



Photo-Fenton process at natural conditions of pH, iron, ions, and humic acids for degradation of diuron and amoxicillin

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Abstract

Effect of ferric ions at concentrations typically found in natural waters (0.05 to 1.06 mg L⁻¹) and low H₂O₂ concentrations (between 0.5 and 17.9 mg L⁻¹) on simulated sunlight-induced (300 W m⁻²) photo-Fenton degradation at initial neutral pH (7.0) of amoxicillin and diuron in Milli-Q water was studied using an rotatable central composite experimental design 2² with a central and two axial points. H₂O₂ concentration was the parameter playing the key role on the degradation of both pollutants. Despite that initial pH was 7.0 in Milli-Q water, this latter decreased rapidly in the first minutes, reaching values of 3.5 and 5.0 for diuron and amoxicillin respectively after 15 min of simulated sunlight irradiation. In contrast, in presence of bicarbonate/carbonate (HCO₃⁻/CO₃⁼), fluoride (F⁻), and humic acids (HAs) at concentrations found often in surface and well waters with ferric ion and H₂O₂ concentrations of 0.3 and 9.7 and 15.2 mg L⁻¹ respectively, both pollutants exhibited a strong degradation keeping the circumneutral pH. Amoxicillin and diuron degradation byproducts found by HPLC/MS were compatible with HO[•] and/or CO₃^{-•} radical attack. Several photo-induced processes such as photo-Fenton (by dissolved ferric-HA complexes), heterogeneous photocatalysis (by colloidal iron), UV-B H₂O₂ photolysis, irradiated-dissolved organic matter, and their reactions with pollutants would be the main oxidative route responsible of degradations. These findings demonstrated that it could be possible using iron concentrations often found in natural waters to oxidize via photo-Fenton processes among other events, organic pollutants at natural pH conditions.

Keywords Circumneutral photo-Fenton · Diuron · Amoxicillin · H₂O₂ photolysis · Water detoxification · Low iron amounts

Introduction

Photo-Fenton processes have arisen as a promising alternative to the abatement of chemical pollutants in water (Ikehata and

El-Din 2006; Pignatello et al. 2006; Oturan and Aaron 2014; Leyva et al. 2018). This makes use of photoactive ferric aqua-complexes, which are predominantly present at acid pH (~ 2.7). Under UV-A irradiation, these aqua-complexes generate

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ferric ion reduction leading to the formation of ferrous iron and HO[•] radicals. Then, in presence of hydrogen peroxide, ferrous ions are oxidized to ferric and HO[•] radicals (Fenton reaction) (Pignatello et al. 2006; Gutierrez-Mata et al. 2017).

Although photo-Fenton processes show encouraging characteristics to degrade chemical pollutants in water, they exhibit two main drawbacks: the first one is related with using acidic pH. Several strategies have been explored in the literature in order to expand the pH range of photo-Fenton processes towards circumneutral or neutral values (Clarizia et al. 2017; Nogueira et al. 2017). For instance, complexing ferric ions with organics such as oxalate, EDTA, and other aliphatic acids have arisen as a successful strategy since most part of these ferric-complexes are stable and photoactive in pH ranges close to the neutrality (Clarizia et al. 2017). However, some questions about its implementation such as increasing of the total organic carbon content and most importantly concerns about the ecotoxicity and biodegradability of chelators and byproducts formed after the photochemical event have emerged (Clarizia et al. 2017). The second important drawback of photo-Fenton processes is the high amounts of both iron and hydrogen peroxide often used. The former could cause the production of important iron-sludge which must be removed from water and subsequently disposed, and the latter could produce alterations on aquatic environments (Wang et al. 2016a).

In this study, two anthropogenic pollutants found often in natural waters, diuron and amoxicillin, were chosen. Diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea) is a water-soluble phenylurea herbicide (42.0 mg L⁻¹ at 25 °C) with low biodegradation and extensively used in cotton and citric crops in USA. Environmental protection agency (USEPA 2003) reported an annual consumption of 4500 ton in 2002 while in Argentina, it was estimated 242 tons in 2016 (SENASA 2016). On the other hand, amoxicillin is a widely used β-lactam antibiotic of broad spectrum (World Health Organization 2018).

Regarding the abatement of diuron and amoxicillin by photo-Fenton processes, several studies have been reported (Mazellier et al. 1997; Malato et al. 2003; Nogueira et al. 2005; Farré et al. 2006, 2007; Maldonado et al. 2007; Catalkaya and Kargi 2008; Trovó et al. 2008, 2011; Elmolla and Chaudhuri 2009; Oturan et al. 2011; Klamerth et al. 2013; Pereira et al. 2014; Rodríguez-Chueca et al. 2014; Alalm et al. 2015; Perini et al. 2018; Liu et al. 2018). A common point for all these studies is the use of high amounts of both ferric and ferrous salts (2–500 mg L⁻¹), hydrogen peroxide (74.0–1500.0 mg L⁻¹), and acidic pH (2.8–3.5). In the literature, there are just few studies about diuron and amoxicillin degradation induced by photo-Fenton reactions at circumneutral pH. All these studies have been performed using complexing agents such as ethylenediamine-N,N-disuccinic acid (EDDS), oxalate, and citric acid with iron and H₂O₂ concentrations of

1.6–5.0 and 17.0–70.0 mg L⁻¹, respectively (Trovó et al. 2008; Klamerth et al. 2009, 2013; Pereira et al. 2014).

Another approach, which has not extensively explored towards removal of organic pollutants, is using photo-Fenton processes under natural conditions. Some authors have argued that natural surface waters irradiated with sunlight may promote low concentrations of HO[•] radicals through several photochemical processes, mainly photo-Fenton reaction with natural iron and H₂O₂ concentrations (Millero and Sotolongo 1989; Nakatani et al. 2007; De Laurentiis et al. 2014; Gligorovski et al. 2015).

Sciacca et al. (Sciacca et al. 2010) published for the first time that simple adding of 10.0 mg L⁻¹ of hydrogen peroxide to natural Sahelian surface waters containing 0.3 mg L⁻¹ of total iron led to the *E. coli* and *Salmonella* inactivation under natural sunlight irradiation demonstrating that H₂O₂ could enhance natural photochemical events including photo-Fenton. Recently, some authors have demonstrated that it is possible to induce photo-Fenton processes at low natural iron concentrations often present in natural waters (0.3–0.6 mg L⁻¹) and H₂O₂ concentrations ranging between 3 and 10 mg L⁻¹ to achieve degradation of several pollutants in water by photo-Fenton processes under simulated and sunlight irradiation (Serra-Clusellas et al. 2018; Ulliman et al. 2018). Furthermore, Gutierrez-Zapata et al. (2016) and Alvear-Daza et al. (2018a, c) have also applied this approach in natural well waters, which already contain natural iron concentrations (0.3 mg L⁻¹), to remove simultaneously 2,4-D and bacteria by the simple addition of H₂O₂ (10 mg L⁻¹) either at laboratory or pilot scale. 2,4-D removal was rapidly achieved while bacteria inactivation required 6 h of either artificial or natural sunlight irradiation. These authors also found that the presence of some anions such as bicarbonate/carbonate and fluoride could enhance the photochemical processes responsible for herbicide and bacteria abatement (Gutiérrez-Zapata et al. 2016, 2017a). Moreover, it is well known that humic substances (HSs) which are common in surface and well waters exhibit an interesting potential to form stable and soluble complexes with ferrous and ferric ions at neutral pH (Voelker et al. 1997; Fukushima and Tatsumi 2001; Georgi et al. 2007; Lipczynska-Kochany and Kochany 2008; Rao et al. 2009; Klamerth et al. 2011; Wang et al. 2016b). These Fe-HS complexes can participate in Fenton and photo-Fenton processes leading to the removal of organic pollutants in water.

Herein, we reported a systematic study for photo-Fenton degradation of diuron and amoxicillin both at initial concentrations of 10.0 mg L⁻¹, iron concentrations ranging from 0.05 to 1.06 mg L⁻¹, and typically found in natural surface and well waters (Sciacca et al. 2010; Avigliano et al. 2015; Gutiérrez-Zapata et al. 2016) and low amounts of hydrogen peroxide (ranging from 0.05 to 17.89 mg L⁻¹) at circumneutral pH (~7.0) in presence of amounts of bicarbonate/carbonate, fluoride, and

humic acids often found in well and surface waters (Sciacca et al. 2010; Gupta et al. 2012; Sadat 2012; Gutiérrez-Zapata et al. 2016). The effect of ferric ion and hydrogen peroxide concentration on photo-Fenton degradation of both pollutants in Milli-Q water was determinate by using a rotatable central composite experimental design 2^2 . Liquid chromatography coupled with mass spectrometry (HPLC/MS) analyses were performed to detect oxidation byproducts of diuron and amoxicillin. This study is focused to show that using low amounts of iron such as those typically found in natural surface or well waters is enough to carry out photo-Fenton reactions at initial neutral pH to remove amoxicillin (a common antibiotic widely used around the world) and diuron (a water-soluble herbicide), and thus avoiding the subsequent elimination of residual reactants. Moreover, the effect of anions also typically found in natural waters such as bicarbonate/carbonate, fluoride, and natural organic matter as humic acids on degradation of both pollutants at initial neutral pH was studied. Detection of byproducts generated during pollutant degradation followed by HPLC/MS may give evidence if removal of amoxicillin and diuron in natural waters should be possible by simply adding hydrogen peroxide without the further addition of ferric/ferrous salts and pH acidification since natural dissolved or colloidal iron could be efficiently used in order to achieve both pollutant removal by photo-Fenton processes at neutral pH.

Experimental methods

Reagents

Amoxicillin trihydrate, diuron (Sigma-Aldrich), acetonitrile HPLC grade (Sigma-Aldrich), humic acids (Alfa-Aesar), H_2O_2 at 30% (v/v) (Merck), $\text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$ (Sigma-Aldrich), $\text{NaF} \cdot 10 \text{H}_2\text{O}$ (Sigma-Aldrich), and Na_2CO_3 (Sigma-Aldrich) were used to perform all the experiments. All reagents were used without further purification.

Experimental design and experiments performed in Milli-Q water

Effect of ferric ions and H_2O_2 concentrations ranging between 0.1–0.9 and 1.0–15.0 mg L^{-1} respectively on photo-Fenton degradation of diuron and amoxicillin was studied by a rotatable central composite experimental design 2^2 with 4 degrees of freedom and one central and two axial points (Table 1). Some experiments such as Fenton reaction (dark), UV- H_2O_2 photolysis, pollutant photolysis, and ions and HS effect were carried out by using the H_2O_2 concentrations recommended by experimental design and iron concentrations often allowed by World Health Organization (WHO) (0.3 mg L^{-1}) in drinking water (WHO 1997). Results were analyzed using the software Statgraphics Centurion XV. All experiments were carried out by duplicate.

Table 1 Ferric ions and H_2O_2 concentrations determined by experimental design 2^2

Experiments	$[\text{H}_2\text{O}_2]$ (mg L^{-1})	$[\text{Fe}^{3+}]$ (mg L^{-1})
E1 (central point)	8.0	0.50
E2	0.5	0.50
E3	8.0	0.05
E4 (+1)	15.0	0.90
E5	1.0	0.90
E6	8.0	0.50
E7	15.0	0.10
E8	7.0	1.06
E9	17.9	0.50
E10 (−1)	1.0	0.10

A total of 80.0 mL of Milli-Q water (at initial pH of ~ 7.0 which was adjusted with NaOH) containing suitable ferric iron and H_2O_2 concentrations with diuron and amoxicillin initial concentrations of 10.0 mg L^{-1} was added to a cylindrical Pyrex bottle. These initial concentrations were chosen in order to permit an adequate detection of photodegradation byproducts by HPLC/MS. Then, these bottles were irradiated by a Hanau Suntest (AM-1) solar simulator (total intensity 300 W m^{-2}) under constant magnetic stirring during 75 min to diuron and 60 min to amoxicillin (Fig. S1 supporting material). The lamp has a spectral distribution with about 0.5% of emitted photons at wavelengths shorter than 300 nm (UV-C range) and about 4% between 300 and 400 nm (UV-B and UV-A ranges). The distribution of the photons emitted between 400 and 800 nm follows the solar spectrum. Temperature of the experiments was never superior to 38 °C. Samples were periodically collected, and H_2O_2 was eliminated by adding sodium bisulfite (NaHSO_3) to follow the reaction kinetics.

Diuron concentration was followed by HPLC (Shimadzu LC20A) equipped with a UV-VIS detector and a C-18 RP column Nucleosil 100-5 with a mobile phase of acetonitrile/acetic acid (45:55) at pH 3.0. Flow was 0.9 mL min^{-1} and the analyte was detected at 254 nm. Amoxicillin was monitored with a mobile phase acetonitrile/phosphate buffer (15:85) at pH 5.0, a flow of 0.5 mL min^{-1} , and a detection wavelength of 230 nm.

Salicylic acid (SA, 110 mg L^{-1}) was used as trapping reagent to detecting hydroxyl radicals. This reacts with H_2O_2 (10.0 mg L^{-1}) under simulated solar light using the same experimental conditions than those to diuron and amoxicillin. HPLC (Shimadzu LC20A) determination of SA and its initial reaction byproducts: catechol, 2,3-, and 2,5-dihydroxybenzoic acid (2,3-DHBA and 2,5-DHBA) were achieved using a mobile phase composed by citrate buffer (80%), acetonitrile (10%), and methanol (10%) at pH 3.0, a flow of 0.5 mL min^{-1} , and a C-18 RP column Nucleosil 100-5. Detection wavelengths were 275 nm (Catechol), 305 nm (AS and 2,3-DHBA), and 326 nm (2,5-DHBA).

Degradation experiments in presence of fluoride, bicarbonate/carbonate, and humic acids

These experiments were carried out in presence of H₂O₂ concentrations suggested by the experimental design for diuron and amoxicillin and ferric iron concentrations recommended by WHO for drinking water (0.3 mg L⁻¹) (WHO 1997). Fluoride, bicarbonate/carbonate, and humic acid concentrations were used at values often found in surface and groundwater samples (Sciacca et al. 2010; Gutiérrez-Zapata et al. 2016).

Determination of total iron by atomic absorption spectroscopy

Total iron concentration was measured by flame atomic absorption spectroscopy (AAS) using a Shimadzu AA-7000 equipment, at λ = 248.3 ± 0.2 nm (LoQ = 0.03 mg L⁻¹). Aliquots of 25 mL were acidified and directly measured by AAS in order to determine total (dissolved and suspended) iron of the solution.

HPLC/MS measurements

Degradation byproducts of diuron and amoxicillin produced during their photo-induced degradation were monitored by using a HPLC (Hitachi Elite LaChrom) equipped with a RP C18 column Nucleosil 100–5 at 30 °C (using the same chromatographic conditions previously mentioned) coupled with a mass spectrometer (Bruker Amazon SL) with an electro-spray ionization (ESI) at a voltage of 140 V and an ionization temperature of 140 °C for diuron and 100 °C for amoxicillin.

Results and discussion

Effect of ferric ion and hydrogen peroxide concentration on photo-Fenton degradation of diuron and amoxicillin in Milli-Q water at initial neutral pH by using an experimental design 2²

Diuron removal experiments are shown in Fig. 1a at initial pH 7.0 in Milli-Q water during 75 min of simulated sunlight irradiation. Experiments with lower and higher hydrogen peroxide concentration (Table 1: E2, E5, E9, and E10) exhibited low diuron removal. When H₂O₂ concentration oscillated between 8.0 and 15.0 mg L⁻¹, it was obtained the highest diuron removal. It is interesting to highlight that low ferric ion concentrations (0.05–1.06 mg L⁻¹) were enough to achieve high rates of diuron degradation under simulated sunlight exposure. However, this removal was not performed at neutral pH. Figure 1 b shows that in all experiments, pH dropped rapidly to 3.5 in the first 15 min of simulated sunlight irradiation. These findings were already reported by Romero et al. (2016) and Barona et al. (2015) who claimed that in photo-

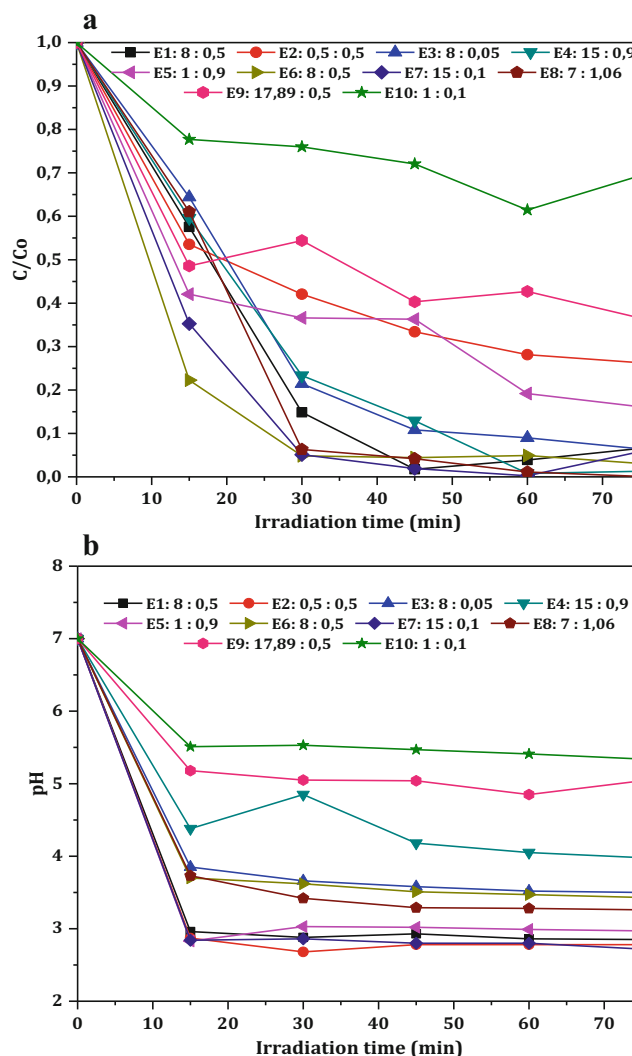


Fig. 1 a Degradation of diuron (10.0 mg L⁻¹) in Milli-Q water at different concentrations of ferric ions and H₂O₂ (H₂O₂/Fe) and initial pH 7.0 under simulated sunlight irradiation (300 W m⁻²). b pH monitoring under sunlight irradiation. Numbers into figure correspond to hydrogen peroxide and iron concentration respectively

Fenton reactions at initial circumneutral pH, this pH dropping could due to formation of resorcinol oxidation byproducts of acidic nature.

Surface response for diuron degradation developed to 45 min of simulated sunlight irradiation (where greater variability in degradation was observed between experiments) revealed that the optimal concentrations of ferric ion and hydrogen peroxide to obtain the highest diuron removal were 0.84 and 9.7 mg L⁻¹, respectively (R² = 0.9927) (Fig. 2a). Pareto diagram (Fig. 2b) shows the main effects of the ferric and H₂O₂ interaction after 45 min of irradiation. Results indicate that the most representative effect in the model is the quadratic term of the H₂O₂ concentration explaining why the surface response exhibited its curvature. Meanwhile, terms of ferric and H₂O₂ concentration and ferric-H₂O₂ interaction showed a minor effect. Another important feature of the surface

response was that at H_2O_2 concentration interval between 7.0 and 10.0 mg L^{-1} , diuron degradation was not strongly affected by the ferric iron concentration. When hydrogen peroxide concentration was high ($15.0\text{--}18.0 \text{ mg L}^{-1}$), a detrimental effect caused on diuron degradation was observed. This could be related by the fact that the hydrogen peroxide at these concentrations could act as a HO_2^\bullet scavenger leading to the production of HO_2^\bullet radicals (Eq. 1) which can undergo further disproportionation reaction producing H_2O_2 (Eq. 2) (Pignatello et al. 2006):



Amoxicillin (AMX) removal during 60 min of simulated sunlight irradiation is depicted on Fig. 3a. Experiments E2, E5, and E10 with low H_2O_2 concentration (Table 1) exhibited the worse results, while those with intermediate and high ferric ion concentrations ($0.1, 0.5, 0.9,$ and 1.06 mg L^{-1}) and highest H_2O_2 concentrations of $7.0, 8.0, 15.0,$ and 17.89 mg L^{-1} (E4, E6, E7,

E8, and E9) showed the best removal results during 60 min of simulated sunlight irradiation. In addition, Fig. 3b revealed that pH dropped as well during the experiments; however, this decrease was minor (5.6) than the value obtained with diuron.

Analysis of surface response for amoxicillin degradation after 10 min of simulated sunlight irradiation (where greater variability in degradation was observed between experiments) showed that the optimal concentrations of ferric ions and H_2O_2 were 1.06 and 15.2 mg L^{-1} , respectively ($R^2 = 0.9987$) (Fig. 4a). Pareto diagram (Fig. 4b) showed this time that parameters involved in the process with positive effect were iron and H_2O_2 concentration while the quadratic effect of hydrogen peroxide and the combination of ferric and H_2O_2 exhibited a minor negative effect. A lineal relationship between AMX degradation and iron and hydrogen peroxide concentration was found. This behavior generates a response surface with an upward shape indicating that it was not possible to find an optimal range in the ferric and hydrogen peroxide concentrations studied.

Since pH decreased rapidly during the first minutes of simulated sunlight irradiation, it is possible to suggest that several water-soluble ferric aqua-complexes could be generated. It is

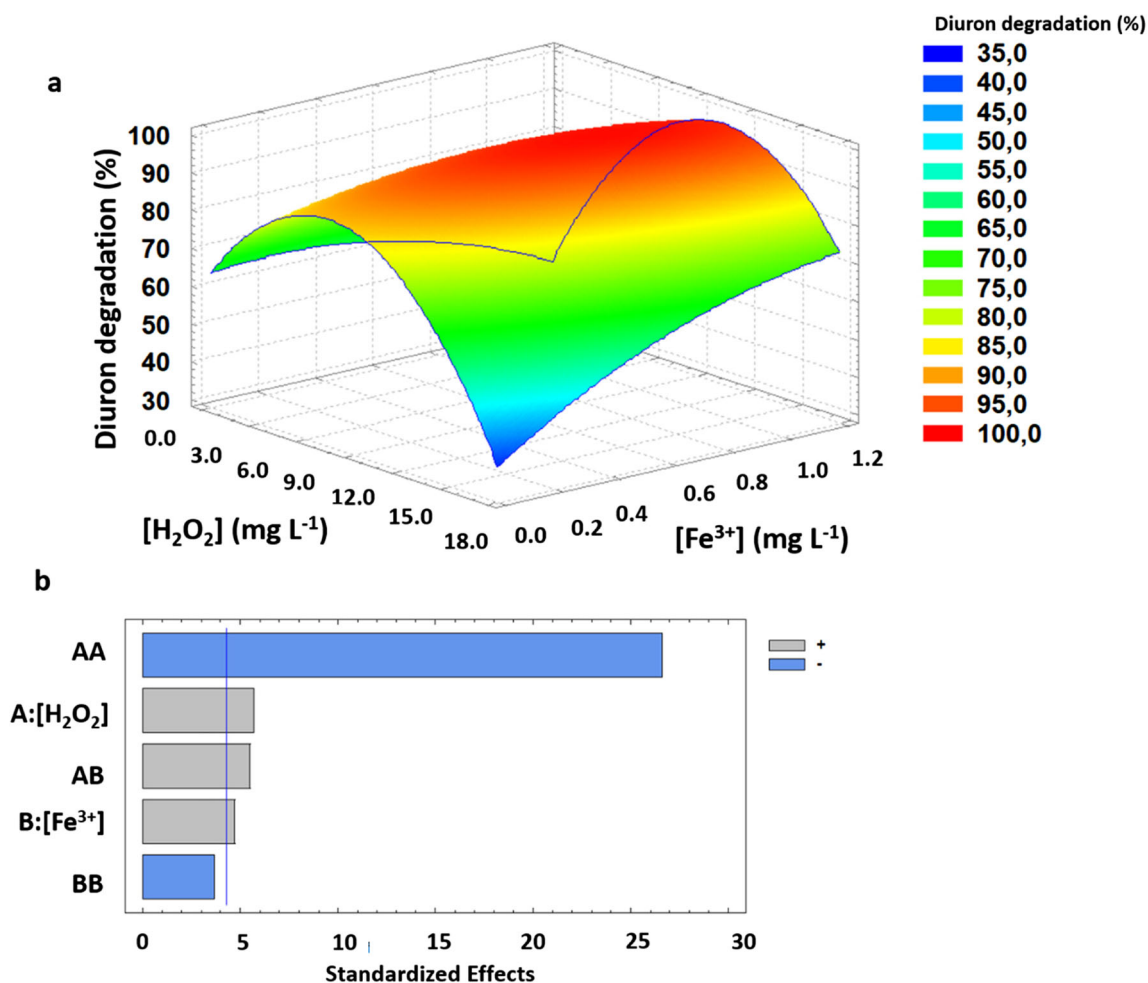
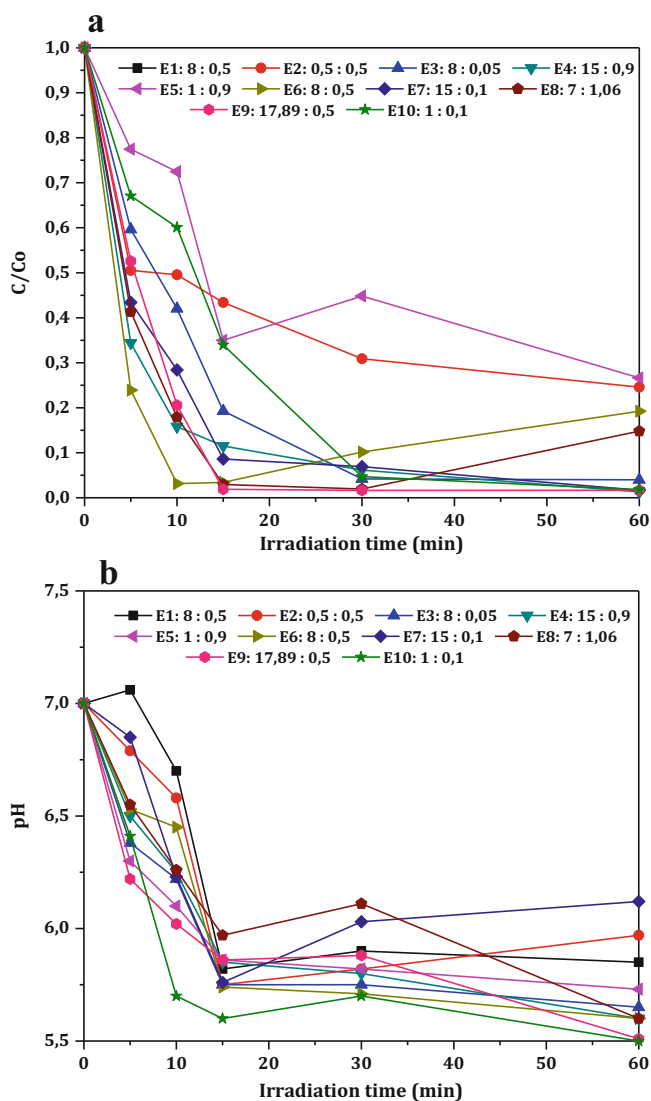


Fig. 2 a Analysis of surface response and b Pareto diagram for diuron degradation obtained from the experimental design 2^2 . $r^2 = 0.9927$

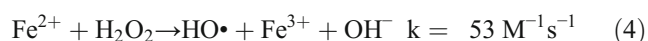
Fig. 3 **a** Degradation of amoxicillin (10.0 mg L⁻¹) in Milli-Q water at different concentrations of ferric ions and H₂O₂ (H₂O₂/Fe) and initial pH 7.0 under simulated sunlight irradiation (300 W m⁻²). **b** pH monitoring under sunlight irradiation. Numbers into figure correspond to hydrogen peroxide and iron concentration respectively



well known that Fe(OH)²⁺ complex is the main ferric specie at pH values between 2.5 and 5.0. Fe(OH)²⁺ is a very photoactive complex absorbing light comprised between 290 and 400 nm leading efficiently to the production of HO[•] radicals (Eq. 3) (quantum yield of HO[•] radical production at λ = 280 nm = 0.31) (Faust and Hoigné 1990; Šima and Makáňová 1997; Feng and Nansheng 2000).



Thus, once pH decreased at values between 5.0 and 3.5 in Milli-Q water experiments, the photolysis of water-soluble Fe(OH)²⁺ aqua-complex would be responsible for diuron and AMX abatement by the formation of HO[•] radicals. In addition, ferrous ions (Fe²⁺) could be re-oxidized to ferric ones by molecular oxygen or by Fenton reaction. This latter would lead the concomitant production of HO[•] extra (Eq. 4) (Pignatello et al. 2006):



Control experiments (Fig. 5a) revealed that diuron photolysis under sunlight irradiation did not play an important role in the herbicide oxidation. In contrast, Fenton reaction (dark conditions) exhibited a diuron removal close to 20% and UV-B photolysis of H₂O₂ achieved diuron removals of 80% after 75 min of simulated sunlight irradiation.

Figure 5 b shows results about control experiments carried out in AMX degradation. This time, AMX photolysis was important since almost 55% of antibiotic was removed while Fenton reaction (dark) exhibited an AMX removal close to 40%. In contrast, UV-B H₂O₂ photolysis led a high AMX removal around 80% after 75 min of simulated sunlight irradiation. Several studies have reported that AMX undergoes photolysis/hydrolysis reactions (Lamm et al. 2009; Pérez-Parada et al. 2011; Arsand et al. 2018). However, these studies

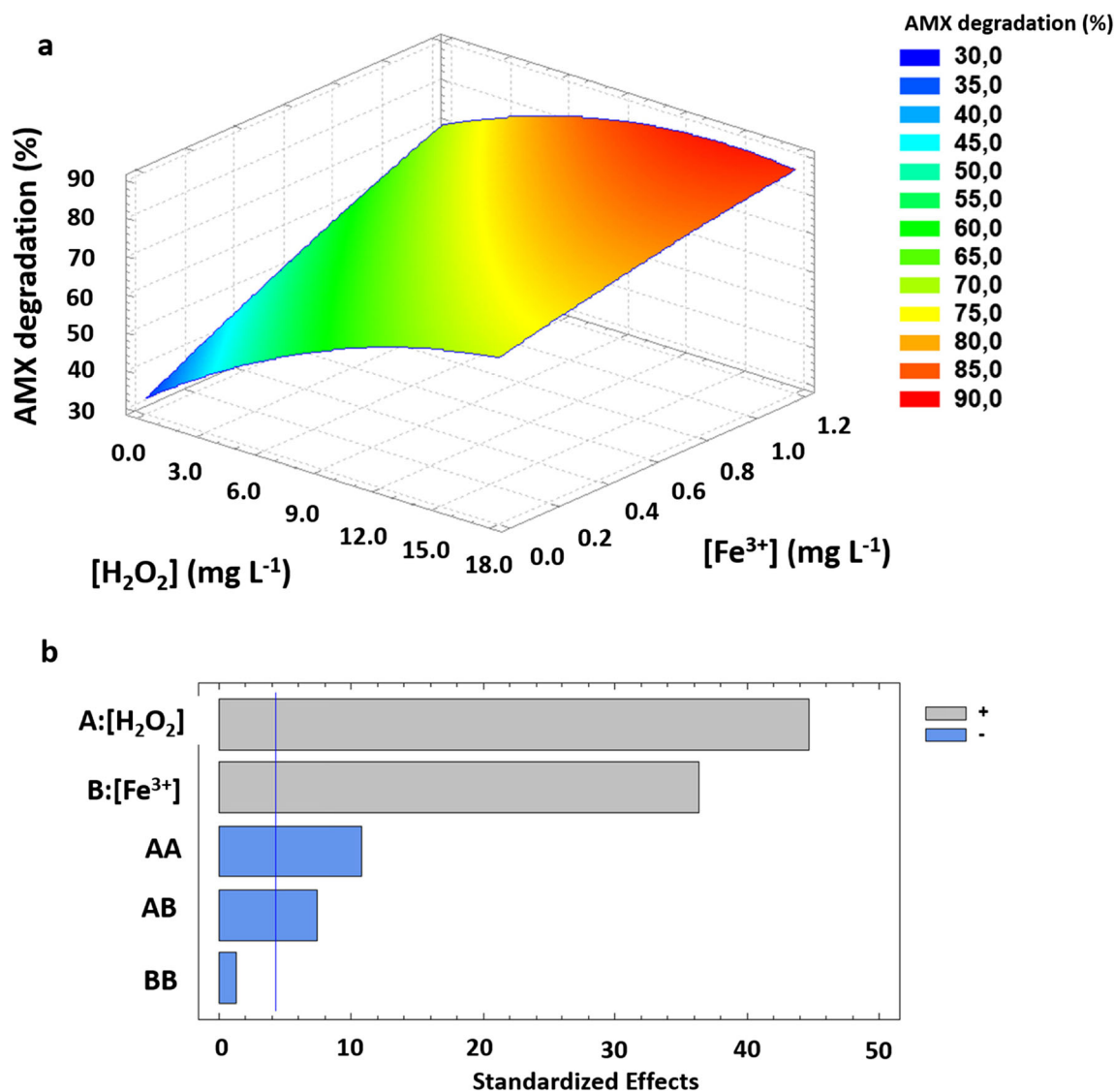


Fig. 4 **a** Analysis of surface response and **b** Pareto diagram for amoxicillin degradation obtained from the experimental design 2^2 . $r^2 = 0.9987$

reported that although AMX suffered photo-transformations, it was still found after 24 h of simulated sunlight irradiation (Arsand et al. 2018). On the other hand, AMX hydrolysis was dependent on the pH values since this reaction was completed quickly at basic pH (10), while at acidic pH, AMX residues were present after 5 h (Nägele and Moritz 2005).

Despite that H_2O_2 absorbs mainly UV-C light leading to the formation of HO^\bullet radicals (Shu et al. 2013; Lopez-Alvarez et al. 2016), it exhibits low UV-B light absorption that also could lead to its photolysis and to the consequent production of these radicals. In our experimental conditions, UV-C light cannot reach the solution because photo-reactor vessels are built of Pyrex glass which cut-off wavelengths below 290 nm. Figure 6 shows the light absorption of H_2O_2 comprised between 290 and 350 nm together with the emission spectrum of the solar simulator and the Pyrex glass light transmission. As it can be observed in Fig. 6, in our experiments,

only UV-B light reaches the reaction solution, being responsible for H_2O_2 photolysis (in a lower extent in comparison with UV-C) and the concomitant production of HO^\bullet radicals. This possible production of HO^\bullet radicals by UV-B light was evaluated by using salicylic acid as HO^\bullet radical-trapping reagent. Production of 2,3-, 2,5-dihydrobenzoic acid and catechol from salicylic acid (110 mg L^{-1}) in presence of 10.0 mg L^{-1} of H_2O_2 at initial pH 7.0 under solar simulated light is indicative of HO^\bullet radicals presence, as was reported by Chang et al. (2008). Insert in Fig. 7 shows that salicylic acid underwent a degradation of around 25% after 14 min of simulated sunlight irradiation and 10.0 mg L^{-1} of H_2O_2 with the concomitant formation of 2,3- and 2,5-dihydrobenzoic acid and catechol. 2,3- and 2,5-DHBA were formed after 10 min of sunlight irradiation while catechol was produced during whole experiment. These byproducts are compatible with attack of HO^\bullet radicals on salicylic acid molecule which could be

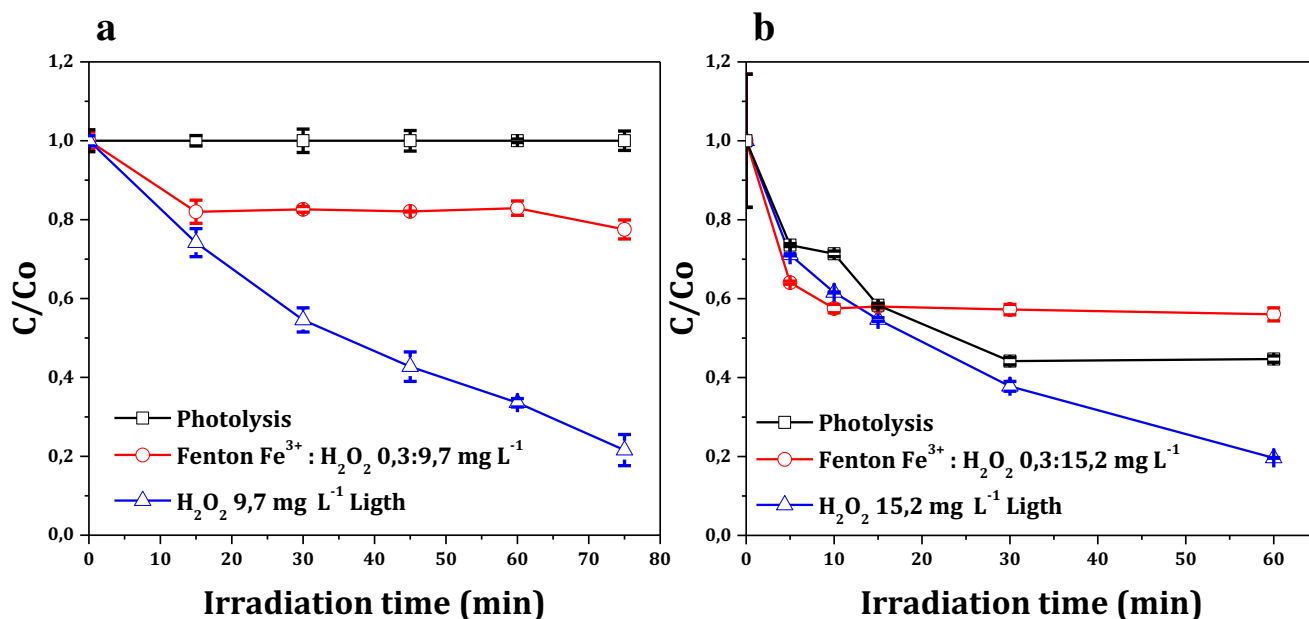


Fig. 5 Control experiments a diuron and b amoxicillin

formed by UV-B H₂O₂ photolysis (Chang et al. 2008). Serra-Clusellas et al. (2018) and others (Cataldo 2014; Huang et al. 2018) recently also showed evidence that UV-B light could induce H₂O₂ photolysis and participate in the degradation of organic pollutants. Therefore, in the same way, we could explain the strong removal of diuron and AMX observed in the degradation control experiments by photolysis of H₂O₂.

Removal of diuron and amoxicillin by photo-Fenton process at neutral pH in presence of fluoride, bicarbonate/carbonate, and humic acids

Two concentrations of fluoride ((-) 0.1 and (+) 1.0 mg L⁻¹) and humic acids (HA) ((-) 2.0 and (+) 5.0 mg L⁻¹) were

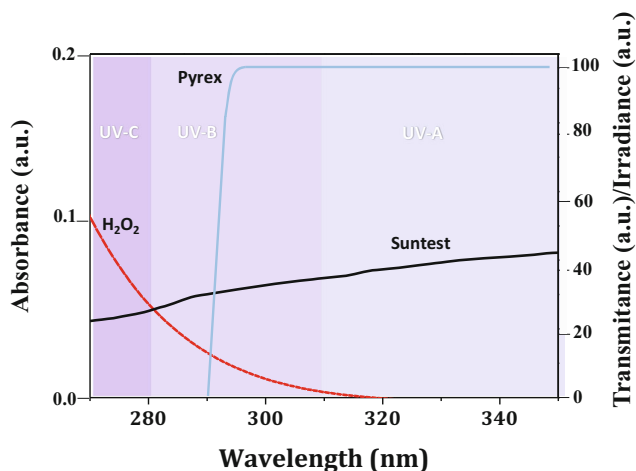


Fig. 6 UV-B-A light H₂O₂ absorption, Pyrex transmittance, and solar simulator emission

chosen while bicarbonate/carbonate concentration was fixed at 100.0 mg L⁻¹ simulating typical concentrations of these anions and HA present in natural surface and well water samples (Sciacca et al. 2010; Avigliano et al. 2015; Gutiérrez-Zapata et al. 2017b; Alvear-Daza et al. 2018b).

Since WHO recommends values of ferric concentrations in drinking water around 0.3 mg L⁻¹ (WHO 1997), this concentration was chosen to perform experiments containing anions and humic acid. At this iron concentration (0.3 mg L⁻¹), the mathematical model calculated by the surface response to diuron (Eq. 5) and AMX (Eq. 6) revealed that pollutant removal did not undergo a major change when optimal H₂O₂ concentrations were used (9.7 and 15.2 mg L⁻¹ for diuron and AMX respectively).

$$\begin{aligned} \text{Diuron deg\%} = & 63.599 + 6.62256 * \text{H}_2\text{O}_2 \\ & + 7.74771 * \text{Fe}^{3+} - 0.448815 * (\text{H}_2\text{O}_2)^2 \\ & + 2.47637 * \text{H}_2\text{O}_2 * \text{Fe}^{3+} - 18.8442 * (\text{Fe}^{3+})^2 \end{aligned}$$

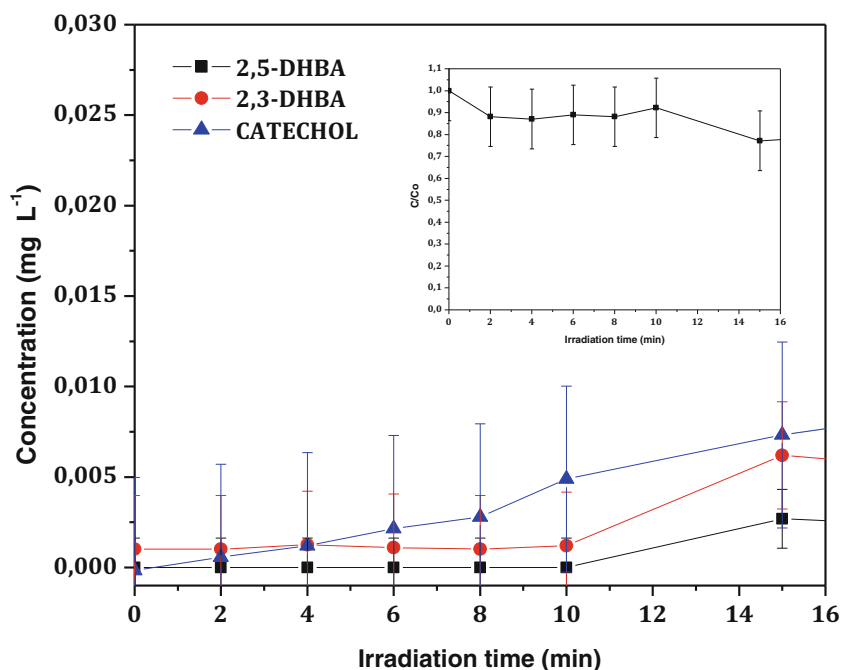
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$$\begin{aligned} \text{AMX deg\%} = & 32.509 + 3.78914 * \text{H}_2\text{O}_2 \\ & + 34.8114 * \text{Fe}^{3+} - 0.0882313 * (\text{H}_2\text{O}_2)^2 \\ & - 1.03737 * \text{H}_2\text{O}_2 * \text{Fe}^{3+} - 3.04702 * (\text{Fe}^{3+})^2 \end{aligned}$$

(6)

Dark reactions in presence of ferric ions (0.3 mg L⁻¹), hydrogen peroxide (9.7 mg L⁻¹), fluoride, HA, and bicarbonates/carbonates revealed that diuron underwent a partial degradation (around 20 and 25%) (Figure S2a supporting material). Experiments carried out in absence of ferric ions and only in presence of 9.7 mg L⁻¹ of hydrogen peroxide showed diuron

Fig. 7 Reaction of salicylic acid (SA, 8×10^{-4} mol L⁻¹) under simulated sunlight irradiation at initial pH 7.0 with H₂O₂ (10.0 mg L⁻¹) and following of SA and byproducts 2,3- and 2,5 dihydroxybenzoic acid (DHBA) and catechol



removal close to 50 and 75% (Fig. 8a). The simultaneous presence of both ferric ions (0.3 mg L⁻¹) and hydrogen peroxide (9.7 mg L⁻¹) under sunlight irradiation in presence of ions and HA exhibited a high diuron degradation (85%) almost comparable with those experiments performed in Milli-Q water (blue line). The pH monitoring (Fig. 8b) revealed that during all experiments where anions and HA were present, this parameter did not undergo changes since it keeps almost unaltered except in experiments performed without the presence of F⁻, HCO₃⁻/CO₃⁼ and HA where pH dropped rapidly below 3.5.

Dark experiments in presence of anions, humic acids, iron, and H₂O₂ revealed that amoxicillin underwent a partial degradation around 40 and 60% (Fig. S2b supporting material). On the other hand, amoxicillin degradation under sunlight irradiation (Fig. 9a) exhibited the same behavior depicted for diuron. In these experiments, both hydrogen peroxide photolysis and photo-Fenton reactions were the photochemical events responsible for antibiotic removal. In presence of ferric (0.3 mg L⁻¹) and hydrogen peroxide (15.7 mg L⁻¹, the optimal value found) and high concentrations of fluorine and HA,

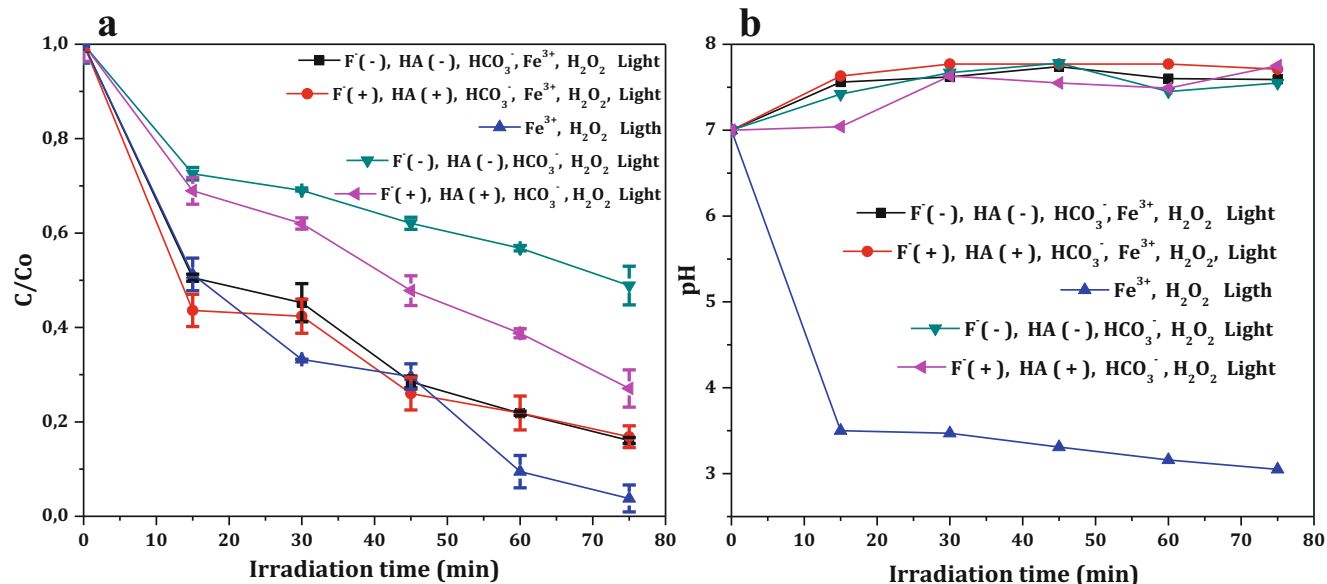


Fig. 8 a Degradation of diuron (10 mg L⁻¹) in presence of fluorine (-): 0.1, (+): 1.0 mg L⁻¹; humic acids (HA) (-): 2.0 mg L⁻¹, (+): 5.0 mg L⁻¹ and carbonates 100.0 mg L⁻¹, [Fe³⁺]: 0.3 mg L⁻¹, [H₂O₂]: 9.7 mg L⁻¹, at

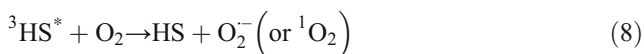
initial pH 7.0 under simulated sunlight irradiation (300 W m⁻²). **b** Monitoring of pH during the photochemical experiment

amoxicillin underwent a strong degradation comparable with the same experiment performed in Milli-Q water (blue line). pH values in experiments carried out in presence of anions and HA are kept constant (pH neutral) (Fig. 9b) while experiments performed in Milli-Q water exhibited a strong pH drop (3.5).

It is well known that humic substances form soluble complexes with ferric ions. These complexes have been already studied in Fenton and photo-Fenton reactions and they are attributed the degradation of several pollutants in water (Voelker et al. 1997; Fukushima and Tatsumi 2001; Georgi et al. 2007; Lipczynska-Kochany and Kochany 2008; Klammerth et al. 2011). It is likely accepted that ferric-humic acid complexes absorb UV-A and visible light irradiation leading to the reduction of ferric to ferrous iron (Eq. 7) and the concomitant oxidation of the HA. Thus, ferrous iron could participate in Fenton reactions with H₂O₂ yielding HO[•] radicals (Eq. 4):



UV-A and visible light can photo-induce triplet excited states in humic acids which can undergo further non-radiative deactivation through energy and/or electronic transfer to molecular oxygen leading to the production of O₂^{•-} radical and singlet oxygen (¹O₂) (Eq. 8). Both ROS exhibit a poor oxidation capacity (Canonica et al. 1995; McNeill and Canonica 2016):

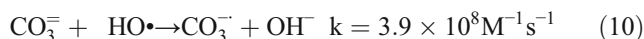


It is possible that at neutral pH, iron can also be forming iron (hydr)oxides such as goethite and lepidocrocite which

have poor photocatalytic activity (Li et al. 2007; Chen et al. 2015). However, Du et al. (2008) have suggested that iron (hydr)oxides in presence of fluoride can be more efficient in the production of HO[•] radicals enhancing their photocatalytic activity since it is possible the formation of surface Fe-F bonds which could oxidize efficiently H₂O.

Total iron determination experiments of filtrated water by 0.22 μm membranes were performed by atomic absorption spectroscopy. Results showed presence of insoluble iron. A strong iron removal by filtration was observed especially in experiments with low HA concentrations (2.0 mg L⁻¹) where iron removal was around almost 50% (iron concentration after filtration was 0.144 mg L⁻¹) while those experiments where water contains 5.0 mg L⁻¹ of HA exhibited an iron removal of 38% (iron concentration after filtration was 0.216 mg L⁻¹). Presence of highest HA concentrations in water would lead to the high formation of dissolved HA-Fe complexes.

On the other hand, it is well known that bicarbonate/carbonate anions act as efficient HO[•] radical scavengers leading to carbonate radical (CO₃^{•-}) formation (Eqs. 9 and 10) (Busset et al. 2007). Equation 10 could explain why there was a slight increasing of pH during the experiments:



Although CO₃^{•-} has a lower oxidation potential (CO₃^{•-}/CO₃⁼ E° = 1.7 V vs NHE) (Busset et al. 2007; Dell'Arciprete et al. 2012) than hydroxyl radical, there are several studies reporting its ability to oxidize organic pollutants in water (Busset et al. 2007; Pétrier et al. 2010;

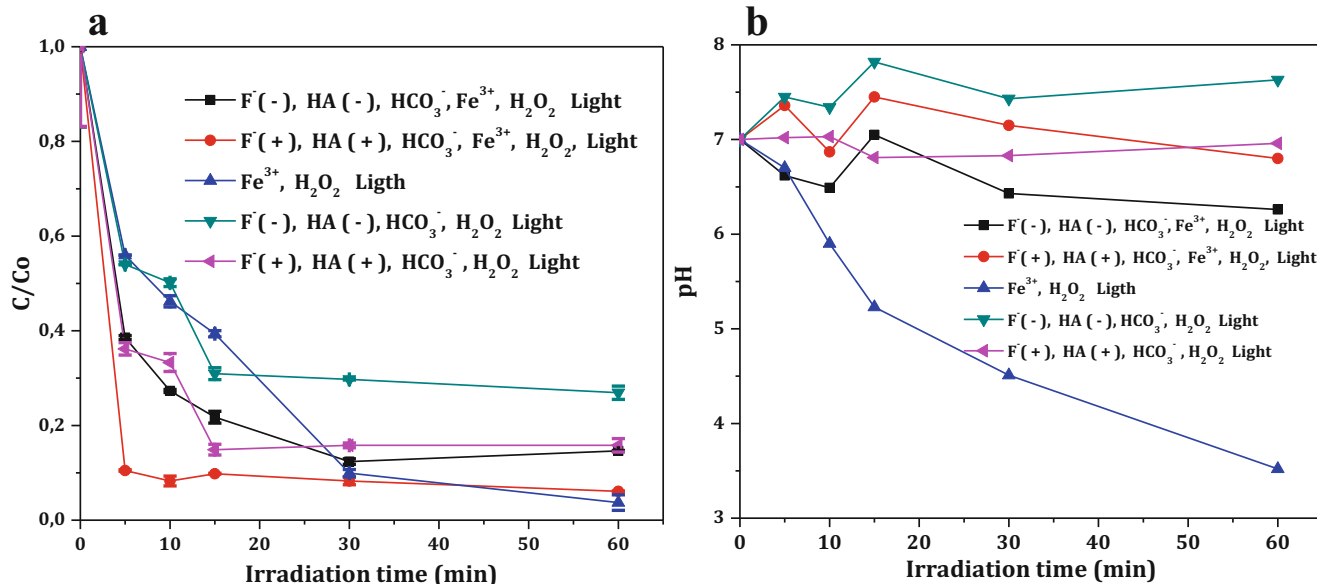


Fig. 9 a Degradation of amoxicillin (10.0 mg L⁻¹) in presence of fluorine (-): 0.1, (+): 1.0 mg L⁻¹; humic acids (HA) (-): 2.0 mg L⁻¹, (+): 5.0 mg L⁻¹ and carbonates 100.0 mg L⁻¹, [Fe³⁺]: 0.3 mg L⁻¹, [H₂O₂]:

15.2 mg L⁻¹, at initial pH 7.0 under simulated sunlight irradiation (300 W m⁻²). b Monitoring of pH during the photochemical experiment

Dell’Arciprete et al. 2012). Thus, in our experimental conditions, bicarbonate/carbonate anions could generate carbonate radicals by reaction with HO^\bullet and the former could also participate in diuron and AMX degradation.

Evaluation of diuron and amoxicillin degradation byproducts by HPLC/MS

Diuron degradation byproducts found in Milli-Q water and samples containing anions and HA are presented in Table 2. The most characteristic feature was the presence of *N*-demethylated byproducts in both experimental conditions corresponding to *m/z* ratios of 232, 248, 250, and 264. A peak with retention time of 4.2 min and *m/z* of 220 was related to the presence of a diuron metabolite produced by the attack of HO^\bullet radicals on the aromatic ring of a demethylated byproduct. All these findings were accorded to previous

studies reported on the literature where it was argued that the main oxidation route of diuron in photo-Fenton process is related with the attack of HO^\bullet radicals on the methylurea group of the molecule (Fig. 10) (Farré et al. 2007). However, in experiments carried out in presence of anions (F^- and $\text{HCO}_3^-/\text{CO}_3^{2-}$), the possible formation of $\text{CO}_3^{\bullet-}$ could also lead to the formation of *N*-demethylated byproducts since carbonate radical can also attack electrophilic sites of the molecule by electron transfer or hydrogen abstraction reactions, such as was reported by Dell’Arciprete et al. (2012) in the oxidation of some neonicotinoid insecticides in the presence of $\text{CO}_3^{\bullet-}$. Byproducts obtained during the reaction demonstrated the possibility of electron transfer and hydrogen abstraction. Regarding toxicity of some byproducts generated by photo-Fenton treatment of diuron aqueous solutions, Farré et al. (2007) found that presence of methylurea or 1,1-methylurea as degradation byproducts could be linked to high

Table 2 *m/z*, chemical structures, retention times, and experimental conditions of diuron byproducts obtained from HPLC/MS measurements in photo-Fenton experiments ($[\text{Fe}^{3+}]$: 0.3 mg L^{-1} ; $[\text{H}_2\text{O}_2]$: 9.7 mg L^{-1}) realized in Milli-Q water and in presence of

fluorine ((-): 0.1 mg L^{-1} ; (+): 1 mg L^{-1}) humic acids ((-) 2.0 mg L^{-1} ; (+) 5.0 mg L^{-1}) and carbonates (100.0 mg L^{-1}) under simulated sunlight irradiation (300 W m^{-2}) at initial pH 7.0

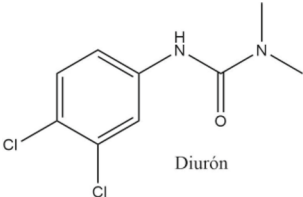
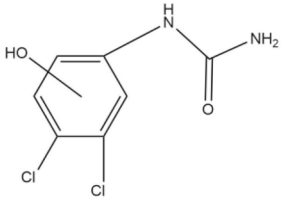
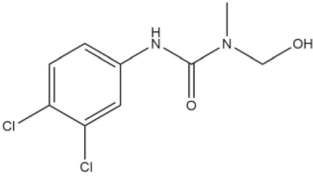
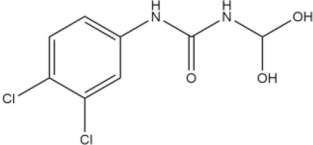
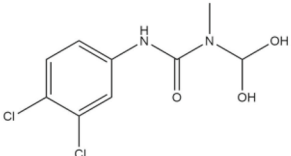
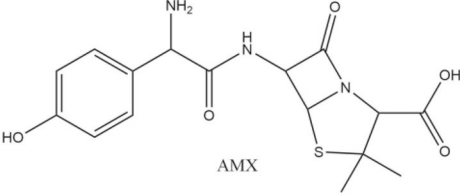
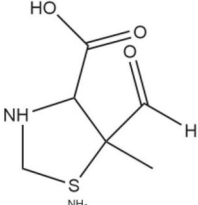
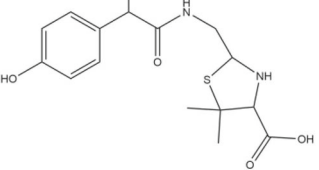
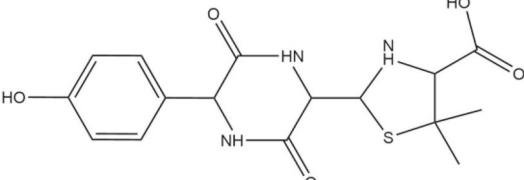
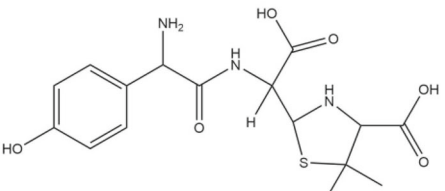
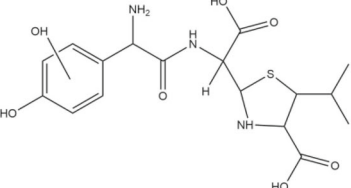
<i>m/z</i>	Chemical structure	Retention time (min)	Sample
232 (Diuron)	 Diuron	4,7	Standard Photo-Fenton Milli-Q water F^- (-), HA (-), Fe^{3+} H_2O_2 F^+ (+), HA (+), Fe^{3+} H_2O_2
220		4,2	F^- (-), HA (-), Fe^{3+} H_2O_2 F^+ (+), HA (+), Fe^{3+} H_2O_2
248		4,1	Photo-Fenton Milli-Q water F^- (-), HA (-), Fe^{3+} H_2O_2 F^+ (+), HA (+), Fe^{3+} H_2O_2
250		4,3	F^- (-), HA (-), Fe^{3+} H_2O_2 F^+ (+), HA (+), Fe^{3+} H_2O_2
264		4,2	Photo-Fenton Milli-Q water F^- (-), HA (-), Fe^{3+} H_2O_2 F^+ (+), HA (+), Fe^{3+} H_2O_2

Table 3 m/z, chemical structures, retention times, and experimental conditions of amoxicillin byproducts obtained from HPLC/MS measurements in photo-Fenton experiments ($[\text{Fe}^{3+}]$: 0.3 mg L^{-1} ; $[\text{H}_2\text{O}_2]$: 9.7 mg L^{-1}) realized in Milli-Q water and in presence of

fluorine (–): 0.1 mg L^{-1} ; (+): 1 mg L^{-1}) humic acids (–) 2.0 mg L^{-1} ; (+) 5.0 mg L^{-1}) and carbonates (100.0 mg L^{-1}) under simulated sunlight irradiation (300 W m^{-2}) at initial pH 7.0

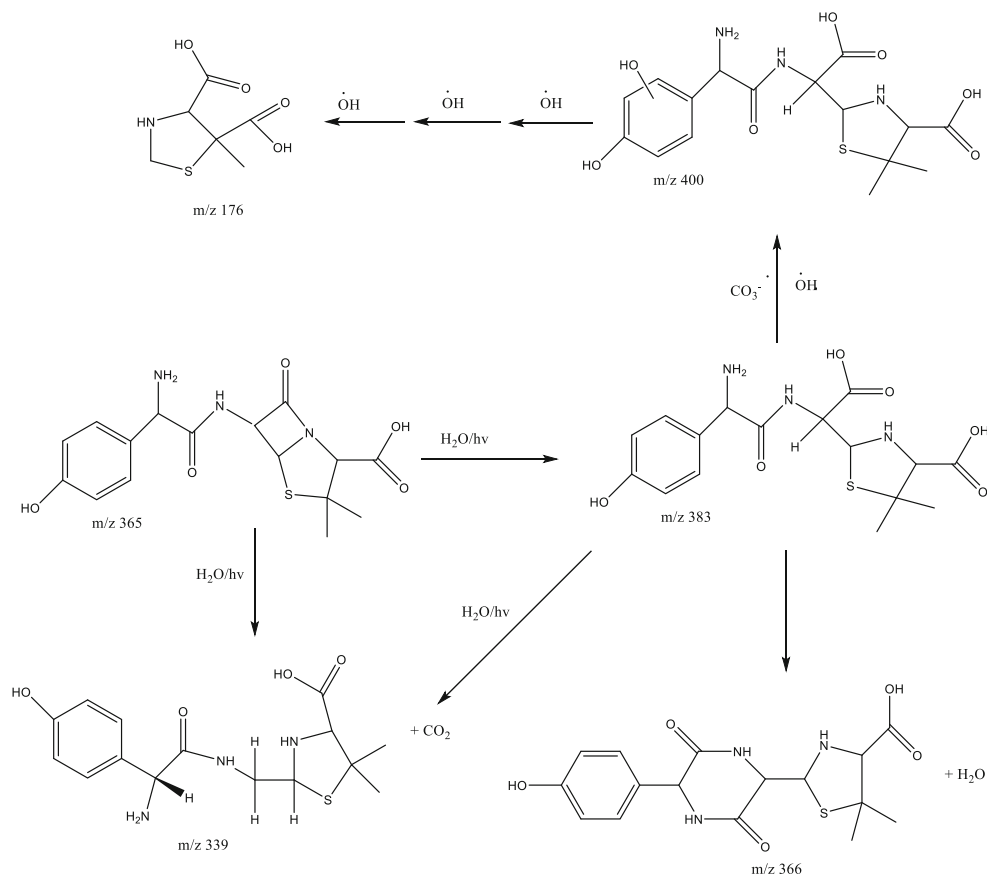
m/z	Chemical structure	Retention time (min)	Sample
365 (AMX)		4.7	F [–] (–), HA (–), Fe ³⁺ H ₂ O ₂ F [–] (+), HA (+), Fe ³⁺ H ₂ O ₂ Photo-Fenton Milli-Q water
176		4.9	F [–] (+), HA (+), Fe ³⁺ H ₂ O ₂
339		4.8	F [–] (–), HA (–), Fe ³⁺ H ₂ O ₂ F [–] (+), HA (+), Fe ³⁺ H ₂ O ₂ Photo-Fenton Milli-Q water
366		4.9	F [–] (–), HA (–), Fe ³⁺ H ₂ O ₂ F [–] (+), HA (+), Fe ³⁺ H ₂ O ₂
383		4.5	F [–] (–), HA (–), Fe ³⁺ H ₂ O ₂ F [–] (+), HA (+), Fe ³⁺ H ₂ O ₂ Photo-Fenton Milli-Q water
400		4.9	Photo-Fenton Milli-Q water F [–] (+), HA (+), Fe ³⁺ H ₂ O ₂

of bicarbonates/carbonates, it could be possible that carbonate radicals attack the aromatic ring of amoxicillin molecule leading to formation of hydroxylated byproducts as well. Busset et al. (2007) have suggested that $\text{CO}_3^{\cdot-}$ radical could attack phenol molecules resulting in the formation of phenoxyl radical by electron transfer or hydrogen abstraction. The subsequent reaction of phenoxyl radical with dissolved oxygen leads to peroxy radical formation whose disproportionation reaction could produce benzoquinone and dihydroxybenzene.

Especially under conditions with high fluoride and humic acid concentrations where amoxicillin underwent the highest degradation at neutral pH, a molecule with m/z around 176 was detected. This byproduct was also detected by Trovó et al. (2011), and it could come from a strong attack of $\text{HO}^{\cdot}/\text{CO}_3^{\cdot-}$ radicals to amoxicillin molecule or on hydrolysis/photolysis byproducts.

Experimental results would suggest that both diuron and amoxicillin molecules can be degraded by photo-Fenton processes using iron at concentrations present naturally and low

Fig. 11 Mechanism of diuron degradation by photo-induced HO[•] or CO₃^{•-} radicals obtained from HPLC/MS measurements



H₂O₂ concentrations mainly through the attack of photo-induced hydroxyl radicals. On the other hand, presence of anions such as bicarbonates/carbonates and fluoride and humic acids leads to the several photochemical reactions such as photo-Fenton (dissolved ferric-humic acid complexes), photocatalysis (colloidal iron) and UV-B H₂O₂ photolysis, photo-inducing HO[•], and CO₃^{•-} radicals at circumneutral pH.

Conclusions

An experiment design 2² evidenced the feasibility to use low ferric ion concentrations as those likely found in natural water sources and low concentrations of H₂O₂ to degrade diuron and amoxicillin in Milli-Q water at initial pH of 7.0. However, this latter parameter decreased during the first minutes of simulated sunlight irradiation reaching acidic value; thus, diuron and amoxicillin were removed by a classical photo-Fenton reaction at acidic pH. In contrast to this, when experiments were performed in presence of HCO₃⁻/CO₃⁼, F⁻, and humic acids (simulating natural conditions), pH did not undergo strong changes maintaining its value around 7.0–6.5. Under these experimental conditions, several photochemical events such as photo-Fenton, photocatalysis, and UV-B H₂O₂ photolysis could be induced being responsible of diuron and amoxicillin abatement. On the

other hand, amoxicillin exhibited the presence of several degradation byproducts, some of them related with hydrolysis/photolysis reactions and others possibly coming from the attack of photo-induced HO[•] or/and CO₃^{•-} radicals. Regarding diuron, it was observed that this molecule underwent an oxidative attack on the methylurea group which could be achieved by the reaction with both HO[•] and CO₃^{•-} radicals. Finally, it could be possible to obtain the degradation of amoxicillin and diuron in natural sources of water containing ferric ions with the addition of low amounts of H₂O₂ by photo-Fenton reaction carried out to circumneutral pH in presence of HCO₃⁻/CO₃⁼, F⁻ and humic acids at natural concentrations.

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