

Abatement of 2,4-D by H₂O₂ solar photolysis and solar photo-Fenton-like process with minute Fe(III) concentrations

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A B S T R A C T

The Photo-Fenton-like (PF-like) process with minute Fe(III) concentrations and the Hydrogen Peroxide Photolysis (HPP), using Xe-lamp or solar light as sources of irradiation, were efficiently applied to eliminate the herbicide 2,4-D from water.

PF-like experiments concerning ferric and H₂O₂ concentrations of 0.6 mg L⁻¹ and 20 mg L⁻¹ respectively, using Xenon lamps (Xe-lamps) as a source of irradiation and 2,4-D concentrations of 10 mg L⁻¹ at pH 3.6, exhibited complete 2,4-D degradation and 77% dissolved organic carbon (DOC) removal after 30 min and 6 h of irradiation respectively whereas HPP (in absence of ferric ions) experiments showed a 2,4-D reduction and DOC removal of 90% and 7% respectively after 6 h of irradiation. At pH 7.0, HPP process achieved a 2,4-D abatement of approximately 75% and a DOC removal of 4% after 6 h. PF-like exhibited slightly improved 2,4-D and DOC removals (80% and 12% respectively) after the same irradiation time probably due to the low pH reduction (from 7.0 to 5.6). Several chlorinated-aromatic intermediates were identified by HPLC-MS. These by-products were efficiently removed by PF at pH 3.6, whereas at neutral PF-like and acid or neutral HPP, they were not efficiently degraded. With natural solar light irradiation, 10 and 1 mg L⁻¹ of 2,4-D were abated using minor H₂O₂ concentrations (3, 6, 10 and 20 mg L⁻¹) and iron at 0.6 mg L⁻¹ in Milli-Q water. Similar results to Xe-lamp experiments were obtained, where solar UV-B + A light H₂O₂ photolysis (HPSP) and solar photo-Fenton-like (SPF-like) played an important role and even at low H₂O₂ and ferric concentrations of 3 and 0.6 mg L⁻¹ respectively, 2,4-D was efficiently removed at pH 3.6. Simulated surface water at pH 3.6 containing 1 mg L⁻¹ 2,4-D, 20 mg L⁻¹ H₂O₂ and 0.6 mg L⁻¹ Fe(III) under natural sunlight irradiation efficiently removed the herbicide and its main metabolite 2,4-DCP after 30 min of treatment while at neutral pH, 40% of herbicide degradation was achieved. In the case of very low iron concentrations (0.05 mg L⁻¹) at acid pH, 150 min of solar treatment was required to remove 2,4-D.

Keywords:

2,4-D
Chlorinated degradation by-products
Solar photo-fenton-like
Hydrogen peroxide solar photolysis
Water treatment

1. Introduction

The overuse of pesticides poses significant health and environmental risks as these compounds contaminate water sources and create a need for remediation (Barbosa et al., 2016; SENASA).

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Among pesticides, 2,4-dichlorophenoxyacetic acid (2,4-D) is one of the most widely used around the world; 7600 tonnes were commercialized in Argentina during 2012 (SENASA), and over 20,000 tonnes applied annually in the US (US EPA, 2015, 2007). Due to its significant solubility in water (c.a. 300 mg L⁻¹) and moderate potential of lixiviation in soils, it was categorised by the US EPA as a highly persistent chemical in aquatic and terrestrial anaerobic environments (US EPA, 2011).

The increase in the type and concentration of pollutants in aquatic systems or urban/industrial effluents, mostly related to anthropogenic activities, generated the need for innovative strategies for water remediation, such as Advanced Oxidation Process (AOPs). In the last few years, research efforts have mainly been devoted to overcoming limitations associated with these processes and improving their efficiency. In this sense and focusing on Fenton and photo-Fenton (PF) processes, the main drawbacks are: i) the optimal pH is acidic; ii) the generation of iron-sludge; and iii) the need for additional reagents (H₂O₂ and iron salts). Fenton-based processes in more environmentally friendly conditions are desirable, i.e. neutral or circumneutral pH, lower reactant consumption, and sunlight as a source of irradiation.

The degradation of organic pollutants in trace levels in urban effluents by PF process at circumneutral pH and low amounts of iron (e.g. 5 mg L⁻¹), H₂O₂ (e.g. 40 mg L⁻¹) was reported in several studies (Klamerth et al., 2009; Miralles-Cuevas et al., 2014, 2015), when iron was kept in solution by complexing agents. Although successful, this strategy presents additional drawbacks such as the extra cost of chelator addition, an increase of the total organic carbon content and most importantly, concerns about the ecotoxicity and biodegradability of chelators and by-products formed after the photochemical event (Clarizia et al., 2017). However, the iron concentration considered was not representative of that typically found in surface or groundwater, which varies from 0.05 to 0.68 mg L⁻¹ in Argentinian rivers (Avigliano et al., 2015).

Previous studies have shown the successful removal of 2,4-D at initial concentrations ranging from 22 to 100 mg L⁻¹ by PF process at acid pH (pH < 3.0) in Milli-Q water using relatively high amounts of ferric or ferrous salts (3–340 mg L⁻¹ Fe) and H₂O₂ (from 50 mg L⁻¹ to 15,266 mg L⁻¹), leading to the generation of 2,4-dichlorophenol (2,4-DCP) as the main oxidation by-product (Sun and Pignatello, 1993; Paterlini and Pupo Nogeira, 2005; Jimenez et al., 2011; Conte et al., 2014). Only a few studies investigated the process at circumneutral pH. For example, Luna et al. (2014) reported the degradation of 2,4-D (700 mg L⁻¹) in saline distilled water by the addition of 379 mg L⁻¹ Fe(II) and 15,200 mg L⁻¹ H₂O₂ subjected to sunlight irradiation, but although initiated at circumneutral conditions, pH dropped to close to 1 as the reaction proceeded, leading to the classic PF process. Similar results were found by Barona et al. (2015) who studied the degradation of dihydroxybenzene isomers in Milli-Q water by PF process using minute Fe(III) concentrations (0.7 mg L⁻¹) and H₂O₂ (40 mg L⁻¹). Conte et al. (2014) evaluated the abatement of 2,4-D (30 mg L⁻¹) by PF treatment at pH 5.0 using iron complexing agents such as citrate and oxalate with 3 mg L⁻¹ Fe(III) and 131.5 mg L⁻¹ H₂O₂ upon UV-A irradiation. Results showed that ferric-citrate and ferric-oxalate complexes led to significant degradation and mineralization of 2,4-D at pH 5.0. However, final pH was not reported. Recently, Gutierrez-Zapata et al. (2017) reported the abatement of 24.3 mg L⁻¹ 2,4-D in groundwater, with a natural iron content of 0.3 mg L⁻¹, at pH 7.0 and an addition of 10 mg L⁻¹ H₂O₂ under simulated solar light. This study demonstrated that low amounts of H₂O₂ can induce an enhancement of photo-induced natural abiotic processes and Reactive Oxygen Species (ROS) production. However, this study did not show evidence of the influence of Hydrogen Peroxide Photolysis (HPP) on the 2,4-D degradation nor the

intermediate compounds generated during the process. Although UV-C absorption is most efficient for •OH production by H₂O₂ photolysis, this reaction is also significant under UV-B + A absorption in wastewater treatment (Pignatello et al., 1999), artificial snow (Jacobi et al., 2004), frozen H₂O₂ (Chu and Anastasio, 2008), nonylphenol degradation (Neamtu and Frimmel, 2006 and Neamtu et al., 2008), and oxidation of *p*-cresol (Rojas et al., 2011).

Herein, the degradation of 2,4-D by HPP and PF-like process in the presence of minute concentrations of Fe(III), using a Xenon lamp and natural sunlight as irradiation sources, was investigated. The levels of Fe(III) considered are representative of those found in Argentinian rivers, e.g. La Plata river 0.6 mg L⁻¹, (Avigliano et al., 2015). The effect of H₂O₂ concentration was also evaluated at acid and neutral pH.

2. Material and methods

2.1. Chemicals

The chemicals 2,4-D, 2,4-DCP, 2-chlorohydroquinone (2-CHQ), 4-chlorocatechol, 4,6-dichlororesorcinol (4,6-DCR), 3,5-dichlorocatechol, and 4-chlorophenol were purchased from Sigma Aldrich (St Louis, MO), with analytical HPLC and GC grade standards with purity > 96%.

Reagent grade 30% H₂O₂ and FeCl₃·6H₂O as source of Fe(III) were obtained from ANEDRA (Buenos Aires, Argentina).

Solutions were prepared with high-purity water from a Classic UVMK2 Purelab Ultra (Elga-Veolia) system (resistivity > 18 MΩ cm, at 25 °C). The simulated surface water was prepared from the following salts of analytical grade: CaCl₂·2H₂O, NaHCO₃ and KCl, all supplied from ANEDRA; MgSO₄·7H₂O, humic acid (sodium salt) and NaF obtained from Sigma Aldrich.

Analytical grade 98% H₂SO₄ and NaOH pellets from ANEDRA were used in the preparation of dilute solutions for pH adjustment. Isocratic grade acetonitrile from Merck Millipore LiChrosolv® and glacial acetic acid from ANEDRA were used as HPLC mobile phase. Analytical grade 98% H₂SO₄ and 1000 mg L⁻¹ Ti standard solution from Merck were applied in the determination of H₂O₂ concentration.

2.2. Instruments and analytical procedures

Analysis of 2,4-D and 2,4-DCP were performed by reverse-phase HPLC, using a HP 1100 Series chromatograph fitted with a *Phenomenex* LUNA C18 column (150 mm × 4.6 mm × 5 μm), at 25 °C and coupled to Agilent Technologies 1200 UV–Vis detector, working at λ = 280 nm; 55% of acetonitrile, 30% of acetic acid at 30% and 15% of Milli-Q water were used as mobile phase at 0.8 mL min⁻¹ (t_r (2,4-D) = 4.2 min; t_r (2,4-DCP) = 4.9 min). Limit of quantification (LoQ) (2,4-D) = 0.007 mg L⁻¹; LoQ (2,4-DCP) = 0.009 mg L⁻¹. Samples were filtered by a 0.45 μm PVdF (Polyvinylidene fluoride) filter and a 20 μL volume was injected.

Dissolved organic carbon (DOC) was monitored by a Shimadzu TOC-V_{CPH} analyser. Samples were previously filtered using 0.45 μm PVdF membranes.

A Shimadzu UV/Vis UV-1650 PC spectrophotometer was used to determine H₂O₂ concentration from absorption of the titanichydrogen peroxide coloured complex at λ = 410 nm (Welcher, 1975), after filtering through 0.45 μm PVdF filters (LoQ (H₂O₂) = 0.6 mg L⁻¹).

Total iron concentration was measured by flame Atomic Absorption Spectroscopy (AAS) in a Thermo Scientific iCE spectrometer 3000 Series, at λ = 248.3 ± 0.2 nm (LoQ = 0.03 mg L⁻¹).

Aromatic intermediates produced during treatments with Xenon lamp were identified by isotope profiling, high resolution

metabolomics analysis (XCMS) and characterized by the integration of the METLIN metabolite database. The concentrations of the identified intermediates were determined by high-performance liquid chromatography coupled with a mass spectrometer (HPLC-MS).

To identify chlorinated degradation products, isotope profiling [^{35}Cl (75.78%) and ^{37}Cl (24.22%)] was performed using the mass spectra acquired from a Waters Alliance 2695 High Performance Liquid Chromatography system coupled with Waters Acquity TQ triple quadrupole mass spectrometer (HPLC-MS/MS). The by-products were separated by a Phenomenex (Torrance, CA) Kinetex C₁₈ (100 mm × 4.6 mm; 2.6 μm particle size) reverse-phase column. The mobile phase consisted of 10 mM ammonium acetate and 0.1% formic acid in water (A) and 100% acetonitrile (B). The gradient conditions were 0–0.5 min, 2% B; 0.5–7 min, 2–80% B; 7.0–9.0 min, 80–98% B; 9.0–10.0 min, 2% B; 10.0–15.0 min, 2% B at a flow rate of 0.5 ml min⁻¹. The MS/MS system was operated using electrospray ionization (EI) in the negative ion mode with capillary voltage of 1.5 kV (ES-). Further details about methodology are presented in supplementary information.

2.3. Experimental setup and operational conditions

Experiments were conducted at initial 2,4-D concentrations of 1 mg L⁻¹ or 10 mg L⁻¹. The higher concentration was used for the investigation of the effects of irradiation source and the identification and quantification of degradation by-products. Afterwards, the initial 2,4-D concentration was reduced for higher environmental relevance.

2.3.1. Abatement of 2,4-D under Xe-lamp irradiation (batch mode)

50 mL of 10 mg L⁻¹ 2,4-D (Milli-Q water) (initial DOC of 4.7 ± 0.4 mg L⁻¹) were treated by HPP and PF-like processes. A Newport 300 W Xe-Arc free ozone lamp with a 66902 Arc Lamp Housing (with horizontal beam) was used to irradiate a cylindrical Pyrex[®] reactor simulating the solar UV average irradiance (3 mW cm⁻²) in a perfect sunny day (see diagram on [figure S1 of Supplementary information](#)). About 30% of the UV irradiance from the Xe lamp corresponded to UV-B; however, the fraction would only be 4–5% of total UV sunlight radiation, at 37° of latitude ([ASTM, 2003](#)).

Starting concentrations of 20 mg L⁻¹ H₂O₂ and 0.6 mg L⁻¹ Fe(III) were selected based on preliminary experiments (at an initial pH of 7 and 3.6 and using a UV-A lamp, see [Figures S2 and S3](#) in Supplementary information). The solution was continuously stirred at 300–400 rpm for 6 h. After each PF-like treatment, the reactor was cleaned in an acid bath overnight in order to remove potential adsorbed iron. The reactor wall (borosilicate 3.3 glass, thickness 1 mm) is expected to significantly filter radiation with λ < 290 nm. To dissociate the influence of UV-B fraction from the rest of wavelengths on H₂O₂ photolysis, a glass filter SQ (FSQ-WG320 Newport), blocking λ < 320 nm, was used between the lamp and the reactor. Experiments were duplicated.

2.3.2. Abatement of 2,4-D under sunlight irradiation (recirculation mode)

A 500 mL of a 2,4-D solution (1 mg L⁻¹ or 10 mg L⁻¹) were treated by Hydrogen Peroxide Solar Photolysis (HPSP) and solar photo-Fenton-like (SPF-like) processes, at two pH conditions (3.6 and 7.0) for 6 h (10 a.m. - 4 p.m.) on clear, sunny days during the summer months of January–March (58° 22' W, 34° 36' S). The experimental setup included a 500 mL feed tank, a Materflex[®] peristaltic pump, a 250 mL cylindrical Pyrex[®] reactor located on a reflecting surface and tilted at a 34° angle with respect to the horizontal. A refrigeration system kept the temperature at 25 ± 3 °C

while exposed to solar radiation. The solution was continuously recirculated at 12 L h⁻¹. UV-B + A radiation was monitored throughout the time by means of a Lutron YK-35UV UV light meter in order to calculate the normalized irradiated time (t_{3mw,n}). This parameter was used to standardize the solar irradiation, assuming an average solar UV flux on a perfect sunny day of 3 mW cm⁻² ([Hincapié-Pérez et al., 2006](#)). Experiments containing 1 mg L⁻¹ 2,4-D were performed with different H₂O₂ concentrations: 3, 6, 10 and 20 mg L⁻¹. Finally, the degradation of 1 mg L⁻¹ 2,4-D was investigated in a simulated surface water (0.1 mg L⁻¹ F⁻, 7.8 mg L⁻¹ Cl⁻, 11.5 mg L⁻¹ SO₄²⁻, 61.0 mg L⁻¹ HCO₃⁻, 5.0 mg L⁻¹ humic acid) ([Stumm and Morgan, 1996](#)).

3. Results

3.1. Abatement of 2,4-D under Xe-lamp irradiation (batch mode)

The evolution of 2,4-D and H₂O₂ concentrations for experiments with an initial pH of 7.0 (a) and 3.6 (b) are depicted in [Fig. 1](#) and [Fig. 2](#), respectively. Control experiments (10 mg L⁻¹ 2,4-D) were conducted with and without UV-B filter and led to less than 10% degradation after 6 h of treatment, at both pH levels tested (data not shown).

In the absence of cut-off filter (UV-B + A and visible irradiation), degradation kinetics of 2,4-D were similar during the first 5 h for the HPP and PF-like treatments at pH 7. This fact indicated that HPP was the dominant process at circumneutral pH. Although the trials started at neutral conditions, the pH dropped to 5.3 ± 0.4 and 5.6 ± 0.6 for PF-like and HPP experiments, respectively. Under these conditions, the contribution of dissolved iron and therefore the PF process became relevant, and a removal improvement was observed after the first 5 h of irradiation when iron was present.

Photolysis of 2,4-D with Fe(III), in the absence of H₂O₂, produced 17% degradation after 6 h of irradiation. When the UV-B filter was used, all photo-induced processes at neutral pH were significantly reduced.

At pH 3.6 and employing UV-B + A and visible irradiation, the PF-like process rapidly and completely degraded 2,4-D, whereas results from HPP treatment were similar to those at pH 7.0. The experiments performed using 0.6 mg L⁻¹ Fe(III) without H₂O₂ led to an increase in 2,4-D degradation with respect to that observed at neutral pH, from 17% to 35%. The use of UV-B filter produced the same detrimental effect observed previously. The pH remained constant at 3.6 throughout the test.

Dissolved organic carbon (DOC) concentration was measured at the end of the treatments. At pH 7.0, UV-B + A + visible HPP and PF-like trials led to a DOC decrease of 4% and 12% whereas at pH 3.6 the reductions were 9% and 77%, respectively. Using the UV-B filter, the efficiency of the processes diminished; it is nevertheless remarkable that a 60% removal of DOC was achieved after 1 h of PF process at pH 3.6.

[Fig. 2](#) depicts the evolution of H₂O₂ consumption. PF-like trials at an initial pH 7.0 or 3.6 upon the UV-B + A + visible irradiation showed the most important change, with 88% of H₂O₂ removed after 6 h at pH 7.0, and 66% consumed after 1 h of treatment at pH 3.6.

3.2. Identification of chlorinated-aromatic intermediates and degradation mechanism

The intermediates identified and categorised by isotope profiling with integration of the METLIN are summarized in Supplementary data and [Table 1](#). Intermediates identified and quantified during PF-like and HPP processes were: 2,4-dichlorophenol (2,4-DCP), 2-chlorohydroquinone (2-CHQ), 4-chlorocatechol (4-

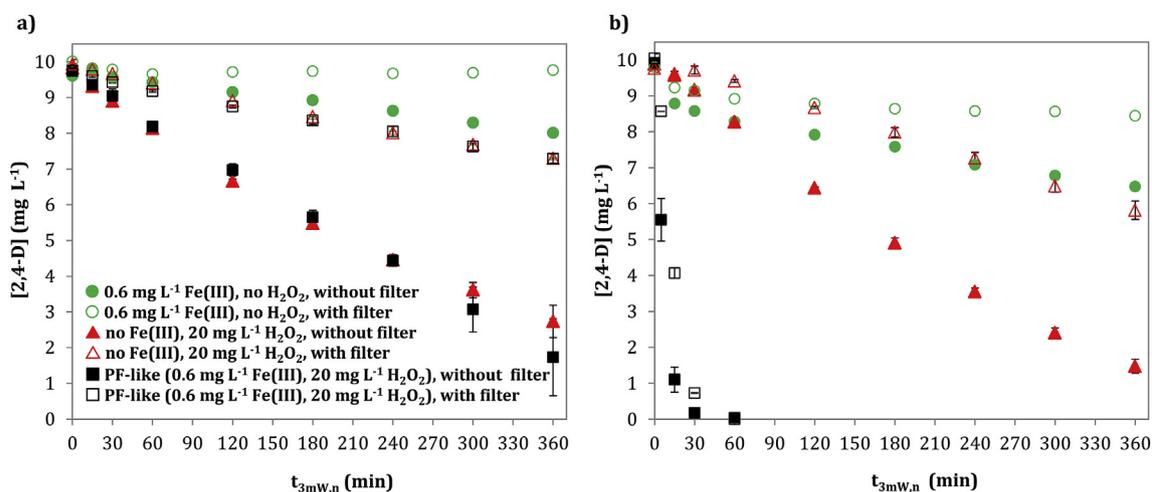


Fig. 1. 2,4-D time course of 50 mL of 10 mg L⁻¹ 2,4-D irradiated by the Xe-lamp at initial pH = 7 (Fig. 1a) and pH = 3.6 (Fig. 1b).

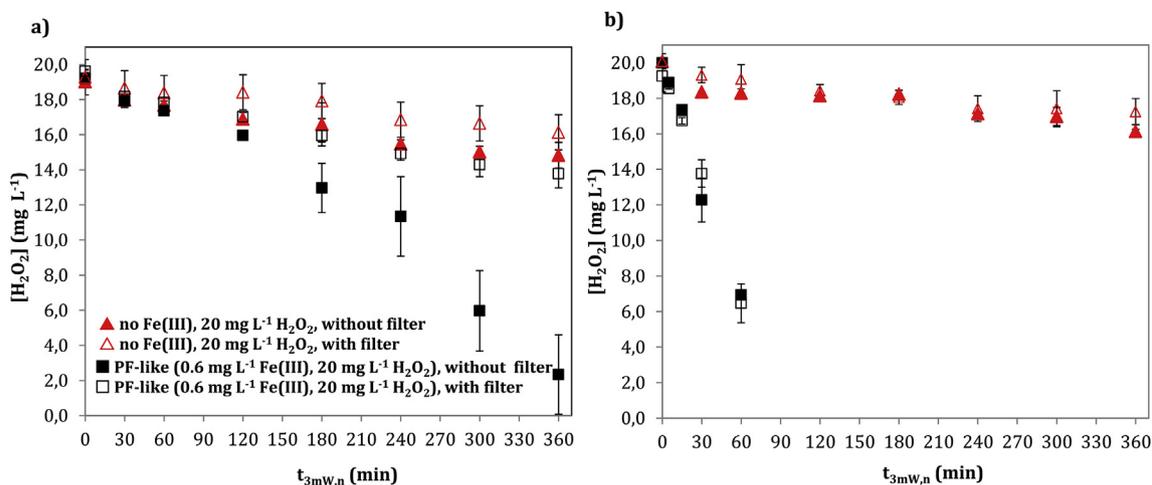


Fig. 2. H₂O₂ evolution when 50 mL of 10 mg L⁻¹ 2,4-D were irradiated by the Xe-lamp at initial pH = 7 (Fig. 2a) and pH = 3.6 (Fig. 2b).

Table 1
Summary of the intermediates identified by XCMS platform.

Intermediates	m/z	Retention time (min)
2,4-dichlorophenol	160.9563	9.01
2-chlorohydroquinone	142.9894	7.14
4-chlorocatechol		
4,6-dichlororesorcinol	176.9518	8.90
3,5-dichlorocatechol		
4-chlorophenol	126.9955	12.95

CC), 4,6-dichlororesorcinol (4,6-DCR), 3,5-dichlorocatechol (3,5-DCC), 4-chlorophenol (4-CP). The evolution of intermediate concentrations is depicted in Figure S5 and S6 (Supplementary information) for PF-like and HPP treatment, respectively. The most predominant intermediate during the early stage of the breakdown was 2,4-DCP. The hydroxyl radical (\bullet OH) attacked the C1-O bond of the aromatic ring, leading to the loss of an alkoxy radical to form 2,4-DCP and glycolic acid (Peller et al., 2004; Kwan and Chu, 2004) (see Table 2).

According to Kwan and Chu (2004), the \bullet OH may replace the chlorine atom of 2,4-DCP at two different positions, *para*-position to form 2-chlorohydroquinone or *ortho*-position to form 4-chlorocatechol. Results in this study (Figures S4 and S5 in

Supplementary data) show that \bullet OH radicals prefer to attack chlorophenols at *para*-positions and form 2-chlorohydroquinone, as was also reported by Bandara et al. (2001) and Ma et al. (2001). The electrophilic hydroxyl radical attacks the electron rich positions at the *ortho*- and *para*-sites. However, the \bullet OH attack at the *para*-position may experience less steric strain than that at the *ortho*-position and the inductive electron-withdrawing effect of the chlorine atom might render attachment of the electrophilic hydroxyl radical to the *ortho*-relative to the *para*-position (Peller et al., 2004). Consequently, *para*-substitution overcomes *ortho*-substitution, resulting in a faster oxidation of 2,4-DCP to 2-CHQ (S5 and S6 in supplementary data). Thus, 2-CHQ may dissociate two hydrogen atoms to give 2-chloro-1,4-benzoquinone upon further hydroxyl radical attacks, which proved undetectable in this case. 2,4-DCP can be hydroxylated by hydroxyl radicals, leading to the formation of 3,5-dichlorocatechol and 4,6-dichlororesorcinol. These two by-products would then undergo further hydroxylation; however, the intermediates were not detectable because they could be rapidly dehydrogenated to their corresponding quinone. 4-chlorophenol was also detected, probably being generated after dechlorinating 2,4-DCP. The degradation pathways were proposed accordingly, to illustrate a series of steps in the degradation of 2,4-D (Fig. 3). Although hydroquinone, benzoquinone, phenol and some

Table 2

The molecular ions, retention times, and calibration equations and coefficients for the analysis of 2,4-D and the identified intermediates.

Compounds	Molecular ion (m/z)	Retention time (min)	Equation and correlation coefficient
2,4-dichlorophenoxyacetic acid	219, [M-H] ⁻	8.46	$y = 1 \cdot 10^{-7}x$, $R^2 = 0.995$
2,4-dichlorophenol	161, [M-H] ⁻	9.63	$y = 4 \cdot 10^{-7}x$, $R^2 = 1$
2-chlorohydroquinone	143, [M-H] ⁻	6.6	$y = 5 \cdot 10^{-5}x$, $R^2 = 0.98$
4-chlorocatechol		7.97	$y = 3 \cdot 10^{-7}x$, $R^2 = 0.944$
4,6-dichlororesorcinol	177, [M-H] ⁻	8.55	$y = 8 \cdot 10^{-7}x$, $R^2 = 0.994$
3,5-dichlorocatechol		8.9	$y = 3 \cdot 10^{-7}x$, $R^2 = 0.975$
4-chlorophenol	127, [M-H] ⁻	8.85	$y = 71 \cdot 10^{-6}x$, $R^2 = 0.994$

carboxylic acids, proposed as compounds generated during last steps of 2,4-D degradation pathway, have been not identified, it is fair to suggest that 2,4-D degradation could yield these by-products specially during experiments carried out at acid pH values where high mineralization is achieved. It is well known that chlorophenols such as 4-chlorophenol and 4-chlorocatechol can undergo upon photocatalytic reactions $\bullet\text{OH}$ radical attack leading to the dechlorination and yielding hydroquinone and benzoquinone as main by-products. Therefore, both chemical substances can undergo ring opening producing aliphatic acids (butanedioic and acetic acid) prior to mineralization (Mylonas and Papaconstantinou, 1996; Li et al., 1999; Lapertot et al., 2006).

3.3. Abatement of 2,4-D under sunlight (recirculation mode)

Results obtained for the treatment of 10 mg L^{-1} 2,4-D at both pH levels were similar and even slightly better, in terms of 2,4-D degradation, mineralization and H_2O_2 evolution, than those obtained with the Xe-lamp (data not shown). This behaviour could be associated with the different experimental setup and/or different irradiation source.

Iron precipitation was detected on the inner walls of the recirculation tubing, especially when silicon tubes were used and at neutral pH. Although the experimental system was carefully cleaned with acid after every trial, minute quantities of iron may have remained adsorbed on the tube walls. Indeed, small quantities

of iron were found at the end of HPSP experiments performed at initial $\text{pH} = 7$ (pH dropped to 4.2 after 6 h of treatment) and $\text{pH} = 3.6$, even though no iron was added. The case of HPSP at $\text{pH} = 3.6$ was particularly remarkable: total 2,4-D degradation and 32% of mineralization were reached after 3 h of treatment ($t_{3\text{mw},n} = 170 \text{ min}$), but in Xe-lamp experiments, the removal of 2,4-D and DOC was only 85% and 9%, respectively ($t_{3\text{mw},n} = 360 \text{ min}$). At the end of this HPSP trial, iron concentration was determined to be 0.07 mg L^{-1} , which supports the hypothesis of iron desorption from the tube walls. In order to evaluate the effect of this minute amount of Fe(III) on the PF-like process, an experiment was conducted under the previous conditions (10 mg L^{-1} 2,4-D, 20 mg L^{-1} H_2O_2 , 0.07 mg L^{-1} Fe(III), $\text{pH} = 3.6$) and Xe-lamp irradiation (UV intensity = 3 mW cm^{-2}). The time evolution of 2,4-D, 2,4-DCP and H_2O_2 is shown in Fig. 4. The results were in agreement with those of the HPSP trial, where 2,4-D and 2,4-DCP were totally eliminated after $t_{3\text{mw},n} = 180 \text{ min}$, the DOC removal was approximately 32% and 35%–40% of H_2O_2 was consumed at the end of the treatment.

The processes were further investigated at the more environmentally relevant initial concentration of 1 mg L^{-1} 2,4-D. In this case, DOC was not monitored due to analytical limitations.

In a first approach, SPF-like (0.6 mg L^{-1} Fe(III)) and HPSP treatments were investigated using initial H_2O_2 concentrations of 3, 6, 10 and 20 mg L^{-1} , and initial $\text{pH} = 7.0$ and 3.6 (Fig. 5).

Results showed no significant differences between SPF-like and HPSP processes at neutral pH for each H_2O_2 concentration

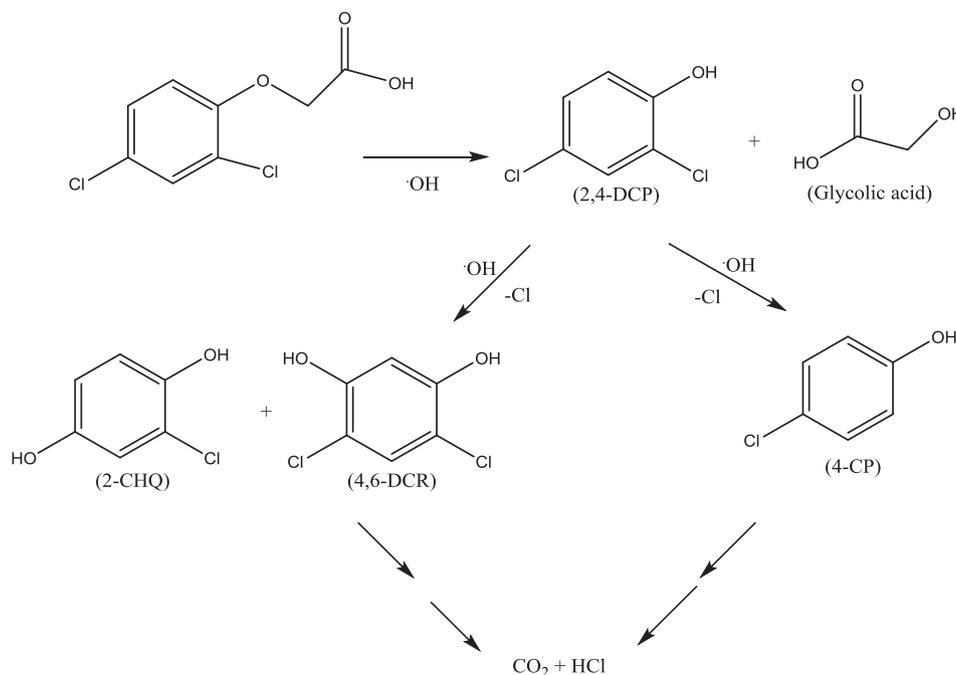


Fig. 3. Formation of chlorinated aromatic by-products during PF-like and HPP treatments under UV-B + A + visible light irradiation.

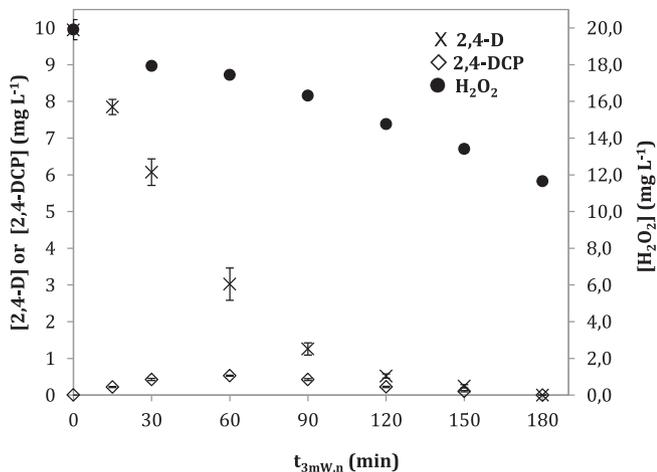


Fig. 4. 2,4-D, 2,4-DCP and H_2O_2 time course of 50 mL of 10 mg L^{-1} 2,4-D irradiated by the Xe-lamp using the following conditions: 0.07 mg L^{-1} Fe (III) and 20 mg L^{-1} H_2O_2 at $\text{pH} = 3.6$.

evaluated during 6 h of treatment ($t_{3\text{mw},n} = 310\text{--}340$ min). Final pH for all the treatments ranged between 5.5 and 6.8. Under these conditions, iron dissolution can be neglected, and HPSP process was likely the main contributor to 2,4-D oxidation.

Faster degradation was observed with increasing initial H_2O_2 concentration up to 10 mg L^{-1} . Similar yields (90%) were achieved after 6 h of treatment when 10 or 20 mg L^{-1} H_2O_2 was added. The addition of 20 mg L^{-1} H_2O_2 appeared to display superior degradation kinetics initially; however, after 120 min of treatment, both experiments (10 and 20 mg L^{-1} H_2O_2) behaved similarly. The lower concentrations (3 and 6 mg L^{-1}) did not reach removal to 2,4-D drinking water standards. The concentration of 2,4-DCP and total iron at the end of HPSP trials at neutral pH were below the corresponding LoQs for all experiments.

At neutral pH, for most of SPF-like experiments, H_2O_2 removal was slightly higher than in HPSP treatments, except for the case of 20 mg L^{-1} concentration, where this behaviour was only noticed at the beginning of the process. Approximately 80%, 50%, 30% and 20% of H_2O_2 were consumed during SPF-like treatments when 3, 6, 10 and 20 mg L^{-1} of this reagent was added as an initial concentration, and the H_2O_2 consumed ranged from 2.5 to 3.6 mg L^{-1} . Thus, no notable differences in total consumption of H_2O_2 were observed.

At $\text{pH} 3.6$, 3 mg L^{-1} H_2O_2 were sufficient to achieve total 2,4-D and 2,4-DCP degradation after $t_{3\text{mw},n} = 25$ min of SPF-like process, (0.6 mg L^{-1} Fe(III)); same outcome was observed at $t_{3\text{mw},n} = 110$ min during the HPSP experiment at this pH. However, total iron at the end of the HPSP experiment was found to be 0.03 mg L^{-1} , indicating that minute amounts of iron previously deposited on the tube walls leached under acidic conditions and was enough to produce the degradation of the pollutant and its by-product by SPF treatment. Under acidic conditions, the H_2O_2 consumption was 60% and 35%, when 0.6 and 0.03 mg L^{-1} of iron species were present, respectively.

Experiments of 2,4-D degradation in simulated groundwater were conducted with initial concentrations of 10 and 20 mg L^{-1} H_2O_2 ; Fig. 6 shows the results corresponding to the latter, since it displayed the highest efficiency. SPF-like and HPSP processes at neutral pH degraded close to 40% of 2,4-D after 6 h of treatment ($t_{3\text{mw}} = 335$ min) in simulated surface water, while pH increased to around 8. Acidification was required to achieve complete 2,4-D and 2,4-DCP abatement (data for 2,4-DCP evolution not shown) after $t_{3\text{mw},n} = 35$ min and DOC elimination close to 50%. The final H_2O_2 concentration was 15 mg L^{-1} .

The HPSP treatment (20 mg L^{-1} H_2O_2) at $\text{pH} = 3.6$, resulted in 0.05 mg L^{-1} of total iron leached from the inner tube walls at the end of the test, which practically converted it into a SPF treatment with minute iron amounts. The process achieved elimination of 2,4-D and 2,4-DCP in $t_{3\text{mw},n} = 140$ min and 35% mineralization. The final H_2O_2 concentration was 17.5 mg L^{-1} .

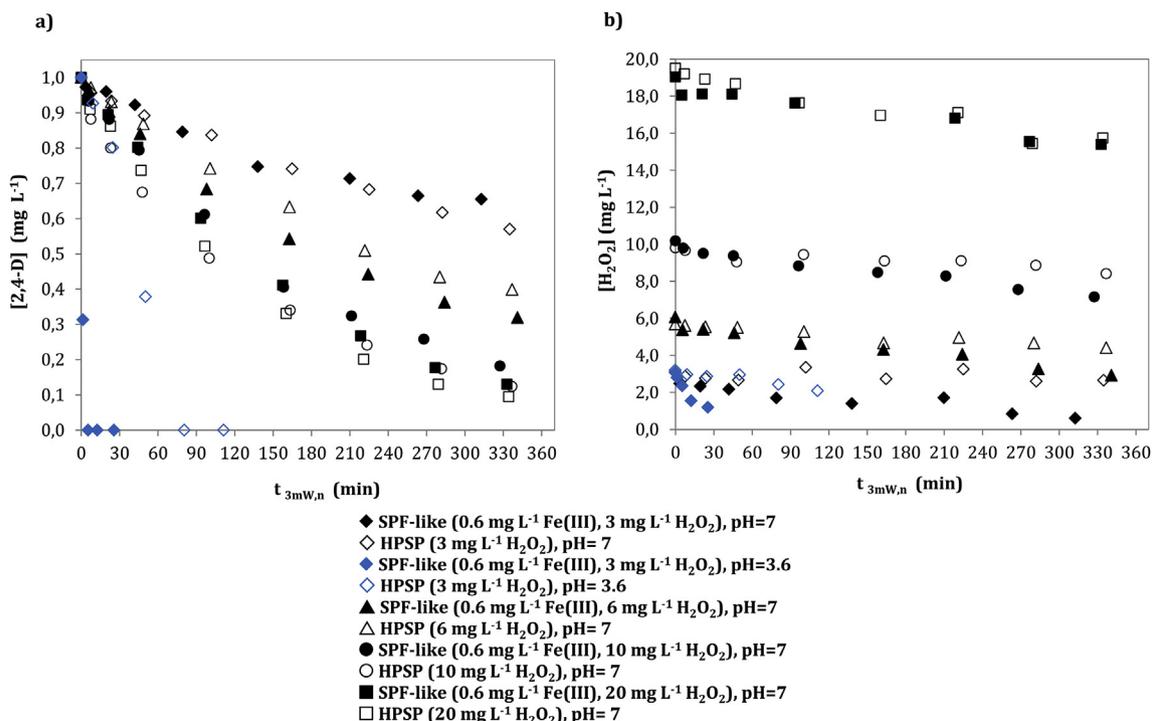


Fig. 5. 2,4-D (Fig. 5 a) and H_2O_2 (Fig. 5 b) time course of 500 mL of 1 mg L^{-1} 2,4-D (Milli-Q water) irradiated by solar light at an initial $\text{pH} = 7$ (black color) and $\text{pH} = 3.6$ (blue color). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

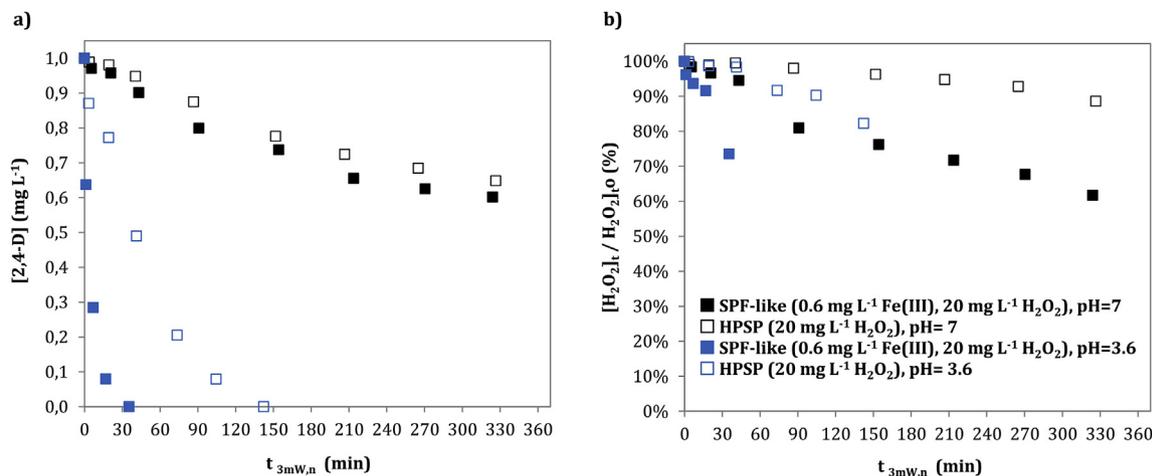
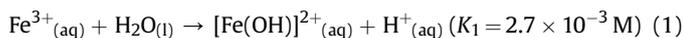


Fig. 6. 2,4-D (Fig. 6 a) and H₂O₂ (Fig. 6 b) time course of 500 mL of 1 mg L⁻¹ 2,4-D (matrix: simulated surface water) irradiated by solar light at an initial pH = 7 (black color) and pH = 3.6 (blue color). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

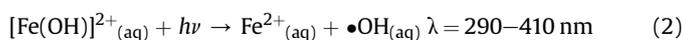
4. Discussion

The results obtained when the Xe-lamp was used demonstrate that degradation of 2,4-D mainly occurs by HPP at neutral pH, whereas under acidic conditions, PF contributes significantly to the process.

At pH between 2.5 and 5.0, Fe(OH)²⁺ is the main ferric-hydroxy complex in aqueous solutions (Pignatello et al., 2006), as described by Eq. (1).

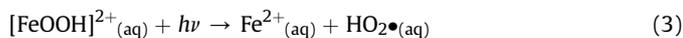


Fe(OH)²⁺ is a highly photo-active ferric aqua complex with two important light absorption maximums at 297 nm ($\epsilon = 2030 \text{ M}^{-1} \text{ cm}^{-1}$) and 205 nm ($\epsilon = 4640 \text{ M}^{-1} \text{ cm}^{-1}$) (Pignatello et al., 2006; Gallard et al., 1999), and enables the photo-production of hydroxyl radicals by UV-B + A and visible light absorption following Eq. (2):



Thus, in mildly acidic conditions and subjected to UV-B + A and visible irradiation, these species contribute to 2,4-D abatement, as observed in the control experiments performed with 2,4-D and Fe(III) at pH 3.6. Moreover, the complex [Fe(OH)₂]⁺, whose photochemistry is still not fully understood, is present at pH values > 5.0 and can also participate in the 2,4-D degradation at circumneutral pH, as suggested by Eq. (2).

Similar H₂O₂ disappearance levels were achieved when UV-B filter was used after 1 h of PF-like treatment at pH 3.6, which indicates that UV-A + visible wavelengths were responsible for the photo-induced reactions during this process when iron was dissolved. Inversely, PF-like trials performed at neutral pH presented a higher H₂O₂ consumption when UV-B contributed to the process. This indicates that UV-B light promotes a higher photolysis of [FeOOH]²⁺ complex ($\epsilon = 0.33$ using a medium pressure mercury arc lamp) that produces HO₂• and Fe(II) (via Eq. (3)) (Pignatello et al., 2006).



It is also noteworthy that 20–22% of final H₂O₂ consumption occurred during the HPP treatment at both studied pH values,

suggesting that pH variations from 3.6 to 7 do not play an important role in the process. When the UV-B filter was used, the H₂O₂ consumption during the first 30 min was reduced by 50%, and to 14–16% in 6 h at both pH values. The experiments showed that UV-B and UV-A can photolyze H₂O₂, but under UV-B, H₂O₂ decomposition and 2,4-D elimination proceed much faster.

Chlorinated phenols such as 3,5-dichlorocatechol, 2-chlorohydroquinone and 4-chlorophenol were detected as intermediates during HPP and PF-like processes at pH 3.6 and 7.0. There were no marked differences in the nature of by-products generated by the processes at either pH value but dissimilarities were observed in the kinetics of by-product abatement and their concentrations. By-products were generated to a lesser extent and they were removed faster during PF-like process at low pH than at neutral pH value or during HPP treatment, underscoring the improved performance of acidic PF processes for organic removal and suggesting that •OH generation and attack was the main mineralization *via* during both treatments and pH values.

The results of the study corroborate the hypothesis that SPF-like process at acidic pH could be performed with minute concentrations of iron (0.07–0.6 mg L⁻¹), found naturally in surface waters, to reach efficient 2,4-D, 2,4-DCP and DOC removals in a Milli-Q water matrix (Fig. 4) and demonstrate the degradation of 1 mg L⁻¹ 2,4-D in a Milli-Q or simulated surface water, respectively, applying SPF process under acidic conditions (pH 3.6), using minute Fe(III) concentrations ($\leq 0.6 \text{ mg L}^{-1}$) (Figs. 5 and 6). For the removal of 1 mg L⁻¹ 2,4-D in Milli-Q water, only 3 mg L⁻¹ H₂O₂ and 0.6 mg L⁻¹ Fe(III) were necessary to reach 2,4-D and 2,4-DCP concentrations below the limit of quantification ([2,4-D] < 0.007 mg L⁻¹ and [2,4-DCP] < 0.009 mg L⁻¹) in less than 30 min. When a simulated surface water matrix was used, a H₂O₂ concentration of 20 mg L⁻¹ was necessary under the same reaction conditions. Therefore, SPF-like process is able to reduce 2,4-D and 2,4-DCP concentrations to the maximum levels established by WHO (2003) ([2,4-D] < 0.030 mg L⁻¹) and US EPA (2015) ([2,4-DCP] < 0.010 mg L⁻¹). However, irradiation times longer than $t_{3\text{mW},n} = 6 \text{ h}$ were required at neutral pH to reach 2,4-D concentrations below 0.1 mg L⁻¹ (maximum contaminant level set by Argentinean legislation for drinking water) (Código Alimentario Argentino, 2007).

The lower herbicide abatement observed in simulated surface water matrix experiments can be associated mainly with the scavenger effect of inorganic anions as well as the competitive effect of the humic acids for ROS produced. Interestingly, during the SPF-

like trials with humic acids at neutral pH, iron remained in solution due to its coordination with these compounds (Georgi et al., 2007; Lipczynska-Kochany and Kochany, 2008) and was available to participate in photo-Fenton reactions as demonstrated by experiments performed with 1 mg L⁻¹ 2,4-D and 5.0 mg L⁻¹ HA at neutral pH in the absence of the dissolved salts (data not shown). Under these conditions, the herbicide was completely eliminated after t_{3mw,n} = 120 min and 180 min when initial H₂O₂ concentration was 20 and 10 mg L⁻¹, respectively. Therefore, the presence of HA accelerates 2,4-D degradation by keeping iron in solution at neutral pH; however, the increase in inorganic species concentrations led to a significant reduction on herbicide removal.

5. Conclusions

Results showed the feasibility of 2,4-D removal by HPSP, which is the dominant mechanism of organic pollutant reduction during the SPF-like process at neutral pH.

The addition of H₂O₂ and direct exposure to solar light produces the removal of 2,4-D from surface water even in the presence of minute iron concentrations such as those found in natural waters (SPF-like process by minute Fe(III) concentrations). Acidification may be required to increase the efficiency of the treatment, depending on the characteristics of the water matrix.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.watres.2018.07.072>.

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