Photocatalytic degradation of propanil and molinate over TiO$_2$ suspensions

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Abstract The light-induced degradation of propanil and molinate under simulated solar irradiation has been investigated in aqueous solutions containing TiO$_2$ suspensions as photocatalysts. The study focuses on the identification of possible intermediate products and the determination of inorganic ions formed during the process, using several powerful analytical techniques such as gas chromatography mass-spectrometry (GC-MS) and ion chromatography (IC). The primary degradation of propanil and molinate has been a fast process with half-lives varying from 4.3 to 2.9 minutes respectively, and followed pseudo-first-order kinetics according to the Langmuir–Hinshelwood model. The stoichiometric transformation of organic chlorine into chloride ion and organic sulfur to sulfate ions was observed for propanil and molinate respectively, whereas oxidation of nitrogen to nitrate ions took place at delayed irradiation times for both herbicides. The mineralization of the organic carbon to CO$_2$ after 240 min of irradiation was found to be $\geq 95\%$ for both herbicides. Various organic intermediates detected during the treatment have been identified by GC/MS techniques. Based on this by-product identification, a possible multi-step degradation scheme was proposed for each herbicide including hydroxylation, dechlorination, dealkylation and oxidation steps that lead to the mineralization of the starting molecule.
Keywords Molinate; photocatalytic oxidation; photoproduct analysis; propanil; TiO$_2$

Introduction

Among the compounds of environmental concern, anilides and thiocarbamate derivatives constitute important classes of herbicides that are widely used for weed control in agricultural crops. Within these families, propanil (3′,4′-dichloropropioanilide) and molinate (S-ethyl-N-hexamethylene-thiocarbamate) are extensively used in Greece and other European countries and as a result their residues have been detected in various natural waters (Albanis *et al*., 1998; Albanis and Galassi, 1995). Therefore, the investigation of remediation treatments of polluted waters containing trace amounts of pesticides is of environmental interest.

Photocatalytic oxidation is one of the emerging technologies for the elimination of organic micropollutants because of the efficiency in their mineralization. Among the semiconductors used, titanium dioxide (TiO$_2$) is considered a very efficient catalyst which, unlike other semiconductors, is non-toxic, stable to photocorrosion, cheap and suitable for work using sunlight as the energy source (Poulios *et al*., 1998). The last fact is particularly relevant for Mediterranean agricultural areas, where solar irradiation is highly available making this process quite attractive.

The present photocatalytic degradation study of propanil and molinate reveals new transformation products for both herbicides and tries not only to identify these intermediates, but also to incorporate them in an integrated degradation pathway. Moreover a complete description of the photocatalytic degradation of each herbicide is given, by monitoring the mineralization products such as carbon dioxide and inorganic ions. Thus, the objectives of the study were: (i) to determine the main transformation products (TPs) by using GC-MS techniques and to propose a degradation pathway, (ii) to evaluate the kinetics

of disappearance of the tested herbicides, and (iii) to monitor the evolution of CO_2 and of the main inorganic ions produced during the process.

Experimental

Chemicals

Propanil and molinate analytical grade standards (99.5% purity) were purchased from Riedel-de Häen (Germany). Pesticide grade n-hexane, was purchased from Labscan Ltd (Dublin, Ireland). Barium hydroxide and sodium sulfate (pro-analysis) was from Merck (Darmstadt, Germany). Titanium dioxide (Degussa P25), was used as received for all degradation experiments. Doubly distilled water, filtered through 0.45 μm HA cellulose acetate membranes (Millipore), was used throughout the work.

Irradiation procedure

Irradiation experiments were carried out on stirred aqueous solutions using a 50 ml cylindrical Pyrex glass UV-reactor under continuous flushing of O_2 at a rate of 15 ml/min. Degradations were performed on 15 ml of aqueous solutions containing the desired concentration of herbicides ($\approx$10 mg/L) and two different amounts of TiO_2 (100 and 500 mg/L) at natural pH. The suspensions were allowed to stay in the dark for 60 min under stirring to reach adsorption equilibrium on to semiconductor surface. The irradiation was carried out using a Suntest CPS+ apparatus from Heraeus (Hanau, Germany) equipped with a xenon arc lamp (1500 W) and special glass filters restricting the transmission of wavelengths below 290 nm.

Analytical procedures

Kinetic studies. After irradiation for specific time intervals samples of 5 ml were withdrawn from the reactor. To remove the TiO_2 particles the solution samples were filtered through HA 0.45 μm filter. The samples were extracted twice with 2.5 ml n-hexane for one minute using a vortex, dried with a small amount of Na_2SO_4 and finally analysed by GC, quantified by internal standard. The analysis of molinate and propanil was performed using Shimadzu 14A gas chromatographs equipped with flame thermionic detector (FTD) and electron capture detector (ECD ^{63}Ni) respectively. The DB-1 capillary column, 30m $\times$ 0.32 mm i.d. used, contained methylsilicone (J&W Scientific, Folsom, CA) followed a temperature program: 150°C for 2 min, from 150 to 210°C with a rate of 5°C/min, at 210°C for 10 min, 210 to 270°C with a rate of 10°C/min, and at 270°C for 3 min. The detector gases were hydrogen and air, and their flow rates were regulated at 150 ml/min and 3.5 ml/min respectively. The ion source was an alkali metallic salt (Rb_2SO_4) bonded to a 0.2 mm spiral of platinum wire. The temperatures were set at 220°C for the injector and 250°C for the detector. For both detectors helium was used as the carrier at 25 cm/s and nitrogen was used as make-up gas at 25 ml/min. For ECD the temperatures were set at 250°C for the injector and 300°C for the detector.

Mineralization studies. Complete mineralization of organic samples to CO_2 is very often obtained by using the photocatalytic method. The kinetics of the evolution of CO_2 formed was followed by using the method of Chemssedine and Boehm (1990). The evolution of inorganic ions (SO_4^{2-}, NO_3^{-}, Cl^-) was followed by suppressed ion chromatography, using a Shimadzu 500 apparatus equipped with a 100 mm long $\times$ 4.6 mm i.d. Shim-pack IC-A1 column (Shimadzu) and a conductometric detector CDD-6A (Shimadzu). The eluent was a mixture of phthalic acid (2.5 mM) and tris (hydroxymethyl) aminomethane (2.5 mM) at a flow rate of 1.5 ml/min.

By-product evaluation. A relatively low amount of TiO_2 (100 mg/L) was used in the experiments for the identification of organic intermediates, which enables slower kinetics and provides favorable conditions for the determination of by-products. The analytical procedure for SPE extraction technique followed by GC-MS analysis in EI mode has been described by our group in previous work (Konstantinou *et al.*, 2001). The GC was equipped with a DB-5-MS capillary column, 30 m × 0.25 mm i.d. coated with methylphenylsiloxane (5% phenyl) (J&W Scientific, Folsom, CA) used at the following chromatographic conditions: Injector temperature 220°C, column program of temperatures 55°C, 55–200°C (5°C/min), 200–210°C (1°C/min) 210°C (2 min), 210–270°C (20°C/min), 270°C (3 min). Helium was used as the carrier gas at 14 psi. The interface was kept at 270°C. Qualitative analyses were performed in the electron impact (EI) mode, at 70 eV potential using full scan mode.

Results and discussion

Photocatalytic degradation of propanil

Adsorption in the dark and direct photolysis. It is generally expected that the observed photocatalytic degradation is governed by the adsorption kinetics. In the present case the adsorption kinetics of propanil onto TiO_2 surface was followed for a period of 180 min. The adsorption was increased for the first 90 min, reaching a plateau after that. The initial concentration of propanil decreased from 13.2 to 10.21 mg/L under vigorous stirring for 3 h in the dark. This corresponds to a coverage of 0.33 molecule/nm^2 which represent a moderately adsorbed organic compound. Irradiation of propanil solution in the absence of TiO_2 shows that photolytic decomposition occurs at a low rate. Thus, photochemical processes are scarcely responsible for the observed fast transformations when the solution was irradiated in the presence of titanium. The photolysis kinetic parameters of propanil are shown in Table 1.

Kinetics of propanil disappearance. The kinetics of propanil disappearance in the presence of different concentrations of TiO_2 (100 and 500 mg l^{-1}) followed an apparent first-order degradation curves which is consistent with the Langmuir–Hinshelwood model resulting from the low coverage in the experimental concentration range ($\approx$10 mg/L). The k_{obs} values (Table 1) in the presence of 100 and 500 mg/L of TiO_2 were 0.0416 and 0.1623 min^{-1} respectively, confirming the positive influence of the increased number of TiO_2 active sites on the process kinetics. However, this beneficial effect tends to level off and then to decrease for TiO_2 concentrations higher than 1–2 g/L depending on the reactor, due to relevant scattering of the incident light (Assabane *et al.*, 2000).

Evolution of the mineralization. The evolution of CO_2 as a function of the irradiation time in the photocatalytic degradation of propanil is shown in Figure 1. Taking into account the fact that complete disappearance of propanil in the irradiated reactor occurs after 40 min, whereas the stoichiometric formation of CO_2 is observed after 240 min under the same

Table 1 Photocatalytic degradation kinetic parameters (rate constants, correlation coefficients, half-lives) of the selected herbicides in distilled water, and in TiO_2 suspensions (100 and 500 mg/L) under simulated solar light

Herbicides	Photolysis			TiO_2 (100 mg/L)			TiO_2 (500 mg/L)		
	k_{obs} (min^{-1})	R^2	$t_{1/2}$ min	k_{obs} (min^{-1})	R^2	$t_{1/2}$ min	k_{obs} (min^{-1})	R^2	$t_{1/2}$ min
Propanil	0.0020	0.951	346.6	0.0416	0.995	16.7	0.1623	0.990	4.3
Molinate	0.0032	0.951	216.6	0.0512	0.997	13.5	0.237	0.969	2.9

working conditions, it is deduced that transient organic intermediates are likely to be present in the reaction system after the complete destruction of the tested herbicide.

The evolution of chloride ions becomes quantitative at 180 min indicating that dechlorination of propanil is faster than mineralization to CO_2. Thus only dechlorinated transient organics are present in the solution after that time. The presence of several identified chlorinated transformation products, discussed below, supports the above observation. Both ammonia and nitrate have been detected generally in different relative concentrations starting from compounds having nitrogen-containing groups, such as amines or nitro derivatives. At long exposure times, conversion of ammonium to nitrate ions has been observed. Under the present experimental conditions, the quantitative recovery of nitrogen as nitrate would be achieved after long irradiation periods (more than 4 h). In four hours time period only 32% of the stoichiometric nitrate was formed for propanil.

Propanil photocatalytic degradation pathway. It is well established that conduction band electrons (e^-) and valence band holes (h^+) are generated when aqueous TiO_2 suspension is irradiated with light energy greater than its band gap energy (e.g. 3.2 eV). The photogenerated electrons could reduce the organic substrate or react with the adsorbed molecular O_2 on the Ti(III)-surface, reducing it to superoxide radical anion $O_2{\cdot}^-$. The photogenerated holes can also oxidize either the organic molecule directly, or the OH^- ions and the H_2O molecules adsorbed at the TiO_2 surface, to ·OH· radicals. Together with other highly oxidant species (peroxide radicals) they are reported to be responsible for the heterogeneous TiO_2 photodecomposition of organic substrates.

The analysis of sample extracts was obtained after 90 min of irradiation in the presence of 100 mg/L TiO_2 and allowed the determination of several transformation products. Up to eight compounds could be detected as possible degradation intermediates. Six of them were unequivocally identified by: (a) using an identification program of NIST library (compounds 2, 3, 4, 5, 8) with a fit value higher than 70% in all cases; (b) by comparing the spectra with previously reported spectra (compounds 2 and 6). Two compounds (1 and 7) not included in the library were identified by interpretation of the mass spectra. Compound 1 exhibited the molecular ion peak at m/z = 233 and two peaks at m/z = 161 (base peak) and m/z = 163 which corresponded to the hydroxylated derivative of propanil (addition of OH group, m/z = [M+16]$^+$) and the characteristic peaks of dichloroaniline respectively. Compound 7 was identified as the ring hydroxylated derivative of propanil, exhibited the
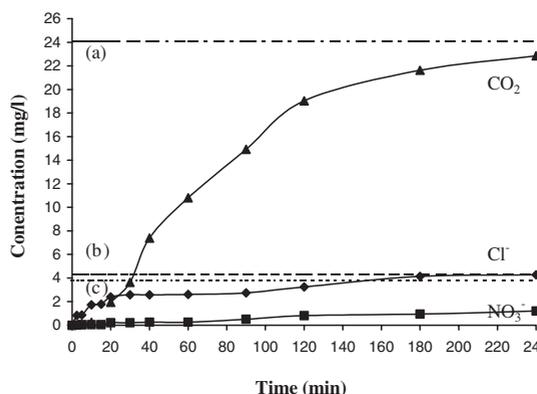

Figure 1 Evolution of carbon dioxide, chloride and nitrate ions originating from propanil photocatalytic degradation under simulated solar light ($TiO_2 = 500$ mg/L). Curves (a), (b) and (c) represent the stoichiometric concentrations of CO_2, Cl^-, and NO_3^- respectively

peaks $[M^+] = 233$ and m/z = 177 (base peak), m/z = 179 which corresponded to the addition of hydroxy group to propanil and the characteristic ions of the hydroxylated dichloroaniline respectively. Based on the previous structure identification of the organic intermediates, a possible photocatalytic degradation pathway of propanil consisting of several steps was proposed in Figure 2.

Photocatalytic degradation of molinate

Adsorption in the dark and direct photolysis. The adsorption kinetics of molinate onto TiO_2 surface was also followed for a period of 180 min. The adsorption was increased for the first 60 min reaching a plateau after that time. The initial concentration of molinate was 9.79 mg/L. After addition of titanium (0.5 g/L) and stirring in the dark for 180 min, it decreased to 7.88 mg/L that corresponds to a moderately absorbed compound (0.25 molecule/nm^2). Irradiation of molinate solution in the absence of TiO_2 shows that photolytic decomposition occurs at a slow rate as well. After 60 min of irradiation, direct photolysis contributed less than 23% to the degradation of molinate. The photolysis kinetic parameters of molinate are shown in Table 1.

Kinetics of molinate disappearance. The kinetics of molinate disappearance follows also an apparent first order degradation curve according to the Langmuir–Hinshelwood model. Table 1 lists the rate constants and the linear regression coefficients arising from the integral linear transformation curves. According to these values the appropriate first-order relationship appears to fit well.

Evolution of the mineralization. The kinetic variation of CO_2 and the related inorganic ions is given in Figure 3. The complete disappearance of molinate occurs after 30 min whereas the stoichiometric formation of CO_2 demands irradiation period longer than 240 min under the same working conditions. Thus, transient organic intermediates are likely to be present in the reaction system after the complete destruction of molinate.
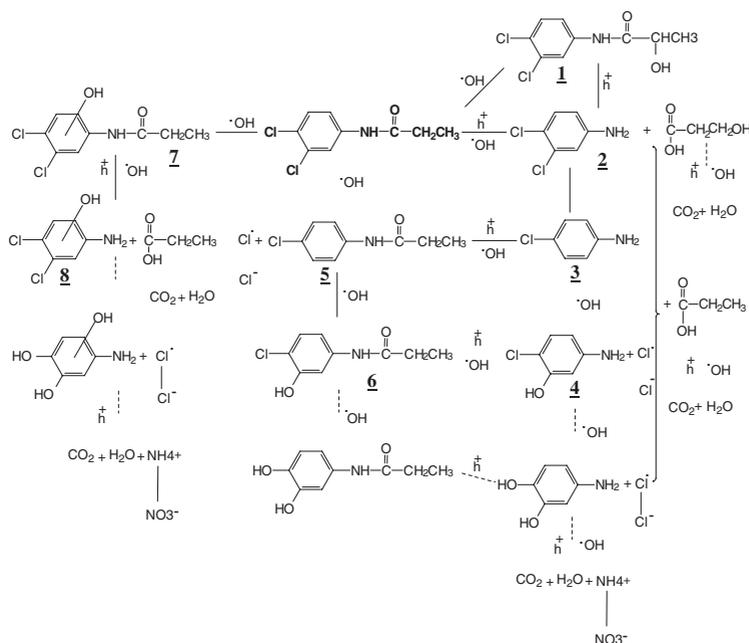

Figure 2 Proposed photocatalytic degradation pathway of propanil in aqueous solutions by TiO_2 and simulated solar light
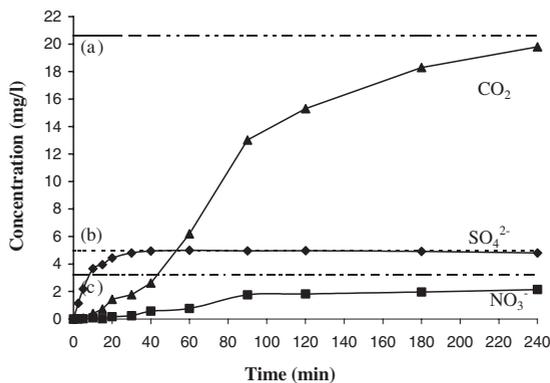
Figure 3 Evolution of carbon dioxide, sulphate and nitrate ions originating from molinate photocatalytic degradation under simulated solar light ($TiO_2 = 500$ mg/L). Curves (a), (b) and (c) represent the stoichiometric concentrations of CO_2, SO_4^{2-}, and NO_3^- respectively

The stoichiometric concentration of SO_4^{2-} was reached just after the complete disappearance of the parent compound in 40 min. This supports the idea that oxidation of thio-alkyl group is a fast process and only nitrogen-containing derivatives are present after that irradiation time.

Under the present experimental conditions, the quantitative recovery of nitrogen as nitrate would be achieved after long irradiation periods. In four hours 66% of the stoichiometric nitrate was formed i.e. twice the percentage formed in the photodegradation of propanil. This is consistent with the fact that a higher nitrate to ammonium concentration ratio is produced for compounds containing ring nitrogen than for compounds with the nitrogen atom bonded to the ring or in lateral chains (Low *et al.*, 1991).

Molinate photocatalytic degradation pathway. Up to nine compounds could be detected as possible degradation intermediates. Three of them were unequivocally identified as the possible ketomolinate isomers (compounds 1a, b, c) by comparing the spectra with the previous reported spectra for keto derivatives of molinate (Sturini *et al.*, 1996). The γ keto derivative was reported in this study for the first time (compound 1c). Their mass spectra lacked the hexahydroazipine isocyanate ion (m/z = 126), the base peak of molinate, and gave oxygenated hexahydroazipine isocyanate ions (m/z = 140) and weak molecular ions (m/z = 201).

Photoproducts 3 and 6 were identified using the identification program of NIST library with a fit value higher than 70% in both cases. Three compounds (2, 4 and 5) not included in the library were identified by interpretation of the mass spectra. Compound 2 was identified as the de-alkylated derivative of ketomolinate and exhibited a peak at m/z = 171 by the loss of the ethyl group (M-29), corresponding to the [M-1]$^+$ ion that is explained by the characteristic cleavage of the S-H bond.

Compound 4, with molecular ion [M]$^+$ = 203 found at Rt = 28.44 min, was associated as the sulphoxide derivative of molinate. Compound 5 was identified as the de-alkylated derivative of molinate and exhibited a peak at m/z = 157 due to the loss of alkyl group, corresponding to the [M-1]$^+$ ion as explained previously. Moreover it exhibits the same ions as molinate. Figure 4 describes some of the possible reaction pathways involving the intermediates identified by GC-EI-MS.

The great number of compounds detected during the degradation of the above compounds shows the complexity of the photocatalytic process and suggests the existence of various degradation routes resulting in multi-step and interconnected pathways.

Figure 4 Proposed photocatalytic degradation pathway of molinate in aqueous solutions by TiO_2 and simulated solar light

Cost-effective treatments to complete compound mineralization are usually not practicable, and the presence of by-products during and at the end of the water treatment appears to be unavoidable.

Conclusions

This work shows that heterogeneous titanium-dioxide photocatalysed decomposition is a feasible and fast treatment for the removal of the selected herbicides present at mg/L level from agricultural effluents or polluted surface waters. The degradation of the herbicides follows first-order kinetics and complete disappearance is observed in less than one hour, working with moderate amounts of TiO_2, under simulated solar light.

A careful study of the parameters, such as CO_2, inorganic ion formation and identification of by-products, obtained in combination with analytical procedures based on mass spectroscopy techniques, provides a thorough knowledge of the degradation mechanism. The analysis of the transformation products reveals the presence of hydroxylation, dechlorination, dealkylation and oxidation steps leading to the mineralization of the starting molecule.

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T.A. Albanis *et al.*

232