

SOLAR PHOTOCATALYSIS

SUMMARY

This unit describes an alternative source of energy that combines sunlight and chemistry to produce chemical reactions. It outlines the basic chemical and physical phenomena that are related with solar chemistry. This unit describes also the experimental systems necessary for performing pilot-plant-scale solar photocatalytic experiments. It outlines the basic components of these pilot plants and the different possibilities for operating them because a pilot plant has to be as versatile as possible in order for any photocatalytic experiment to be performed with sufficient confidence. It describes also the fundamental parameters related to solar heterogeneous photocatalysis reactions: photolysis, radiation intensity and initial substrate concentration. It outlines the basic tests for understanding experimental system behavior when these parameters change and why these changes affect the photocatalytic reaction rate. Photolysis tests have to be performed always before photocatalysis tests in order to find out decomposition rates without the semiconductor. Above a certain flux of UV photons, reaction rate changes depending on intensity and the use of additional oxidants, for trapping the photogenerated electrons and/or producing extra oxidizing species, is commented. The direct application of the Langmuir-Hinshelwood model produces an empirical equation, which fits the degradation experimental data accordingly. This equation is useful in a wide range of initial concentrations and is necessary for engineering plant design but experimentation at pilot plant level is essential to obtain these equations. Examples for better comprehension of all these questions are shown. Finally, an overview of other factors affecting solar photocatalysis is presented: catalyst concentration and particle diameter, photoreactor diameter, oxygen, pH, temperature are also shown.

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2.1. INTRODUCTION

The dramatic increases in the cost of oil beginning in 1974 focussed attention on the need to develop alternative sources of energy. It has long been recognised that the sunlight falling on the earth's surface is more than adequate to supply all the energy that human activity requires. The challenge is to collect and convert this dilute and intermittent energy to forms that are convenient and economical or to use solar photons in place of those from lamps. It must be kept in mind that today there is a clear world-wide consensus regarding the need for long-term replacement of fossil fuels, which were produced million of years ago and today are merely consumed, by other inexhaustible or renewable energies. Under these circumstances, the growth and development of Solar Chemical Applications can be of special relevance. These technologies can be divided in two main groups:

1. Thermochemical processes: the solar radiation is converted into thermal energy that causes a chemical reaction. Such a chemical reaction is produced by thermal energy obtained from the sun for the general purpose of substituting fossil fuels.
2. Photochemical processes: solar photons are directly absorbed by reactants and/or a catalyst causing a reaction. This path leads to a chemical reaction produced by the energy of the sun's photons, for the general purpose of carrying out new processes.

It should be emphasized, as a general principle, that the first case is associated with processes that are feasible with conventional sources of energy. The second is related only to completely new processes or reactions that are presently carried out with electric arc lamps, fluorescent lamps or lasers.

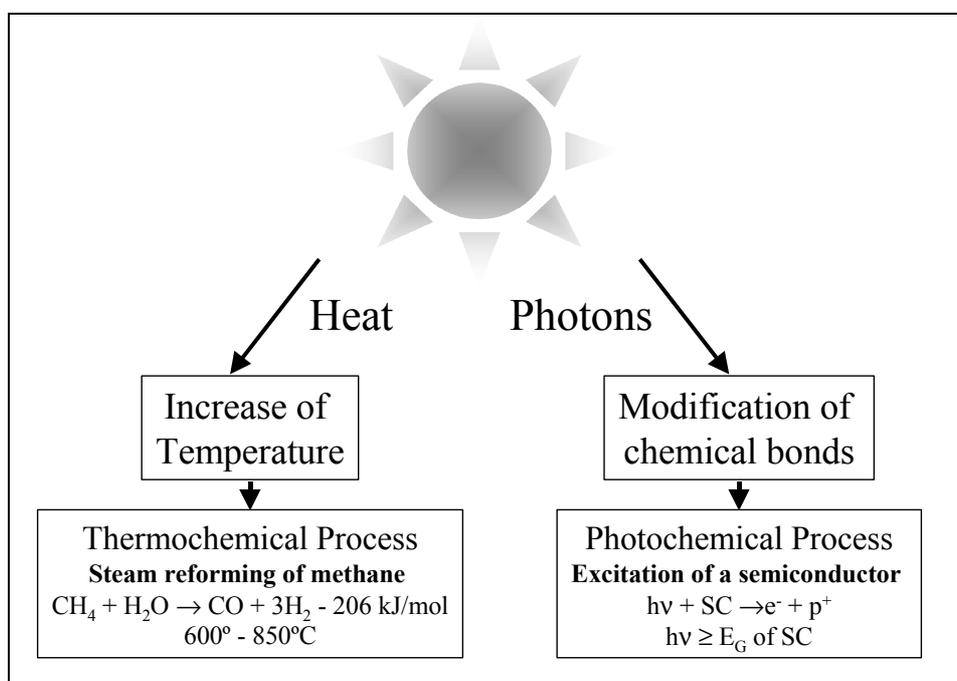


Figure 2.1. Schematic view of Solar Chemical Applications

From the outset, it was recognized that direct conversion of light to chemical energy held promise for the production of fuels, chemical feedstock, and the storage of solar energy. Production of chemicals by reactions that are thermodynamically ‘uphill’ can transform solar energy and store it in forms that can be used in a variety of ways. Wide ranges of such chemical transformations have been proposed. A few representative examples are given in Table 2.1 to illustrate the concept.

	ΔH (kJ/mol)
$\text{CO}_2(\text{g}) \rightarrow \text{CO}(\text{g}) + 1/2\text{O}_2$	286
$\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g}) \rightarrow \text{CH}_3\text{OH}(\text{l}) + 3/2\text{O}_2$	727
$\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2(\text{g}) + 1/2\text{O}_2$	286
$\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 1/6\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + \text{O}_2$	467

Table 2.1 Representative chemical reactions that can store solar energy (Thermochemical processes)

These processes generally start with substances in low-energy, highly-oxidized forms. The essential feature is that these reactions increase the energy content of the chemicals using solar energy. For such processes to be viable, they must fulfil the following requirements:

- The thermochemical reaction must be endothermic.
- The process must be cyclic and with no side reactions that could degrade the photochemical reactants.
- The reaction should use as much of the solar spectrum as possible.
- The back reaction should be very slow to allow storage of the products, but rapid when triggered to recover the energy content.
- The products of the photochemical reaction should be easy to store and transport.

The other pathway for the use of sunlight in photochemistry is to use solar photons as replacements for those from artificial sources. The goal in this case is to provide a cost-effective and energy-saving source of light to drive photochemical reactions with useful products. Photochemical reactions can be used to carry out a wide range of chemical syntheses ranging from the simple to the complex. Processes of this type may start with more complex compounds than fuel-producing or energy-storage reactions and convert them to substances to which the photochemical step provides additional value or destroy harmful products. The principles of photochemistry are well understood and examples of a wide range of types of synthetic transformations are known (Figure 2.2). Therefore, the problem becomes one of identifying applications in which the use of solar photons is possible and economically

feasible. The processes of interest here are photochemical, hence, some component of the reacting system must be capable of absorbing photons in the solar spectrum.

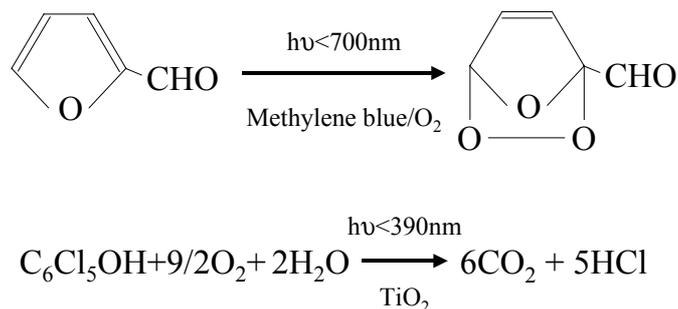


Figure 2.2. Furfural photo-oxidation and pentachlorophenol mineralization (Photochemical processes).

Because they are very technologically and environmentally attractive, solar chemical processes have seen spectacular development in recent years. In the beginning, research in solar chemistry was centered only on converting the solar energy into chemical energy, which could then be stored and transferred over long distances. Together with this important application, other environmental uses have been developed, so that today the entire range of solar chemical applications has a promising future. In principle, any reaction or process requiring an energy source can be supplied by solar energy.

2.1.1 Phodegradation Principles

For the benefit of those who may have a limited background in photochemistry, a brief outline of some basic concepts of photochemistry is presented here. In order for photochemistry to take place, photons of light must be absorbed. The energy of a photon is given by

$$U = \frac{hc}{\lambda} \quad (2.1)$$

where h is Planck's constant ($6.626 \cdot 10^{-34}$ J s), c is the speed of light and λ is the wavelength. For a molecule's bond to be broken, U must be greater than the energy of that bond.

When a given wavelength λ of light enters a medium, its spectral irradiance E_λ ($\text{W m}^{-2} \text{nm}^{-1}$) is attenuated according to the Lambert-Beer law, which is expressed in two ways, one for gas phase and the other for liquid phase:

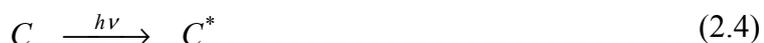
$$\ln(E_\lambda^o / E_\lambda^l) = \alpha_\lambda p_i l \quad \text{gas phase} \quad (2.2)$$

$$\log(E_\lambda^o / E_\lambda^l) = \varepsilon_\lambda c_i l \quad \text{liquid phase} \quad (2.3)$$

E_λ^o and E_λ^l are the incident spectral irradiances and at a distance l into the medium, α_λ is the absorption coefficient ($\text{cm}^{-1} \text{atm}^{-1}$), p_i is the partial pressure (atm) of component i , ε_λ is the extinction coefficient ($\text{M}^{-1} \text{cm}^{-1}$), and c_i is the concentration (M) of component i . The absorbance A_λ at wavelength λ is the product $\varepsilon_\lambda c_i l$. The photochemical quantum yield (ϕ) is

defined as the number of molecules of target compound that reacts divided by the number of photons of light absorbed by the compound, as determined in a fixed period of time. Normally, the unit is the maximum quantum yield attainable.

The term photocatalysis implies the combination of photochemistry with catalysis. Both light and catalyst are necessary to achieve or to accelerate a chemical reaction. Photocatalysis may be defined as the “acceleration of a photoreaction by the presence of a catalyst”. Heterogeneous processes employ semiconductor slurries for catalysis, whereas homogeneous photochemistry is used in a single-phase system. Any mechanistic description of a photoreaction begins with the absorption of a photon, being sunlight the source of photons in solar photocatalysis. In the case of homogeneous photocatalytic processes, the interaction of a photon-absorbing species (transition metal complexes, organic dyes or metalloporphyrines), a substrate (e.g. the contaminant) and light can lead to a chemical modification of the substrate. The photon-absorbing species (C) is activated and accelerates the process by interacting through a state of excitation (C*). In the case of heterogeneous photocatalysis, the interaction of a photon produces the appearance of electron/hole (e⁻ and h⁺) pairs, the catalyst being a semiconductor (e.g. TiO₂, ZnO, etc). In this case, the excited electrons are transferred to the reducible specimen (Ox₁) at the same time that the catalyst accepts electrons from the oxidizable specimen (Red₂) which occupies the holes. In both directions, the net flow of electrons is null and the catalyst remains unaltered.



2.1.2 Photocatalysis

The methods based on catalysis and photochemistry have been denominated Advanced Oxidation Processes. Among them, those which produce hydroxyl radicals ([•]OH) have had growing success. As mentioned before, UV light can be used in several ways but direct photolysis can occur only when the chemical compounds absorb incident light efficiently. By contrast, these radicals can also be generated with a semiconductor (photocatalysis) which absorbs UV radiation when this is in contact with the water. In heterogeneous photocatalysis, dispersed solid particles absorb larger fractions of the UV spectrum efficiently and generate chemical oxidants in situ from dissolved oxygen or water. These advantages make heterogeneous photocatalysis a particularly attractive method for environmental

detoxification. The most important features of this process making it applicable to the treatment of contaminated aqueous effluents are:

- The process takes place at ambient temperature.
- Oxidation of the substances into CO₂ is complete.
- The oxygen necessary for the reaction is obtained from the atmosphere.
- The catalyst is cheap, innocuous and can be reused.
- The catalyst can be attached to different types of inert matrices.

Whenever different semiconductor materials have been tested under comparable conditions for the degradation of the same compounds, TiO₂ has generally been demonstrated to be the most active. Only ZnO is as active as TiO₂. TiO₂'s strong resistance to chemical and photocorrosion, its safety and low cost limits the choice of convenient alternatives. This semiconductor is of special interest, since it can use natural (solar) UV because it has an appropriate energetic separation between its valence and conduction bands which can be surpassed by the energy content of a solar photon ($\lambda > 300$ nm). Other semiconductor particles, e.g., CdS or GaP absorb larger fractions of the solar spectrum and can form chemically activated surface-bond intermediates, but unfortunately, these photocatalysts are degraded during the repeated catalytic cycles involved in heterogeneous photocatalysis. Therefore, degradation of the organic pollutants present in wastewater using irradiated TiO₂ suspensions is the most promising process and R&D in this field has grown very quickly during the last years.

To date, evidence supports the idea that the hydroxyl radical ($\bullet\text{OH}$) is the main oxidizing specimen responsible for photooxidation of the majority of the organic compounds studied. The first effect, after absorption of near ultraviolet radiation, $\lambda < 390$ nm, is the generation of electron/hole pairs (see Figure 2.3), which are separated between the conduction and valence bands. In order to avoid recombination of the pairs generated, if the solvent is oxidoreductively active (water) it also acts as a donor and acceptor of electrons. Thus, on a hydrated and hydroxylated TiO₂ surface, the holes trap $\bullet\text{OH}$ radicals linked to the surface. In any case, it should be emphasized that even trapped electrons and holes can rapidly recombine on the surface of a particle. This can be partially avoided through the capture of the electron by preadsorbed molecular oxygen, forming a superoxide radical.

Whatever the formation pathway, it is well known that O₂ and water are essential for photooxidation with TiO₂. There is no degradation in the absence of either. Furthermore, the oxidative species formed (in particular the hydroxyl radicals) react with the majority of organic substances. For example, in aromatic compounds, the aromatic part is hydroxylated and successive steps in oxidation/addition lead to ring opening. The resulting aldehydes and

carboxylic acids are decarboxylated and finally produce CO_2 . However, the important issue governing the efficiency of photocatalytic oxidative degradation is minimizing electron-hole recombination by maximizing the rate of interfacial electron transfer to capture the photogenerated electron and/or hole. This issue is discussed in more detail later.

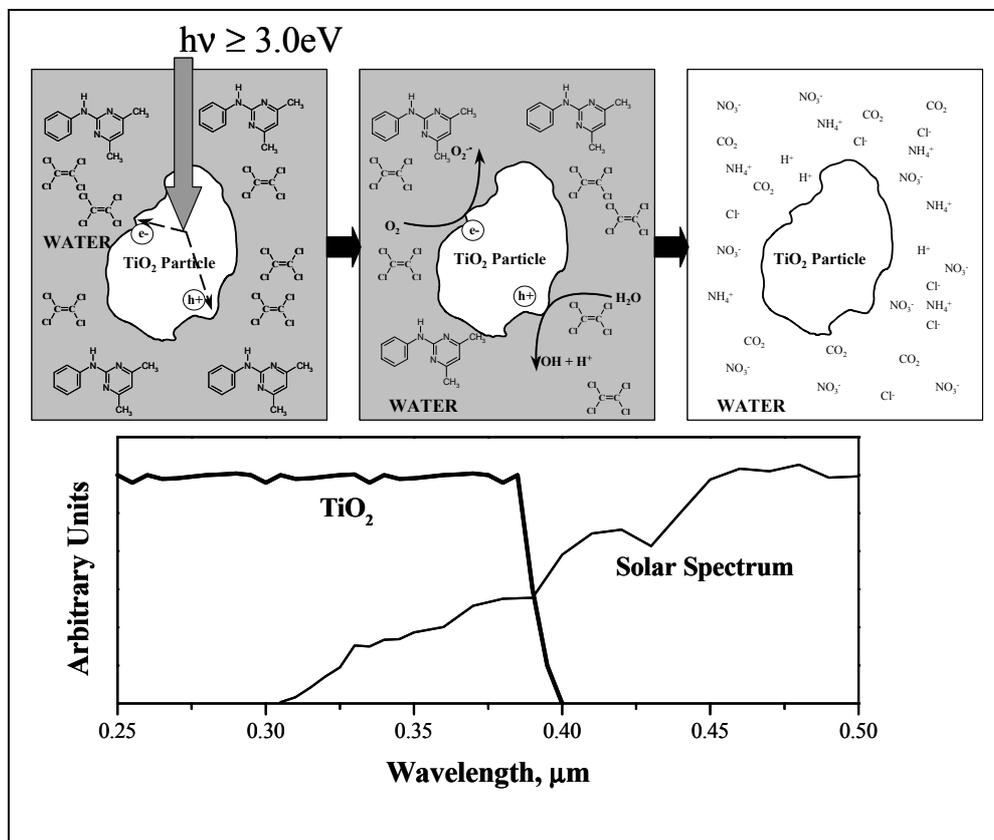


Figure 2.3. Effect of UV radiation on a TiO_2 particle dispersed in water and subsequent destruction of the organics dissolved in water. TiO_2 absorption spectrum compared with Solar spectrum is also shown.

Despite encouraging laboratory-scale data and some industrial-scale tests, chemical oxidation detoxification is still restricted to a few experimental plants. The broader application of those technologies requires: i) reactor optimization and modeling and ii) assessment of the efficiency of oxidation technology to reduce the toxicity of effluents.

2.2 SOLAR DETOXIFICATION PILOT PLANTS

The treatment of contaminated water necessarily includes the design of an efficient photoreactor. Basic laboratory research on the process has mostly been performed with experimental devices in which efficiency was not as important as obtaining appropriate conditions that would permit reproducibility of the results and exhaustive knowledge of the effects of all the important parameters. This is correct when the goal is a fundamental

knowledge of the process, but not always sufficient to attempt a change of scale. The UV-light is provided by a lamp introduced in a water-cooled envelope or solar simulators, All the IR beams, which could heat the slurry suspensions, are removed by a water cell, which contains an optical disk transparent to the wavelengths domain desired. During photocatalytic degradation experiments some parameters as pH, CO₂ and O₂ can be monitored in situ by specific electrodes.

The design procedure for a pilot solar detoxification system requires the selection of a reactor, catalyst operating mode (suspension or fixed matrix), reactor-field configuration (series or parallel), treatment-system mode (once-through or batch), flow rate, pressure drop, pre-treatment, catalyst and oxidant loading method, pH control, etc., so a pilot plant has to be as versatile as possible to allow for these variables and, at the same time, provide sufficient confidence in the experiments carried out in it. A pilot plant must fulfill all the present and future requirements of the research to be performed in it. In Figure 2.4 a detailed drawing of a plant is given. Usually, a detoxification pilot plant is constructed with several solar collectors. All the modules are connected in series, but with valves that permit to bypass any number of them (see Figure 2.4, “collector by-pass”). Sampling valves are in the outlet of each of the modules. All the tubes and valves are black HDPE, material chosen because it is strongly resistant to chemicals, weather-proof and opaque, in order to avoid any photochemical effect outside of the collectors. There are storage-feeder tanks available, also made of HDPE and having different capacities, where the test mixtures are prepared. Four different operating modes are possible: recirculation, once-through, partial recirculation, and system cleaning.

When concentrating solar collectors are used, the temperature of the water, which flows through them, rises considerably. Obviously, the slower the flow rate used in once-through experiments and the longer recirculation experiments, the greater the increase of temperature is. Therefore, to avoid evaporation and damage to plastics, cooling is necessary, and a closed-circuit water-cooling system has to be installed. A centrifugal pump with an electric motor (calculated to provide sufficient flow when the maximum length of the system is used) has to be installed to move the water to be tested in the reactor. The flow rate (in batch mode) has to be such that it guarantees only a small amount of reactant is converted each time through the reactor, and the concentration throughout the system remains relatively constant (this reasoning will become clear below). Either a flow-rate control loop made up of a flow meter connected to a controller, which in turn governs an automatic electric valve, or an electric pump with a speed controller has to be installed to regulate the flow to the rate desired. The most important sensors required for the system are temperature, pressure and dissolved oxygen (at least in the reactor outlet). As oxygen is required for the oxidation of organics, an injection system at the reactor inlet allows oxygen to be added to the reactor. Atmospheric oxygen can be also stirred into the reaction medium in the reservoir tank. A UV-radiation

sensor must be placed in a position where the solar UV light reaching the photoreactor can be measured, permitting the evaluation of the incident radiation as a function of hour of the day, clouds, atmospheric or other environmental variations. All these data have to be sent by an appropriate transmitter from the sensors to a computer, which stores the results for later evaluation. To clean the system, a drainage tube, with an active carbon filter to retain any organic compound not decomposed during the experiments, must be hooked up to the sewage pipelines.

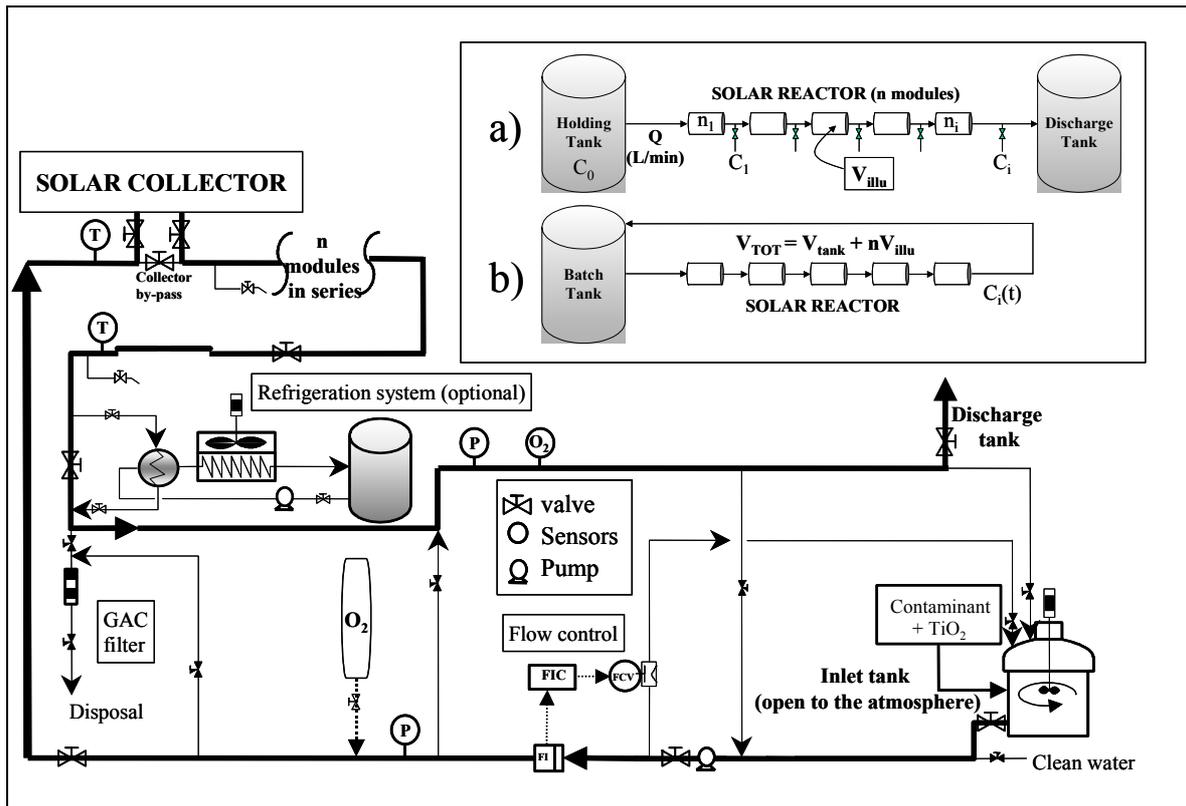


Figure 2.4. Photocatalytic Detoxification Pilot Plant scheme (once-through mode is shown).

In the inset is shown the schematic of two pilot plant operation concepts: A once-through operation (a) and a batch operation (b).

2.2.1 Operation of pilot plants

In the once-through mode (shown in Figure 2.4) the experimental procedure begins when the pump is turned on and the system is filled with clean water. Those modules necessary are selected and the corresponding valves are set to bypass the rest. Then the water is pumped through the circuit and the modules are covered. Obviously, the maximum pump flow rate is necessary for this procedure. The amounts required for obtaining the initial concentrations of catalyst, contaminant and any other ingredient in the experiment are added to the holding tank. When the time needed for mixture to be completed has expired, this is verified by taking samples at two different points in the reactor at the same time for analysis. A few minutes

later two more samples are taken and, if the four coincide, the concentration of the reactives may be considered to be the same throughout the reactor. Simultaneously, the automatic control sets the flow rate (Q), which will then be kept constant during the experiment, oxygen injection is activated and valves are adjusted so that the fluid goes to the discharge tank. After that the modules to be used are put into operation (uncovered). This marks the beginning of the experiment.

The modules are kept illuminated a little longer (experimental time) than necessary to allow the water in the holding tank to go through the reactor and approach the discharging tank. This time (t_{exp}) is:

$$t_{exp} = \frac{V_{tube} + nV_{mod}}{Q} \quad (2.10)$$

where Q is the flow rate, V_{tube} is the volume in the pipes between the modules and the tank and V_{mod} is the volume in each module, with n the number of modules in series. At this time, samples are taken at all the valves in the outlets of each of the modules in the experiment. This provides “ n ” number of samples with different residence or illumination times ($t_{R,i}$) to enable determination of kinetics. Under these conditions, the reactor behaves according to the ideal plug-flow model as explained later. The residence time corresponding to each sample collected at the end of the experiment is calculated with the following equation:

$$t_{R,i} = \frac{n_i V_{illu}}{Q} \quad (2.11)$$

where i is the number of modules through which the samples have passed before being collected and V_{illu} is the volume in the illuminated section of each module. When the test is over, n samples have been obtained with a reactor residence time that is a function of the flow rate. Thus, if the procedure is repeated at a different flow rate, that group of samples has a different t_R and the number of points ($t_{R,i}$, *Concentration*) necessary to evaluate any experiment can be obtained.

Solar detoxification pilot plants are frequently operated in a recirculating batch mode. In this scheme, the fluid is continuously pumped between the reactor and a tank in which no reaction occurs, until the desired degradation is achieved. The systems are operated in a discontinuous manner by recirculating the solution with an intermediate reservoir tank and centrifugal pump. This type of operation differs little from the previous one. When concentration of the reactives is the same throughout the reactor, oxygen injection (if necessary) is activated and the position of the valves is maintained so that the fluid begins and ends up in the holding tank (now called the batch tank). The automatic control sets the maximum flow rate which has to be such that it guarantees that only a small amount of reactant is converted each time it goes through the reactor. Then the modules that are going to be used are put into operation. This begins the experiment. Recirculation is continued and the test lasts however long

required, even up to several days. Samples may now be taken at any of the sampling ports, since as the system is in recirculation mode, t_R is the same for samples taken at any point in the system. The ($t_{R,i}$, *Concentration*) pairs are thus obtained (Eq. 2.12).

$$t_{R,i} = \frac{V_{illu}}{V_{TOT}} t_{exp,i} \quad (2.12)$$

where V_{TOT} is the volume of the entire pilot plant. V_{illu} and V_{TOT} are defined at the beginning of the experiment by the number of modules used and the level of water in the batch tank. The experimental time (t_{exp}) is the difference in time between the initial sample (initial concentration of the pollutant, $t_{exp} = 0$) and samples collected during the experiment ($t_{exp} > 0$).

2.3. FUNDAMENTALS PARAMETERS IN SOLAR PHOTOCATALYSIS

2.3.1 Direct photolysis

As mentioned before, some pollutants can be dissociated in the presence of UV light. For this, the pollutant must absorb the light with a reasonable photodissociation quantum yield. Although organic pollutants absorb light over a wide range of wavelengths, this is generally stronger at the lower wavelengths. In any case, the focus here is on fundamental photocatalytic parameters and therefore the photolytic effect will be discussed from this point of view. These tests have to be performed in order to find out the decomposition rates without the semiconductor. As TiO_2 readily sticks to the glass in the photoreactors, it is necessary to carry out these tests at the beginning, before the catalyst comes into contact with the photoreactors. In pilot-plant-scale experiments, removal of the thin coating of catalyst on the tubes after TiO_2 suspensions have circulated through them is a very hard, complex and expensive task. After these tests have been performed, the photocatalytic experiment results may be considered accurate and the kinetic parameters can be determined properly. Any side effect of the photocatalytic reaction rate can be quantified and subtracted from the global rate, resulting in the real photocatalytic reaction rate.

The case of acrinathrin is a good model of this effect (see Figure 2.5). Its spectrum overlap slightly in the 300-330 nm region with the Solar spectrum and, therefore, solar photons can produce photoalteration processes after being exposed to the environment. But such natural photodegradation is very slow: $E = 400 \text{ kJ/L}$ to reach 10 % of the initial concentration under aerobic well-illuminated conditions. And the TOC content is near 50 % of the initial at this moment. This effect should be very similar when acrinathrin is present in natural waters. In surface water degradation is extremely slow and in ground water almost negligible. So disposal of acrinathrin into the environment could be very risky. When TiO_2 is used (Figure 2.5), the degradation rate is increased and acrinathrin degradation is practically complete. A commercial formulation (Rufast®, acrinathrin 15%) has been used and the presence of other

organics in the formulation produces TOC to be the double than the stoichiometric quantity corresponding to acrinathrin.

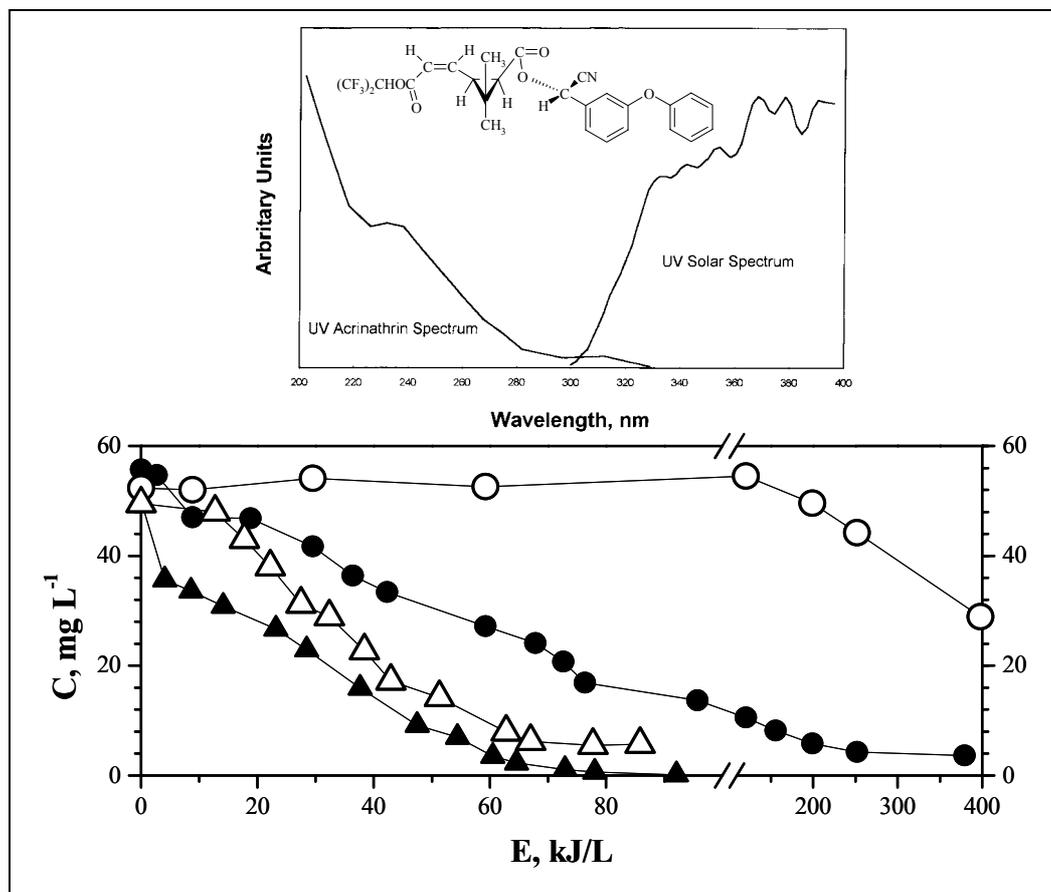


Figure 2.5. Disappearance of commercial acrinathrin by photolysis (●) and photocatalysis (▲) and evolution of Total Organic Carbon (open symbols). UV spectra between 200 and 400 nm of acrinathrin and sunlight is also shown.

2.3.2 Radiant flux

Since 1990 there has been a clarification of the kind of solar technology which should be involved in detoxification. The question was if to concentrate the radiation is really necessary for the photocatalysis technology and if a non-concentrating collector can be as efficient as concentrating ones. Initially it was thought that the last ones were the ideal alternative and in fact, the first large pilot plants operate with them. However, their high cost and the fact that they can only operate with direct solar radiation (this implies their location in highly insolated areas) led to consider the alternative of static non-concentrating collectors. The reason of using one-sun systems for water treatment is firmly based on two factors, first the high percentage of UV photons in the diffuse component of solar radiation and second the low order dependence of rates on light intensity.

It has been experimentally measured that above a certain flux of UV photons, reaction rate changes from one to half-order dependence to the intensity. This modification does not seem to happen at determined radiation intensity, as different researchers obtain different results. It is presumable that the experimental conditions affect significantly. Most authors impute the transition of $r = f(I^{1.0})$ to $r = f(I^{0.5})$, to the excess of photogenerated species (e^- , h^+ and $\bullet OH$). A very simple explanation could be the following (based on the first stages of the process). The first stages considered are: (i) formation of electron/hole pairs (Eq. 2.13), (ii) recombination of the pairs (Eq. 2.14) and (iii) oxidation of a reactant R (Eq. 2.15).



From these reactions, the concentration of holes is:

$$\frac{d[h]}{dt} = k_f I - k_R [e][h] - k_o [h]R \quad (2.16)$$

where I is the intensity of incident radiation. If it is considered that $[e] \approx [h]$, then in stationary state:

$$\frac{d[h]}{dt} = 0 \rightarrow k_f I = k_R [h]^2 + k_o [h]R \quad (2.17)$$

When I is very high, a large number of holes and electrons are generated and therefore $k_R [h]^2 \gg k_o [h]R$:

$$k_f I \approx k_R [h]^2 \rightarrow [h] \approx K I^{0.5} \quad (2.18)$$

As the reaction rate depends on the amount of hydroxyl radicals present, and these are generated in the holes (see Figure 2.3), then $r \propto I^{0.5}$ when I is high. Under these conditions, the quantum yield diminishes because of the high rate of recombination of e^-/h^+ pairs formed. In the same manner, when I is small, the inverse is true, $k_R [h]^2 \ll k_o [h]R$:

$$k_f I \approx k_o [h]R \rightarrow [h] \approx K' I \quad (2.19)$$

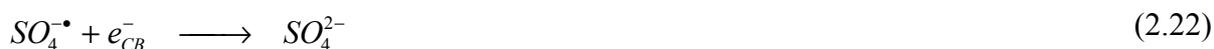
At higher radiation intensities, another transition from $r = f(I^{0.5})$ to $r = f(I^0)$ is produced. At this moment, the photocatalytic reaction leaves its dependence on the received radiation, to depend only on the mass transfer within the reaction. So, the rate is constant although the radiation increases. This effect can own to different causes, as can be the lack of electrons scavengers (i.e. O_2), or organic molecules in the proximity of TiO_2 surface and/or excess of products occupying active centers of the catalyst, etc. Really, these phenomena appear more frequently when working with supported catalyst, and/or at low agitation level. This implies low catalyst surface in contact with the liquid and smaller turbulence. This does not favor the contact of reactants with the catalyst and the diffusion of products, from the proximity of the catalyst to the liquid.

These effects may be appreciably attenuated if some product that reduces the importance of the electron/hole recombination is added. When the electrons are trapped, recombination of e^-/h^+ is impeded. Either way, 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 due to their strong oxidizing character. The use of inorganic peroxides has been demonstrated to enhance the rate of degradation of different organic contaminants remarkably because they trap the photogenerated electrons more efficiently than O_2 . It must be mentioned here that in many highly toxic wastewaters where degradation of organic pollutants is the major concern, the addition of an inorganic anion to enhance the organic degradation rate may be justified. Another advantage related to the use of this type of oxidant comes up when solar energy is the photon source. Although scientific research on photocatalytic detoxification has been conducted for at least the last three decades, industrial/commercial applications, engineering systems and engineering design methodologies have only been developed recently. The increase of the photocatalytic reaction rate with these additives would decrease photoreactor dimensions proportionally and dramatically decrease overall costs. The oxidizing substance should not generate any toxic by-product. Hydrogen peroxide is the obvious candidate and it has been tested with a large number of compounds. Also, it is a very commonly used chemical and, so, very cheap.

Being an electron acceptor, hydrogen peroxide can be a beneficial oxidizing agent because could react with conduction band electrons to generate hydroxyl radicals which are required for the photomineralization of organic pollutants. The effect depends on H_2O_2 concentration, generally showing an optimum range of concentration. At higher concentration values the improvement starts to lessen. Inhibition could be explained in terms of TiO_2 surface modification by H_2O_2 adsorption, scavenging of photoproducted holes and reaction with hydroxyl radicals.



Peroxydisulphate can be also a beneficial oxidizing agent in photocatalytical detoxification because $SO_4^{\cdot-}$ is formed from the oxidant compound by reaction with the semiconductor photogenerated electrons (e^-_{CB}). The peroxydisulfate ion accepts an electron and dissociates (Eq. 2.21). The sulfate radical proceeds through the reactions shown in Eqs 2.22 and 2.23. In addition, the strongly oxidizing $SO_4^{\cdot-}$ ($E^0 = 2.6$ V) can directly participate in the degradation processes.



The effect of both oxidants is shown in Figure 2.6. 25 mg/L of PCP is used as model compound in a 2-axis parabolic trough photoreactor (see Solar Photochemistry Technology). 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_{hv} , incident on the reactor. E_{hv} is calculated by Eq. 3.1.

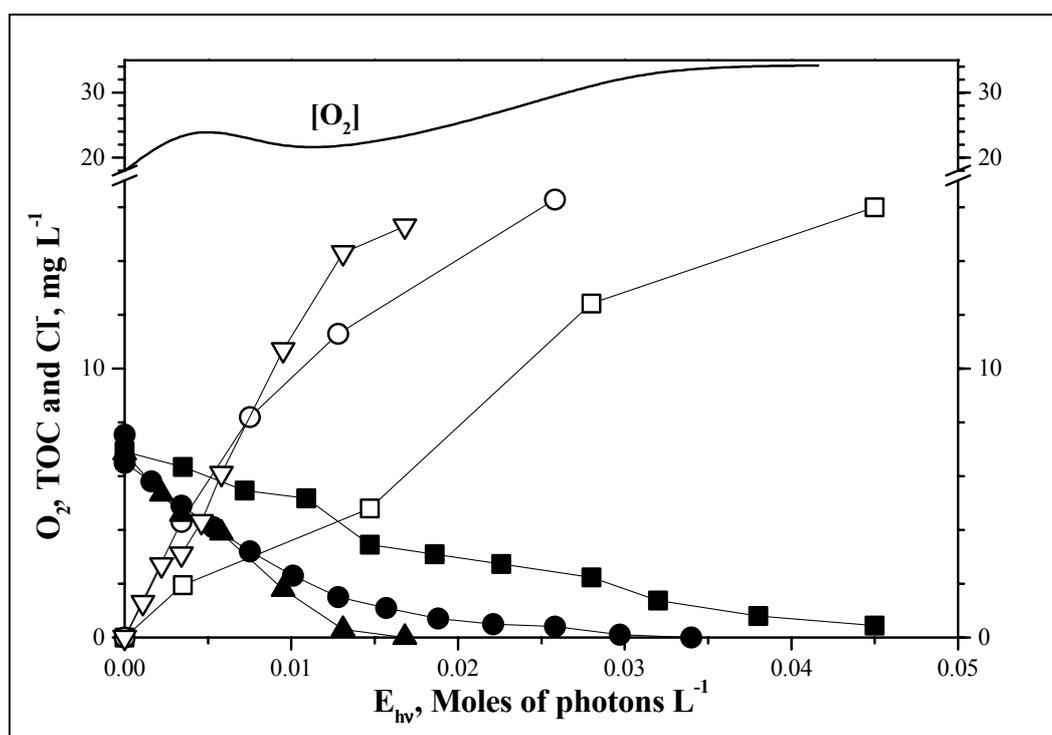


Figure 2.6. Pentachlorophenol (shown as TOC) mineralization (■), with H_2O_2 10 mM (●) and with $S_2O_8^{2-}$ 1 mM (▲) with a TiO_2 amount of 0.2 g L^{-1} . Chloride production (open symbols) and O_2 evolution during H_2O_2 experiment are also shown.

The results presented in Figure 2.6 demonstrate that hydrogen peroxide and peroxydisulphate enhance the photocatalytic reaction rate. The first increases the reaction rate by a factor of two and the second by a factor of five, respectively. The $S_2O_8^{2-}$ effect is more noticeable in the last part of the reaction. The presence of peroxydisulphate seems to affect essentially the mineralization of the degradation intermediates. Oxygen has not been injected during the H_2O_2 experiment but it reaches a value near 4 times more than the usual dissolved oxygen in water at ambient pressure (see point 2.4.2). This demonstrates that the application of hydrogen peroxide could be very useful when it is not possible to obtain an adequate concentration of oxygen in the reactor (a difficult engineering problem when the reactor is very long and narrow very usual in solar tubular reactors).

But, other oxidants have been used in photocatalysis for reducing solar (or artificial) UV exposure time: ClO_3^- , BrO_3^- , IO_4^- , HSO_5^- . Nevertheless, these additives are very expensive compared to hydrogen peroxide and peroxydisulphate, and their application would dramatically increase treatment cost. Even more importantly, they do not dissociate into harmless products (Br^- and I^-), because hundreds of mg/L of these anions are undesirable in water.

2.3.3 Initial concentration of contaminant

It is well known that in photocatalysis the degradation rate observed for an organic substrate follows saturation behavior. After a certain concentration is achieved, the rate increments very little and in some cases a decrease is observed. The optimum contaminants concentration in water before the photocatalytic treatment must permit the maximum reaction rate. So, the initial concentration of contaminants in the wastewater can be optimized, when possible. Since hydroxyl radicals react non-selectively, numerous intermediates are formed en-route to complete mineralization at different concentrations. Because of this, all tests have to be carried out using TOC as crucial parameter, because the photocatalytic treatment must destroy not only the initial contaminant, but any other organic compound as well. The results shown in Figure 2.7 are examples of the experiments carried out with mixtures of different commercial pesticides. 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.

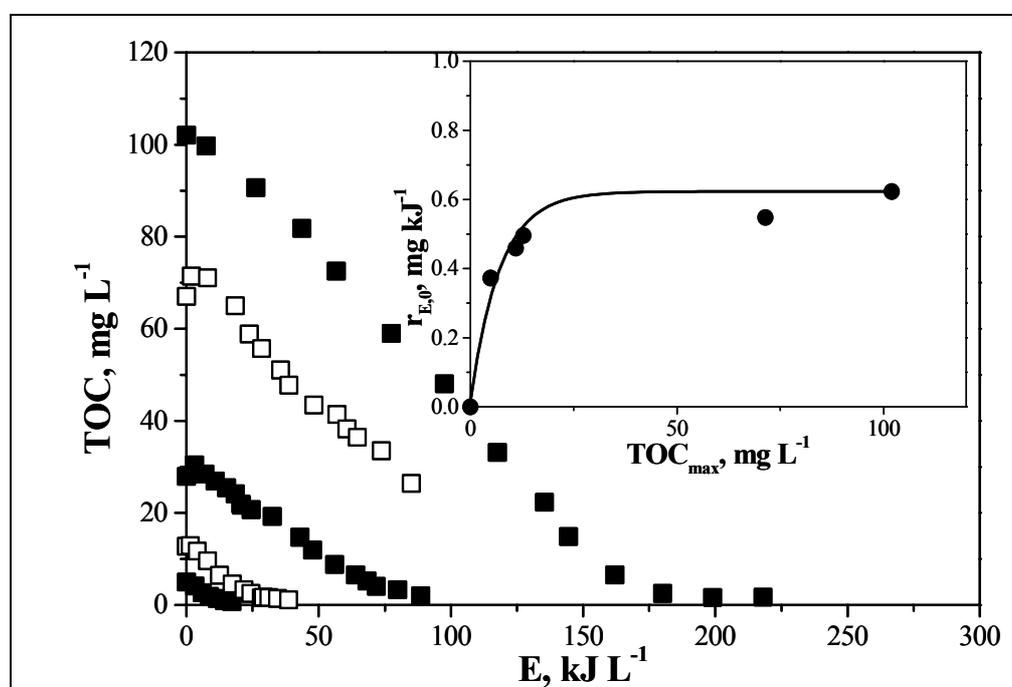


Figure 2.7. Pesticides decomposition at different initial concentrations. "Maximum rate" as function of TOC maximum TOC is shown in the inserted graphic.

As the reaction is 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 a lot of products that undergo manifold reactions. One parameter is proposed 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 ($r_{E,0}$). 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 $r_{E,0}$ is referred to as “maximum rate”. In the graphic insert in Figure 2.7, 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 is known, a model for predicting plant behavior is necessary. This model must allow calculation of the area of solar collectors required for treating water contaminated with different amounts of pesticides. Although different authors admit that the Langmuir-Hinshelwood (L-H) model is not a perfect explanation of the mechanism of the photocatalytic process, they do agree on its usefulness, since the behavior of the reaction rate versus reactant concentration can very often be adjusted to a mathematical expression with it. In the present case, instead of using the L-H model ($r = kKC/(I+KC)$) directly, the use of an alternative model is preferred for fitting experimental data in large solar photocatalytic plants, by an approximate kinetic solution of the general photocatalytic kinetic system, which has the analytical form of an L-H equation. With these considerations, the rate of TOC disappearance is given by Eq. 2.24 (analogous to L-H model but without its original significance).

$$r_{E,0} = \frac{\beta_1 [TOC]_{max}}{\beta_2 + \beta_3 [TOC]_{max}} \quad (2.24)$$

The experimental results shown in Figure 2.7 have been used to calculate the constants (β_i). By inversion of Eq. 2.24 these constants can be calculated from the intercept and the slope of the line of fit (Eq. 2.25), which is shown in the inset in Figure 2.8.

$$\frac{1}{r_{E,0}} = \frac{\beta_3}{\beta_1} + \frac{\beta_2}{\beta_1} \frac{1}{[TOC]_{max}}; \quad \frac{\beta_3}{\beta_1} = 1.67 \text{ mg}^{-1} \text{ kJ}; \quad \frac{\beta_2}{\beta_1} = 5.07 \text{ kJ L}^{-1} \quad (2.25)$$

Using these values, experimental results and the corresponding lines of fit are shown in Figure 2.8. The lines of fit were drawn with Eq. 2.26 using the constants reported previously.

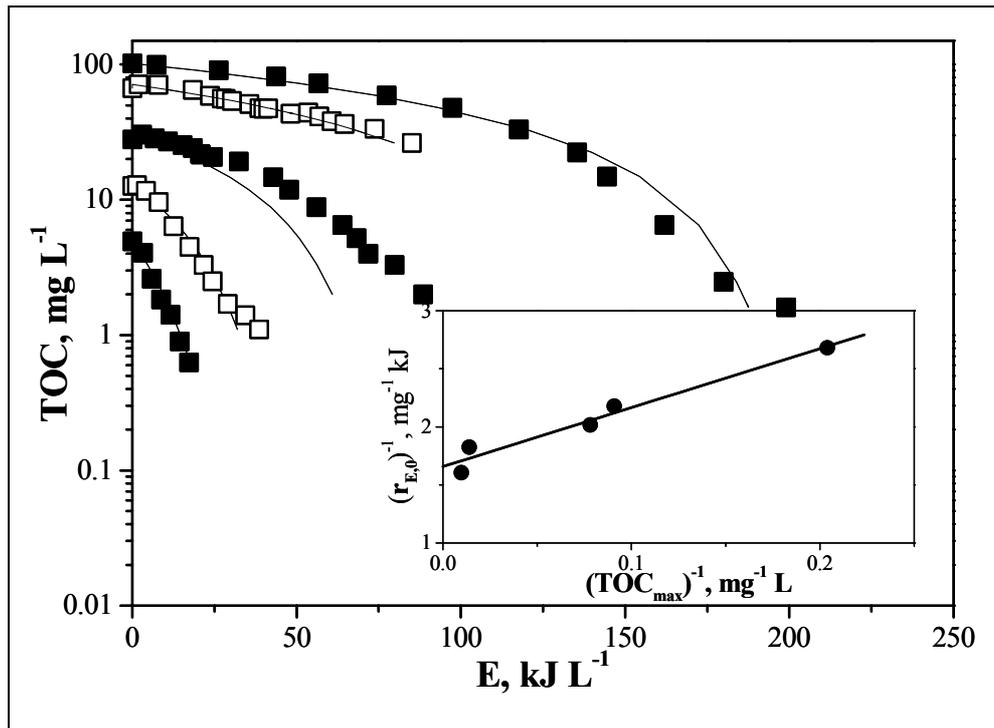


Figure 2.8. Application of the proposed kinetic model for mineralization of a pesticide mixture. The inset shows the fit of Eq. 2.25.

$$\frac{1}{\beta_1} \left\{ \beta_2 \ln \left(\frac{[TOC]_{max}}{[TOC]} \right) + \beta_3 ([TOC]_{max} - [TOC]) \right\} = E_{UV} \quad (2.26)$$

The experimental results agree reasonably well with the model proposed and the constants calculated. This equation allows TOC degradation to be predicted as a function of initial TOC and available radiation, and the reverse, incident energy on the reactor necessary to reach a specific degree of mineralization. As seen in Figure 2.8, fits are not perfect, but taking into account the experimental and accumulative errors, the adjustment may be considered acceptable. These errors could have been produced in the following measurements: (i) reactor volume and experiment time; (ii) analytical determinations; (iii) UV radiation measurement and (iv) calculation of $r_{E,0}$ from the maximum slope of each of the experiments shown in Figure 8. Therefore, useful design equations may be obtained with a Langmuir-Hinshelwood type model, in spite of not fitting the heterogeneous photocatalytic reaction mechanism. For now these equations must be obtained at pilot plant size, however, they will be useful for larger plants if the same type of collector is used

2.4. FACTORS AFFECTING SOLAR PHOTOCATALYSIS

2.4.1. Relationship between particle size, reactor diameter and TiO₂ concentration

There are a number of studies in the literature on the influence of catalyst concentration on process efficiency. Although the results are quite different, it may be deduced from all of them that incident radiation on the reactor and length of path inside the reactor are fundamental in determining optimum catalyst concentration. This summarizes the conclusions if the radiation comes from a source of radiation placed outside the photoreactor (as in a reactor illuminated by solar radiation):

- If the path length is short (1-2 cm max.), maximum reaction rate is obtained with 1-2 g L⁻¹ of TiO₂.
- If the path length is several centimeters long, the appropriate catalyst concentration is several hundred milligrams per liter.

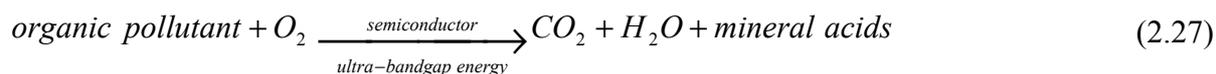
In all the cases described above, a “screening” effect is produced when the TiO₂ concentration is very high. The reaction rate diminishes due to the excessive opacity of the solution, which prevents the catalyst farthest in from being illuminated. Approximately, 1 g L⁻¹ of catalyst reduces transmissivity to zero in a 1-cm-inner-diameter cylinder. For the solar reactors, it is therefore necessary to find out the optimum catalyst concentration experimentally. That is, the minimum concentration at which the maximum reaction rate is obtained. When catalyst concentration is very high, after traveling a certain distance on an optical path length, turbidity impedes further penetration of light in the reactor. The percentage of photons absorbed by the suspension and the percentage of photons scattered by the TiO₂ particles is a very complex problem that cannot be solved experimentally, but must be experimentally estimated.

The titanium dioxide employed in the photocatalytic experiments is disposed as a colloidal suspension. The great difference between considering the TiO₂ from dry powder and TiO₂ particles suspended in an aqueous medium is the mean size of the particles. If two samples with the same catalyst concentration but dispersed with different protocols (ultrasounds and stirring) are compared; sonicated samples are found to be more efficient. Although in stirred samples there are fewer TiO₂ clusters, larger clusters screen light better than small ones. The photocatalytic experiments carried out with different particle sizes have demonstrated that efficiencies are better with small particles than with larger particles only when reactor diameter and catalyst concentration are optimized to allow UV photons to penetrate along the entire photoreactor path length. In this case, it is not possible to talk about particle radius, because TiO₂ powder is irregularly shaped, and when it is dispersed in an aqueous medium the “particles” (300-600 nm sized) are clusters of primary particles (20-40 nm sized), not spherical or monodisperse. This leads to the conclusion that light extinction in colloidal suspensions is a determining parameter for solar photoreactor design. It should also be recalled that small particle sizes cause additional problems for catalyst separation after photocatalytic treatment. The best inner reactor diameter, for solar photocatalytic applications

is in the range of a few centimeters with a few hundred mg of TiO₂ per liter. The area/volume ratio is also a crucial parameter, and if this ratio is optimized the reactor efficiency would also be increased.

2.4.2. Influence of oxygen

In semiconductor photocatalysis for water purification, the pollutants are usually organic and, therefore, the overall process can be summarized by Eq.24. Given the reaction stoichiometry of this equation, there is no photomineralization unless O₂ is present. The literature provides a consensus regarding the influence of oxygen. It is necessary for complete mineralization and does not seem to be competitive with other reactives during the adsorption on TiO₂ since the places where oxidation takes place are different from those of reduction (see Figure 2.3). Therefore, injection of pure O₂ becomes necessary in once-through experiments (see Figure 2.4) at low flow rates. At high flow rates or with recirculation, the addition of oxygen is not always necessary since the illumination time per pass is short. The water again recovers the oxygen consumed when it reaches the tank (open to the atmosphere and stirred).



The concentration of oxygen also affects the reaction rate but it seems that the difference between using air ($p_{O_2} = 0.21$ atm) or pure oxygen ($p_{O_2} = 1$ atm) is not drastic. In an industrial plant it would be purely a matter of economy of design. Therefore, injection of pure O₂ becomes necessary in once-through designs at low flow rates. At high flow rates or with recirculation, the addition of oxygen is not always necessary since the illumination time per pass is short. The water again recovers the oxygen consumed when it reaches the tank (open to the atmosphere and stirred).

2.4.3. pH influence

The oxide/electrolyte interface has an electrical surface charge, which strongly depends on the pH of the medium. The electrokinetically mobilized charge is a determining parameter in the colloidal stability of the oxide particle suspensions. This involves the study of particle sizing depending on the pH; if the pH is equal to the Point of Zero Charge (PZC) the particles aggregate and ensembles are larger. The pH of the aqueous solution significantly affects TiO₂, including the charge of the particle and the size of the aggregates it forms. 300 nm sizes increase to 2-4 μm when dispersion reaches PZC. The zero surface charge yields zero electrostatic surface potentials that cannot produce the interactive rejection necessary to separate the particles within the liquid. This induces a phenomenon of aggregation and TiO₂ clusters become larger. This effect is clearly related to the capability of the suspension for transmitting and/or absorbing light. Furthermore, larger clusters sediment more quickly than small particles, thus the agitation necessary to maintain perfect homogeneity must be more

vigorous. The PZC for TiO₂ is around 7. Above and below this value, the catalyst is negatively or positively charged according to:



The abundance of all the species as a function of pH: TiOH ≥ 80% when 3 < pH < 10; TiO⁻ ≥ 20% if pH > 10; TiOH₂⁺ ≥ 20% when pH < 3. Under these conditions, the photocatalytic degradation of the ionisable organic compounds is affected by the pH. At first sight a very acidic solution appears to be detrimental and a very basic solution to be favorable, since the variations are modest or non-existent around neutrality. In many cases, a very important feature of photocatalysis is not taken into account when it is to be used for decontamination of water, is that during the reaction, a multitude of intermediate products are produced that may behave differently depending on the pH of the solution. To use only the rate of decomposition of the original substrate could yield an erroneous pH as the best for contaminant degradation. Therefore, a detailed analysis of the best pH conditions should include not only the initial substrate, but also the rest of the compounds produced during the process.

2.4.4. Temperature influence

Because of photonic activation, photocatalytic systems do not require heating and operate at room temperature. The true activation energy is nil, whereas the apparent activation energy is often very low (a few kJ/mol) in the medium temperature range (20°C-80°C). However, at very low temperatures (-40°C-0°C), activity decreases and activation energy becomes positive. The decrease in temperature favors reactants adsorption, which is a spontaneous exothermic phenomenon, but also favors adsorption of the final reaction products, desorption of which tends to be the rate-limiting step. By contrast, at "high" temperatures (>70-80°C) for various types of photocatalytic reactions, the activity decreases and the apparent activation energy becomes negative. When temperature increases above 80°C, nearing the boiling point of water, the exothermic adsorption of reactants is disfavored and this tends to become the rate-limiting step.

In addition to these mechanical effects, other consequences of plant engineering must be considered. If temperature is high, the materials used for the plant should be temperature-resistant and oxygen concentration in water decreases. Consequently, the optimum temperature is generally between 20 and 80°C. This absence of need for heating is attractive for photocatalytic reactions carried out in aqueous media and in particular for environmental purposes (photocatalytic water purification). There is no need to waste energy heating water that already possesses a high thermal capacity.

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