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Abstract: The technical feasibility and performance of photocatalytic degradation of six water-soluble pesticides (cymoxanil, methomyl, oxamyl, dimethoate, pyrimethanil and telone) have been studied at pilot-plant scale in two well-defined systems which are of special interest because natural solar UV light can be used: heterogeneous photocatalysis with titanium dioxide and homogeneous photocatalysis by photo-Fenton. TiO₂ photocatalysis tests were performed in a 35-L solar pilot plant with three Compound Parabolic Collectors (CPCs) under natural illumination and a 75-L solar pilot plant with four CPC units was used for homogeneous photocatalysis tests. The initial pesticide concentration studied was 50 mg.L⁻¹ and the catalyst concentrations employed were 200 mg.L⁻¹ of TiO₂ and 20 mg.L⁻¹ of iron. Both toxicity (*Vibrio fischeri*, Biofix □) and biodegradability (Zahn-Wellens test) of the initial pesticide solutions were also measured. Total disappearance of the parent compounds and nearly complete mineralization were attained with all pesticides tested. Treatment time, hydrogen peroxide consumption and release of heteroatoms are discussed.

Solar photocatalytic degradation of some hazardous water-soluble pesticides at pilot-plant scale.

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ABSTRACT

The technical feasibility and performance of photocatalytic degradation of six water-soluble pesticides (cymoxanil, methomyl, oxamyl, dimethoate, pyrimethanil and telone) have been studied at pilot-plant scale in two well-defined systems which are of special interest because natural solar UV light can be used: heterogeneous photocatalysis with titanium dioxide and homogeneous photocatalysis by photo-Fenton. TiO₂ photocatalysis tests were performed in a 35-L solar pilot plant with three Compound Parabolic Collectors (CPCs) under natural illumination meanwhile, and a 75-L solar pilot plant with four CPC units was used for homogeneous photocatalysis tests. The initial pesticide concentration studied was 50 mg.L⁻¹ and the catalyst concentrations employed were 200 mg.L⁻¹ of TiO₂ and 20 mg.L⁻¹ of iron. Both toxicity (*Vibrio fischeri*, Biofix®) and biodegradability (Zahn-Wellens test) of the initial pesticide solutions were also measured. Total disappearance of the parent compounds and nearly complete mineralization were attained with all pesticides tested. Treatment time, hydrogen peroxide consumption and release of heteroatoms are discussed.

Keywords

Solar photocatalysis, Photo-Fenton, Organophosphates, Carbamates, Organochlorines.

1. INTRODUCTION

During the last few decades, the development of the agrochemical industry has dramatically increased due to widespread intensive agriculture. Consequently, human health is threatened by high concentrations of pesticides, heavy metals, hydrocarbons, chlorinated hydrocarbons, etc., present in continental and marine natural waters as a result of low-to-medium contaminant concentrations ($< 500 \text{ mg.L}^{-1}$) in industrial effluents. EU legislation is constantly being adapted to protect and improve the quality of Europe's fresh water resources [1].

Most pesticides require more effective treatment systems due to their high chemical stability and/or low biodegradability [2-4]. Among these persistent water contaminants are the six water-soluble pesticides studied in this work: cymoxanil, methomyl, oxamyl, dimethoate, pyrimethanil and telone (of special interest because of their extremely easy transport in the environment).

The strong potential of Advanced Oxidation Processes (AOPs) for bio-recalcitrant wastewater treatment is universally recognized today. Many studies have focused on the development of these processes using different reaction systems [5-7]. AOPs are characterized by the production of hydroxyl radicals ($\bullet\text{OH}$), the second strongest known oxidant after fluorine (2.8 V vs. standard hydrogen electrode). It is able to oxidize and mineralize almost every organic molecule, yielding CO_2 and inorganic anions. Many oxidation processes, such as TiO_2/UV , $\text{H}_2\text{O}_2/\text{UV}$, photo-Fenton and ozone (O_3 , O_3/UV , $\text{O}_3/\text{H}_2\text{O}_2$) are currently employed. The advantage of AOPs is enhanced by the fact that there are different $\bullet\text{OH}$ radical production possibilities, so they can be adapted to specific treatment requirements. On the other hand, the relatively high operating costs of these processes compared to those of a biological treatment are the main disadvantage. The use of AOPs for wastewater treatment has been studied extensively, but UV

radiation generation by lamps or ozone production is expensive. Therefore AOPs which can be driven by solar radiation (photo-Fenton and heterogeneous catalysis with UV/TiO₂) are of special interest, making the development of suitable technologies for practical applications very attractive [8-9].

Different semiconductor materials have been tested under comparable conditions for the degradation of the same compounds, among which TiO₂ has generally been demonstrated to be the most suitable [10]. In the photo-Fenton process, the Fenton reagent produces [•]OH radicals by the addition of H₂O₂ to Fe²⁺ salts. The organic pollutant degradation rate is strongly accelerated by irradiation with UV-Vis light in photo-Fenton [11]. Under these conditions, the photolysis of Fe³⁺ complexes promotes Fe²⁺ regeneration ~~and the Fenton reaction due to the presence of H₂O₂~~ and iron may be considered a true catalyst.

This work evaluates these two well-defined AOP systems in two different pilot-plant photoreactors illuminated by sunlight. The efficiency of both treatment methods in the degradation of six medium to highly-soluble pesticides (cymoxanil, methomyl, oxamyl, dimethoate, pyrimethanil and telone) was evaluated. These contaminants, belonging to well-known pesticides families (organophosphorous, organochlorines, etc), were selected due to their wide application in agriculture and their high water solubility (of special interest because of their extremely easy transport in the environment).

2. EXPERIMENTAL.

2.1. Chemicals.

Cymoxanil (98.2% technical grade $C_7H_{10}N_4O_3$, Aragonesas Agro S.A.), methomyl (99.4% technical grade $C_5H_{10}N_2O_2S$, Aragonesas Agro S.A.), oxamyl (Vydate 24% commercial grade $C_7H_{13}N_3O_3S$, Du Pont Iberica S.A.), dimethoate (98.2% technical grade $C_5H_{12}NO_3PS_2$, Aragonesas Agro S.A.), pyrimethanil (98.2% technical grade $C_{12}H_{13}N_3$, Agrevo S.A.) and telone (90% technical grade $C_3H_4Cl_2$, 1,3-dichloropropene, Aldrich Chemical) were used as received (**scheme 1**). Analytical standards for chromatography analyses were purchased from Sigma-Aldrich. Distilled water used in both pilot plants was obtained from the Plataforma Solar de Almería (PSA) distillation plant (conductivity $<10\mu S.cm^{-1}$, $Cl^- = 0.7-0.8 mg.L^{-1}$, $NO_3^- = 0.5 mg.L^{-1}$, organic carbon $<0.5 mg.L^{-1}$). The heterogeneous photocatalytic degradation tests were carried out using a slurry suspension ($200 mg.L^{-1} TiO_2$) of Degussa (Frankfurt, Germany) P-25 titanium dioxide (surface area $51-55 m^2.g^{-1}$, **Degussa TiO_2 datasheets**). Photo-Fenton experiments were performed using iron sulphate ($FeSO_4.7H_2O$), reagent-grade hydrogen peroxide (30% w/v) and sulphuric acid for pH adjustment (to around 2.7-2.9).

SCHEME 1

2.2. Analytical determinations.

Mineralization was followed by measuring the Total Organic Carbon (TOC) by direct injection of filtered samples into a Shimadzu-5050A TOC analyser provided with an NDIR detector and calibrated with standard solutions of potassium phthalate. The concentration of the six pesticides was analysed using reverse-phase liquid chromatography (flow rate $0.5 ml.min^{-1}$) with UV detector in an HPLC-UV (Agilent Technologies, series 1100) with C-18 column (LUNA $5\mu m$, $3 mm x$

150 mm from Phenomenex). Ultrapure distilled-deionised water obtained from a Milli-Q (Millipore Co.) system and HPLC-graded organic solvents were used to prepare all the solutions. **Table 1** shows the mobile-phase composition and wavelength in each case. **The analytical error of these measurements was estimated to be 5%.**

TABLE 1

Cation concentrations (NH_4^+ and methylamine) were determined with a Dionex DX-120 ion chromatograph equipped with a Dionex Ionpac CS12A 4-mm-x-250-mm column. Isocratic elution was done with H_2SO_4 (10 mM) at a flow rate of $1.2 \text{ mL}\cdot\text{min}^{-1}$. Anion concentrations were measured with a Dionex DX-600 ion chromatograph using a Dionex Ionpac AS11-HC 4-mm-x-250-mm column. The gradient programme was pre-run for 5 min with 20 mM NaOH, an 8-min injection of 20 mM of NaOH, and 7-min with 35 mM of NaOH, at a flow rate of $1.5 \text{ mL}\cdot\text{min}^{-1}$.

Total iron concentration was determined according to ISO 6332 with 1,10-phenantroline. Hydrogen peroxide was determined by iodometric titration.

2.3. Toxicity evaluation.

Toxicity of initial pesticide solutions was evaluated with Biofix®Lumi-10, a commercial assay. The reagent is a freeze-dried preparation of a specially selected strain of the marine bacterium *Vibrio fischeri* (formerly known as *Photobacterium phosphoreum*, NRRL number B-11177). To monitor the effective concentration at which 50% of the normal bacteria activity was inhibited due to compound toxicity (EC_{50}), different dilutions of the test sample, made with a specially prepared non-toxic 2% sodium chloride solution, were mixed with the bacterial suspension. The drop in light emission was measured after contact periods of 5 and 15 minutes.

Careful control of temperature was essential because light emission is sensitive to temperature, therefore a thermoblock was used to maintain the optimum test temperature of 15°C. Light production from luminescent bacteria was measured with Biofix®Lumi-10. Sample inhibition effect was compared with a toxicant-free control (2% sodium chloride solution) to obtain EC₅₀. To monitor inhibition during the photo-Fenton process, sample salinity was adjusted to 2% and the drop in light emission was also measured after a contact period of 15 minutes. Hydrogen peroxide present in the samples from Photo-Fenton experiments was removed prior to toxicity analysis using catalase (2500 U/mg bovine liver; 100 mg/L) acquired from Fluka Chemie AG (Buchs, Switzerland) after adjusting the sample pH to 7

2.4. Biodegradability evaluation.

The Zahn-Wellens test was used according to the EC protocol (Directive 88/303/EEC) to evaluate the biodegradability of water-soluble, non-volatile organic contaminants. Activated sludge from a municipal wastewater treatment plant in Almería, mineral nutrients and the initial pesticide solutions as the sole carbon source were mixed together with proper aeration and agitation. The degradation process was monitored daily, or at other appropriate regular time intervals, by determination of the DOC (with the TOC analyser) in the filtered solution [12].

Biodegradability of Telone, the only volatile pesticide present in our study, was analysed by a Biological Oxygen Demand test (BOD₅) using a WTW 2000 Oxitop[®] unit thermostated at 20°C. An inoculum of activated sludge, mineral nutrients and thioallyl urea as a nitrification inhibitor were added to the pesticide solution.

2.5. Experiment set-up.

Heterogeneous photocatalytic experiments with TiO₂ were carried out under sunlight in a pilot plant at the PSA (latitude 37°N, longitude 2.4°W). The pilot plant

operates in batch mode and has three compound parabolic collectors (CPCs), one tank and one recirculation pump (20 L min^{-1}). This system is outdoors and is not thermally insulated, so the temperature inside the reactor was continuously recorded by a PT-100 inserted in the tank. The total volume (V_T) of 35 L is separated into two parts: 22 L (transparent borosilicate-glass tubes in the CPC, Schott-Duran Type 3.3, Germany) of total irradiated volume (V_i) and the dead unilluminated reactor volume (tank + high-density polyethylene tubes), as recently described in detail elsewhere [13].

Photo-Fenton experiments were also carried out under sunlight in a different pilot plant specially developed for photo-Fenton applications. This solar reactor is composed of four Compound Parabolic Collector units. The total volume of the reactor (75 L) is separated into two parts: 44.6 L (glass tubes) total irradiated volume (V_i), and the dead unilluminated reactor volume (tank + tubes). The flow rate was 25 L min^{-1} . The collector is covered with tailor-made aluminium sheets to perform the experiment steps previous to illumination. A diagram of this system has recently been published elsewhere [14]. This pilot plant is also outdoors, but temperature control was achieved by trace heating on part of the tubing, and cooling with a secondary-cycle cooling-water heat exchanger, which maintained the temperature at the set point of 30°C .

All the experiments were performed twice.

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), which provides data in terms of incident $W_{UV}\cdot\text{m}^{-2}$. The energy reaching any surface in the same position with regard to the sun can be measured in this way.

With **Equation 1**, combination of the data from several days' experiments and their comparison with other photocatalytic experiments is possible.

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

where t_n is the experimental time for each sample, UV is the average solar ultraviolet radiation measured during Δt_n , and t_{30W} 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). **A 2% UV radiation measurement error was estimated for t_{30W} .**

All the Photo-Fenton experiments were performed at a pH adjusted to 2.7-2.9 with sulphuric acid in order to avoid iron hydroxide precipitation. The initial dose of hydrogen peroxide was 100 mL in all the experiments and was always added after pH adjustment and iron addition. The concentration of peroxide in the reactor had to be maintained in the $200\text{-}500 \text{ mg.L}^{-1}$ range throughout the process, so it was analysed frequently and controlled to avoid complete disappearance by adding small amounts as consumed. The corresponding pesticide was previously dissolved in a 5-litre flask and added directly to the pilot plant. After 15 minutes of homogenisation, with the collectors covered to avoid illumination, a sample was taken (initial concentration, Point 1) and sulphuric acid was added. After 15 minutes, a sample was taken to confirm that pH was around 2.7-2.9. Then iron salt was added ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 20 mg.L^{-1} of Fe^{2+} , Point 2), homogenized, and another sample taken. Finally the initial dose of hydrogen peroxide was added (100 ml, Point 3) and a sample was taken 15 minutes later (“dark Fenton” reaction started). At that moment collectors were uncovered, and photo-Fenton began.

For titanium dioxide treatment, first the compound was added to the pilot plant (previously dissolved in a 5-litre flask), and homogenised for 15 minutes, then a

sample of the initial concentration was taken. Finally, the catalyst TiO_2 (200 mg.L^{-1}) was added. After 15 minutes, another sample was taken and the collectors were uncovered. Initial pH in all cases was 6 ± 0.5 .

3. RESULTS AND DISCUSSION.

First, the original toxicity and biodegradability of the target pesticides (50 mg.L^{-1}) were analysed to justify using AOPs (TiO_2 and photo-Fenton processes) for pesticide degradation rather than a conventional biological treatment. **Table 2** shows the results of toxicity assays and Zahn-Wellens tests (DBO_5 for Telone) carried out for each pesticide. It may be observed that all the tested compounds are toxic at concentrations of less than 50 mg.L^{-1} except telone (toxic at concentrations $> 85 \text{ mg.L}^{-1}$). Methomyl, dimethoate and telone are clearly non-biodegradable, while biodegradability of oxamyl, cymoxanil and pyrimethanil was low for several days.

TABLE 2

AOP treatment of telone is justified despite its non-toxicity, because of the possibly chronic environmental toxicity which could appear due to its high water solubility and non-biodegradability. In all other cases, the toxicity is in the range of tens of mg.L^{-1} . It is difficult to find such a high concentration in natural water or sewage, but could be found in industrial wastewater (intensive agriculture, pesticide formulation sites, etc.). Moreover, it has also been demonstrated that those contaminants cannot be detected in a conventional sewage treatment plant.

The main parameters used to monitor the degradation and mineralization of each pesticide studied were the TOC, the inorganic species produced (chloride, nitrate, ammonium, phosphate and sulphate), concentration of the parent compounds and hydrogen peroxide consumption throughout the process. All the pesticides were tested at an initial concentration of 50 mg.L^{-1} . As stated in previous publications [15], the

optimal iron concentration for homogeneous experiments would be between 2 mg.L⁻¹, which is enough to provide satisfactory reaction rates, and 55 mg.L⁻¹ (maximum concentration), therefore an intermediate value of 20 mg.L⁻¹ of iron was selected for this work. The optimal TiO₂ concentration for heterogeneous experiments was found to be 200 mg.L⁻¹ in several previous studies [16, 17].

~~Photo Fenton treatment of each pesticide is based on the following equations (4-9), where combination of the mineralization reaction (equation 2) and the decomposition of hydrogen peroxide (equation 3) are shown:~~

Equations 4 to 9 show the simplified stoichiometry of the whole photo-Fenton process, a combination of the mineralization reaction (**Eq. 2**) and decomposition of hydrogen peroxide (**Eq. 3**).



Methomyl :



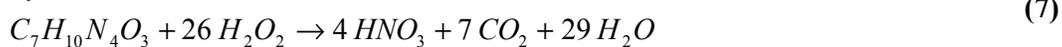
Dimethoate :



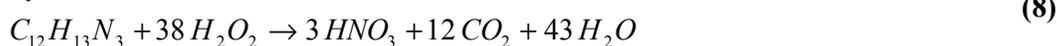
Oxamyl :



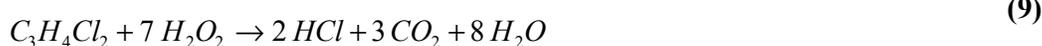
Cymoxanil :



Pyrimethanil :



Telone :



Before discussing the results found in the individual pesticide treatments, the significant degradation common to all of them during “dark Fenton” (with the collectors covered) should be mentioned. On the other hand, no degradation has ever been detected with TiO_2 in the dark.

Figure 1 a shows the degradation of methomyl and the mineralization (i.e., disappearance of TOC), with both TiO_2 and photo-Fenton treatments, as well as the evolution of hydrogen peroxide consumption during the whole photo-Fenton process. Almost complete mineralization was achieved (around 80% of initial TOC disappeared), in both photocatalytic experiments, however the necessary illumination time for the photo-Fenton test appeared to be around 4 times less than the TiO_2 test (see **Tables 3 and 4**).

FIGURE 1

Methomyl photolysis and hydrolysis studies have already been performed by other researchers [18,19] with no appreciable loss of methomyl in solution observed (in hydrolysis tests less than 10% at pH 1.5, and 0% at pH 2.7 and 5). Therefore, in this work no photolysis or hydrolysis experiments were carried out with this pesticide.

Concerning inorganic species produced, it is important to mention how the whole amount of sulphur present in the pesticide molecule was released as sulphate anion, in the TiO_2 test (**Figure 1 c**). Sulphate was not measured during any of the photo-Fenton experiments due to the addition of sulphuric acid for pH adjustment. On the other hand, ammonium, methylamine and nitrate anions were also detected in various relative concentrations during both photocatalytic experiments (**Figure 1 b and c**). Nonetheless, the nitrogen mass balance was always incomplete at the end of treatment (around 43% of the **theoretical inorganic** nitrogen expected in both processes). A methylamine peak was also detected next to the ammonium peak on the ionic chromatogram, but the

concentrations are not given over illumination time as, due to methylamine's high volatility, results were inconsistent. Consequently, this methylamine may close the incomplete nitrogen mass balance, as it has been reported as methomyl degradation metabolites elsewhere [20]. This effect has also been observed in the nitrogenous pesticides studied here, dimethoate, oxamyl and cymoxanil.

Figure 2 a shows the degradation of dimethoate and TOC disappearance in both TiO₂ and photo-Fenton treatments, as well as hydrogen peroxide consumption during photo-Fenton. The maximum percentage of mineralization achieved was also 80% in both processes, with a reaction rate 2.5 times higher with photo-Fenton than with TiO₂ (see **Tables 3 and 4**).

FIGURE 2

Hydrolysis and photolysis experiments were not performed in this work as they have been widely reported in previous publications [21,22], in which no degradation of dimethoate in darkness and very low oxidation exclusively under solar light (only 2%) were observed.

Measurements of ammonium and nitrate depicted in **Figures 2 b and c**, show an incomplete total nitrogen mass balance at the end of both photocatalytic processes. In the photo-Fenton test, **theoretical inorganic** nitrogen was 49% of expected, and in the TiO₂ experiment 67%. Release of sulphate and phosphate ions in the TiO₂ test (**Figure 2d**) reached the maximum expected at the end of the treatment. Nevertheless in the photo-Fenton experiment, released phosphate (**Figure 2 d**) disappeared due to precipitation with ferric ions from the oxidation of ferrous ions in photo-Fenton reactions.

Figure 3a shows the degradation of oxamyl and the reduction in TOC in both photocatalytic experiments, as well as the evolution of hydrogen peroxide consumption

during photo-Fenton. A significant percentage of mineralization was achieved in both cases (80% of initial TOC disappeared), however the illumination time required for photo-Fenton test appeared to be nearly 3 times less than for TiO₂ test (see **Tables 3 and 4**). Notice the additional organic carbon (TOC) from the oxamyl in the commercial Vydate formula (no technical-grade product was available), 76% of which is not described by the manufacturer.

FIGURE 3

Before the photocatalytic experiments, several hydrolysis and photolysis tests were performed in 250-mL flasks. First, two 50-mg.L⁻¹ oxamyl solutions were kept in the dark for around 12 days at pH 6, which was expected to be the natural pH at the beginning of the TiO₂ experiment, and 2.8, which is the optimal pH for photo-Fenton tests. No hydrolysis was observed in either case. Apart from this, another two 50-mg.L⁻¹ oxamyl solutions were exposed to the solar radiation for approximately 24 hours, at the same two pH values as in the hydrolysis experiments. This time, only 20% of the pesticide was eliminated during photolysis at pH 6. These results show that oxamyl is hardly degraded in the environment, and therefore, AOP treatment is justified.

Ammonium and nitrate anions released from the initial pesticide molecule were detected in different relative concentrations during both photocatalytic experiments (**Figures 3 b and c**), but the nitrogen mass balance was incomplete at the end of both treatments. Only 17% of the **theoretical inorganic** nitrogen expected **appeared** **was found** in the TiO₂ test, while 30% was detected in the photo-Fenton experiment. **Figure 3 c** shows the evolution of sulphur released from the oxamyl molecule as sulphate anions during the process. As may be observed, it was impossible to achieve the stoichiometric amount of sulphur during heterogeneous photocatalysis. The explanation for this

seemed to be an unquantified methylsulphonate peak in the ionic chromatograph, which could close the sulphur mass balance.

It is worth mentioning that the photo-Fenton test was not only quicker and more effective than TiO₂ treatment, but total nitrogen concentration released was also higher at the end (**Figure 3 b**). Indeed, a significant increase can be observed in the total amount of nitrogen released (3 mg.L⁻¹ between $t_{30w} = 63$ and 114 minutes) during photo-Fenton.

Figure 4 a shows the degradation of cymoxanil and TOC disappearance in both TiO₂ and photo-Fenton treatments, as well as the hydrogen peroxide consumption during photo-Fenton. In both photocatalytic processes, 80% of TOC was mineralised, and the illumination time necessary for this appeared to be twice as high for TiO₂ as for photo-Fenton (see **Tables 3 and 4**).

Hydrolysis and photolysis experiments with cymoxanil were also performed following the same procedure as with oxamyl. The percentage of degradation detected in the hydrolysis tests at pH 5.4 (the natural pH of cymoxanil at the beginning of the TiO₂ experiment), was 47%, and at pH 2.8 it was 26%, after around 12 days. In the photolysis tests, pesticide elimination measured after 24 hours of exposure to solar radiation was 22% and 46% at pH 5.4 and 2.8 respectively. Other researchers have also performed cymoxanil hydrolysis and photolysis studies at different pH and temperature conditions establishing this pesticide's half-life in the environment [23,24]. The results presented in this work are in agreement with the literature.

FIGURE 4

In **Figures 4 b and c** the ammonium and nitrate concentrations measured during both photocatalytic experiments are plotted over illumination time. Although mineralization by photo-Fenton was twice as fast as with TiO₂ treatment, the total nitrogen released at

the end of the tests was similar (6 mg.L^{-1} and 5.3 mg.L^{-1} respectively). In addition, the nitrogen mass balance was incomplete, and total inorganic nitrogen at the end of TiO_2 and photo-Fenton experiments was 37% and 44% of the theoretical expected amount, respectively. **Figure 4 b** shows a significant increase detected in total nitrogen concentration (approximately 2.2 mg.L^{-1} between t_{30w} 62 and 109 min), which is a TOC decrease of exactly 2.7 mg.L^{-1} .

Figure 5 a shows the degradation of pyrimethanil and elimination of the TOC found in the two photocatalytic experiments, as well as the evolution of hydrogen peroxide consumption during photo-Fenton over illumination time. The percentage of mineralization was significant in both cases (80% of initial TOC disappeared), however photo-Fenton appeared to require around 4.5 times less illumination time than TiO_2 (see **Tables 3 and 4**).

Pyrimethanil degradation was also studied in hydrolysis and photolysis tests, with the same procedure as for the above two pesticides. No significant elimination of the pesticide was detected at pH 6.3 (natural pH of pyrimethanil), or pH 2.8, in any of these experiments.

FIGURE 5

As may be observed in **Figure 5 a** most of the TOC eliminated (over 70%), during TiO_2 photocatalysis was detected between 54 and 273 minutes. Indeed when no pyrimethanil was detected measured ($t_{30w} = 126$ minutes), TOC still remained high (21 mg.L^{-1}), suggesting the presence of a significant number of photocatalytic intermediates. ~~These results are in agreement with previous studies on this pesticide performed by other researchers [25].~~ In the same figure, the photo-Fenton results show a significant decrease in TOC (nearly 80%). This took place from the dark Fenton reaction up to 65 minutes after illumination. This time, total disappearance of the pesticide was detected

at $t_{30w} = 30$ minutes, and TOC was much lower than with TiO_2 , 8.9 mg.L^{-1} , demonstrating that photo-Fenton treatment is more effective.

Ammonium and nitrate anions released from the initial pesticide molecule were measured in different relative concentrations during both photocatalytic experiments (**Figure 5 b and c**). In both cases, total nitrogen released was quite far from the stoichiometric amount expected. This could be explained if the intermediate aliphatic formation were acetylurea, acetamide and formamide, as detected by other researchers [25], as the result of the pyrimidine ring opening. In these previous studies, low concentrations of acetamide and formamide remained in the solution for a rather long time, showing the relative stability of these compounds to oxidation, and keeping the nitrogen mass balance from being closed.

Figure 6 a shows the degradation of telone (1,3-dichloropropene) and TOC disappearance with TiO_2 and photo-Fenton treatments, as well as hydrogen peroxide consumption in the photo-Fenton process. In this case, the illumination time required for 80% mineralization in both photocatalytic experiments appeared to be around 20 times higher for the TiO_2 treatment than photo-Fenton (see **Tables 3 and 4**).

Since telone is a volatile pesticide (boiling point: 93°C , vapour pressure 40 mbar at 20°C), blank experiments were necessary not only to study hydrolysis and photolysis, but also to establish the percentage of telone released into the atmosphere. The hydrolysis test was performed under the same conditions described above, while photolysis was carried out in the pilot plant used for TiO_2 experiments, maintaining recirculation and with collectors uncovered, so photolysis and volatilization could be evaluated at the same time. Telone disappearance was found by the decrease in TOC and chloride analysis. The hydrolysis experiment was performed at pH 6.1, the natural pH of telone, and the maximum TOC decrease measured after 3 days was 30% from the

initial value. A slight chloride release (2.53 mg.L^{-1} , 10% of the initial organic chlorine present in the telone molecule), which caused the pH to drop to 4.5, was also detected. From these results, the disappearance of telone can be attributed mainly to its high volatility. No additional effect was detected in the experiment performed in the pilot plant (photolysis and volatilisation), as telone does not absorb at UV spectra. The same decrease in TOC was detected as in the hydrolysis test: 30% of the initial amount in **only** 4 hours. In this case, a chloride release of around 1.51 mg.L^{-1} (approximately 6% of the initial organic chlorine present in telone molecule), was measured, which caused a **a natural** drop in pH from 5.4 to 4.0. Therefore, it can be concluded that telone underwent slight hydrolysis, but also considerable volatilisation. This effect should be taken into account in photocatalytic testing.

FIGURE 6

As commented above, the elimination of this pesticide was monitored using the mineralization rate (TOC decrease) and chloride released during both photocatalytic processes. In **Figure 6 b** the concentration of chloride is plotted against the illumination time. It may be observed that the amount of chloride released was exactly the **theoretical** concentration expected only in the photo-Fenton treatment. Meanwhile, at the end of the TiO_2 process, the chloride mass balance was not closed, indeed, the amount of lost chloride necessary to reach the stoichiometric value was around 28%, which means approximately 30% of TOC. This is just the TOC decrease detected after four hours in the “photolysis-volatilization” experiment. This effect was not observed in the photo-Fenton process due to the higher mineralization rate, which allowed almost 100% of TOC to be eliminated in only 25 minutes of illumination.

Before discussing reaction kinetics, it should be emphasised that the pilot plants are plug flow photoreactors (22 L in glass tubes and 8 L in piping and valves for the TiO_2

experiments; 44.6 L in glass tubes and 20 L in piping and valves for the photo-Fenton experiments) and mixing tank. Since the system is dynamic, the photoreactor outlet concentration is not exactly the same as the mixing tank outlet concentration. Thus, unless properly accounted for, the presence of the tank will alter the perceived performance of the photoreactor. A very high flow rate to achieve low conversion each time through is a possible solution to this problem. Flow rates (see experimental section) are very high compared to the total volume of the plug flow photoreactor. This means once through every 2-3 minutes, and therefore very little conversion per pass. Likewise, such low conversion per pass and the small volume included in the dark zones of the photoreactor do not permit any discussion of reactions taking place in the dark (mainly in the photo-Fenton process).

Finally several kinetics studies were also performed for each pesticide, assuming that the reaction between $\bullet\text{OH}$ radicals and the pesticide is the rate-determining step. Pesticide degradation in all the experiments may be described by a first-order reaction (**Equation 10**):

$$r = k_{OH}[\bullet\text{OH}]C = k_{ap}C \quad (10)$$

Where C represents the pesticide concentration, k_{OH} is the reaction rate constant and k_{ap} is a pseudo first-order constant. This was confirmed by the linear behaviour of $\ln(C_0/C)$ as a function of t_{30w} , for all the tests performed (see **Tables 3 and 4**).

As the reaction is not expected to follow such simple first or zero order kinetics models, overall reaction rate constants cannot be calculated. The complexity of the results is caused by the fact that the TOC is a sum parameter often including several hundred products that undergo manifold reactions. The maximum gradient of the degradation curve has been chosen in order to have one parameter as a practical point of comparison

for various experiments. Furthermore, this parameter was calculated for all the pesticides taking into account the tangent to the TOC curve at the point of its greatest drop. This is referred to as the “maximum mineralization rate” (r_{\max}) (see **Tables 3 and 4**).

Tables 3 and 4 also show the initial degradation rate and the maximum mineralization rate for each pesticide (when treated with photo-Fenton or TiO_2 , respectively), and the treatment time necessary for 80% of TOC to be eliminated. For such practical purposes as designing a treatment plant, all these parameters should be taken into account depending on whether the end requirements are to completely degrade the contaminant, to degrade it only up to a certain point, or up to a certain percentage of mineralisation, etc.

From the data presented in these two tables, it can be concluded that photo-Fenton is more effective than TiO_2 for all the pesticides tested, except for dimethoate mineralization, in which case both treatments were quite similar. As can be observed, the initial photo-Fenton treatment degradation rates were higher than those for TiO_2 photocatalysis.

TABLE 3

TABLE 4

It is worth mentioning that the initial mineralization rate was quite similar in the TiO_2 treatment for all the pesticides, while for photo-Fenton it seemed to be quite different for oxamyl and telone. This effect could be explained by the commercial oxamyl preparation (Vydate) employed, as 76% of the formulation contained compounds not described by the manufacturer. In fact, as confirmed by the appearance of additional TOC, some of those compounds are organic substances. Telone’s simple chemical structure led to a higher initial mineralization rate in the photo-Fenton treatment.

Table 3 summarizes the consumption of hydrogen peroxide necessary to eliminate approximately 80% of the initial TOC for each pesticide during photo-Fenton experiments as a function of t_{30w} . This parameter is of interest for evaluation of process economics. The consumption of this oxidant is directly proportional to treatment time and not to pollutant concentration, except for oxamyl due to the high percentage of unknown organic substances in its commercial formula. From the table it may be concluded that hydrogen peroxide consumption is not directly related to initial TOC or its decrease. Hydrogen peroxide consumption was actually quite similar for all pesticides except for cymoxanil and telone, which required longer and shorter treatment times, respectively, for 80% of mineralization.

After testing the pure compounds, mixtures simulating a more realistic effluent were tested to determine any constraints related to the simultaneous presence of different pesticides (**Figure 7**). Telone is not included in this mixture because it is so volatile. As these tests were longer than those performed with each pesticide alone, the expected substantial volatilisation could cause misinterpretation of results. These tests also showed that photo-Fenton is more efficient than TiO_2 . Mineralisation was not complete (part of the intermediates formed seem to be recalcitrant to the treatment) but only 10% remained at the end, which is a lower ratio than with the pure compounds. It could be expected that, as the treatment is longer (> 500 min and 1500 min for photo-Fenton and TiO_2 , respectively), there would be more mineralisation than in the tests with pure compounds.

As photo-Fenton treatment was more efficient for pesticide degradation than TiO_2 , toxicity analyses were performed during these tests (Table 5). As shown in Table 2, all the compounds were toxic at the initial concentrations tested. **Table 5** shows that the

photo-Fenton treatment was successful in reducing toxicity in most cases, considering that the *Vibrio fischeri* test is usually more sensitive than activated sludge, and might be useful in ensuring safe discharge of the water into a biological treatment plant and/or predicting biodegradability. Chemicals added to the water for photocatalysis were removed prior to bioassay. Experiments were extended until TOC mineralisation was significant (over 80%). Telone was a special case as the percentage of inhibition was not as high at the beginning (coherent with the high EC50 shown in Table 1) and increased during the treatment. Note that chlorinated compounds remain throughout treatment, reaching complete dechlorination only at the end (see Figure 6).

4. CONCLUSIONS.

It has been demonstrated that wastewater contaminated by six medium to highly soluble pesticides (cymoxanil, methomyl, oxamyl, dimethoate, pyrimethanil and telone), can be treated successfully by photo-Fenton and TiO₂ photocatalytic processes, within a reasonable length of time. Photo-Fenton treatment was more efficient than TiO₂, not only for pesticide degradation, but also for TOC mineralization, except for dimethoate for which the mineralization rate was quite similar in both photocatalytic treatments.

It may also be concluded that in photo-Fenton treatment of organophosphorous pesticides, iron precipitation as ferric phosphate must be taken into account so that the amount of iron necessary to keep the process from stopping can be added.

Treatment time required for maximum elimination of TOC using 20 mg.L⁻¹ of Fe²⁺ was always much shorter (between 1.5 times for dimethoate and 20 times for telone), than with 200 mg.L⁻¹ of TiO₂.

Finally, the identification of a methylamine peak in the ionic chromatogram of nitrogenous pesticides in both photocatalytic treatments provided the explanation for the

nitrogen mass balance not closing in any of the pesticides tested. In the case of Pyrimethanyl, the formation of several stable intermediates, such as acetamide and formamide, which remained at the end of the experiments, kept total expected stoichiometric nitrogen from being obtained.

5. ACKNOWLEDGMENTS.

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6. REFERENCES.

- [1] The Water Framework Directive. Directive 2000/60/EC of the European Parliament and of the Council.
- [2] P.R. Gogate, A.B. Pandit, A review of imperative technologies for wastewater treatment I: oxidations technologies at ambient conditions, *Adv. Environ. Res.* 8 (2004) 501-551.
- [3] I.K. Konstantinou, T.A. Albanis, Photocatalytic transformation of pesticides in aqueous titanium dioxide suspensions using artificial and solar light: intermediates and degradation pathways, *Appl. Catal., B: Environ.* 42 (2003) 319-335.
- [4] M. Pera-Titus, V. García-Molina, M.A. Baños, J. Giménez, S. Esplugas, Degradation of chlorophenols by means of advanced oxidation processes: a general review, *Appl. Catal. B: Environ.* 47 (2004) 219-256.
- [5] O. Legrini, E. Oliveros, A.M. Braun, Photochemical processes for water treatment, *Chem. Rev.* 93 (1993) 671-698.

- [6] R. Andreozzi, V. Caprio, A. Insola, R. Martota, Advanced oxidation processes (AOP) for water purification and recovery, *Catal. Today* 53 (1999) 51-59.
- [7] S. Esplugas, J. Jiménez, S. Contreras, E. Pascual, M. Rodríguez, Comparison of different advanced oxidation processes for phenol degradation, *Water Res.* 36 (2002) 1034-1042.
- [8] D. Bahnemann, *Photocatalysis*, *Sol. Energy* 77 (2004) 445.
- [9] S. Malato, J. Blanco, A. Vidal, C. Richter, Photocatalysis with solar energy at a pilot-plant scale: An overview, *Appl. Catal. B: Environ.* 37 (2002) 1-15.
- [10] J. Cunningham, G. Al-Shayyed, P. Sedlak, J. Caffrey, Aerobic and anaerobic TiO₂-photocatalysed purification of water containing organic pollutants, *Catal. Today* 53 (1999) 145-148.
- [11] A. Safarzadeh-Amiri, J.R. Bolton, S.R. Cater, The use of iron in advanced oxidation processes, *J. Adv. Oxid. Technol.* 1 (1996) 18-26.
- [12] M. Lapertot, C. Pulgarín, P. Fernández-Ibáñez, M.I. Maldonado, L. Pérez-Estrada, I. Oller, W. Gernjak, S. Malato, Enhancing biodegradability of priority substances (pesticides) by solar photo-Fenton, *Water Res.* (2006) in press.
- [13] M. Kositzki, I. Poullos, S. Malato, J. Cáceres, A. Campos. Solar photocatalytic treatment of synthetic municipal wastewater, *Water Res.* 38 (2004) 1147-1154.
- [14] I. Oller, W. Gernjak, M.I. Maldonado, P. Fernández-Ibáñez, J. Blanco, J.A. Sánchez-Pérez, S. Malato, Photocatalytic treatment of Dimethoate by solar photocatalysis at pilot plant scale, *Environ. Chem. Lett.* 3 (2005) 118-121.
- [15] M. Hincapié, M.I. Maldonado, I. Oller, W. Gernjak, J.A. Sánchez-Pérez, M.M. Ballesteros, S. Malato, Solar photocatalytic degradation and detoxification of EU priority substances, *Catal. Today* 101 (2005) 203-210.

- [16] P. Fernández-Ibáñez, S. Malato, F.J. de las Nieves, Relationship between TiO₂ particle size and reactor diameter in solar photoreactors efficiency, *Catal. Today* 54 (1999) 195-204.
- [17] S. Malato Rodríguez, J. Blanco Gálvez, M.I. Maldonado Rubio, P. Fernández Ibáñez, D. Alarcón Padilla, M. Collares Pereira, J. Farinha Mendes, J. Correia de Oliveira, Engineering of solar photocatalytic collectors, *Sol. Energy* 77 (2004) 513-524.
- ~~[18] A.R. Fernández-Alba, D. Hernando, A. Agüera, J. Cáceres, S. Malato, Toxicity assays: a way to increase solar AOP efficiency, *Water Res.* 36 (2002) 4255-4262.~~
- [19] S. Malato, J. Blanco, J. Cáceres, A.R. Fernández-Alba, A. Agüera, A. Rodríguez, Photocatalytic treatment of water-soluble pesticides by photo-Fenton and TiO₂ using solar energy, *Catal. Today* 76 (2002) 209-220.
- [20] T.J. Strathmann, A.T. Stone, Reduction of the carbamate pesticides oxamyl and methomyl by dissolved FeII and CuI, *Environ. Sci. and Technol.* 35 (2001) 2461-2469.
- [21] C. Domínguez, J. García, M.A. Pedraz, A. Torres, M.A. Galán, Photocatalytic oxidation of organic pollutants in water, *Catal. Today* 40 (1998) 85-101.
- [22] E. Evgenidou, K. Fytianos, I. Poullos, Photocatalytic oxidation of dimethoate in aqueous solutions, *J. Photochem. Photobiol. A: Chemistry* 175 (2005) 29-38.
- [23] P. Morrica, S. Trabue, J.J. Anderson, S. Lawler, S. Seccia, P. Fidente, R. Scout Swain and L. Mattson, Kinetics and Mechanism of cymoxanil Degradation in Buffer Solutions, *J. Agric. food Chem.* 52 (2004) 99-104.
- [24] P. Morrica, P. Fidente and S. Seccia, Performance liquid chromatographic mass spectrometric identification of the photoproducts of cymoxanil, *Biomed. Chromatogr.* 19 (2005) 506-512.
- ~~[25] A. Agüera, E. Almansa, A. Tejedor, A.R. Fernández-Alba, S. Malato and M.I. Maldonado, Photocatalytic pilot scale degradation study of pyrimethanil and of its main~~

degradation products in waters by means of solid-phase extraction followed by gas and liquid chromatography with mass spectrometry detection, *Environ. Sci. Technol.* 34 (2000) 1563-1571.

Figure captions:

Figure 1. (a) Degradation and mineralization of methomyl by photo-Fenton and TiO₂. Points 1, 2 and 3 refer to the steps prior to the system illumination (see subsection “experiment set-up” for details). (b) and (c) Inorganic ions released from the pesticide in photo-Fenton (empty symbols) and TiO₂ (stuffed symbols) experiments: (○) total nitrogen, (◁) N coming from NO₃⁻, (◇) N coming from NH₄⁺ and (+) S coming from SO₄²⁻.

Figure 2. (a) Degradation and mineralization of dimethoate by photo-Fenton and TiO₂. Points 1, 2 and 3 as in figure 1. (b), (c) and (d) Inorganic ions released from the pesticide in photo-Fenton and TiO₂ experiments. See legend explanation in figure caption 1. (▽) P from PO₄³⁻.

Figure 3. (a) Degradation and mineralization of oxamyl by photo-Fenton and TiO₂. Points 1, 2 and 3 as in figure 1. (b) and (c) Inorganic ions released from the pesticide in photo-Fenton and TiO₂ experiments. See legend explanation in figure caption 1.

Figure 4. (a) Degradation and mineralization of cymoxanil by photo-Fenton and TiO₂. Points 1, 2 and 3 as in figure 1. (b) and (c) Inorganic ions released from the pesticide in photo-Fenton and TiO₂ experiments. See legend explanation in figure caption 1.

Figure 5. (a) Degradation and mineralization of pyrimethanil by photo-Fenton and TiO₂. Points 1, 2 and 3 as in figure 1. (b) and (c) Inorganic ions released from the pesticide in photo-Fenton and TiO₂ experiments. See legend explanation in figure caption 1.

Figure 6. (a) Mineralization of telone by photo-Fenton and TiO₂. Points 1, 2 and 3 as in figure 1. (b) Chloride released from the pesticide molecule in TiO₂ and photo-Fenton experiments. See legend explanation in figure caption 1. (▷) total chloride.

Figure 7. Mineralization of the mixture of pesticides by TiO₂ and photo-Fenton (20 mg·L⁻¹ of Fe²⁺), at a concentration of 50 mg·L⁻¹ each one.

Scheme 1. Chemical structure of pesticides tested.

Table 1. HPLC methods for target compounds.

Target compounds	Mobile phase (ratio)	Wavelength
Cymoxanil	H ₂ O/Acetonitrile (80/20)	240 nm
Methomyl	H ₂ O/Acetonitrile (90/10)	234 nm
Oxamyl	H ₂ O/Methanol (80/20)	234 nm
Dimethoate	H ₂ O/Acetonitrile (80/20)	210 nm
Pyrimethanil	H ₂ O/Acetonitrile (50/50)	270 nm

Table 2. Toxicity and Biodegradability of each initial pesticide solution (50 mg L⁻¹).

	Methomyl	Dimethoate	Oxamyl	Cymoxanil	Pyrimethanil	Telone
Toxicity (EC₅₀, mgL⁻¹)	34.1	14.9	9.10	39.1	36.1	85.1
Biodegradability (%)	10 (13 d*)	13 (13 d)	40 (18 d)	60 (18 d)	60 (20 d)	0 ⁽¹⁾

* d = days of biotreatment once biodegradability reached a constant value (28-day tests);⁽¹⁾ Telone BOD₅ analysis.

Table 3. Kinetic parameters and consumption of hydrogen peroxide as function of initial TOC for photo-Fenton experiments.

Target compounds	Fe 20 mg.L ⁻¹					
	TOC ₀ mg.L ⁻¹	t _{30v,80} ⁽¹⁾ min	k _{ap} min ⁻¹	r ₀ ⁽²⁾ mM.min ⁻¹	H ₂ O ₂ CONS ⁽⁴⁾ mM	r _{max} (TOC) mg.L ⁻¹ .min ⁻¹
Methomyl	22	101	0.25±0.01	0.084±0.004	60	0.27±0.01
Dimethoate	15	77	0.25±0.03	0.056±0.003	39	0.19±0.01
Oxamyl	56 ⁽³⁾	126	0.13±0.01	0.035±0.002	39	0.51±0.03
Cymoxanil	24	236	0.41±0.05	0.103±0.005	131	0.37±0.02
Pyrimethanil	32	66	2.5±0.3	0.48±0.02	46	1.10±0.06
Telone	13	8	-	-	5	0.39±0.02

⁽¹⁾ Treatment time necessary for to eliminate approximately 80% of initial TOC. ⁽²⁾ Initial degradation rate.

⁽³⁾ Commercial oxamyl which contains 76% of unknown compounds. ⁽⁴⁾ Amount of hydrogen peroxide consumed to eliminate approximately 80% of initial TOC.

Table 4. Kinetic parameters for TiO₂ experiments.

Target compounds	TiO ₂ 200 mg.L ⁻¹				
	TOC ₀ mg.L ⁻¹	t _{30w,80} ⁽¹⁾ min	k _{ap} min ⁻¹	r ₀ ⁽²⁾ mM.min ⁻¹	r _{max} (TOC) mg.L ⁻¹ .min ⁻¹
Methomyl	19	401	0.044±0.002	0.014±0.001	0.094±0.005
Dimethoate	14	208	0.062±0.003	0.014±0.001	0.21±0.01
Oxamyl	55 ⁽³⁾	369	0.025±0.001	0.0064±0.0003	0.16±0.01
Cymoxanil	23	457	0.046±0.002	0.011±0.001	0.064±0.003
Pyrimethanil	39	306	0.038±0.002	0.0093±0.0005	0.13±0.01
Telone	17	161	-	-	0.16±0.01

⁽¹⁾ Treatment time necessary to eliminate approximately 80% of initial TOC. ⁽²⁾ Initial degradation rate.

⁽³⁾ Commercial oxamyl which contains 76% of unknown compounds.

Table 5. Percentage of inhibition of each pesticide during photo-Fenton treatment (20 mg·L⁻¹ of Fe²⁺).

	Methomyl	Dimethoate	Oxamyl⁽¹⁾	Cymoxanil	Pyrimethanil	Telone
Inhibition (15 min) (beginning photo-Fenton)	73%	80%	98%	60%	73%	24%
Inhibition (15 min) (50% TOC eliminated)	70%	40%	87% ⁽²⁾	85%	60%	32% ⁽³⁾
Inhibition (15 min) (80- 90% TOC eliminated)	58%	40%	57%	74%	52%	40%

⁽¹⁾ Commercial product: Vydate. ⁽²⁾ Toxicity after 80% of the initial TOC eliminated. ⁽³⁾ Toxicity after 50% of the initial TOC eliminated.

Figure 1.

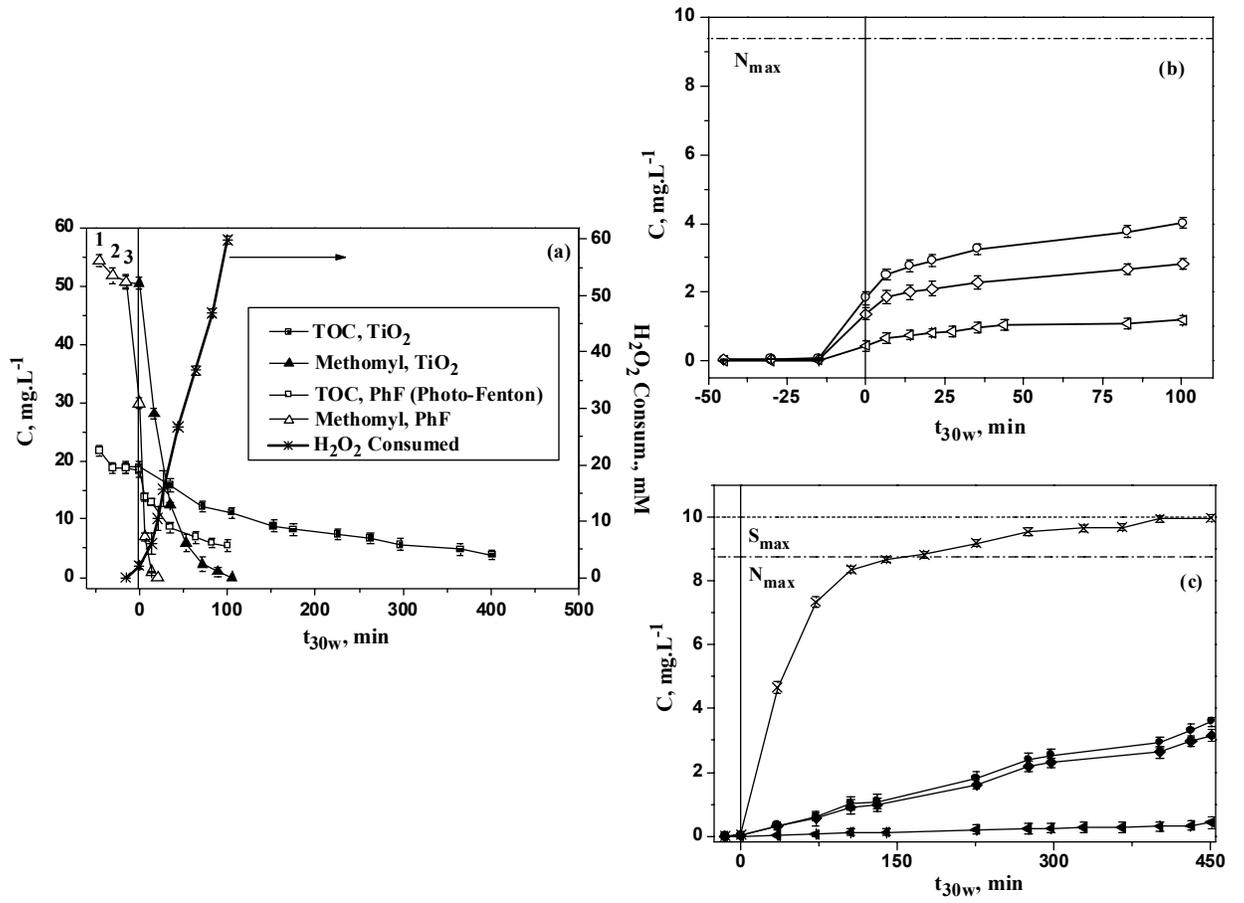


Figure 2.

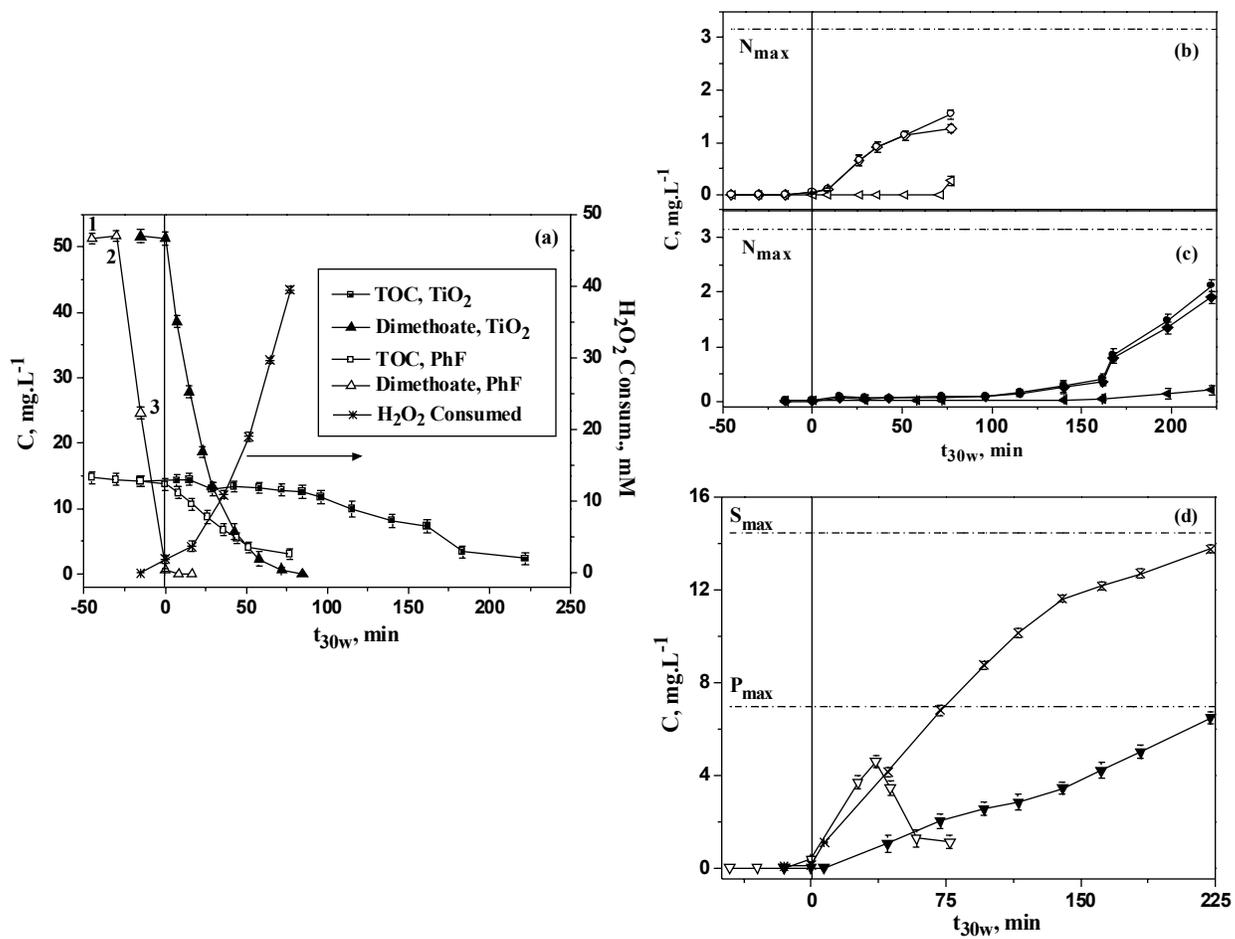


Figure 3.

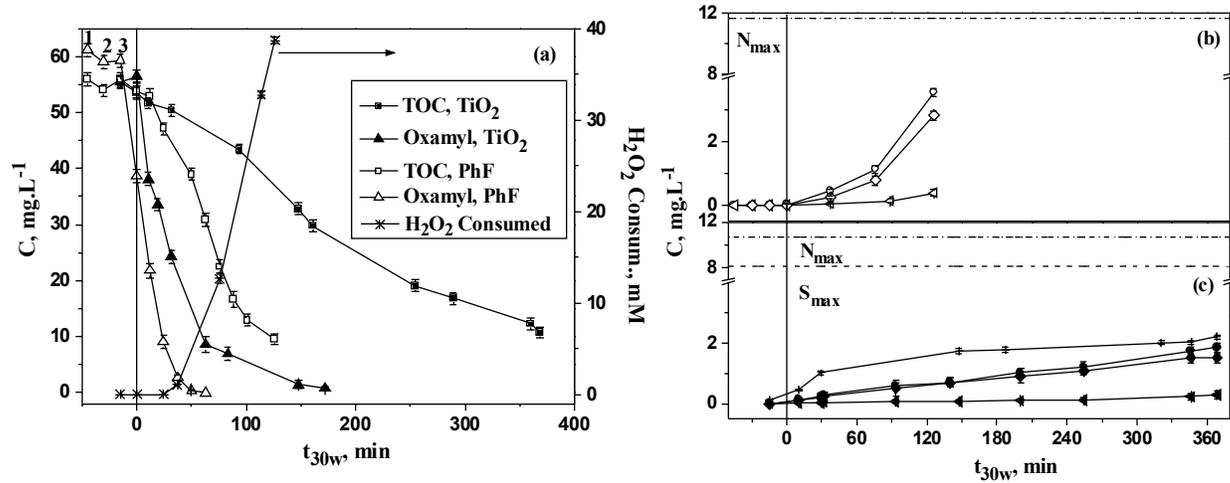


Figure 4.

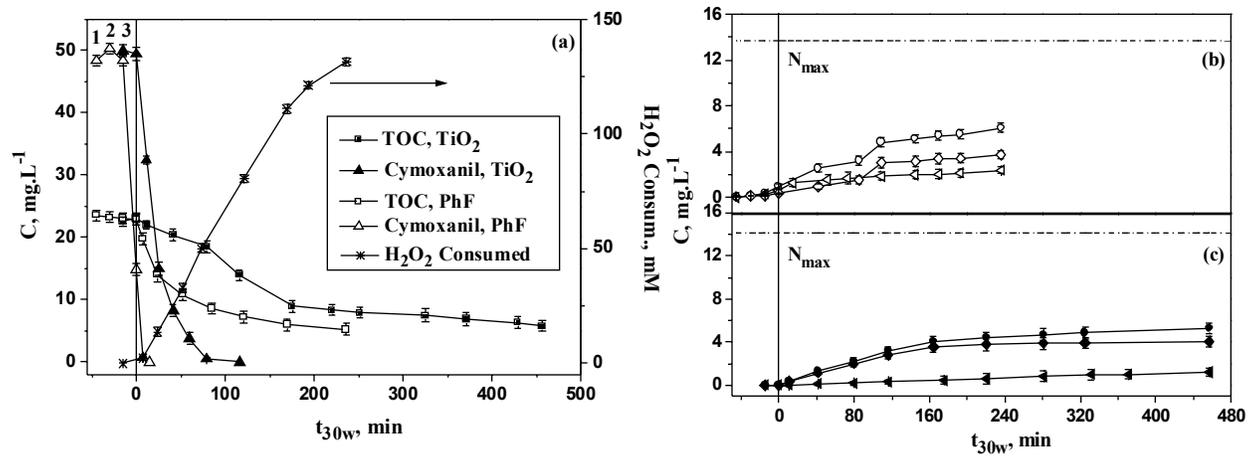


Figure 5.

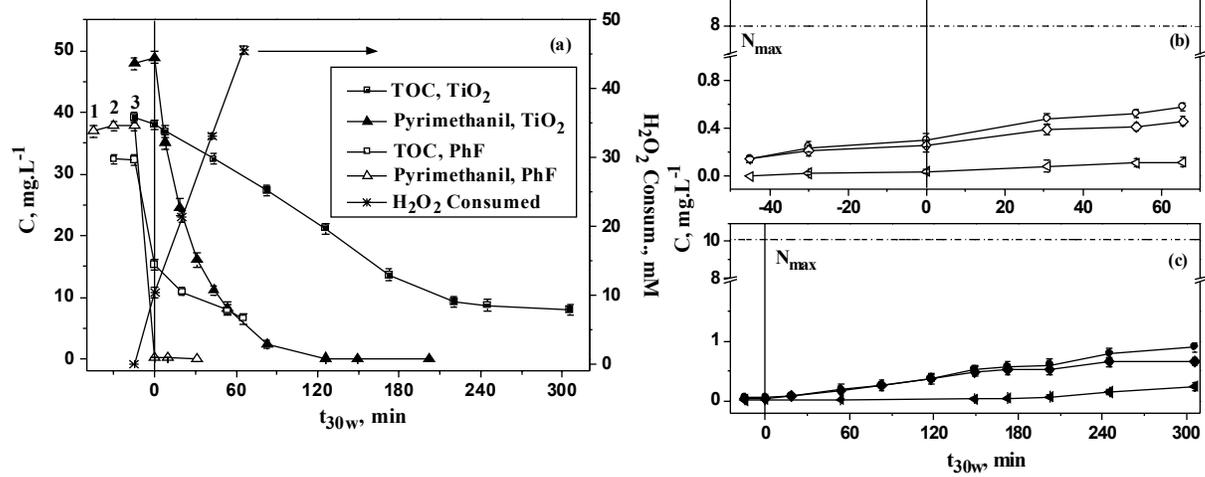


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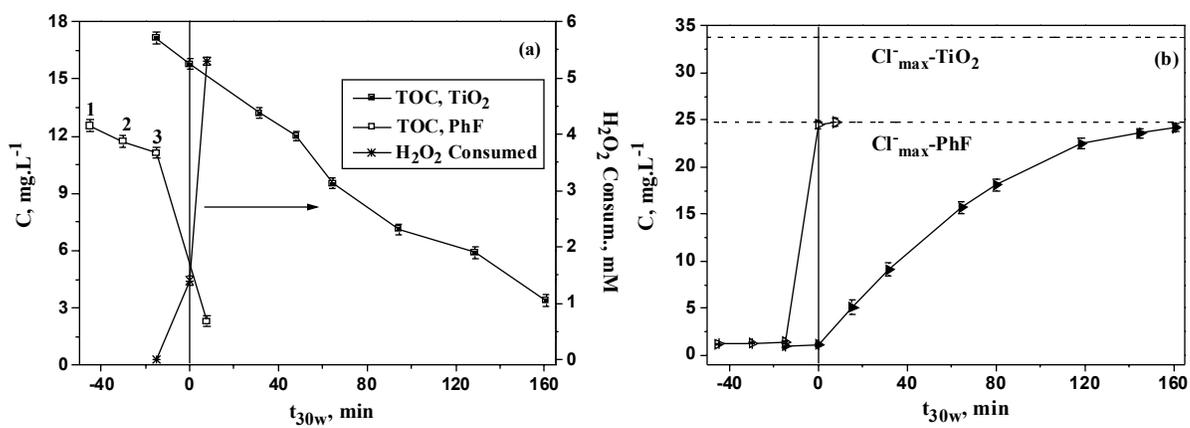
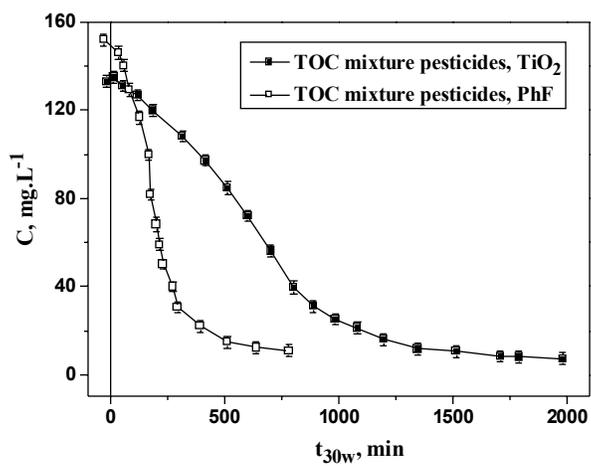


Figure 7.



Scheme 1.

