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Factors affecting diclofenac decomposition in water by UV-A/TiO_2 photocatalysis

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ABSTRACT

In this work, the photocatalytic conversion and mineralization of non-steroidal, anti-inflammatory drug diclofenac (DCF) was studied. UV-A irradiation at 3.37×10^{-6} einstein/s photon flux was provided by a 9 W lamp, while emphasis was given on the effect of catalyst type and loading (50–1600 mg/L), initial DCF concentration (5–20 mg/L) and the use of H_2O_2 (0.07–1.4 mM) as an additional oxidant on conversion and mineralization in various matrices (i.e. deionized water, groundwater and treated municipal effluent). Conversion was assessed by measuring sample absorbance at 276 nm, while mineralization by measuring total organic carbon.

Of six commercially available TiO_2 samples tested, Degussa P25 was found to be highly active for the DCF decomposition, whose extent was affected adversely by the complexity of the water matrix and at increased initial concentrations but it was maximized at optimal catalyst to DCF and H_2O_2 to DCF concentration ratios. DCF at 10 mg/L initial concentration was not toxic to freshwater species *D. magna*, unlike its photocatalytic degradation by-products that exhibited considerable toxicity.

1. Introduction

Over the past few years, pharmaceuticals are considered as an emerging environmental problem due to their continuous input and persistence into the aquatic ecosystem even at low concentrations. Diclofenac (DCF) is a non-steroidal, anti-inflammatory drug commonly used as analgesic, antiarthritic and antirheumatic, whose about 15% is excreted unchanged after human consumption [1]. In this view, it is commonly detected at the outlets of domestic wastewater treatment plants and in the receiving aquatic bodies since its biodegradation and/or natural attenuation are limited [2]. Since DCF can escape conventional wastewater treatment, new processes have to be tested and/or developed for its removal.

In recent years, advanced oxidation processes (AOPs) have been employed to treat pharmaceuticals and personal care products in various water matrices and representative studies have been thoroughly reviewed recently [3]. In the majority of the existing processes the parameter responsible for an effective degradation is the existence of highly reactive hydroxyl radicals [4]. DCF has been treated by various AOPs including homogeneous photo-Fenton oxidation driven by UV-C irradiation [5] or natural sunlight [6], H_2O_2/UV-C oxidation [7], ozonation [7–10], sonolysis based on low [11] or high [12] frequency ultrasound and electrochemical oxidation over boron-doped diamond anode [13].

Although semiconductor photocatalysis based on titania and induced by UV/Vis illumination comprises a promising technology for water purification with many applications over the past several years, it has not been extensively employed for DCF degradation. Rizzo et al. [14] studied the photocatalytic degradation of DCF in Degussa P25 TiO_2 suspensions irradiated by a 125 W black light fluorescent lamp to assess the effect of substrate concentration and catalyst loading on kinetics, as well as determine post-oxidation ecotoxicity to daphnids, freshwater algae and marine crustaceans. Méndez-Arriaga et al. [15] investigated DCF degradation by artificial solar irradiation in a tubular, recirculation reactor to elucidate the effect of TiO_2 loading, dissolved oxygen concentration, recycle flowrate and temperature on conversion, as well as evaluate post-treatment aerobic biodegradability and ecotoxicity to marine bacteria. In other studies, Calza et al. [16] applied response surface methodology to determine the statistically important factors in DCF degradation by artificial solar irradiation. They also identified reaction intermediates and proposed a detailed pathway for the photocatalytic degradation of DCF. The widespread use of TiO_2 as an effective photocatalyst, however, has been curbed by its poor light absorption in the visible region due to its large band gap [17].

The aim of this work was to investigate the effect of various operating conditions such as TiO_2 type and loading, DCF initial concentration, water matrix and the addition of H_2O_2 on DCF photocatalytic decomposition and mineralization induced by UV-A

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Table 1
TiO_2 catalysts used in this study. A: anatase; R: rutile; ND: not determined.

Catalyst	Crystal form	BET area (m^2/g)	Particle size (nm)	Supplier
Degussa P25	75% A:25% R	50	21	Degussa AG
Hombicat UV100	100% A	>250	5	Sachleben Chemie GmbH
Aldrich	100% A	190–290	15	Aldrich
Tronox AK-1	100% A	90	20	Kerr-McGee Chemicals LLC
Tronox TRHP-2	100% R	7	ND	Kerr-McGee Chemicals LLC
Tronox TR	100% R	5.5	300	Kerr-McGee Chemicals LLC

irradiation, a work that has not been done before for this specific compound in a systematic way. Moreover, the ecotoxicity of DCF to *D. magna* prior to and after photocatalytic treatment was assessed.

2. Materials and methods

2.1. Chemicals

DCF sodium salt (99.5% purity) was purchased from Sigma–Aldrich and used as received. Hydrogen peroxide (35%, w/w, perhydrol) was purchased from Merck. Milli-Q water system (Millipore, USA) was used for the preparation of model solutions in deionized water (DW). Groundwater (GW) taken from a pumping well and the effluent of municipal wastewater treatment plant of Limassol, Cyprus were also spiked with DCF to assess the effect of water matrix on degradation. Six commercially available TiO_2 samples, whose main properties are summarized in Table 1, were employed in this study for slurry photocatalytic experiments.

2.2. Experimental procedures

Photocatalytic experiments were conducted in an immersion well, batch type, laboratory scale photoreactor purchased from Ace Glass (Vineland, NJ, USA) and described in detail elsewhere [18]. In a typical run, 350 mL of aqueous solution containing DCF at initial concentration between 5 and 20 mg/L and inherent pH of about 6 were slurried with the appropriate amount of catalyst and magnetically stirred for 30 min in the dark to equilibrate. It should be noticed that the range of DCF concentrations employed is substantially higher than that typically found in environmental samples which is at the μg/L level [3,14]. This was done though to allow (i) the assessment of treatment efficiency within a measurable time scale and (ii) the accurate determination of residual concentrations with the analytical techniques employed in this work. Irradiation was provided by a UV-A lamp (Radium Ralutec, 9W/78, 350–400 nm) of 9 W nominal power under continuous oxygen flow and a constant temperature of 23 °C to start the reaction. The lamp was positioned vertically inside the reaction vessel and housed in an inner glass tube. The photon flux of the lamp was determined actinometrically using the potassium ferrioxalate method [19] and found equal to 3.37×10^{-6} einstein/s.

2.3. Analytical procedures

Samples drawn from the reaction vessel were first filtered with 0.22 μm filters to remove catalyst particles. The progress of photocatalytic reaction was then monitored measuring sample absorbance with a UV-Vis Jasco V-530 spectrophotometer at 276 nm [11,14] since this wavelength corresponds to the maximum DCF absorbance in the UV spectrum. The linearity between absorbance and concentration was tested using solutions at various DCF concentrations in the range 0–25 mg/L and the response was found to be linear over the whole range of concentrations under consideration. It should be noted here that measuring absorbance in treated solutions may not represent absolutely the concentration of unreacted DCF since some of the reaction by-products may also absorb at 276 nm, thus contributing to the recorded absorbance. In this respect, the reported concentration values used to compute reaction conversions and rates may account for the residual substrate and possibly some of its reaction intermediates. Total organic carbon (TOC) was measured with a Shimadzu VCPH/CPN analyzer.

2.4. Toxicity assay

DCF solutions were assessed with respect to their ecotoxicity to freshwater species *D. magna* prior to and after photocatalytic treatment. The tests were performed using the Daphtoxkit FTH magna. Ephippia were activated by rinsing in tap water and were then hatched for 72–90 h in standard freshwater (prepared using $NaHCO_3$, $CaCl_2$, $MgSO_4$ and KCl) suitable for Daphnia at 20–22 °C under continuous illumination of 6000 lx. Dissolved oxygen was measured and it was always at acceptable levels, while pH was adjusted to 7 ± 0.5.

Two hours prior to testing, the neonates were fed using a dilution of *Spirulina* microalgae in order to reduce mortality caused by starvation, which can bias the test results. During the subsequent 48 h test exposure the organisms were not fed. One hundred and twenty neonates were used to perform the tests. Five daphnids were tested in quadruplicate in specific test plates covered and incubated at 20 °C, in the dark. After 24 and 48 h of incubation the number of dead and immobilized neonates was calculated. Each sample was run in duplicate and mean values are quoted as results with standard deviation never exceeding 1.1%.

3. Results and discussion

3.1. Catalyst screening

Screening runs were conducted to assess the relative catalytic activity of various TiO_2 samples and the results are shown in Fig. 1. As clearly seen in Fig. 1a, Degussa P25, Hombicat UV100 and Tronox AK-1 are highly active yielding about 85% conversion after 240 min of reaction, while the respective value for the other three samples is 60–70%. With regard to initial rate computed over the first 15 min of reaction and shown in Fig. 1b, Degussa P25 and Hombicat UV100 are far more effective than the rest. These findings can be assessed in the context of the main mechanisms occurring during semiconductor photocatalysis which, in the case of TiO_2, are briefly described as follows.

It is well documented [20] that irradiation of an aqueous TiO_2 suspension with light energy greater than the band gap energy of the semiconductor (e.g. >3.2 eV for anatase) yields conduction band electrons (e^-) and valence band holes (h^+). Part of the photogenerated carriers recombine in the bulk of the semiconductor, while the rest reach the surface, where the holes, as well as the electrons, act as powerful oxidants and reductants respectively. The photogenerated electrons react with the adsorbed molecular O_2 on the Ti(III) sites, reducing it to superoxide radical anion $O_2^{\bullet -}$, while the photogenerated holes can oxidize either the organic molecules directly, or the OH^- ions and the H_2O molecules adsorbed onto the TiO_2 surface to hydroxyl radicals. These radicals together with other highly

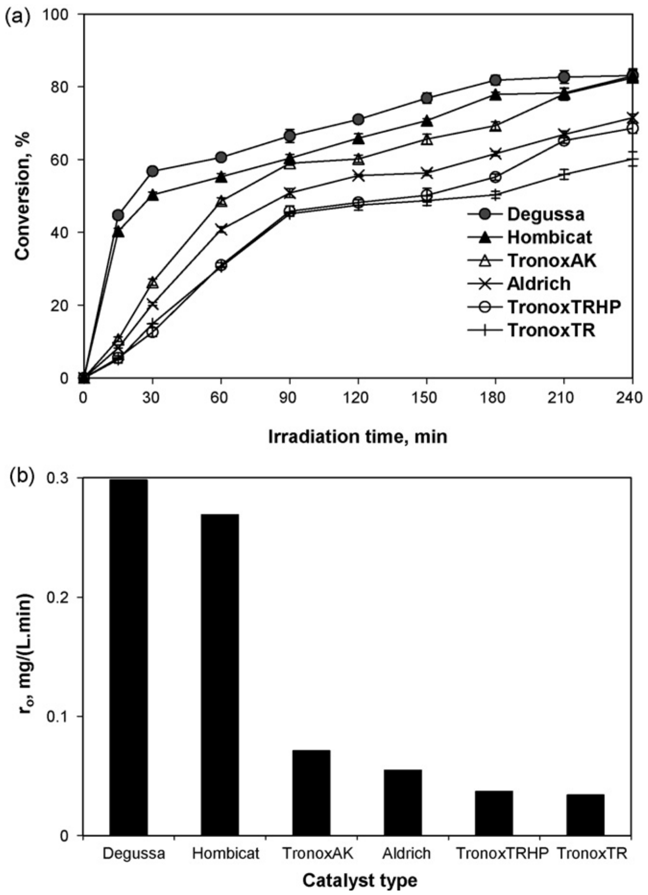

Fig. 1. Effect of TiO_2 type (250 mg/L) on DCF (10 mg/L) degradation: (a) conversion–time profiles and (b) initial rate.

reactive species (e.g. peroxide radicals) are thought to be the primary oxidizing step in photocatalysis. The hydroxyl radicals formed on the illuminated semiconductor surface are very strong oxidizing agents, with a standard oxidation potential of 2.8 V. They can easily attack the adsorbed organic molecules or those located close to the surface of the catalyst, thus leading eventually to their complete mineralization.

As seen in Fig. 1, pure anatase samples exhibit greater activity than pure rutile samples which is in accordance with previous reports stating that anatase has usually a better photocatalytic activity than rutile [21–23]. This may be attributed to several reasons including (i) the different position of the conduction band (more positive for rutile), (ii) the higher recombination velocity of electron/hole pairs in rutile, and (iii) the higher capacity of anatase to adsorb oxygen due to higher density of superficial hydroxyl groups [23]. Moreover, pure anatase samples have larger specific surface areas than pure rutile samples (Table 1) and this may also explain their increased activity. This is so since the rates of electron transfer amongst electrons, holes and the reactants increase with increasing specific surface area particularly at conditions of slow electron/hole recombination [22].

Comparing the pure anatase samples, Hombicat UV100 is notably more active than Aldrich although both samples have similar properties, namely crystalline form, surface area and particle size as seen in Table 1; it is possible that different preparation methods have been employed for the two samples and this could affect properties such as active site density, aggregate particle size in solution and other nano-structural parameters and consequently alter reactivity [24–26]. In addition to the aforementioned argument, the increased activity of Hombicat UV100 compared to Tronox AK-1 may also be due to the fact that the former has a far greater surface area than the latter.

Regarding the two more active catalysts, namely Degussa P25 and Hombicat UV100, the former owes its activity to a slow electron/hole recombination rate, while the high photoreactivity of the latter is due to a fast interfacial electron transfer rate which is typical of pure anatase [27]. Both mechanisms appear to play a critical role for DCF degradation and this would explain the nearly identical activities of Hombicat UV100 and Degussa P25 shown in Fig. 1. Nonetheless, one could argue that Degussa P25 is more active than Hombicat UV100 if comparison were based on a common surface area rather than catalyst loading since, for the same catalyst mass, the surface area of Hombicat UV100 is at least five times greater than Degussa P25. In view of these results, all subsequent runs were done with Degussa P25.

It should be pointed out here that the primary goal of the catalyst screening experiments was to confirm the suspected high activity of Degussa P25 (in the sense that this particular catalyst has been successfully employed in numerous photocatalytic applications) for the degradation of DCF rather than clarify the mechanisms through which different TiO_2 samples exhibit different activities.

3.2. *Effect of catalyst loading*

TiO_2 loading in slurry processes is a significant factor that can affect performance. Fig. 2a shows the effect of catalyst loading on 10 mg/L DCF conversion. As seen, the final (i.e. after 240 min of irradiation at a nominal fluence 0.69 kWh/m^2) conversion is common at about 85% regardless the catalyst loading employed. The reason why conversion levels off and, for instance, it does not reach 100%

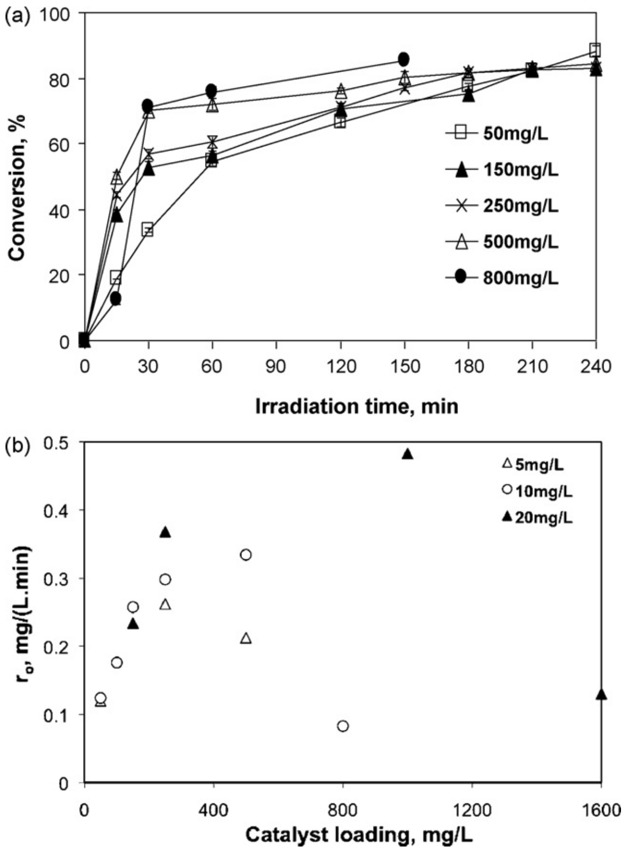

Fig. 2. Effect of Degussa P25 TiO_2 loading on DCF degradation: (a) conversion–time profiles at 10 mg/L DCF and various loadings; (b) initial rate at 5, 10 and 20 mg/L DCF and various loadings.

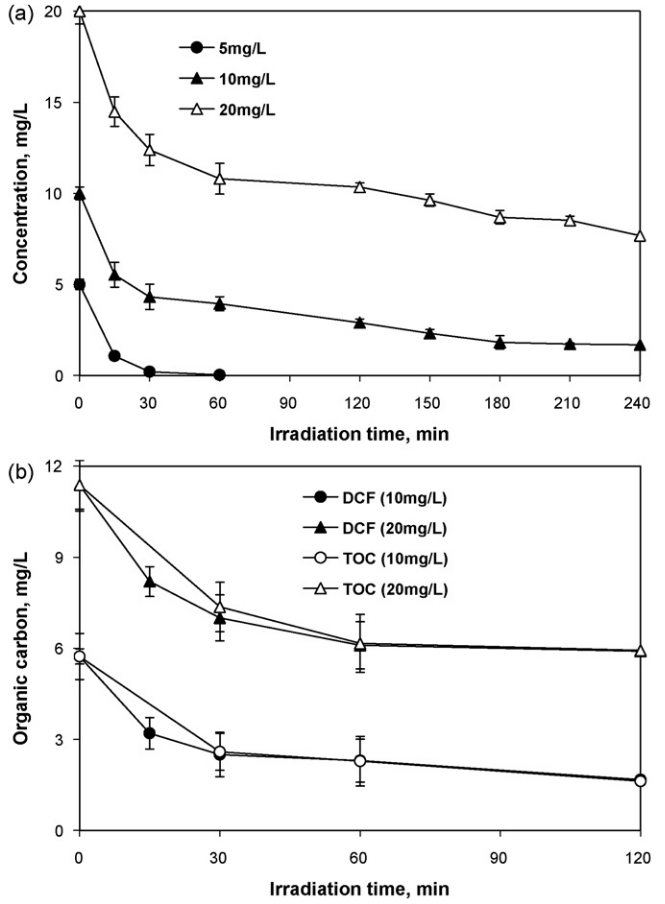

Fig. 3. Effect of initial DCF concentration (5, 10 and 20 mg/L) on degradation at 250 mg/L Degussa P25 TiO_2: (a) concentration–time profiles; (b) comparison between TOC and carbon contained in DCF.

may be the presence of some stable end-products in the reaction mixture that contribute to the measured sample absorbance.

On the contrary, catalyst loading appears to affect the early stages of reaction as seen in Fig. 2b which shows initial degradation rates as a function of catalyst loading at various DCF concentrations (5, 10 and 20 mg/L). The initial rate increases with increasing catalyst loading and reaches a maximum beyond which it drops. At increased catalyst loadings, the excess of catalyst particles may mask part of the photosensitive surface and consequently hinder or even reflect light penetration [28,29], thus resulting in the observed lag-phase. This threshold loading depends on the reactor geometry and operating conditions, as well as the initial substrate concentration [30]; the effect of the latter is clearly seen in Fig. 2b. Interestingly and at the conditions employed in this study, maximum initial rates occur at a common catalyst to DCF concentration ratio of 50. This implies that, during the early reaction stages, kinetics are determined by both the catalyst and substrate concentration.

3.3. Effect of DCF concentration

Fig. 3a shows the effect of initial DCF concentration on degradation at 250 mg/L Degussa P25 TiO_2. Conversion expectedly decreases with increasing initial concentration, i.e. at 60 min (nominal fluence 0.17 kWh/m^2) it becomes 99.5%, 61% and 46% at 5, 10 and 20 mg/L initial concentration, respectively. Nonetheless, process efficiency, in terms of mass of DCF destroyed, is enhanced at increased concentrations, i.e. at 60 min it takes values of 5, 6.1 and 9.2 mg/L, respectively. Rizzo et al. [14] reported that the time needed to achieve 50% conversion (also evaluated measuring absorbance at 276 nm) by means of UV-A irradiation with 200 mg/L Degussa P25 TiO_2 was 16.3 and 82.5 min at 5 and 20 mg/L initial DCF concentration, respectively; these values are in agreement with the results of Fig. 3a.

Fig. 3b shows a comparison of liquid phase TOC and DCF temporal profiles at 10 and 20 mg/L initial concentration, where DCF concentration is expressed in terms of its organic content. Interestingly, the respective curves nearly overlap which implies that the mineralization rates of DCF degradation intermediates are at least equal to the DCF conversion rate. This is rather surprising since photocatalysis is a degrading process and, hence, several intermediates of varying reactivity are likely to be formed prior to mineralization; some of them are expected to be quite recalcitrant to further decomposition, thus not justifying the relative position of the TOC and DCF curves in Fig. 3b (on the contrary, mineralization should be slower than DCF conversion). However, this may happen due to the presence of intermediates that (i) absorb at 276 nm and, thus, misleadingly contribute to the organic content of the DCF curve, and/or (ii) are strongly adsorbed onto the catalyst surface and, thus, do not contribute to the measured TOC.

3.4. Effect of electron acceptor

In further experiments, the effect of adding H_2O_2 at various concentrations (0.07–1.4 mM) on DCF degradation was studied and the results are shown in Fig. 4. In general, H_2O_2 is expected to promote degradation since it may react with conduction band electrons and the superoxide radical anion to yield hydroxyl radicals and anions as follows [27]:

$$H_2O_2 + e^- \rightarrow OH^- + HO^\bullet \tag{1}$$

$$H_2O_2 + O_2^{\bullet -} \rightarrow OH^- + HO^\bullet + O_2 \tag{2}$$

Reactions (1) and (2) enhance reactivity due to (i) the formation of additional oxidizing species and (ii) the suppression of e^-/h^+ recombination, a major cause of low TiO_2 photocatalytic quantum yield. Nonetheless, it is well documented that, depending on the reaction conditions and system in question, there is an optimum H_2O_2 concentration above which H_2O_2 acts as electron and radical scavenger, thus leading to reduced degradation [31,32]. This behavior is clearly demonstrated in Fig. 4; for the run performed at 20 mg/L DCF concentration, H_2O_2 has a beneficial effect for the whole range of concentrations studied. Conversely, for the run at 10 mg/L conversion increases with increasing oxidant concentration up to 0.14 mM above which scavenging effects become important. Noticeably, for the run at 5 mg/L adverse effects occur for the whole range of oxidant concentrations in question, thus showing that the critical factor is the oxidant to substrate concentration ratio rather than the oxidant concentration alone. This is also evident comparing Fig. 4a and c, where the respective runs were performed at a constant catalyst to DCF concentration ratio of 50, thus excluding the effect of catalyst loading on conversion.

Although an exhaustive kinetic analysis was outside the scope of this work, an attempt was made to elucidate degradation kinetics. At a simple level, the rate of reactive oxygen species (ROS) formation is only a function of the operating conditions (e.g. irradiation intensity, catalyst loading) and should remain constant; in this view, DCF degradation may be approximated by:

$$-\frac{d[C]}{dt} = k_{app}[C]^n \tag{3}$$

where k_{app} is an apparent reaction constant incorporating the (constant) concentration of reactive moieties and n is the reaction order. Fig. 5 shows the integrated form of Eq. (3) for $n = 1$ for the three runs of Fig. 4 without H_2O_2 (closed symbols). As seen, pseudo-first order kinetics fit data reasonably well; for instance,

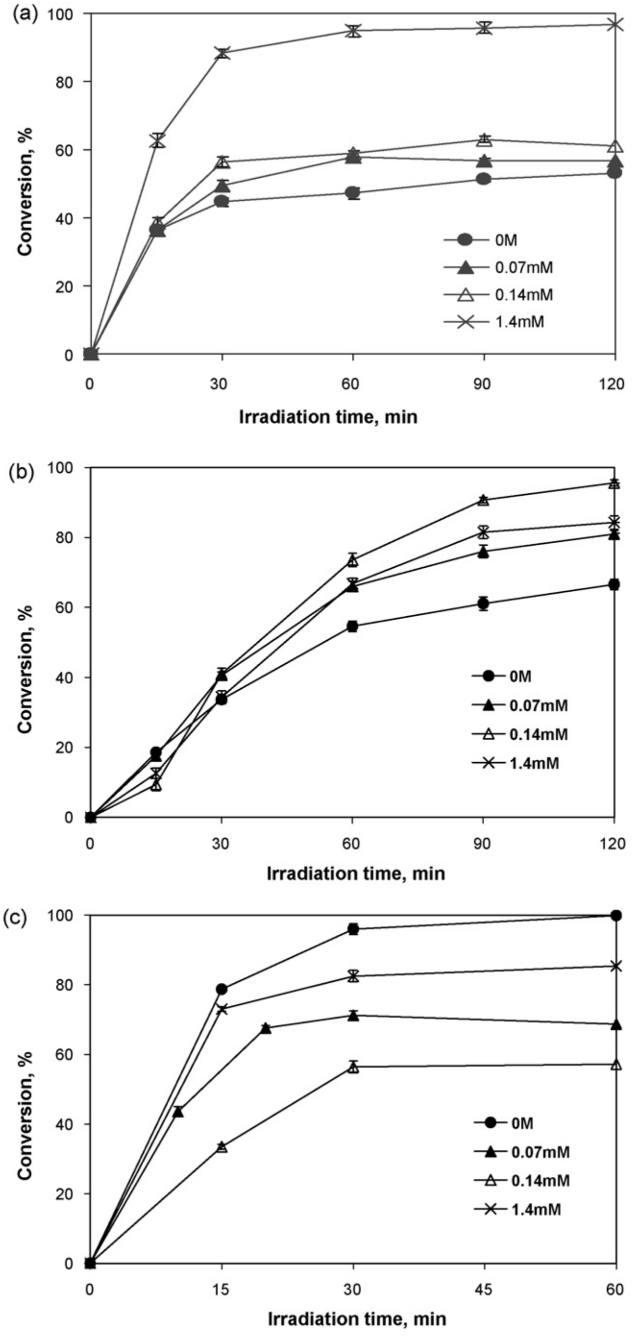

Fig. 4. Effect of H_2O_2 addition (0.07, 0.14 and 1.4 mM) on DCF degradation: (a) 20 mg/L DCF, 1000 mg/L Degussa P25 TiO_2; (b) 10 mg/L DCF, 50 mg/L Degussa P25 TiO_2; (c) 5 mg/L DCF, 250 mg/L Degussa P25 TiO_2.

the regression coefficient of the linear fitting, r^2, is 0.99 for the run at 5 mg/L DCF and from the slope of the straight line k_{app} is computed equal to 0.1 min^{-1}. For the runs at higher concentrations, two regimes appear to exist with different kinetic constants: a fast one at the beginning of the reaction followed by a slower one. For the run at 20 mg/L, k_{app} is 0.03 min^{-1} over the first 15 min and decreases by an order of magnitude thereafter (changes in slope are indicated by dashed lines). As the reaction proceeds, fewer DCF molecules become available to react with ROS (concentration gradients become smaller), while the latter are also consumed to reactions with refractory degradation intermediates; both would justify slower kinetics at prolonged times. Fig. 5 also shows representative data of Fig. 4 in the presence of H_2O_2 (open symbols). The existence of two kinetic regimes is, in this case, more pronounced due to either the beneficial (i.e. fast removal of most DCF at 20 mg/L) or adverse (i.e. occurrence of strong scavenging at 5 mg/L DCF) role of peroxide.

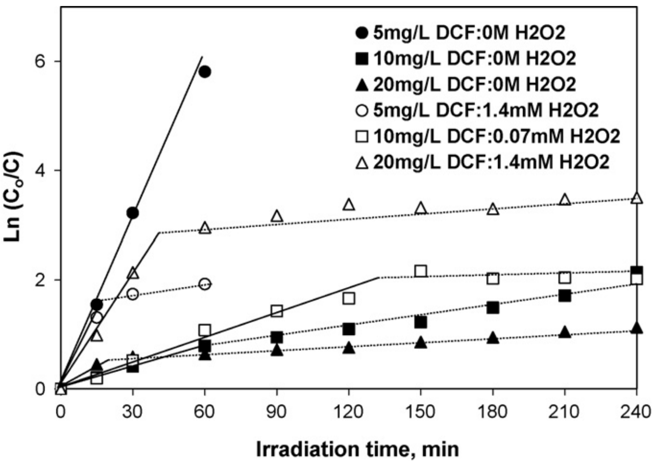

Fig. 5. Pseudo-first order kinetics of DCF degradation with (open symbols) and without (closed symbols) H_2O_2. Other conditions as in Fig. 4.

Fig. 6 shows a comparison between TOC and the organic carbon contained in DCF during representative experiments with H_2O_2 (i.e. at conditions where H_2O_2 promotes reactions). TOC reduction after 120 min (nominal fluence 0.35 kWh/m^2) is 71% and 80% for the runs at 10 and 20 mg/L DCF, respectively. The respective values for the runs without oxidant are 72% and 47% (Fig. 3b). Although data of Figs. 3b and 6 may not be directly comparable to each other since different catalyst loadings were employed, it can be inferred that the addition of H_2O_2 accelerates primarily DCF conversion to intermediates and, to a lesser extent, their subsequent mineralization to carbon dioxide and water. This is clearly demonstrated in Fig. 6, where the discrepancy between the TOC values and the organic carbon contained in DCF corresponds to the carbon content of reaction intermediates.

To exclude the possibility that increased degradation in the presence of H_2O_2 is due to bleaching and/or photobleaching rather than to the contribution of reactions (1) and (2), DCF at a concentration of 10 mg/L was subject to photolysis (i.e. without catalyst) with and without H_2O_2 yielding only 10% and 15% TOC reduction respectively after 120 min of reaction (nominal fluence 0.35 kWh/m^2). The

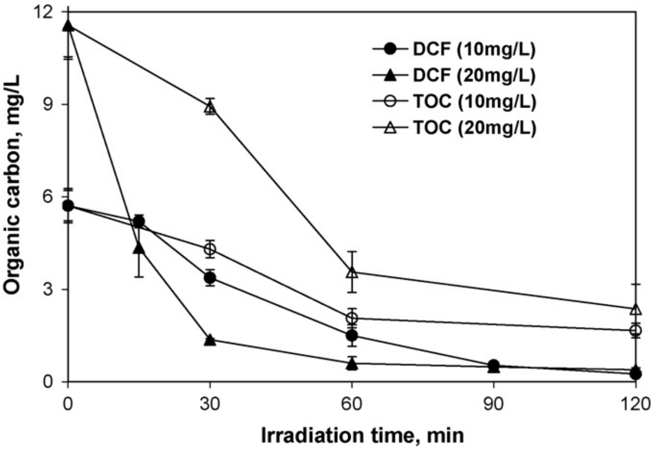

Fig. 6. Temporal profiles of TOC and carbon contained in DCF during irradiation of 10 mg/L DCF (0.14 mM H_2O_2, 50 mg/L Degussa P25 TiO_2) and 20 mg/L DCF (1.4 mM H_2O_2, 1000 mg/L Degussa P25 TiO_2).

Table 2
Extent of mineralization after 120 min at various water matrices.

Sample	Matrix	DCF (mg/L)	TiO_2:TOC ratio	H_2O_2:TOC ratio	Mineralization (%) (SD)
1	DW	10	44	0	73 (±0.50)
2	GW	10	79	0	40 (±0.67)
3	DW	20	22	0	48 (±0.80)
4	Effluent	10	32	0	47 (±0.40)
5	DW	10	9	0.8	71 (±1.20)
6	GW	10	79	0.8	42 (±0.77)

experiment with H_2O_2 was repeated in the dark resulting in only 5% removal.

3.5. *Effect of water matrix*

All runs described so far were conducted in deionized water (DW); to evaluate the effect of water matrix on mineralization, 10 mg/L of DCF were spiked in GW and effluent samples and results are shown in Fig. 7. As seen, the final (i.e. after 120 min, nominal fluence 0.35 kWh/m^2) TOC reduction is 45 ± 5% regardless the matrix and the addition or not of H_2O_2. Table 2 shows data from runs at various matrices and, as clearly seen, organics and other species initially present in GW and the effluent clearly impede degradation (GW and effluent samples already contain about 1.5 and 10 mg/L TOC respectively). For instance, DCF oxidation in DW at a catalyst to TOC ratio of 44 (Sample 1) yields 73% mineralization, while the respective value in GW (Sample 2) is only 40% although the catalyst to TOC ratio is nearly double. It should be noted here that the catalyst to TOC ratio of 44 in Sample 1 corresponds to a catalyst to DCF ratio of 25, i.e. half of the optimum value recorded in Fig. 2b. Therefore, the respective value in Sample 2 would nearly correspond to the optimum ratio (assuming that TOC is exclusively due to DCF). Samples 3 and 4 yield identical mineralization although the latter operates at a 50% greater catalyst to TOC ratio; this implies that the residual organic matter in the treated municipal effluent (which typically consists of macromolecules like humic and fulvic acids, as well as biopolymers) is quite stable to advanced oxidation as has also been reported elsewhere [33].

3.6. *Toxicity*

DCF at 10 mg/L initial concentration was treated photocatalytically with 500 mg/L Degussa P25 TiO_2 and toxicity was monitored as a function of treatment and exposure times, as seen in Fig. 8. The original, unoxidized DCF is slightly toxic to the test microorganism with toxicity expectedly increasing with increasing exposure time. Blank samples containing titania only without DCF were also tested to exclude the possibility that toxicity is owing to catalyst particles. Toxicity steeply increases within the first 15 min of reaction and gradually decreases thereafter up to 60 min. This profile is typical for model solutions of organic pollutants since early degradation by-products are responsible for individual and synergistic toxic effects that are greater than that of the initial compound [34]; at longer treatment times, toxicity decreases to acceptable levels as toxic intermediates are degraded further. Interestingly, the sample taken after 120 min of reaction is highly toxic, thus implying that some of the deep oxidation end-products accumulating in the reaction mixture introduce severe inhibition. A similar trend was observed by Rizzo et al. [14] who investigated the toxicity of photocatalytically treated DCF (20 mg/L of substrate in the presence of 1600 mg/L TiO_2) to *D. magna* and *P. subcapitata*.

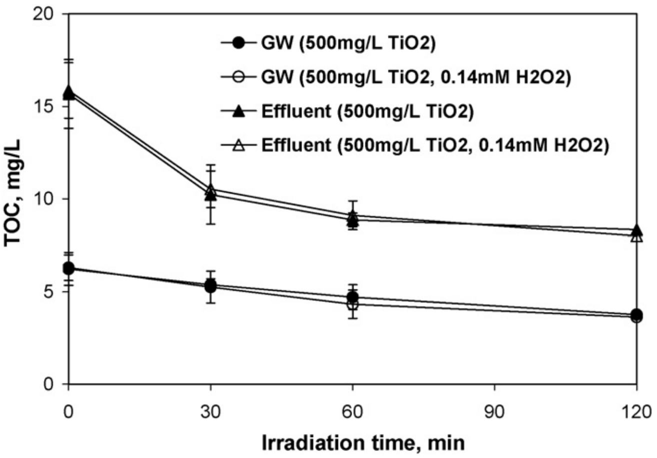

Fig. 7. Effect of water matrix on 10 mg/L DCF mineralization.

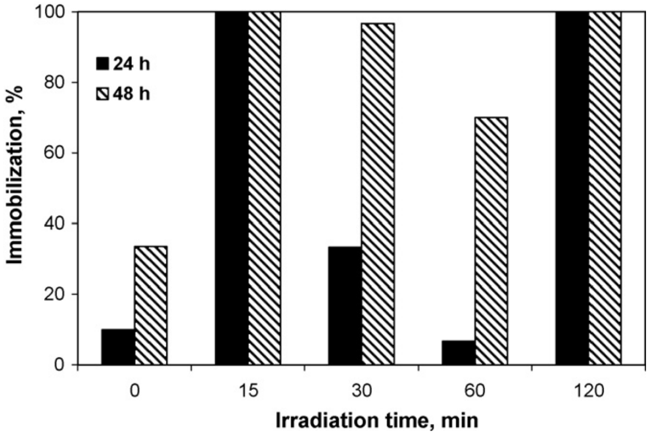

Fig. 8. Evolution of toxicity to *D. magna* at 24 and 48 h exposure times during the photocatalytic degradation of 10 mg/L DCF with 500 mg/L TiO_2.

4. Conclusions

The conclusions drawn from this study can be summarized as follows:

(1) Semiconductor photocatalysis based on titania is an efficient method for the destruction and mineralization of diclofenac in aqueous systems. Process performance is affected by several factors, namely: irradiation time, photocatalyst type, catalyst to substrate concentration ratio and the water matrix (i.e. presence of other scavenging organics, additional oxidants, etc.).
(2) Reaction rate constants increase with decreasing initial concentration. Since the levels of diclofenac and alike compounds in environmental samples are relatively low, their degradation is likely to occur readily at mild operating conditions.
(3) Freshwater microorganisms *D. magna* are more sensitive to DCF degradation by-products than to DCF itself. This is a point of concern, should the treated solution be discharged in aquatic receivers.

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