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Decomposition of diclofenac by solar driven photocatalysis at pilot plant scale

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Abstract

Pilot plant experiments applying solar titanium dioxide photocatalysis and solar photo-Fenton treatment at different pH and iron concentrations with an initial diclofenac concentration of 50 mg L^{-1} are described.

In preliminary experiments absence of hydrolysis and slow photolysis under solar irradiation of diclofenac solutions were observed. Solar photo-Fenton treatment with freshly precipitated iron at pH around 7 showed first order kinetics, the reaction taking place on the surface of the iron precipitate. Simultaneous oxidation, precipitation and re-dissolution processes of diclofenac governed photo-Fenton decomposition kinetics at pH 2.8. The use of different iron concentrations (0.03–0.75 mM) showed no influence on the reaction rate in a neutral medium due to reactor geometry. Similar behaviour (no influence of iron concentration) was observed at pH 2.8, due to precipitation problems. A pH of around 4, close to the pK_a of diclofenac, showed promising results, partly overcoming both iron and diclofenac precipitation. Solar titanium dioxide photocatalysis with Degussa P-25 followed first order kinetics and no precipitation or adsorption occurred.

Decomposition of diclofenac took around 100 min under all photo-Fenton treatment conditions employed. Decomposition by titanium dioxide photocatalysis took about 200 min. In photo-Fenton treatment, hydrogen peroxide consumption to diclofenac decomposition was about 80–110 mM at pH 2.8 and 40 mM in the other two treatments (neutral pH and pH = 4).

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1. Introduction

“Emerging contaminants” are mostly unregulated, and may be candidates for future regulation depending on research on their potential effects on health and monitoring data regarding their occurrence [1]. Examples of compounds that have recently emerged as particularly relevant are surfactants, pharmaceuticals and personal care products. These groups of contaminants do not need to persist in the environment to cause a negative effect, since their high transformation/removal rates can be compensated for by their continuous introduction into the environment. Recently non-steroidal anti-inflammatory drugs (NSAD) have been found in natural water sources, such as rivers, lakes and wells, and in outflows of sewage treatment plants [2–5]. Some studies have also shown that pharmaceutical compounds can reach detectable concentrations due to their large production (hundreds of tons per year) and extended use [6–8]. Diclofenac is an NSAD, mostly used as the sodium salt in medical care as an analgesic, antiarthritic and antirheumatic, and is an important drug in outpatient care. Pollution in the aquatic environment can be attributed to several different sources such as, emission from production sites, direct disposal in households, excretion and human and animal medical care. Balance of the input and output of pharmaceuticals in sewage treatment plants reveals that not all pharmaceuticals are removed during this treatment [9–11] as they have been designed to be lipophilic and biologically persistent to maintain their therapeutic activity

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until their specific physiological function on humans or animals has been performed. Diclofenac is one of the pharmaceutically active compounds most frequently detected in the water-cycle. It is considerably stable under normal environmental conditions and the most probable decomposition pathway for its onsite elimination is photodecomposition [3,9,12].

Due to incomplete removal during the wastewater treatment process, the NSAD have received increasing attention as an emerging class of environmental pollutants [1]. Moreover, many NSAD are photochemically active and a number of adverse responses have been recorded [13]. Diclofenac is transformed producing a carbazole structure (which absorbs visible light) that is an efficient generator of singlet oxygen [14].

Although adopted as the best available technology, biological treatment only partially removes diclofenac, which is discharged into the final effluent. It has thus become evident that the application of more enhanced technologies may be crucial to meeting municipal and industrial wastewater recycling requirements. Recent studies on new treatment technologies for such wastewater frequently consider AOPs (advanced oxidation processes) the most appropriate methods of removing non-biodegradable compounds [15–17]. Advanced oxidation processes (AOP) are characterized by the production of hydroxyl radicals ($^{\bullet}$OH), which are very reactive and produce pollutant mineralisation in the final stages. The AOPs are versatile because they offer several different options for production of radicals, depending on the requirements of the specific treatment target. Recently some research on the removal of diclofenac from contaminated water and drinking water using AOPs have appeared [18–21]. Although diclofenac and AOPs have long been known, it is only recently that they have been put together, as diclofenac becomes more important as an emerging contaminant.

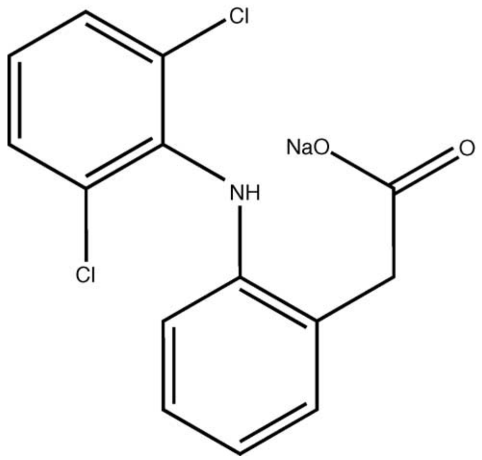
A big advantage of the AOPs is that solar radiation can be used, diminishing the cost of generating the UV radiation required by them. Photo-Fenton is one of the AOPs for which the solar technologies have been most extensively studied and developed [16,22,23]. The Fenton reagent is a mixture of Fe^{2+} salts with hydrogen peroxide (H_2O_2). It can easily oxidize organic compounds, and in recent years has been applied for water and soil treatment [24]. This reagent is an attractive oxidative system, which produces $^{\bullet}$OH radicals in a very simple way. Due to the fact that iron is very abundant and non-toxic and hydrogen peroxide is easy to handle and is environmentally safe, it is a good option for wastewater treatment. Furthermore, it has been found that the reaction can be enhanced by UV–vis light (artificial or natural), producing additional $^{\bullet}$OH radicals and leading to the regeneration of the catalyst. This light-enhanced process is called photo-Fenton. The solar heterogeneous photocatalytic detoxification process consists in utilising the near-ultraviolet (UV) solar spectrum to photoexcite a semiconductor catalyst in the presence of oxygen, generating $^{\bullet}$OH radicals. The most commonly used catalyst is the semiconductor TiO_2.

This article reports on the oxidation of diclofenac at pilot plant scale using solar light with photo-Fenton and TiO_2, two widely used AOP systems with established effectiveness and a highly developed technology [25], which, to our knowledge, have never been applied to diclofenac. The specific aims of the study were to investigate the kinetics of the processes and determine the best conditions of those tested.

2. Experimental

Diclofenac sodium salt was from Sigma–Aldrich and used as obtained (see Scheme 1). $Fe_2(SO_4)_3{\cdot}xH_2O$ (75%) was used as the iron source, H_2SO_4 and NaOH for pH-adjustments. H_2O_2 was 30% (w/v). TiO_2 was Degussa P-25. Standard freshwater was reconstructed by addition of 96 mg L^{-1} $NaHCO_3$, 60 mg L^{-1} $CaSO_4{\cdot}2H_2O$, 60 mg L^{-1} $MgSO_4$ and 4 mg L^{-1} KCl to distilled water, which resembles the composition of a moderately hard freshwater [26]. We did not add any humic substances to this ‘‘standard fresh water’’ because their concentration varies widely in different regions and water sources (groundwater, river water, etc.), and is very low in the arid and semi-arid regions where solar technologies can be applied. Our intention was not to test the effect of humic substances, but to perform photocatalytic tests in the presence of inorganic anions and cations that could also affect the reaction kinetics due to $^{\bullet}$OH radical scavenging and solubility equilibrium. A sentence has been added in the experimental section clarifying these statements. All reagents were analytical grade except H_2O_2 (reagent grade) and TiO_2 (commercial product quality).

Dissolved organic carbon (DOC) was measured after filtration (0.22 μm, nylon) by means of a TOC analyser, model Shimadzu TOC 5050A equipped with an ASI5000 autosampler. Diclofenac concentration was determined using reverse-phase liquid chromatography (flow rate 0.5 mL min^{-1}) with UV detector in an HPLC-UV (Agilent



Scheme 1. Diclofenac structure.

Technologies, series 1100) with C-18 column (LUNA 5 μm, 3 mm × 150 mm, from Phenomenex). Diclofenac was determined by isocratic elution with a 50% aqueous of 10 mM ammonium formiate buffer solution/50% acetonitrile. The sample was prepared by dilution with acetonitrile and subsequent filtration. Cation concentrations were determined with a Dionex DX-120 ion chromatograph equipped with a Dionex Ionpac CS12A 4 mm × 250 mm column. Isocratic elution was done with H_2SO_4 (10 mM) at a flow rate of 1.2 mL min^{-1}. Anion and carboxylic acid concentrations were measured with a Dionex DX-600 ion chromatograph using a Dionex Ionpac AS11-HC 4 mm × 250 mm column. Flow rate was 1.5 mL min^{-1} and elution was done with NaOH gradient programmes. pH measurements were carried out with a Crison pH-meter, model micro pH 2002. H_2O_2 concentration was determined by iodometric titration and temperature was measured directly in the pilot plant.

Photo-Fenton and TiO_2 experiments were performed in a compound parabolic collector solar pilot plant (Almería, Spain, latitude 37°N, longitude 2.4°W) with a total volume of 35 L, illuminated volume of 22 L and irradiated collector surface of 3.08 m^2 [23]. The plant works in batch mode, continuously recirculating the whole volume in the reactor, maintaining turbulent flow in the absorber tubes. The temperature inside the reactor depends on season and weather, but is usually between 30 and 40 °C.

At the beginning of the experiments, with collectors covered, all the chemicals are added to the tank and mixed until constant concentration is achieved throughout the system. Then the cover is removed and samples are collected at predetermined times (t). Hydrogen peroxide concentration was maintained around 200–400 mg L^{-1} by continual additions as it was consumed. Solar ultraviolet radiation (UV) was measured by a global UV radiometer (KIPP&-ZONEN, model CUV3), mounted on a platform tilted 37° (the same angle as the CPCs), which provides data in terms of incident W_{UV} m^{-2}. This gives an idea of the energy reaching any surface in the same position with regard to the sun. With Eq. (1), combination of the data from several days' experiments and their comparison with other photocatalytic experiments is possible.

$$t_{30W,n} = t_{30} + \Delta t_n \frac{UV}{30}\frac{V_i}{V_T}, \quad \Delta t_n = t_n - t_{n-1} \qquad (1)$$

where t_n is the experimental time for each sample, UV the average solar ultraviolet radiation measured during Δt_n, and t_{30W} a "normalized illumination time". In this case, time refers to a constant solar UV power of 30 W m^{-2} (typical solar UV power on a perfectly sunny day around noon).

Hydrolysis and photolysis experiments were performed in 3 L Pyrex beakers (UV transmissivity > 80% between 320 and 400 nm, around 40% at 300 nm, internal diameter 15 cm) and covered with a Pyrex top (not airtight) to avoid sample contamination and evaporation. During hydrolysis tests, the beakers were kept in the dark. The pilot plant was not used for this purpose to avoid any slight effect of TiO_2 deposits on the photoreactor tubes, as removal of the thin catalyst coating remaining on the tubes after TiO_2 suspensions have circulated through them, is a very hard, complex and expensive task due to the dimensions of the tubes and the plant itself. The maximum temperature inside the beakers was 35 °C.

3. Results and discussion

3.1. Hydrolysis and photolysis

Several blank experiments, at the same initial concentrations as the photocatalytic experiments were performed, first to guarantee that the results obtained during the photocatalytic tests were consistent and not due to hydrolysis and/or photolysis. Hydrolysis experiments were performed at different pH (3, 7 and 9). No hydrolysis was detected at pH 7 and 9 after 72 h. Results at pH 3 (90% disappearance of diclofenac and TOC in 3 h) should be discussed in detail, because they are related to several points that are very important to the overall results. Diclofenac is a very soluble in neutral-alkaline medium (50 g L^{-1}) and acidic pharmaceutical (pK_a = 4.15; [12]) that becomes almost insoluble below pH 4, so below this pH value, diclofenac precipitates. But it was demonstrated that no diclofenac was really degraded because the complete volume of diclofenac (water + precipitate) was re-dissolved using acetonitrile and all the initial diclofenac was recovered. This finding was very important for the rest of the results reported in this paper, as an acid medium is very easily achieved during diclofenac decomposition due to chloride release. Results could be inconsistent if "precipitation" were not clearly stated and confused with "decomposition".

At this point it should be remarked that the review of the literature (as commented on in Section 1) has not reported this effect. Almost all the AOPs used before to degrade diclofenac have been carried out in a neutral or basic medium, as mainly O_3, O_3/UV, H_2O_2/UV have been applied. In all these cases pH was set at 7 or higher by adding sodium hydroxide. The only work where the photo-Fenton degradation of diclofenac was carried out at pH 2.8 [21] does not mention precipitation of this pharmaceutical.

Table 1 shows the results of photolysis experiments with diclofenac dissolved in demineralised water and in

Table 1
Photolysis expressed as % disappearance of diclofenac

$t_{illum.}$ (A) (h)	%	$t_{illum.}$ (B) (h)	%
4	28	7	36
11	47	27	71
18	59	34	75
32	68	62	85

C_0 = 50 mg L^{-1}. A: demineralised water at pH 7.5; B: standard freshwater at pH 7.2.

reconstructed freshwater. The results obtained indicate that the photolytic decomposition due to solar illumination is important. Photolysis in demineralised water showed a spontaneous drop of pH due to chloride release. In order to avoid diclofenac precipitation, small quantities of sodium hydroxide had to be added to maintain the pH above the pK_a. This was not necessary in the case of the experiment performed with standard freshwater due to the pH buffer capacity of this type of water. Results of demineralised and standard freshwater were very similar.

Diclofenac and solar UV (latitude 37°N, longitude 2.4°W) spectra overlap in the 300–330 nm region because diclofenac has a maximum at 273 nm that tails well over 300 nm [21], showing that absorption of solar photons can produce photodegradation. But such natural photodecomposition is very slow under well-illuminated aerobic conditions (transparent glass, 15 cm i.d.) and mineralisation (measured by TOC analysis) never occurred. The effect has been described before in natural water [3,9,12,27] in which the solution becomes red-brown, presumably as a consequence of formation of carbazole structures, as stated by Moore [13], and release of chlorine substituents. Photolysis produced significant substrate decay during the first hours and afterwards was slowed down markedly, probably because of the accumulation of reaction intermediates acting as ‘‘inner’’ filters. In any case, the environmental fate of diclofenac has not yet been clearly stated and, therefore, disposal into the environment could be very risky.

3.2. Photo-Fenton decomposition in standard freshwater in a neutral medium

It is well known that ferric iron precipitates at neutral pH, but iron precipitation and aging of the precipitate is a complex process. First oligomers are formed, which grow and then dehydrate until finally thermodynamically stable precipitates are formed [28,29]. Furthermore, the solutions are irradiated in the experiments, so parallel to the thermal aging processes photoreductive decomposition of colloidal iron and iron precipitate can release ferrous iron to the solution, which will be re-oxidised with hydrogen peroxide present (Fenton reaction producing hydroxyl radical) or oxygen. This photoreduction is a ligand-to-metal charge transfer reaction, where the ligand can be water or an organic substance [30,31]. In addition, ferric iron precipitates can have semiconductor properties, so further possible reactions are the production of electron–hole pairs upon incidence of a photon and the consecutive oxidation of contaminants adsorbed on the surface [31,32].

In view of the above, photo-Fenton treatment with freshly precipitated iron at pH 7 was performed to prevent diclofenac insolubilisation. Experiments were carried out with standard freshwater to provide a neutral medium. Addition of iron has an acidifying effect due to the formation of different ferric iron precipitates as mentioned. If iron concentrations are high enough, this acidifying effect can exceed the buffer capacity of standard freshwater due to the hydrogen carbonate added. Therefore, the amount of sodium hydrogen carbonate added was raised according to the concentration of iron added (molar ratio 3:1) compared to indications in the literature [26].

Results of dissolved organic carbon (DOC) mineralisation, diclofenac decomposition and hydrogen peroxide consumption are depicted in Fig. 1a and b. Diclofenac decomposition behaves like a first order reaction, while hydrogen peroxide consumption and DOC mineralisation trends are steady like zero order kinetics. Diclofenac decomposition and hydrogen peroxide consumption are

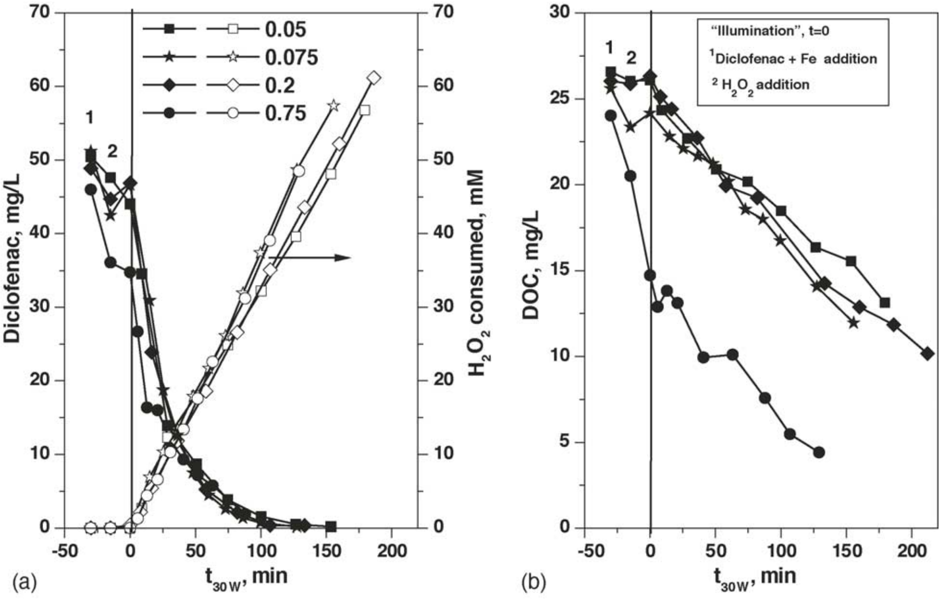


Fig. 1. Photo-Fenton treatment in neutral standard freshwater medium. Different series (0.05, 0.075, 0.2, 0.75 mM) are the different iron concentrations employed.

observed to be similar for all iron concentrations. In contrast, at first sight, DOC mineralisation seems to depend upon iron concentration. If the initial rapid decrease in the experiment with higher iron concentrations were not reconsidered, there would seem to be a steady decrease, regardless of iron concentration. The explanation could be that transient amorphous iron precipitates are positively charged [29], while diclofenac at pH 7 is mostly deprotonated, i.e., negatively charged. Chemical adsorption of diclofenac on the iron precipitates is thereby favoured. The more iron precipitate present, the stronger this effect is. It should therefore be stated that due to the adsorption phenomena, under these reaction conditions a decrease in DOC does not guarantee detoxification. The way in which samples are analysed permits diclofenac dissolved and adsorbed on iron oxide to be measured at the same time. The samples are mixed with an equivalent amount of acetonitrile, which desorbs diclofenac from the precipitate. Afterwards they are filtered and injected in HPLC.

The similar decomposition performance for all iron concentrations could be explained by combining reactor geometry considerations, light absorption and diclofenac adsorption. The CPC absorber tube has an inner diameter of 29.7 mm. The penetration depth of photocatalytically active radiation depends upon the optical density of the solution. Amorphous iron oxide is very strongly light absorptive, so that all the available active radiation is absorbed, even in the experiment with the lowest iron concentration (0.05 mM), leading to a reaction rate independent of the iron concentration. This would explain the linear hydrogen peroxide consumption if a ligand-to-metal charge-transfer reaction with water as the ligand were responsible for photoreduction of iron and subsequent re-oxidation by hydrogen peroxide, producing hydroxyl radicals by the Fenton reaction. The reaction of diclofenac might also be a Langmuir–Hinshelwood mechanism on the surface of the iron precipitate causing first order behaviour. This would be a ligand-to-metal charge transfer or oxidation by photo-generated electron–holes [31].

In all the experiments, diclofenac decomposition took around 100–110 min. Hydrogen peroxide consumption to achieve this decomposition is around 35–40 mM. This by far exceeds the theoretical stoichiometric demand of hydrogen peroxide for oxidation of 50 mg L^{-1} of diclofenac (5.3 mM). If the mechanism responsible for diclofenac oxidation is a reaction on the surface of the iron precipitates, an alternative treatment without addition of hydrogen peroxide could be proposed, because ferrous iron is readily oxidised to ferric iron and consequently precipitated in a neutral medium [30].

3.3. Photo-Fenton treatment in standard freshwater acidified to pH 2.8

Photo-Fenton treatment is usually performed in an acid medium to maintain the iron in solution. Some authors have worked in a certain range of low pH values, but most have followed the suggestion of Pignatello [33], who proposed a pH of 2.8 as optimal. In acid medium, diclofenac becomes practically insoluble. Consequently, oxidising species (e.g., hydroxyl radicals) have to diffuse the pollutant precipitate (a heterogeneous process) or react with the small dissolved share of the pollutant (a homogeneous process with pollutant solubility equilibrium as an influencing factor).

DOC mineralisation, diclofenac decomposition and chloride and ammonium evolution are shown for an experiment with a 0.075 mM iron concentration, in Fig. 2, in which DOC and diclofenac are already seen to decrease after the addition of acid and iron, but before the addition of hydrogen peroxide, indicating the precipitation of diclofenac. The following unusual behaviour during the experiment is provoked by continuous decomposition, precipitation and re-dissolution processes.

Therefore, measurement of DOC and diclofenac concentration during the experiment cannot guarantee correct evaluation of diclofenac decomposition. However, the evolution of inorganic ions can give an indication of the oxidation process, as these ions are soluble and can be measured by ion chromatography. Chloride release from the aromatic ring is often one of the first steps in the oxidation of aromatic compounds taking place in treatment with advanced oxidation processes. Evolution of the theoretical amount of chloride to be released of the known initial diclofenac concentration indicates that the original compound is fully degraded. The evolution of chloride can thus be used to compare the results of the HPLC analysis of diclofenac in the experiments performed in a neutral medium and the experiments at pH 2.8. The mineralisation of the organic nitrogen in the diclofenac molecule, which joins the two aromatic rings, is a bit slower than chloride evolution (see Fig. 2). Almost no organic nitrogen was mineralised to nitrate compared to ammonium (less than 3%). Consequently, only ammonium evolution was considered. The evolution of the theoretical amount of ammonium indicates a rather well-advanced mineralisation

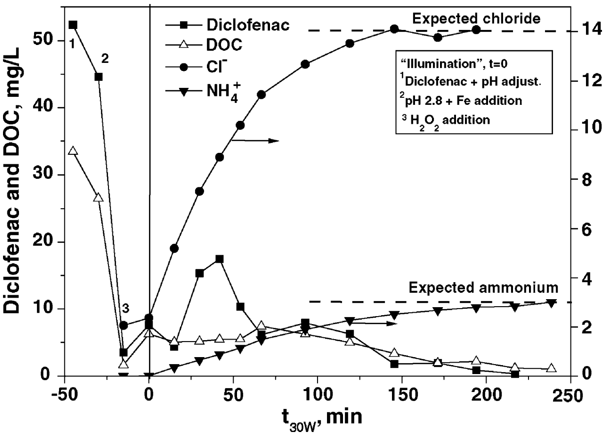


Fig. 2. Photo-Fenton treatment at pH 2.8 with 0.075 mM iron in standard freshwater.

of the compound. Due to the molecular structure of diclofenac it is probable that nitrogen release is one of the last steps before the molecular structure becomes completely mineralised (cf. Scheme 1).

Fig. 3a–c shows the release of chloride and ammonium and the hydrogen peroxide consumption in photo-Fenton experiments at 0.03, 0.075, 0.3 and 0.75 mM of iron. Even though the iron concentrations are quite different (factor 25 between lowest and highest concentrations) in the four experiments, the differences in chloride and ammonium evolution, as well as the consumption of hydrogen peroxide are slight. Only the experiment with the highest iron concentration is notably faster. Stoichiometric chloride evolution takes around 100 min in all the experiments, which is quite similar to disappearance of diclofenac as measured with HPLC in the experiments at pH around 7. Stoichiometric ammonium evolution takes 160–250 min. So the differences in ammonium evolution for the four iron concentrations are slightly more pronounced. The same is true for hydrogen peroxide consumption. Nevertheless, as mentioned above with regard to the rather different iron concentrations, hydrogen peroxide decomposition rates are quite similar. Blank experiments with only hydrogen peroxide and iron without any organic substance showed similar behaviour (experiments not shown). One explanation could be that hydroxyl radical generation is higher at higher iron concentrations, but due to the low concentrations of scavenging substances (almost no pollutant dissolved) radical recombination reconstituting hydrogen peroxide is a major fate of the hydrogen peroxide produced. It is therefore suggested that the radical concentrations in the solution are also higher at higher iron concentrations, which could explain why soluble intermediate decomposition products are mineralised and ammonium production is quicker at higher iron concentrations. On the other hand, diclofenac oxidation, as indicated by chloride release, seems to depend on the solubilisation of the compound. This is also indicated by the high hydrogen peroxide consumption until complete dechlorination (80–110 mM, see Fig. 3c), which is about 15–20 times the stoichiometric demand of complete diclofenac mineralisation.

3.4. Photo-Fenton treatment in distilled water without control of pH

Both treatment in neutral and acid media were shown to be disadvantageous to iron and diclofenac precipitation. Therefore, photo-Fenton treatment was performed starting at pH around 7 but with water with no pH buffer capacity, so that the resulting pH would change from 7 to 3.7 during treatment due to the formation of intermediate carboxylic acids and dechlorination. This means that diclofenac is more soluble because the pH is close to the pK_a (4.15; [12]) and iron precipitation should be slowed down, possibly yielding an overall accelerated decomposition.

The results of this experiment are depicted in Fig. 4. In this experiment diclofenac decomposition as measured by HPLC and chloride evolution almost coincide, although the slight increase in chloride concentration after disappearance of diclofenac indicates that some diclofenac had precipitated due to the decreased pH. Note that this precipitation could not be clearly determined because diclofenac decomposition was so fast. Again, ammonium formation is slower than chloride evolution. The DOC mineralisation profile also indicates that the process is determined by the solubility equilibrium of diclofenac as influenced by the pH. The DOC increase after several minutes is due to oxidation of soluble intermediates that are formed and in the further course of the

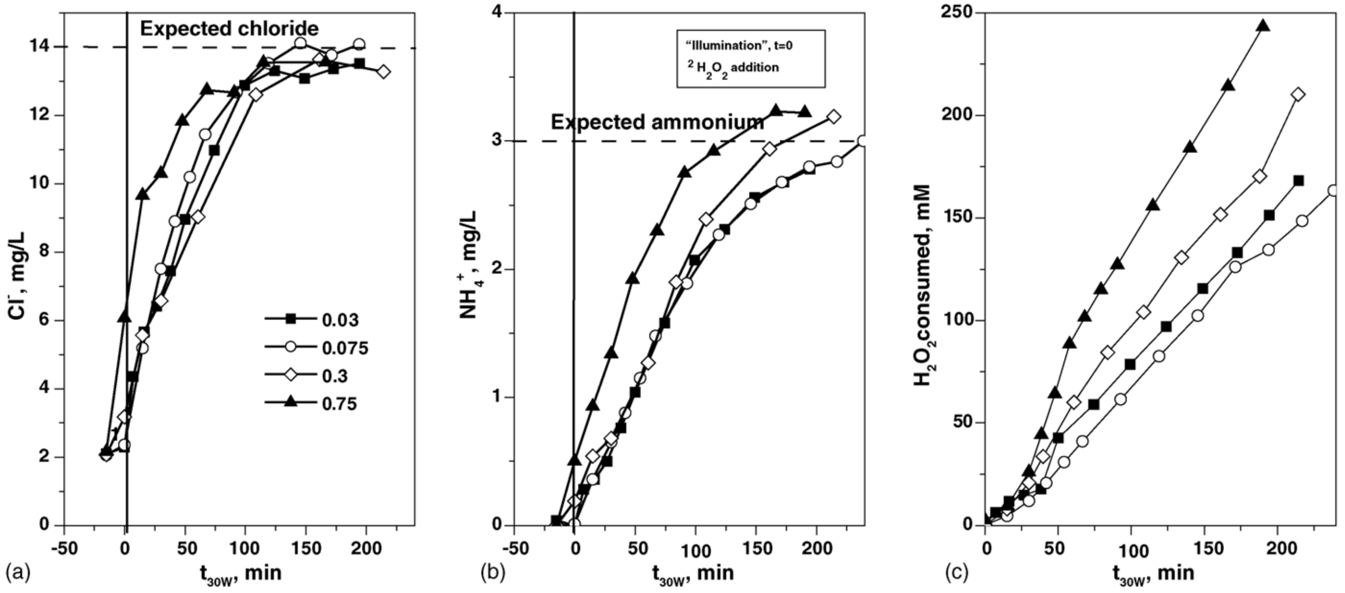


Fig. 3. Photo-Fenton treatment at pH 2.8 at four different iron concentrations (0.03, 0.075, 0.3, 0.75 mM) in standard fresh water. No H_2O_2 consumption was detected before the start of illumination.

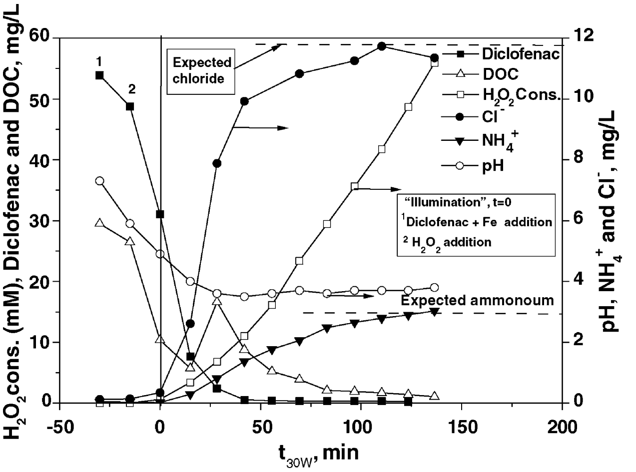


Fig. 4. Photo-Fenton treatment at 0.05 mM iron concentration starting at pH 7 with no pH buffer capacity (distilled water).

reaction mineralised. To identify part of these oxidation products, carboxylic acids were determined. Maleic, acetic, formic and oxalic acids were detected. Coinciding with the maximum DOC after 30 min, the maximum acid concentrations detected were around 0.1, 1.5, 4.0 and 7.0 mg L^{-1} for maleic, acetic, formic and oxalic acid, respectively. Acetic acid seemed to be the most recalcitrant of them and along with oxalic acid, the only one that was found in low concentrations until the end of the experiment. No acids containing three carbon atoms were found.

When HPLC measurements are used to assess the process, diclofenac decomposition takes around 50 min and H_2O_2 consumption up to this point is around 15 mM. This is considerably faster than in the other two cases, and H_2O_2 consumption is also much lower. When stoichiometric chloride evolution is used to assess the experiment, decomposition time again increases to around 100 min as in the other two photo-Fenton treatments, and H_2O_2 consumption increases to around 40 mM.

From the results obtained, pH control around pH 4.5–5 seemed promising. At the same time, addition of iron complexing substances could also enhance the process at this elevated pH, as proposed by several authors, to prevent iron precipitation [34–36].

3.5. TiO_2 photocatalysis in a neutral medium

After all the difficulties encountered due to the insolubility of diclofenac at low pH, titanium dioxide photocatalysis was employed, because it can be conducted without adjustment of pH. The experiment was performed in standard freshwater and with 0.2 g L^{-1} TiO_2 in suspension, because this value is near the optimum according to the reaction rate in previous experiments [37].

The results are depicted in Fig. 5. Again chloride evolution coincides with diclofenac decomposition measured by HPLC. Total diclofenac decomposition takes place after around 200 min, which is slower than in all the photo-Fenton treatments applied. As can be seen in Fig. 5, the decomposition kinetics perfectly fit pseudo-first order kinetics according to the generally accepted Langmuir–Hinshelwood mechanism for titanium dioxide photocatalysis [38]. DOC oxidation begins after an initial lag phase of more than 100 min, which is typical for photocatalytic oxidation, because the first reactions taking place do not induce mineralisation but only partial oxidation of the compound.

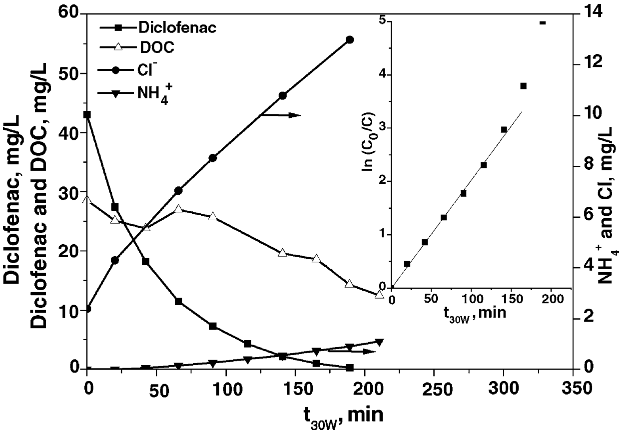


Fig. 5. TiO_2 (0.2 g L^{-1}) photocatalysis in standard freshwater.

4. Conclusions

Diclofenac is a weak acid, soluble in its deprotonised form, but practically insoluble when protonised. In the present study, no hydrolysis was detected at pH 7 or 9. Precipitation occurred at pH 3. Solar photolysis experiments at pH 7 led to slow diclofenac decomposition and the solution became red-brown.

The solubility equilibrium dependent on the pH of diclofenac and iron were also shown to be determining for application of solar-driven iron/hydrogen peroxide catalysed decomposition of diclofenac. At pH 7, undefined fresh iron precipitates degrade diclofenac under solar irradiation following pseudo-first order kinetics. Different iron concentrations showed like decomposition rates due to shading effects of the highly absorptive iron precipitates inside the photoreactor absorber tubes.

Results of photo-Fenton treatment at pH 2.8 indicated that diclofenac decomposition takes place in the homogeneous phase, and the process kinetics are governed by the continuous re-dissolution of diclofenac. As a consequence, different iron concentrations again showed no influence on the pollutant decomposition rate.

Photo-Fenton treatment starting at a pH of around 7 but with no pH buffer capacity, caused a decrease to pH 3.7 during the experiment, and diclofenac and iron precipitation could be partly overcome. Diclofenac decomposition with titanium dioxide photocatalysis in the same reactor followed pseudo-first order kinetics and no precipitation occurred.

Comparison of diclofenac decomposition shows that, it was complete after around 100 min in all photo-Fenton treatments, but hydrogen peroxide consumption was more than double at pH 2.8. Diclofenac decomposition with titanium dioxide took around twice as long. So although diclofenac and the photo-Fenton process seem to be incompatible at first sight due to the compound's insolubility at low pH, the reaction rate is still significantly higher in the photo-Fenton process under all the reaction conditions employed.

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