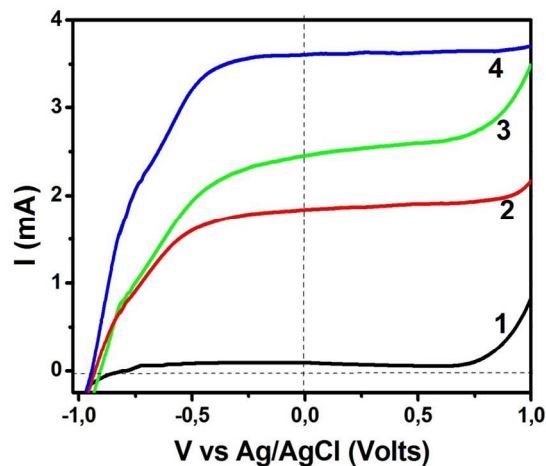

Figure 3. *IV curves obtained with a nc-TiO_2/FTO photoanode: (1) in the dark or (2-4) under illumination. Aqueous electrolyte contained 0.25 mol.L^{-1} NaOH and various CIP concentrations: (2) zero; (3) 12.5 x 10^{-5} mol.L^{-1}; and (4) 25 x 10^{-5} mol.L^{-1}.*

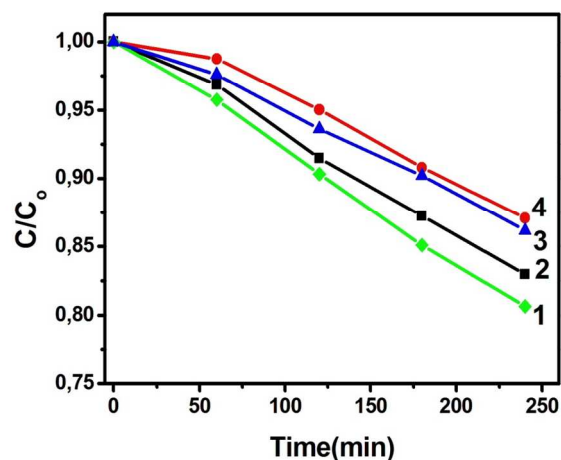***Figure 4.*** *Variation of the relative absorbance at 321 nm of 9.1 x 10^{-5} mol.L^{-1}CIP during photoelectrocatalytic degradation at various applied electric biases: (1) +1V; (2) no bias; (3) -1V; and (4) 0 V. The aqueous electrolyte contained 0.25 mol.L^{-1} NaOH.*

alkaline electrolyte slowed down decay rate. This may be explained by the data reported in a previous study[14], where it was shown that fluoroquinolone adsorption on titania is favored at neutral pH and discouraged at high pH. Of

course, adsorbed CIP may degrade faster than in the bulk. The presence of NaOH will surely affect protonation of CIP and thus modify its interaction with titania. Unfortunately, the range of influence of NaOH on CIP, as reflected on the value of the degradation rate, was rather limited. Thus degradation was insensitive to the increase of NaOH concentration above the presently used one and of course it decreased at lower NaOH concentration. Such data are incapable of offering information on the protonation issue. It is at least verified that CIP photocatalytic degradation was slower at high pH. On the other hand, anodic bias did have a small positive effect on photodegradation rate (Curve 1) while negative or zero bias vs Ag/AgCl (Curves 3 and 4, respectively) had adverse effects on the photodegradation rate. Forward bias may enhance degradation rate by assisting electron-hole separation and possibly by stronger adsorption to the titania film surface. This is apparently what was presently observed. Negative (reverse) bias may repel CIP away from the photoanode and adversely act with respect to electron-hole separation. The decrease of the rate constant in this last case also indicates that the presence of electric tension does not produce any important electrocatalytic effect under the present conditions. This is anyway expected by the fact that no degradation was observed in the dark under moderate applied bias (up to ± 1.0 V vs. Ag/AgCl).

Going back to Fig.3, it is interesting to note that an enhanced photocurrent can be obtained in the presence of CIP. Organic material photoelectrocatalytic oxidation may give rise to electricity production by a PhotoFuelCell operation[2] that may be employed to produce renewable energy by consuming organic wastes or water pollutants. A PhotoFuelCell is a photoelectrochemical cell where a fuel is consumed photocatalytically to produce electricity[2]. Even though, the energy input in the present case is low, it points to the right direction for the employment of PhotoFuelCells.

Finally, photoelectrocatalytic degradation was studied in the presence of NaCl and the results are shown in Fig.5. As can be seen in Table 1, photoelectrocatalytic decay rates where substantially enhanced in the presence of NaCl. Some decay was observed also in the dark (curves 4 of Fig.5), but it was very limited and its differentiation as a function of the applied bias was without importance.
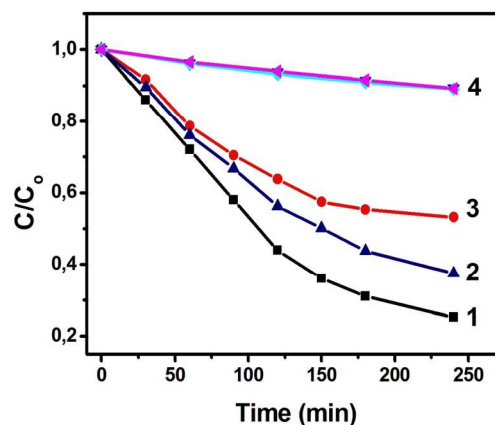

Figure 5. *Variation of the relative absorbance at 321 nm of 9.1 x 10^{-5} mol.L^{-1}CIP during photoelectrocatalytic degradation at various applied electric biases: (1) +1V; (2) no bias; and (3) -1V; Curves 4 (3 coinciding curves) correspond to the same corresponding conditions but recorded in the dark. The aqueous electrolyte contained 0.25 mol.L^{-1} NaCl.*

Curve 2 of Fig.5 demonstrates an important photocatalytic effect, which was absent in the presence of NaOH (curve 2 of Fig.4) or in the absence of any salt (Fig.2). The data of curve 2 were recorded in the absence of any bias and of any wiring or electrodes other than the photoanode electrode. The only additional component was NaCl. These data then correspond to photocatalytic degradation of CIP in the presence of NaCl. The presence of Cl^- may lead to photocatalytic radical formation by interaction with photogenerated holes[1,4]. These $Cl^{\bullet}$ radicals may accelerate CIP photodegradation. Indeed the rate constant in that case was 4.8×10^{-3} min^{-1}. Interestingly, this is more effective than the formation of hydroxyl

radicals in the presence of NaOH, obviously because $Cl^{\bullet}$ radicals are formed at higher density than $OH^{\bullet}$, even though, the concentration of the two salts was the same. Application of an electric bias had a similar effect as in the case of NaOH electrolyte (Fig.4). An anodic bias further accelerated degradation while a cathodic bias decreased degradation rate. We are again faced with enhancement of electron-hole separation in the presence of forward bias and possibly enhancement of CIP attraction towards the titania film, which naturally results in increasing decay rate constant. The maximum value of the decay rate constant was then equal to $6.8 \times 10^{-3} min^{-1}$ and was observed in the presence of NaCl under +1V forward bias vs. Ag/AgCl.

Conclusions

CIP can be photocatalytically degraded by using nanostructured titania films. In the presence of an alkaline electrolyte photocatalytic degradation was slower than in pure water. It could be increased only to a limited degree by application of forward bias, obviously, assisting electron-hole separation and CIP attraction to the photoanode. On the contrary, in the presence of NaCl, the photodegradation rate was substantially enhanced. The photoelectrocatalysis rate could be further enhanced by applying a forward bias. Electrocatalytic effects, i.e. degradation in the dark or in the absence of photocatalyst under applied bias, were not detected in the case of NaOH and were of limited importance in the case of NaCl. In short, photoelectrocatalysis does not offer any spectacular results at moderate applied bias as in the present case, however, the presence of Cl^- ions offers an important enhancement of photocatalytic degradation.

Acknowledgement

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