

# **SOLAR PHOTOCATALYSIS AND WATER TREATMENT: DETOXIFICATION AND DISINFECTION**

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**Keywords:** Inorganic peroxides, photolysis, solar disinfection, solar photocatalysis, solar pilot plants, titanium dioxide, wastewater treatment

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## **Summary**

This chapter describes 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 discussed. 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 presented. Finally, an overview of other factors affecting solar photocatalysis is presented, such as catalyst concentration and

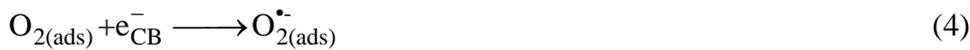
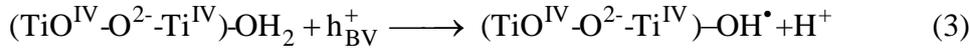
particle diameter, photoreactor diameter, oxygen, pH, and temperature. The chapter also summarizes most of the research related to solar photocatalytic degradation of water contaminants carried out during recent years, and how it could significantly contribute to the treatment of very persistent toxic compounds, as well as the use of the solar photocatalytic processes to inactivate microorganisms present in water.

## 1. Introduction

The latest advances in water purification have been in the oxidation of very persistent organic compounds dissolved in water. The methods based on catalysis and photochemistry is known as advanced oxidation processes. Among them, those which produce hydroxyl radicals ( $\cdot\text{OH}$ ) have had growing success. Methods based on UV,  $\text{H}_2\text{O}_2/\text{UV}$ ,  $\text{O}_3/\text{UV}$  and  $\text{H}_2\text{O}_2/\text{O}_3/\text{UV}$  combinations utilize photolysis of  $\text{H}_2\text{O}_2$  and ozone to produce the hydroxyl radicals. As mentioned in *Photochemical Conversion of Solar Energy* 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  $\text{CO}_2$  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,  $\text{TiO}_2$  has generally been demonstrated to be the most active. Only  $\text{ZnO}$  is as active as  $\text{TiO}_2$ .  $\text{TiO}_2$ 's strong resistance to chemical and photocorrosion, its safety and low cost, limit 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 (see Figure 1) which can be surpassed by the energy content of a solar photon ( $\lambda > 300 \text{ nm}$ ). Other semiconductor particles, e.g.,  $\text{CdS}$  or  $\text{GaP}$  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  $\text{TiO}_2$  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,  $\lambda < 390 \text{ nm}$ , is the generation of electron/hole pairs, which are separated between the conduction and valence bands (Eq. (1)). In order to avoid recombination of the pairs generated (Eq. (2)), if the solvent is oxidoreductively active (water) it also acts as a donor and acceptor of electrons. Thus, on a hydrated and hydroxylated  $\text{TiO}_2$  surface, the holes trap  $\bullet\text{OH}$  radicals linked to the surface (Eq. (3)). In any case, it should be emphasized that even trapped electrons and holes can rapidly recombine on the surface of a particle (Eq. (2)). This can be partially avoided through the capture of the electron by preadsorbed molecular oxygen, forming a superoxide radical (Eq. (4)).

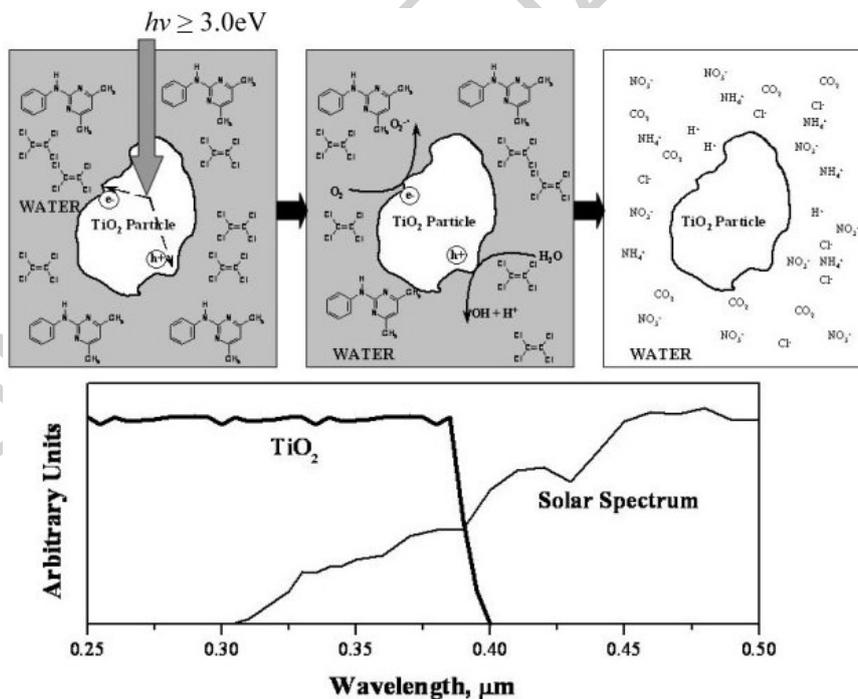


Figure 1. Effect of UV radiation on a  $\text{TiO}_2$  particle dispersed in water and subsequent destruction of the organics dissolved in water.  $\text{TiO}_2$  absorption spectrum compared with solar spectrum is also shown.

Whatever the formation pathway is, it is well known that  $O_2$  and water are essential for photooxidation with  $TiO_2$ . There is no degradation in the absence of either substance. 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 details in the following sections.

## 2. Fundamental Parameters in Solar Photocatalysis

### 2.1. Direct Photolysis

As mentioned in *Photochemical Conversion of Solar Energy*, 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. 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.

	$t_{illum.}$	%	$t_{illum.}$	%
<b>Imidacloprid</b>	24 h	27	48 h	55
<b>Methomyl</b>	24 h	0	48 h	0
<b>Diuron</b>	24 h	20	48 h	44
<b>Formetanate</b>	24 h	10	48 h	10

Table 1. Photolysis expressed as % disappearance of the selected pesticides.

Table 1 shows results of photolysis experiments with four pesticides. The results obtained indicate that the spontaneous degradation due to solar illumination is always unimportant. Methomyl is not degraded at all. Figure 2 shows the spectra of aqueous solutions of the four pesticides and solar spectrum. Methomyl and solar UV spectra do not overlap, showing that capacity for absorption of solar photons cannot produce

photoalteration processes after being exposed to the environment. Imidacloprid, diuron and formetanate and solar UV (latitude 37°N, longitude 2.4°W) spectra slightly overlap in the 300-to-330-nm region (Figure 2) showing that absorption of solar photons can produce photoalteration after exposure to the environment.

But such natural photodegradation is very slow under well-illuminated aerobic conditions. The effect must be very similar when these pesticides are disposed of in natural waters. In surface water degradation is extremely slow and in ground water almost negligible. So disposal into the environment could be very risky.

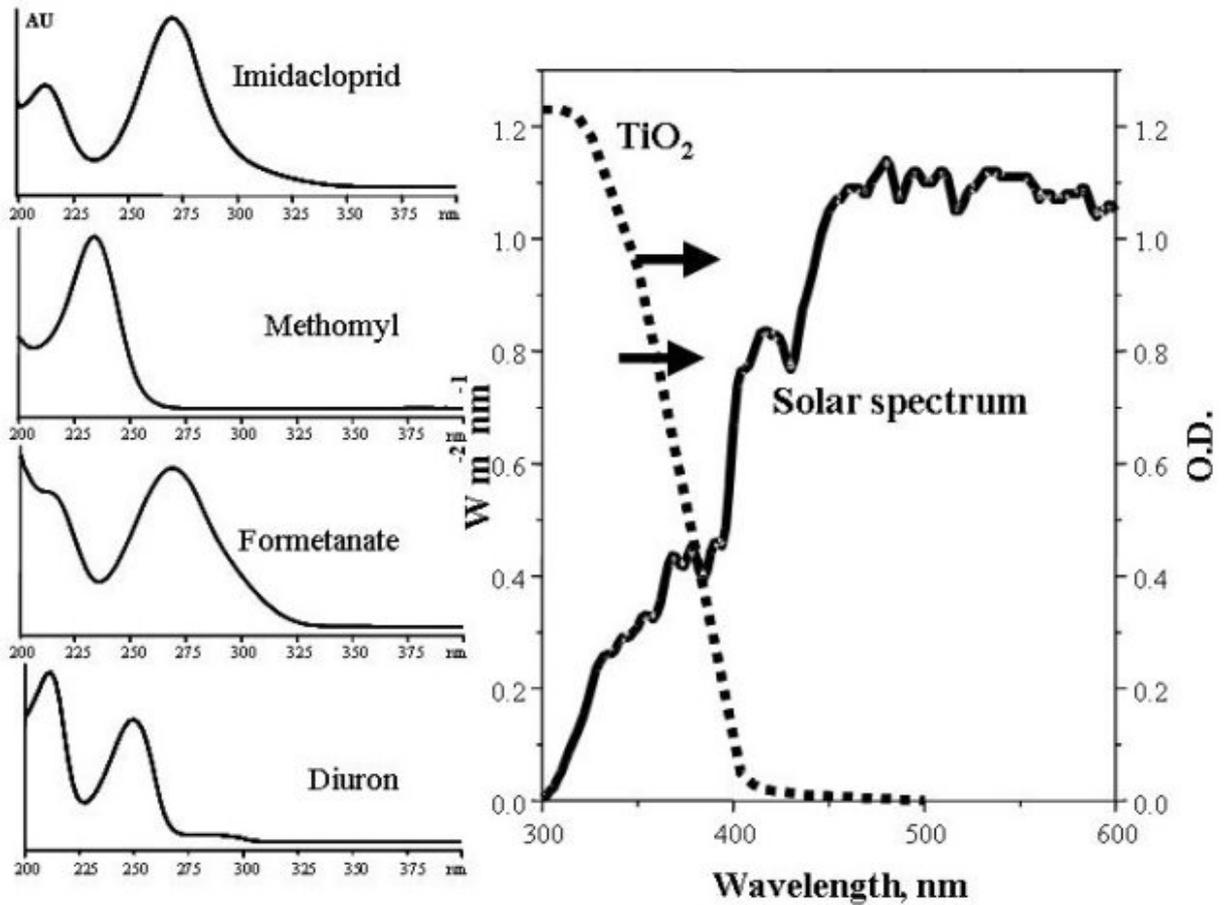


Figure 2. UV spectra of the four pesticides and solar spectrum.  $\text{TiO}_2$  absorption spectrum is also shown.

Figure 3 shows photocatalytic degradation of all pesticides. It may be observed that all the pesticides are degraded in a short time (less than 150 min). The order is the following: diuron > methomyl > imidacloprid > formetanate. Excluding methomyl (an “aliphatic” pesticide), the  $\text{TiO}_2$  order seems to be related with pesticides solubility. As more soluble, less reaction rate was observed. It is reasonable to induce that the less soluble pesticides absorb easily on  $\text{TiO}_2$  and react quicker.

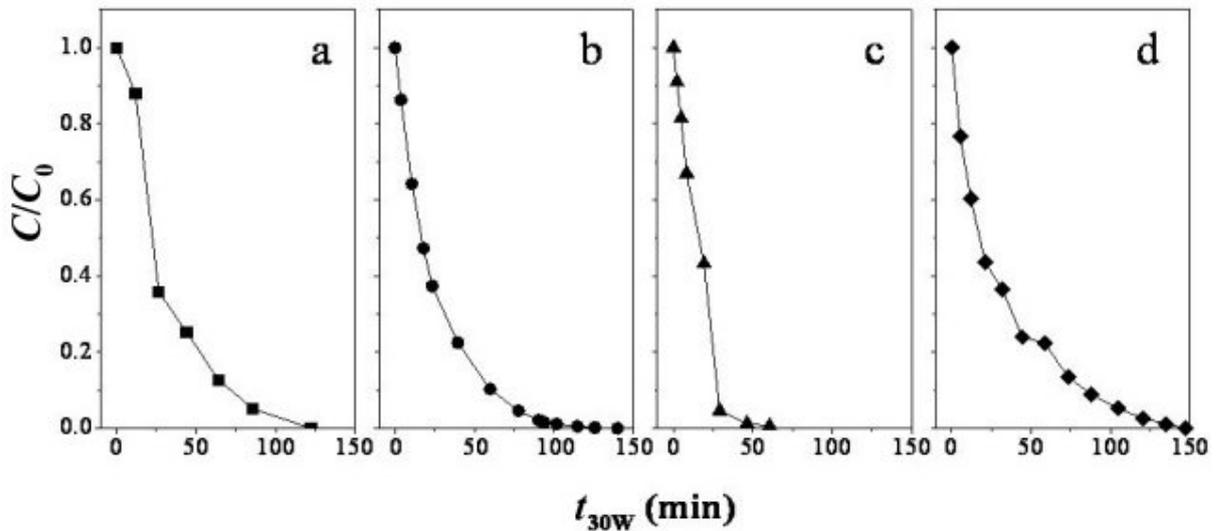


Figure 3. Disappearance of imidacloprid (a), methomyl (b), diuron (c) and formetanate (d) as a function of  $t_{30W}$  (illumination time, see *Photochemical Conversion of Solar Energy*).  $\text{TiO}_2$  (200 mg/L).

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### Biographical Sketches

**Sixto Malato**. Born in Almería (Spain) on 10<sup>th</sup> May, 1964. Dipl. Chemistry (Chemical Engineering) by Facultad de Ciencias of University of Granada (1987). Master in Environmental Sciences by the Instituto de Investigaciones Ecológicas (Málaga, 1994). PhD in Chemical Engineering at the University of Almería (1997). 18 years of experience having worked at different sectors.

His professional activities started in 1987 as Junior Researcher in Chem. Eng. Department of Univ. of Almería; in 1988 he joined the Production Department in an oil refinery (REPSOL S.A.) in Puertollano (Spain). Since 1990 he works at the Plataforma Solar de Almería (PSA-CIEMAT) in all the EU R&D projects linked to the Solar Detoxification of water. Concretely, he has been involved in 11 EU, 13 National R&D Projects and 6 R&D Contracts (with Private Companies) related to the development of solar wastewater treatment technologies, and has been involved in the design and construction of all the experimental pilot plants for solar detoxification of industrial waste water in Europe. He author of 1 book and co-author of 5 books as well as 21 chapters in others. He has also co-authored more than 100 publications in indexed international journals, 21 articles in technical journals and more than 140 contributions to 68 different International Congress and Symposiums and 4 patents. He has attended 31 Workshops and Conferences on Water Treatment and participated as a teacher in 17 courses on Advanced Wastewater Treatment. He has directed 4 PhD dissertations. The Jury's Grand Prix of "European Grand Prix for Innovation Awards" (Monaco, December 2004)

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