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PRE-INDUSTRIAL EXPERIENCE IN SOLAR PHOTOCATALYTIC MINERALIZATION OF REAL WASTEWATERS. APPLICATION TO PESTICIDE CONTAINER RECYCLING

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ABSTRACT

Particulate suspensions of TiO_2 irradiated with natural solar light in a large experimental plant catalyse the oxidation of organic contaminants. The problem in using TiO_2 as a photocatalyst is electron/hole recombination. One strategy for inhibiting e^-/h^+ recombination is to add other (irreversible) electron acceptors to the reaction. In many highly toxic waste waters where degradation of organic pollutants is the major concern, the addition of an inorganic anion to enhance the organic degradation rate may be justified. For better results, these additives should fulfil the following criteria: dissociate into harmless by-products and lead to the formation of $\cdot\text{OH}$ or other oxidising agents. In this paper, we attempt to demonstrate the optimum conditions for the treatment of commercial pesticide rinsates found in the wastewater produced by a pesticide container recycling plant. The experiments were performed in one of the pilot plants of the largest solar photocatalytic system in Europe, the Detoxification Plants of the Plataforma Solar de Almería (PSA), in Spain. After testing ten different commercial pesticides, results show that peroxydisulphate enhances the photocatalytic mineralization of all of them. This study is part of an extensive project focused on the design of a solar photocatalytic plant for decontamination of agricultural rinsates in Almería (Spain).

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KEYWORDS

Peroxydisulphate, pesticides, solar photocatalysis, titanium dioxide.

INTRODUCTION

Various ongoing water-monitoring surveys in the EC and the USA have shown the presence of herbicides (Kopling *et al.*, 1996), some of their metabolites (Meyer and Thurman, 1996) and, to a lesser extent, insecticides (Chiron *et al.*, 1995), in surface and ground water at concentrations ranging from sub- $\mu\text{g/L}$ to mg/L levels. Such levels have aroused public concern and the removal of persistent organic chemicals from water has turned into a pressing ecological problem. As a consequence, research programs to develop technologies for reducing pesticide input into runoff waters have been implemented in the EU. Water pollution from pesticides originates in four major sources: (i) pesticide treatments in agriculture may generate water pollution of up to $10 \mu\text{g/L}$; (ii) rinse water from containers and spray equipment, $10\text{-}100 \text{ mg/L}$; (iii) wastewater from agriculture-related industries, $10\text{-}100 \text{ mg/L}$; (iv) wastewater from pesticide

manufacturing plants, 10-1000 mg/L. Whatever the concentration found, they have to be removed, either to protect our water resources or to achieve drinking water quality.

Developments in the field of the chemical treatment of water have made several oxidative degradation procedures available for the elimination of pesticides: TiO_2/UV , Fenton reagent, O_3 , O_3/UV and $\text{O}_3/\text{H}_2\text{O}_2$. Of these, TiO_2/UV is perfect for use with solar energy but, in spite of the promising laboratory-scale results, this process is still restricted to a few experimental plants (Goswami, 1995). One of these plants is installed at Plataforma Solar de Almería (Spain). This paper is focused on the application of the Solar Photocatalytic Technology to the treatment of commercial pesticide rinsates found in the wastewater produced by a pesticide-container recycling plant, but the results obtained could be applied to any of the previously mentioned (ii-iv) major causes of water pollution by pesticides.

The province of Almería has experienced significant economic growth in the last 15-20 years due to, among other reasons, the widespread installation of greenhouses. This has led to the intensive use of a large variety of pesticides and the accumulation of their plastic containers until it has become an environmental problem. So far, these empty plastic bottles have simply been discarded. Although the amount of product remaining in each bottle after use is minimal, the numbers are so important (around 1.5 million units per year) that they cause high risk to the environment (poisoning of flora and fauna, dumping of these bottles in the sea by floods, water supply contamination by ground filtration, etc). A solution to this problem has come up with the possibility of recycling the plastic bottles for other uses. After selective collection and transport to the recycling plant, the plastic must be washed for processing in order to allow its reutilization. The water used for this becomes contaminated with a mixture of different pesticides and must then be treated to eliminate them. It is in this water detoxification that Solar Photocatalysis intervenes.

MATERIALS AND METHODS

The present paper reports on the photocatalytic behaviour of commercial pesticides in one of the pilot plants (Compound Parabolic Collectors, CPCs) that form part of the largest solar photocatalytic system in Europe, the Detoxification Plants at the Plataforma Solar de Almería (PSA) in Spain. The current configuration of the PSA-CPCs field has 6 modules (collector surface 8.9 m², photoreactor volume 108 L, total plant volume 247 L) mounted on a fixed platform tilted 37° (local latitude). This plant has been operating since 1994 as previously described in detail elsewhere (Malato *et al.*, 1997). The schematic configuration of the system is shown in Malato *et al.* (1996). The 6 modules are connected in series and the water flows directly from one to the other and finally to a tank. A centrifugal pump then returns the water to the collectors. At the beginning of the experiments, with collectors covered, all the chemicals are added to the tank and mixed until constant concentration is achieved throughout the system. Then the cover is removed and samples are collected at predetermined times (t).

Evaluation of Solar UV Radiation

Solar ultraviolet radiation (UV) is an essential parameter for the correct evaluation of data obtained from experiments in a solar- TiO_2 water decontamination pilot plant. A global UV radiometer (KIPP&ZONEN, model CUV3) with typical sensitivity of 264 $\mu\text{Volts W}^{-1} \text{m}^2$, mounted on a platform tilted 37° (the same angle as the CPCs), provides data in terms of incident $W_{\text{UV}} \text{m}^{-2}$, which gives an idea of the energy reaching

any surface in the same position with regard to the sun. The UV_G data measured are sent to a computer where they are stored. Obviously, Solar-UV power varies during experiments, made still more noticeable by clouds. With Eq. 1, combination of the data from several days' experiments and their comparison with other photocatalytic experiments is possible.

$$Q_{UV,n} = Q_{UV,n-1} + \Delta t_n \overline{UV}_{G,n} \frac{A_{CPC}}{V_{TOT}} \quad (1)$$

where t_n is the experimental time for each sample, $\overline{UV}_{G,n}$ is the average UV_G during Δt_n , A_{CPC} is the collector surface, V_{TOT} is the total plant volume and $Q_{UV,n}$ is the accumulated energy (per unit of volume, kJ L^{-1}) incident on the reactor for each sample taken during the experiment. Consequently, when Q_{UV} is used, the reaction rate (r_Q) is expressed in terms of mg per kJoule of UV incident on the collector surface. Sometimes it is necessary to explain the results in terms of illumination time instead of Q_{UV} . For this purpose it may be assumed that the average Solar UV on a perfectly sunny day for 2 hours around noon is about $30 \text{ W}_{UV} \text{ m}^{-2}$. Under these conditions and in the reactor used in this work, 1 kJ/L is equivalent to 6.5 minutes illumination time. When this simplification is used, the illumination time calculated by this procedure is called t_{30W} .

Reagents

All tests have been carried out using commercial products, because the treatment plant must destroy not only active, but any other organic compound contained in the formulation as well, since they also intervene in the process and must obviously be considered. The simulated rinsates were prepared by combining 10 commercial biocides, extensively used in the industrial greenhouses of Almería with an initial Total Organic Carbon (TOC) of 100 mg/L (10% of each formulation). Rhône-Poulenc Rufast® (Acrinathrin, $\text{C}_{26}\text{H}_{21}\text{F}_6\text{O}_5$, 15% w/v), Merck Vertimec® (Avermectine B₁, $\text{C}_{48}\text{H}_{72}\text{O}_{14}$ 1.8% w/v), AgrEvo Thiodan® (Endosulphan- α - β , $\text{C}_9\text{H}_6\text{Cl}_6\text{O}_3\text{S}$ 35% w/v), AgrEvo Dicarzol® (Formetanate, $\text{C}_{11}\text{H}_{16}\text{ClN}_3\text{O}_2$ 50% w/w), Bayer Confidor® (Imidacloprid, $\text{C}_9\text{H}_{10}\text{ClN}_3\text{O}_2$ 20% w/v), Ciba-Geigy Match® (Lufenuron, $\text{C}_{17}\text{H}_8\text{Cl}_2\text{F}_8\text{N}_2\text{O}_3$ 5% w/v), Bayer Tamaron 50® (Methamidophos, $\text{C}_2\text{H}_8\text{NO}_2\text{PS}$ 50% w/v), Dupont Vydate® (Oxamyl, $\text{C}_7\text{H}_{13}\text{N}_3\text{O}_3\text{S}$ 24% w/v), AgrEvo Scala® (Pyrimethanil, $\text{C}_{12}\text{H}_{13}\text{N}_3$ 40% w/v) and AgrEvo Previcur® (Propamocarb, $\text{C}_9\text{H}_{20}\text{N}_2\text{O}_2$ 72.2% w/v). When only one formulation is tested, the amount required to obtain the desired initial concentration is added to the tank at the beginning of the experiment.

The P-25 titanium dioxide catalyst (Degussa) was selected since it is the most widely used in photocatalytic decontamination. The TiO_2 /water mixtures were prepared by adding the powder directly, rapidly obtaining a homogeneous milky suspension (200mg/L). The water used in the pilot plant experiments comes from the PSA Desalination Plant and has an equivalent laboratory quality (Type III-IV ASTM), with a TOC content of a little over ($<0.5 \text{ mg L}^{-1}$). Raw water was used in one test with 10 biocides simulating rinsates. The most important characteristics of this water are: Conductivity 2.0 mS, pH 8.1, HCO_3^- 160 mg/L, Cl^- 575 mg/L and SO_4^{2-} 380 mg/L. The reagent-grade persulphate used as an additional oxidant was applied directly without any prior treatment or purification.

Analytical Determinations.

Simulated rinsates mineralization rates was followed by Total Organic Carbon analysis using direct injection of the slurries into a Heraeus-Foss Electric TOC-2001 (UV-Peroxydisulfate method). This type of analysis is vital for the photodegradation experiments because the presence of other unknown organics makes it crucial

to identify the moment at which no TOC remains and water may be considered decontaminated (Chiron *et al.*, 1997). In some cases, the active ingredient of biocide was analysed with a Hewlett-Packard 1050 HPLC-UV system. Persulphate ($\text{Na}_2\text{S}_2\text{O}_8$) additive has been proven to be a very powerful accelerator of the photocatalytic reaction (Pelizzetti *et al.*, 1991). Sulphates were analysed to find out their concentration, since during photocatalysis $\text{S}_2\text{O}_8^{2-}$ becomes 2SO_4^{2-} . Therefore, once the initial amount of sulphate and the amount at any given moment have been determined, the amount of peroxydisulphate that has been decomposed can also be found, and thereby, the quantity that has to be added. The sulphates were measured by turbidimetry after filtering the samples to remove TiO_2 (EPA Method 375.4).

RESULTS AND DISCUSSION

The first tests were aimed at finding out the behaviour of certain products separately, that is, with bottle residues from only one pesticide in the water. Figure 1 summarises tests carried out with 3 of them. The initial TOC obtained from adding 90 mL of Scala® (40% w/v of pyrimethanil) to 247 L of water is very similar to what would be expected with all the organic content from the pyrimethanil. Hence, 100 mL of Vydate (24% w/v oxamyl) produced a TOC of almost 100 mg L^{-1} , of which only 37 mg L^{-1} come from oxamyl, and the rest come from the formulation. Likewise, with 62 mL of Confidor® (20% w/v imidacloprid) the initial TOC obtained is 130 mg L^{-1} , of which 21 mg L^{-1} of TOC are imidacloprid. As it is impossible to find out the rest of the compounds in these formulations, because the manufacturers refuse to reveal them, they must be considered potential contaminants which the treatment must eliminate.

In Figure 1B, active ingredient of biocide may also be observed to disappear very rapidly in comparison with the TOC (Figure 1A). 38 kJ/L ($t_{30\text{W}} = 5.8 \text{ h}$) are required to eliminate 50 mg L^{-1} of imidacloprid, 85 kJ/L ($t_{30\text{W}} = 13.1 \text{ h}$) for 120 mg L^{-1} of pyrimethanil and 83 kJ/L ($t_{30\text{W}} = 12.7 \text{ h}$) for 80 mg L^{-1} of oxamyl. But mineralization of all the organic content in the water is very slow unless persulphate is used. In Figures 1A and B (open dots), the intensifying effect of persulphate is shown. The use of persulphate increases the degradation rate of all organic compounds.

Table 1 shows different parameters to compare the efficiencies in all the experiments with Confidor®, Scala® and Vydate®. $Q_{\text{UV},95\% \text{TOC}}$ is defined as the accumulated energy per unit of volume incident on the reactor necessary to mineralise 95% of the initial TOC. This is used because there is an induction period typical of photocatalysis (see Figure 1A) before TOC abatement due to partial oxidation of the organics (Tahiri *et al.*, 1996). This effect has to be taken into consideration when results are compared and reaction rate only is insufficient. It was not possible to determine $Q_{\text{UV},95\% \text{TOC}}$ experimentally without persulphate because the reaction rate is too slow and the tests would be extremely long. Therefore, this information (Table 1) has been calculated by extrapolating the results shown in Figure 1A for which zero order kinetics has been considered. This is not completely realistic in photocatalysis, because there is a change of order whenever reactant concentration is low (the asymptotic shape of the curves shows it). So to extrapolate TOC degradation using zero order kinetics always yields a lower $Q_{\text{UV},95\% \text{TOC}}$ and this difference is more noticeable without persulphate. In other words, Confidor and Scala are improved at least 3 times and Vydate is improved at least 6 times when persulphate is used. The size of the solar field, which is the most expensive component of a photocatalytic solar plant, is directly related to the reaction rate. So that for the same amount of water, with a certain initial concentration of contaminant, a 3 times smaller collector field would be necessary for Confidor and Scala and 6 times smaller for Vydate.

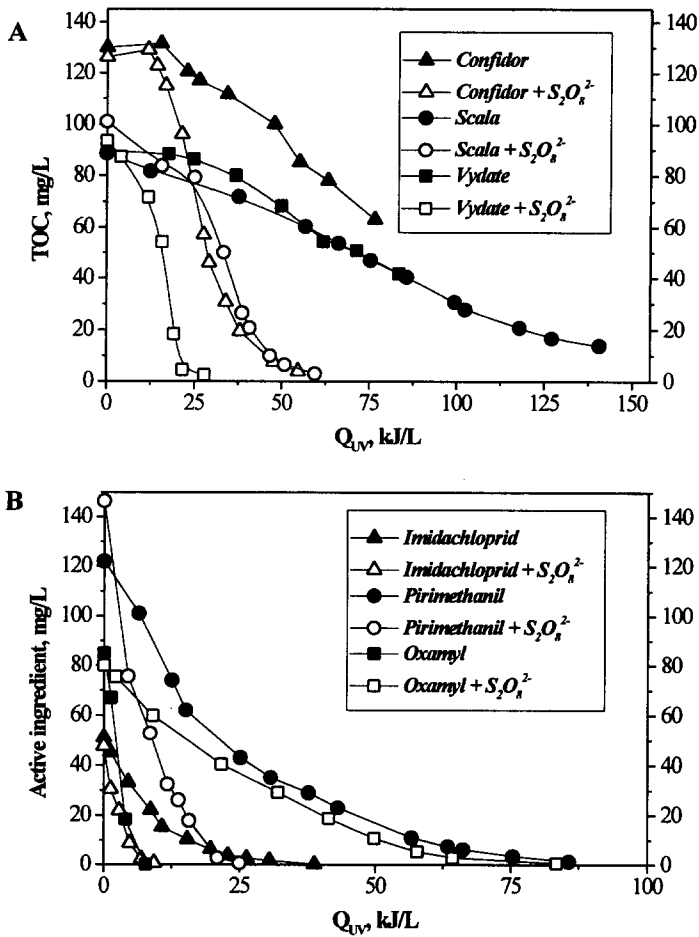


Figure 1. Mineralization of 3 biocides with TiO_2 (200 mg/L) as a function of accumulated solar energy. A: Disappearance of the TOC set at an initial concentration around 100 mg TOC/L. B: Decomposition of the active ingredient of biocide (AI). Open dots correspond to experiments with 10 mM peroxydisulphate.

Table 1. Degradation rates of 3 commercial biocides with and without additional oxidant.

	$Q_{UV,95\%TOC}$, kJ/L	$t_{30W}(95\%TOC)$, min	r_Q (AI), mg/kJ
Confidor	130	845	2.7
Confidor + $S_2O_8^{2-}$	50	325	8.0
Scala	160	1040	4.0
Scala + $S_2O_8^{2-}$	53	345	9.8
Vydate	130	845	1.4
Vydate + $S_2O_8^{2-}$	21	137	11.6

These experiments have demonstrated the viability of the treatment applied to formulations containing biocides and other types of organics. Afterwards it is necessary to demonstrate that the process is effective when applied to complex mixtures of them. Therefore, in order to simplify the study, we have assumed that:

- The organics remaining in the water after the washing process is determined by on-line TOC analysis.
- The design concentration of organics in the water before photocatalytic treatment has been set at TOC = 100 mg/L. The water is reused until this concentration is reached.
- The formulations selected are sufficiently representative of all those used in Almería greenhouses.

For this purpose, a test was prepared with the ten pesticides mentioned above. Thus the total TOC, containing 10% of each one of the formulations was 100 mg L⁻¹. With these assumptions, degradation experiments were performed using the same conditions described for the previous test, the results of which are presented in Figure 2.

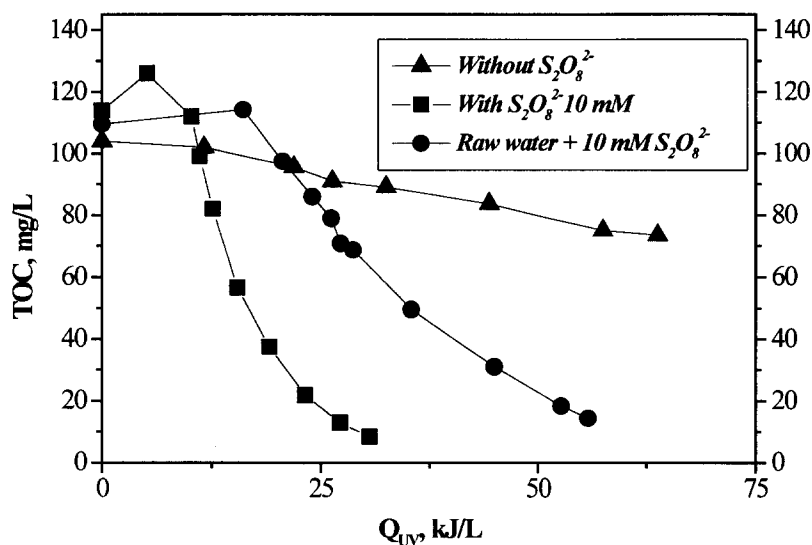


Figure 2. Mineralization of all the biocides tested (10% TOC from each) with TiO₂ (200 mg/L) as a function of accumulated solar energy. Experiment with raw PSA water is also included.

At first sight, it is evident that the addition of this oxidant is substantially beneficial. An induction period corresponding to 12 kJ/L is obtained with peroxydisulphate and around 25 kJ/L without it, after which the total organic carbon is transformed into CO₂. After this, the TOC curve slopes sharply towards 0 in the presence of 10 mM peroxydisulphate, suggesting that the additive strongly accelerates degradation of intermediates. This leads to a very important reduction (at least 6 times) of the energy necessary for total mineralization. This reduction would also reduce the solar collector surface necessary to degrade the organics in the process water by the same factor. The size of the photoreactor is the most important barrier to solar photocatalysis commercialisation. It has been demonstrated that the reaction rate is not critically shortened by the use of normal water, despite the highly saline raw water at the PSA. The mineralization rate is 2 times higher with distilled water than with raw water.

The total volume of water was about 250 L and the collector used is 9 m². From these data and the degradation rate of the TOC (in tests using raw water with persulphate), the capacity of the treatment plant could be calculated in the following manner:

$$t_{30W} = Q_{UV,95\%TOC} \times 6.5 \text{ min}; \quad \text{Treatment capacity} = \frac{(\Delta\text{TOC}) V_{\text{TOT}}}{A_{\text{CPC}} t_{30W}} \quad (2)$$

As example:

$$Q_{UV,95\%TOC} = 60 \text{ kJ/L} \longrightarrow t_{30W} = 390 \text{ min} \xrightarrow[250 \text{ L}; 9 \text{ m}^2]{\Delta\text{TOC} = 114 \text{ mg/L}} \text{Treatment capacity} = \frac{8.0 \text{ mg TOC}}{\text{min m}^2}$$

This factor, calculated with an average intensity of 30 W_{UV} m⁻², will be very useful for extrapolating the experimental results to other volumes and different environmental conditions. The average yearly UV radiation at the PSA is 18.6 W_{UV} m⁻² (sunny hours about 4380 h year⁻¹). Considering TOC to be 50% of the total weight, the average yearly treatment capacity in this case would be approximately:

$$\frac{16.0 \text{ mg}}{\text{min m}^2} \times \frac{18.6 \text{ Wm}^{-2}}{30 \text{ Wm}^{-2}} \times \frac{4380 \text{ sun hours}}{\text{year}} \times 60 \times 10^{-6} = 2.6 \text{ kg m}^{-2} \text{ year}^{-1}$$

More tests must be carried out to optimise the process, but, directly used, the results can give an idea of the size of the treatment plant. According to 1995 data, 1.5 million plastic pesticide bottles were emptied in the province of Almería. Experiments determining the residues remaining in empty bottles have been carried out at the PSA. If the bottles are not rinsed, approximately 1 gr. per bottle (1500 kg of pesticides per year) remains. But if the bottle is rinsed once, which is not unusual due to the high cost of the product, the residue becomes 0.1 gr per bottle (150 kg per year). So, the treatment plant would have a collector surface of between 600 and 60 m², if we managed to collect all the bottles generated in the province of Almería. It has been proven that bottle rinsing is essential, because the wastewater effluent can be reduced up to ten times. If the treatment plant were located in an area with sun conditions similar to PSA, the average yearly UV radiation would also be the same. Treatment costs are not examined here because much more experimentation is needed to optimise the pesticide wastewater treatment. Our results have demonstrated that one way to markedly enhance the TiO₂ photocatalytic degradation of organic pollutants in water is to add an efficient (S₂O₈²⁻) electron acceptor to the system.

CONCLUSIONS

The detoxification of water contaminated by pesticides (usually at low-medium concentrations, but highly toxic) is a field where solar photocatalysis could be applied in the future. But effluents are never contaminated by pure pesticides because they are not marketed that way. Therefore, the decontamination procedure has to be analyzed by an appropriate method. TOC analysis is highly recommendable because of its versatility and, at the same time, its suitability for "on-line" treatment plant installations.

The use of additional oxidants is recommendable when the organic content of the water is relatively high and/or the mineralization rate is low. For better results, these additives should fulfil the following criteria: dissociate into harmless by-products and lead to the formation of •OH or other oxidising agents. Peroxydisulphate fits these conditions quite well and is a cheap, widely used chemical. It enhances the degradation rate of a mixture of 10 commercial biocides dissolved in water (100 mg TOC/L) by a factor of 6 compared to TiO₂ alone. This permits an important reduction in treatment cost because photoreactor

dimensions are directly related to the mineralization rate. When the major concern is to mineralise the organic pollutants, the use of an additional oxidant is perfectly justified.

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