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Photocatalytic treatment of water-soluble pesticides by photo-Fenton and TiO_2 using solar energy

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Abstract

The technical feasibility and performance of photocatalytic degradation of four water-soluble pesticides (diuron, imidacloprid, formetanate and methomyl) have been studied at pilot scale in two well-defined systems of special interest because natural-solar UV light can be used: heterogeneous photocatalysis with titanium dioxide and homogeneous photocatalysis by photo-Fenton. The pilot plant is made up of compound parabolic collectors (CPCs) specially designed for solar photocatalytic applications. Experimental conditions allowed disappearance of pesticide and degree of mineralisation achieved in the two photocatalytic systems to be compared. In order to assure that the photocatalytic results are consistent, hydrolysis and photolysis tests have been performed with the four pesticides. The initial concentration tested with imidacloprid, formetanate and methomyl was 50 and 30 mg/l with diuron, and the catalyst concentrations were 200 mg/l and 0.05 mM with TiO_2 and iron, respectively. Total disappearance of the parent compounds and 90% mineralisation have been attained with all pesticides tested, methomyl being the most difficult to be degraded with both treatments. First-order rate constants, initial rate, time necessary for mineralising 90% of the initial TOC and hydrogen peroxide consumption were calculated in all cases, enabling comparison both of treatments and of the selected pesticide reactivity.

Keywords: Diuron; Imidacloprid; Formetanate; Methomyl; Pesticides; Photocatalysis; Photo-Fenton; Titanium dioxide

1. Introduction

Since the first European directive in 1975, much progress has been made in tackling point source contamination of European waters [1]. But severe pressure remains on priority hazardous substances (PHSs) [2] and persistent organic pollutants [3]. Human health is threatened by high concentrations of pesticides, heavy metals, hydrocarbons, chlorinated hydrocarbons, etc. dissolved in water, the source of which is usually industrial wastewater containing PHSs at low-to-medium concentration (<500 mg/l). In this context, the IPPC (integrated pollution prevention and control) Directive [4] requests the development of technologies and management practices for specific industrial sectors (see Annex I of the Directive) for the minimisation of pollution and recycling of water. Due to the lack of available on-site treatment technologies, a large number of the industrial activities included in Annex I of the IPPC Directive are not treating wastewater appropriately. As a consequence, simple, low cost, available technologies are strongly required [5].

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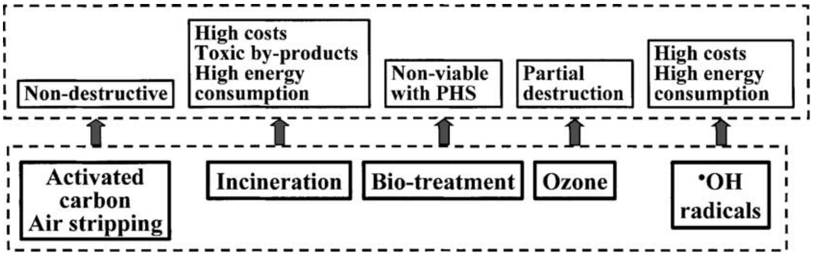


Fig. 1. PHS-treatment methods and their disadvantages.

The main cause of water contamination by PHSs is industrial discharge. The treatment of wastewater is based upon various mechanical, biological, physical and chemical processes. After filtration and elimination of particles in suspension, biological treatment is the ideal process. Unfortunately, there is a class of products labelled bio-recalcitrant (non-biodegradable). Almost all PHSs are in this category. In such cases, it is necessary to adopt much more effective reactive systems [6]: air stripping, adsorption on granulated activated carbon, incineration, ozone and oxidation. Their disadvantages are summarised in Fig. 1.

Advanced oxidation processes (AOPs) have been proposed as an alternative for the treatment of this type of wastewater. Many researchers have concentrated on this goal [7,8] pointing out that these processes, although making use of different reacting systems, are all characterised by the same chemical feature: production of OH radicals ($^{\bullet}$OH). These radicals are extraordinarily reactive (oxidation potential 2.8 V) and attack most organic molecules. They are characterised by their not very selective attack, which is a useful attribute for an oxidant used in pollution problems. Here it should be pointed out that only wastewater with a relatively low COD (chemical oxygen demand) content (<1.0 g/l) are suitable for treatment with AOPs, since a higher COD would require the consumption of large amounts of reactants and energy. The versatility of AOPs is also enhanced by the fact that they offer different possibilities for OH radical production, thus allowing them to conform to specific treatment requirements. The main problem with AOPs is their high cost. The application of solar technologies to these processes could help to diminish that problem by reducing the energy consumption required to generate UV radiation. From the point of view of their practical application, heterogeneous TiO_2 photocatalysis and homogeneous photo-Fenton are the AOPs for which the solar technologies have been most extensively studied and developed [9–12].

Research devoted to environmental protection has developed rather quickly as a consequence of the special attention paid to the environment by international social, political and legislative authorities [13], leading in some cases to very severe regulations [14]. Compliance with strict quality standards is especially called for in the case of those toxic substances that affect the biological sphere and prevent activation of biological degradation processes. Among those substances, pesticides present one of the greatest problems, because as the world population is expected to continue increasing during the 21st century the requirement for continued increase in agricultural productivity will also be an unavoidable necessity. Associated with this is a proportionally even greater increase in the production and consumption of agrochemical products. Pesticides and agrochemical compounds in general have been detected in water since the 1950s. As these contaminants are non-biodegradable, this is an accumulative problem with unpredictable consequences for the mid-term future [15].

This work evaluates two well-defined AOP systems that use natural UV light in a large pilot plant, heterogeneous photocatalysis with TiO_2 and photo-Fenton. The processes were applied to the degradation of four pesticides: diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea], imidacloprid [1-(6-chloro-3-pyridylmethyl)-*N*-nitroimidazolidin-2-ylideneamine], formetanate [3-dimethylaminomethyleneaminophenyl methylcarbamate] and methomyl [*S*-methyl *N*-(methylcarbamoyloxy)thioacetamidate]. Four different pesticides were selected for the following two main reasons: they have two different structures that are representative of a wide range of modern pesticides (containing different heteroatoms and bonding structures) and they are highly soluble in water (of special interest because of their extremely easy transport in the environment, seriously threatening all surface and groundwater).

2. Materials and methods

2.1. Photoreactor

All the experiments were carried out under sunlight in compound parabolic collectors (CPCs) at the Plataforma Solar de Almería (PSA, latitude 37°N, longitude 2.4°W). The pilot plant [16] is made up of twin systems, each having three collectors, one tank and one pump. Each collector ($1.03\,\mathrm{m}^2$ each) consists of eight Pyrex tubes connected in series and mounted on a fixed platform tilted 37° (local latitude). The water flows at 20 l/min (see Fig. 2) directly from one module to another and finally into a tank. The total volume (V_T) of the reactor (40 l) is separated into two parts: 22 l (Pyrex tubes) total irradiated volume (V_i) and the dead reactor volume (tank + high density polyethylene tubes). At the beginning of the experiments, with collectors covered, all the chemicals are added to the tank and mixed until constant concentration is achieved throughout the system. Then the cover is removed and samples are collected at predetermined times (t). Solar ultraviolet radiation (UV) was measured by a global UV radiometer (KIPP&ZONEN, model CUV3), mounted on a platform tilted 37° (the same angle as the CPCs), which provides data in terms of incident $\mathrm{W_{UV}\,m^{-2}}$. This gives an idea of the energy reaching any surface in the same position with regard to the sun. With Eq. (1), combination of the data from several days' experiments and their comparison with other photocatalytic experiments is possible:

$$t_{30\,\mathrm{W},n} = t_{30\,\mathrm{W},n-1} + \Delta t_n \frac{\mathrm{UV}}{30}\frac{V_\mathrm{i}}{V_\mathrm{T}},$$
$$\Delta t_n = t_n - t_{n-1} \qquad (1)$$

where t_n is the experimental time for each sample, UV the average solar ultraviolet radiation measured during Δt_n, and $t_{30\,\mathrm{W}}$ is a "normalised illumination time". In this case, time refers to a constant solar UV power of $30\,\mathrm{W\,m^{-2}}$ (typical solar UV power on a perfectly sunny day around noon). As the CPCs do not concentrate light inside the photoreactor, the system is outdoor and, as it is not thermally insulated, the maximum temperature achieved inside the reactor has been 40 °C. All "blank tests" (hydrolysis and photolysis) were performed in 3 l Pyrex beakers (UV transmission > 80% between 320 and 400 nm, internal diameter 15 cm) and covered with a Pyrex top to avoid sample contamination and evaporation. During

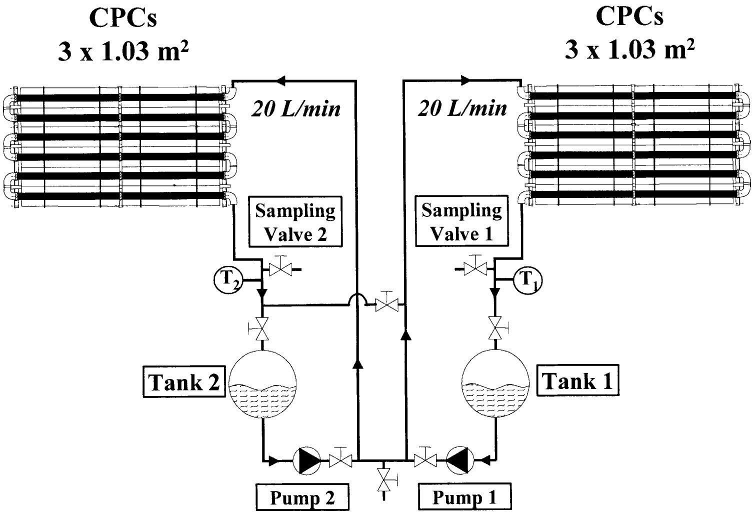


Fig. 2. Diagram of the twin pilot plants.

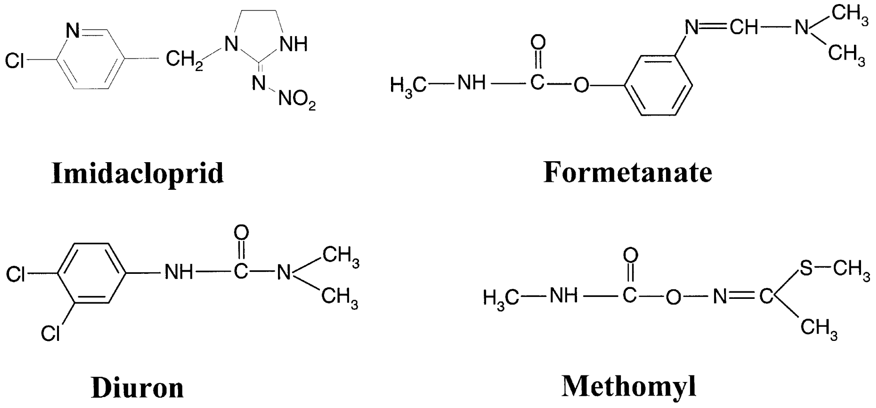
hydrolysis tests the beakers were kept in the dark. The pilot plant was not used for this purpose to avoid any slight effect of TiO_2 deposits on the photoreactor tubes, as removal of the thin catalyst coating remaining on the tubes after TiO_2 suspensions have circulated through them is a very hard, complex and expensive task due to the dimensions of the tubes and the plant itself. The maximum temperature inside the beakers was 35 °C.

2.2. Chemicals

Technical-grade imidacloprid (97.9%) was supplied by Bayer Hispania S.A. (Barcelona, Spain). Technical-grade methomyl (98%) and diuron (98.5%) were supplied by Aragonesas Agro S.A. (Madrid, Spain). Technical-grade formetanate (50%) was supplied by Argos Shering AgrEvo, S.A. (Barcelona, Spain). Analytical-standard (Pestanal®) imidacloprid, methomyl and formetanate hydrochloride were purchased from Riedel-deHaën (Seelze, Germany). Analytical-standard diuron was purchased from “Dr. Ehrenstorfer GmbH” (Augsburg, Germany). The pesticides are shown in Scheme 1. Analytical-grade organic solvents and inorganic salts were used for HPLC-UV (high pressure liquid chromatography with ultraviolet detector). The heterogeneous photocatalytic degradation tests were carried out using a slurry solution (200 mg/l of TiO_2) of Degussa (Frankfurt, Germany) P-25 titanium dioxide (surface area 51–55 $m^2\,g^{-1}$). For the photo-Fenton experiments (0.05 mM iron), the following chemicals were used: iron sulphate ($FeSO_4{\cdot}7H_2O$), hydrogen peroxide reagent grade (30%) and sulphuric acid for pH adjustment (around 2.7–2.8). The concentration of peroxide in the reactor was determined by frequent analyses (iodometric titration) and maintained constant (around 15 mM) by adding small amounts as consumed. Two thousand and five hundred units per milligram of bovine liver catalase acquired from Fluka Chemie AG (Buchs, Switzerland) was used to eliminate the remaining H_2O_2 after sampling in photo-Fenton experiments. With this porpoise 0.5 ml of catalase solution (0.1 g/l) was added to 25 ml of sample ($6 < pH < 7$) and after 10 min hydrogen peroxide was completely decomposed. By this procedure up to 20 mM of hydrogen peroxide can be decomposed. The water used in the experiments was obtained from the PSA distillation plant (conductivity $< 10\,mS\,cm^{-1}$, $Cl^- = 0.2$ mg/l, $NO_3{}^- = 0.5$ mg/l, organic carbon $< 0.5\,mg\,l^{-1}$).

2.3. Analytical determinations

HPLC-UV. Imidacloprid, methomyl, diuron and formetanate were analysed using reverse-phase liquid chromatography (at 0.5 ml/min) with UV detection in an HPLC-UV (Hewlett-Packard, series 1100) with C-18 column (LUNA 5 micron-C18, 3 × 150 mm from Phenomenex). The mobile-phase composition and wavelength was in each case: H_2O (pH = 3)/acetonitrile (ACN) at 80/20 ratio at 270 nm (imidacloprid), H_2O/ACN at 90/10 ratio at 234 nm (methomyl), H_2O/methanol at 40/60 ratio at 254 nm



Scheme 1. Pesticides tested.

(diuron) and K_2HPO_4 (18.4 mM in water, pH = 8.9)/ACN at 80/20 ratio at 252 nm (formetanate).

TOC. Total organic carbon (TOC) was analysed by direct injection of the filtered samples into a Shimadzu-5050A TOC analyser calibrated with standard solutions of hydrogen potassium phthalate.

LC-IC. Formation of inorganic anions was followed by LC-IC (Dionex-120, anions column IonPAc AS14, 250 mm long). The eluent for inorganic anions was $Na_2CO_3/NaHCO_3$ (1 mM/3.5 mM). Nessler spectrophotometric methods were used for ammonium.

3. Results and discussion

The renewed interest of researchers in the photo-assisted Fenton processes (classic old reactive system discovered by Fenton in the last century) is today underlined by a significant number of studies devoted to wastewater treatment. Production of OH radicals by Fenton reagent occurs by means of the addition of H_2O_2 to Fe^{2+} salts. The degradation rate of organic pollutants is strongly accelerated with photo-Fenton by irradiation with UV–Vis light. Under these conditions, the photolysis of Fe^{3+} complexes allows Fe^{2+} regeneration and the occurrence of Fenton reactions due to the presence of H_2O_2 and iron may be considered a true catalyst. This is a simple way of producing OH radicals, neither special reactants nor special apparatus being required. Iron is very abundant non-toxic element and hydrogen peroxide is easy to handle and environmentally safe. Hydroxyl radicals can also be generated with a semiconductor that absorbs radiation when in contact with water. References and patents related to the heterogeneous photocatalytic removal of toxic and hazardous compounds from water and air published during the last decade can be counted in the thousands [17] and applications and target compounds are numerous. Whenever semiconductor materials have been tested under comparable conditions for the degradation of the same compounds, TiO_2 has generally been demonstrated to be the most active [18]. In spite of the possible advantages of a supported catalyst configuration, slurry systems are much more efficient [19]. So recovery of the catalyst from slurry and its reuse has also been previously studied and developed. Catalyst recuperation is achieved by induced accelerated sedimentation of TiO_2 particles [16,20], which depends on the colloidal stability, mobility and size of the particles. Both catalytic systems (TiO_2 and photo-Fenton) are of special interest because solar light can be used (see Fig. 3).

Detoxification of wastewater is today the most successful photochemical application of solar photons with several relevant facilities already in operation [12]. The first European industrial-scale solar CPC photocatalytic plant has recently been erected with commercially available components. It has demonstrated that the solar photocatalytic technology is sufficiently developed for industrial use [21,22]. In this context, the scope of this paper is to demonstrate that the solar technology already developed is able to degrade different hazardous compounds by both photo-Fenton and TiO_2 using the same set-up.

Diuron [23], an EPA (Environmental Protection Agency, USA) Type III pesticide, that is toxic and slightly hazardous, is considered a PHS by the EC (European Commission) [2] and is soluble in water (36.4 mg/l, 25 °C). Furthermore, it is a highly persistent herbicide with a half-life in soil of over 300 days. Formetanate, classified as Type I, that is a very toxic and highly hazardous pesticide, is also highly soluble in water (822 g/l, 25 °C). Imidacloprid is Type II, which means that it is a toxic and moderately hazardous pesticide, and it is very soluble in water (0.61 g/l, 25 °C). Methomyl has been classified by the WHO (World Health Organisation), EPA and EC as a very toxic and hazardous pesticide and is highly soluble in water (57.9 g/l). It also has a low sorption affinity to soils and can therefore easily cause groundwater contamination in agricultural areas [24,25].

Several blank experiments, at the same initial concentrations as the photocatalytic experiments, were performed first to guarantee that the results obtained during the photocatalytic tests were consistent and not due to hydrolysis and/or photolysis. Hydrolysis experiments were done at different pH but without repeating those results found in the literature [23]. In any case, hydrolysis at pH 2.7 has been performed in all cases because photo-Fenton tests were done at this pH. Table 1 shows these results. Only slight hydrolysis was detected at pH 2.7 in the case of formetanate but after 144 h, and only formetanate presented relevant hydrolysis at higher pHs. In any case, hydrolysis is irrelevant compared to the photocatalytic results (see

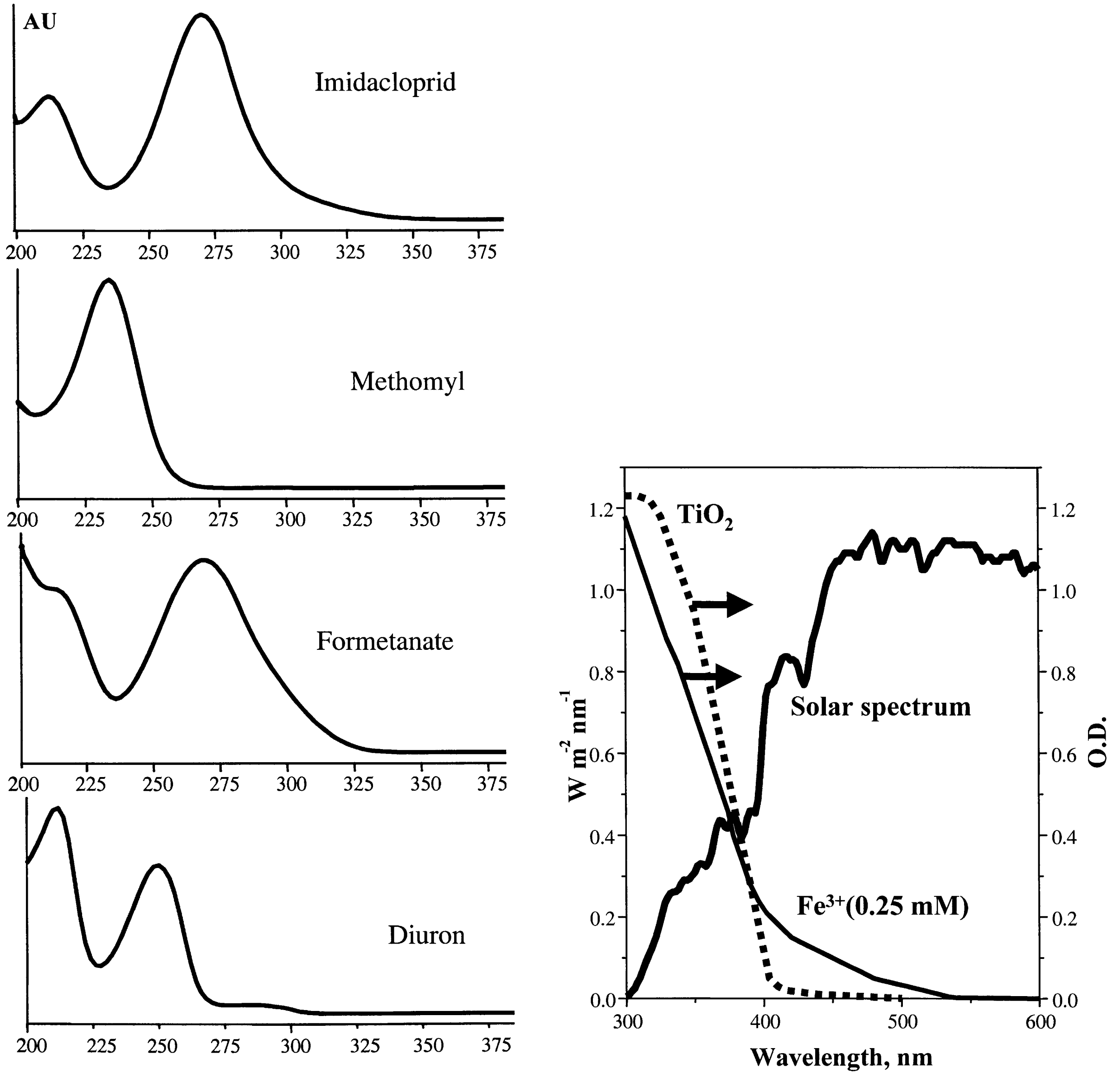


Fig. 3. UV spectra of the four pesticides and solar spectrum. TiO_2 and Fe(III) absorption spectra are also shown.

Table 1
Hydrolysis expressed as % of disappearance of the selected pesticides at different pHs (d: days)

	pH 2.7		pH 5		pH 7		pH 8–9	
	t (h)	%	*t* (h)	%	*t* (h)	%	*t* (h)	%
Imidacloprid	36	0	36	0	–	–	36	0
Methomyl	20 d	0	20 d	0	–	–	–	–
Diuron	72	0	72	0	–	–	–	–
Formetanate	144	2	144	18	48	24	24	82

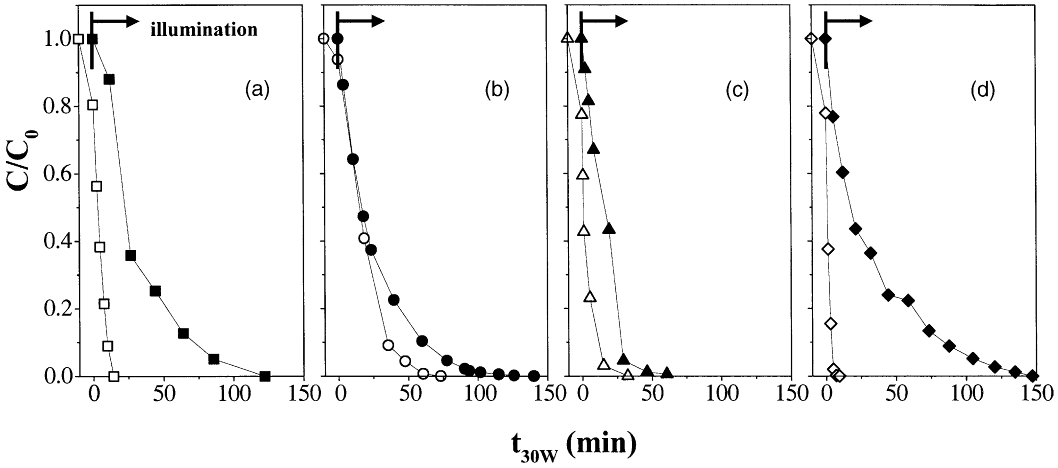


Fig. 4. Disappearance of imidacloprid (a), methomyl (b), diuron (c) and formetanate (d) as a function of $t_{30\,W}$ (illumination time). TiO_2 (200 mg/l): black symbols. Photo-Fenton (0.05 mM Fe): white symbols.

Fig. 4). TOC degradation has never been measured under irradiation without catalysts.

Table 2 shows results of photolysis experiments with the four pesticides. The results obtained indicate that the spontaneous degradation due to solar illumination is always unimportant. Methomyl is not degraded at all. Fig. 3 shows the spectra of aqueous solutions of the four pesticides and solar spectrum.

Methomyl and solar UV spectra do not overlap, showing that capacity for absorption of solar photons cannot produce photoalteration processes after being exposed to the environment. Therefore, all the results obtained during tests in the pilot plant are related to "photocatalytic effects". Imidacloprid, diuron and formetanate and solar UV (latitude 37°N, longitude 2.4°W) spectra slightly overlap in the 300–330 nm region (Fig. 3) showing that absorption of solar photons can produce photoalteration after exposure to the environment. But such natural photodegradation is very slow under well-illuminated aerobic conditions (transparent glass, 15 cm inner diameter) and mineralisation never occurs. The effect must be very similar when these pesticides are disposed of in natural waters. In surface water degradation is extremely slow and in ground water almost negligible. So disposal into the environment could be very risky. Several authors have determined the wide range of intermediate photoproducts generated by these pesticides when they are illuminated under natural sunlight: diuron [26], imidacloprid [27,28] and formetanate [29].

Table 2
Photolysis expressed as % disappearance of the selected pesticides

	$t_{illum.}$ (h)	%
Imidacloprid	24	27
	48	55
Methomyl	24	0
	48	0
Diuron	24	20
	48	44
Formetanate	24	10
	48	10

Fig. 4 shows the experiments performed with all the pesticides at 50 mg/l except diuron, which was tested at a lower concentration (30 mg/l) due to its lower solubility. But in any case, this does not affect the comparison because all of them present first-order kinetics. It may be observed that all the pesticides are degraded in a short time (less than 150 min) and that in all cases photo-Fenton is quicker than TiO_2 (this is discussed in detail below). The "dark" Fenton reaction (see Eq. (8)) always produces slight disappearance of the pesticide before illumination. This disappearance of pesticide in the dark has been described by a multitude of authors, but in this case, it is very slight because of the small quantity of Fe^{2+}

used (0.05 mM), which is rapidly (less than 10 min) converted to Fe^{3+} by hydrogen peroxide. The reason for using such a low concentration of iron was to demonstrate that a small amount is enough for complete degradation in a reasonable time, permitting disposal of water after treatment without removing iron. This could reduce process costs and will drastically facilitate the operation of these plants. It can also be observed that methomyl and diuron degradation rates are quite similar with photo-Fenton and TiO_2, while with imidacloprid and formetanate photo-Fenton is clearly quicker. The order is the following: diuron > methomyl > imidacloprid > formetanate (for TiO_2) and formetanate > imidacloprid > diuron > methomyl (for photo-Fenton). Excluding methomyl (an "aliphatic" pesticide, whose behaviour is explained after), the TiO_2 order seems to be related with pesticides solubility. If more soluble, less reaction rate was observed. It is reasonable to induce that the less soluble pesticides absorb easily on TiO_2 and react quicker. Concerning photo-Fenton, nothing can be concluded from these results for explaining formetanate, imidacloprid and diuron relative reactivity.

The four pesticides were successfully degraded as shown in Fig. 4. The "dark" Fenton reaction produced very slight mineralisation of the pesticide before illumination. Nevertheless, total mineralisation (i.e., complete disappearance of TOC) can be attained only after very long irradiation (see Fig. 5). In any case, the by-products detected as the last steps prior to mineralisation are always very simple (usually carboxylic acids [28–31]) and the complete release of heteroatoms as inorganic acids have been confirmed by anion analyses (ionic chromatography, see Section 2) according to the stoichiometry proposed in reactions (2), (3), (4) and (5) (corresponding to methomyl, diuron, imidacloprid and formetanate, respectively). It should be remarked that nitrogen released has very often been measured as a combination of ammonia and nitrate, but as ammonia is oxidised to nitrate after long irradiation [32] reactions are given here only to their most oxidised state.

$$C_5H_{10}O_2N_2S + \tfrac{21}{2}O_2 \rightarrow 2HNO_3 + H_2SO_4 + 5CO_2 + 3H_2O \quad (2)$$

$$C_9H_{10}Cl_2N_2O + 13O_2 \rightarrow 2HNO_3 + 2HCl + 9CO_2 + 3H_2O \quad (3)$$

$$C_9H_{10}ClN_5O_2 + \tfrac{33}{2}O_2 \rightarrow 5HNO_3 + HCl + 9CO_2 + 2H_2O \quad (4)$$

$$C_{11}H_{15}N_3O_2 + \tfrac{35}{2}O_2 \rightarrow 3HNO_3 + 11CO_2 + 6H_2O \quad (5)$$

Photocatalytic disappearance with TiO_2 follows apparent first-order kinetics as usual in heterogeneous photocatalysis when initial concentration is low enough and there is no catalyst saturation. It should

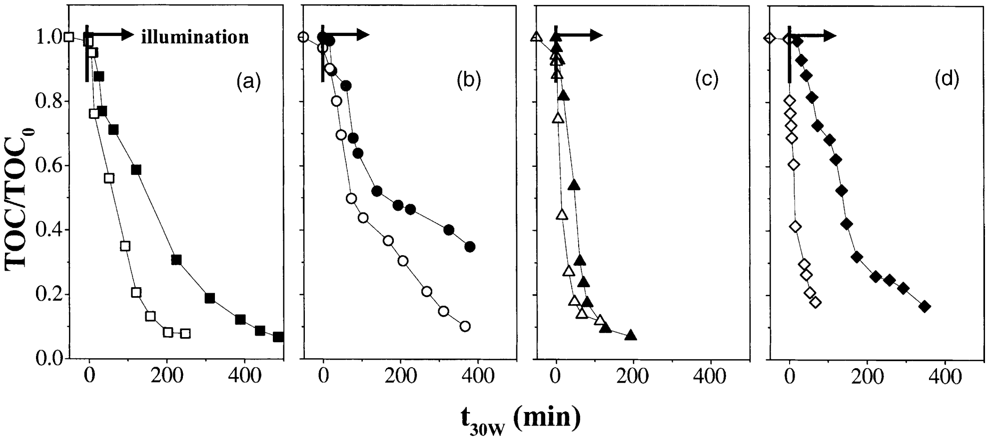


Fig. 5. Mineralisation of imidacloprid (a), methomyl (b), diuron (c) and formetanate (d) as a function of t_{30W} (illumination time). TiO_2 (200 mg/l): black symbols. Photo-Fenton (0.05 mM Fe): white symbols.

be emphasised that all pesticides decompose giving rise to by-products, which could also be competitive on the surface of the TiO_2. Their concentration varies throughout the reaction up to their mineralisation and thus the following equation (based on the Langmuir–Hinselwood kinetic model and commonly used for describing photocatalysis by TiO_2 kinetics) could describe the kinetics:

$$r = \frac{k_r KC}{1 + KC + \sum_{i=1}^{n} K_i C_i} \quad (i = 1, \ldots, n) \tag{6}$$

where k_r is the reaction rate constant, K the reactant adsorption constant, C the concentration at any time, K_i the by-products adsorption constant and C_i is the by-products concentration at any time. When C_0 is low enough, Eq. (6) can be simplified $(1 + KC + \sum \ldots = 1)$ to a first-order reaction rate equation:

$$r = k_{ap} C \tag{7}$$

This was confirmed by the linear behaviour of $\mathrm{Ln}(C_0/C)$ as a function of $t_{30\,\mathrm{W}}$ for all the tests performed (see Table 3). Similar behaviour was observed with photo-Fenton if the C_0 used for the calculation corresponds to the beginning of illumination and the dark reaction is not considered. The Fenton reactant consists of an aqueous solution of hydrogen peroxide and ferrous ions providing hydroxyl radicals (Eq. (8)). When the process is complemented with UV/visible radiation (Eq. (9)), it is called photo-Fenton and becomes catalytic.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \tag{8}$$

$$Fe^{3+} + H_2O \xrightarrow{h\nu} Fe^{2+} + H^+ + {}^{\bullet}OH \tag{9}$$

$${}^{\bullet}OH + \text{pesticide} \rightarrow \text{By-products} \tag{10}$$

Assuming that the reaction between the ${}^{\bullet}OH$ radicals and the pesticide is the rate-determining step, the rate equation is written as

$$r = k_{OH}[{}^{\bullet}OH]C = k'_{ap} C \tag{11}$$

where C is the pesticide concentration, k_{OH} the reaction rate constant and k'_{ap} is a pseudo-first-order constant.

Table 3 also shows the initial disappearance rate for each pesticide and the time necessary for a given amount of mineralisation ($t_{30\,\mathrm{W},90\%\,\mathrm{TOC}}$). As mineralisation does not follow simple models like first- or zero-order kinetics, overall reaction rate constants cannot be calculated (see Fig. 5). The complexity of the results, of course, is caused by the fact that the TOC is a sum parameter often including several hundred products that undergo manifold reactions. This parameter appears to be easy to handle and therefore was chosen in order to obtain a practical point of comparison. From the data in Table 3 photo-Fenton is seen to be more effective than TiO_2 for treating all the pesticides tested, except for diuron mineralisation, in which case both treatments are quite similar. Moreover, the parent compounds disappear very quickly by photo-Fenton compared with TiO_2, but this difference is attenuated if TOC degradation is considered. An important measure of the success of an AOP is the extent of mineralisation of target compounds to CO_2 and inorganic ions because it signifies the overall destruction of possible toxic intermediates in addition to the parent compound itself.

Huston and Pignatello [30] have determined photo-Fenton efficiency in the mineralisation of several pesticides and have described low mineralisation rates for aliphatic chain pesticides. Haag and Yao [33] have described rate constants for reaction of hydroxyl

Table 3
First-order rate constants, initial rate and time necessary for mineralising 90% of the initial TOC for the four pesticides tested with TiO_2 and photo-Fenton

Pesticide	k (min)		r_0 (mg l^{-1} min^{-1})		$t_{30\,\mathrm{W},90\%\,\mathrm{TOC}}$ (min)	
	k_{ap}	k'_{ap}	TiO_2	Photo-Fenton	TiO_2	Photo-Fenton
Imidacloprid	−0.035	−0.22	−0.61	−4.73	421	187
Methomyl	−0.046	−0.08	−1.34	−1.44	635	368
Diuron	−0.092	−0.20	−0.69	−1.06	124	159
Formetanate	−0.026	−0.85	−0.87	−10.79	399	105

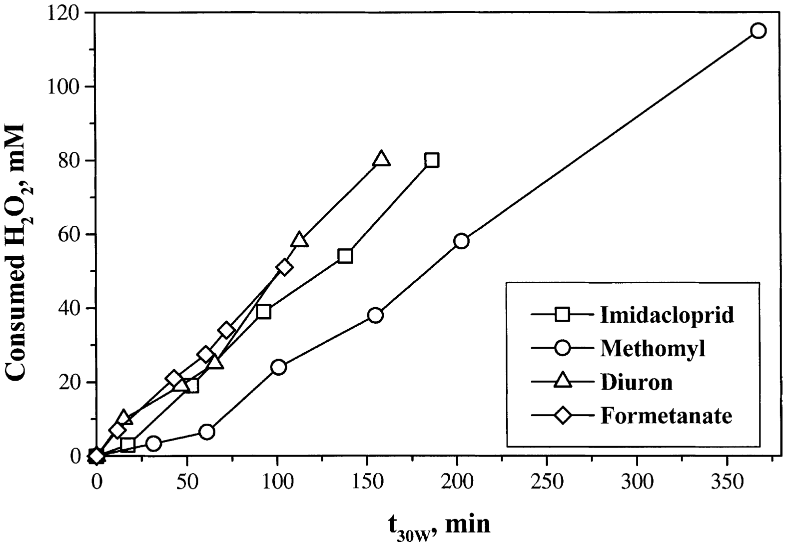


Fig. 6. Consumption of hydrogen peroxide during the photocatalytic treatment of the four pesticides. The last point for each pesticide corresponds to $t_{30\,W,90\%\,TOC}$ as shown in Table 3.

radicals with 44 water contaminants and the results demonstrate that $^{\bullet}$OHs are least reactive with aliphatic compounds. A similar effect was also described by Fallmann et al. [34] in a study with 10 different pesticides. In agreement with those results, methomyl (the unique “aliphatic” pesticide of this study) was the least reactive pesticide (with regard to TOC degradation) in our study. Methomyl was also the least reactive pesticide with photo-Fenton treatment. Furthermore, the methomyl reaction rates with TiO_2 and photo-Fenton treatment were the most similar. It is well known [35,36] that in photocatalysis with TiO_2 the role of photogenerated electrons is significant. Therefore, the “slow” reaction between hydroxyl radicals and methomyl could be compensated by the photoreduction provoked by the electrons of TiO_2 conduction band. This is consistent with the similar results obtained with this pesticide by both treatments.

Another important aspect related to both treatments concerns consumption of chemicals. During TiO_2 treatment only the catalyst is necessary and it can be reused [20,37,38]. As commented above, the iron concentration used during photo-Fenton treatment is such that it does not require separation previous to water disposal, which reduces operating costs. The hydrogen peroxide consumed during treatment has to be evaluated to find out which treatment is more economical. Fig. 6 shows the consumption of hydrogen peroxide during the test represented in Figs. 4 and 5. It should be observed that the consumption of the oxidant is directly proportional to treatment time and not to pesticide concentration. This means that the hydrogen peroxide degradation rate is only a function of its concentration and iron concentration (see Eq. (8)). In all the tests, the concentration of peroxide remaining in the reactor was determined by frequent analyses and maintained constant (around 15 mM) by adding small amounts as consumed. The consumption required in each case to attain 90% mineralisation was 80, 115, 80 and 51 mM for imidacloprid, methomyl, diuron and formetanate, respectively. From Figs. 5 and 6 it can be estimated that 50% of the hydrogen peroxide consumed is required to degrade the last 20% of the TOC. Such heavy consumption could be a drawback for employing photo-Fenton treatment to substantially reduce the TOC.

4. Conclusions

AOPs driven by solar energy appear to be an efficient method of removing pesticides from water.

Complete mineralisation of the initial compounds has been obtained. In this study, we have demonstrated the feasibility of such process under solar irradiation and at an upscaled volume in a CPC reactor. Furthermore, we have attempted to demonstrate that the comparison of different AOPs is not a trivial matter. Comparison of only the rate of decomposition of a single original substrate could lead to erroneous conclusions and/or classifications. Therefore, a detailed analysis should include not only the rate of disappearance of several substrates (containing different heteroatoms and bonding structures) but also that of the compounds produced during the process or at least of an integral parameter such as TOC.

It has been also demonstrated that photo-Fenton was more efficient than TiO_2 not only for parent compound degradation but also for TOC mineralisation. TiO_2 and photo-Fenton have similar efficiencies only in the case of methomyl, an aliphatic-chain pesticide. It is also worth mentioning that the concentration in the photocatalyst (iron) used is low enough to make the treated solution directly compatible with a safe environment. The major drawback of the photo-Fenton treatment is the high consumption of hydrogen peroxide if total mineralisation is to be achieved. It should be mentioned that this process seems suitable for pre-treatment of highly toxic and biorecalcitrant compounds before biological treatment. In this case, total mineralisation would not be necessary.

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References

[1] European Commission, EU Focus on Clean Water, 1999.
[2] European Commission, Socio-Economic Impacts of the Identification of Priority Hazardous Substances under the Water Framework Directive, Directorate-General Environment, 2000.
[3] United Nations, Inventory of Information Sources on Chemicals. Persistent Organic Pollutants, Environment Programme, 1999.
[4] European Union, Integrated Pollution Prevention and Control Directive, 96/61/EC.
[5] European Commission, EU Freshwater, A Challenge for Research and Innovation, A Concerted European Response, DG XII, EUR 18098, 1998.
[6] G.A. Zinkus, W.D. Byers, W.W. Doerr, Chem. Eng. Prog. (May 1998) 19.
[7] R. Andreozzi, V. Caprio, A. Insola, R. Martota, Catal. Today 53 (1999) 51.
[8] S. Chiron, A.R. Fernández-Alba, A. Rodríguez, E. García-Calvo, Wat. Res. 34 (2) (2000) 366.
[9] S. Malato, J. Blanco, J.M. Herrmann (Eds.), Solar Catalysis for Water Decontamination, Catal. Today 54 (2–3) (1999), complete issue.
[10] O.M. Alfano, D. Bahnemann, A.E. Cassano, D. Dillert, R. Goslich, Catal. Today 58 (2000) 199.
[11] J. Blanco, S. Malato, Solar Detoxification, UNESCO Natural Sciences World Solar Programme, http://www.unesco.org/science/wsp, 2001.
[12] S. Malato, J. Blanco, A. Vidal, Ch. Richter, Appl. Catal. B 37 (2002) 1.
[13] S.C. Nixon, T.J. Lack, D.T.E. Hunt, A.F. Boschet, Sustainable use of Europe's water? State, prospects and issues, European Environmental Agency, Environmental Assessment Series No. 7, 2000.
[14] A.N. Angelakis, M.H.F. Marekos, L. Bontoux, T. Asano, Wat. Res. 33 (10) (1999) 2201.
[15] M.G. Hayo, Agric. Ecosyst. Environ. 60 (1996) 81.
[16] J. Blanco, S. Malato, P. Fernández, A. Vidal, A. Morales, P. Trincado, J.C. Oliveira, C. Minero, M. Musci, C. Casalle, M. Brunote, S. Tratzky, N. Dischinger, K.-H. Funken, C. Sattler, M. Vincent, M. Collares-Pereira, J.F. Mendes, C.M. Rangel, Solar Energy 67 (4–6) (2000) 317.
[17] D.M. Blake, Bibliography of work on the photocatalytic removal of hazardous compounds from water and air, Technical Information Service, US Department of Commerce, Springfield, VA 22161, USA, 1994. Update Number 1 to June 1995, 1995. Update Number 2 to October 1996, 1997. Update Number 3 to January 1999, 1999. Update Number 4 to October 2001, 2001.
[18] J. Cunningham, G. Al-Shayyed, P. Sedlak, J. Caffrey, Catal. Today 53 (1999) 145.
[19] R.L. Pozzo, M.A. Baltanás, A.E. Casano, Catal. Today 39 (1998) 219.
[20] J. Blanco, S. Malato, F.J. de las Nieves, P. Fernández, EU Patent P9902508, 1999.
[21] K.-H. Funken, C. Sattler, B. Milow, L. de Oliveira, J. Blanco, P. Fernández, S. Malato, M. Brunotte, N. Dischinger, S. Tratzky, M. Musci, J.C. de Oliveira, Wat. Sci. Technol. 44 (5) (2001) 271.
[22] S. Malato, J. Blanco, A. Vidal, P. Fernández, J. Cáceres, P. Trincado, J.C. Oliveira, M. Vincent, Chemosphere 47 (2002) 235.

[23] C.D.S. Tomlin, The Pesticide Manual, 11th ed. British Crop Protection Council, 1997.

[24] D. Barceló, S. Chiron, A.R. Fernández-Alba, A. Valverde, M.F. Alpendurada, in: M.T. Meyer, E.M. Thurman (Eds.), American Chemical Society, 1996, p. 237.

[25] T.J. Strathmann, A.T. Stone, Environ. Sci. Technol. 35 (12) (2001) 2461.

[26] J. Jirkovski, V. Faure, P. Boule, Pest. Sci. 50 (1997) 42.

[27] A. Agüera, E. Almansa, S. Malato, I. Maldonado, A.R. Fernández-Alba, Analuses 26 (1998) 245.

[28] S. Malato, J. Caceres, A. Agüera, M. Mezcua, D. Hernando, J. Vial, A.R. Fernández-Alba, Environ. Sci. Technol. 35 (2001) 4359.

[29] A. Marinas, C. Guillard, J.M. Marinas, A.R. Fernández-Alba, A. Agüera, J.M. Herrmann, Appl. Catal. B 34 (2001) 241.

[30] P.L. Huston, J.J. Pignatello, Wat. Res. 33 (5) (1999) 1238.

[31] K. Tanaka, S.M. Robledo, T. Hisanaga, R. Ali, Z. Ramli, W.A. Baka, J. Mol. Catal. A 144 (1999) 425.

[32] E.M. Bonsen, S. Schroeter, H. Jacobs, J.A.C. Broekaeet, Chemosphere 35 (7) (1997) 1431.

[33] W.R. Haag, C.D. Yao, Environ. Sci. Technol. 26 (1992) 1005.

[34] H. Fallmann, T. Krutzler, R. Bauer, S. Malato, J. Blanco, Catal. Today 54 (1999) 309.

[35] E. Pelizzetti, C. Minero, Colloid. Surf. A 151 (1999) 321.

[36] P. Calza, C. Minero, A. Hiskia, E. Papaconstantinou, E. Pelizzetti, Appl. Catal. B 29 (2001) 23.

[37] R.J. Watts, S. Kong, W. Lee, J. Environ. Eng. 121 (10) (1995) 730.

[38] W. Xi, S.V. Geisen, Wat. Res. 35 (5) (2001) 1256.