



## Effect of organic species on the solar detoxification of water polluted with pesticides

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### ABSTRACT

The effect of organic species on a solar-driven photo-Fenton treatment of a mixture of pesticides (methyl-oxydemethon, methidathion, carbaryl and dimethoate) has been studied in this paper. Triethoxyisododecyl alcohol, acetophenone and ethylenediaminetetraacetic acid (EDTA) have been used as examples of surfactants, solvents and complexing agents, respectively. An inhibitory effect on mineralization as well as on the elimination of the pesticides was observed in the case of the aliphatic surfactants, most probably due to the competition between the pesticides and the added organic matter for reaction with the relatively unselective hydroxyl radical. A methodology combining chemical analyses and bioassays was tested in order to explore the applicability of coupling a photo-Fenton process with a biological treatment in the presence of the surfactant. Despite the complexity of the mixture under study, a reliable monitoring of the process was accomplished; the biocompatibility of the mixture was enhanced and the optimal irradiation intensity was achieved just after complete removal of the pesticides.

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### 1. Introduction

Water polluted with pesticides constitutes an important environmental problem as increasing volumes of aqueous solutions of these hazardous chemicals are being generated, mainly in rural areas where the control and treatment of these residues is not easy; hence, they can potentially contaminate surface and ground water [1]. Solar photochemical processes, and in particular the photo-Fenton process, have been demonstrated to be useful to deal with this problem. This reagent consists of the use of catalytic concentrations of iron and sacrificial amounts of hydrogen peroxide, which acts as an oxidising agent [2]. The removal of pollutant can be achieved after moderate irradiation periods [3–5], and in general, the biocompatibility of the solution can be significantly enhanced [6–8]. In some cases, a biological treatment has been successfully applied to the photochemically treated effluent [9,10].

However, most of the published work deals with the elimination of model pesticides and very little information is currently available on the role of other species commonly present in real systems, which could interfere with the photo-Fenton reaction, and hence, modify the biocompatibility of the photo-treated effluent. In fact,

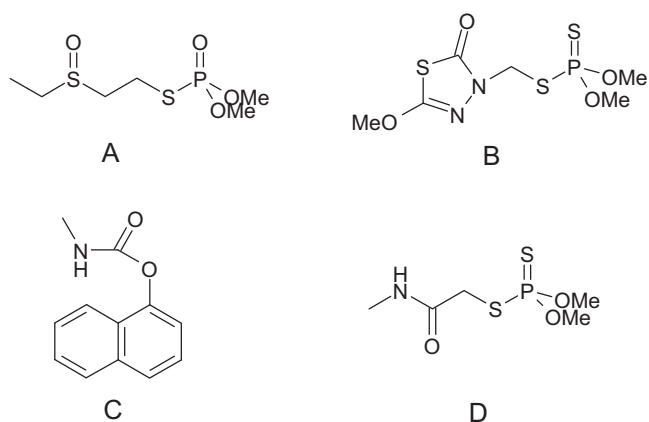
some papers have reported a loss of efficiency of the photo-Fenton process in the presence of some inorganic ions, such as chlorides [11–15]. Determining the effects of such interfering species on the biocompatibility of an effluent submitted to a solar photo-Fenton process is of paramount interest in order to determine if using a hybrid treatment is still possible, as well as the effect of those species on the coupling point.

Rinsing empty agricultural product bottles or plastics from greenhouses, a potential source of this kind of contamination, is expected to generate not only pesticides and inorganic ions, but also some other organics are commonly present. For instance, surfactants or organic solvents can be commonly found in the composition of commercial pesticides because of the low solubility of their active ingredients in water; in addition, extra amounts of surfactants are added when rinsing, and bottles containing other products widely used in intensive agriculture, such as chelating agents, could be mixed with those containing pesticides. As far as we know, no study has been published on the influence of these organics on the detoxification of this kind of wastewater by a photo-Fenton process, although they are expected to have a significant effect on mineralization, pesticide removal and the biocompatibility of the mixture.

Bearing all of this in mind, the aim of this paper is to gain further insight into the applicability of solar photo-Fenton as a pre-treatment to enhance the biocompatibility of aqueous solutions containing pesticides. In particular, the effect of three organic

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**Scheme 1.** Chemical structures of oxydemeton-methyl (A), methidathion (B), carbaryl (C) and dimethoate (D).

species, namely a surfactant (triethoxyisododecyl alcohol) a solvent (acetophenone) and a complexing agent (EDTA) in the photochemical process will be determined. In addition, a reliable methodology based on the combination of chemical analyses and bioassays will be assessed in order to compare the process in the presence or absence of extra organics.

## 2. Experimental

### 2.1. Reagents

High purity pesticides employed in this work (methidathion, carbaryl and dimethoate) were obtained from Aldrich (Pestanal). The four commercial pesticides used in the experiments were: (a) Ultracid™, containing 40% (w/v) of methidathion, supplied by Syngenta, (b) SevnoI™ (85%, w/w of carbaryl) was purchased from MAFA, (c) Laition™ (40%, w/v of dimethoate) was obtained from Lainco, and (d) Metasystox R™ (Bayer), which contained 25% (w/v) of methyl-oxydemeton (see Scheme 1 for structures).

EDTA, employed as a 0.1 M solution of disodium salt, and acetophenone (reagent grade) were supplied by Panreac. Triethoxyisododecyl alcohol (C<sub>12</sub>H<sub>25</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>OH, mixture of isomers, technical grade) was provided by BASF. Hydrogen peroxide (330 g/l), ferrous sulphate, and other chemicals used in this work were reagent grade and obtained from Panreac and used as received. The water used was Milli Q grade.

### 2.2. Photochemical reactions

Experiments carried out to determine the effect of added organics on the reaction were performed in open glass vessels, in which 250 ml of an aqueous solution containing 50 mg/l of the following three pesticides was placed: carbaryl, dimethoate and methidathion. Later, the organics were added at a concentration of 200 mg/l. The pH was adjusted to 2.8 with sulphuric acid and the concentration of Fe<sup>2+</sup> was 20 mg/l; this concentration of iron was chosen because it is able to absorb most of the solar irradiation reaching the treatment plant and it is compatible with discharge limits in many countries [13]. Hydrogen peroxide (24.8 mM, twice the stoichiometric amount needed to mineralize the pesticides, determined from the initial chemical oxygen demand) was added and then, the samples were irradiated with a solar simulator (Oriol Instruments, Model 81160 equipped with a 300 W xenon lamp). Magnetic stirring was maintained throughout the reaction time, and water was added periodically in order to compensate for loss through evaporation.

Scaled-up reactions with commercial pesticides were carried out in a solar photoreactor based on compound parabolic collectors, which has been described in detail elsewhere [14]; the irradiated surface and volume were 0.26 m<sup>2</sup> and 1.83 l respectively. The equipment was loaded with 4 l of an aqueous solution containing four commercial pesticides, Ultracid™, SevnoI™ Laition™ and Metasystox R™ (50 mg/l of each active ingredient, methidathion, carbaryl, dimethoate and methyl-oxydemeton) and later, triethoxyisododecyl alcohol (200 mg/l) was added. The pH was 2.8 (adjusted with sulphuric acid) and the iron concentration was 20 mg/l; hydrogen peroxide was periodically analysed and the required amount was added to maintain a concentration in the solution of between 200 and 500 mg/l throughout the process. Samples were taken at selected accumulated irradiation energies in order to be analysed. Samples free of H<sub>2</sub>O<sub>2</sub> employed in bioassays were obtained in parallel experiments in which addition of peroxide was stopped when DOC was close to selected values and irradiation was kept until complete exhaustion of this reagent; these samples were neutralised before analysis.

In order to normalize the intrinsically changing conditions of solar irradiation, *t*<sub>30W</sub> was employed. This is a commonly used parameter in solar photocatalysis [16]. It can be calculated according to Eq. (1), where UV is the average solar ultraviolet irradiance during Δ*t*<sub>n</sub> (W/m<sup>2</sup>), *V*<sub>i</sub> the irradiated volume (l), *V*<sub>t</sub> the total volume (l) and *I* a standard value for UV irradiance, typically 30 W/m<sup>2</sup> in the South East of Spain.

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

### 2.3. Chemical analysis

The concentration of the pesticides was determined by means of liquid chromatography (Perkin Elmer XL Autosystem, equipped with a diode-array detector and an autosampler). A reverse phase column (LiChrosphere 100 RP-18) was used. The eluent was an isocratic mixture of acetonitrile/water (50/50). The detection wavelengths were 280 nm for carbaryl, 215 nm for methidathion and 210 nm for dimethoate and methyl-oxydemeton.

Dissolved organic carbon (DOC) was determined by means of a TOC-V CSH analyser (Shimadzu), based on catalytic combustion onto a platinum catalyst and infrared (IR) analysis of the formed CO<sub>2</sub>. All samples passed through polypropylene filters (Teknokroma, 0.45 μm) before analysis.

Chemical oxygen demand (COD) was determined spectrometrically according to the standardized dichromate method [17]; digestions were performed at 148 °C in a Thermoreaktor TR300 (Merck) and a Spectroquant NOVA 60 (Merck) was used for the photometric determination. Hydrogen peroxide was measured by iodometric titration, following the standardized procedure [17] in the laboratory scale experiments, when accuracy was required; alternatively, a colorimetric method with test strips (Merckoquant), purchased from Merck, was employed in pilot plant experiments to ensure that the remaining amount of H<sub>2</sub>O<sub>2</sub> was within the desired range (200–500 mg/l). The concentration of iron was determined according to the o-phenantroline standardized procedure [17]; briefly, all the iron was reduced to iron(II) by addition of hydroquinone, the pH was adjusted to 3.5, then o-phenantroline was added and the red complex formed was determined spectrophotometrically at 508 nm.

The average oxidation state (AOS), which relates COD to DOC, was calculated according to Eq. (2), where DOC is the dissolved organic carbon of the solution and COD is the chemical oxygen demand at the sampling time (both parameters expressed as mg/l)

$$AOS = 4 - 1.5 \frac{COD}{DOC} \quad (2)$$

The carbon oxidation state (COS) was estimated by means of Eq. (3), where  $\text{DOC}_0$  is the initial total organic carbon of the solution and COD is the chemical oxygen demand at the sampling time (both parameters expressed as mg/l). Note that in this formula,  $\text{CO}_2$  eliminated from the solution (with an oxidation state +4) is also considered in the calculation.

$$\text{COS} = 4 - 1.5 \frac{\text{COD}}{\text{DOC}_0} \quad (3)$$

#### 2.4. Biological measurements

$\text{BOD}_5$  was determined according to OECD-301F test, (ready biodegradability, manometric respirometry).  $\text{KH}_2\text{PO}_4$ ,  $\text{K}_2\text{HPO}_4$ ,  $\text{Na}_2\text{HPO}_4$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{CaCl}_2$ ,  $\text{MgSO}_4$  and  $\text{FeCl}_3$  were added to the mixture. The bottle was sealed with an OxiTop®(WTW), able to monitor depression inside the recipient.

Zahn–Wellens test was performed according to the OECD-302B, Zahn–Wellens/EMPA test [18,19]. The pollutant solution (2l) was magnetically stirred in an open glass reactor and kept in the dark at room temperature. Activated sludge (1 g/l) and mineral substances ( $\text{KH}_2\text{PO}_4$ ,  $\text{K}_2\text{HPO}_4$ ,  $\text{Na}_2\text{HPO}_4$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{CaCl}_2$ ,  $\text{MgSO}_4$  and  $\text{FeCl}_3$ ) were added to the mixture; air was bubbled throughout the experiment and samples were taken daily. A blank control consisting in a mixture of 2l of distilled water, activated sludge and the mineral species was also run. The biodegradation ( $D_t$ ) was estimated by means of Eq. (4), where  $C_0$  is the initial DOC value (determined three hours after the beginning of the experiment),  $C_t$  the DOC at the sampling time,  $C_{Bt}$  the DOC of the blank experiment at the sampling time and  $C_{B0}$  the initial DOC of the blank (measured after three hours).

$$D_t = \left[ 1 - \frac{(C_t - C_{Bt})}{C_0 - C_{B0}} \right] \times 100 \quad (4)$$

The standardized ISO 11348-3 norm was followed for the inhibition of the luminescent of *Vibrio fischeri* assays, in which lyophilised bioluminescent bacteria (NRRL B-11177, Macherey-Nagel) were used [20]. The standard procedure was employed for reconstitution of the bacteria, using a saline solution obtained from Macherey-Nagel. The luminescence was measured with a Lumimeter Lumiflux-Bio-10, also purchased from Macherey-Nagel. Toxicity was determined after 15 min incubation. Distilled water and zinc sulphate were used in control experiments. All samples were filtered and neutralised before analysis.

#### 2.5. Experimental design and statistical methods

A complete factorial design,  $2^k$ , with one replicate ( $2 \times 2^3$ , hence 16 experiments) was employed to determine the significance of the organic additives under study. Each component was studied at a low level (absence) and at a high level (200 mg/l). The influence of the ions on the response variable (remaining DOC,  $\text{H}_2\text{O}_2$  consumption) was determined after 30 min, 60 min and 120 min. The significance of the components was estimated according to the ANOVA multifactor methodology. The statistical  $F$  needed for the study of significance was calculated by means of the software STATGRAPHICS 5.1. For the sake of simplicity a Pareto chart showing the components was employed.

### 3. Results and discussion

#### 3.1. Solar simulator photo-Fenton experiments

Preliminary experiments were carried out in order to determine the role of three organics, namely a surfactant (triethoxyisododecyl alcohol), a solvent (acetophenone) and a complexing agent (EDTA)

on the solar-driven photo-Fenton treatment of a mixture of pesticides. The experimental design methodology described above was used for this purpose. First, the effect of organics on the mineralization was determined. Relative DOC values ( $\text{DOC}/\text{DOC}_0$ ) were used in calculations, as the presence of the organic interferent resulted in higher initial DOC. Response surfaces were calculated after 30, 60 and 120 min irradiation in solar simulator and based on these data, Pareto diagrams were employed to determine the significance of each organic (see Fig. 1 for equations and diagrams).

Only the presence of the aliphatic surfactant was significant and it resulted in a slower mineralization. This inhibitory role of triethoxyisododecyl alcohol in the process could be attributed to the more refractory behaviour of the surfactant molecules towards the oxidising media. In addition, a possible scavenging role of triethoxyisododecyl alcohol towards  $\cdot\text{OH}$  should not be ruled out, as this is a well known behaviour of other aliphatic alcohols, such as *t*-butanol [21]. These results are in agreement with recent work carried out by Hwang et al., who have also reported on the negative role of an aliphatic alcohol, namely isopropanol on the Fenton elimination of methyl *tert*-butyl ether [22].

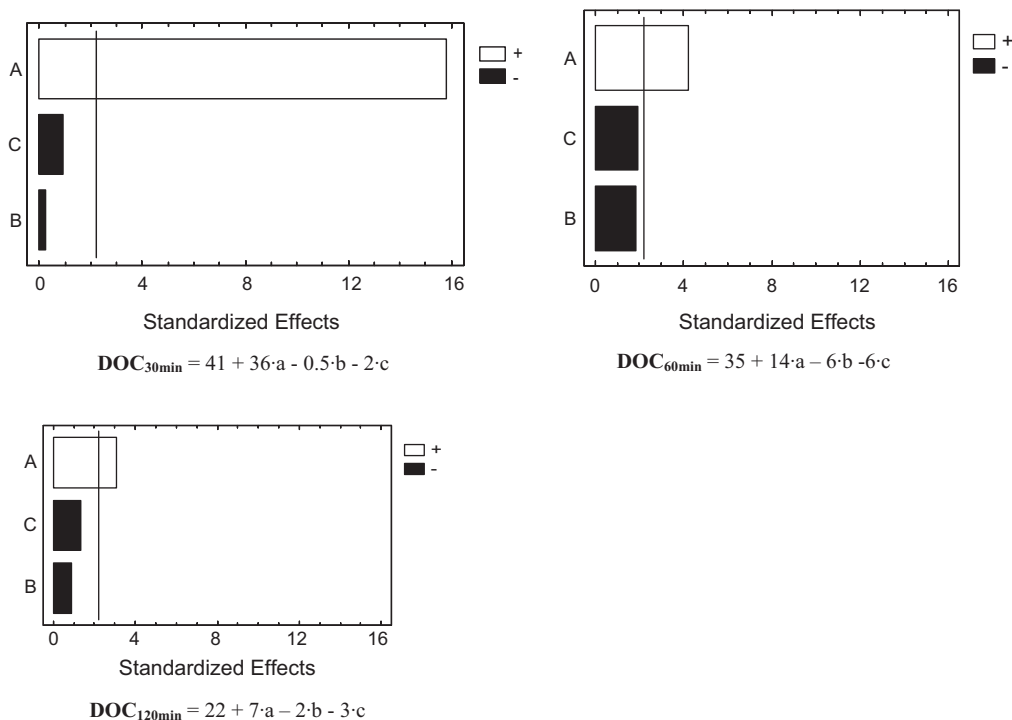
The presence of acetophenone and EDTA had no significant effect on the percentage of mineralization achieved despite the higher initial amount of organics. The efficient oxidation of these two compounds could explain this fact. In this context, Ghiselli et al. attributed to EDTA the ability to form chelates with Fe(III) which, upon absorption in the UV-visible range photolyze through an intramolecular electron transfer mechanism [23].

In order to gain further insight into the oxidation process, possible changes in the hydrogen peroxide consumption were also analysed. Again in this case, the absolute  $\text{H}_2\text{O}_2$  consumption did not seem to be a reliable parameter, as it was affected by the initial amount of organic matter (in all cases, higher consumptions were detected when compared with the blank experiment without organics); hence a relative parameter was used, namely the ratio between the DOC decrease and the  $\text{H}_2\text{O}_2$  consumption ( $\Delta\text{DOC}/\Delta\text{H}_2\text{O}_2$ ). Fig. 2 shows that the highest ratio was achieved in the presence of EDTA, hence indicating an improved efficiency in the photo-Fenton process; different behaviour was observed for the surfactant, as no significant increase of  $\Delta\text{DOC}/\Delta\text{H}_2\text{O}_2$  was measured, despite the presence of higher amounts of organics.

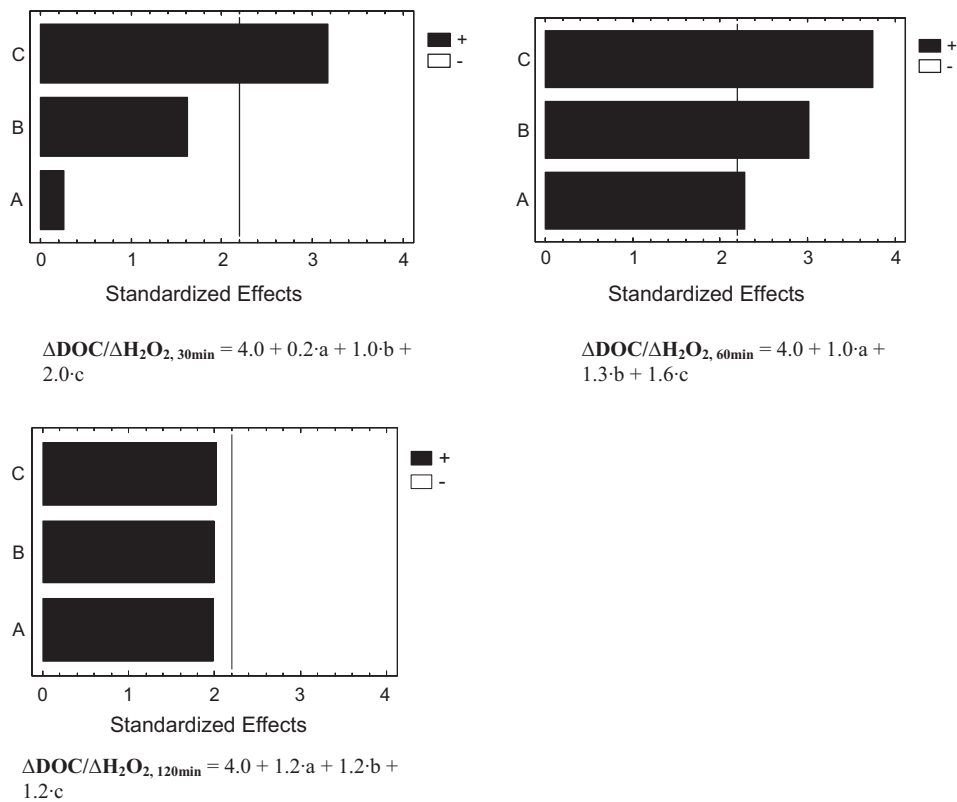
#### 3.2. Sunlight driven photo-Fenton experiments

The reaction was scaled-up employing real sunlight as the irradiation source. For this purpose, a mixture of four commercial pesticides described in the experimental section was employed. The presence of organics resulted in a slower mineralization of the mixture (see Fig. 3), the same as occurred with the laboratory scale experiments. In addition, the organics had also a remarkable effect on the elimination of the pesticides as analysed by HPLC: in the experiment carried out with the surfactant, a  $t_{30W}$  of ca. 180 min was needed to accomplish the complete removal of the pesticides, while ca. 60–70 min were required in the case of EDTA and acetophenone; in all cases, this value was well above the 30–40 min employed in the experiment carried out without extra organics. The pH of the sample was measured all along the reaction and, although some decrease was observed due to the formation of acidic intermediates, such as carboxylic acids [8], this parameter was in the range 2.4–2.8 throughout the process.

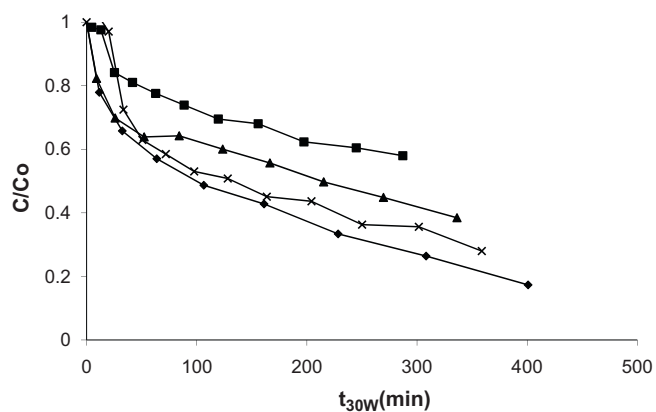
All experiments gave similar results and displayed the disfavoured role of triethoxyisododecyl alcohol on the photo-Fenton process as mineralization was significantly slower, the  $\Delta\text{DOC}/\Delta\text{H}_2\text{O}_2$  was not increased despite the higher initial DOC and longer irradiation periods were required to achieve complete removal of the pesticides. In addition, this alcohol was only moderately biodegradable, as shown by its  $\text{BOD}_5/\text{COD}$  ratio, which was



**Fig. 1.** Pareto diagrams obtained to determine the significance of the presence of triethoxyisododecyl alcohol (A), acetophenone (B) and EDTA (C), on the relative DOC values of a solution also containing three pesticides after 30 min, 60 min and 120 min of solar driven photo-Fenton process. The limit value for significance is indicated by the vertical line.



**Fig. 2.** Pareto diagrams obtained to determine the significance of the presence of triethoxyisododecyl alcohol (A), acetophenone (B) and EDTA (C), on the ratio between the DOC decrease and the H<sub>2</sub>O<sub>2</sub> consumption ( $\Delta DOC / \Delta H_2O_2$ ) after 30 min, 60 min, 120 min and 300 min of solar driven photo-Fenton process in a solution containing three pesticides. The limit value for significance is indicated by the vertical line.

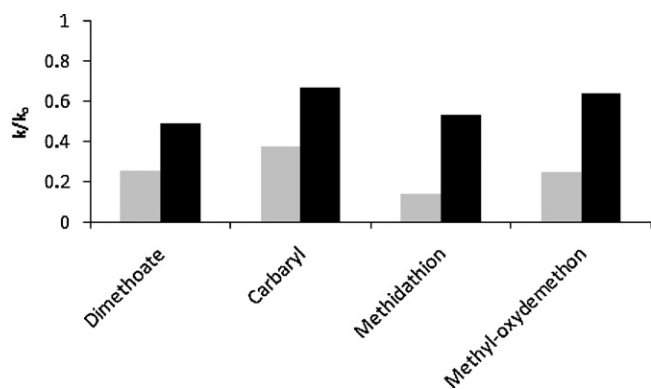


**Fig. 3.** Relative DOC values ( $DOC/DOC_0$ ) measured along a solar-driven photo-Fenton reaction for a mixture of 4 commercial surfactants: with no extra organics (♦), also containing triethoxyisododecyl alcohol (■), also containing acetophenone (▲) and also containing EDTA (×).

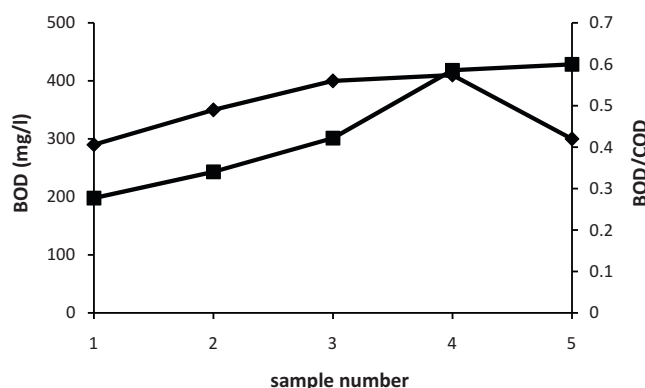
below 0.20. Based on these results, this compound was chosen for a more detailed study on the effect of this organic on changes in the biocompatibility of the effluent throughout the photo-Fenton process.

The pseudo first order reaction rate constants ( $k$ ) were determined for the four pesticides studied (see Fig. 4). The  $k$  values obtained were clearly lower in the presence of the surfactant, confirming that the pesticide removal was strongly inhibited by this organic additive. Some inhibition was also observed when the role of chlorides was studied [14]; nonetheless, Fig. 4 shows that the inhibitory effect was more remarkable in the case of the surfactant, as the  $k$  values were 3–5 times lower than those obtained in the absence of interfering species. However, the lower  $k$  values measured in the presence of organics should be attributed to competition between the pesticides and the added organic matter for reaction with the relatively unselective hydroxyl radical, while in the case of chloride, it was due to a scavenging role of  $Cl^-$ , that transforms the hydroxyl radical into a much less reactive dichlorine radical anion [11,15,24].

When changes in biocompatibility throughout a photo-Fenton process were compared in the presence and absence of chloride, it was found that samples submitted to the same  $t_{30W}$  showed different biocompatibility, as the lower efficiency of the photo-Fenton when  $Cl^-$  was in the solution shifted the optimal biodegradability towards higher  $t_{30W}$  values. On the other hand, it was proven that samples showing similar percentages of mineralization exhibited



**Fig. 4.** Relative pseudo-first order rate constants for the elimination of the four studied pesticides in the presence of chloride (black bars) and surfactant (grey bars). Data are expressed as  $k/k_0$ , where  $k_0$  is the constant calculated for each pesticide in the absence of interfering species.



**Fig. 5.**  $BOD_5$  (♦), and  $BOD/COD$  ratio (■, right axis) for 5 samples taken at different irradiation intensities (see Table 1 for details) of a mixture of 4 commercial pesticides and triethoxyisododecyl alcohol.

a comparable biocompatibility [14]. The system studied here was more complex, as the initial DOC values were very different with and without the surfactant (ca. 320 mg/l and 150 mg/l, respectively) and more than 50% of the DOC was attributable to the surfactant in the first case.

In order to gain further insight into the behaviour of the mixture of the pesticides in the presence of the surfactant, samples were taken after different periods of photo-treatment. The chosen sampling points were: the initial (sample 1), slightly before complete removal of the pesticides (sample 2), in coincidence with the pesticides removal (sample 3), slightly after complete elimination of the pesticides (sample 4) and after stronger mineralization (sample 5); see Table 1 for DOC values. Table 1 shows the COD and DOC of the samples studied, the percentage of mineralization and the AOS and COS values. The AOS parameter is considered to be a good indicator when monitoring changes in the composition of the dissolved organic matter [25]. As a result of an oxidation process, an increase in this parameter could be expected; this behaviour was observed from samples 3 to 5, as AOS increased progressively from  $-0.95$  to  $+0.79$ . However, this is not the trend at the early stages of the reaction, as no significant variation was detected. This apparently anomalous behaviour could be attributed to the faster mineralization of the most oxidised fraction of the organic matter, namely pesticides; hence, the proportion of the more reduced aliphatic surfactants among the remaining dissolved organics increased. The oxidation of organic matter even at the beginning of the process was demonstrated by the increase of the carbon oxidation state (COS) from  $-0.90$  to  $+1.65$ . Contrary to AOS, this parameter also includes in the calculations of the carbon atoms eliminated as  $CO_2$  (as the initial DOC is related with the COD at the sampling time) and this has been considered to be a better indicator of the efficiency of a redox process [26].

### 3.3. Inhibition and toxicity tests

A set of bioassays was performed to determine the biocompatibility of the sample and the possibility of coupling a bioprocess. None of the toxicity assays proposed for biocompatibility assessment gave reliable results (see [8] for a detailed discussion on this methodology), although an overview of the available data seemed to point to the existence of detoxification. In particular, the inhibition of luminescence of *V. fischeri* showed very high values even in sample 5 (more than 95%) and only when it was diluted could some differences be observed (100% inhibition in sample 1 and 70% in sample 5, see Table 1, last row); this is attributable to the high sensitivity of this species when compared with other bioassays.

**Table 1**  
Main characteristics of the samples taken at different irradiation intensities of a mixture of 4 commercial pesticides and triethoxyisododecyl alcohol submitted to a photo-Fenton process: initial (sample 1), slightly before complete removal of the pesticides (sample 2), in coincidence with the pesticides removal (sample 3), slightly after complete elimination of the pesticides (sample 4) and after stronger mineralization (sample 5).

|                                | Sample 1 | Sample 2 | Sample 3 | Sample 4 | Sample 5 |
|--------------------------------|----------|----------|----------|----------|----------|
| $t_{30W}$ (min)                | 0        | 110      | 180      | 220      | 280      |
| DOC (mg/l)                     | 320      | 302      | 287      | 269      | 234      |
| Mineralization (%)             | –        | 5.6      | 10.4     | 16.0     | 26.9     |
| COD (mg/l)                     | 1046     | 1028     | 948      | 703      | 500      |
| AOS                            | –0.90    | –1.10    | –0.95    | 0.10     | 0.79     |
| COS                            | –0.90    | –0.81    | –0.44    | 0.71     | 1.65     |
| Toxicity (1:10 diluted sample) | 100      | 97       | 100      | 84       | 71       |

The BOD<sub>5</sub> of samples 1–5 was calculated. Data shown in Fig. 5 indicate that this parameter remained in the range 200–400 mg/l throughout the photochemical reaction; however, BOD also depends on the oxidation state of organic matter and it increased considerably, as indicated by the AOS. Hence, the BOD/COD ratio has been considered as a more reliable parameter to monitor biodegradability, as the effect of the oxidation state is eliminated [27]. A clear increase in this parameter was observed, from an initial ratio of 0.25 to reach values of 0.60 for samples 4 and 5. This indicates that there was an enhancement in the biodegradability of the sample, which is consistent with the elimination of the pesticides. The highest BOD/COD ratio was achieved slightly after the removal of the pesticides; this behaviour was already observed in the absence of additives [8] and in the presence of chlorides [14] and it was attributed to the elimination of the toxic pesticides and the primary oxidation by-products to form more biodegradable compounds. Although the mixture was too complex to obtain reliable data from GC–MS analyses because of the presence of extra organics, and more sophisticated analytical methods would be required for this purpose, a similar process might explain the trends observed.

To confirm these data, a Zahn–Wellens test was carried out with samples 1 and 4. Fig. 6 indicates that the photo-Fenton was able to enhance the long-term biodegradability of the sample, as less than 60% of the biodegradation was reached after 28 days in the untreated sample 1 and this value was increased to more than 80% in sample 4. In addition, 80% biodegradation was achieved after 10 days in sample 4 while this value was only ca. 40% after 10 days in sample 1. Nonetheless, this increase was more moderate than in the experiments carried out in the absence of organics [8], when it increased from 20% in the untreated sample to ca. 90% for the photo-Fenton treated solution. These differences can be attributed to presence of isododecyl alcohol, which is the major

component of the mixture: the biodegradation of sample 1 (60% after 28 days) was well above that of the sample containing only the pesticides (less than 20%); this indicates that micro-organisms are able to metabolize the surfactant although the pesticides are reluctant to this process and hence, a chemical pre-treatment is required (see Fig. 6). Furthermore, the behaviour of sample 4 was equivalent to that containing only the surfactant and; this supports the hypothesis that this more biodegradable alcohol is more resistant to chemical oxidation than pesticides and that at the end of the process it is the predominant source of organics; as a consequence, an enhancement of the biodegradability is observed.

#### 4. Conclusions

Solar photocatalysis has been demonstrated to be a good method to treat water polluted with pesticides; the presence of other organic species in the mixture, particularly triethoxyisododecyl alcohol resulted in a slower mineralization and pesticides removal. The biocompatibility of the mixture was enhanced to reach the optimal value slightly after the elimination of the active ingredients, as happened in the absence of additives. However, the coupling point with a bioprocess was shifted towards longer irradiation periods because of the lower efficiency of the photo-Fenton in the presence of organics.

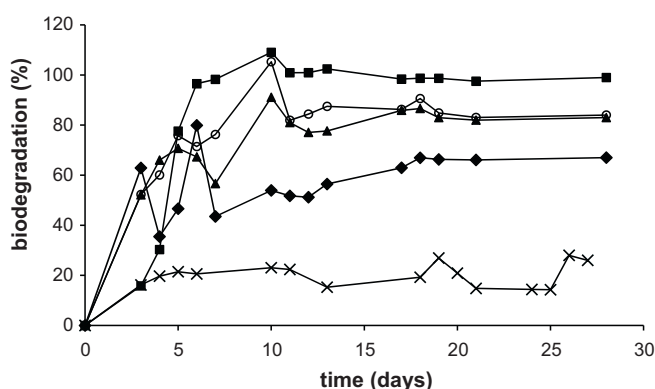
The methodology of combining chemical and bioassays has also been applied in this case. Although some of the assays could not be applied because of the high complexity of this mixture, a good general understanding of the process could be obtained when results on the removal of the pesticides, mineralization and biodegradability assays (BOD and Zahn–Wellens) are combined with those previously obtained in the absence of the organics.

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**Fig. 6.** Zahn–Wellens test performed for an untreated solution of the four commercial pesticides and the surfactant (sample 1) (♦), for the photo-treated solution after removal of the pesticides (sample 4) (▲), for a solution containing only the surfactant (○), for a solution containing only the pesticides (×) and for a solution of diethyleneglycol, used as a control (■).

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