

## RESEARCH AND ENVIRONMENTAL ISSUES IN THE 1990S

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### Summary

This chapter summarizes part of the research carried out at Plataforma Solar de Almería related with solar photocatalytic degradation of water contaminants. A description is given of how solar photocatalysis could become a significant segment of the wastewater treatment technologies related with the degradation of very persistent toxic compounds. It outlines the decomposition of organic and inorganic contaminants and different examples are also given for better comprehension of the ability of solar energy for carrying out oxidation and reduction processes.

These examples include chlorophenols, chlorinated solvents, pesticides and cyanide at concentrations of tens of milligrams per liter. Moreover, commercial formulations of pesticides have been tested and the degradation of the active ingredient at the same time that the coadjutants have been demonstrated. All of them have been successfully converted by solar-TiO<sub>2</sub> photocatalysis to harmless products. Besides, the possibility of using the Photo-Fenton reaction illuminated with solar light opens the possibility where solar photocatalysis could be applied to wastewater with higher contaminant concentration. Application of Photo-Fenton to pesticidal and olive mill wastewaters is presented.

A new photoelectrochemical reactor (in which the photoanode has a cylindrical form) installed in a solar collector is presented. By applying an external anodic bias to a thin TiO<sub>2</sub> layer deposited on a conducting substrate, the recombination between the

photogenerated charge carriers can be suppressed and thus the quantum efficiency enhanced and the separation of the catalyst after the treatment avoided.

## 1. Introduction

Environmental pollution is a pervasive problem with widespread ecological consequences. Decontamination of drinking water is mainly by procedures that combine flocculation, filtration, sterilization and conservation, to which a limited number of chemicals are added. Normal human sewage water can be efficiently treated in conventional biological processing plants. But very often, these methods are unable to reduce the power of the contaminant. In these cases, some form of advanced biological processing is usually preferred in the treatment of effluents containing organic substances. Biological treatment techniques are well established and relatively cheap. However, these methods are susceptible to toxic compounds that render the waste degrading microorganisms inactive. An alternative to air stripping and adsorption on granulated activated carbon, merely transferring toxic materials from one medium to another, is not a long-term solution to the problem of loading hazardous waste on the environment. Incineration is capable of converting toxic compounds to carbon dioxide, water and inorganic acids, but unfavorable public perception has slowed and very often prevented its implementation. Concerns over emissions of undestroyed components and organic products of incomplete combustion have caused incineration to be a source of continuing controversy. To solve this problem, apart from reducing emissions, two main water treatment strategies are followed: (i) chemical treatment of drinking water, contaminated surface and groundwater and (ii) chemical treatment of waste waters containing non-biodegradable compounds.

This type of treatment is suitable when a biological processing plant cannot be adapted to certain types of pollutants that did not exist when it was designed. In such cases, a potentially useful approach is to partially pre-treat the toxic waste by oxidation technologies to produce intermediates that are more readily biodegradable. Light can be used, under certain conditions, to enable chemicals to break down the pollutants to harmless by-products. Light can have a dramatic effect on a molecule or solid, because, when it absorbs light, its ability to lose or gain electrons is often altered. This electronically excited state is both a better oxidizing and a better reducing agent than its counterpart ground state. Electron transfer processes involving excited-state electrons and the contact medium (for example water) can therefore generate highly reactive species like hydroxide ( $\bullet\text{OH}$ ) radicals. This radical is strongly oxidative ( $E^\circ=2.8$  V), much greater than other traditional oxidants (e.g. ozone: 2.07 V, hydrogen peroxide: 1.78 V, chloride dioxide: 1.57, chlorine: 1.36 V, etc.). These can then be used to chemically decompose a pollutant into harmless end products. Alternatively, light can be used directly to break up pollutant molecule bonds photolytically. These processes are called Advanced Oxidation Processes (abbreviated as AOPs). Many oxidation processes, such as  $\text{TiO}_2/\text{UV}$ ,  $\text{H}_2\text{O}_2/\text{UV}$ , Photo-Fenton and ozone processes ( $\text{O}_3$ ,  $\text{O}_3/\text{UV}$ ,  $\text{O}_3/\text{H}_2\text{O}_2$ ) are currently employed for this purpose.  $\text{TiO}_2/\text{UV}$  and Photo-Fenton are of special interest since they can use solar light.

The Solar Department of CIEMAT-DER (Renewable Energy Department) and the Plataforma Solar de Almería (PSA), main research center of DER and the largest

European facility on Solar Energy Applications, have been participating in the chemical application to water solar detoxification since 1990, in particular in projects of photocatalytic decontamination of used water, both at national and international levels. The experience acquired with solar detoxification systems at the engineering level, led to the development and the installation at PSA of the largest European Solar Detoxification Facility at pilot plant scale that has been successfully used by many European Research Institutions. It is expected that this work will illustrate the cross-linked synergistic relationships that have been developed between the different European Research Groups involved in the PSA photocatalysis research program during the last few years.

## 2. Solar-TiO<sub>2</sub> Photocatalytic Treatment of Chlorophenols

Phenols are highly toxic pollutants present in the aqueous effluents of the wood and paper and other chemical industries that produce this organic as an intermediate product. Chlorinated phenols have been used as insecticides, antiseptics and disinfectants, and have been found in drinking water following chlorination. As a result of the toxicity of these compounds, the US Environmental Protection Agency has included them in the Priority Pollutant list. Different chlorophenols have been successfully degraded by photocatalysis and 4-chlorophenol, 2,4-dichlorophenol and pentachlorophenol has been selected to be presented here as representative of this family of Priority Pollutants. The chlorophenols have been tested at around 20 mg L<sup>-1</sup> using TiO<sub>2</sub> slurries (200 mg L<sup>-1</sup>) in a 2-axis parabolic trough photoreactor (see Figure 5 of *Solar Photocatalysis*, total volume 260 L, total solar collector surface 32 m<sup>2</sup>).

Figure 1 shows the degradation of these three typical contaminants as function of the energy incident inside the photoreactor. According to Eq. (16) in *Photochemical Conversion of Solar Energy*, the value of  $I_E^*$  was given in moles of photons L<sup>-1</sup> s<sup>-1</sup>, as calculated from the measurements of UV radiation. As radiation data was collected over certain periods of time, it is very easy to gather the average incident radiation in the reactor, in any time range, and use that average in this equation. It is possible to find the amount of photons collected in the reactor (per unit of volume) from the start up of the experiment until each sample is collected:

$$E_{hv,n} = E_{hv,n-1} + \Delta t_R I_{E,n}^* \quad (1)$$

$$\Delta t_R = t_{R,i} - t_{R,i-1}$$

where  $t_{R,i}$  is the time each sample has been illuminated,  $E_{hv}$ , is the energy accumulated (per unit of volume, moles of photons L<sup>-1</sup>) inside the reactor for each sample taken during the experiment and  $I_{E,n}^*$  are the moles of incident photons corresponding to the average UV radiation during the sampling period.

As observed in Figure 1, the chlorophenols disappear completely at a very similar rate. However, many new organic compounds appear and the TOC behavior is different. An induction period is followed by transformation of the total organic carbon into CO<sub>2</sub>. During this induction period the chlorophenols produce more oxidized substances, but these are not mineralized. Mineralization only occurs when the last step of the oxidation

process yields  $\text{CO}_2$ . In the case of 2,4-dichlorophenol the effect is more evident, when  $E_{hv} = 0.05$  moles of photons  $\text{L}^{-1}$  the initial compound has been completely destroyed (solid squares, Figure 1) but at least 50 % of the organic carbon still remains (open squares, Figure 1).

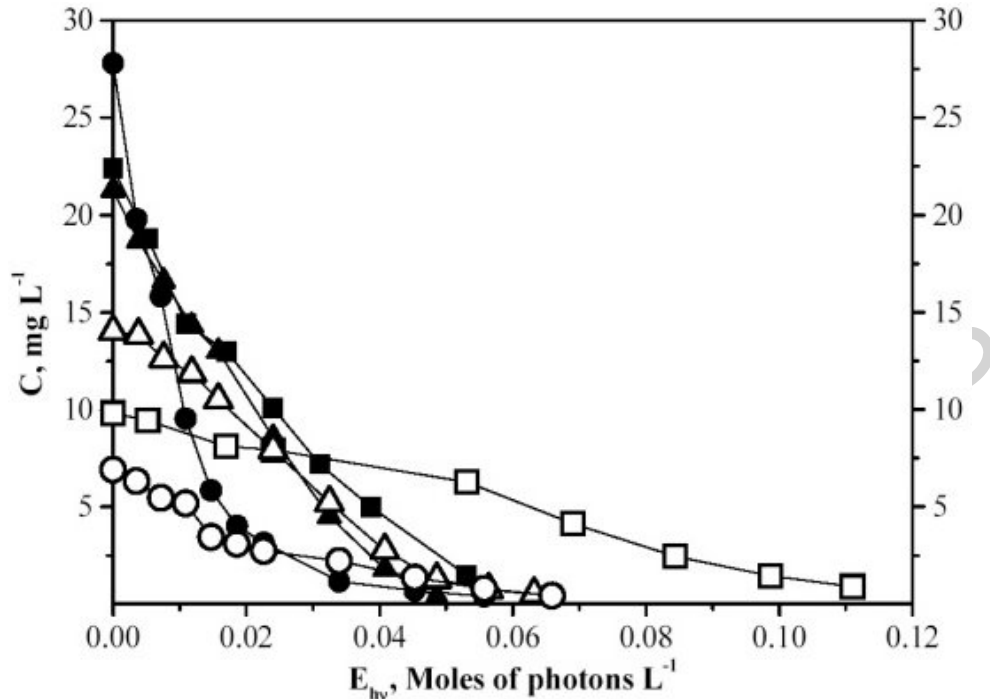


Figure 1. Solar photocatalytic degradation of 4-chlorophenol (CP, ▲), 2,4-dichlorophenol (DCP, ■) and pentachlorophenol (PCP, ●) with a catalyst amount of  $0.2 \text{ g L}^{-1}$ . TOC corresponding to each compound is also shown (open symbols).

It is necessary to relate the mineralization reaction rate with the solar photon flux reaching the collector surface. The process efficiency could be explained in terms of grams of mineralized TOC per mol of photons incident inside the photoreactor. In this case, the efficiency (including the induction period) is  $0.117 \text{ g}$ ,  $0.09 \text{ g}$  and  $0.233 \text{ g}$  of TOC per mol of photons for PCP, DCP and CP respectively. The total volume of water was  $260 \text{ L}$  and the collector used was  $32 \text{ m}^2$ . From these data and the degradation of the TOC the capacity of the treatment plant could be calculated. 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,  $4.14$  moles of photons are equivalent to 1-hour illumination time.

Therefore, the “mineralization treatment capacity” of the photoreactor for each chlorophenol and  $\text{m}^2$  of radiation collecting surface are:  $0.015 \text{ g}$  of TOC (PCP),  $0.012 \text{ g}$  of TOC (DCP) and  $0.030 \text{ g}$  of TOC (CP) per hour and square meter. Recalculating for each chlorophenol considering the molecular weight of each one:  $0.055 \text{ g}$  of PCP  $0.027 \text{ g}$  of DCP and  $0.053 \text{ g}$  of CP per hour and square meter. The treatment capacity, calculated with an average intensity of  $30 \text{ W}_{UV} \text{ m}^{-2}$ , will be very useful for extrapolating the experimental results to other volumes and different environmental conditions. The average yearly UV radiation at the Plataforma Solar de Almería is  $18.6 \text{ W}_{UV} \text{ m}^{-2}$  (sunny

hours about 4380 h year<sup>-1</sup>). The average yearly treatment capacity in the case of PCP would be approximately:

$$\frac{55 \text{ mg}}{\text{h m}^2} \times \frac{18.6 \text{ Wm}^{-2}}{30 \text{ Wm}^{-2}} \times \frac{4380 \text{ sun hours}}{\text{year}} \times 10^{-6} = 0.15 \text{ kg of PCP m}^{-2} \text{ year}^{-1}$$

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### Biographical Sketches

**Sixto Malato** Dipl. Chemistry (Chemical Engineering) by *Facultad de Ciencias of University of Granada* (1987). Master in Environmental Sciences by the *Instituto de Investigaciones Ecológicas* (Málaga, 1994).

PhD in Chemical Engineering at the *University of Almería* (1997). 14 years of experience having worked at different sectors. His professional activities started in 1987 as Junior Researcher in Chem. Eng. Department of Univ. of Almería; in 1988 he joined the Production Department in an oil refinery (REPSOL S.A.) in Puertollano (Spain).

Since 1990 he works at the Plataforma Solar de Almería (PSA-CIEMAT) in all the EU R&D projects linked to the Solar Detoxification of water. Concretely, he has been involved in 6 EU, 7 National R&D Projects and 5 R&D Contracts (with Private Companies) related with wastewater treatment. He was involved in the design and construction of the three pilot plants for experimentation in solar detoxification of industrial waste waters existing in Europe.

He is author of 1 book, co-author of other 2 books, 40 international publications in refereed journals, 80 contributions to 49 different International Congress and Symposiums (15 of them personally presented), 17 contributions to 13 different National Symposiums, 11 technical journals. Also, he has directed 1 PhD Thesis and participated as teacher in 7 courses related with Advanced Wastewater Treatment.

**Julian Blanco Gálvez** Dipl. Industrial Engineer by the *Escuela Superior de Ingenieros* (Seville, 1984), and Master in Environmental Sciences by the *Instituto de Investigaciones Ecológicas* (Málaga, 1994) has 16 years of experience having worked at different industrial sectors. His professional activities started in 1985 as Production Manager in a machinery assembly factory in Gerona (Spain); in 1988 he joined the engineering department of the American multinational electrical company AMP Inc. in Barcelona (Spanish branch). During 1989 he was also consultant of Spanish Normalization Institution AENOR.

Since 1990 he works at the Plataforma Solar de Almería (PSA-CIEMAT) in R&D projects linked to the solar and environmental areas. He was the project leader for the design and construction of the first pilot plant for experimentation in solar detoxification of industrial wastewaters existing in Europe (E.U. DGXII Direction C Project nº BRPR-CT97-0424.). Besides, he has been involved in 7 EU, 9 National R&D Projects and 5 R&D Contracts (with Private Companies) related with wastewater treatment.

In 1993 he became the leader of PSA Solar Chemistry department. Since 1994 he is the head of the Solar Chemistry Area of CIEMAT, being several scientific installations in Almería and in Madrid under his responsibility. In 1995 he became the Spanish National Representative in the Task II group of IEA-SolarPACES.

He is co-author of 2 books, 13 specific technical reports, 28 international publications and 64 contributions to National and International Congress and Symposiums (19 of them personally presented), up to date. Also, he has participated as teacher in 12 courses and has given multiple lectures in conferences and seminars.