

Review

Photocatalysis with solar energy at a pilot-plant scale: an overview

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Received 4 August 2001; accepted 3 November 2001

Abstract

Advanced oxidation processes (AOPs) are characterized by a common chemical feature: the capability of exploiting the high reactivity of $\bullet\text{OH}$ radicals in driving oxidation processes which are suitable for achieving the complete abatement and through mineralization of even less reactive pollutants. This paper reviews the use of sunlight to produce $\bullet\text{OH}$ radicals. The experimental systems necessary for performing pilot-plant scale solar photocatalytic experiments are described. It outlines the basic components of these pilot plants and the fundamental parameters related to solar photocatalysis reactions. This paper summarizes also most of the research carried out at Plataforma Solar de Almería (PSA) 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 also 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. Besides, the possibility of using the photo-Fenton reaction illuminated with solar light opens the boundary where solar photocatalysis could be applied. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Photocatalysis; Photo-Fenton; Solar energy; Solar collectors; Titanium dioxide; Water treatment

1. Introduction

The main causes of surface water and groundwater contamination are industrial discharges (even in low quantities), excess use of pesticides, fertilizers (agrochemicals) and landfilling domestic wastes. The wastewater treatment is based upon various mechanical, biological, physical and chemical processes. In fact, this is a combination of many operations like filtration, flocculation, sterilization or chemical oxidation of organic pollutants. After filtration and

elimination of particles in suspension, the biological treatment is the ideal process (natural decontamination). Unfortunately, all organic pollutants are not biodegradable and there is a class of products noted as bio-recalcitrant organic compounds. The last progresses in the decontamination of water concern the treatment of these compounds [1,2]. These methods rely on the formation of highly reactive chemical species, which degraded the more recalcitrant molecules into biodegradable compounds. These are called the advanced oxidation processes (AOPs). These processes although making use of different reacting systems [3–7] are all characterized by same chemical feature: production of OH radicals ($\bullet\text{OH}$). These radicals are extraordinarily reactive species

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(oxidation potential 2.8 V). They attack most of the organic molecules with rate constants usually in the order of 10^6 – $10^9 \text{ M}^{-1} \text{ s}^{-1}$. They are also characterized by a little selectivity of attack which is a useful attribute for an oxidant used in wastewater treatment and for solving pollution problems. The versatility of AOPs is also enhanced by the fact that they offer different possible ways for hydroxyl radicals production, thus allowing a better compliance with the specific treatment requirements.

A suitable application of AOP to wastewater treatments must consider that they make use of expensive reactants such as H_2O_2 , and/or O_3 and, therefore, it is obvious that their application should not replace, whenever possible, the more economic treatments such as the biological degradation [8,9]. The potentialities offered by AOP can be exploited to integrate biological treatments by an oxidative degradation of toxic or refractory substances entering or leaving the biological stage. Another aspect concerning the opportunity of AOP application is that referring to the polluting load of wastes normally expressed as chemical oxygen demand (COD). Only wastes with relatively small COD contents ($<2.0 \text{ g l}^{-1}$) can be suitably treated by means of these techniques since higher COD contents would require the consumption of too large amounts of expensive reactants. Wastes with higher pollutant contents can be more conveniently treated by means of wet oxidation or incineration. This work evaluates two well-defined AOP systems of special interest because natural solar UV-light [10–13] can be used: heterogeneous photocatalysis with TiO_2 and homogeneous photocatalysis by photo-Fenton process.

The solar heterogeneous photocatalytic detoxification process consists in utilizing the near-UV part of the solar spectrum (wavelength shorter than 380 nm), to photoexcite a semiconductor catalyst in the presence of oxygen. In these circumstances oxidizing species, either bound hydroxyl radical ($\bullet\text{OH}$) or free holes, which attack oxidizable contaminants, are generated producing a progressive breaking of molecules yielding to CO_2 , H_2O and dilute inorganic acids. The most commonly used catalyst is the semiconductor TiO_2 (cheap, non-toxic and abundant product) [14,15]. The solar homogeneous photocatalytic detoxification process (photo-Fenton) is based on the production of $\bullet\text{OH}$ radicals by Fenton reagent (H_2O_2 added to Fe^{2+} salts).

The rate of degradation of organic pollutants with Fenton-like reagents is strongly accelerated by irradiation with UV–VIS light. This is an extension of Fenton process which takes advantage from UV–VIS light irradiation at wavelength values higher than 300 nm. In these conditions, the photolysis of Fe^{3+} complexes allows Fe^{2+} regeneration and the occurrence of Fenton reactions due to the presence of H_2O_2 [16,17].

PSA (a large European scientific installation and the largest European laboratory for solar energy applications) is actively participating in demonstrative applications, both at national and international level, of solar technology (www.psa.es). PSA is exploring innovative uses of our oldest renewable source of energy, solar energy, to drive photochemical processes since early 1990s. One of the applications in which PSA has been deeply involved is solar detoxification with the use of solar photons to degrade hazardous toxic compounds in water by photocatalytic processes. Although scientific research on these processes has been conducted for at least the last three decades [18–21], industrial/commercial applications, engineering systems and engineering design methodologies have only been developed recently [22]. The experience acquired on solar detoxification systems at engineering level, particularly through EU projects, led to the development and installation at PSA of different pilot plants (with different collector fields, see www.psa.es), which have been used successfully by many European Research Institutions. This paper summarizes the work done during the last decade.

2. Solar collectors for photochemistry

2.1. Concentrating collectors

Contrary to solar thermal processes, which are based on the collection of large quantities of photons of all wavelengths to reach a specific temperature range, solar photochemical processes are based on the collection of only high-energy short-wavelength photons to promote photochemical reactions. Most of the solar photochemical processes use UV or near-UV sunlight (300–400 nm), but in some photochemical synthesis processes, up to 500 nm sunlight can be absorbed and photo-Fenton heterogeneous photocatalysis uses sunlight up to 580 nm. Sunlight

at wavelengths over 600 nm is normally not useful in any photochemical process. Nevertheless, the specific hardware needed for solar photochemical applications has much in common with those used for thermal applications. As a result, both photochemical systems and reactors have followed conventional solar thermal collector designs, such as parabolic troughs and non-concentrating collectors. At this point, their designs begin to diverge, since:

- the fluid must be directly exposed to solar radiation and, therefore, the absorber must be transparent to the photons, and
- temperature usually does not play a significant role in photochemical processes, so no insulation is required.

The original solar photoreactor designs for photochemical applications were based on line-focus parabolic-trough concentrators (PTCs). In part, this was a logical extension of the historical emphasis on trough units for solar thermal applications. Furthermore, PTC technology was relatively mature and existing hardware could be easily modified for photochemical processes. The first outdoors engineering-scale reactor developed (in USA) was a converted solar thermal parabolic-trough collector in which the absorber/glazing-tube combination had been replaced by a simple pyrex glass tube through which contaminated water could flow [23,24]. The

first engineering-scale solar photochemical facility for water detoxification in Europe was developed by CIEMAT [25] using 12 two-axis PTCs (see Fig. 1), each consisting of a turret and a platform supporting four parallel PTCs, with an absorber at the focus of each collector. The platform has two motors controlled by a two-axis (azimuth and elevation) tracking system. Thus, the collector aperture plane is always perpendicular to the solar rays, which are reflected by the parabola onto the reactor tube (concentrating ratio ≈ 10) at the focus through which circulates the contaminated water to be detoxified.

Typical overall optical efficiencies obtained in this PTC were around 50% [26,27]. Parabolic-trough collectors make efficient use of direct solar radiation and, as an additional advantage, the thermal energy collected from the concentrated radiation could simultaneously be used for other applications. The reactor is small, while receiving a large amount of energy per unit volume. The flow is turbulent and volatile compounds do not evaporate, so that handling and control of the liquid to be treated is simple and cheap. The main disadvantages are that the collectors (i) use only direct radiation, (ii) are expensive, and (iii) have low optical and quantum efficiencies (at least for TiO_2 applications) [28]. Several different substances have been successfully degraded with these collectors: chromium(VI) [29], dichloroacetic acid [30–32], phenol [33,34], 4-chlorophenol (CP) [35],

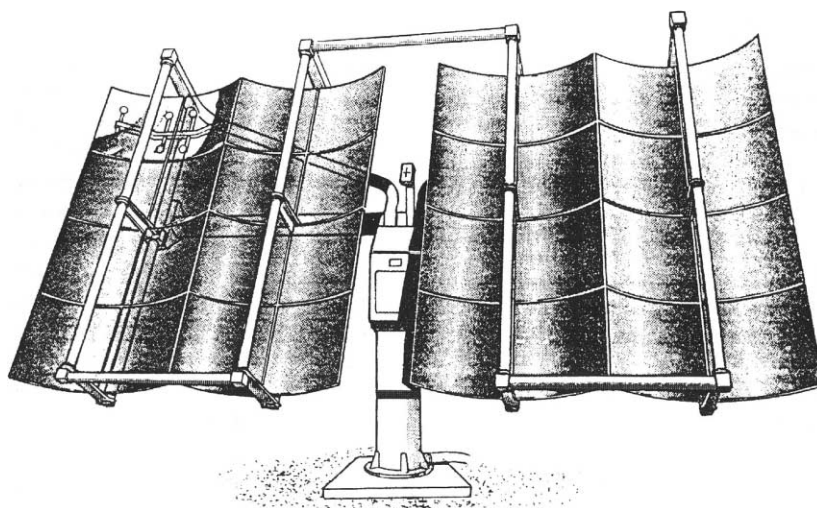


Fig. 1. Two-axis parabolic trough.

dichlorophenol (DCP) [36], pentachlorophenol (PCP) [37], atrazine [35], and industrial wastewaters [38,39]. The pilot-plant experiments described in these references processed hundreds of liters of water with tens of milligrams per liter of substrates and 200 mg l^{-1} TiO_2 slurries (the optimum concentration found for this reactor [40]). In all cases, the photonic efficiencies (moles of substrate degraded/incident moles of photons inside the reactor) were about 1%. Another small PTC (3 m^2 , one-axis) has also been tested [41] for degrading lindane. Results were similar to those obtained with the two-axis PTCs.

2.2. Non-concentrating collectors

One-sun (non-concentrating) collectors are, in principle, cheaper than PTCs as they have no moving parts or solar tracking devices. They do not concentrate radiation, so that efficiency is not reduced by factors associated with concentration and solar tracking. Manufacturing costs are cheaper because their components are simpler, which also means an easy and low-cost maintenance. Also, the non-concentrating collector support structures are easier and cheaper to install and the surface required for their installation is smaller, because, since they are static, they do not project shadows on the others. An extensive effort in the design of small non-tracking collectors, has resulted in the testing of several different non-concentrating solar reactors:

- Free-falling film: the process fluid falls slowly over a tilted plate with a catalyst attached to the surface, which faces the sun and is open to the atmosphere [32,42].
- Pressurized flat plate: consists of two plates between which the fluid circulates using a separating wall [43–45].
- Solar ponds: small, shallow on-site pond reactors [34,46].

Although one-sun collectors are simple, the design of a robust one-sun photoreactor is not trivial, since they must be weather-resistant, chemically inert and UV-transmissive. In addition, flow in non-concentrating systems is usually laminar, which presents mass transfer problems and vaporization of reactants. Consequently, the use of tubular photoreactors has a decisive advantage because of the inherent structural efficiency of tubes, which are also available in a large variety of materials and sizes and are a natural choice for a pressurized fluid system.

2.3. Compound parabolic concentrator (CPC)

CPCs, extensively employed for evacuated tubes, are an interesting cross between trough concentrators and one-sun systems and are a good option for solar photochemical applications. Among the collectors currently available, they constitute our choice for optimal possibilities [47–49]. CPCs are static collectors

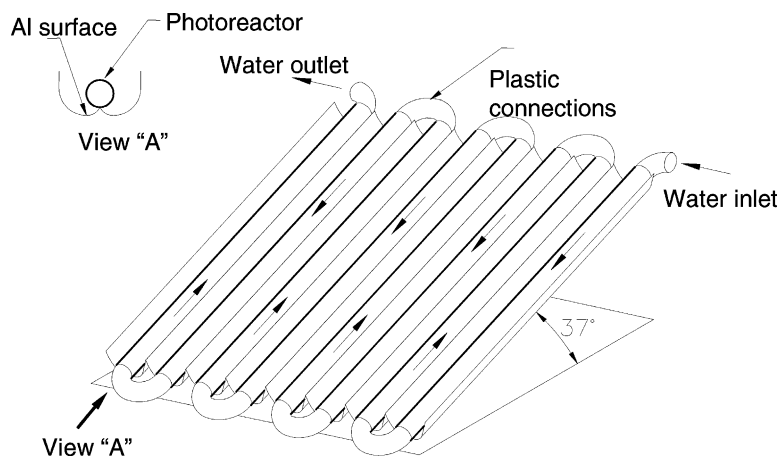


Fig. 2. Schematic drawing of a CPC.

with an involute reflective surface around a cylindrical reactor tube (see Fig. 2). They have been found to provide the best optics for low concentration systems and can be designed with a concentrating ratio close to one, thus having the advantages of both PTCs and one-sun collectors [33,46,50] since these static collectors can capture both direct and diffuse UV-sunlight [24,36,51,52].

The beauty of the solar CPC system is its intrinsic simplicity, while it is also cost-effective, easy to use, and requiring low capital investment. The reflector design enables almost all the UV-radiation arriving at the CPC aperture (not only direct, but also diffuse) to be collected and available to the process in the reactor. The light reflected by the CPC is distributed around the back of the tubular photoreactor so that most of the reactor tube circumference is illuminated. Because of the CPC aperture-to-tube diameter ratio, the incident light on the reactor is very similar to that of a one-sun photoreactor. As in a parabolic trough, water is easier to pipe in and to distribute than in many one-sun designs. All these factors contribute to excellent CPC collector performance in solar photochemical and photocatalytic applications [36,48,49,53–56].

3. Solar plant design and operation

Most of the components of solar photochemical systems are made of standard materials with no special requirements, except for the reactor, the reflective surface and the catalyst/sensitizer, since almost all the solar photochemical processes require a catalyst or a sensitizer [10,51].

3.1. Absorber tube

The photochemical reactor must contain the working fluid, including the catalyst or the sensitizer, and must transmit solar UV-light efficiently with minimal pressure-drop across the system. It must also provide good mass transfer from the fluid stream to an illuminated photocatalyst or a sensitizer surface. An adequate flow distribution inside the reactor must be assured, since a non-uniform distribution leads to a non-uniform residence time inside the reactor and to a decreased performance compared to that of an ideal flow. The choice of materials that are

both transparent to UV-light and resistant to its destructive effects is limited. Temperatures inside solar photochemical reactors can easily reach 40–50 °C. Therefore, photochemical reactors must be able to withstand summer temperatures of 70–80 °C. Furthermore, reactor material must be inert to chemicals and resistant to high or low pH. Quartz has excellent UV-transmission and resistance to temperature and chemicals, but its high cost makes it completely unrealistic. Fluoropolymers are a good choice because of their good UV-transmittance and chemical inertness [39]. One of their greatest disadvantages is that, in order to achieve a desired minimum pressure rating, the wall thickness of a fluoropolymer tube may have to be increased, which in turn will lower its UV-transmittance. Glass is a natural alternative for photoreactors. Low iron-content borosilicate glass has good transmissive properties in the solar range with a cut-off of about 285 nm and therefore, would seem to be the most adequate [29,57,58]. Two undesired effects reduce the performance of a glass reactor for the purposes of solar detoxification [59]: (i) absorption in the solar UV-range between 300 and 400 nm; (ii) a further decrease of the UV-transmissivity during operation because of the damaging impact of solar radiation (UV-solarization). Both effects are caused by valence changes of transition metal cations. The effect of Fe ions in glass is especially harmful, since Fe²⁺ ions are oxidized into Fe³⁺ by photons with wavelengths shorter than 400 nm. Furthermore, Fe³⁺ absorbs in the UV. It may be assessed that the enhancement of transmissivity in the 300–400 nm region can only be attained by a strong reduction in iron content down to 50 mg kg⁻¹ [49].

3.2. Reflective surface

The requirements for the optical quality of reflective surfaces in solar applications are usually related to the solar concentration. In the case of solar photochemical applications, the strictest requirements are those of PTCs. This is an important additional factor in favor of low or non-concentrating systems, since lower quality means lower manufacturing cost. With regard to the reflector/concentrator, aluminum is the best option owing to its low cost and high reflectivity. The ideal reflective surface for solar photochemical applications must be highly UV-reflective,

acceptably weather-resistant for long lifetime and reasonably priced. The surfaces currently available at PSA that best fit these requirements are electropolished anodized aluminum [29,39,49,58] and organic plastic films with an aluminum coating. In both cases, a compromise between outdoor resistance and UV-reflectance must be achieved. Commercial coated plastic films have been used successfully in parabolic troughs installed in PSA applications [37,57]. Because of their lack of rigidity, these films must be bonded over a stiff substrate and about 2% reflectivity is lost in this process.

3.3. Radiation absorption

In a photochemical process, solar radiation is normally absorbed and transferred to the catalyst or to the sensitizer that is excited by the solar photons. Some catalytic systems, different from TiO_2 slurries, have been tested at PSA: photo-Fenton [60–63], decatungstate anion [64–66], TiO_2 attached to a glass surface [31,32], TiO_2 attached to glass tubes [67], TiO_2 deposited on glass fibers [68] and Ti/TiO_2 photoanodes [69,70]. Fixed catalyst/sensitizer configurations [32,67–70] eliminate the need for catalyst/sensitizer recovery, but reduce system efficiency considerably. Up to now, no efficient supported

catalysts have yet been achieved [71]. Moreover, an important question is how long a supported catalyst/sensitizer will last in the fluid stream. By contrast, homogeneous and slurry configurations have the advantages of higher throughput, low pressure-drop through the reactor and excellent fluid-to-catalyst mass transfer. After their use, titania powders can be agglomerated and sedimented [72–75].

Another important design parameter for tubular photoreactors is the diameter, since in both homogeneous or heterogeneous processes, all incident efficient photons must be kept inside the reactor and not allowed to get through without intercepting an absorption target particle. The intensity of illumination affects the relationship between reaction rate and catalyst/sensitizer concentration. The dispersion and absorption of light causes photon density to diminish almost exponentially over the length of the optical path within a catalyst suspension. At higher light intensities, the catalyst/sensitizer concentration can be higher [33,43,47]. When catalyst/sensitizer concentration is too high, a “screening” effect produces excessive solution opacity and the system efficiency is reduced [72]. The lower the catalyst/sensitizer concentration, the less opaque the suspension. For example, in the case of titanium dioxide photocatalysis, 1 g l^{-1} of TiO_2 catalyst reduces transmittance to zero



Fig. 3. Partial view of the demonstration plant based on CPCs.

over a 10 mm path length with six-fold concentrated light in a parabolic-trough collector [76]. Therefore, in a tube with a wider diameter, only the outer layer would be illuminated. This means that larger i.d. reactors allow lower optimum catalyst concentrations. So the practical i.d. for tubular photoreactors must be optimized to any specific process taking into account all the relevant factors. For TiO₂ slurries in the photoreactors tested at PSA, the optimum reactor diameter is in the range of a few centimeters with a few hundreds milligrams of TiO₂ per liter.

Based on this accumulated experience in pilot-plant design, construction and testing a full-size demonstration plant has been erected at the facilities of HIDRO-CEN (Madrid, Spain). This plant was designed to treat 1 m³ of water with 100 m² of collector aperture area (see Fig. 3). The CPC reflector is made of a highly reflective anodized aluminium sheet supporting 16 parallel 1.5 m long tubes. A complete module is formed by a series of collectors connected in a row. The final prototype plant consists of E–W oriented parallel rows of 21 collectors each. Final system design is completely modular. Collectors are connected in series using HDPE quick connections between glass reactor tube absorbers. Water flows simultaneously through all parallel tubes and there is no limit to the number of collector components modules may have. As this plant is to be a demonstration of what a commercial plant would be like, operation is fully automatic and maintenance requirements are minimum. General plant design and operation has been previously described [49]. This industrial-scale solar photocatalytic plant, designed and erected with commercially available components according to previous pilot-plant results, has demonstrated that the solar photocatalytic technology is sufficiently developed for industrial use.

4. Basic photocatalysis parameters

4.1. Direct photolysis

Although organic pollutants absorb light over a wide range of wavelengths, it is generally stronger at the lower wavelengths. In any case, the focus here is on basic photocatalytic parameters and therefore, the photolytic effect will be discussed from this point of view. Such tests are performed to find out the decomposition

rates without the semiconductor. Any side effect of the photolytic reaction rate can be quantified and subtracted from the global rate, to get the true photocatalytic reaction rate. A good model of this is the case of acrinathrin [77]. Its spectrum slightly overlaps with the solar spectrum in the 300–330 nm region and, therefore, solar photons can produce photoalteration processes after being exposed to the environment. But such natural photodegradation is very slow: $Q = 400 \text{ kJ l}^{-1}$ to reach 10% of the initial concentration under aerobic well-illuminated conditions. Q is the amount of energy collected by the reactor (per unit of volume) from the start up of the experiments until each sampling:

$$Q_{UV,n} = Q_{UV,n-1} + \Delta t_n \overline{UV}_{G,n} \frac{A_r}{V_t},$$

$$\Delta t_n = t_n - t_{n-1} \quad (1)$$

where t_n is the experimental time of each sample, A_r the radiation collecting surface of the photoreactor, V_t the total pilot-plant volume and $Q_{UV,n}$ is the cumulated energy (per unit of volume, kJ l^{-1}) having entered the reactor for each sample taken during the experiment. Sometimes, it is useful (for those readers not interested in solar energy) 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 (300–400 nm) on a perfectly sunny day for 2 h around noon is about $30 W_{UV} \text{ m}^{-2}$. Under these conditions and using reactors similar to those shown in Figs. 2 and 3, 1 kJ l^{-1} is equivalent to 6.5 min illumination if $A_r = 9 \text{ m}^2$ and $V_t = 250 \text{ l}$. When this simplification is used, the illumination time calculated by this procedure can be called t_{30W} . In this case, 2600 min were necessary for destroying 90% of 50 mg l^{-1} of acrinathrin by photolysis. The same objective was attained using TiO₂ but 50 times faster. Other photolysis studies concerning different products have been performed on atrazine [35] and PCP [37].

4.2. Radiant flux

Since 1990, the kind of solar technology that should be involved in detoxification has been clarified [28,33,36,40,48,49,51,78–80]. Experimental measurements [32,34,40,43,47,48,81,82] have shown that above a certain UV photon flux (around one to two suns, i.e. $60\text{--}120 \mu\text{Einstein m}^{-2} \text{ s}^{-1}$) the reaction rate

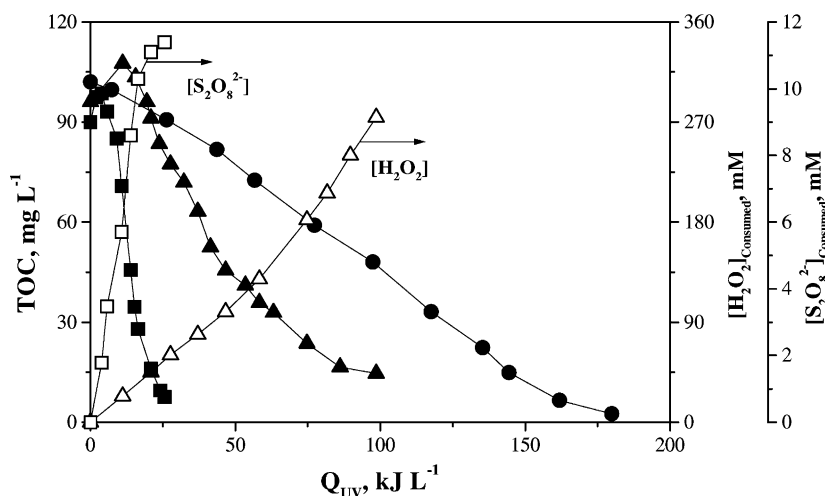


Fig. 4. Mineralization of commercial pesticides: (●) TiO_2 alone; (▲) with H_2O_2 , 25 mM; (■) with $\text{S}_2\text{O}_8^{2-}$, 10 mM. Both oxidants kept at constant concentrations throughout the experiment. H_2O_2 (Δ) and $\text{S}_2\text{O}_8^{2-}$ (\square) consumption are also shown.

becomes proportional to radiation intensity square root. Adding a product that reduces the importance of electron/hole recombination may appreciably attenuate this effect. When the electrons are trapped, recombination of e^-/h^+ is impeded. Addition of oxidants can improve the efficiency of the process at high illumination intensities. Moreover, this type of compounds can increase the quantum yield even at low irradiation levels owing to their strong oxidizing nature. The use of certain inorganic peroxides (hydrogen peroxide and sodium persulphate, see Fig. 4) has been demonstrated to remarkably enhance the rate of degradation of organic contaminants because they trap the photogenerated electrons more efficiently than O_2 [35,39,83–95]. The increase in the photocatalytic reaction rate with these additives decreases the photoreactor dimensions proportionally and correlatively decreases the overall investment costs.

4.3. Degradation pathways

A variety of degradation products (DPs) are formed during photocatalytic processes. Nevertheless, in most cases, no attention is paid to the possible formation of these DPs which, on the other hand, allow the degradation processes to be better understood and evaluated. Cost-effective treatment to complete compound mineralization is usually not feasible and the generation of

by-products appears to be unavoidable with photocatalytic degradation. Identification of those by-products is the key to maximizing overall process efficiency. Since hydroxyl radicals react non-selectively, numerous by-products are formed at low concentrations. On the other hand, some of the DPs obtained may be more toxic and persistent than the parent compound. Pilot-plant scale compound degradation pathway studies (using HPLC–UV–MS and GC–MS) have been performed with atrazine [35], PCP [40], imidacloprid [96,97], CP [98], and pyrimethanil [99]. They all indicated a total disappearance of their corresponding DPs.

5. Solar UV-photocatalytic degradation of contaminants

Up to now, practical applications of solar technologies have been studied and developed most intensively for heterogeneous TiO_2 photocatalysis and homogeneous photo-Fenton. In this context, treatment of industrial wastewater, in spite of inefficient production of hydroxyl radicals and slow kinetics, which may limit economic feasibility, seems to be one of the most promising fields of application of solar detoxification. The only really general rule is that there is no general rule at all, each real case being completely different [100]. Consequently, preliminary research is always

required to assess potential pollutant treatments and optimize the best option for any specific problem, on a nearly case-by-case basis. In this section, an attempt will be made to summarize the results obtained with different contaminants in solar pilot plants.

5.1. Single compound degradation by UV-irradiated TiO_2 slurries

Some chlorophenols have been successfully degraded [36,37,40,43,47,76,83,98,101,102] by photocatalysis and CP, DCP and PCP are presented here as representative of this family of priority pollutants and how solar pilot-plant experiments can be very useful for obtaining “design parameters”. Chlorophenols have been tested at around 20 mg l^{-1} using TiO_2 slurries (200 mg l^{-1}) in a two-axis parabolic-trough photoreactor (see Fig. 1, total volume 260 l, total solar collector surface 32 m^2). Fig. 5 shows the degradation of these three typical contaminants as a function of the photonic energy entering the photoreactor.

Mineralization only occurs when the last step of the oxidation process yields CO_2 . The mineralization reaction rate must be related to the solar photon flux reaching the collector surface. The process efficiency could be explained in terms of grams of mineralized TOC per mole of incident photons. In this case, the

efficiency (including the induction period) is 0.117, 0.09 and 0.233 g of TOC per mole of photons for PCP, DCP and CP, respectively in a total volume of 260 l of water in a 32 m^2 collector. It may be assumed that the mean solar UV-radiation during 2 h around noon on a perfectly sunny day is about $30 \text{ W}_{\text{UV}} \text{ m}^{-2}$. Under these conditions and in the reactor used in this work, 4.14 mol of photons are equivalent to 1 h illumination. Therefore, the “mineralization treatment capacity” of the photoreactor for each type of chlorophenol can be expressed in grams of TOC removed per hour and per square meter of collector. It was found equal to 0.015 , 0.012 and $0.030 \text{ g TOC h}^{-1} \text{ m}^{-2}$ for PCP, DCP and CP, respectively. Taking into account the stoichiometric ratios between TOC and the various contaminants, this correspond to 0.053 , 0.027 and 0.053 g of pollutant mineralized per hour and per square meter for PCP, DCP and CP, respectively. The treatment capacity, calculated for a mean intensity of $30 \text{ W}_{\text{UV}} \text{ m}^{-2}$, is very useful for extrapolating experimental results to other volumes and ambient conditions. Information concerning degradation of other single compounds at pilot-plant scale using solar collectors is available: phenol [33], atrazine [35], 2,4-dichlorophenoxyacetic acid and of benzofuran [103], chlorinated solvents [49,104], imidacloprid [96,97,105], pirimicarb [105], acrinathrin [77],

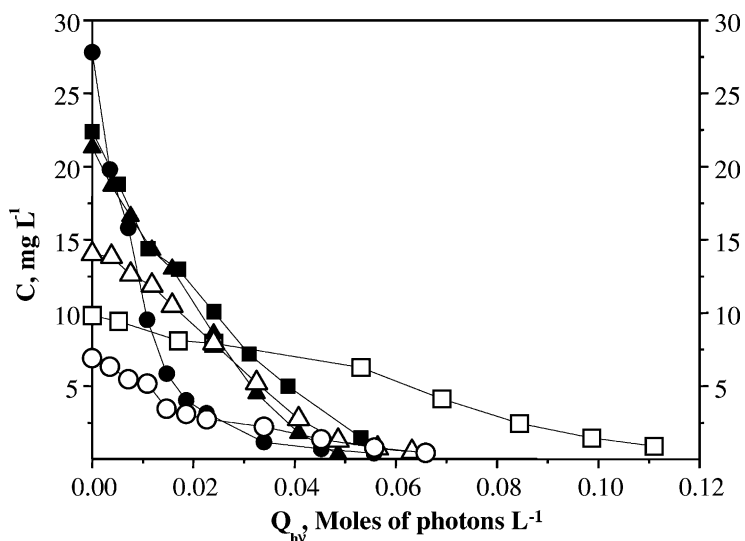


Fig. 5. Solar photocatalytic degradation of CP (\blacktriangle), DCP (\blacksquare), and PCP (\bullet) with a catalyst amount of 0.2 g l^{-1} . TOC corresponding to each compound is also shown (open symbols).

lindane [41,55], butiphos and EPTC [55], cyanide [87], methamidophos [84], oxamyl [88], pyrimethanil [99], dichloroacetic acid [31,43], and Cr(VI) [29,57]. Preliminary results have also been obtained in water disinfection [55].

5.2. Real wastewater treatment by UV-irradiated TiO_2 slurries

Solar photocatalytic degradation technology may be considered as feasible for the treatment of wastewaters containing hazardous contaminants for which biological waste treatment plants are impossible at medium or low pollutant concentrations. The technology may be considered as linearly dependent on the energy flux and, therefore, the associated investment is also linearly dependent on the collector surface. Reasonable orders of magnitude for inflow into typical treatment plants would be in the range of several dozens up to a few hundreds of cubic meters per day [39,53,56,89,106,107]. The results shown in Fig. 6 are examples of experiments carried out with real wastewaters at different initial concentrations and will be used to explain the general procedure for obtaining “design

parameters”. Since the reaction is not expected to follow simple models like first or zero order kinetics, overall reaction rate constants cannot be calculated. Therefore, another parameter has been chosen. The maximum gradient of the degradation curve, which is the gradient of the tangent at the inflection point ($r_{Q,0}$) is employed to obtain a practical point of comparison for different experiments, since it has a zero order rate constant ($mg\ kJ^{-1}$ instead of $mg\ min^{-1}$) and, therefore, appears 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. This parameter $r_{Q,0}$ is referred to as the “maximum rate”. In the graphic inset in Fig. 6, it may be observed that the initial rate is steady from 20–30 mg of TOC per liter. At this concentration, saturation occurs and the reaction rate becomes constant.

Once the optimum initial concentration for degradation is known, a model for predicting plant behavior is necessary. This model should enable one to calculate the solar collector area required for treating water contaminated with different amounts of pesticides. A previously developed model [40], which has

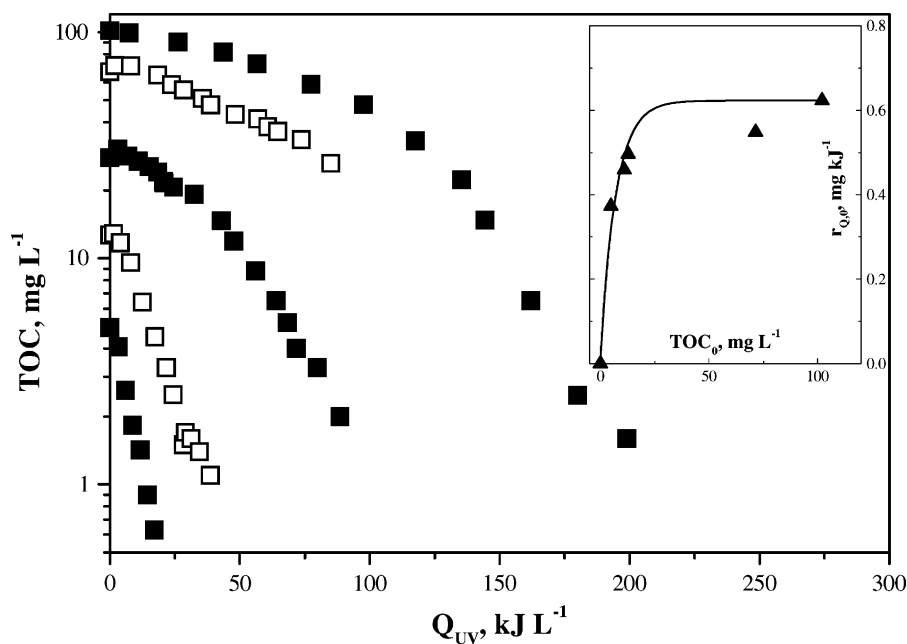


Fig. 6. Decontamination of wastewater containing pesticides at different initial concentrations. “Maximum rate” as a function of maximum TOC is shown in the inset.

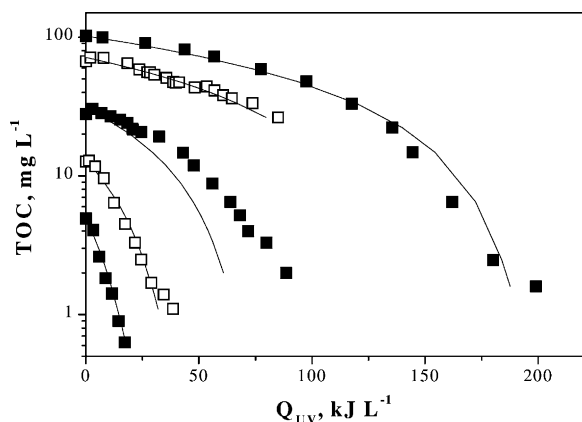


Fig. 7. Application of the proposed kinetic model for mineralization of a pesticide mixture.

the analytic form of a Langmuir–Hinshelwood equation, has been preferred to the direct use of the L–H model ($r = kKC/(1 + KC)$) for fitting experimental data in large solar photocatalytic plants, by approximate solution of the general photocatalytic kinetic system. With these considerations, the rate of TOC disappearance is given by

$$r_{Q,0} = \frac{\beta_1[\text{TOC}]_{\max}}{\beta_2 + \beta_3[\text{TOC}]_{\max}} \quad (2)$$

The experimental results shown in Fig. 6 were used to calculate the constants (β_i) by inversion of Eq. (2). Using these values, experimental results and the corresponding lines of fit are shown in Fig. 7. The lines of fit were drawn with:

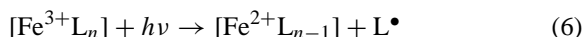
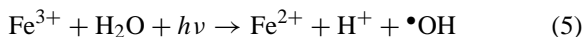
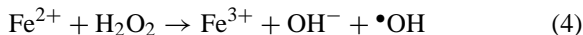
$$\frac{1}{\beta_1} \left\{ \beta_2 \ln \left(\frac{[\text{TOC}]_{\max}}{[\text{TOC}]} \right) + \beta_3([\text{TOC}]_{\max} - [\text{TOC}]) \right\} = Q_{UV} \quad (3)$$

This equation enables one to predict TOC degradation as a function of the initial TOC and of the available radiation energy, and reciprocally, to predict the incident energy on the reactor necessary to reach a specific degree of mineralization. Nevertheless, UV-radiation data for the final plant location must be available. The inset in Fig. 6 shows 20–30 mg of TOC per liter as the initial steady state rate. So 25 mg of TOC per liter has been chosen as the initial concentration for photocatalytic treatment plant design. Applying Eq. (3),

56.4 kJ l⁻¹ will be necessary to reduce the TOC from 25 to 1 mg l⁻¹. Considering 5000 m³ of wastewater per year, 2.8 × 10⁸ kJ per year of solar UV-energy will be necessary. Considering a yearly mean UV-radiation as measured for the PSA (latitude 37°5', longitude 2°21', 500 m above sea level) of 18.6 W_{UV} m⁻² (4380 sunny hours per year), 2.93 × 10⁵ kJ m⁻² per year are available. Therefore, the treatment plant would have a collector surface of 1000 m². Information concerning real wastewater degradation is available in [38,39,83–85,89,106–109].

5.3. Solar photo-Fenton

The Fenton reactant (described by Fenton at the end of the 19th century) consists of an aqueous solution of hydrogen peroxide and of ferrous ions providing another important source of hydroxyl radicals (Eq. (4)). Under acidic conditions (pH 2–4), this reactant is readily a powerful oxidant of organic compounds [4,12,16,110,111], and when the process is complemented with UV–VIS radiation, the degradation rate increases significantly [112–115]. Although the oxidizing power of the combination of Fe²⁺ with H₂O₂ (i.e. the Fenton reaction, Eq. (5)) has been known since more than 100 years, the fact that the reaction can be enhanced by UV–VIS irradiation ($\lambda < 580$ nm) was only discovered a few years ago. The so-called photo-Fenton reaction (Eq. (5)) produces additional hydroxyl radicals and leads to reduction of the photocatalyst by the irradiated light. A very simplified description is given in Eqs. (4)–(6). The main advantage of the photo-Fenton process is its sensitivity to light up to wavelengths ≤ 600 nm (see Fig. 8). Light penetration is deep and the contact between pollutant and the oxidizing agent is intimate, because of the homogenous phase. Disadvantages are the low pH required (usually below pH 4) and the need to remove iron after the reaction:



The use of sunlight instead of artificial light for the photo-Fenton reaction would dramatically lower the costs of the process and, thus, provide a major step

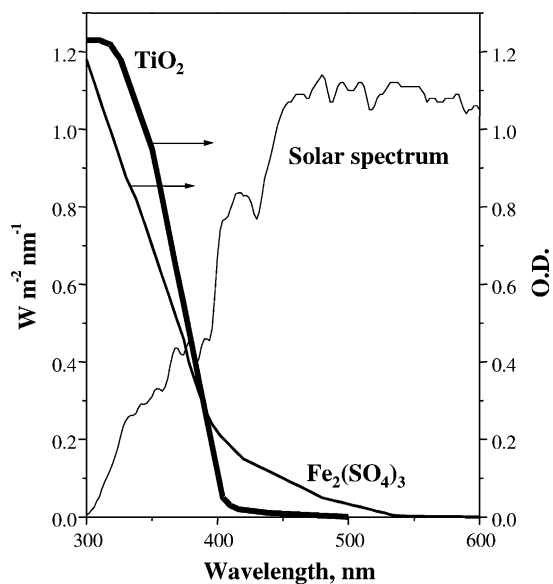


Fig. 8. PSA typical solar spectrum compared to the optical density (O.D., optical path length 1 cm) of a $\text{Fe}_2(\text{SO}_4)_3$ solution (0.25 mM as Fe) and the absorption spectrum of TiO_2 powder.

towards industrial application [53]. The feasibility of the photo-Fenton process for treating highly contaminated wastewaters has been demonstrated during experiments with CP [61], metobromuron and isoproturon [116], *p*-nitrotoluene-*o*-sulfonic acid [117], and a mixture of 10 pesticides [60].

Acknowledgements

The authors thank the European Commission (DG XII) for its economical support to the development of the Solar Photocatalysis at Plataforma Solar within the framework of the following projects: (i) "Enhancement and new developments in industrial process through solar radiation". Contract no. ERGBE 1-CT000019, Access to Large-Scale Scientific Installation Program, 1990–1993; "Enhancement and developments of industrial applications of solar energy technologies". Project no. CHGE-CT93-0038 (DG-12 COMA), Human Capital Program, 1994–1995; (iii) "Innovative training horizons in applied solar thermal and chemical technologies". Project no. ERBMFGE-CT95-0023,

1996–1998; (iv) "Solar detoxification technology to the treatment of industrial non-biodegradable persistent chlorinated water contaminants". Project no. BRPR-CT97-0424, 1997–2000; (v) "Water recovery from olive mill wastewaters after photocatalytic detoxification and disinfection". Project no. FAIR-CT98-3807 (DG12-SSMI), 1998–2001; (vi) "Trans-national Access to Plataforma Solar de Almería: the European Solar Thermal Test Centre". Contract no. HPRI-CT1999-00013, Improving Human Potential Program, 2000–2003. The authors also thank Prof. Jean Marie Herrmann (Ecole Centrale de Lyon) for his valuable comments and Mrs. Deborah Fuldaer for correcting the English.

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