

Research Article

Photocatalytic Degradation of Pesticides in Natural Water: Effect of Hydrogen Peroxide

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The aim of this paper is to evaluate the effectiveness of photocatalytic treatment with titanium dioxide in the degradation of 44 organic pesticides analyzed systematically in the Ebro river basin (Spain). The effect of the addition of hydrogen peroxide in this treatment is studied, and a monitoring of effectiveness of photocatalytic processes is carried out by measurements of physical-chemical parameters of water. The application of photocatalytic treatment with 1 g L^{-1} of TiO_2 during 30 minutes achieves an average degradation of the studied pesticides of 48%. Chlorine demand, toxicity, and dissolved organic carbon (DOC) concentration of water are reduced. If hydrogen peroxide is added with a concentration of 10 mM, the average degradation of pesticides increases up to 57%, although chlorine demand and toxicity of water increase while DOC concentration remains unchanged with this treatment. The application of either photocatalytic treatments does not produce variations in the physical-chemical parameters of water, such as pH, conductivity, colour, dissolved oxygen, and hardness. The pesticides which are best degraded by photocatalytic treatments are parathion methyl, chlorpyrifos, α -endosulphan, 3,4-dichloroaniline, 4-isopropylaniline, and dicofol while the worst degraded are HCHs, endosulphan-sulphate, heptachlors epoxide, and 4,4'-dichlorobenzophenone.

1. Introduction

During recent years, numerous organic substances considered to be hazardous have been detected in waters of Ebro river basin (Spain). These substances have been detected in surface and ground waters and they can be considered hazardous substances according to the current legislation because they are toxic, persistent, and bioaccumulative substances.

Pesticides, artificially synthesized substances used to fight pests and improve agricultural production, are especially problematic. These are monitored by the Pesticides Control Network (Ebro river basin), which systematically analyzes 44 organic pesticides in surface waters. These pesticides were selected because of their appearance in lists of hazardous substances and/or their high level of use in Spanish agriculture. The 44 pesticides analyzed in the Ebro river basin are alachlor, aldrin, ametryn, atrazine, chlorfenvin-fos, chlorpyrifos, pp'-DDD, op'-DDE, op'-DDT, pp'-DDT,

desethylatrazine, 3,4-dichloroaniline, 4,4'-dichlorobenzophenone, dicofol, dieldrin, dimethoate, diuron, α -endosulphan, endosulphan-sulphate, endrin, α -HCH, β -HCH, γ -HCH, δ -HCH, heptachlor, heptachlor epoxide A, heptachlor epoxide B, hexachlorobenzene, isodrin, 4-isopropylaniline, isoproturon, metholachlor, methoxychlor, molinate, parathion methyl, parathion ethyl, prometon, prometryn, propazine, simazine, terbutylazine, terbutryn, tetradifon, and trifluralin.

Due to the presence of hazardous substances, both natural water used to supply the population and water which is to be reused have to be treated in water treatment plants to ensure that they comply with the minimum criteria established in the current legislation [1–3].

Water treatments consist of several operations which often do not achieve the removal of hazardous substances or entail other problems deriving from the treatment.

In the case of drinking water production, an important successful development is the possible formation of

organic-halogenated compounds, potentially carcinogenic and chlorinated deriving from methane, as reaction products between chlorine (common disinfectant product) and the organic matter in water. The most abundant of these are trihalomethanes (THMs) whose concentration is limited by Spanish Royal Decree 140/2003 at to $100 \mu\text{g L}^{-1}$.

The drawbacks in the use of compounds with chlorine, among others, have derived in the research of other alternative treatments for removing pollutants in water treatments. Among these, advanced oxidation processes (AOPs) are based on the generation of reactive oxygen species, which are highly reactive, nonselective, and do not generate toxic byproducts [4, 5]. These species are capable of degrading a substantial number of pollutants by radicalary mechanisms. The generation of these species can be carried out by processes with ozone, hydrogen peroxide, metallic catalysts, UV radiation, and so forth.

One of the most frequently investigated AOPs in recent years is the photocatalytic process. Photocatalysis entail the combination of radiation and catalyst. Both are necessary in order to achieve or accelerate a chemical reaction, and therefore photocatalysis can be defined as the “acceleration of a photoreaction by the presence of a catalyst.”

Catalysts used in these processes are semiconductor metallic oxides materials. The surface of semiconductor metallic oxides provides a place where oxidation-reduction reactions can be started by radiation. Semiconductors have bands associated with energy levels spaced between them. Photoexcitation with energy equal to or greater than that of the gap between the valence and conduction bands moves an electron from the valence band to the conduction band, generating a hole deficient in electrons. The oxidation of an adsorbed molecule can be produced in holes and simultaneously the reduction of another molecule can be produced in the opposite part of the catalyst.

Numerous semiconductor substances have been tried as catalyst in photocatalytic processes. Generally, it is known that titanium dioxide is one of the most effective. Moreover, it has a high stability and photoactivity, low cost, nontoxicity, and solubility. The activation of titanium dioxide is produced with radiation at $\lambda < 387 \text{ nm}$.

As a result of the application of photocatalytic processes based on titanium dioxide, the number of references in the literature in recent decades related to the degradation of toxic and hazardous substances in water can be counted in their thousands. As regards the group of pesticides under study, photocatalytic processes have been applied in several ways and there are many references to the degradation of such pesticides such as triazines [6, 7], organic-phosphorated pesticides [8–10], alachlor [11, 12], diuron [7, 13], and parathion methyl [14].

The addition of hydrogen peroxide to photocatalytic treatment with titanium dioxide can be used to increase the effectiveness of the latter process because, as hydrogen peroxide is a more powerful oxidant than oxygen, it generates a larger collection of electrons and this avoids the recombination of electron-hole pairs formed in the photocatalytic process. Hydrogen peroxide is an electron acceptor and it

can react with electrons in the conduction band and generate radicals.

Similarly, there are several references concerning the removal of pesticides by photocatalytic treatments with hydrogen peroxide, such as the degradation of atrazine, isoproturon, alachlor and diuron [7], organic-phosphorated pesticides [9, 10], and other triazines [15].

However, the results show a big disparity with respect to the effect of hydrogen peroxide. It is sometimes beneficial while at other times it is damaging to the effectiveness of the process. This phenomenon, the effect of hydrogen peroxide in photocatalytic treatments, produces additional drawbacks when complex mixtures of pollutants are used. The damaging effect in the degradation rate is produced by a modification of the catalyst surface by hydrogen peroxide adsorption [16] and the inhibition of generated holes in the valence band and reaction with hydroxyl radicals [17]. When the effect of hydrogen peroxide is beneficial, a substantial consumption of hydrogen peroxide is sometimes necessary in order to obtain only a small increment of the degradation rate.

The aim of this research work is to evaluate the degradation of the 44 pesticides systematically analyzed in the Ebro river by photocatalytic treatment with titanium dioxide and to study the effect of hydrogen peroxide in this treatment. Moreover, a monitoring of the effectiveness of the photocatalytic processes is carried out by measuring the physical-chemical parameters of water.

2. Materials and Methods

2.1. Samples. Samples of natural water from the Ebro river upstream from Zaragoza (Spain) were prepared by fortification with 44 pesticides in concentrations of 500 ng L^{-1} . These 44 organic pesticides, listed in the introduction section, are systematically analysed in surface waters by the Network of Control of Pesticides in the Ebro river basin.

2.2. Sample Characterization. The characterization of the samples was carried out using the parameters shown in Table 1. The equipment used and standard methods applied are detailed below.

The analysis of the chromatographic conditions of the pesticides is shown in Table 2 and the results of the validation of this analysis in Table 3.

Previously to the analysis of pesticides by GC/MS a solid-liquid extraction was carried out. This extraction consisted of the retention of organic compounds in a solid phase and subsequent elution with an organic solvent.

The extraction was carried out using an AUTOTRACE WorkStation automatic extractor (Zymark). Before extraction, 100 ng L^{-1} of surrogate compounds used to control the extraction process (simazine-D5, atrazine-D5, and prometryn-D6) were added to the water sample. During solid-liquid extraction, 900 mL of the sample was passed through cartridges containing a solid ENV+ filter (polystyrene divinyl benzene copolymer) (ISOLUTE cartridges, 200 mg 6 mL^{-1}). The pesticides contained in the sample were retained in

TABLE 1: Parameters, equipment, and standardized methods used for the characterization of samples.

Parameter	Equipment	Standard method	Reference
pH and temperature	pH-meter CRISON GLP21	SM 4500-HB	[18]
Conductivity	Conductivity-meter CRISON Basic30	UNE-EN 27888: 1994	[19]
Dissolved organic carbon (DOC) concentration	Analyzer Shimadzu TOC-VCSH	SM 5310B	[18]
Chlorine Demand	—	SM 5710B	[18]
Turbidity	Turbidity-meter Hanna LP2000	ISO 7027: 1999	[20]
Color	Multiparametric Photometer Hanna C99	SM 2120B	[18]
Dissolved oxygen concentration	Multiparametric Photometer Hanna C99	SM 4500-O C	[18]
Hydrogen peroxide concentration	—	—	[21]
Hardness	Multiparametric Photometer Hanna C99	SM 2340B	[18]
Suspended solids concentration	Multiparametric Photometer Hach Lange DR2800	SM 2540D	[18]
Phosphorous concentration	Multiparametric Photometer Hanna C99	SM 4500-P C	[18]
Ammonia concentration	Multiparametric Photometer Hanna C99	SM 4500-NH3 C	[18]
Cyanide concentration	Multiparametric Photometer Hanna C99	SM 4500-CN E	[18]
Fluoride, chloride, nitrate, phosphate, and sulphate concentration	Ionic Chromatographer DIONEX ICS-1000	SM 4110B	[18]
Toxicity	Toxicity-meter LUMISTox 300	ISO 11348: 1999	[22]
Pesticides	Gas chromatographer TRACE2000 and mass spectrometer POLARIS	EPA 525.2	[23]

TABLE 2: Conditions of pesticide analysis.

Gas chromatographer TRACE GC 2000 (Thermo Finnigan)	
Column	DB5-MS (J&W, 30 m, 0.25 mm, 0.25 μ m)
Program of temperatures	90°C (1 min), 20°C min ⁻¹ , 180°C (1 min), 2°C min ⁻¹ , 240°C (1 min), 20°C min ⁻¹ , 310°C (10 min)
Injector temperature	250°C
Injection volume	1 μ L, splitless 0.8 min
Carrier gas	He (N55), 1 mL min ⁻¹
Mass spectrometer POLARIS (Thermo Finnigan)	
Ionization energy	70 eV
Acquisition mode	Full scan
Mass interval	50–450 amu
Screen speed	1 scan s ⁻¹
Acquisition time	32.5 min

the solid phase and dried under N_2 for 10 minutes. They were then eluted by passing 10 mL of ethyl acetate (SDS for pesticide analysis) through the cartridge, thus facilitating the passage of these compounds from the water phase to an organic phase. The extracts thus obtained were concentrated under a N_2 flow until an approximate volume of 1 mL was obtained, after which 3 mL of isooctane was added (SDS for pesticide analysis) in order to carry out a change of solvent. The extract was then concentrated until obtaining an approximate volume of 0.5 mL. Anthracene deuterate (D10, SUPELCO) was added to each extract as an internal standard for subsequent quantification of the pesticides present in the samples. These extracts were analysed by GC/MS.

2.3. Experimental Procedure in Photocatalytic Treatments. The titanium dioxide used in this work was Degussa P25. The tests were carried out with a dose of 1 g L⁻¹, the same as that used in previous studies and determined as optimal in the stages of disinfection [24–26]. The TiO₂ was added to 1 L of sample to be treated and shaken at 300 rpm to promote contact between the sample and the catalyst and provide oxygen to the reaction medium. The reaction time was 30 minutes.

For tests with hydrogen peroxide, the compound was added to the sample H₂O₂ 30% v/v (Carlo Erba) with a concentration of 10 mM. This same dose has been used and determined as optimal in many research works evaluating

TABLE 3: Results of the methodology validation of the pesticide analysis.

Pesticide	Quantification limit ($\mu\text{g L}^{-1}$)		Calibration interval ($\mu\text{g L}^{-1}$)	Validity interval ($\mu\text{g L}^{-1}$)	Recovery interval (%)	
	Instrumental step	Full method			Instrumental step	Full method
Isoproturon	20	0.030	20–500	0.030–300	75–130	63–110
Diuron	20	0.030	20–500	0.030–300	82–128	70–123
3,4-Dichloroaniline	20	0.030	20–500	0.030–300	88–130	47–106
4-Isopropylaniline	20	0.030	20–500	0.030–300	80–130	60–125
Desethylatrazine	20	0.030	20–500	0.030–300	76–130	80–129
Trifluralin	20	0.015	20–500	0.030–300	70–130	70–127
Dimethoate	20	0.030	50–500	0.030–300	66–124	54–137
Simazine	50	0.030	20–500	0.030–600	75–135	64–127
Prometon	20	0.030	20–500	0.030–300	76–124	0–125
Atrazine	200	0.100	200–5000	0.100–300	78–130	75–127
Propazine	20	0.015	20–500	0.015–300	86–130	73–127
Terbuthylazine	20	0.015	20–500	0.015–300	79–130	83–128
Parathion methyl	50	0.030	50–500	0.030–300	78–139	72–130
Parathion ethyl	20	0.030	20–500	0.030–300	74–122	64–128
Alachlor	20	0.015	20–500	0.015–300	75–125	70–124
Ametryn	20	0.030	20–500	0.030–300	78–130	0–116
Prometryn	20	0.030	20–500	0.030–300	80–120	17–116
Terbutryn	20	0.030	20–500	0.030–300	80–120	13–114
Chlorpyrifos	20	0.015	20–500	0.015–300	75–120	73–116
Chlorfenvinfos	20	0.015	20–500	0.015–300	76–130	70–126
HCHs	20	0.015	20–500	0.015–300	84–124	70–120
Hexachlorobenzene	20	0.030	20–500	0.030–300	70–130	74–136
Heptachlor	20	0.015	20–500	0.015–300	75–130	58–113
Heptachlor epoxide A	20	0.015	20–500	0.015–300	85–125	62–112
Heptachlor epoxide B	20	0.015	20–500	0.015–300	84–130	58–113
Aldrin	20	0.015	20–500	0.015–300	85–125	64–126
4,4'-Dichlorobenzophenone	20	0.015	20–500	0.015–300	75–120	68–126
Isodrin	20	0.015	20–500	0.015–300	85–125	66–120
α -Endosulphan	20	0.015	20–500	0.015–300	70–125	70–93
pp'-DDE	20	0.015	20–500	0.015–300	89–122	64–107
Dieldrin	20	0.015	20–500	0.015–300	70–125	62–120
Endrin	20	0.015	20–500	0.015–300	80–125	74–122
pp'-DDD + op'-DDT	40	0.030	40–1000	0.030–600	79–125	66–139
Endosulphan-sulphate	20	0.015	20–500	0.015–300	83–125	73–126
pp'-DDT	20	0.030	20–500	0.030–300	76–130	50–120
Dicofol	50	0.030	50–500	0.030–300	80–148	63–136
Methoxychlor	20	0.015	20–500	0.015–300	77–126	75–130
Metholachlor	20	0.015	20–500	0.015–300	76–115	73–128
Molinate	20	0.015	20–500	0.015–300	91–130	75–113
Tetradifon	20	0.015	20–500	0.015–300	85–130	70–116

the effectiveness of photocatalytic treatment with hydrogen peroxide on the degradation of different compounds, or even on the generation of ROS: degradation of dyes [27–30], pesticides [31, 32], antibiotics [33], and ROS production [34]. In these tests, hydrogen peroxide was removed after the treatment.

The UV/VIS radiation source was provided using an ATLAS SUNTEST CPS+/XLS+ solar chamber. This chamber is an instrument equipped with a xenon lamp used for lighting and the ageing of materials. It can be used as simulator of natural sunlight. The chamber also includes an agitation system, a quartz filter, UV radiation, visible light,

temperature control. It is equipped with a programmable system for measuring and for regulating the irradiation intensity. The irradiation range of the equipment is from 250 to 785 W m⁻² with a wavelength of 300 to 800 nm. The samples were subjected to a radiation intensity from 500 W m⁻² which corresponds to 50% of the intensity of natural solar radiation at midday [35].

All the tests were performed in duplicate, using glass beakers of 1 L and with shaking. Moreover, blank tests were carried out.

3. Results and Discussion

The results of the two photocatalytic treatments (TiO₂/radiation and TiO₂/H₂O₂/radiation) on the solutions of natural water fortified with the 44 pesticides under study relating to the sample characterization and the removal of pesticides are presented below.

3.1. Sample Characterization. The characterization of the initial sample and the samples treated with the two photocatalytic processes is shown in Table 4.

The results show the following.

- (i) The application of photocatalytic treatments does not produce significant variations with respect to the initial values of pH, conductivity, color, dissolved oxygen, hardness, ammonium concentration, and concentration of ions in solution.
- (ii) The turbidity of the sample, in both cases, declines slightly, and solids in suspension make it significantly through the chemical oxidation of organic matter produced in the treatment.
- (iii) Chlorine demand in the TiO₂/radiation-treated sample is reduced significantly, up to a value of 1 mg L⁻¹. However, the application of TiO₂/H₂O₂/radiation treatment produces an enormous increase in this parameter. This is possibly due to the various byproducts formed after the application.
- (iv) Regarding the toxicity of treated sample, TiO₂/radiation treatment reduces the initial toxicity of the sample to approximately half its initial value. On the other hand, the application of TiO₂/H₂O₂/radiation produces an increase in the initial toxicity, due to the formation of byproducts more toxic than the original. This has occurred in other research works concerning the application of these photocatalytic treatments [14, 36–38].
- (v) The COD undergoes no variation through the TiO₂/H₂O₂/radiation treatment while it is reduced by 36% after the application of TiO₂/radiation. This suggests the mineralization of organic matter present in the process with hydrogen peroxide [39].
- (vi) Suspended solids are removed by both photocatalytic treatments. This is due to the organic matter present in the water by this advanced oxidation process.

- (vii) Hydrogen peroxide appears after the TiO₂/radiation treatment formed as a by-product in photocatalytic reactions. In the case of the TiO₂/H₂O₂/radiation treatment, where it is used initially as a reagent, almost its total consumption is observed.

3.2. Pesticide Removal. Photocatalytic experiments were carried out in duplicate. Table 5 shows the average concentration of each pesticide studied in the initial sample and the final concentration after the photocatalytic treatments. It is worth noting that average concentrations are shown because the variations obtained in these analyses were very low, always below 2%.

In addition to the photocatalytic treatments, blank tests were carried out. These blank tests were solution of pesticides with titanium dioxide without radiation and with radiation without catalyst. The results obtained are shown in Table 6. Only for some pesticides were degradations different to zero achieved.

As can be observed, some of the studied pesticides can be degraded by TiO₂ without radiation and by radiation without TiO₂. The degradation of these pesticides by TiO₂ only is due to their adsorption in the catalyst. The degradation of these pesticides by radiation only is due to the advanced oxidation process with UV by which hydroxyl radicals are generated.

Table 7 shows the average removal percentages of the pesticides.

The photocatalytic treatments achieved an average degradation of 48% by photocatalysis (TiO₂/radiation) and 57% by photocatalysis with hydrogen peroxide (TiO₂/H₂O₂/radiation).

The photocatalytic treatments were very effective in the removal of parathion methyl, chlorpyrifos, α -endosulphan, 3,4-dichloroaniline, 4-isopropylaniline, and dicofol. The treatments were less effective in the degradation of HCHs, endosulphan-sulphate, heptachlors epoxide, and 4,4'-dichlorobenzophenone.

As can be seen in Tables 5 and 7, the addition of hydrogen peroxide to the process slightly improves the average percentage of pesticide removal. However, this improvement does not occur for all the pesticides studied. In fact, some of them present the same removal percentages by both photocatalytic treatments. The increase in the average percentage of degradation is due to an improvement in some of the studied pesticides to add hydrogen peroxide. These are some triazines, α -endosulphan, molinate, trifluralin, and anilides, for which removal is improved by 5–20% using hydrogen peroxide; isodrin, aldrin, DDTs, and 4,4'-dichlorobenzophenone, for which removal is improved by 25–50% using hydrogen peroxide.

The degradation percentages of the pesticides in their individual group are as follows.

Triazines. The rates of degradation of triazines obtained by the photocatalytic treatments are between 35 and 60%. By photocatalysis, these percentages are from 35 to 55%. Degradation of these pesticides is very similar, 40–60%, when

TABLE 4: Characterization of samples of surface water fortified with pesticides in photocatalytic treatments.

Initial sample			
Physical-chemical parameters			
pH	8.0	Colour (PCU)	0
Conductivity ($\mu\text{S cm}^{-1}$)	508	Dissolved oxygen (mg L^{-1})	9.9
Turbidity (NTU)	69	Hardness ($\text{mg CaCO}_3 \text{ L}^{-1}$)	108
Suspended solids (mg L^{-1})	27	NH_4^+ concentration (mg L^{-1})	0.15
Phosphorous (mg L^{-1})	0.8	CN^- concentration (mg L^{-1})	0.002
DOC (mg C L^{-1})	22	Toxicity (% inhibition)	33.6
Chlorine demand ($\text{mg Cl}_2 \text{ L}^{-1}$)	6.0		
Anion concentrations in solution (mg L^{-1})			
Fluorides	0.1	Nitrates	10.8
Chlorides	63.8	Phosphates	<0.2
Sulphates	98		
Sample after treatment TiO_2 /radiation			
Physical-chemical parameters			
pH	8.0	Colour (PCU)	0
Conductivity ($\mu\text{S cm}^{-1}$)	589	Dissolved oxygen (mg L^{-1})	6.2
Turbidity (NTU)	54	Hardness ($\text{mg CaCO}_3 \text{ L}^{-1}$)	109
Suspended solids (mg L^{-1})	7	NH_4^+ concentration (mg L^{-1})	0.15
Phosphorous (mg L^{-1})	0.4	CN^- concentration (mg L^{-1})	0.0015
DOC (mg C L^{-1})	14	Toxicity (% inhibition)	18.9
H_2O_2 concentration (mg L^{-1})	5	Chlorine demand ($\text{mg Cl}_2 \text{ L}^{-1}$)	1.0
Anion concentrations in solution (mg L^{-1})			
Fluorides	<0.1	Nitrates	11.6
Chlorides	66.4	Phosphates	<0.2
Sulphates	101.0		
Sample after treatment $\text{TiO}_2/\text{H}_2\text{O}_2$ /radiation			
Physical-chemical parameters			
pH	8.0	Colour (PCU)	0
Conductivity ($\mu\text{S cm}^{-1}$)	625	Dissolved oxygen (mg L^{-1})	9.8
Turbidity (NTU)	56	Hardness ($\text{mg CaCO}_3 \text{ L}^{-1}$)	95
Suspended solids (mg L^{-1})	5	NH_4^+ concentration (mg L^{-1})	0.15
Phosphorous (mg L^{-1})	0.2	CN^- concentration (mg L^{-1})	0.001
DOC (mg C L^{-1})	22	Toxicity (% inhibition)	43.3
H_2O_2 concentration (mg L^{-1})	0.5	Chlorine demand ($\text{mg Cl}_2 \text{ L}^{-1}$)	55.6
Anion concentrations in solution (mg L^{-1})			
Fluorides	<0.1	Nitrates	11.4
Chlorides	65.0	Phosphates	<0.2
Sulphates	99.2		

hydrogen peroxide is added to the treatment. Therefore, the addition of this reagent is not compensated for by the increase of the effectiveness in the degradation of triazines by photocatalytic treatment. Among the triazines studied are atrazine and desethylatrazine, the most difficult to degrade by photocatalytic treatments.

Organic Phosphorated. The five organic-phosphorated pesticides studied are degraded between 40 and 90% by photocatalytic treatments. The degradation percentages obtained for these pesticides are similar whether or not hydrogen

peroxide is added. The degradation of dimethoate and chlorfenvinfos only slightly improves when hydrogen peroxide is added. Methyl parathion and chlorpyrifos are the pesticides that degrade best by photocatalysis (degradation of 80–90%) while chlorfenvinfos is the most difficult organic-phosphorated pesticide to degrade (maximum degradation of 55%).

HCHs and HCB. With regard to HCHs, the degradation percentages obtained by the photocatalytic treatments are the lowest. In all cases, adding hydrogen peroxide makes

TABLE 5: Concentration of pesticides in samples in photocatalytic treatments.

Pesticide	Concentration (ng L ⁻¹)		
	Initial	After TiO ₂ /radiation	After TiO ₂ /H ₂ O ₂ /radiation
Alachlor	505	253	177
Aldrin	512	230	26
Ametryn	501	225	225
Atrazine	551	358	331
Chlorfenvinfos	492	295	221
Chlorpyrifos	520	104	104
pp'-DDD	510	332	102
op'-DDE	480	288	144
op'-DDT	482	313	96
pp'-DDT	482	386	145
Desethylatrazine	593	385	356
3,4-Dichloroaniline	658	0	0
4,4'-Dichlorobenzophenone	519	493	363
Dicofol	568	57	57
Dieldrin	508	356	356
Dimethoate	608	274	243
Diuron	501	125	125
α -Endosulphan	475	48	0
Endosulphan-sulphate	483	459	435
Endrin	486	243	243
α -HCH	511	109	409
β -HCH	519	441	441
γ -HCH	521	443	417
δ -HCH	504	428	428
Heptachlor	491	246	246
Heptachlor epoxide A	495	347	347
Heptachlor epoxide B	487	341	341
Hexachlorobenzene	503	327	327
Isodrin	516	206	0
4-Isopropylaniline	512	0	0
Isoproturon	521	78	78
Metholachlor	524	262	210
Methoxychlor	519	234	130
Molinate	551	248	165
Parathion ethyl	507	228	228
Parathion methyl	508	51	51
Prometon	492	271	271
Prometryn	489	220	220
Propazine	508	330	305
Simazine	554	305	277
Terbuthylazine	524	262	262
Terbutryn	514	231	206
Tetradifon	493	296	296
Trifluralin	566	255	170

no difference to the degradation percentages obtained so its use is redundant. The HCB is degraded 35% by the photocatalysis, and the addition of hydrogen peroxide does not produce any improvement.

Heptachlors. Degradation rates obtained for the heptachlors are 50% while the heptachlors epoxides are more difficult to degrade (30%). The addition of hydrogen peroxide to the process does not improve the degradation percentages

TABLE 6: Degradation of pesticides in blank experiments.

Pesticide	Removal by TiO ₂	Removal by radiation
Trifluralin	0	28
Heptachlor	14	45
Aldrin	20	50
Isodrin	24	55
pp'-DDE	33	46
pp'-DDD + op'-DDT	21	13
pp'-DDT	25	28

of these pesticides. In case of heptachlors, the blanks experiments show a degradation of 45% by radiation. The photocatalytic treatment does not therefore improve its degradation with respect to radiation only.

Endosulphans. Under photocatalysis, α -endosulphan shows almost total degradation while endosulphan-sulphate is practically undegraded by photocatalytic treatments. Both have the same behavior after the addition of hydrogen peroxide, showing an improvement of 5%, although again this small improvement does not compensate for its use.

Drins. With regard to these pesticides, it can be seen by these treatments that aldrin and isodrin (isomers between them) are more easily degradable than endrin and dieldrin (isomers between them), especially in the case of using hydrogen peroxide. The rates of degradation of dieldrin and endrin, 50% and 30% respectively, do not improve when adding hydrogen peroxide. In the case of aldrin and isodrin, blank experiments show an important degradation by radiation. Thus radiation and not the photocatalytic treatment is responsible for their degradation. However, the degradation of aldrin and isodrin is noticeably more effective when using hydrogen peroxide treatment, achieving their complete degradation.

DDTs. The DDTs studied degrade between 20% and 40% under the photocatalytic treatments. However, similar degradations are achieved in the blank experiments. The degradation could thus occur by the effect of titanium dioxide or radiation only, not by photocatalytic treatment. These degradation rates increase significantly by adding hydrogen peroxide, reaching 70–80%. Therefore, for the DDTs the presence of hydrogen peroxide notably favours their degradation.

Anilines. The two studied anilines, 3,4-dichloroaniline and 4-isopropylaniline, are completely degraded by the photocatalytic treatments. Therefore, the use of hydrogen peroxide is not necessary for increasing the effectiveness of the treatment.

Ureas. Isoproturon and diuron, the studied pesticides that are derivatives of urea, present high degradation rates under the photocatalytic treatments, being 85% and 75%,

respectively. The same percentages are obtained when using hydrogen peroxide, so that its use does not improve the process.

Anilides. The three anilides studied also show the same behaviour with photocatalytic treatments, and the addition of hydrogen peroxide produces a slight improvement, from 5% to 20%. Under photocatalysis, the degradation percentages are 50–55%. These percentages increase slightly when hydrogen peroxide is added to the treatment system, achieving rates of 60–75% degradation in this case.

Other Pesticides. For the rest of the pesticides under study, molinate, trifluralin, tetradiphon, dicofol, and 4,4'-dichlorobenzophenone, very different degradations are achieved. Molinate and trifluralin are degraded 55% by the photocatalysis and this percentage increases to 70% when hydrogen peroxide is added. Therefore, the use of this reagent represents a significant improvement in the degradation of these two pesticides. In the case of trifluralin, the blank experiment with radiation produced 30% degradation but its removal is greater by photocatalysis. Degradation of dicofol is very effective by the photocatalytic treatment, being 90%. The presence of hydrogen peroxide does not favour degradation in this case. The same applies to tetradiphon, which degrades to a lesser extent (40%), but hydrogen peroxide does not increase the effectiveness of the process. The 4,4'-dichlorobenzophenone is barely degraded at all by photocatalysis but its degradation increases up to 30% when adding hydrogen peroxide to the treatment.

4. Conclusions

After the completion of this study, the following conclusions can be drawn.

- (i) The pesticides most effectively removed by the photocatalytic treatments, reaching yields higher than 80%, are parathion methyl, α -endosulphan, chlorpyrifos, 3,4-dichloroaniline, 4-isopropylaniline, and dicofol. The least degraded, below 30%, are HCHs, endosulphan-sulphate, heptachlors epoxides, and 4,4'-dichlorobenzophenone.
- (ii) Photocatalytic treatment, TiO₂/radiation, achieves a partial removal of the studied pesticides of 48%. When hydrogen peroxide is added the average percentage increases to 57%. The addition of hydrogen peroxide improves the degradation of some of the pesticides studied, mainly isodrin, aldrin, DDTs, 4,4'-dichlorobenzophenone, some triazines, molinate, α -endosulphan, trifluralin, and anilides.
- (iii) TiO₂/radiation treatment produces a reduction of 36% of the initial COD, 43% of the initial toxicity, and chlorine demand is reduced to 1 mg L⁻¹. The same treatment with hydrogen peroxide produces a large increase in toxicity and chlorine demand of the treated sample and there is no variation in the COD due to the generation of intermediate compounds

TABLE 7: % Removal of pesticides by photocatalytic treatments.

Group	Pesticide	Removal after TiO ₂ /radiation (%)	Removal after TiO ₂ /H ₂ O ₂ /radiation (%)
Triazines	Simazine	45	50
	Atrazine	35	40
	Propazine	35	40
	Terbuthylazine	50	50
	Prometon	45	45
	Ametryn	55	55
	Prometryn	55	55
	Terbutryn	55	60
	Desethylatrazine	35	40
Organic phosphorated	Parathion methyl	90	90
	Parathion ethyl	55	55
	Chlorpyrifos	80	80
	Chlorfenvinfos	40	55
	Dimethoate	55	60
HCHs	α -HCH	20	20
	β -HCH	15	15
	χ -HCH	15	20
	δ -HCH	15	15
HCB	Hexachlorobenzene	35	35
Heptachlors	Heptachlor	50	50
	Heptachlor epoxide A	30	30
	Heptachlor epoxide B	30	30
Endosulphans	α -Endosulphan	90	100
	Endosulphan-sulphate	5	10
Drins	Endrin	50	50
	Dieldrin	30	30
	Isodrin	60	100
	Aldrin	55	95
DDTs	pp'-DDE	40	70
	pp'-DDD + op'-DDT	35	80
	pp'-DDT	20	70
Anilines	3,4-Dichloroaniline	100	100
	4-Isopropylaniline	100	100
Ureas	Isoproturon	85	85
	Diuron	75	75
Carbamate	Molinate	55	70
Nitroderivate	Trifluralin	55	70
Anilides	Alachlor	50	65
	Metholachlor	50	60
	Methoxychlor	55	75
Chlorophenols	Tetradiphon	40	40
	Dicofol	90	90
Chlorinated diphenyl	4,4'-Dichlorobenzophenone	5	30
Average		48	57

(no mineralization) that can be more toxic than the original.

- (iv) Both the studied photocatalytic processes produce a reduction of turbidity and of the solids in suspension in the treated samples.

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References

- [1] "Royal Decree 140/2003 de 7 de febrero, por el que se establecen los criterios sanitarios de la calidad del agua de consumo humano," BOE 54 de 21 de febrero de 2003.
- [2] Royal Decree 1620/2007 of 7 December 2007, which establishes the legal category for the reuse of purified water, Bulletin Official of the State 294, of 8 December 2007.
- [3] "Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008, on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council," Official Journal of the European Union L 348/84, 2008.
- [4] G. R. Peyton and W. H. Glaze, "Destruction of pollutants in water with ozone in combination with ultraviolet radiation. 3. Photolysis of aqueous ozone," *Environmental Science and Technology*, vol. 22, no. 7, pp. 761–767, 1988.
- [5] S. J. Masten and S. H. R. Davies, "The use of ozonation to degrade organic contaminants in wastewaters," *Environmental Science Technology*, vol. 28, no. 4, pp. 181A–185A, 1994.
- [6] E. Evgenidou, E. Bizani, C. Christophoridis, and K. Fytianos, "Heterogeneous photocatalytic degradation of prometryn in aqueous solutions under UV-Vis irradiation," *Chemosphere*, vol. 68, no. 10, pp. 1877–1882, 2007.
- [7] S. Sanches, M. T. Barreto Crespo, and V. J. Pereira, "Drinking water treatment of priority pesticides using low pressure UV photolysis and advanced oxidation processes," *Water Research*, vol. 44, no. 6, pp. 1809–1818, 2010.
- [8] S. F. Chen, Z. Mengyue, and T. Yaowu, "Photocatalytic degradation of organophosphorous pesticides using TiO_2 supported on fiberglass," *Journal of Microchemistry*, vol. 54, pp. 54–58, 1996.
- [9] P. Oancea and T. Oncescu, "The photocatalytic degradation of dichlorvos under solar irradiation," *Journal of Photochemistry and Photobiology A*, vol. 199, no. 1, pp. 8–13, 2008.
- [10] L. Wei, C. Shifu, Z. Wei, and Z. Sujuan, "Titanium dioxide mediated photocatalytic degradation of methamidophos in aqueous phase," *Journal of Hazardous Materials*, vol. 164, no. 1, pp. 154–160, 2009.
- [11] P. N. Moza, K. Hustert, S. Pal, and P. Sukul, "Photocatalytic decomposition of pendimethalin and alachlor," *Chemosphere*, vol. 25, no. 11, pp. 1675–1682, 1992.
- [12] C. C. Wong and W. Chu, "The direct photolysis and photocatalytic degradation of alachlor at different TiO_2 and UV sources," *Chemosphere*, vol. 50, no. 8, pp. 981–987, 2003.
- [13] A. E. Kinkennon, D. B. Green, and B. Hutchinson, "The use of simulated or concentrated natural solar radiation for the TiO_2 -mediated photodecomposition of basagran, diquat, and diuron," *Chemosphere*, vol. 31, no. 7, pp. 8663–8671, 1995.
- [14] T. S. Kim, J. K. Kim, K. Choi, M. K. Stenstrom, and K. D. Zoh, "Degradation mechanism and the toxicity assessment in TiO_2 photocatalysis and photolysis of parathion," *Chemosphere*, vol. 62, no. 6, pp. 926–933, 2006.
- [15] O. Borio, B. M. Gawlik, I. R. Bellobono, and H. Muntau, "Photooxidation of prometryn and prometon in aqueous solution by hydrogen peroxide on photocatalytic membranes immobilising titanium dioxide," *Chemosphere*, vol. 37, no. 5, pp. 975–989, 1998.
- [16] E. Pelizzetti, "Concluding remarks on heterogeneous solar photocatalysis," *Solar Energy Materials and Solar Cells*, vol. 38, no. 1–4, pp. 453–457, 1995.
- [17] S. Malato, P. Fernández-Ibáñez, M. I. Maldonado, J. Blanco, and W. Gernjak, "Decontamination and disinfection of water by solar photocatalysis: recent overview and trends," *Catalysis Today*, vol. 147, no. 1, pp. 1–59, 2009.
- [18] A. D. Eaton, L. S. Clesceri, E. W. Rice, A. E. Greenberg, and M. A. H. Franson, *Standard Methods for the Examination of Water and Wastewater*, 21st edition, 2005.
- [19] UNE-EN Norm 27888:1994. Determinación de la conductividad eléctrica (ISO 7888:1985). Ediciones AENOR.
- [20] ISO Norm 7027:1999. Water quality. Determination of turbidity.
- [21] R. F. P. Nogueira, C. O. Mirela, and W. C. Paterlini, "Simple and fast spectrophotometric determination of H_2O_2 in photo-Fenton reactions using metavanadate," *Talanta*, vol. 66, pp. 86–91, 2005.
- [22] ISO Norm 11348:1999. Water quality. Determination of the inhibitory effect of water samples on the light emission of *Vibrio fischeri* (Luminescent bacteria test).
- [23] EPA Method 525.2. Determination of organic compounds in drinking water by liquid-solid extraction and capillary column gas chromatography/mass spectrometry-Revision 2.0.
- [24] A. G. Rincón and C. Pulgarín, "Photocatalytic inactivation of *E. coli*: effect of (continuous-intermittent) light intensity and of (suspended-fixed) TiO_2 concentration," *Applied Catalysis B*, vol. 44, no. 3, pp. 263–284, 2003.
- [25] H. M. Coleman, C. P. Marquis, J. A. Scott, S. S. Chin, and R. Amal, "Bactericidal effects of titanium dioxide-based photocatalysts," *Chemical Engineering Journal*, vol. 113, no. 1, pp. 55–63, 2005.
- [26] M. Lanao, M. P. Ormad, C. Ibarz, N. Miguel, and J. L. Ovelleiro, "Bactericidal effectiveness of O_3 , $\text{O}_3/\text{H}_2\text{O}_2$ and O_3/TiO_2 on *Clostridium perfringens*," *Ozone Science & Technology*, vol. 30, no. 6, pp. 431–438, 2008.
- [27] A. Riga, K. Soutsas, K. Ntampegiotis, V. Karayannis, and G. Papapolymerou, "Effect of system parameters and of inorganic salts on the decolorization and degradation of Procion H-exl dyes. Comparison of $\text{H}_2\text{O}_2/\text{UV}$, Fenton, UV/Fenton , TiO_2/UV and $\text{TiO}_2/\text{UV}/\text{H}_2\text{O}_2$ processes," *Desalination*, vol. 211, no. 1–3, pp. 72–86, 2007.
- [28] M. Saquib, M. Abu Tariq, M. Faisal, and M. Muneer, "Photocatalytic degradation of two selected dye derivatives in aqueous suspensions of titanium dioxide," *Desalination*, vol. 219, no. 1–3, pp. 301–311, 2008.
- [29] N. Sobana, K. Selvam, and M. Swaminathan, "Optimization of photocatalytic degradation conditions of Direct Red 23 using nano-Ag doped TiO_2 ," *Separation and Purification Technology*, vol. 62, no. 3, pp. 648–653, 2008.
- [30] J. C. Garcia, J. I. Simionato, A. E. C. D. Silva, J. Nozaki, and N. E. D. Souza, "Solar photocatalytic degradation of real textile effluents by associated titanium dioxide and hydrogen peroxide," *Solar Energy*, vol. 83, no. 3, pp. 316–322, 2009.
- [31] M. Qamar, M. Muneer, and D. Bahnemann, "Heterogeneous photocatalysed degradation of two selected pesticide derivatives, triclopyr and daminozid in aqueous suspensions of titanium dioxide," *Journal of Environmental Management*, vol. 80, no. 2, pp. 99–106, 2006.
- [32] W. Bahnemann, M. Muneer, and M. M. Haque, "Titanium dioxide-mediated photocatalysed degradation of few selected organic pollutants in aqueous suspensions," *Catalysis Today*, vol. 124, no. 3–4, pp. 133–148, 2007.
- [33] M. M. Haque and M. Muneer, "Photodegradation of norfloxacin in aqueous suspensions of titanium dioxide," *Journal of Hazardous Materials*, vol. 145, no. 1–2, pp. 51–57, 2007.

- [34] B. G. Kwon, "Characterization of the hydroperoxy/superoxide anion radical formed from the photolysis of immobilized TiO_2 in a continuous flow," *Journal of Photochemistry and Photobiology A*, vol. 199, pp. 112–118, 2008.
- [35] T. Yuranova, O. Enea, E. Mielczarski, J. Mielczarski, P. Albers, and J. Kiwi, "Fenton immobilized photo-assisted catalysis through a Fe/C structured fabric," *Applied Catalysis B*, vol. 49, no. 1, pp. 39–50, 2004.
- [36] A. Bozzi, M. Dhananjeyan, I. Guasaquillo et al., "Evolution of toxicity during melamine photocatalysis with TiO_2 suspensions," *Journal of Photochemistry and Photobiology A*, vol. 162, no. 1, pp. 179–185, 2004.
- [37] E. C. Catalkaya and F. Kargi, "Advanced oxidation treatment of pulp mill effluent for TOC and toxicity removals," *Journal of Environmental Management*, vol. 87, no. 3, pp. 396–404, 2008.
- [38] V. A. Sakkas, P. Calza, M. A. Islam et al., " $\text{TiO}_2/\text{H}_2\text{O}_2$ mediated photocatalytic transformation of UV filter 4-methylbenzylidene camphor (4-MBC) in aqueous phase: statistical optimization and photoproduct analysis," *Applied Catalysis B*, vol. 90, no. 3–4, pp. 526–534, 2009.
- [39] I. K. Konstantinou and T. A. Albanis, "Photocatalytic transformation of pesticides in aqueous titanium dioxide suspensions using artificial and solar light: intermediates and degradation pathways," *Applied Catalysis B*, vol. 42, no. 4, pp. 319–335, 2003.

