



Photodegradation of eight miscellaneous pesticides in drinking water after treatment with semiconductor materials under sunlight at pilot plant scale

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HIGHLIGHTS

- ▶ Heterogeneous photocatalytic oxidation of pesticides in water.
- ▶ ZnO and TiO₂ strongly enhances photodegradation.
- ▶ The treatment cost was estimated to be 27.18 €/m³ for ZnO.
- ▶ Half lives ranged from 9 to 38 min by use of the tandem ZnO/Na₂S₂O₈.

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ABSTRACT

Heterogeneous photocatalysis with different semiconductor materials such as zinc oxide (ZnO), titanium dioxide (TiO₂), tungsten (VI) oxide (WO₃), tin (IV) oxide (SnO₂) and zinc sulphide (ZnS) in aqueous suspensions has been investigated for the removal of eight miscellaneous pesticides (ethoprophos, isoxaben, metolaxyl, metribuzin, pencycuron, pendimethalin, propanil and tolclofos-methyl). The experiments were carried out at pilot plant scale using compound parabolic collectors under natural sunlight, comparison of catalysts showed that ZnO is the most efficient for catalyzing the removal of these compounds. The photocatalysis of these compounds using ZnO followed first-order kinetics. The residual levels at the end (240 min) of the ZnO experiment were lower than 0.8 µg L⁻¹.

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1. Introduction

Leaching of pesticides into the groundwater from agricultural practices is receiving increasing attention in European countries because groundwater represents about 98% of the available fresh water of our planet. Thus, the European Directive 2000/60/EC concerning water used for human consumption establishes maximum concentrations for pesticides and their related products in drinking waters to safeguard people from harmful effects. In the leaching process, soil properties (total organic carbon content, pH, texture, mineralogy and structure), land use and management (pesticide application rate and timing, tillage), climate, subsoil and vadose zone characteristics, groundwater, and pesticide properties play a decisive role [1–3].

The frequent occurrence of pesticides in surface and groundwaters [4] has prompted the search for suitable methods that can easily destroy these bio-recalcitrant organic contaminants. Although conventional biological treatments of water offer some advantages such

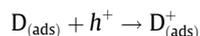
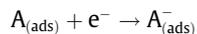
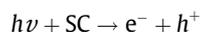
as their low cost and easy operation, most studies concerning the treatment of pesticides have concluded that they are not very effective due to the low biodegradability of these compounds [5–7]. In the recent years, research for new techniques for water decontamination that can overcome these disadvantages has led to processes that involve light, which are called advanced oxidation process (AOPs). Among these techniques, photocatalytic methods in the presence of artificial or solar light, like heterogeneous photocatalysis or the photo-Fenton treatment have been proven to be effective for the degradation of various pesticides (s-triazine herbicides, phenylurea pesticides, organochlorine pesticides, etc.) found in wastewater [8–13]. These catalysis systems are characterized by the generation of very reactive and oxidizing free radicals in aqueous solutions, such as the hydroxyl radicals, one of the most powerful oxidants known (oxidation potential 2.8 V).

Heterogeneous photocatalysis is based on the irradiation of semiconductor (SC) particles, usually suspended in aqueous solutions, with wavelengths energy $h\nu \geq E_g$ (band gap energy), an electron e^- is propelled in the conduction band (cb), remaining a positive hole h^+ in the valence band (vb); both the electron and the hole migrate towards the particle surface (Fig. 1). The e_{cb}^- and

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the h_{vb}^+ can recombine on the surface or in the bulk of the particle in a few nanoseconds (and the energy dissipated as heat) or can be trapped in surface states where they can react with donor (D) or acceptor (A) species adsorbed or close to the surface of the particle according to the following reactions [6]:



The photocatalytic degradation of pesticides is largely dependent on the solution pH, pollutant type and concentration, UV light intensity, catalyst loading, ionic composition of wastewater, and oxidant concentration [8].

The present study describes the photocatalytic degradation of eight miscellaneous pesticides (ethoprophos, isoxaben, metalaxyl, metribuzin, pencycuron, pendimethalin, propanil and tolclofos-methyl) using aqueous suspensions of different semiconductors (ZnO, TiO₂, SnO₂, WO₃, and ZnS) in order to know the effectiveness on disappearance of these pollutants in drinking water under natural sunlight.

2. Experimental

2.1. Pesticides and reagents

Analytical standards were purchased from Dr. Ehrenstorfer (Augsburg, Germany): Ethoprophos (93% purity), isoxaben (96% purity), metalaxyl (99.5% purity), metribuzin (99% purity), pencycuron (99.5% purity), pendimethalin (98.5% purity), propanil (99.5%

purity) and tolclofos-methyl (99.5% purity). The main physical-chemical properties of the active ingredients are shown in Table 1. The molecular structures of the pesticides selected for this study are illustrated in Fig. 2. Experimental values of octanol/water partition coefficient (K_{OW}), soil/organic partition coefficient (K_{OC}), aqueous solubility (S_w), aqueous hydrolysis, and GUS (Groundwater Ubiquity Score) index were taken from The Pesticide Properties DataBase [14]. Zinc oxide (99.99%, powder < 70 μ m), and tungsten (VI) oxide (99.8%, powder < 20 μ m) were purchased from Alfa Aesar (Karlsruhe, Germany). Titanium dioxide P25 Degussa (99.5%, <21 nm) was supplied from Nippon Aerosil Co. Ltd. (Osaka, Japon). Tin (IV) oxide (99.9%, powder < 44 micron) and zinc sulphide (99.99%, powder < 10 micron) were supplied from Sigma-Aldrich Química S.A. (Madrid, Spain). Sodium peroxydisulfate (98%) was purchased from Panreac Química (Barcelona, Spain). Acetonitrile was supplied by Scharlau (Barcelona, Spain). Deionized water (18 M Ω cm resistivity) was obtained from a Milli-Q ultrapure water purification system (Millipore, Bedford, MA, USA).

2.2. Preparation of solutions

For identification and quantification of analytes in water samples, stocks solutions (1000 μ g mL⁻¹) of each pesticide standard were prepared in acetonitrile, protected from light and stored at 5 °C. A pesticide intermediate standard solution was prepared by dilution in the same solvent to obtain a concentration of 10 μ g mL⁻¹. Several standard solutions, with concentrations of 2–200 μ g L⁻¹, were injected to obtain the linearity of detector response and the detection limits of the pesticides studied. The correlation coefficient was found to be >0.99 and the limits of detection (LOD, obtained at signal-to-signal noise ratio 3) ranged from 0.05 to 3 μ g L⁻¹.

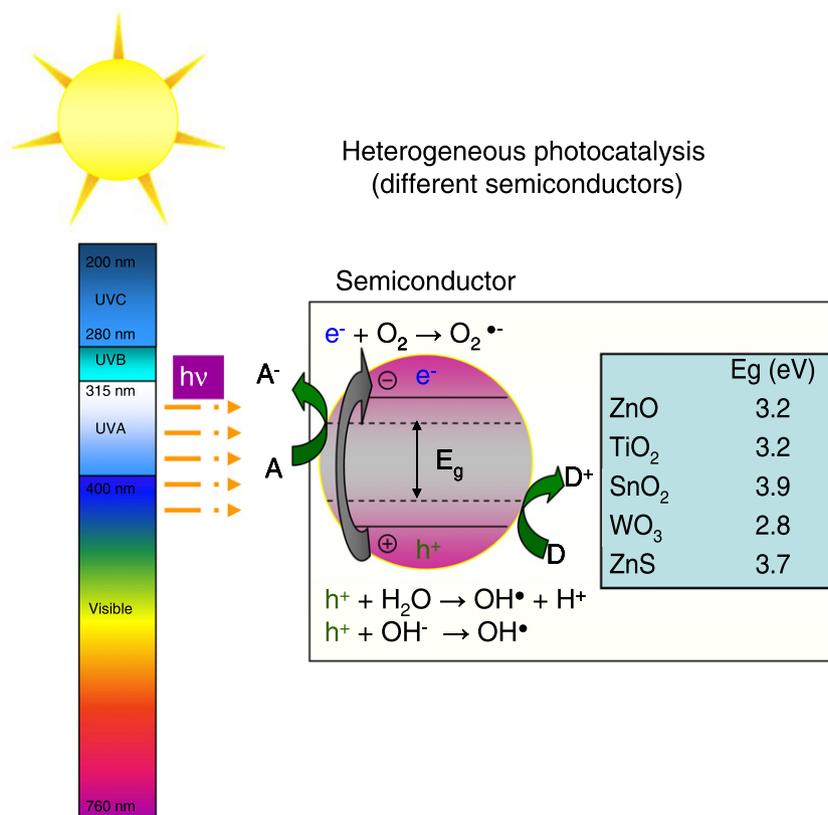


Fig. 1. Scheme for the heterogeneous photocatalysis.

Table 1
Physical–chemical characteristics of the pesticides used in this study.

Commercial names	Active ingredient	Molecular weight	Log K_{ow}	S_w^a	Aqueous hydrolysis ^b	Log K_{oc}	GUS index ^c
MOCAP 10% GR (Bayer)	Ethoprophos	242.3	3.0	1300	Stable	2.0	2.4 (M)
ROKENYL 50 50% w/v (Dow AgroSciences)	Isoxaben	332.4	3.9	0.9	Stable	2.5	2.9 (H)
RIDOMIL 46.5% w/v SC (Syngenta)	Metalaxyl	279.3	1.6	7100	106	2.7	2.1 (M)
SENCOR 70% WG (Bayer)	Metribuzin	214.3	1.6	1165	Stable	1.6	2.6 (M)
TROTIS 25 25% w/v SC (Bayer)	Pencycuron	328.8	4.7	0.3	156	3.7	0.6 (L)
STOMP LE 33% w/v EC (BASF)	Pendimethalin	281.3	5.2	0.3	Stable	4.2	−0.4 (L)
STAM NOVEL FLO 48% w/v SC (Kenogard)	Propanil	218.1	2.3	95	365	2.7	−0.5 (L)
RIZOLEX 50% WP (Kenogard)	Tolclofos-methyl	301.1	4.6	0.7	97	3.6	0.3 (L)

^a Water solubility (mg L^{-1}).

^b DT_{50} (days) at 20 °C and pH = 7.

^c Groundwater Ubiquity Score (GUS) Index. Leachability in parentheses: (L, Low; M, Medium; H, High).

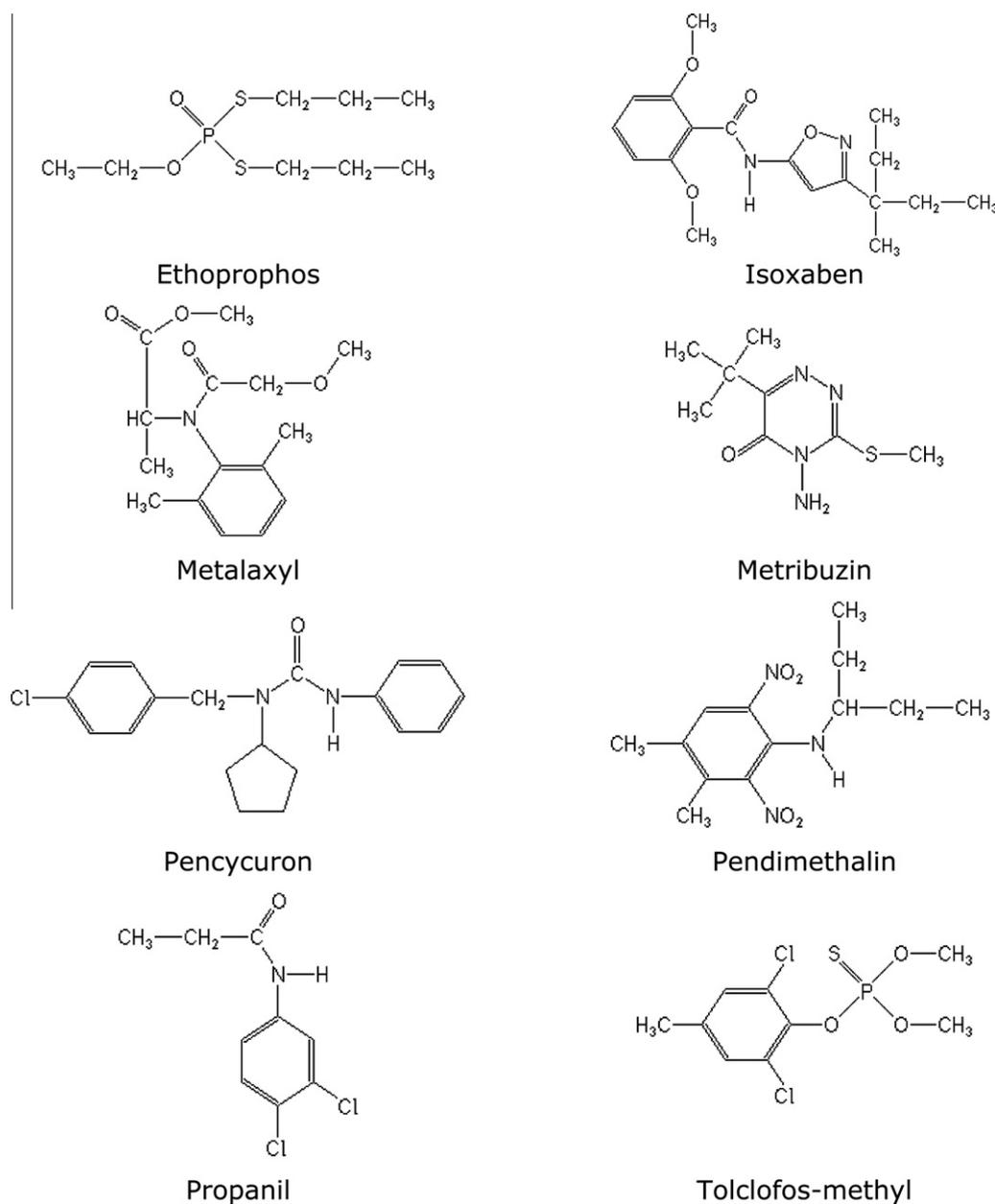


Fig. 2. Molecular structures of the studied pesticides.

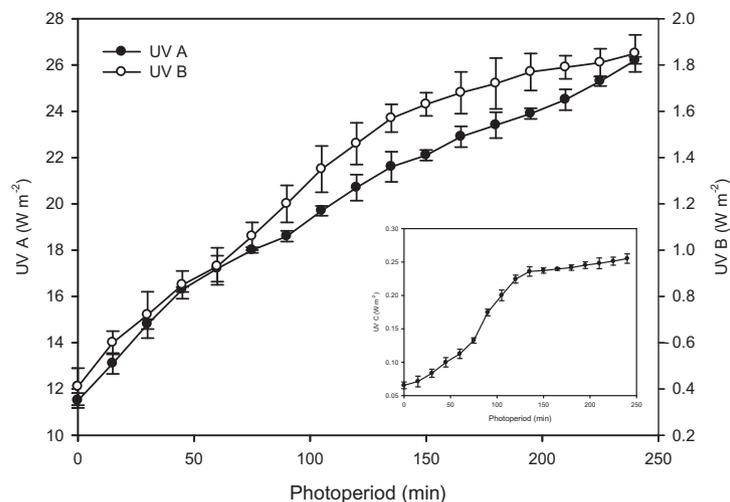


Fig. 3. Mean values ($n = 15$) for UV-A and UV-B radiation recorded in the different sample points of the photoperiod. Insert graphic shows UV-C radiation. Error bars denote standard deviation.

2.3. Solar photocatalysis experiment

2.3.1. Solar photocatalytic plant

The experiment was carried out in a pilot plant in Murcia, SE Spain (latitude $37^{\circ}59'N$, longitude $1^{\circ}08'W$) using natural sunlight irradiation during July, 2011. The values (mean \pm SD) of visible plus near-infrared (400–1100 nm), UVA (315–400 nm), UVB (280–315 nm) and UVC (200–280 nm) radiation were taken with a portable photoradiometer Delta Ohm HD 2102.2 (Caseelle di Selvazzano, Italy). The mean values of VIS + NIR, UVA, UVB and UVC at 13 h were 950.2 ± 30.6 , 23.6 ± 2.1 , 1.6 ± 0.2 and 0.2 ± 0.1 (all in $W m^{-2}$), respectively while $102,645 \pm 5,022$ lx were recorded. Fig. 3 shows the mean values recorded for UV radiation during the sampling.

The solar pilot plant used in this experiment is based on compound parabolic collector (CPC) technology (Fig. 4). This small prototype consists of one photoreactor module ($1.27 m^2$) with five borosilicate tubes (200 cm length \times 4 cm i.d.) mounted on curved polished aluminium reflectors (0.9 cm radius of curvature) running in east–west line. The water flows directly from tube one to another connected in series and finally to the reservoir tank (250 L) and a centrifugal pump (0.55 kw) before returning ($45 L min^{-1}$) to the collector tubes in a closed circuit. The reaction system was continuously stirred to achieve a uniform suspension and thermostated by circulating water to keep the temperature at $25 \pm 2^{\circ}C$. The illuminated volume was 12.55 L and the dead volume in the PVC tubes about 6.5 L. Storage tank, flowmeter, sensors (pH, O_2 and T), pipes, and fittings completed the installation.

2.3.2. Photocatalysis design

At the beginning of the photocatalytic assay, the commercial products (Table 1) were added all together to 150 L of drinking water (pH = 8.26 ± 0.07 , EC = 1.04 ± 0.11 dS m^{-1} , TOC = 1.63 ± 0.15 mg L^{-1} ; Ca^{2+} = 109.0 ± 3.4 mg L^{-1} , Mg^{2+} = 50.6 ± 1.5 mg L^{-1} , Na^{+} = 51.4 ± 1.3 mg L^{-1} , K^{+} = 2.90 ± 0.11 mg L^{-1} , Mn^{2+} = 0.03 ± 0.00 mg L^{-1} , SO_4^{2-} = 251.0 ± 5.9 mg L^{-1} , Cl^{-} = 81.4 ± 4.2 mg L^{-1} , HCO_3^{-} = 184.3 ± 7.1 mg L^{-1} , NO_3^{-} = 1.72 ± 0.21 mg L^{-1} and NO_2^{-} below the detection limit) to reach a spiking level of about 0.1 mg L^{-1} of each. The respective mixtures were homogenized by shaking for 20 min to constant concentration in the dark with collectors covered by a black awning.

In all cases, the photocatalysts (ZnO, TiO_2 , SnO_2 , WO_3 , and ZnS) and electron acceptor reactant ($Na_2S_2O_8$), were added at 200 and 150 mg L^{-1} , respectively, and the cover was removed after

15 min. Several samples (0, 10, 20, 40, 60, 120, and 240 min) were taken during the photoperiod (4 h), from 10 to 14 h. One practical problem in using photosensitizers is e^{-}/h^{+} recombination, which can be avoided in the presence of a suitable electron acceptor. For this purpose, air was periodically injected into the tank to maintain the O_2 concentration around 8–10 mg L^{-1} . In heterogeneous photocatalysis, the principal role of dissolved oxygen in the photodegradation process is to act as an electron sink. A parallel blank assay, without semiconductor and $Na_2S_2O_8$ (photolysis experiment), was carried out. In all cases, assays were replicated three times.

2.4. Analytical determinations

Water samples were extracted and analyzed according to the procedure described by Fenoll et al. [15]. The separation, identification and quantification of the selected pesticides were carried out using an HPLC system (consisting of vacuum degasser, autosampler and a binary pump) (Agilent Series 1100, Agilent Technologies, Santa Clara, CA, USA) equipped with a reversed phase C8 analytical column of 150 mm \times 4.6 mm and 5 μm particle size (Zorbax Eclipse XDB-C8) and an G6410A triple quadrupole mass spectrometer from Agilent equipped with an ESI interface operating in positive ion mode. The mobile phases A and B were acetonitrile and 0.1% formic acid, respectively. The gradient program started with 10% A, constant for 5 min, followed by a linear gradient to 100% A after 35 min. After this 35 min run time, 10 min of post-run time followed using initial 10% of A.

Blank samples were used to establish the limit of detection (LOD) and the limit of quantification (LOQ). Both, LODs and LOQs were calculated from the signal-to-noise (S/N) ratio 3 and 10, respectively. The repeatability study was carried out with 25 and 100 $\mu g L^{-1}$ matrix-matched standard calibration points, injected five times, to evaluate the intra-day (within 1 day) and inter-day (between days) precision. For determining inter-day precision, samples were stored at $-20^{\circ}C$. Intra-day and inter-day relative standard deviations (RSDs) were below 8% and 10%. In order to evaluate the accuracy of the method, the recoveries were determined by the standard addition technique. The average recovery by the LC–MS–MS method obtained for these compounds varied from 87.6% to 105.2% with a relative standard deviation between 3.5% and 5.9%. The calibration samples were analyzed by spiking pesticides at 2–200 $\mu g L^{-1}$ levels into water samples in five replicates. Additives in the commercial

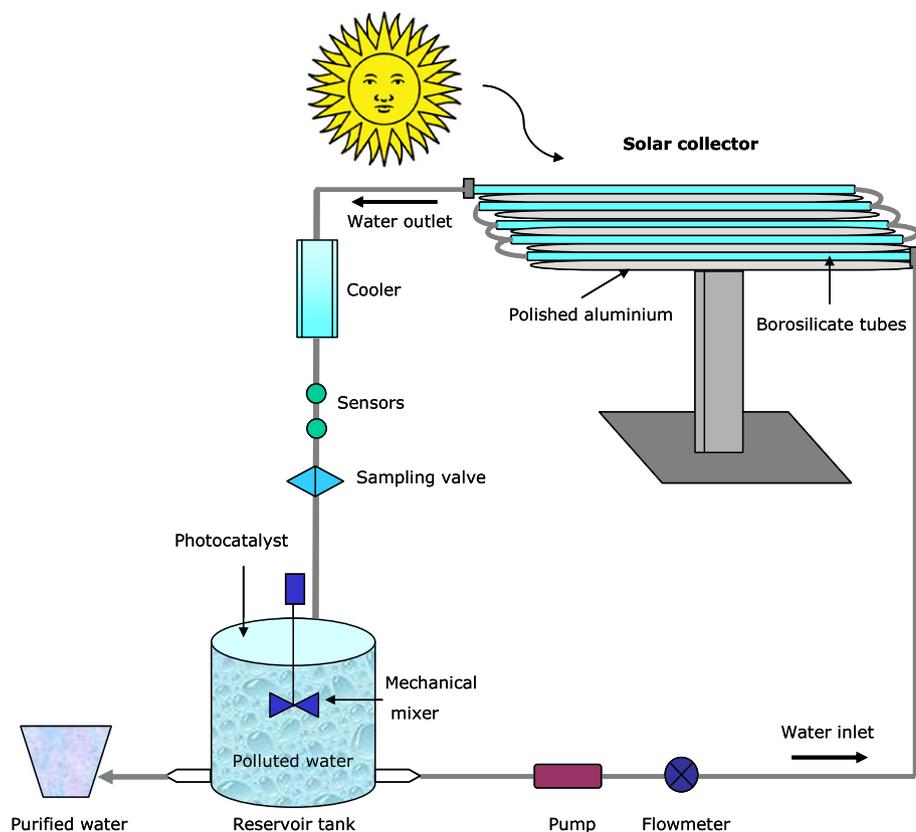


Fig. 4. Scheme of the pilot plant used for the photocatalytic experiments.

pesticide product do not affect the analytical performance of the analytical method.

3. Results and discussion

3.1. Direct photolysis

After addition of pesticides, their initial concentration in water ranged from 65 to 115 $\mu\text{g L}^{-1}$. Fig. 5 shows the disappearance of ethoprophos, isoxaben, metalaxyl, metribuzin, penicuron, pendimethalin, propanil, tolclofos.methyl in drinking water using semiconductor materials (photocatalysis), or not (photolysis), during the studied photoperiod (240 min). Irradiation of water in the absence of the photocatalyst showed very low efficiencies as compared to the reactions in the presence of semiconductors (especially ZnO and TiO_2). The final pesticide carryover in photolysis experiment ranged from 51% to 98% for metribuzin and propanil, respectively. The small decay in pesticide concentration could be due to direct photolysis since the pesticide spectra show a weak absorption in the 280–320 nm range (Fig. 6) which overlaps the emission spectrum of sunlight, particularly metribuzin. Also, the presence of dissolved organic matter (DOM) may act as influential factors in herbicide dissipation although the photocatalytic effect of DOM is contradictory in the literature [16,17]. Moreover, ions such Ca^{2+} and Mg^{2+} [18], which were present at high concentration in the used water, and other such Mn^{2+} , Cu^{2+} [13], nitrite and nitrate [19–22] can also enhance photodegradation.

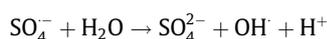
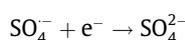
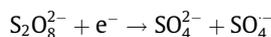
3.2. Effect of photocatalyst loading, $\text{Na}_2\text{S}_2\text{O}_8$ concentration and pH

Screening experiments were performed to assess the catalytic activity of ZnO and TiO_2 . The variables studied for optimization

of photocatalytic heterogeneous process were catalyst loading, $\text{Na}_2\text{S}_2\text{O}_8$ concentration and initial pH of the aqueous suspension.

The effect of the photocatalyst loading on the disappearance kinetics of the studied pesticides has been investigated using different concentrations of catalyst (ZnO and TiO_2) varying from 50 to 250 mg L^{-1} . The reaction rate is directly proportional to the mass of catalyst. However, above a certain value the reaction rate levels off and becomes independent of the concentration the catalyst. The limit depends on the geometry and the working conditions of the photoreactor [11]. This plateau fits with to the maximum amount of catalyst in which all the particles are totally illuminated, after this limit a screening effect excess particles occurs. In our study, it can be observed from Fig. 7A, that the optimum value for ZnO was about 200 mg L^{-1} . At this concentration, more than 93% of the studied pesticides were decomposed. Above this concentration, the suspended catalyst particles may block the passage of light and increase light scattering. Similar results were observed for TiO_2 .

The addition of an electron acceptors, such as inorganic peroxides ($\text{S}_2\text{O}_8^{2-}$), to a semiconductor suspension usually enhances the photodegradation rate of organic pollutants [8], because these substances capture the photogenerated electrons more efficiently than dissolved oxygen, leading to a reduction in the electron-hole recombination generating $\text{SO}_4^{\cdot-}$ radicals, which are also a very strong oxidizing species ($E^0 = 2.6 \text{ V}$). The reactions where $\text{Na}_2\text{S}_2\text{O}_8$ is involved and responsible for its efficiency are the following:



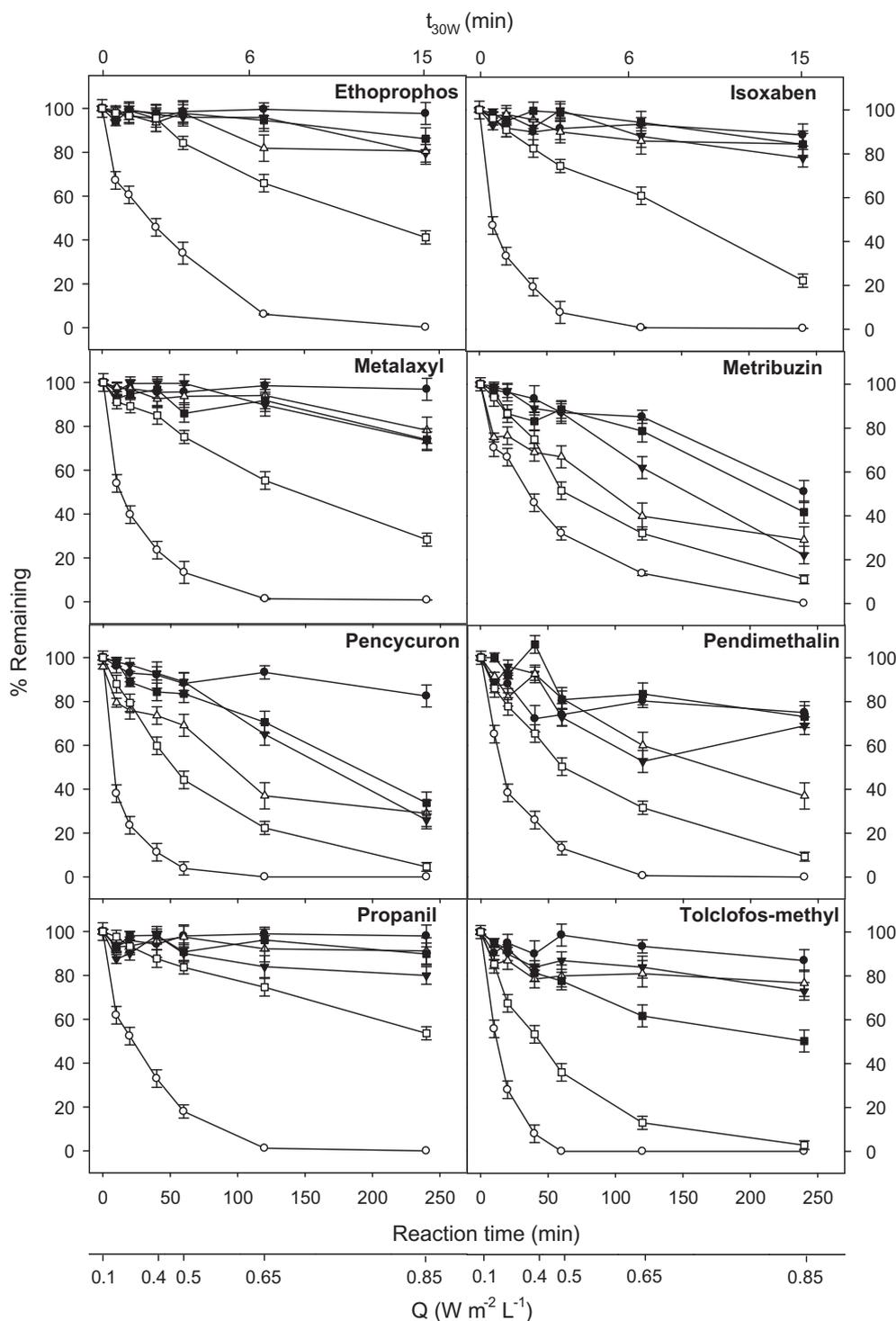
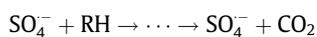


Fig. 5. Percentage remaining of the pesticides by photolysis (●), and heterogeneous photocatalysis with ZnO (○), TiO₂ (□), SnO₂ (▲) WO₃, (Δ), and ZnS (■) during the photoperiod. (Q, accumulated UV energy incident on the reactor per liter of water).



In this study, the effect of adding electron acceptor reactant on the disappearance kinetics of the studied pesticides has been evaluated using different concentrations of peroxydisulfate (from 50 to 200 mg L⁻¹). Increased concentration of peroxydisulfate in tandem with a fixed concentration of ZnO led to an increase on the reaction rate for these pesticides until it reached a plateau (Fig. 7B). The optimum value for peroxydisulfate was 150 mg L⁻¹. Similar results were observed for TiO₂.

The pH of the solution appears to play an important role in the photocatalytic degradation of various pollutants. The effect of pH on the photocatalytic reaction is generally attributed to the surface charge of semiconductor, the size of the aggregates it forms and the position of the conductance and valence bands [11]. The influence of the initial pH value on the photodegradation rate of these compounds was studied for ZnO and TiO₂. No significant differences were observed in the reaction rate when the pH was increases from 6 to 9 which it has the advantage of not being necessary to adjust the pH of the water. The surface charge of the photocatalyst and the

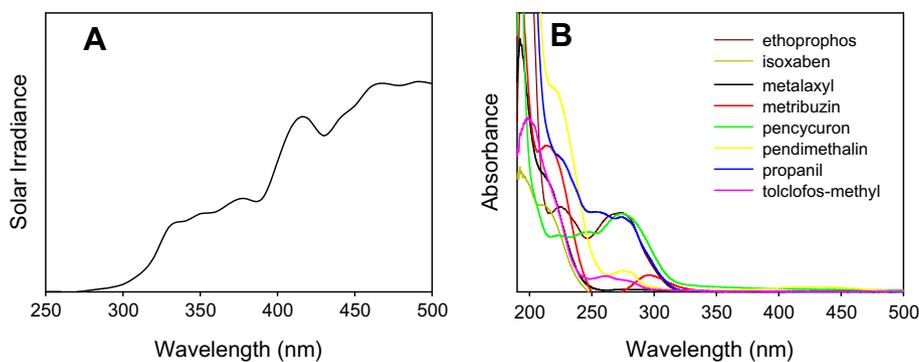


Fig. 6. Available solar spectrum for photochemical processes (plot A) and absorption spectra of the studied pesticides (plot B, [pesticide = 10 mg L⁻¹]).

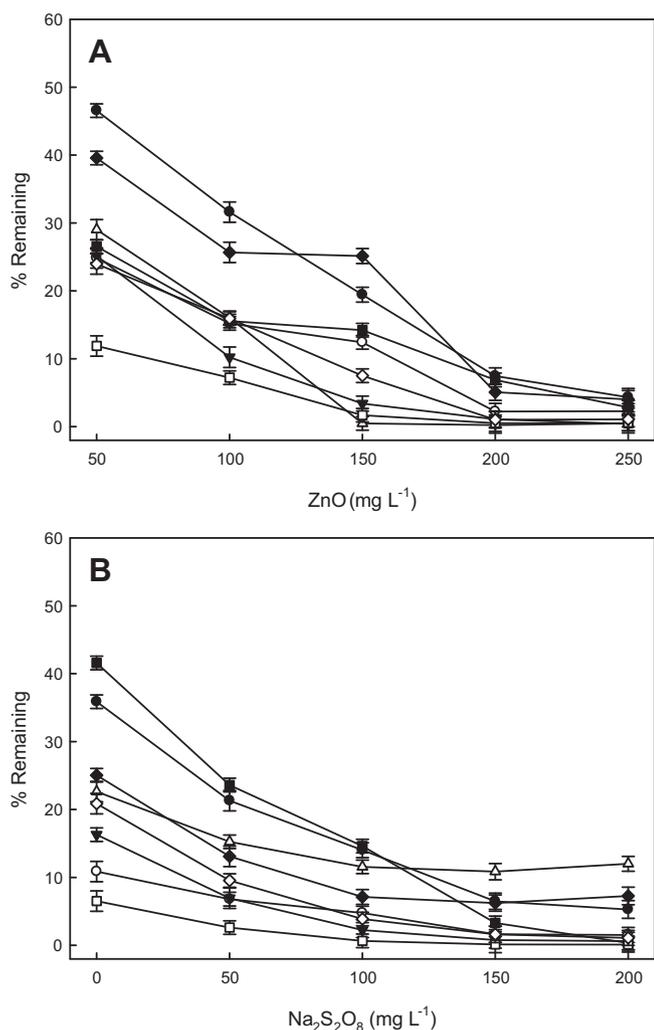


Fig. 7. Photodegradation of the pesticides as function of initial concentrations of ZnO (plot A, fixed [Na₂S₂O₈ = 100 mg L⁻¹]) and Na₂S₂O₈ (plot B, fixed [ZnO = 150 mg L⁻¹]). *t* = 100 min, pH₀ = 8.2. (●) Ethoprophos, (○) Isoxaben, (▼) Metalaxyl, (■) Metribuzin, (□) Pencycuron, (◆) Pendimethalin, (◇) Propanil and (Δ) Talclofos-methyl.

ionization of the pesticides can be profoundly affected by the solution pH. The point of zero charge (pzc) of TiO₂ and ZnO is about 6.2 and 9.0, respectively. Therefore, the TiO₂ and ZnO surface is predominantly positively charged below those pHs and negatively charged above those values. Electrostatic attraction or repulsion between pesticide and catalysts take place and consequently, the pesticide photodegradation rate can be enhanced or inhibited. The ionization

state of the surface of photocatalyst can also be protonated and deprotonated depending of the pH as occurs for pesticides. In the case of TiO₂, the abundance of all the species as a function of pH are TiOH ≥ 80% when 3 < pH < 10; TiO⁻ ≥ 20% if pH > 10 and TiOH₂⁺ ≥ 20% when pH < 3 [23].

3.3. Heterogeneous photocatalytic experiments

In the recent years, semiconductor-induced photocatalysis, especially titanium dioxide (TiO₂), has received intensive attention as an environmental remediation technology for the treatment of polluted water combining the low cost, the mild conditions and the possibility of using sunlight as the source of irradiation [11,24,25]. However, the effect of other semiconductors like zinc oxide (ZnO), tungsten (VI) oxide (WO₃), tin (IV) oxide (SnO₂) and zinc sulphide (ZnS) is less known than titanium oxide (TiO₂). Fig. 5 shows concentration–time profiles during photocatalytic oxidation of the pesticides studied at 100 μg L⁻¹ as initial concentration with addition of 200 mg L⁻¹ of catalyst and 150 mg L⁻¹ of Na₂S₂O₈. ZnO appeared to be more effective for the oxidation all pesticides than TiO₂, WO₃, SnO₂ and ZnS, the first showing more than 99% of the pesticide initially present in the drinking water being degraded after 4 h of illumination. Thus, after 4 h of irradiation almost 20% of the total organic carbon (TOC) is still present. It should be due to the formation of transient organic intermediates more persistent than the initial substrate produced under our experimental conditions and/or other organic compounds present in the commercial herbicide samples. The presence of additives in commercial products could decrease the rate of degradation of these herbicides. ZnO is a very interesting wide band gap semiconductor material because of its direct band gap and large excitation binding energy. The band gap of this semiconductor is ca. 3.2 eV, which corresponds to a radiation wavelength of around 390 nm. The efficiency of this catalyst for the photodecomposition of different classes of pesticide has been demonstrated [26]. The lower activity observed for WO₃ than for ZnO could be related to the lower energy of conduction band, whereas the lower activity observed for SnO₂ and ZnS can be attributed to the significantly shorter wavelength necessary to activate the catalyst (318 and 336 nm for SnO₂ and ZnS, respectively). The observed differences for ZnO and TiO₂ are certainly related to the structure, diameter of particles and electrical properties of the photocatalyst [27]. Thus, its non-stoichiometry leads to electron mobility of at least two orders of magnitude higher than TiO₂. This results in a quicker charge transfer with the various species in the solution and consequently to lower recombination rates in comparison to TiO₂ [28,29].

3.4. Interfering substances

Some water components like calcium, magnesium, iron, zinc, copper, bicarbonate, phosphate, nitrate, sulfate, chloride and

dissolved organic matter can affect the photocatalytic degradation rate of organic pollutants since they can be adsorbed onto the surface of the catalyst [8]. Fig. 8 depicts the evolution of electrical conductivity (EC), chloride, nitrate and sulfate during the experiment carried out with ZnO/Na₂S₂O₈. As can be seen in this figure, EC increases along the experiment due the evolution of some inorganic ions, mainly sulfate. A weak increase in the concentrations of chloride (81.3–85 mg L⁻¹) and nitrate (1.7–2.5 mg L⁻¹) was observed after 240 min of illumination while sulfate strongly increases its concentration from 251.6 to 381.3 mg L⁻¹. Mahmoodi et al. [30] observed an inhibitive effect of those anions in the order SO₄²⁻ < NO₃⁻ < Cl⁻ during the photolytic degradation of diazinon and imidacloprid attributing the detrimental effect to their competition for the active sites on the TiO₂ surface and catalyst deactivation which subsequently, decreased the reaction rate.

Although ·OH scavenging by some inorganic anions results in corresponding anion radicals, they have lower oxidation potential. In our case, the oxidation–reduction potential (ORP) measures recorded showed a weak increase from 270 mV (initial sampling) to 299 mV at the end of the experiment in the ZnO/Na₂S₂O₈ system which indicates that the oxidizing strength of the solution was maintained during the experiment.

On the other hand, the toxicity in the illuminated ZnO system can be magnified by the increase of Zn²⁺ in the solution as consequence of the photogenerated holes (ZnO + 2h⁺ → Zn²⁺ + ½O₂). The measurements made of Zn²⁺ by inductively coupled plasma (ICP) during the illumination time confirm the dissolution and photodissolution of ZnO, especially during the first 30 min. The initial [Zn²⁺] was 0.51 mg L⁻¹ at the beginning of the assay reaching 23 mg L⁻¹ after 240 min of irradiation. However, the concentration of Zn²⁺ in water after pH adjustment to about 9.5 to form the precipitate was below 0.1 mg L⁻¹. Metal removal is not complete until the metal solid is physically removed from the water, by subsequent sedimentation and filtration.

3.5. Kinetics

Langmuir–Hinshelwood (L–H) kinetics is the most commonly used model to explain the kinetics of the heterogeneous photocatalytic process. The usual kinetic expression is described by following equation:

$$r = -dC/dt = k_{LH}K_L C / (1 + K_L C) \quad (1)$$

in which r is the rate of reaction, C the concentration of the target compound, k_{LH} the apparent L–H rate constant for the reaction and K_L ($K_{ads/des}$) is the photon-flux-independent Langmuir equilibrium adsorption/desorption constant.

The L–H model assumes a fast adsorption/desorption equilibrium step and a subsequent slow surface step. However, Ollis [31] showed that for at least some photocatalyzed reactions, adsorption/desorption reaction equilibrium are not established during reaction, because the substantial reactivity of an adsorbed active species like hole (h⁺), radical (·OH), etc., causes a continued displacement from equilibrium of the adsorbed reactant concentration. Therefore, as the L–H model is based on the degree of pollutant adsorption on the photocatalytic surface, it is not able in some cases to explain the degradation when the contaminant is not adsorbed on the surface of catalyst [32]. Moreover, some authors [33,34] have described the influence of the photon flux (Φ) on both the k_{LH} and K_L . Emeline et al. [33] and Ollis [31] both proposed to use a pseudo-steady-state analysis to explain the intensity dependence of the L–H kinetic parameter and the apparent adsorption parameter based on the surface coverage of reactant, θ_R , and ·OH concentration, respectively. Also, Brosillon et al. [34] assumed the pseudo-steady-state for the concentration of ·OH either with L–H model under certain conditions and Eley–Rideal model to explain the dependence of the apparent kinetic parameters with the light intensity.

Despite the unmodified L–H model may not be used to explain surface process bearing in main the above findings, the LH kinetic model will no doubt continue to be used by many researchers because of its simplicity in fitting the experimental results while waiting for finding a useful tool for describing the active species involved in oxidation [11,35].

In view of these, most of researchers approximated Eq. (1) to first order kinetics for the condition $k_{LH}C \ll 1$. Thus, the photocatalytic degradation rate of organic compounds, including pesticides, is commonly described by a pseudo-first order kinetic expression, which is rationalized in terms of the Langmuir–Hinshelwood (L–H) model:

$$-dC/dt = k_{ap}C_p$$

where C is the concentration of the pesticide and k_{ap} (in units of time⁻¹) is the apparent first-order rate constant and, by integration, we obtain:

$$C = C_0 e^{-k_{ap}t} \text{ or } \ln C_0 - k_{ap}t$$

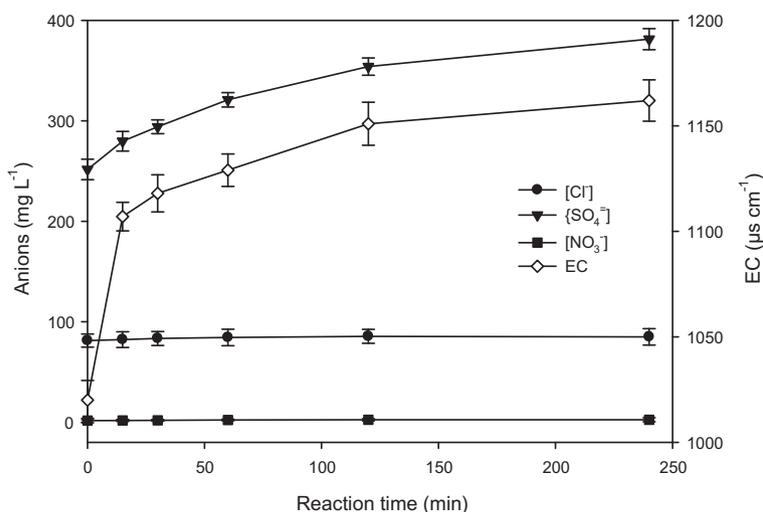


Fig. 8. Evolution of Electric Conductivity and anions concentration during the experiment with ZnO/Na₂S₂O₈.

Table 2
Kinetic parameters for photocatalysis (ZnO and TiO₂) of the pesticides in drinking water under natural sunlight.

Pesticides	ZnO					TiO ₂				
	$C_t = C_0 e^{-kt}$	R^2	$S_{y/x}^a$	$t_{1/2}$ (min)	t_{90} (min) ^b	$C_t = C_0 e^{-kt}$ or $C_t = C_0 - kt$	R^2	$S_{y/x}^a$	$t_{1/2}$ (min)	t_{90} (min) ^b
Ethoprophos	$C_t = 93.1e^{-0.019t}$	0.987	6.10	35.7	118.7	$C_t = 101.0 - 0.256t$	0.984	3.08	197.1	354.7
Isoxaben	$C_t = 96.2e^{-0.054t}$	0.988	5.90	12.9	42.7	$C_t = 97.4 - 0.316t$	0.992	2.61	154.1	277.4
Metalaxyl	$C_t = 95.1e^{-0.042t}$	0.989	5.75	16.6	55.1	$C_t = 95.2 - 0.291t$	0.982	3.65	163.5	294.2
Metribuzin	$C_t = 94.7e^{-0.018t}$	0.993	4.53	38.1	126.5	$C_t = 102.7e^{-0.010t}$	0.989	3.87	71.4	237.4
Pencycuron	$C_t = 98.2e^{-0.080t}$	0.992	4.83	8.7	28.9	$C_t = 100.5e^{-0.013t}$	0.999	1.33	53.3	177.1
Pendimethalin	$C_t = 97.8e^{-0.039t}$	0.994	4.26	17.8	59.1	$C_t = 97.5e^{-0.010t}$	0.995	2.41	68.6	228.0
Propanil	$C_t = 95.1e^{-0.030t}$	0.992	4.96	23.3	77.3	$C_t = 97.5 - 0.188t$	0.985	2.19	259.8	467.6
Tolclofos-methyl	$C_t = 100.6e^{-0.062t}$	0.999	1.45	11.1	37.0	$C_t = 99.5e^{-0.017t}$	0.997	2.12	41.3	137.1

^a Standard deviation of the fitting (standard error of estimate).

^b Time required for 90% of the initial pesticide concentration to disappear.

Table 3
Economic assessment for water treatment by heterogeneous photocatalysis (ZnO and TiO₂).

	ZnO	TiO ₂
I. Collector costs (€/year) ^a	2969.42	2969.42
II. Engineering costs (€/year)	200.00	200.00
III. Operation and maintenance costs (€/year)	2.5% I + II	79.24
IV. Consumable costs (€/year)	Unit price	79.24
Na ₂ S ₂ O ₈ (€/kg)	3.00 €	91.18
ZnO (€/kg)	30.00 €	1367.70
TiO ₂ (€/kg)	7.00 €	410.3
	Total reagent	1458.88
V. Service costs (€/year)	Unit price	
Water (€/L)	0.001	26.40
Electricity (€/kW h ⁻¹)	0.16	397.12
	Total service	423.52
	Total I + II + III + IV + V	5131.06
VI. Overheads (€/year)	10% I + II + III + IV + V	408.24
	Total I + II + III + IV + V + VI	5644.16
	t_{90}	126.54
	TC (m ³ /year)	207.68
Treatment cost (€/m ³)		27.18
		157.40

^a The collector cost was calculated on the basis of a 10 years period.

The half-life time ($t_{1/2}$) is the time needed for the concentration of pesticide to drop to one-half the original value. Unlike the half-life, the disappearance time does not assume a specific degradation model (e.g., first-order degradation).

To facilitate comparison with other photocatalytic experiments, the “normalized illumination time” (t_{30W}) was calculated according to the following equation:

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

$$\Delta t_n = t_n - t_{n-1}$$

where t_n is the exposition time for each sample (min), UV the average solar ultraviolet radiation (W m⁻²) measured during Δt (min), V_i the total irradiated volume (l), and V_T is the total volume (l) of the reactor (illuminated and unilluminated). In this expression, which has been used by several authors working on this topic [11], 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 knowledge of kinetics is required to assess the efficiency of systems used for the photooxidation of pesticides. The photocatalysis kinetic parameters of pesticides are shown in Table 2, where the apparent rate constants and half-lives are listed. In the case of ZnO for all pesticides and in the case of TiO₂ for metribuzin, pencycuron, pendimethalin and tolclofos-methyl, the kinetics of dissipation followed an apparent first-order degradation curve with R^2 ranging from 0.987 to 0.999 and a standard error of estimate lower than 6.1 in the most unfavorable case. However, the kinetics of dissipation of ethoprophos, isoxaben, metalaxyl and propanil using

TiO₂ as catalyst followed a zeroth-order reaction with a rate independent of the concentration of the reactant. This behavior is typically found when the surface of the catalyst is saturated by the reactants.

The half-lives in the presence of ZnO ranged from 9 to 38 min (t_{30W} 0.3–1.7 min) for pencycuron and metribuzin, while in the presence of TiO₂, the calculated values ranged from 41 to 260 (t_{30W} 1.9–16.3 min) for tolclofos-methyl and propanil, respectively. The found photocatalytic activity order (ZnO > TiO₂) agreed with the previously described for other pesticides [36,37]. However, contradictory results have been reported when comparing the effect of both catalysts on the degradation of other pollutants [38–41].

HO· is indiscriminate in its reactivity and a multitude of by-products can be expected in most cases. The reactions of HO· with organic compounds, like the studied pesticides, lead to the formation of carbon-centered radicals [42]. The hydroxyl radical react in well-known ways with pesticides, principally by abstracting H from C–H, N–H, or O–H bonds, adding to C=C bonds, or adding to aromatic rings [43]. The organic intermediates formed in the first stage of the oxidation may react further with HO· and oxygen, with the overall process leading eventually to mineralization to CO₂, and H₂O. Evolution of CO₂ is slower than disappearance of the initial compound and ordinarily decreases in rate with time as products become less and less reactive with HO·. Also, when the organic substrate contains heteroatoms, mineralization often leads to the formation of inorganic acids. All the pesticides used in this study, except ethoprophos and tolclofos methyl are nitrogen-containing compounds and they could form HNO₃ and NH₄⁺ as phenylurea

herbicides [44]. In addition, ethoprophos, metribuzin and tolclorofos methyl are sulfur pesticides and they could form sulphuric acid as sulfur aromatic compounds [45].

3.6. Cost estimate for water treatment

A comparison of the treatment cost of the heterogeneous photocatalysis with ZnO with regard to the cost of the heterogeneous photocatalysis with TiO₂ under the same experimental conditions is showed in Table 3. Bearing in mind that the SE of Spain receives about 3000 h of sunlight per year and that the average of useful minutes of the pilot plant (UM) is 480 min/day, the treatment capacity (TC) of our system was calculated according to the following equation:

$$TC(\text{L/year}) = (UM \times V \times 365) / (t_{90})$$

where V is the volume of drinking water treated and t_{90} was calculated according to the following equation:

$$t_{90} = \ln 10 / k = 2.303 / k$$

where k is the rate constant. In our case, the selected t_{90} was the t_{90} of the pesticide with lower value of k .

The treatment cost was estimated to be 27.18 €/m³ for the ZnO/Na₂S₂O₈ system and 157.40 €/m³ for the TiO₂/Na₂S₂O₈ system. The significant differences found in cost between both treatments are attributed to the high reaction rate ($t_{90} < 130$) observed for the studied compounds by ZnO/Na₂S₂O₈ system. From these results, it appears that, although the cost of treatment with TiO₂/Na₂S₂O₈ system is more expensive than the ZnO/Na₂S₂O₈ system, it is still far below the cost for other physico-chemical treatment process.

4. Conclusions

The photocatalytic oxidation of eight pesticides under natural sunlight by heterogeneous photocatalysis with different semiconductors (ZnO, TiO₂, WO₃, SnO₂ and ZnS) has been studied. ZnO proved to be more efficient photocatalyst since the oxidation of the pesticides proceeded at higher reaction rates. The primary degradation of the pesticides using ZnO followed a pseudo-first order kinetics according to the Langmuir–Hinshelwood model and parameters such as catalyst and oxidant concentrations played an important role affecting the reaction rate. The amount of time required for 90% of its initial pesticide concentration to be dissipated ranged from 29 to 126 min ($t_{30\text{W}}$ 1.1–5.8 min) for pencycuron and metribuzin, respectively, in the ZnO/Na₂S₂O₈ system. Finally, the total investment and water treatment cost for decontamination of these pesticides was carefully estimated, showing that ZnO/Na₂S₂O₈ system in combination with a renewable source of energy like sunlight can be used advantageously.

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