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Solar photo-Fenton degradation of herbicides partially dissolved in water

M. Jiménez[b], I. Oller[a], M.I. Maldonado[a], S. Malato[a], A. Hernández-Ramírez[b], A. Zapata[a], J.M. Peralta-Hernández[b,*]

[a] Plataforma Solar de Almería (CIEMAT), Carretera Senés, Km 4, 04200, Tabernas (Almería), Spain
[b] Universidad Autónoma de Nuevo León, Facultad de Ciencias Químicas-CELAES, Pedro de Alba s/n, Cd. Universitaria, San Nicolás de los Garza, NL, C.P. 66400, Mexico

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ABSTRACT

This study evaluates the solar photo-Fenton decontamination of wastewater containing a highly polluted mixture of two common herbicides, one of them partially dissolved. The mixture was composed by the commercial formulations Hierbamina® (479.5 g/L 2,4-dichlorophenoxyacetic acid, 2,4-D) and Gesaprim® (90% atrazine, ATZ), in a 5:9 (v/v) ratio, as they are commonly dosed in Mexico. All solar photo-Fenton experiments were performed in a Compound Parabolic Collector (CPC) pilot-plant with a total volume of 35 L (22 L illuminated volume). The influence of some operating variables (e.g., iron concentration, matrix salinity and initial pollutant concentration) and their relationship to photo-Fenton process efficiency were studied. Experiments were performed at three iron concentrations (5, 10 and 20 mg/L), in two types of waters (demineralized and fresh) and at two initial herbicides amounts (90 and 170 mg/L of ATZ and 50 and 100 mg/L of 2,4-D). Solution ecotoxicity and biodegradability during the photo-treatment was also evaluated, since it has been demonstrated that some photo-degradation by-products of ATZ and 2,4-D can be more toxic and/or persistent than the parent compounds. It was found that 10 mg/L of iron was a suitable concentration, the use of fresh water did not reduce photo-Fenton efficiency and H_2O_2 consumption becomes more efficient with higher starting pollutant concentration. Moreover, the study of toxicity and biodegradability during photo-Fenton degradation allowed the selection of the most favourable design parameters for the detoxification of the water.

1. Introduction

In developing countries, such as Mexico, agriculture is one of the main water consuming activities, employing 76% of the national water resources [1]. Due to the intense agricultural activity, the use of agrochemicals (pesticides) is a common practice that has considerably increased environmental pollution in Latin America in recent years [2]. The majority of these compounds (either in their parent form or in others resulting from diverse biotic or abiotic processes) are normally still toxic in the long term, recalcitrant to conventional water treatments, and consequently, represent a serious threat both to the environment and human health.

One of the main ways pesticides are disposed of is by dumping solutions used for fumigating or for dosing irrigation water into the environment. These solutions are generally prepared where they are used, and the equipment must be cleaned after use or drained of unused pesticide. It is therefore necessary to propose treatment methods to eliminate this source of contamination before it enters in the environment, where diffuse pollution would be more difficult to address. Pesticide solutions are very often prepared in water at very high concentration in emulsions or foams where the pesticides are not really dissolved. The proposed treatment method takes this into consideration.

Advanced oxidation processes (AOPs) have been described as effective methods for oxidizing these compounds because of their capacity for mineralizing almost any organic pollutant due to the production of hydroxyl radicals (•OH), powerful unselective oxidants (2.8 V vs. NHE (pH 0)) [3]. Among them, solar photo-Fenton is considered one of the most promising AOPs for the treatment of recalcitrant organic compounds in aqueous solutions [4–6]. This paper reports on the solar photo-Fenton decontamination of a mixture containing two common herbicides at high concentrations, one over its solubility limit. The aim was to propose an efficient on-site solution for the remediation of these highly polluted effluents before their discharge into the environment. This mixture was composed of the commercial formulations Hierbamina® (479.5 g/L 2,4-Dichlorophenoxyacetic Acid, 2,4-D) and Gesaprim® (90% atrazine, ATZ), in a 5:9 (v/v) ratio, as they are normally dosed in Mexico. This mixture is commonly employed in broadleaf control in corn, bean and sorghum crops [7,8].

ATZ is a widely used triazine-herbicide used in broadleaf control that has been characterized as bio-recalcitrant and toxic [9–11].

* Corresponding author. Tel.: +52 81 83294000x6288.
E-mail address: juan.peraltahr@uanl.edu.mx (J.M. Peralta-Hernández).

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This herbicide, classified as a possible human carcinogen by the US EPA and included in the Water Framework Directive list of priority hazardous substances, has been banned in some countries [12]. Its degradation by AOPs has been widely studied for a long time [13–16], but usually as a pure compound in demineralized water below its solubility threshold (30 mg/L) and not as an emulsion. In this paper, ATZ degradation has been addressed under more realistic conditions. 2,4-D is a common, persistent, and highly toxic phenoxyl herbicide also used in broadleaf control [17,18]. 2,4-D degradation by AOPs has also been studied before [7,19,20], but not at such a high concentration or as part of a real pesticide solution as usually applied to crops.

The main novelty of this paper is related with decontamination of wastewater containing partially dissolved pesticides. The proposed treatment method takes this into consideration, since it is able to degrade the parent compounds, permitting continuous dissolution/degradation of the undissolved fraction. This study of photo-Fenton degradation of a commercial herbicide mixture focuses on the influence of some operating variables (e.g., iron concentration, matrix salinity and initial pollutant concentration) and their relationship to process efficiency parameters (treatment time required and H_2O_2 consumption). Solution ecotoxicity and biodegradability during the photo-treatment was also evaluated, since it has been demonstrated that some photo-degradation by-products of ATZ and 2,4-D can be more toxic and/or persistent than the parent compounds [18,21,22]. Both, a commercial assay based on *Vibrio fischeri* and respirometry with activated sludge was employed for toxicity evaluation as it is recommended to evaluated toxicity by more than one bioassay.

2. Experimental

2.1. Chemicals

Commercial formulations of Hierbamina® (479.5 g/L 2,4-D, $C_8H_6Cl_2O_3$) and Gesaprim® (solid, 90% ATZ, $C_8H_{14}ClN_5$), were used as received. Analytical standards (>98%) for chromatographic analyses were purchased from Sigma-Aldrich. Water solubility of these compounds is 0.03 g/L, 20 °C (ATZ) and 0.9 g/L, 20 °C (2,4-D). Hierbamina® was tested diluted in 0.01–0.02% (v/v) water and Gesaprim® in 0.01–0.02% (w/v) water to an initial concentration of 50–100 mg/L of 2,4-D and 90–170 mg/L of ATZ, respectively. Demineralized water (DW) used for the test was supplied by the Plataforma Solar de Almería (PSA) demineralisation plant (conductivity < 10 μS/cm, Cl^- = 0.2–0.3 mg/L, NO_3^- < 0.2 mg/L, organic carbon <0.5 mg/L). Fresh water (FW) used in the experiments contained 2 mg/L DOC, 1 mS/cm, 185 mg/L Cl^-, 150 mg/L SO_4^{2-}, Na^+: 240 mg/L, Ca^{2+}: 60 mg/L; 35 mg/L Mg^{2+}. Experiments were performed using iron sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$, >98%), reagent-grade hydrogen peroxide (30%, w/v) and sulfuric acid (>98%) for pH adjustment (around 2.7–2.9), all purchased from Panreac. The photo-treated solutions were neutralized by NaOH (reagent-grade >98%, Panreac) for toxicity and biodegradability analyses.

2.2. Analytical determinations

HPLC-UV-DAD (Agilent Technologies, series 1100) was used to monitor the pesticide concentration with a C-18 column (Gemini 5 μm, 3 mm × 150 mm from Phenomenex). The mobile phase consisted of a mixture of 55% acetic acid (0.2%) and 45% acetonitrile. Detection was done at 223 nm (ATZ) and 202 nm (2,4-D). HPLC analytical samples were prepared by mixing the pesticide solution with acetonitrile in a 1:1 proportion. Samples were evaluated with acetonitrile dilution before and after filtration (0.22 μm) to distinguish between the soluble and non-soluble fraction of ATZ at any given time. When the unfiltered and organic samples were mixed, all the ATZ present was dissolved, permitting total quantification when it was over its solubility limit. Concomitantly, when the unfiltered and organic samples were not mixed, all the undissolved ATZ was retained in the filter. Mineralization was followed by measuring the total organic carbon (TOC) by direct injection of the samples into a Shimadzu-5050A TOC analyzer. Anion concentrations (Cl^- and SO_4^{2-}) were determined with a Dionex DX-600 ion chromatograph using a Dionex Ionpac AS11-HC 4 mm × 250 mm column. Chemical oxygen demand (COD) was measured with Merck® Spectroquant kits. The COD method was unable to identify the triazine ring, and photo-Fenton was unable to mineralize it. Therefore, the corresponding theoretical amount of oxygen required for triazine ring oxidation was added in all the experimental measurements. Total iron concentration was monitored by colorimetric determination with 1,10-phenanthroline, according to ISO 6332, using a Unicam-2 spectrophotometer. Hydrogen peroxide was analyzed by a fast, simple spectrophotometric method using ammonium metavanadate [23].

2.3. Toxicity and biodegradability assays

A commercial assay marketed by Macherey-Nagel® as Biofix®Lumi-10 was employed to evaluate the toxicity using a specially selected freeze-dried strain of the marine bacterium *V. fischeri* (NRRL number B-11177). Hydrogen peroxide present in the samples was removed prior to toxicity analysis using catalase (100 mg/L of 2500 U/mg bovine liver) acquired from Fluka Chemie AG (Buchs, Switzerland) after adjusting the sample pH to between 6 and 8. Respirometry with activated sludge was employed for toxicity and biodegradability evaluation of the partially photo-treated samples using a BMT Respirometer (SURCIS, S.L). For both purposes, the respirometer was loaded with a certain volume of activated sludge from the Aqualia Municipal Wastewater Treatment Plant in Almería (Spain). 3 mg of N-allythiourea per g of VSS (volatile suspended solids) were added to the sludge to inhibit nitrification and measure the sample's effect on only the heterotrophic bacteria. For toxicity analysis (800 mL of activated sludge), the maximum oxygen uptake rate of activated sludge (mg O_2/L h) was measured in presence of a certain volume of photo-treated sample (200 mL). The percentage of inhibition was then calculated by comparing with the maximum oxygen uptake rate from the addition of 0.5 g of sodium acetate per g of VSS (as a non-toxic reference) to the activated sludge. For biodegradability analysis (1000 mL of activated sludge), the amount of easily biodegradable chemical oxygen demand (COD_{eb}, mg/L) was recorded by the respirometer in presence of 30 mL of filtered pre-aerated sample. The biodegradability of the samples was evaluated by the COD_{eb}/COD_{total} ratio. When $COD_{eb}/COD_{total} > 0.1$, the sample is considered biodegradable.

2.4. Experimental setup

2.4.1. Solar reactors

Photo-Fenton experiments were performed in a Compound Parabolic Collector (CPCs) pilot-plant designed for solar photocatalytic applications. This reactor is made up of two modules with 12 Pyrex glass tubes mounted on a fixed platform tilted 37° (local latitude). The total illuminated area is 3 m^2 and the volume is 40 L, 22 L of which are irradiated.

Solar ultraviolet radiation (UV) was measured by a global UV radiometer (KIPP&ZONEN, model CUV 3) mounted on a platform tilted 37° (the same as the CPCs). With Eq. (1), combination of the data from several days' experiments and their comparison with

Table 1
Hydrogen peroxide consumption and illumination time required for different stages of photo-Fenton degradation of the commercial pesticide mixture (TOC_0 = 80 mg/L, 90 mg/L ATZ, 50 mg/L 2,4-D) at different starting iron concentrations in two different matrixes (DW and FW).

Fe (mg/L)/matrix	Complete degradation of the active ingredients		60% mineralization	
	$t_{30\,W}$ (min)	H_2O_2 (mM)	$t_{30\,W}$ (min)	H_2O_2 (mM)
5/DW	45	12	200	38
5/FW	45	10	180	34
10/DW	34	13	130	40
10/FW	32	11	115	33
20/DW	32	11	100	35
20/FW	33	16	105	40

other photocatalytic experiments is possible [24].

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

where t_n is the experimental time for each sample, UV is the average solar ultraviolet radiation measured during Δt_n, and $t_{30\,W}$ is 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). V_T is the total volume of the water loaded in the pilot plant (40 L), V_i is the total irradiated volume (22 L).

Photo-Fenton experiments were carried out at two different initial concentrations of each pesticide (90 and 170 mg/L of ATZ; 50 and 100 mg/L 2,4-D), corresponding to an initial TOC of 50–90 and 30–60 mg/L, respectively. Two water qualities were tested (DW and FW) at three different iron concentrations (5, 10 and 20 mg/L). The pH was adjusted to 2.7–2.9 (H_2SO_4 2N) and hydrogen peroxide concentration was kept between 50 and 100 mg/L throughout the process.

The mixture of pesticides was added directly into the pilot plant and homogenized by turbulent recirculation for half an hour. With the collectors covered, the pH was adjusted and iron salt was added. Then 200 mg/L of hydrogen peroxide were added and the collectors were uncovered, which is when photo-Fenton began. Hydrogen peroxide was measured frequently and consumed reagent was continuously replaced so as to avoid lack of H_2O_2.

3. Results and discussion

3.1. Photo-Fenton studies

Photo-Fenton degradation of a mixture of two commercial pesticides [Hierbamina® (479.5 g/L 2,4-D) and Gesaprim® (90% ATZ)] was evaluated at a high concentration. The original amount of ATZ was always higher than its solubility point in water at room temperature, and consequently the original mixture was an emulsion in which ATZ was only partially dissolved. However, after less than 15 min of photo-treatment the mixture was homogenized in all cases by the continuous degradation and subsequent redissolution of ATZ, which allowed calculation of kinetics and comparison of different experimental conditions.

The first study was focused on the behavior of the mixture in DW during photo-Fenton treatment and evaluation of the effect of iron concentration on the degradation process. The initial operating conditions were 80 mg/L of TOC (90 mg/L ATZ and 50 mg/L 2,4-D) at three different Fe^{2+} concentrations (5, 10 and 20 mg/L). Table 1 summarizes the results.

In all the cases, photo-Fenton successfully eliminated the active ingredients and mineralized at least 60% of the original TOC. Blank experiments using H_2O_2 without irradiation or irradiated in the same photoreactor during at least 3 h did not produced any ATZ nor 2,4-D degradation. From the beginning of the process, ATZ was gradually degraded and redissolved down to a maximum amount detected of 25–30 mg/L. Nevertheless, the HPLC analysis of samples predissolved with acetonitrile before filtering allowed the total amount of ATZ in the mixture, including the non-soluble fraction, to be assessed. Total elimination of ATZ was observed after 30–45 min of illumination time and 11–15 mM of H_2O_2 consumed with different iron concentrations. On the other hand, 2,4-D was totally degraded after only 6–8 min of photo-treatment and 3–5 mM of H_2O_2 consumed. Chloride concentration was monitored throughout the process in order to confirm complete degradation of the pesticides. For instance, with 20 mg/L of Fe^{2+}, the amount of Cl^- found after 55 min of illumination time and 45% mineralization (30 mg/L of Cl^-) demonstrated that the original parent compounds were totally eliminated and the remaining intermediates were unchlorinated.

Due to the nature of the photo-Fenton reaction, and considering that the triazine ring is not oxidized by hydroxyl radicals [13], the remaining TOC at the end of the process should come mainly from triazine ring (3 of the 8 carbons initially present in the ATZ molecule) and some aliphatic carboxylic acids (from ATZ lateral chains and from 2,4-D), which are more biodegradable than ATZ. In the experiment with 20 mg/L Fe^{2+} (highest mineralization of all the tests shown in Table 1, 25 mg/L of TOC at the end of the test), 15 mg/L of the remaining TOC was carbon from the triazine ring contained in the original amount of ATZ (90 mg/L). Photo-Fenton degradation of single ATZ (0.01% w/v of Gesaprim®) was also evaluated with 10 mg/L of Fe^{2+} in DW (starting TOC 50 mg/L, 90 mg/L ATZ). After 120 min of illumination time and 30 mM of H_2O_2 consumed, mineralization was 60%. The 20 mg/L remaining TOC was entirely carbon from the triazine ring in the original ATZ content (19 mg/L).

Regarding iron concentration, photo-Fenton was noticeably less efficient at 5 mg/L of Fe^{2+}, mainly due to the lack of absorption of light by Fe^{3+} complexes (iron-aquo and ferric iron-carboxylic acid) present at low concentrations [25]. Nevertheless, there were no significant differences in the hydrogen peroxide required for achieving the total degradation of the active ingredients or 60% of mineralization (see Table 1). This means that despite the different degradation rates, hydrogen peroxide was still being used efficiently in all the experiments. It is well known that when hydrogen peroxide concentration in the solution is too high, some simultaneous reactions that consume H_2O_2 can occur in the matrix reducing the efficiency of hydroxyl radical generation [26,27]. Therefore, in all the experiments described in this paper, H_2O_2 concentration was kept within the range of 50–100 mg/L to avoid undesirable reactions.

On the other hand, degradation efficiency at 10 and 20 mg/L was similar in terms of elimination of active ingredients, mineralization rates, and H_2O_2 consumption; although, as expected, the overall efficiency was slightly higher with 20 mg/L of Fe^{2+} (see Table 1). This is explained by the photoreactor design [28], in which iron concentration is enough to absorb all the solar irradiation in both cases permitting quick regeneration of the ferrous ions.

More realistic experiments were then performed using FW to evaluate any influence of its components on photo-Fenton degra-

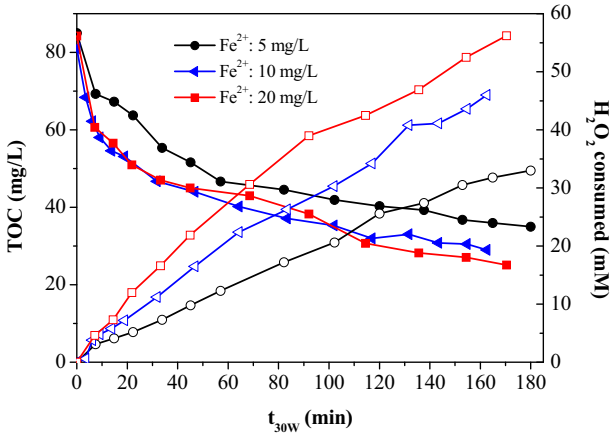

Fig. 1. Mineralization (solid symbols) and H_2O_2 consumed (open symbols) during photo-Fenton treatment in FW of the pesticide mixture at TOC_0: 80 mg/L.

dation of the pesticide mixture, since it has been demonstrated that some inorganic ions present in natural wastewater may affect generation of hydroxyl radicals [29]. We have previously demonstrated by response surface methodology, [30] that the main components of natural waters do not seriously affect the efficiency of the process in the range of 100–2000 mg/L chloride and 50–500 mg/L sulfate, respectively, but as the specific FW used in this study contains not only chloride and sulfate, this should be confirmed by testing at different iron concentrations. These tests were carried out under the same experimental conditions as the previous tests in DW (TOC_0: 80 mg/L, 90 mg/L ATZ, 50 mg/L 2,4-D at 5, 10 and 20 mg/L of Fe^{2+}). Mineralization and H_2O_2 consumption results are summarized in Fig. 1. A comparison of the results for both matrixes (DW and FW) at the three iron concentrations is shown in Table 1.

As clearly observed, no significant differences were found between the degradation results in DW and FW matrixes. This means that the use of real water did not noticeably reduce photo-Fenton efficiency (treatment time and H_2O_2 consumption). In view of these results, the following experiments were carried out in FW at 10 mg/L of iron. Photo-Fenton degradation of the selected mixture was also run at a higher starting concentration (double the one previously tested: TOC_0: 150 mg/L, 170 mg/L ATZ and 100 mg/L 2,4-D). Comparison of the experiments at the two different pollutant concentrations in FW and 10 mg/L of Fe^{2+} is summarized in Fig. 2.

As expected, as the original concentration was higher, overall H_2O_2 consumption and illumination time required for total elimination of the active ingredients and 60% mineralization increased. Higher organic load requires more hydroxyl radicals and consequently, degradation of the pesticide mixture takes longer. However, H_2O_2 consumption was more efficient at higher initial TOC. 25 and 16 mg H_2O_2 consumed/mg TOC mineralized for 80 and 150 mg/L of original TOC, respectively. As the process was run at a similar H_2O_2 concentration in both cases, part of it could have been consumed by parallel reactions that do not produce •OH or part of the •OH produced are reacting with components that are not organic. A detailed explanation of these mechanisms can be found in the excellent review by Pignatello et al. [25]. Therefore, the lower the starting TOC, the higher the H_2O_2 consumption ratio (mg H_2O_2 consumed/mg TOC mineralized). This information could be useful for H_2O_2 dosing in a system for treating pesticide-polluted wastewater: the lower pesticides concentration in the wastewater, the lower H_2O_2 concentration should be kept during the treatment.

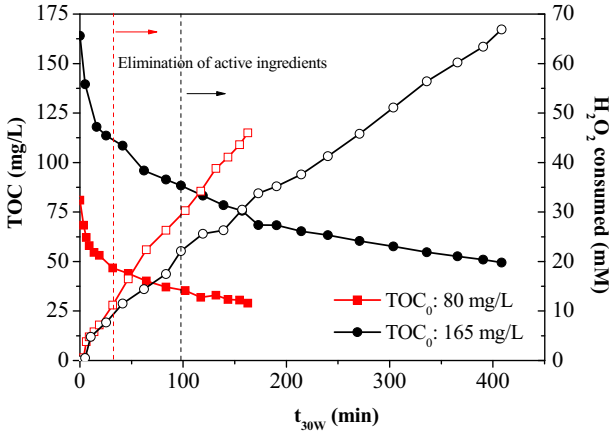

Fig. 2. Mineralization (solid symbols) and H_2O_2 consumed (open symbols) during photo-Fenton treatment of the pesticide mixture at 10 mg/L Fe^{2+} in FW at TOC_0: 80 mg/L and TOC_0: 150 mg/L.

3.2. Toxicity and biodegradability analyses

Toxicity and biodegradability of partially photo-treated samples was monitored during photo-Fenton degradation of the pesticide mixture at TOC_0: 150 mg/L (170 mg/L ATZ, 100 mg/L 2,4-D) and 10 mg/L Fe^{2+} in FW. These assays were designed to evaluate likely variations in toxicity and biodegradability. This information is very relevant for the disposal of the treated effluent into the environment or into a conventional biotreatment plant, since it is known that some intermediates generated during photo-oxidation can be more toxic and/or recalcitrant than the parent compounds [31,32].

In this case, photo-Fenton treatment was extended until 62% of the original mixture was mineralized (250 min of illumination time, 45 mM of H_2O_2 consumed). Total elimination of active ingredients occurred at 42% of mineralization, 65 min of illumination time and 12 mM of H_2O_2 consumed, and full dechlorination was observed at 46% of mineralization, 80 min of illumination time and 15 mM of H_2O_2 consumed. COD was also measured to evaluate the average oxidation state (AOS) of the photo-treated solution according to Eq. (2) [33]

$$\mathrm{AOS} = \frac{4 \cdot (\mathrm{TOC} - \mathrm{COD})}{\mathrm{TOC}} \quad (2)$$

where TOC and COD are expressed in molar concentrations. AOS is between +4 for CO_2, the most oxidized state of C, and −4 for CH_4, the most reduced state of C. This parameter can be used to estimate oxidation in a complex solution consisting of the original substances and their oxidation by-products. It can also provide indirect information on its biodegradability, as it indicates variations in the composition of the effluent that could result in changes in biodegradability/toxicity of the solution [34,35]. Fig. 3 shows TOC, COD and AOS during pesticide mixture degradation by photo-Fenton, and includes several chromatograms of the HPLC analysis at different stages of the photo-treatment.

As observed, AOS increased sharply at the beginning of the treatment and after approximately 50 min of illumination time remained almost constant until the end of the treatment. These results suggest that more oxidized organic intermediates are formed at the beginning of the treatment, and after a certain time, the chemical nature of most of them no longer varies substantially, even if the photo-Fenton treatment continues. This behavior is correlated with TOC during the process. At the beginning there is a sharp decrease in TOC due to fast mineralization of the aromatics and unsaturated hydrocarbons present in the mixture, which can easily be oxidized to CO_2 by •OH radicals. This stage corresponds to the increase in the AOS. This stage includes the degradation intermediates generated from the parent compounds up to total dechlorination. After that, the mineralization rate slows down, due to the formation of carboxylic and aliphatic compounds [36], which

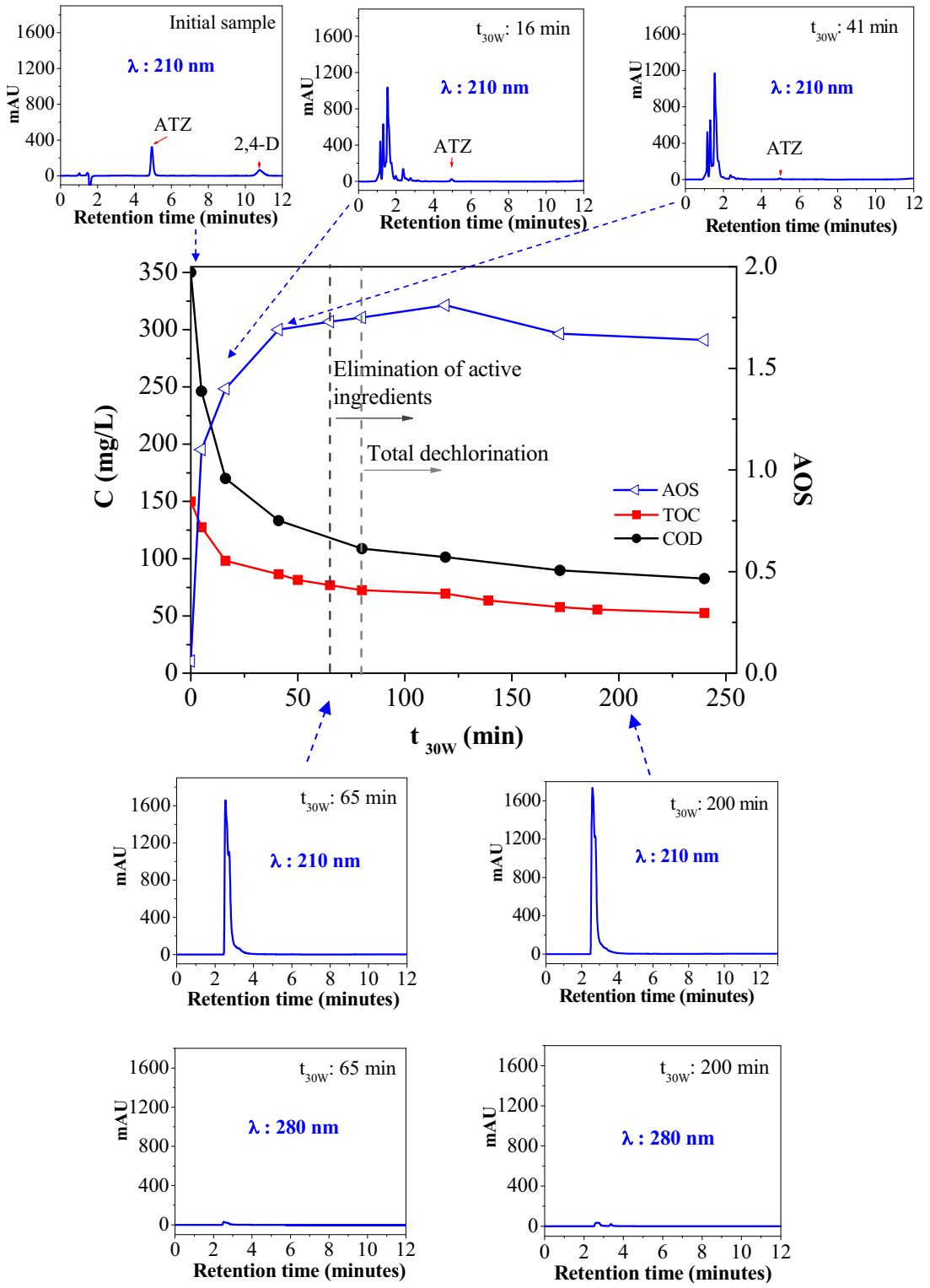

Fig. 3. TOC, COD and AOS during photo-Fenton degradation of the pesticide mixture with starting TOC_0 of 150 mg/L and 10 mg/L of Fe^{2+} including HPLC chromatograms at different stages of photo-treatment.

are hardly attacked by the •OH radicals, and due to the presence of the triazine ring coming from the ATZ, which is refractory to oxidation [13]. This explains AOS stabilization. The chromatograms shown also corroborate these results. At the beginning of photo-treatment (16 and 41 min of illumination time) the chromatograms at 210 nm show the appearance of reaction intermediates and the disappearance of ATZ and 2,4-D, verifying the changing chemical nature of the solution. After 65 min of photo-treatment (elimi-

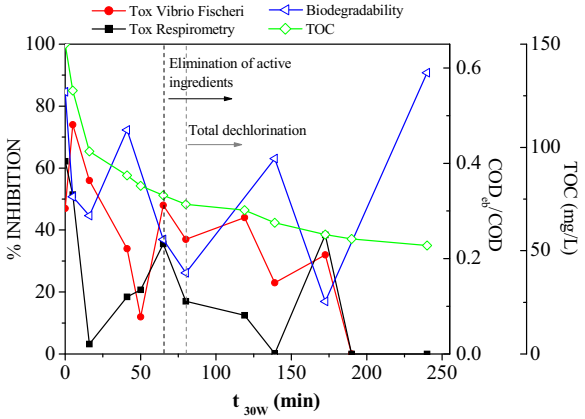

Fig. 4. Toxicity (percentage of *Vibrio fischeri* and activated sludge inhibition) and biodegradability (CODeb/COD) of samples partially treated by photo-Fenton at TOC_0: 150 mg/L, 170 mg/L ATZ, 100 mg/L 2,4-D and 10 mg/L of Fe^{2+} in FW.

nation of active ingredients, stabilization of AOS and TOC) the chromatograms show only one peak at 210 nm, which remains stable until the end of the treatment (200 min illumination time), confirming that the chemical nature of the mixture did not substantially change. This peak corresponds to the presence of carboxylic acids and cyanuric acid, compounds with maximum absorbance at 210 nm, which do not absorb at 280 nm. The chromatograms at 280 nm (typical wavelength at which aromatic compounds show maximum absorbance) confirm the absence of other oxidation intermediates.

As mentioned above, toxicity was evaluated using both *Vibrio ficheri* and respirometry with activated sludge. In the first case, the toxicity was calculated as a percentage of bacteria inhibition when exposed to samples for 30 min. In the second, the inhibition percentage was found by comparing the maximum oxygen uptake rate of the sludge when exposed to the sample with the one of a nontoxic reference. The biodegradability from respirometry measurements was calculated as the CODeb/COD ratio. A sample can be considered biodegradable when CODeb/COD > 0.1. Fig. 4 shows the results of these analyses.

It is worth mentioning that both toxicity curves show a similar tendency, although as expected, the inhibition percentages evaluated by *V. fischeri* are slightly higher than in respirometry, since one bacterial species is more sensitive than the biomass found in activated sludge. The first sample showed relatively high toxicity (60% respirometry inhibition) and during the photo-Fenton treatment, the toxicity curve was observed to vary (rises and falls). The changes in toxicity from the beginning of treatment until total dechlorination ($t_{30\,W}$ = 80 min) can be attributed to photogeneration of some toxic degradation by-products of ATZ; either chlorinated (e.g., amide derivatives atraimine (2-chloro-4-ethylimino-6-isopropylaminos-triazine) and CDIT (4-acetamido-2-chloro-6-ethylamino-s-triazine)) [21] or dechlorinated (as ammeline and ammelide) [37] as described above. In addition, the main product of hydrolysis of 2,4-D (2,4-dichlorophenol), has been described as toxic and more resistant to oxidative degradation than the parent compound [18]. After total dechlorination, toxicity tended to decrease. However, a slight rise in toxicity was observed at approximately 175 min of illumination time, which can be attributed to the presence of some toxic carboxylic acids. Nevertheless, at the end of the process, the mixture showed no relevant toxicity, confirming the ability of photo-Fenton to detoxify the pesticide solution.

The first sample was biodegradable according to the respirometry assay, even though these substances are reported to be recalcitrant. This may be partly attributed to the fact that the mixture contains commercial formulations of not only the active ingredients, but also some more biodegradable additives. Another point to consider is that the first sample was an emulsion in which the majority of the ATZ was not dissolved (only 18% of the total amount in solution) and consequently, the biomass was not affected by the insoluble fraction. Although the analysis revealed that the photo-treated samples were biodegradable throughout the process (CODeb/COD > 0.1), according to toxicity analyses, there was some variation in biodegradability over time (see Fig. 4). A drop in toxicity was usually correlated with an increase in biodegradability, and the points of maximum toxicity were those that showed minimum biodegradability. Knowledge of these profiles during photo-Fenton treatment of a specific wastewater allows the extent of degradation necessary for minimum toxicity and maximum biodegradability of a solution to be determined. It therefore permits selection of the most suitable moment for the disposal to the conventional sewage system. This information is very important for process operating design (setting treatment time and H_2O_2 dosage), since shortening photo-Fenton time is one of the major concerns in cost and energy optimization of the process. In this case, it is obvious that the photo-Fenton treatment should be extended at least until total elimination of the parent compounds. In view of the toxicity and biodegradability curves, the best point to end the photo-treatment to ensure biocompatibility of the mixture may be said to be after at least 42% of mineralization, 65 min of illumination time and 12 mM of H_2O_2 consumed. Nevertheless, a more conservative approach ensuring detoxification of the wastewater would be to extend the photo-treatment until full dechlorination of the mixture (46% mineralization, 80 min of illumination time, 15 mM of H_2O_2 consumed).

4. Conclusions

Photo-Fenton treatment has been demonstrated to be a feasible approach for the decontamination of wastewater containing a highly polluted mixture of two common herbicides, one of them partially dissolved (Hierbamina® (479.5 g/L 2,4-D) and Gesaprim® (90% ATZ)), since it is able to degrade the parent compounds, permitting continuous dissolution of the undissolved fraction, partly mineralize the mixture, reduce toxicity and improve biodegradability.

The main conclusions drawn from this work are summarized as follows:

(1) The use of 10 or 20 mg/L of Fe in tubular solar photoreactors with a diameter of a few cm is not critical, since the results were comparable in terms of treatment time and H_2O_2 consumed. However, the process efficiency was lower at 5 mg/L.
(2) The use of fresh water did not reduce photo-Fenton efficiency.
(3) H_2O_2 consumption becomes more efficient with higher starting pollutant concentration.
(4) Study of toxicity and biodegradability allows the most favorable design parameters (treatment time and H_2O_2 dosage) to be selected.

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