SOLAR PHOTOCHEMISTRY APPLICATIONS

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Summary

Detoxification of contaminated water and air streams is clearly the most successful photochemical application of solar photons. Particularly, heterogeneous TiO_2 photocatalysis and homogeneous Photo-Fenton are the processes for which the solar technologies are most extensively studied and developed today from the point of view of practical applications to treat water contaminants. Other solar photochemical processes are still at a very early research stage. These photocatalytic processes can be applied to hazardous non-biodegradable contaminants, with no easy conventional treatment, in the range of several hundred mg L^{-1} of maximum organic concentration. The process can also be valid to complex mixtures of organic contaminants.

Solar photocatalytic technology can be considered tested and useful for addressing hazardous contaminants such as phenols, agrochemical wastes, halogenated hydrocarbons, biocide compounds from the pharmaceutical industry, wood preserving waste, hazardous metal ions, cyanides and aqueous munitions waste. Other interesting

applications are the treatment of groundwater contamination, seaport tank terminals, cleaning of contaminated landfills and water disinfection.

Biological treatment of residual waters, when feasible, is always the most economical. However, biological processes are only applicable to biodegradable water contaminants so more expensive treatments, such as photocatalytic ones, only make sense to be applied to hazardous non-biodegradable pollutants. In this way, an optimized approach is the combination of both processes. Biologically recalcitrant compounds can be treated with photocatalytic technologies until biodegradability is achieved, transferring later the water to a conventional biological plant. Operation and investment costs of solar photocatalytic plants are estimated to be competitive when compared with conventional technologies for the treatment of hazardous contaminants, at locations with a yearly average solar UV irradiation higher than 15 W m^{-2}.

Solar gas-phase applications are in a preliminary stage as some crucial questions related to the basic fundamentals and the technology still persists. In gas gas-phase PCO, catalyst must be supported and diverse materials (glass fibers, ceramic substrates, inert plastic materials, monoliths, etc) have been used as supporting substrates. Some potential gas-phase applications are gas treatment from contaminated landfill recovering, degradation of emissions in the semiconductor industry, air purification, air disinfection, and self-cleaning windows.

1. Introduction

Detoxification is currently the most successful photochemical application of solar photons, with several relevant installations and projects already in operation. This is due not only to the fact that solar detoxification is an outstanding demonstration of how well suited solar energy is to environmental conservation, but also because, contrary to most photochemical processes, it is non-selective and can be employed with complex mixtures of contaminants. During the 1990s, there are a number of references and related patents on heterogeneous photocatalytic removal of toxic and hazardous compounds from water and air as well as a number of applications and target compounds. Other photochemical processes are still at a very early research stage.

From the point of view of practical applications, heterogeneous TiO_2 photocatalysis and homogeneous Photo-Fenton are the processes for which the solar technologies are most extensively studied and developed today. In other solar photochemical options, such as sensitized-photochemical oxidation by singlet oxygen, there is still very limited experience to date.

Photocatalytic oxidation processes (PCO) currently under development are included in the same group of Advanced Oxidation Technologies (AOT) with other radical-promoting processes like plasma and electron-beam. The main advantage of PCO over other AOTs is its potential for incorporating solar energy in the form of solar photons, whereby the degradation process acquires significant additional environmental value. If solar photons can be collected and used efficiently at low cost, the number of opportunities for PCO may increase dramatically. Although solar driven PCO was at first considered a universal method of degrading organic pollutants, a profusion of contradictory results during recent years (positive results in almost real problems together with other experimental results pointing out uncertainties and negative performance) has lead to confused public perception. Solar PCO technology is currently viewed as very sensitive to many parameters and scientific opinion is evolving toward a more conservative phase of specific applications.

Within this context, treatment of industrial wastewater seems to be one of the most promising fields of application of solar detoxification. However, the main obstacle to the full development of this application is the slow kinetics and the low efficiency in the production of hydroxyl radicals because it may limit the economic feasibility. When industrial wastewater are considered, there is no general rule at all to previously determine the potential feasibility of solar photocatalytic applications**,** each case being completely different from the other. As a consequence, preliminary research is always required to assess the potential pollutant treatment and optimizing the best option for any specific problem, nearly on a case-by-case basis. In an attempt to provide some guidelines, based on the accumulated experience, the following general affirmations may be made:

- <u>Maximum organic concentration of several hundred mg L^{-1}</u>. Photodegradation processes work well in low or medium concentrations up to a few hundred mg L^{-1} of organics. The limit always depends on the nature of the contaminants, but concentrations over 1 g L^{-1} normally are not suitable for solar photocatalytic processes unless previously diluted.
- <u>Non-biodegradable contaminants</u>. When possible, biological treatments are always the most cost-effective processes. Only when the contaminants are persistent (non-biodegradable) photocatalytic processes do make sense.
- <u>Hazardous contaminants present within complex mixtures of organics</u>. One of the main advantages of solar photocatalysis is that it is non-selective, so non-biodegradable contaminants can be treated within a complex mixture of other organic compounds. Solar detoxification also works very well with individual contaminants, but a mixture could be an indication of its utility. Hazardous contaminants also usually appear in concentrations susceptible to photocatalytic treatment.
- <u>Contaminants with no easy conventional treatment</u>. An additional hint of whether solar photocatalysis will be useful can be provided by the fact that contaminants are present in concentrations that make conventional treatment difficult.

The above recommendations provide an indication of the type of industrial waste water for which solar detoxification can potentially be employed. Nevertheless, several additional conditions are needed before a complete solar detoxification feasibility study can be undertaken.

- <u>Throughputs should be reasonable</u>. Spatial velocities or surface throughputs in the solar collector and solar-photon consumption related to the total volume to be treated should be acceptable. The treatment capacity must be high enough to make photocatalytic degradation practical. Many aqueous organic oxidation processes are too slow to be economically viable.

- Solar photons must be used efficiently. The technology to be applied must optimize the collection of solar photons to be used. The overall energy needed per molecule destroyed must also be low enough to make the process feasible and the use of external oxidants, such as electron scavengers, like $S_2O_8^{=}$, H_2O_2 or O_3, must be possible to increase the quantum yield.
- The photocatalytic process should be reliable (no catalyst deactivation). The degradation process must work continuously without problems, such as catalyst deactivation. Collectors, components, catalyst and overall system must also be durable, guaranteeing long periods of operation without incident.
- Operation and maintenance processes must be simple. The implementation of any real solar detoxification technology application requires minimum operation and system supervision. Operation and maintenance costs must be reduced to a minimum.
- Batch system treatment. It is clear that water treatment with solar detoxification should be run in recirculation mode with batch loads of contaminants to guarantee complete destruction. This means that the treatment must be independent of the process generating the wastewater and that online treatments normally are not feasible.

Applications that fulfill both groups of requirements may be considered candidates for solar detoxification and a detailed feasibility test study would be worth to be considered.

2. Solar Photocatalytic Treatment Plants

Solar photocatalytic treatment plants are normally designed to be operated in batch mode. The operation philosophy beyond these plants is described in Figure 1.

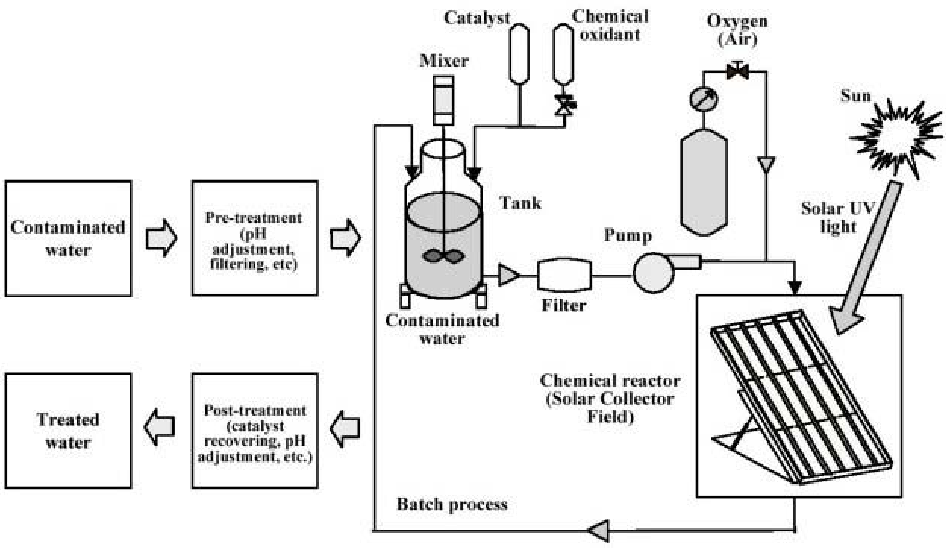

Figure 1. Conceptual design of a solar photocatalytic treatment plant

Contaminated water must be firstly pre-treated to address the organic destruction process in the best possible conditions. Also, pre-treatment objective could be the elimination of possible constituents of the contaminated waters that interfere with the process. After this the catalyst is added and the mixture is pumped in a batch process through the chemical reactor (solar collector field) until the contaminants are degraded. Depending on the nature of the contaminants to be treated, some potentially useful chemical oxidants can be added to enhance the process efficiency. Once the process is completed, the post-treatment processes must adjust the water chemistry to conditions suitable for discharge. In the case of industrial wastewater with a posterior biological treatment, the post-treatment could only be reduced to a pH adjustment and catalyst recovery.

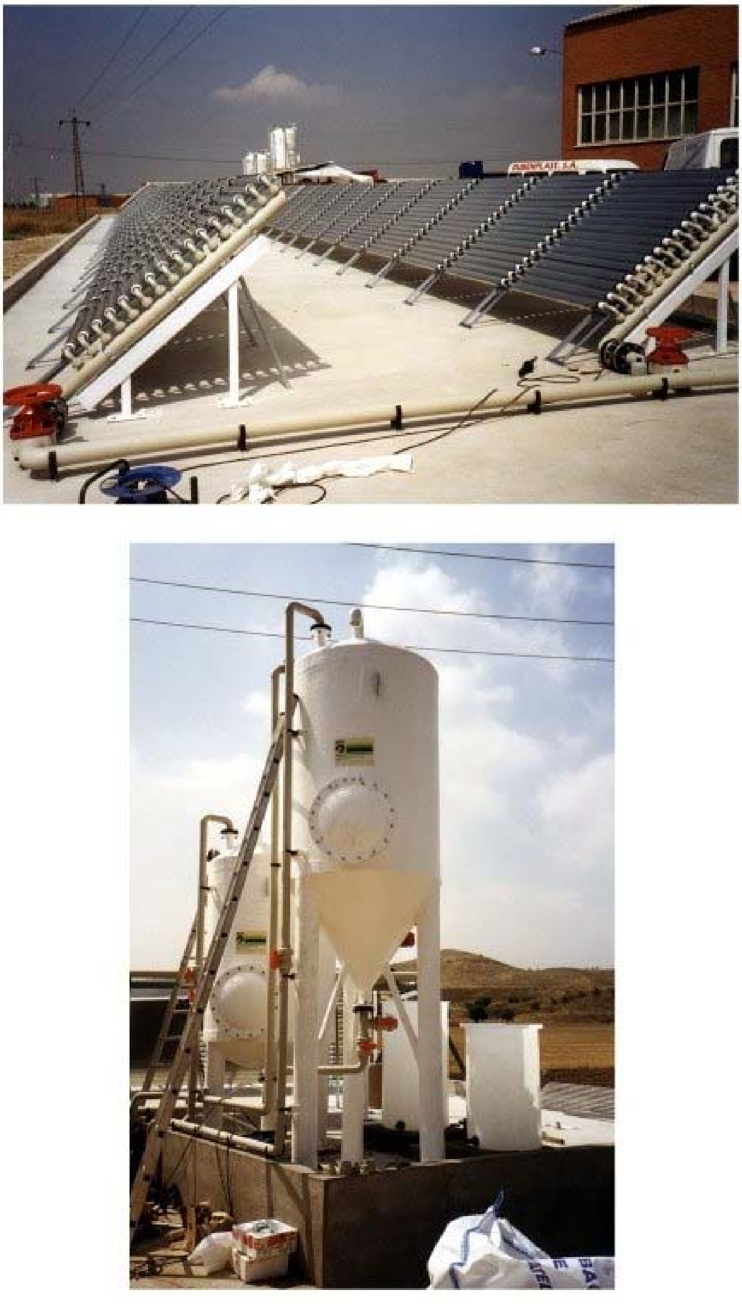

Figure 2. Two views of an industrial solar photocatalytic treatment plant setup (Madrid, Spain, 1999)

An experimental solar photocatalytic plant to industrial wastewater treatment with the previously indicated conceptual design is shown in Figure 2. In this plant, the water to be treated is initially stored in the storage tank, from where the buffer tank and all the hydraulic circuit of solar collectors is completely filled just by gravity. Here, water is continuously recirculated through the reactors until the desired destruction is achieved. TiO_2 catalyst and chemical additives are prepared separately in small deposits and are fed into the treatment circuit during the equivalent of two recirculation cycles, to guaranty a complete homogenization. About 75 percent of the total volume of the treatment circuit is continuously exposed to the solar radiation in the solar reactors. Once the desired destruction is obtained, the water is transferred to the catalyst separation tank, and the treatment circuit is filled again with new wastewater to be treated, restarting the process.

The plant is designed with full automatic control systems and minimum operation and maintenance requirements. Achieved level of water treatment is indirectly measured by measuring sunlight availability. In this way, a solar UV-A sensor is incorporated within the electronic control devices, with the function of solar UV integration from the beginning of the treatment process. This sensor is connected to a Programmable Logic Controller (PLC) and, once the level of energy to fulfill the treatment has been achieved (previously determined from preliminary test for plant design, according to each specific contaminated wastewater to be treated), the PLC stops the main pump, transfer the water to the catalyst separation tank and advise the operator that the treatment has been completed. The PLC receives also other data signals (such as flow rate, tanks level, and temperature) to control the pumps and valves of the system. Specifically developed software controls all normal operation procedures and sequences, so very little direct human intervention is needed. Orders are introduced throughout a keyboard and a printer indicates alarms and main system events.

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Biographical Sketches

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

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

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

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

Sixto Malato Dipl. Chemistry (Chemical Engineering) by *Facultad de Ciencias of University of Granada* (1987). Master in Environmental Sciences by the *Instituto de Investigaciones Ecológicas* (Málaga, 1994). PhD in Chemical Engineering at the *University of Almería* (1997). 14 years of experience having worked at different sectors. His professional activities started in 1987 as Junior Researcher in Chem. Eng. Department of Univ. of Almería; in 1988 he joined the Production Department in an oil refinery (REPSOL S.A.) in Puertollano (Spain).

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

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