RECENT RESEARCH AND ENVIRONMENTAL ISSUES

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 shown 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 destroyed by solar–TiO_2 photocatalysis to non-harmful products. Besides, the possibility of using the Photo-Fenton reaction illuminated with solar light opens the boundary where solar photocatalysis could be applied to wastewater with higher contaminant concentration. Application of Photo-Fenton to pesticidal and olive mill wastewater is presented.

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3.1. INTRODUCTION

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 on 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.

3.2. SOLAR-TIO_2 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^{-1} using TiO_2 slurries (200 mg L^{-1}) in a 2-axis parabolic trough photoreactor (see Chapter 4).

Figure 3.1 shows the degradation of these three typical contaminants as function of the energy incident inside the photoreactor. The value of I^*_E was given in moles of photons L^{-1} s^{-1}, as calculated from the measurements of UV radiation. As radiation data was collected every certain period 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 (see Eq. 2.12):

$$E_{h\nu,n} = E_{h\nu,n-1} + \Delta t_R \, I^*_{E,n}$$
$$\Delta t_R = t_{R,i} - t_{R,i-1} \qquad (3.1)$$

where $t_{R,i}$ is the time each sample has been illuminated, $E_{h\nu}$ is the energy accumulated (per unit of volume, moles of photons L^{-1}) 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.

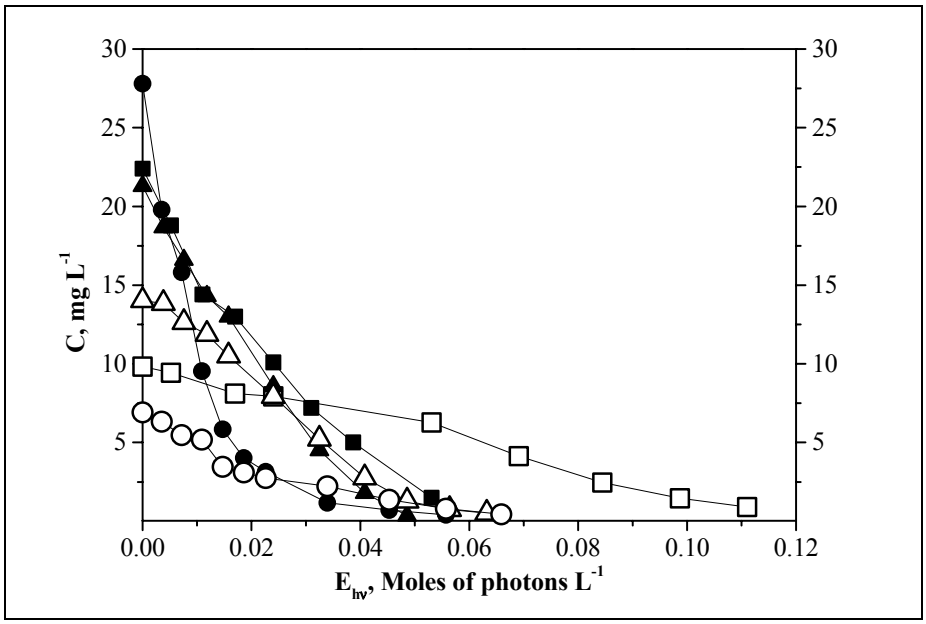

Figure 3.1. *Solar photocatalytic degradation of 4-chlorophenol (CP, ▲), 2,4-dichlorophenol (DCP, ■) and pentachlorophenol (PCP, ●) with a catalyst amount of 0.2 g L^{-1}. TOC corresponding to each compound is also shown (open symbols).*

As observed in Figure 3.1, 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_2. 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 CO_2. In the case of 2,4-dichlorophenol the effect is more evident, when $E_{h\nu}$ = 0.05 moles of photons L^{-1} the initial compound has been completely destroyed (solid squares, Figure 3.1) but at least 50 % of the organic carbon still remains (open squares, Figure 3.1). 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 g, 0.09 g and 0.233 g of TOC per mol of photons for PCP, DCP and CP respectively. The total volume of water was 260 L and the collector used was 32 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 W_{UV} 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 m^2 of

radiation collecting surface are: 0.015 g of TOC (PCP), 0.012 g of TOC (DCP) and 0.030 g of TOC (CP) per hour and square meter. Recalculating for each chlorophenol considering the molecular weight of each one: 0.055 g of PCP 0.027 g of DCP and 0.053 g of CP per hour and square meter. The treatment capacity, 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 Plataforma Solar de Almería is 18.6 W_{UV} m^{-2} (sunny hours about 4380 h $year^{-1}$). The average yearly treatment capacity in the case of PCP would be approximately:

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

3.3 SOLAR-TIO_2 PHOTOCATALYTIC TREATMENT OF PESTICIDES

The contamination of soil, surface water and ground water with mixtures of pesticides has received considerable attention. Such chemicals are included in several pollutant priority lists owing to their widespread use and strong toxicity. Water-monitoring surveys in the EC and the USA have shown the presence of herbicides and their metabolites in surface and ground water at concentrations ranging from sub-μg to mg L^{-1} levels. In any case, the danger limits of the ecotoxicological parameters used to determine the possible effects on aquatic organisms (e.g. LC_{50}) are usually very far above actual pesticide concentrations due to nature's strong power of dilution. On the other hand, once rivers or groundwater have already been contaminated, the solution is very expensive and very often even impossible, because of a lack of treatment methods for wastewater with low concentrations (in the range of μg L^{-1}) of pesticides.

Such levels have aroused public concern and the removal of persistent organic chemicals from water has turned into a pressing ecological problem. Their persistence in natural waters has led to a search for a highly effective method to mineralize them into environmentally compatible compounds. It should be noted that the microbial purification of water polluted by organic micropollutants at parts-per-million levels is extremely difficult, as biodegradation is quite inefficient at low substrate levels. It is also known that pesticides are toxic for many of the bacteria used in biological wastewater treatment. Unlike the low level contamination involved in drinking water, waste water from agricultural or industrial activities may be highly contaminated. Water pollution from pesticides originates in four major sources: (i) pesticide treatments in agriculture may generate water pollution of up to 10 μg L^{-1}; (ii) rinse water from containers and spray equipment, 10-100 mg L^{-1}; (iii) wastewater from agriculture-related industries, 10-100 mg L^{-1}; (iv) wastewater from pesticide manufacturing plants, 10-

1000 mg L^{-1}. It must be noted that the first point leads to widely-dispersed pollution while the other three points lead to well-defined sites at typical concentrations of around 10-100 mg L^{-1} of pesticides. Whatever the concentration found, they have to be removed, either to protect our water resources or to achieve drinking water quality. The main characteristics of this wastewater are its extreme toxicity, low volume and well-defined location. Suitable treatment is therefore required to prevent it, which is easier than cleaning up the environment afterwards. Such point sources of pollution may be ideally treated in small-scale treatment units.

In the Mediterranean area intensive agriculture of greenhouses consumes thousands of tons of pesticides per year. Solar Photocatalysis is a very promising process made even more by the availability of strong sunlight throughout the year as a cheap energy source in this region. By employing sunlight, the common drawback of the relatively high cost of UV-lamps and electricity can be overcome. Thus the availability of sunlight and the lack of other alternatives justify the application of a new technology that has not yet been evaluated on an industrial scale.

Three specific pesticides (imidacloprid, pyrimethanil and formetanate technical grade, purity higher than 95%) have been tested as model substrates at around 50 mg L^{-1} using TiO_2 slurries (200 mg L^{-1}) in a CPC photoreactor with a total volume of 247 L and a solar collector surface 9 m^2 (see Chapter 4). The model wastewater was prepared by adding the appropriate pesticide amount to distilled water. The same procedure was used for all the experiments carried out with pesticides commented below. The chemical structure of the pesticides selected and their photocatalytic degradation is illustrated in Figure 3.2, where the degradation is plotted as a function of the amount of energy, supplied by irradiation from the sun (UV-range of the solar spectrum), per volume of the illuminated reactor unit. The values of E were calculated from the irradiance data, by using the following procedure. In this case a radiometer mounted at the same angle as the solar collector is always necessary for data evaluation. This radiometer sends a signal to a computer in which the data are stored. This method is a mathematical approach for the treatment of such data obtained in real solar experiments using a relationship between experimental time (t), plant volume (V_t), collector surface (A_r) and the radiant power density (Q = W m^{-2}) measured by the radiometer. As radiation data are collected continuously, it is very easy to calculate the average incident radiation on the collector surface (I), for each period of t, and apply Eq. 3.2 to that average. Consequently, the amount of energy collected by the reactor (per unit of volume) from the start of the experiment until each sample is collected may be found by:

$$E_n = E_{n-1} + \Delta t_n \overline{\overline{Q}}_n \frac{A_r}{V_t} \qquad (3.2)$$

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

where t_n is the experimental time at which each sample was taken and E_n is the accumulated energy (per unit of volume, kJ L^{-1}) incident on the reactor for each sample taken during the experiment. Although the accumulated energy is expressed in terms of kJ L^{-1}, it corresponds to energy reaching the collector surface and therefore, the collector efficiency (ratio A_r/V_t, collector reflectivity and photoreactor trasmissivity) is included in it. Consequently, when *E* is used, the reaction rate (*ΔC/ΔE*) is expressed in terms of grams (or moles) per kJoule of light incident on the entire collector surface. If reaction rate is expressed in these units, collector efficiency is already included in it through the use of incident surface radiation, since different reaction rates with the same substance and different solar collectors mean collector efficiency is different.

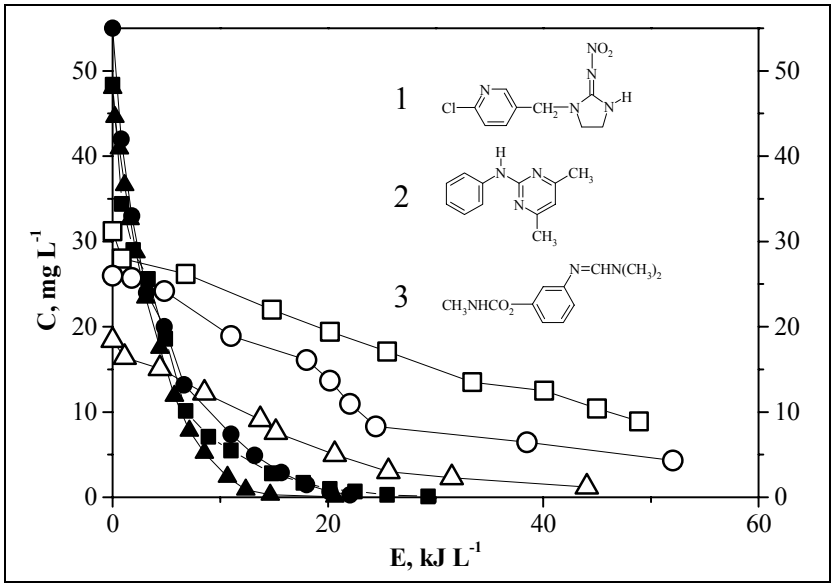

Figure 3.2. *Solar photocatalytic degradation of imidacloprid (1, ▲), pyrimethanil (2, ■) and formetanate (3, ●) with a catalyst amount of 0.2 g L^{-1}. TOC corresponding to each pesticides is also shown (open symbols).*

The total disappearance of all pesticides is obtained for an energy input of near 20 kJ/L (around 3 hours of solar irradiation) but the TOC disappearance of each one presents a different behavior. Two different effects produce this. One is the different TOC content of each one pending on its chemical structure, and the second is related with the different comportment of each one through the degradation pathway. It seems that more persistent intermediates are formed during pyrimethanil degradation because the TOC disappearance is the slowest one. It is important to emphasize that, in practical oxidative degradation, such as those envisaged in water treatment technology, it is not simply the disappearance of the

pollutant that is relevant, but the conversion of all organic carbon into inorganic carbon. The pertinent process is therefore the mineralization of the total organic carbon (TOC), which ensures that the substrate and any intermediate product formed during the process are degraded. Besides, effluents are almost never contaminated by pure pesticides (only in the case "iv" cited before), because they are not marketed in that way. So tests are more realistic when they are carried out with commercial products than with pure compounds. Very often these products contain other organics which have a strong effect on the mineralization process. Therefore, the decontamination procedure must be checked with commercial formulations. The use of commercial formulation permitted a better approach to real decontamination conditions where the presence of inert ingredients affect to the pesticide degradation rate. Figure 3.3 shows an example of this reasoning where commercial formulations of pyrimethanil and imidacloprid are compared with pure compounds.

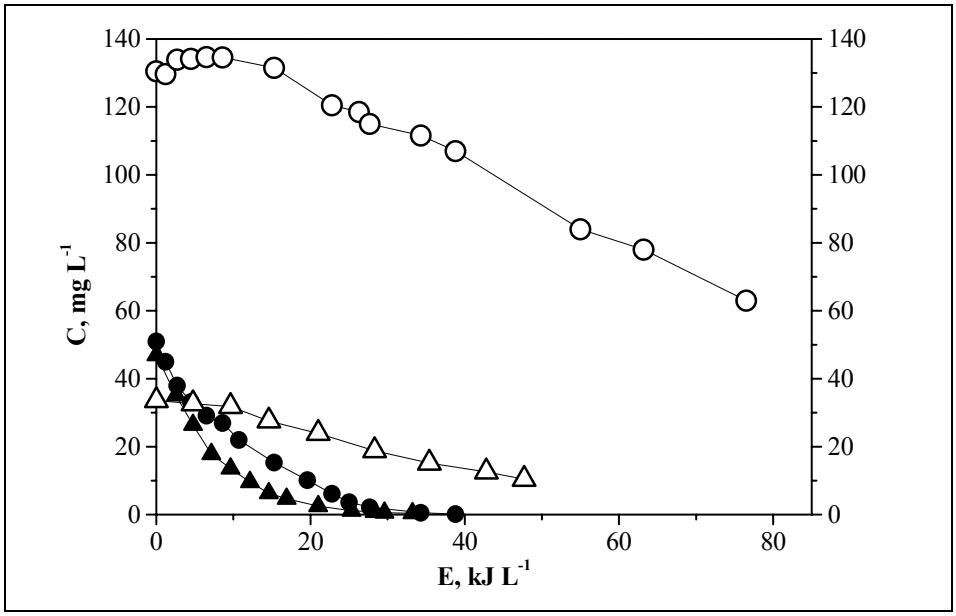

Figure 3.3 *Disappearance of commercial imidacloprid (●) and pyrimethanil (▲) and evolution of Total Organic Carbon (open symbols).*

Bayer Confidor® (Imidacloprid 20% w/v) and AgrEvo Scala® (Pyrimethanil 40% w/v) were used without purification, i.e. all impurities and additives contributed to the total organic carbon (TOC) content. A decrease in the imidacloprid concentration is observed with complete disappearance at around 35 kJ/L but when technical Imidacloprid was used (see Figure 3.2), at the same initial concentration (50 mg L^{-1}), a faster degradation rate was observed achieving total disappearance of imidacloprid after 15 kJ L^{-1}. This fact is a consequence of the competence existing between the pesticide and the formulation components for the reaction with hydroxyl radicals, principal responsible for the initial attack on organic solutes during the photocatalytic process over semiconductor metal oxides. Initial TOC measurements higher than 120 mg L^{-1} in the Confidor (commercial imidacloprid) solution confirmed the presence of a high concentration of additional ingredients

corresponding to the commercial formulation. These compounds produce a high decrease in the mineralization rate. Initial TOC concentration in the case of technical grade was only 20 mg L^{-1} (see Figure 3.2). The total disappearance of commercial pyrimethanil is obtained for an E of ca. 30 kJ L^{-1} at an initial concentration 50 mg L^{-1}. Almost the same result was obtained for the technical product (see Figure 3.2). This similar behavior is explained by the TOC values measured at the beginning of the experiments with commercial and technical pyrimethanil. A good stoichiometric correlation between initial pyrimethanil concentration and initial TOC is observed in both cases. This fact indicates the absence of significant amounts of organic compounds in the commercial solution avoiding any competition between the pesticide and the formulation components for the reaction with hydroxyl radicals.

Commercial Product	Active Ingredient	Manufacturer
Rufast	acrinathrin 15%	Rhône-Poulenc
Vertimec	abamectin 1.8 %	Merck
Match	lufenuron 5%	Ciba-Geigy
Tamaron 50	methamidofos 50%	Bayer
Confidor	imidacloprid 20%	Bayer
Vydate	oxamyl 24%	Du Pont
Thiodan	endosulfan α-β 35%	AgrEvo
Dicarzol	formetanate 50%	AgrEvo
Scala	pyrimethanil 40%	AgrEvo
Previcur	propamocarb 72.2%	AgrEvo

Table 3.1. *Information on commercial pesticides used in the 10 pesticides mixtures experiments.*

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, which is the most usual situation found in the case "ii" and "iii" commented before. Since hydroxyl radicals react non-selectively, numerous intermediates are formed en-route to complete mineralization at different concentrations. Furthermore, formulation adjutants may affect the degradation process and, unfortunately, very little information on the effects of adjutants in photocatalysis degradation is available. Because of this, all tests should be carried out using commercial products, because the treatment plants must destroy not only active matter, but any other organic compound contained in the formulation as well. Hundreds of different formulations are currently used it is impossible to carry out experiments with all of them. For this purpose, an example with ten different commercial pesticides is shown in Figure 3.4.

The 10 commercial products selected were chosen because they belong to the most usual pesticide families and/or they have very different chemical structures (see Table 3.1). In all the experiments, the same TOC (e.g. 10 mg L^{-1}) of each pesticide was added to achieve the initial TOC concentration (e.g. 100 mg L^{-1}). For each pesticide the TOC content was determined by pre-experiments. In Figure 3.4, it is possible to see that mineralization, once begun, maintains the same slope until at least 60-70% of the initial TOC has been degraded. As these reactions are not expected to follow simple models like first or zero order kinetics, overall reaction rate constants cannot be calculated. The complexity of the results, of course, is caused by the fact that the TOC is a sum parameter often including several hundred products that undergo manifold reactions. One parameter could be chosen in order to obtain a practical point of comparison for various experiments: the maximum gradient of the degradation curve, which is the gradient of the tangent at the inflection point. It has the unit of a zero-order rate constant (mg/kJ instead of mg/min) and therefore appears to be easy to handle. Furthermore this gradient can be roughly considered as the initial rate of the mineralization reaction, because it is preceded by a period of nearly constant TOC level. This parameter could be referred to as “maximum rate”.

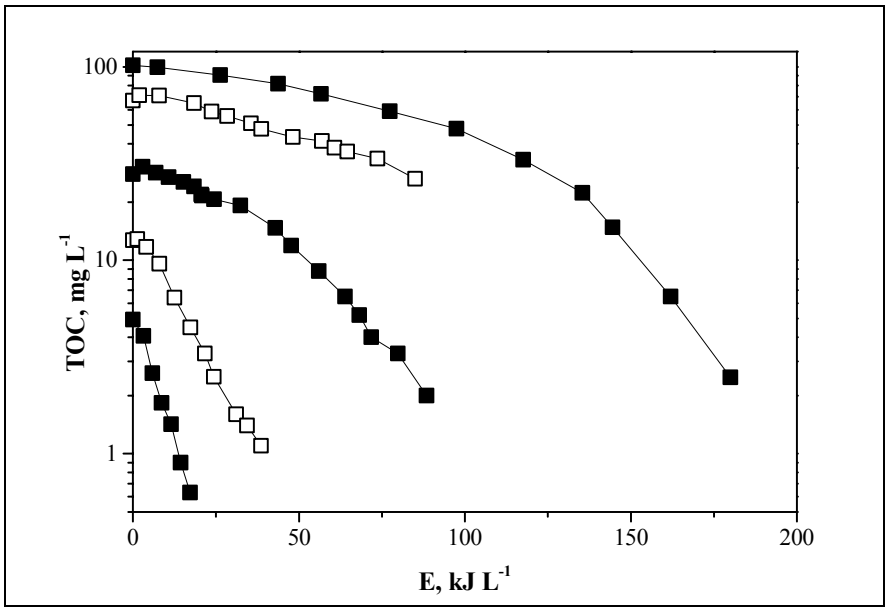

Figure 3.4. *10 commercial pesticides mixture decomposition at different initial concentrations*

3.4. SOLAR-TIO_2 PHOTOCATALYTIC TREATMENT OF NBCS

Many traditional solvents are on environmental "hit list", and the chlorinated ones are facing the big-best challenges; particularly the highly Volatile Organic Compounds (VOCs) have been reduced from many applications and products as the increasing concern about the health effects of VOCs in air and waste water have resulted in a comprehensive attempt to regulate

all sources of VOC emissions. Historically, solvents have been used to mobilize solids preparing them for reactions, to carry particles onto surfaces in coating and then evaporate, and to clean parts and equipment by separating grease and grime and carrying them away. Now industry is minimizing or eliminating solvents to cut hazardous waste costs as well as chemical emissions. C1 and C2 Non Biodegradable Chlorinated hydrocarbon Solvents (NBCS), such as methylene chloride, trichloroethylene, tetrachloroethylene, chloroform, methyl chloroform, etc., are difficult to replace because they have influence in process reaction and are compatible with most substrate materials. Facilities that rely on scrubbers to remove VOCs from air still have a contaminated aqueous solution to treat, and the traditional water-treatment methods (stripping, adsorption by activated carbon, biological treatment, thermal or catalytic oxidation and chemical oxidation) have strong inconveniences or limitations in the treatment of low concentration of organic pollutants (from 20 to 50 mg L^{-1}), in water solution.

Four specific chlorinated solvents (dichloromethane CH_2Cl_2, tetrachloroethylene C_2Cl_4, chloroform $CHCl_3$, and trichloroethylene C_2HCl_3) has been tested as model substrates, including a mixture in the respective ratio of 20, 50, 200 and 50 mg/L respectively. TiO_2 slurries (200 mg/L) have been used in a CPC photoreactor (total volume 39 L, total solar collector surface 3.08 m^2). The mechanism of degradation of C1 halogenated compounds has extensively studied, leading to the formulation of degradation schemes and to the identification of all major intermediates. The final products of degradation are Cl^-, CO_2, HCOOH, HCHO, Oxalic acid, glyoxilic acid and glyoxal, depending on the degradation time. The evolution of chlorides closely matched the disappearance of TOC, but at long degradation times, when the TOC is not completely abated, the residual organic molecules do not contain bound chlorine. Thus, for the purpose of decontamination, it is not necessary to obtain a complete conversion to CO_2. Toxicity related to chlorinated compounds disappears, as the compounds are completely dechlorinated. Therefore, the appearance of chloride can be used as a parameter to determine the degradation of the NBCS. The degradation of the single compounds are illustrated in Figure 5a, where the rate of degradation is plotted as a function of the amount of energy, supplied by irradiation from the sun (UV-range of the solar spectrum), per volume of the illuminated reactor unit. The values of E were calculated from the irradiance data, by using the procedure explained before (Eq. 3.2).

During these experiments it has been detected that complete dechlorination is not achieved if the reactor is open to the atmosphere because an important lost of NBCS is produced. But a complete degradation is obtained with the reactor completely hermetically sealed. This last produces a defect of dissolved oxygen and, therefore, the degradation must be related with reduction pathways. This can be rationalized by the following equations:

$$TiO_2 \xrightarrow{h\nu} e^- + h^+ \quad (3.3)$$

$$h^+ + H_2O \rightarrow {}^{\bullet}OH + H^+ \quad (3.4)$$

$$e^- + O_2 \rightarrow O_2^{\bullet -} \quad (3.5)$$

When O_2 is present, it accepts the electrons formed after radiation absorption by the catalyst but if O_2 is not present the electrons are free for reduction reactions. These reactions are the responsible of the photocatalytic reduction of the NBCS:

$$CCl_4 + 2e^- + H^+ \rightarrow CHCl_3 + Cl^- \quad (3.6)$$

$$CHCl_3 + 2e^- + H_2O \rightarrow HCOH + 2Cl^- + HCl^+ \quad (3.7)$$

$$CH_2Cl_2 + 2e^- + H_2O \rightarrow CH_3OH + 2Cl^- \quad (3.8)$$

Figure 3.5b shows the degradation of a mixture of all the NBCS at the same concentration than in the individual tests. The effect of the absence or presence of oxygen is very clear. It can be observed that the reaction rate is very similar in both cases, but only in the closed reactor the stoichiometric quantity of chloride is obtained. It can be also observed that the energy (kJ/L) necessary for degrading the mixture is very similar to the sum of the energy of the individual experiments (Figure 3.5a).

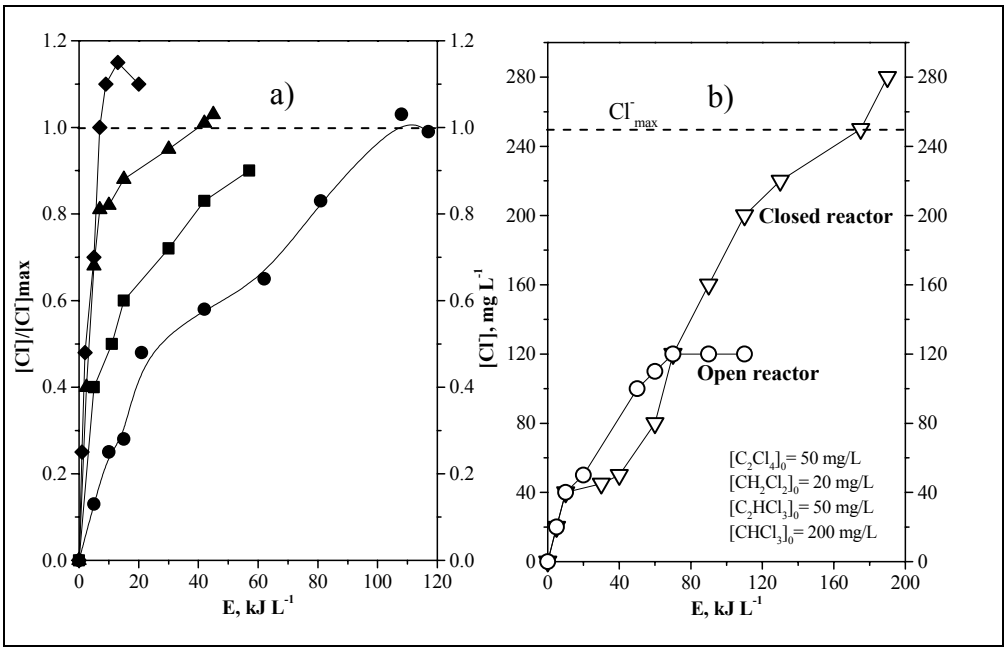

***Figure 3.5**. (a) Dechlorination of 20 mg/L of dichloromethane (◆), 50 mg/L of tetrachloroethylene (▲), 50 mg/L of trichloroethylene (■) and 200 mg/L of chloroform (●) in a closed photoreactor. (b) Chloride appearance during the photodegradation of a mixture of four NBCS. Cl^-_{max} is the maximum stoichiometric concentration of Cl^- expected if the NBCS are completely dechlorinated.*

3.5. SOLAR-TIO_2 PHOTOCATALYTIC TREATMENT OF CYANIDE

Free cyanides species are generated in large quantities in heat-treating operations and in metal finishing industries. The greatest amounts of cyanide-containing wastes are produced by precious metals milling operations and coal gasification processes. The conventional processes used to treat wastewater polluted with cyanides are mainly chemical and biological. These methods present some drawbacks; for instance, in the alkaline chlorination process the formation of highly toxic cyanogen chloride gas can occur while for biologic processes, even when the difficult problem of activated sludge disposal is overcome, the reaction rate values can be very low. Although the literature reports exhaustive studies on the kinetic and mechanistic aspects of cyanides photo-oxidation carried out in laboratory photoreactors using different lamps as radiation source, the use of solar energy to remove CN^- ions is of great interest as it would drastically reduce the operational costs of a treatment process based on heterogeneous photocatalysis. So, here are summarized the first results free cyanides photocatalytic oxidation by using polycrystalline TiO_2 (P25 Degussa) in a CPC photoreactor (total volume 247 L, total solar collector surface 9 m^2).

The reacting mixture was prepared in the stirred tank by firstly adding NaOH to distilled water to adjust the pH to 10; then the required amounts of NaCN and catalyst were added. These experiments indicated that cyanate, nitrite, nitrate and carbonate were the main products. For comparing photoreactivity results obtained under different conditions of irradiation, the measured values of the different species concentration have been considered as a function not of the reaction time but of the cumulative photonic energy, $E_{h\nu}$, incident on the reactor. This quantity is given by Eq. 3.1.

For a typical run carried out with a catalyst amount of 0.2 g/L, Figure 3.6a reports the experimental values of cyanide, cyanate, nitrite and nitrate concentrations versus $E_{h\nu}$. In this Figure the nitrogen mass balance is also reported. It can be observed that the balance is satisfied during the course of cyanide photo-oxidation but it is not satisfied during the subsequent cyanate photo-oxidation. In order to better understand this behavior, which was shown by all the runs, some runs were carried out using cyanate as the starting reagent and by adding hydrogen peroxide to the system during the occurrence of the photoreaction. For a representative run Figure 3.6b reports the experimental results of cyanate concentration versus $E_{h\nu}$. It can be noticed that the nitrogen molar balance is closed only after the addition of hydrogen peroxide to the reacting system. The CPC photoreactivity results indicate that cyanate ion is the first photo-oxidation product of cyanide; the subsequent cyanate photooxidation eventually determines the formation of nitrite and nitrate ions whose amounts, however, denote a lacking of nitrogen mass balance in the course of the reaction. The addition

of H_2O_2 to the reacting system determines the closure of nitrogen mass balance even if the photo-oxidation rate of CNO^- does not significantly change in the presence of H_2O_2.

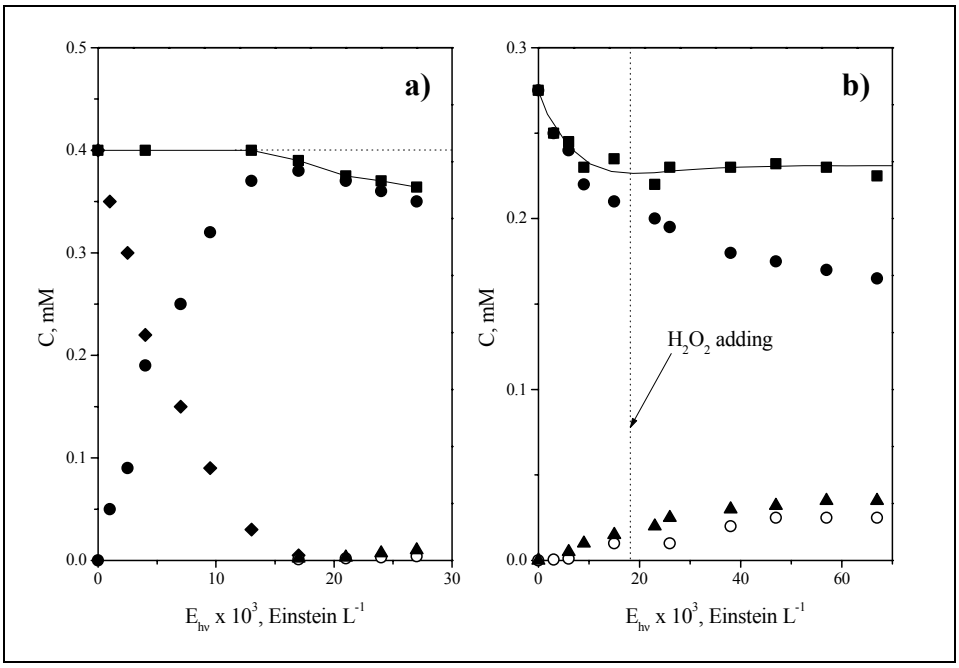

Figure 3.6 *(a) Typical cyanide degradation test with a catalyst amount of 0.2 g/L. (b) Cyanate degradation adding hydrogen peroxide after certain time. Concentrations of cyanide (◆), cyanate (●), nitrite (▲), nitrate (○), and nitrogen balance (■) versus the cumulative photonic energy, E_{hv}.*

The absence of nitrogen mass balance can be justified by considering the oxidative experimental conditions under which the cyanate photooxidation was carried out. The CPC operative conditions, such as the low values of incident photon flow (non solar concentrated radiation) and of oxygen concentration in the dispersion (reactor open to the atmosphere, 6-8 mg O_2 L^{-1}) can determine mild oxidation conditions and, as a consequence, the formation of volatile nitrogen-containing species (such as NH_3, N_2, N_2O, etc.) together with that of nitrite and nitrate ions. At strong oxidant conditions, such as determined in the presence of large amounts of H_2O_2, volatile nitrogen-containing species are not produced or are quickly photooxidized to NO_2^- and NO_3^-.

$$CN^- + 2h^+ + 2OH \rightarrow CNO^- + H_2O \quad (3.9)$$

$$CNO^- + 4O_2 + 2OH^- + 3H_2O \rightarrow CO_3^{2-} + NO_3^- + 4H_2O_2 \quad (3.10)$$

The results of this work indicate that the photocatalytic method can be successfully used for eliminating cyanide ions from wastewater by using the sun as radiation source. The main

oxidation products of cyanide ions are cyanate, nitrite, nitrate and carbonate ions. At mild oxidation conditions of the photoprocess the nitrogen mass balance, carried out on the dissolved compounds, is not satisfied in the course of cyanate photooxidation thus indicating the formation of some volatile species. The nitrogen mass balance is however closed at strong oxidation conditions determined by the addition of H_2O_2 to the solution.

3.6. SOLAR PHOTO-FENTON

Although the oxidizing power of the combination of Fe^{2+} and H_2O_2 (see Chapter 1) has been known for more than hundred years, the fact that the reaction can be enhanced by UV/Vis irradiation ($\lambda < 580$ nm) was found out only a few years ago. The so-called Photo-Fenton reaction (Eq.1.4) produces additional hydroxyl radicals and leads to a reduction of the photocatalyst by the irradiated light. Only a very simplified description is given in Eqs. 1.2, 1.3, 1.4. The main advantage of the Photo-Fenton process is the light sensitivity up to a wavelength of 600 nm (see Figure 3.7a). The depth of light penetration is high and the contact between pollutant and oxidizing agent is close, since a homogenous solution is used. Disadvantages are the low pH values required (usually below pH 4) and the necessity of iron removal after the reaction. The possibility of applying solar light instead of artificial light for the Photo-Fenton reaction would dramatically lower the costs of the process and thus provide a major step towards industrial application.

3.6.1 Photo-Fenton treatment of pesticides

The viability of the photo-Fenton process for treating highly contaminated wastewater has been demonstrated during experiments using a mixture of ten model pesticides, which were presented in Table 3.1. These compounds were selected in order to cover a wide range of organic substance classes. For these experiments 10% of each pesticide (as TOC) were to clean water in a CPC photoreactor (total volume 247 L, total solar collector surface 9 m^2).

Tests were conducted with initial concentrations of 100 mg/L of TOC and Fe concentration from 0.25 mM to 2 mM. The pH was adjusted to 2.5 or 2.8 by addition of concentrated sulfuric acid and ferrous sulfate was added immediately afterwards. H_2O_2 was added in portions of 10-20% of the stoichiometry until the experiment was finished. TOC disappearance was used as the parameter to determine the degradation of the pesticides. Figure 3.7b shows different degradation curves of experiments with pesticides and different quantities of iron. As it can be observed, an increase of the iron concentration did not improve the degradation speed as much as expected. The poor performance of the test with 0.5 mM iron is most probably caused by a slight deviation in pH adjustment. The values of E were calculated from the irradiance data, by using the procedure explained before (Eq. 3.2).

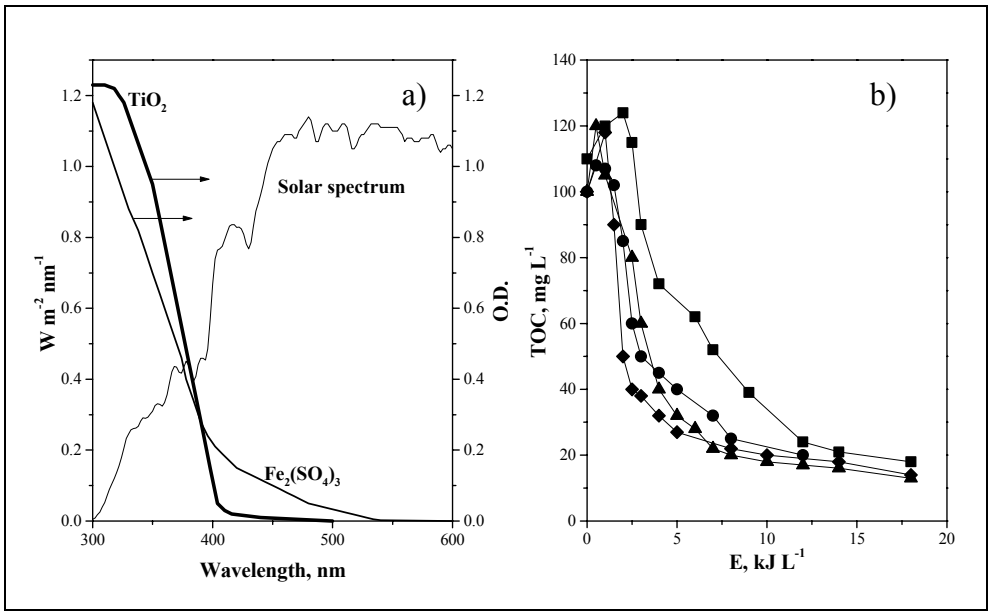

Figure 7. *PSA typical solar spectrum compared to the optical density (O.D., optical path length 1 cm) of a $Fe_2(SO4)_3$ solution (0.25 mM as Fe) and the absorption spectrum of TiO_2 powder. (b) Comparison of different iron concentrations during the degradation of commercial pesticides. (●) 0.25 mM Fe, (■) 0.5 mM Fe, (▲) 1 mM, (◆) 2 mM Fe.*

3.6.2 Photo-Fenton treatment of olive mill wastewater

Olive oil production is a large-scale agricultural activity of the European southern regions with a very strong economical significance. The wastewater from the olive milling process (OMW) are highly pollutant due to a high organic carbon and suspended solids content and to the presence of recalcitrant components. These compounds, mainly aromatics like phenols and polyphenols, are difficult to be degraded by micro-organisms and some of them present biostatic action, which reduces the effectiveness of OMW treatment in conventional biological treatment stations. Our objective is the development of the best (e.g. cheapest) possibility of utilizing sunlight for wastewater treatment by photochemical detoxification technology, to pilot plant scale, for the mineralisation of the recalcitrant phenolic contaminants typically found in the soluble organic fraction of the olive mill wastewater (OMW).

The OMW has been collected from a small olive mill directly from the wastewater effluent of this factory. It has been maintained in the dark but not frozen. The unique pre-treatment has consisted of TSS sedimentation for avoiding excessive quantity of solids in the photocatalytic reactors. All the experiments have been carried out during 2 months after the harvest of the OMW and no significant changes have been detected, during the storing, in the most relevant parameters related with the photocatalytic treatment (total phenols, COD, TOC).

Photo-Fenton photocatalysis have been applied in a CPC photoreactor (total volume 30 L, total solar collector surface 3.08 m^2). During the experiments different H_2O_2 and iron concentrations have been tested. One typical experiments performed with pure OMW (H_2O_2 20 g/L and Fe 1 mM) is shown in Figure 3.8. Hydrogen peroxide has been maintained invariable around 20 g/L adding the necessary quantity of reactive after checking the concentration by titration with thiosulphate. In all the experiments, pH has been fixed at 2.4-2.8 with sulfuric acid. A dark reaction happens with the Fenton reagent. Around 15% of the initial phenols are degraded but no COD. This reaction does not proceed further in the dark (after 2 days the same concentration of phenols, COD and H_2O_2 remains in the sample). Iron has been analysed during the experiment and different quantities of Fe^{2+} and Fe^{3+} have been detected, but the total quantity of iron found in the samples have been always around 1 mM.

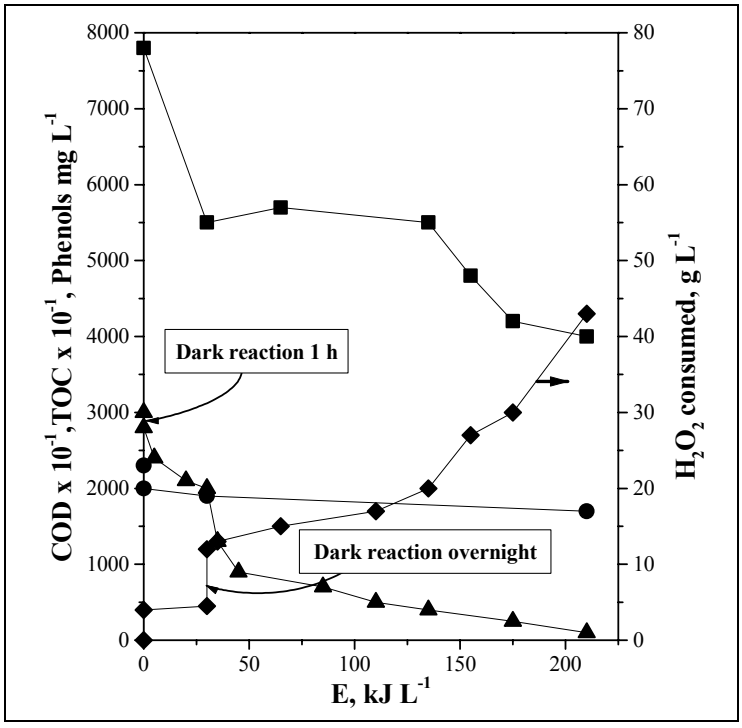

Figure 3.8. *OMW Photocatalytic treatment with Photo-Fenton reagent. Fe = 1 mM and H2O2 = 20 g/L (constant concentration along the experiment). (●) TOC, (■)COD, (▲)Phenols, (◆) H_2O_2.*

Phenols have been degraded from 3000 mg/L until 100 mg/L in a reasonable experimental time (200 kJ/L is equivalent to approximately 14 h of solar irradiation). COD has been reduced also from 81000 mg/L until 38000 mg/L. The consumption of H_2O_2 has been 42.8 g per liter of OMW. During overnight a small degradation happens, presumably due the high temperature (around 55 ºC) reached during the afternoon because the very dark color of the OMW. This high temperature remains in the reactor at least one hour after sunset. This effect has not been detected in the samples maintained at ambient temperature in the sample flasks.

Photo-Fenton reagent is clearly effective. Iron 5 mM with hydrogen peroxide 20 g/L (constant concentration) is the most effective for COD degradation between the different Photo-Fenton experiments carried out. In any case, phenols (the most important contaminants of the OMW) are easily degraded with lower iron concentration (1 mM).

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