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Photocatalytic decontamination and disinfection of water with solar collectors

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Abstract

In recent years, there has been a tremendous amount of research and development in the area of photocatalysis, a process included in a special class of oxidation techniques defined as advanced oxidation processes (AOPs), all characterized by the same chemical feature, production of $^{\bullet}OH$ radicals. This paper reviews the use of sunlight to produce the $^{\bullet}OH$ radicals. The systems necessary for performing solar photocatalysis are described. The paper 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. Various solar reactors for photocatalytic water treatment based mainly on non-concentrating collectors erected during the last few years are also described in detail in this review, as well as the use of the solar photocatalytic processes to inactivate microorganisms present in water, placing special emphasis on some experimental systems erected to optimize this disinfecting technique.

Keywords: Photo-Fenton; Solar collectors; Solar disinfection; Solar photocatalysis; Wastewater treatment

1. Introduction

The main causes of surface and groundwater contamination are industrial effluents (even in small amounts), excessive use of pesticides, fertilizers (agrochemicals) and domestic waste landfills. Wastewater (WW) treatment is usually based on physical and biological processes. After elimination of particles in suspension, the usual process is biological treatment (natural decontamination). Unfortunately, some organic pollutants, classified as bio-recalcitrant, are not biodegradable. In the near future, advanced oxidation processes (AOPs) may become the most widely used water treatment technologies for organic pollutants not treatable by conventional techniques due to their high chemical stability and/or low biodegradability [1–4]. These processes involve generation and subsequent reaction of hydroxyl radicals ($^{\bullet}OH$), which are one of the most powerful oxidizing species. Many oxidation processes, such as TiO_2/UV, H_2O_2/UV, photo-Fenton and ozone (O_3, O_3/UV, O_3/H_2O_2) are currently employed for this purpose. Their attack is not very selective, which is a useful attribute for use in pollution treatment. The versatility of AOPs is also enhanced by the fact that there are different $^{\bullet}OH$ radical production possibilities, so they can be adapted to specific treatment requirements. Their main disadvantage is their high cost. The use of AOPs for WW treatment has been studied extensively, but UV radiation generation by lamps or ozone production is expensive [5]. So future applications of these processes could be improved through the use of catalysis and solar energy. Therefore, research is focusing more and more on those AOPs which can be driven by solar irradiation, photo-Fenton and heterogeneous catalysis with UV/TiO_2. Several reviews have appeared during the last few years [6–12] and a especial effort has been made to supplement these reviews (not repeat information). Photo-Fenton combines Fenton (addition of H_2O_2 to Fe^{2+} salts) and UV–vis light. Photolysis of Fe^{3+} complexes allows Fe^{2+} to be regenerated producing additional radicals and Fenton reactions to take place in the presence of H_2O_2. Under these conditions, iron can be considered a real catalyst. Hydroxyl radicals can also be generated with a solid semiconductor that absorbs radiation (according to its band-gap) when in contact with

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water and generates pairs of valence-band holes and conduction-band electrons. Electron/hole pairs (e^-/h^+) are generated by the absorption of photons with energy greater than necessary to move an electron from the valence band to the conduction band of the semiconductor. When electron/hole pairs are generated, the electron moves away from the surface to the bulk of the semiconductor as the hole migrates towards the surface. If the solvent is oxidoreductively active (water) it also acts as a donor and acceptor of electrons. Thus, on a hydrated and hydroxylated semiconductor surface, the holes produce $^\bullet$OH radicals. Whenever different semiconductor materials have been tested under comparable conditions for the degradation of the same compounds, TiO_2 has generally been demonstrated to be the most active. Since 1976, photocatalytic detoxification has been discussed in the literature as an alternative method for cleaning up polluted water [13] but industrial/commercial applications with solar energy, engineering systems and engineering design methodologies have only been developed recently [14]. This paper summarizes engineering work and recent developments in this area during the last few years.

Another important application related to solar photocatalysis is disinfection. Well-known disinfection processes like chlorination, UV-irradiation, membrane filtration and ozone, all have their advantages and disadvantages. The most widely used disinfection process is chlorination. However, due to natural organic matter (NOM) found in the water, disinfection by-products generated may present a health risk [15,16]. Other frequently used processes are ozonation and irradiation by germicide lamps (254 nm), which also have problems and limitations, such as generation of toxic disinfection by-products [17] and lack of residual effect [18]. Moreover, some microorganisms, like the pathogen *Cryptosporidium parvum*, have a very robust oocyst structure that cannot be treated effectively by conventional processes such as chlorination or UV disinfection [19]. There is therefore a growing interest in developing alternative, effective low-cost disinfection technologies. Killing microbial cells through the use of photoexcited semiconductor powder was first reported by Matsunaga et al. [20]. Since then, an increasing number of scientific contributions have developed new materials, supported photocatalysts, photoreactors and procedures for both gas and aqueous-phase purification and disinfection.

2. Solar collectors for photocatalytic applications

2.1. Concentrating collectors

Contrary to solar thermal processes, which collect large amounts of photons at any wavelength to reach a specific temperature range, solar photochemical processes use only high-energy short-wavelength photons. TiO_2 photocatalysis uses UV or near-UV sunlight (300–400 nm) and photo-Fenton heterogeneous photocatalysis uses sunlight up to 580 nm. Sunlight at wavelengths over 600 nm is normally not useful. Nevertheless, the specific hardware needed for solar photocatalytic 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 [21].

The original solar photoreactor designs [22] for photochemical applications were based on line-focusing parabolic-trough concentrators (PTCs). The parabolic-trough collector consists of a structure that supports a reflective concentrating parabolic surface (Fig. 1). This structure has one or two motors controlled by a solar tracking system on one or two axes, respectively, that keep the collector aperture plane perpendicular to the solar rays. In this situation, all the solar radiation available on the aperture plane is reflected and concentrated on the absorber tube that is located at the geometric focal line of the parabolic trough. The first outdoor engineering-scale reactor developed was designed and built at the National Solar Thermal Test Facility at the Sandia laboratories in Albuquerque, New Mexico (USA), in 1989 (Fig. 1, right). The facility was made up of 6 aligned parabolic-trough collectors with single-axis solar tracking for a total of 465 m^2 aperture area. The collector concentrated the sunlight about 50 times on the photoreactor [23,24].

In 1990, a similar facility designed using PTCs and built at the Plataforma Solar de Almería, was the first engineering-scale solar photochemical facility for water detoxification in Europe [25] (Fig. 1, left). It was made up of 12 two-axis solar-tracking parabolic-trough collectors, each having a total of 32 mirrors in 4 parallel parabolas with a collecting area of 32 m^2.

The solar radiation that reaches ground level without being absorbed or scattered, is called direct radiation, while radiation

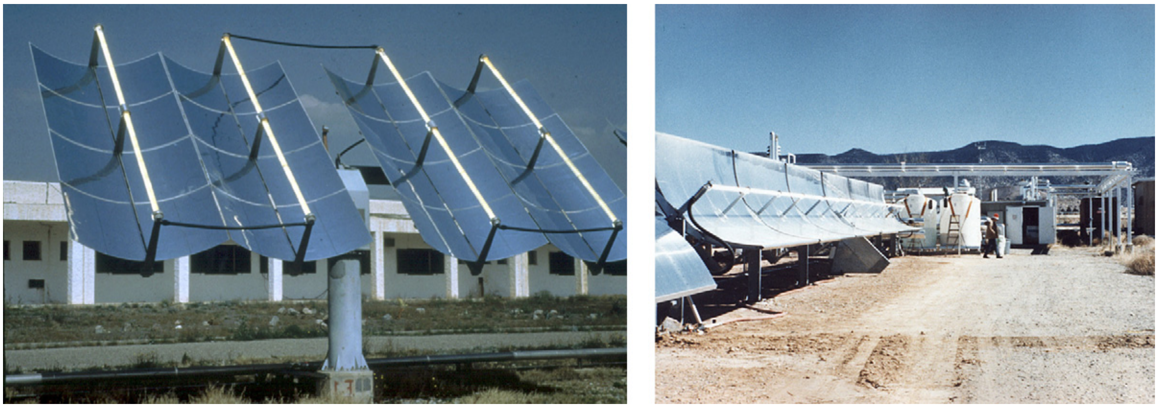

Fig. 1. Parabolic-troughs with two-axis solar tracking (left) and single-axis solar tracking (right).

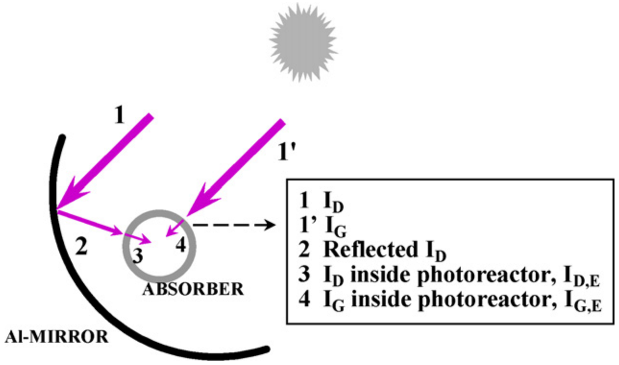

Fig. 2. Photon flux (*I*) inside a parabolic-trough collector photoreactor.

which has been dispersed before reaching the ground is called diffuse radiation, and the sum of both is called global radiation. Fig. 2 shows the path of direct solar radiation (I_D) until it arrives inside the absorber tube. It must arrive at the surface and be reflected (part is lost due to mirror reflectivity, $\eta_{R,\lambda}$) in the right direction (here affected by accurate sun tracking, η_s) by the mirror, before penetrating (part is lost due to glass transmissivity, $\eta_{T,\lambda}$) in the tube. Furthermore, the parabolic trough concentration factor must also be considered (ratio of surface area of the parabola capturing the radiation and surface area of the tube, S_p/S_T). Global radiation (I_G) is also collected by the PTCs, but global radiation is collected directly by the transparent absorber tube without intervention of the collector and is only affected by the transmissivity of the glass, $\eta_{T,\lambda}$.

All the details of these first developments were included several years ago in an excellent review by [22], and the main results were recently reviewed by [6]. Later, at the beginning of the 1990s, attempts were made to use non-concentrating solar collectors as an alternative to PTCs, because PTCs are unsuitable for photocatalytic applications for several reasons [26]: water is heated, radiation flux is too high, most of the photons are not used efficiently [27–30] and their cost is high. The main advantages and disadvantages of these collectors are summarized in Table 1. Among other advantages, when supported catalysts are used in these collectors, a smaller amount can be used, as the photoreactor is smaller than in non-concentrating systems for the same solar collector area. Similarly, fewer tubes (smaller photoreactor tube area) are needed.

Table 1
Comparison between parabolic and non-concentrating solar photoreactors

Advantages	Disadvantages
Concentrating collectors	
Turbulent flow	Only direct radiation
No vaporization of compounds	High cost (sun tracking)
More practical use of a supported catalyst	Low optical efficiency
Smaller reactor tube area	Low quantum efficiency ($r = kI^{<1}$ with TiO_2)
	Water overheating
Non concentrating photoreactors	
Direct and diffuse radiation	Laminar flow (low mass transfer)
No heating	Vaporization of reactants
Low cost	Reactant contamination
High optical efficiency	Weather resistance, chemical inertness and ultraviolet transmission
High quantum efficiency ($r = kI$ with TiO_2)	

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 [31]. They do not concentrate radiation, so efficiency is not reduced by factors associated with concentration and solar tracking. Manufacturing costs are cheaper because their components are simpler, which also means easy, low-cost maintenance. Non-concentrating collector support structures are easier and cheaper to install as well, and the surface required for their installation is smaller, because, since they are stationary, there is no shading. They are able to make use of the diffuse as well as the direct solar UV-A. Extensive effort in the design and testing of small non-tracking collectors has resulted in several different non-concentrating solar reactor prototypes. Most of this work has already been reviewed by our group [6] and only a few papers have been published since then about non-concentrating collectors [32–40]. One example of a non-concentrating collector is shown in Fig. 3. It consists of a rectangular stainless-steel staircase vessel having 21 steps. The photoreactor is provided with a Pyrex glass (UV-transparent) cover to limit water evaporation. The photoreactor, with a solar radiation-collecting surface of 1 m^2, is mounted on a fixed rack tilted at the same angle as the latitude of the site.

Although one-sun collector designs possess important advantages, the design of a robust one-sun photoreactor is not trivial, due to the need for weather-resistant and chemically inert ultraviolet-transmitting reactors. In addition, non-concentrating systems require significantly more photoreactor area than concentrating photoreactors and, as a consequence, full-scale systems (normally composed of hundreds of square meters of collectors) must be designed to withstand the operating pressures anticipated for fluid circulation through a large field. Finally, its construction must be economical and should be efficient, with a low pressure drop. As a consequence, the use of tubular photoreactors has a decisive advantage because of the inherent structural efficiency of tubing. Tubing is also available in a large variety of materials and sizes and is a natural choice for a pressurized fluid system. Based on all of the above, reports by several different authors [11,41–49] and experience acquired by the authors [27,50–53], the main advantages and disadvantages of each of the different technologies for solar photocatalytic applications are as summarized in Table 1. Among other advantages, it should be mentioned that they use not only direct radiation but also diffuse radiation. As there is no concentrating system (with its inherent reflectivity), the optical efficiency is higher than for PTCs. In uncovered, non-concentrating systems exposed to the ambient, reactants could become contaminated. Very often the chemical inertness of the materials used (to resist corrosion caused by outdoor operation and exposure to solar irradiation)

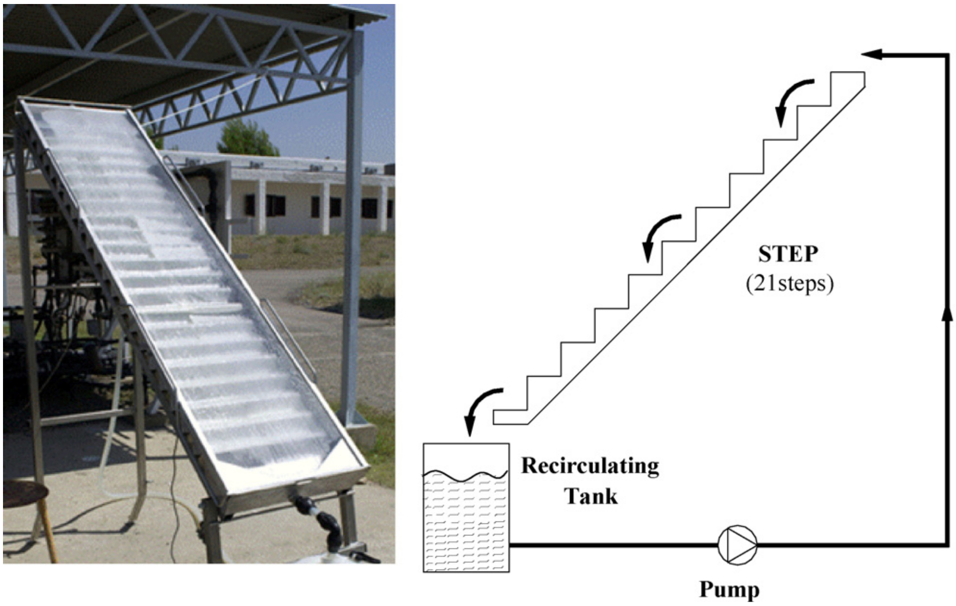

Fig. 3. Non-concentrating solar collector tested at Plataforma Solar de Almería (Spain). Latitude 37°N (Guillard et al. [39]).

for constructing the non-concentrating collector should be guaranteed.

2.3. *Compound parabolic concentrator (CPC)*

Compound parabolic concentrators, a type of low-concentration collector used in thermal applications [54], is an option of interest. Between parabolic concentrators and flat stationary systems, they combine the characteristics of both. While they concentrate solar radiation, they retain the stationary and diffuse-radiation collection properties of flat plate collectors. They have therefore been chosen as a good option for solar photochemical applications by various research groups [45,47,55–65]. Summarizing, the advantages of CPCs are their turbulent flow conditions, no vaporization of volatile compounds, no tracking, no overheating, they can make use of both direct and diffuse solar radiation, are low-cost, weatherproof, reactants are not contaminated, and they have both high optical and high quantum efficiency, since there is a lower e^{-}/h^{+} density than in a concentrating system (as the photonic density is lower) and therefore recombination is also lower. Having the advantages of both non-concentrating and concentrating

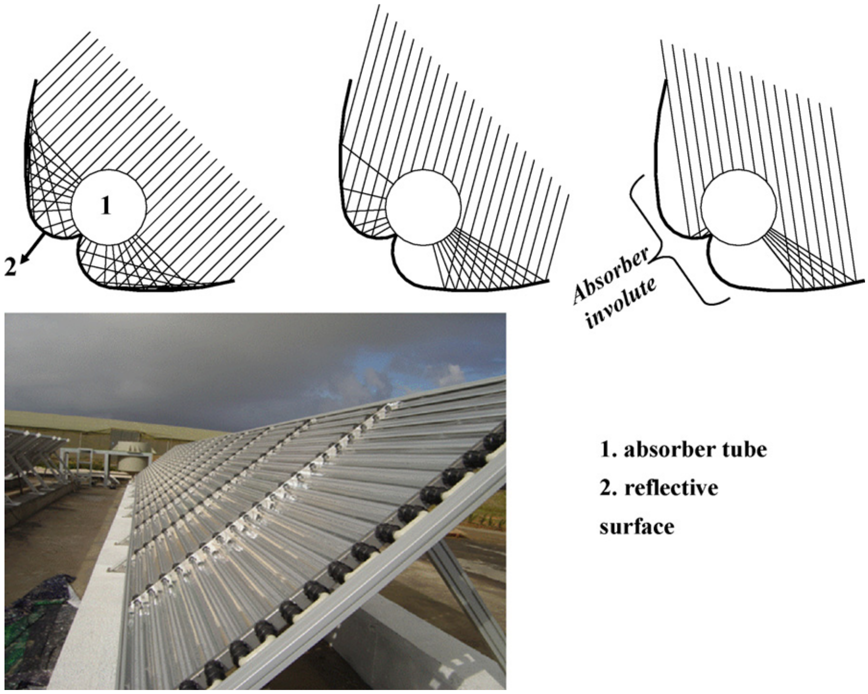

Fig. 4. Schematic drawing and photograph of a compound parabolic concentrator (see also Fig. 8).

systems and none of the disadvantages, CPCs seem to be the best option for solar photocatalytic processes.

The reason for this is that they illuminate the complete perimeter of the receiver, rather than just the ‘‘front’’ of it, as in conventional flat plates or tubes laid side by side (very often used as non-concentrating collectors in solar photocatalysis). The concentration factor (C_{CPC}) of a two-dimensional CPC collector is given by Eq. (1).

$$C_{\mathrm{CPC}} = \frac{1}{\sin\theta_a} = \frac{a}{2\pi r} \qquad (1)$$

The semi-angle of acceptance (θ_a) for photocatalytic applications is usually between 60 and 90°. A special case is the one in which $\theta_a = 90^\circ$, whereby $C_{\mathrm{CPC}} = 1$ (non-concentrating solar system), and each CPC curve is an ordinary involute (Fig. 4). When this occurs, all the UV radiation that reaches the aperture area of the CPC (direct and diffuse) can be collected and redirected to the reactor [53,66]. If the CPC is designed for an acceptance angle of $+90^\circ$ to -90°, all of the diffuse solar radiation incident on the collector plane also impinges directly or indirectly on the photoreactor tube. The light reflected by the CPC is distributed all around the tubular receiver (Fig. 4) so that almost the entire circumference of the receiver tube is illuminated and the light incident on the photoreactor is the same as would impinge on a flat plate.

3. Solar photocatalytic degradation of contaminants

Solar photocatalysis aims at mineralizing the contaminants into carbon dioxide, water and inorganics, and treatment of industrial waste water seems to be one of the most promising fields of application of solar photocatalysis; however, each case is completely different [67,68]. Consequently, preliminary research is always required to assess potential pollutant treatments and optimize the best option for any specific problem on a case-by-case basis. The following paragraphs summarize the main scientific articles that have appeared on this subject during recent years, all of them using solar energy as the photon source.

In photodegradation, the parent organic compound is transformed to eliminate its toxicity and persistence. The oxidation of carbon atoms into CO_2 is relatively easy. In general, however, it is markedly slower than the dearomatization of the molecule. Until now, the absence of total mineralization has been observed only in s-triazine herbicides, for which the final product obtained was essentially 1,3,5-triazine-2,4,6, trihydroxy (cyanuric acid), which is, fortunately, nontoxic [69]. This is because the triazine nucleus is so highly stable that it resists most methods of oxidation. Cl^- ions are easily released into the solution from chlorinated molecules [70–72]. Nitrogen-containing molecules are mineralized mostly into NO_3^- and NH_4^+. Ammonium ions are relatively stable, and the proportion depends mainly on the amount of oxidation of organic nitrogen and irradiation time [73,74]. Organophosphorous contaminants (mainly pesticides) produce phosphate ions. However, in the pH range used (usually <4), phosphate ions remain adsorbed on TiO_2. This strong adsorption somewhat inhibits the reaction rate, though it is still acceptable [75]. In photo-Fenton, phosphate sequestrates iron forming the corresponding non-soluble salt and retarding the reaction rate. Therefore, more iron is necessary when water containing phosphates is treated by photo-Fenton [76]. Until

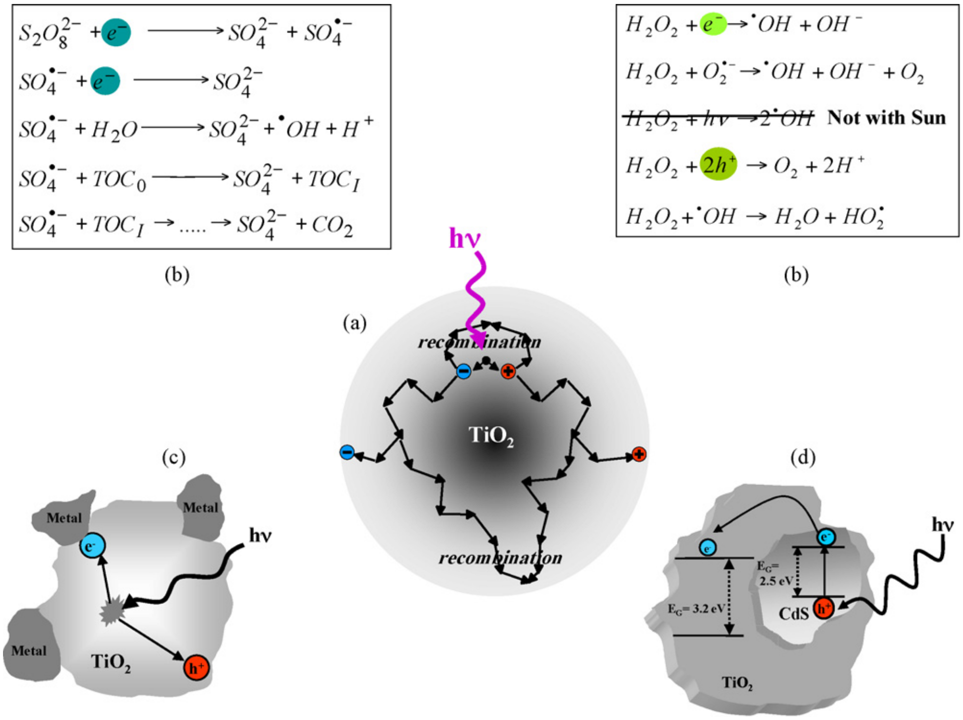

Fig. 5. Electron/hole recombination (a) and ways of improving solar photocatalysis reaction rates; (b) use of electron acceptors; (c) electron capture by a metal in contact with a semiconductor surface; (d) semiconductor–semiconductor photocatalyst.

now, the analyses of fragments resulting from the degradation of the aromatic ring have revealed formation of aliphatics (organic acids and other hydroxylated compounds), which explains why total mineralization takes much longer than dearomatization [77–81], as mineralisation of aliphatics is the slowest step.

Special attention has recently been given the so called ‘‘emerging contaminants’’, mostly unregulated compounds that may be candidates for future regulation depending on research on their potential effects on health and monitoring data regarding their occurrence [82]. Particularly relevant examples of such emerging compounds are surfactants, pharmaceuticals and personal care products, which do not need to persist in the environment to cause a negative effect, because their high transformation/removal rates can be compensated by their continuous introduction into the environment [83]. The solar photocatalytic degradation of these new environmental contaminants, many until recently unknown, is the focus of much research [84–88].

3.1. Improving solar photocatalysis efficiency

However, as concentration and number of contaminants increase (as in real waste water with complex mixtures of organics), the process becomes more complicated and challenging problems such as slow kinetics caused mainly by low photoefficiency need to be solved. Electron/hole recombination (Fig. 5a) in the absence of proper electron acceptors, is extremely efficient and thus represents a major energy-wasting step and quantum yield limiting factor. Besides, the TiO_2 band-gap represents only 5% of the solar spectrum. It is therefore a rather inefficient process even for a high-added-value application. Two basic lines of R&D have been working on modifying catalyst structure and composition (Fig. 5c) and addition of electron acceptors to increase the solar photocatalytic reaction rate (Fig. 5b). A third approach has focused on finding new catalysts able to work with band-gaps which coincide better with (Fig. 5d) the solar spectrum [89–92]. There have been many attempts using the first and third approach, such as improving specific surface [39,68,93,94] by doping and deposition with metal ions and oxides [95–98]. Successful innovative catalyst compositions have been developed, but they have not been used in large-sized plants because no ‘‘cheap’’ solution has yet been developed. Our experience in testing at large solar facilities with different contaminants qualifies the use of electron acceptors as the most versatile way of improving reaction rates for now, opening the opportunity for extending the use of heterogeneous photocatalysis to complicated waste water [99–102].

3.2. Combining solar photocatalysis and biotreatment

Apart from developments increasing the photocatalytic reaction rate, the most important progress in solar photocatalysis in recent years has been related to its combination with biological treatment and the application of toxicological analytical methods. Both approaches have been successful in decreasing treatment time (i.e. plant size), which is another way of increasing overall process efficiency, in contrast to increasing the reaction rate itself. Contaminant treatment, in its strictest meaning, is the complete mineralisation (TOC = 0) of the contaminants; however, today photocatalytic processes only make sense for nonbiodegradable hazardous pollutants. When feasible, biological treatment is usually a good solution. Therefore, biologically recalcitrant compounds could be treated with photocatalytic technologies until biodegradability

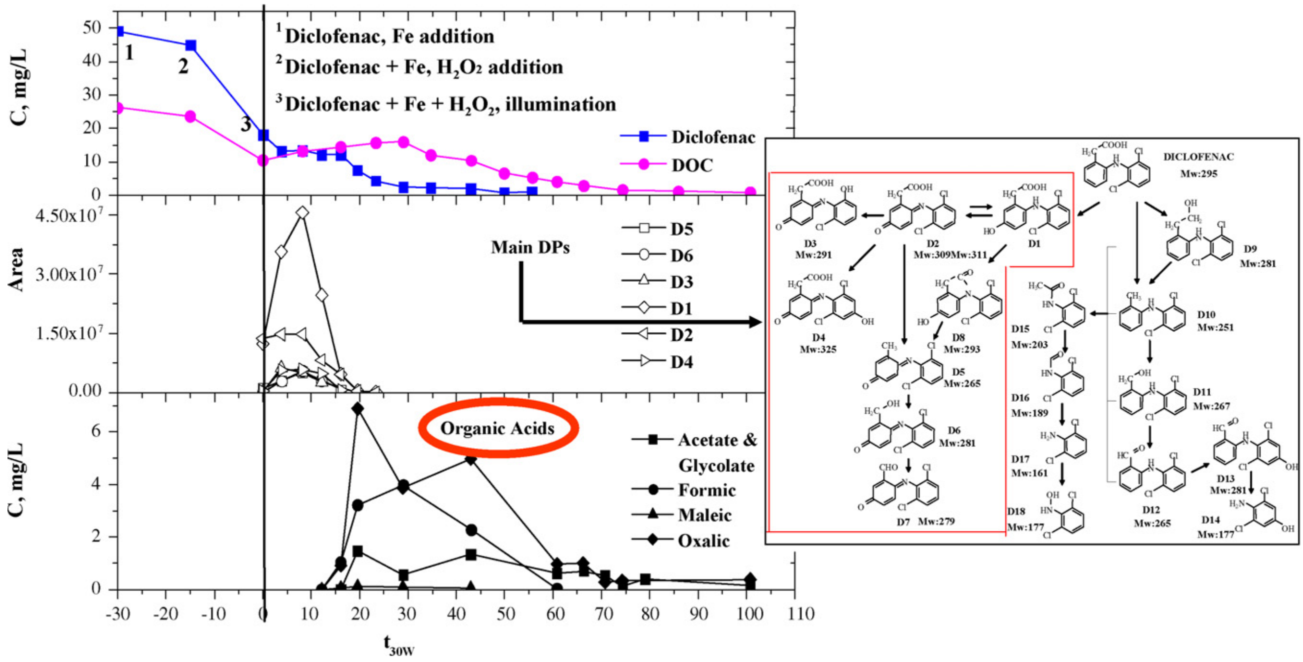

Fig. 6. Evolution over time of the main degradation products and carboxylic acids detected during solar photocatalytic treatment of diclofenac (non-steroidal anti-inflammatory drug considered an ‘‘emerging contaminant’’). Taken from (Pérez-Estrada et al. [88]).

is achieved and then the water would be discharged to a conventional biological plant. One of the main obligations for urban wastewater treatment imposed by European Union Council Directive 91/271/EEC is that wastewater collecting and treatment systems (generally involving biological treatment) should be provided by 31 December 2005 in all agglomerations of between 2000 and 15,000 population equivalent (p.e.). The deadline for agglomerations of more than 15,000 p.e. should have been met by the end of 2000 [103]. Therefore, in the near future, most of the AOP plants developed in the EU could discharge pre-treated wastewater into a nearby conventional biological treatment, without the necessity of installing a specific biotreatment coupled to the AOP. Future evaluation of AOP efficiency should therefore be done from this perspective, instead of attempting to completely mineralise the contaminants using the $^{\bullet}$OH radicals, which is always more expensive. Such a combination reduces treatment time and optimizes the overall economics, since the solar detoxification system can be significantly smaller [61,104,105]. Process kinetics make the first part of the photocatalytic treatment the quickest. It may be observed in Fig. 6 that most of the degradation products (DPs) with high molecular weight appear after exposure to sunlight and reach their maximum concentration after around 10 min of treatment. From here on, they begin to decrease and carboxylic acids appear. In any case, and for purposes of wastewater treatment, the complete mineralisation by photocatalysis is unnecessary in view of the DPs detected, because they could easily be treated in a conventional biological treatment plant.

Therefore, the use of AOPs as a pretreatment can be justified if the intermediates resulting from the reaction (more oxidized compounds, such as carboxylic acids, alcohols, etc.) are readily degraded by microorganisms. The feasibility of such a photocatalytic-biological process combination must always be considered, as it could mean a significant cost reduction due to the smaller solar collector field necessary. Biotreatment and solar photocatalysis combination has only been developed recently, and there are not many papers on the subject [63,106–110]. An ''on-going'' project (''A Coupled Advanced Oxidation-Biological Process for Recycling of Industrial Wastewater Containing Persistent Organic Contaminants'', CADOX) sponsored by the European Commission and with the participation of nine EU partners (http://www.psa.es/webeng/projects/cadox/index.html), focusing on this new hybrid technology, attempts to demonstrate how the treatment cost of water containing persistent contaminants can be drastically reduced. Fig. 7 and Table 2 show an example of evaluation of photo-Fenton treatment of real waste water containing a pesticide (imazalil) taking into account biodegradability results. The overall reaction (Eq. (2)) for oxidation of imazalil shows that inorganic species produced are nitrate and chloride. As clearly shown in Fig. 7, when imazalil has disappeared ($t = 45$ min and $t = 90$ min by Fe = 0.5 mM and Fe = 0.1 mM, respectively), mineralisation is still very low.

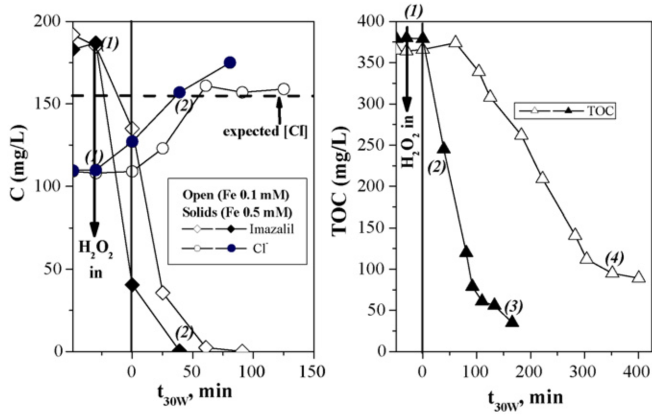

Fig. 7. Disappearance of imazalil and evolution of chloride and total organic carbon (TOC) as a function of illumination time during photo-Fenton treatment of real wastewaters (see Table 2). Points 1–4 refer to data shown in Table 2.

Table 2
Main characteristics of real wastewater containing imazalil (1) and after photo-Fenton treatment at different stages (2, 3 and 4)

	(1)	(2)	(3)	(4)
COD (mg/L)	950	384	82	119
BOD (mg/L)	0.00	123	36.9	64.3
BOD/COD ratio	0.00	0.32	0.45	0.54
BOD/COD rating	Very poor	Good	Good	Very good
Imazalil (mg/L)	199.8	<0.1	<0.1	<0.1
Conductivity (mS/cm)	1.61	2.55	2.44	2.89
Cl^- (mg/L)	105	164	161	163
TOC (mg/L)	285	195	34.6	93.9

Photo-Fenton experiments shown in Fig. 7.

$$C_{14}H_{14}Cl_2N_2O + 19O_2 + 2H_2O \xrightarrow{Fe/H_2O_2/h\nu} 14CO_2 + 5H_2O + 2NO_3H + 2HCl \tag{2}$$

Chloride analyses (determined during degradation of chlorinated compounds) showed very fast degradation/dechlorination compared to disappearance of TOC. Therefore, residual TOC remaining in the water when imazalil has completely disappeared did not correspond to any chlorinated compound. In order to find out the conditions for biocompatibility using the photo-Fenton reaction as a pre-treatment step, the biodegradability of the wastewater was evaluated by the Biochemical Oxygen Demand (BOD_5) test, using unacclimated municipal sludge as the initial inoculum. The results are shown in Table 2. Different stages of the treatment were taken as the reference for the biocompatibility study. It should be noted that complete disappearance of imazalil and chloride release were considered the key-parameter for selection of the treatment stage to be tested by BOD_5. Table 2 shows that there was some degradation of imazalil intermediates by the microorganism in all cases, after pesticide disappearance. It may easily be concluded that biodegradability is enhanced during the treatment (BOD/COD ratio), although biodegradability was better if the treatment was not excessively prolonged (compare samples 3 and 4). In view of these results, and to the intrinsic uncertainty of biodegradable methods, the best value for discharging waste water to a biotreatment could be been set within a wide interval between 195 and 35 mg/L of TOC. The most suitable conditions for biotreatment are therefore obtained when the phototreatment time is just long enough for high biological efficiency (not too much mineralisation so the effluent has a high enough biodegradable organic charge). Longer phototreatment times produce unnecessary photodegradation of biologically degradable substances, and higher energy consumption uncompensated by any benefit.

4. Installed solar photocatalytic treatment plants

Despite its obvious potential for the detoxification of polluted water, there has been very little commercial or industrial use of photocatalysis as a technology to date. Several years ago, according to a review by Goswami [21], only two engineering-scale demonstrations, one for groundwater treatment in the U.S. and one for industrial wastewater treatment in Spain (at Plataforma Solar de Almería) had been published. But more installations have recently been erected, mainly based on non-concentrating collectors. Dillert et al. have treated biologically pretreated industrial waste water from the Volkswagen AG factories in Wolfsburg (Germany) and Taubaté (Brazil). The results of the experiments, which were performed using the Double Skin Sheet Reactor (DSSR) [111], were so promising, that a pilot plant was installed in the Wolfsburg factory during the summer of 1998 [112]. The flowchart of a more recent version of this pilot plant, which was installed in 2000, has recently been published by Bahnemann [8]. In 1997, Freudenhammer et al. reported their results from a pilot study with the Thin Film Fixed Bed Reactor (TFFBR) in various Mediterranean countries [113,114]. Based on these results, a pilot plant, financed by the European Commission, has been built at the site of a textile factory in Tunisia (Menzel Temime). The pilot plant description and the flow chart have recently been published [8,36].

Under the "SOLARDETOX" project (Solar Detoxification Technology for the Treatment of Industrial Non-Biodegradable Persistent Chlorinated Water Contaminants), a consortium coordinated by Plataforma Solar de Almería, Spain, was formed in Europe for the development and marketing of solar detoxification of recalcitrant water contaminants [115]. The main goal of the project (financed by the EC-DGXII through the Brite Euram III Program, 1997–2000) was to develop a commercial non-concentrating solar detoxification system using the compound parabolic collector technology, with a concentration ratio = 1. A full-size demonstration plant for field demonstration to identify any pre- or post-processing requirements, potential operating problems, and capital and operating costs [115] was erected at the facilities of HIDROCEN (Madrid, Spain). Since late 1999, this plant (main characteristics and results published elsewhere [116]), including the catalyst separation procedure also developed under the SOLARDETOX project and installed for the first time in this plant, has been fully operative [117]. The same collectors have also been used by other researchers for treating paper mill effluents in Brazil and Germany [62,118–120], and paper mill effluents [64], surfactants [121], and textile dyes [65] in Spain.

More recently (2004), a new CPC-based plant, has been installed (Fig. 8) in a project focusing on problems in the rapidly growing intensive greenhouse agriculture sector in the Mediterranean Basin. The environmental problems caused are one of its greatest disadvantages. One of these problems is the uncontrolled dumping of plastic pesticide containers, which usually still contain residues. The solution is to selectively collect these containers for recycling. Plastic container recycling starts with shredding and then industrial washing of the shredded plastic, which produces water polluted with highly toxic persistent compounds (pesticides + excipients). This hazardous water containing the dissolved toxic organic matter that was in the pesticide containers must be treated. This rinse water is then continuously recycled and reused. The ALBAIDA company and CIEMAT (Spain) jointly presented a project entitled "Environmental Collection and Recycling of Plastic Pesticide Bottles using Advanced Oxidation Process driven by Solar Energy" to the European LIFE-ENVIRONMENT program, which was approved and began in October 2001. The plant is now in routine operation.

The photo-Fenton treatment mineralizes 80% of the TOC in the rinse water in a batch process. The plant design, based on CPC solar collectors (150 m^2), has 4 parallel rows of 14 photocatalytic reactor modules (20 tubes/module, 2.7 m^2/module) mounted on a 37°-tilted platform (local latitude). The total collector surface is 150 m^2 and total photo reactor volume is 1060 L. The 14 modules in each row are connected in series so the water flows from one module to another and finally to a tank. However, each row is independent and connected in parallel, so they can be operated separately. The system is run in batch mode using a recirculation tank with only one centrifugal

Fig. 8. View of the solar detoxification demonstration plant erected by ALBAIDA at La Mojonera (Almería, Spain).

pump. The treated water from washing plastic pesticide bottles is returned to the washing system by a second pump and the system can again be refilled with contaminated water from the bottle-washing plant. Before entering the solar CPC field, solids are eliminated from the contaminated water and the reagents needed (hydrogen peroxide and Fe^{2+}) for the photo-Fenton reaction are added. As the CPCs have a concentration factor of approximately 1 and there is no thermal insulation, the maximum temperature reached inside the photo reactor is around 40 °C. After treatment, the Fe need not be removed because the water will either be reused or, when discharged, transferred to a 20,000-m^3 irrigation pool where it is not only not a problem, but is an advantage, as it is one of the elements usually added to greenhouse irrigation water.

5. Solar photocatalytic disinfection of water

5.1. *Effect of solar radiation on microorganisms*

Natural sunlight as a killing agent for microorganisms was first described in 1877 [122]. Modern research in the field aimed at supplying microbe-free drinking water has placed particular emphasis on minimization of costs. During recent years, work has concentrated on batch exposition to natural solar radiation, mainly small volumes (1–1.5 L) of untreated (or polluted) water in transparent vessels irradiated for periods of up to 8 h. This simple method, commonly known as Solar Water Disinfection (SODIS) [http://www.sodis.ch/], has been proven successful for a wide variety of pathogens [123,124]. SODIS is very suitable for household drinking water treatment anywhere the lack of safe drinking water is an important problem. Nevertheless, this method is unfeasible for large or channeled volumes of water. The resistance of microorganisms to solar radiation has been studied by several authors and found to vary from one type to another [125]. *Escherichia coli* is often chosen as the reference enteric coliform bacterium in many studies. This bacterium is also widely recognized as an ‘‘easy’’ target for disinfection, since it is relatively simple to inactivate by solar radiation as shown in a number of related articles [124,126–128].

Rincón and Pulgarín [129] reported that the inactivation rates under simulated sunlight of several bacteria groups like *E. coli*, other coliforms, Gram-negative and *Enterococcus* species showed the following sequence: *E. coli* > Gram-negative > -other coliform ⋙ *Enterococcus* species. From all the cases evaluated, they concluded that the least and most resistant species are *E. coli* and *Enterococcus* species, respectively. Other authors, like Sinton et al. [130] also found that *Enterococcus* species were inactivated by natural solar light less rapidly than *fecal coliforms*. Those authors attribute this behavior to the inherent response and resistance of each specimen to the nature of the solar radiation. Other types of organisms like bacterial endospores cannot be inactivated only by solar radiation. Specifically, the *Bacilus cereus*, used as a surrogate of the *Bacilus anthracis* (the bacterium that causes anthrax), has been proven resistant to simulated solar-UV radiation by Lee et al. [131].

Lonnen et al. [124] demonstrated that the solar disinfection batch-process is unfeasible for the inactivation of cysts of the waterborne protozoan pathogen *Acanthamoeba polyphaga* and for *Bacilus subtilis* spores. Nevertheless, the study also showed that fungal pathogens such as *Candia albicans* and *Fusariun solani* are readily inactivated using the solar disinfection technology. Kehoe et al. [132] proved that Type I *Shigella dysenteriae* is very sensitive to solar disinfection batch processing and is easily inactivated even under overcast conditions, and they also proved this process to be appropriate for use in developing countries during *S. dysenteriae* Type I epidemics. Méndez et al. [133] investigated the feasibility of using batch-process solar disinfection for *C. parvum* oocysts in water. Their study showed that solar disinfection was effective for *oocyst* suspensions under simulated sunlight conditions. Bacteriophages like *Poliovirus*, *phage MS-2* or *phage Q-beta* can be inactivated under laboratory conditions (not in real contaminated water) by solar disinfection methods [125].

5.2. *Microorganism inactivation by titanium dioxide photocatalysis*

From the work on photocatalytic disinfection by Matsunaga et al. [20] to date, a relatively large number of related articles have been published. The majority of them report on aqueous photocatalytic mechanisms and dynamics, and most of them have used *E. coli* as model target microorganism [129,134–138]. In the above-mentioned pioneer work [20], the photooxidation of Coenzyme A (CoA) in *Lactobacillus acidophilus* (bacteria), *Saccharomyces cerevisiae* (yeast) and *E. coli* (bacteria) was demonstrated in suspensions of irradiated TiO_2. Decreased CoA in those cells caused their metabolic activity to diminish, leading to cell death, which they reported was inversely proportional to the thickness and complexity of the cell wall. In further research to better understand bactericidal activity of photo-excited titanium dioxide, other authors [139–142] investigated the sites of cellular damage and their contribution to cell death in *E. coli*. These authors suggest that oxidative damage first takes place on the cell wall, where the TiO_2 photocatalytic surface first makes contact with whole cells. Photocatalytic action progressively increased cell permeability and thereafter, the open flow of intracellular components, allowing TiO_2 particles easier access and photo-oxidation of intracellular elements, accelerating cell death. At the present time, the photochemical mechanism of the TiO_2 biocidal action remains largely unclear. It is uncertain what reactive oxygen species are directly involved in the photokilling process [143], especially the identities of the main reactive oxygen species (ROS), which not only include the OH radical, but also $O_2^{\bullet -}$, and H_2O_2. A recent contribution by Cho et al. [127] demonstrates the important role of the $^{\bullet}OH$ -acting either independently or in collaboration with other ROS- in the inactivation of *E. coli* in presence of UV-illuminated TiO_2 particles with excellent linear correlation between steady-state concentrations of $^{\bullet}OH$ and the rates of *E. coli* inactivation.

5.3. Solar photoreactors for disinfection

One of the first contributions to solar photocatalytic disinfection of water is the work performed by Zhang et al. [144], who observed a four-order decrease in the *E. coli* concentration in TiO_2 suspensions when exposed to sunlight for 23 min in a batch reactor. The work of Block et al. [145] on solar photocatalytic disinfection studied bacterial behavior in the presence of TiO_2 powder irradiated by either UV-lamps or sunlight. Their study showed that several common bacteria (*Serratia Marcescens*, *E. coli*, and *Streptococcus Aureus*) were inactivated in less than 10 min. No attempt at optimizing the process was made in these cases. When designing and operating a water disinfection system based on a photocatalytic reactor, a number of points have to be taken into account. The most important are the characteristics of the aqueous system, the source of UV-photons (type of lamps or sun), whether the catalyst is fixed or suspended in the fluid, total daily volume of water to be treated, continuous or batch operation, etc. When the aim of a disinfection system is to provide drinking water, the catalyst might be immobilized on a robust, inert support that allows the catalyst to be irradiated, avoiding post-treatment separation of the catalyst. However, the efficiency of photocatalytic decontamination depends strongly on how the catalyst is employed. Systems that use TiO_2 powder dispersions usually degrade organic pollutants more efficiently than those based on supported catalysts. Although this behavior is also expected and it has in fact been proven for some microorganisms [129,135,136,146,147], it cannot be assumed, since the adsorption substrate–catalyst process preceding photo-degradation is not valid for microorganisms due to the respective sizes of catalyst particle and cell.

To date, the development of supported TiO_2 materials is unable to provide a feasible method for wastewater and drinking water disinfection. Some researchers have made a great effort to improve immobilized TiO_2 reactors. One of the earliest studies in the field is a photoreactor built by Ireland et al. [148], basically composed of several photocatalytic modules, made up of a UV lamp (300–400 nm) coaxially wrapped with TiO_2 coated fiberglass mesh, connected in series. Sunada et al. [140] proposed a photoreactor based on black-light (10 W/m^2) illumination of a thin titanium dioxide film. Belhakova et al. [149] used a flow-through reactor with a glass plate coated by a layer of TiO_2 to inactivate suspensions of *E. coli* and *bacteriophage NM1149*. Vidal et al. [128,150] published the first study on a TiO_2 solar photocatalysis pilot plant for water disinfection. This team built up a new low-cost CPC (see Section 2.3) prototype for better use of available solar radiation. The results obtained for *E. coli* and *Enterococcus faecalis* (initial concentration $\sim 10^2$ to 10^4 CFU/mL) with this solar photo-reactor with a 4.5-m^2 CPC aperture and TiO_2 suspensions (0.5 g/L), showed a 5-log decrease after 30 min of solar irradiation (average solar UV of around 25 W/m^2). Very recent work has studied improvement of solar disinfection using supported TiO_2 on flexible resistant materials, in the shape of cylinders, pills, balls, mesh, etc. One example is TiO_2 deposited on fiberglass [151] inserted in a tubular photoreactor in a CPC solar collector [146]. The authors demonstrated that the CPC solar photoreactor is efficient for *E. coli* inactivation by solar photocatalysis with TiO_2 slurries and supported TiO_2 with treatment periods of around 60–80 min (Fig. 9).

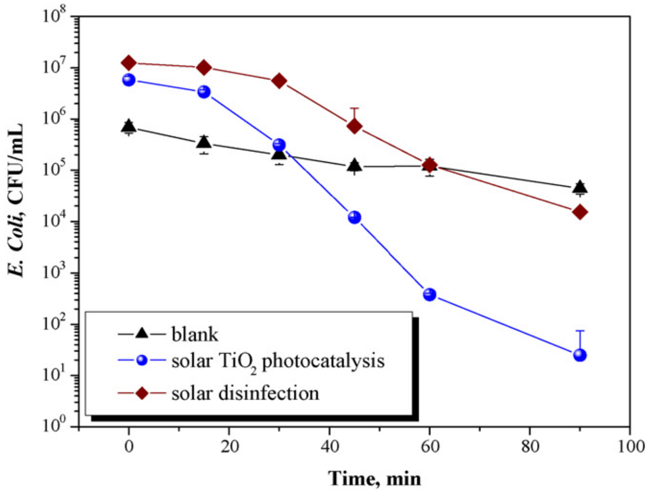

Fig. 9. *E. coli* K-12 inactivation in a solar CPC photoreactor. Solar photocatalysis with immobilized Ahlstrom catalyst (TiO_2-P25 20 g/m^2), solar disinfection (without TiO_2) and blank (photoreactor dark) tests. Average solar UV radiation during the experiments: 28.3 W/m^2.

McLoughlin et al. [152] studied the use of three types of static solar collectors for the disinfection of water containing *E. coli*. Solar disinfection using low cost CPCs was analyzed in depth in another study by Mcloughlin et al. [153], using solar radiation and *E. coli* as the target microorganism. The results proved that bacterial deactivation rates using sunlight alone can be enhanced by low concentrations of titanium dioxide suspended in the water. Proper evaluation of the solar radiation standardization parameters used for photocatalytic treatments is obviously a critical matter. In this sense, Rincón and Pulgarín have made a fundamental contribution to establishing a method of assessing the bactericidal inactivation rate in solar photocatalytic processes for drinking water [136,154]. They proved that the solar UV dose necessary to reach a target disinfection level is not a good system efficiency indicator. They therefore proposed a new parameter, ‘‘effective disinfection time (EDT)’’, defined as the treatment time necessary to avoid bacterial regrowth after 24 (or 48 h) in the dark after phototreatment. This parameter impedes ambiguous interpretation of disinfection results, for example, when reactivation (or regrowth) of microorganisms occurs. They found that the EDT is strongly affected by the residence time of water in the illuminated part of the system, light intensity and the moment of the day selected for the treatment (morning or afternoon) when exposed to solar radiation, and not only by the number of photons entering the solution.

In this context, the European Union International Cooperation (INCO) has recently sponsored two different projects with the aim of developing a cost effective technology based on solar photocatalysis for water decontamination and disinfection in rural areas of developing countries (SOLWATER Project: http://www.psa.es/webeng/solwater/index.html; AQUACAT Project:

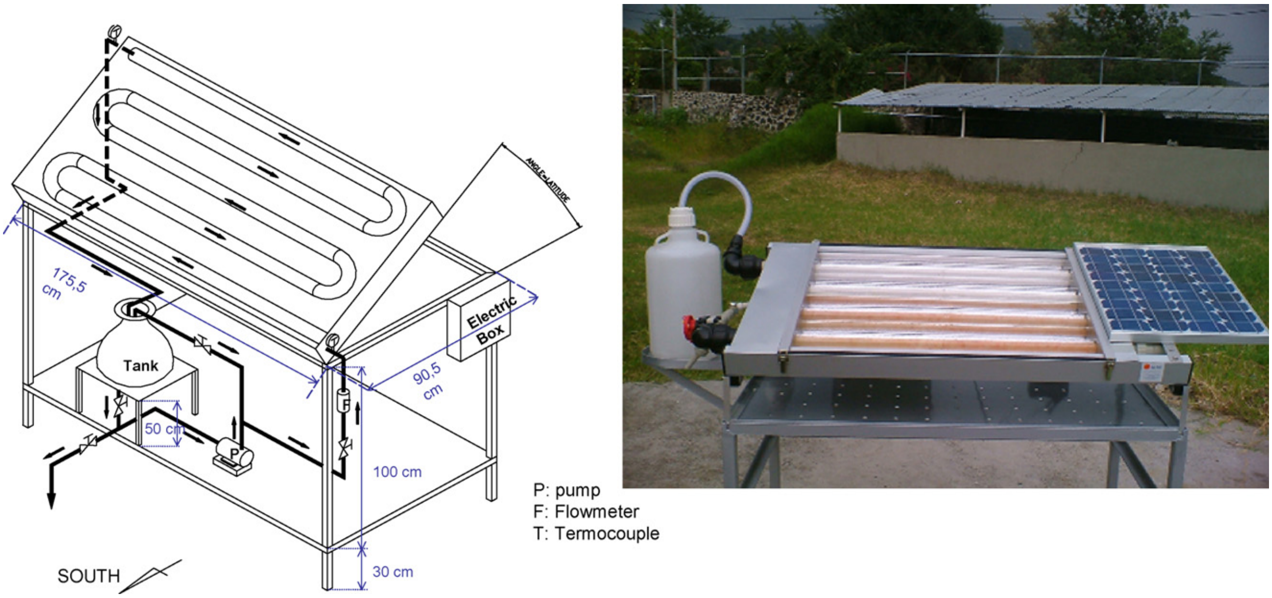

Fig. 10. Schematic diagram and photograph of the photoreactor developed in AQUACAT and SOLWATER projects for photocatalytic disinfection in developing countries.

http://aquacat.univ-lyon1.fr/) [155]. Both projects explore development of a solar reactor to decontaminate and disinfect small volumes of water. Field tests with the final prototypes were carried out in 2005 to validate operation under real conditions [92,156]. Similar tests have been performed in photoreactors installed in Argentina, Egypt, France, Greece, Mexico, Morocco, Perú, Spain, Switzerland and Tunisia. Fig. 10 shows a flow diagram of the reactors and a photograph of the prototypes. Water from the feed tank is pumped through illuminated tubes connected in series in a CPC at a recirculation rate of 13 L min^{-1}. Electricity is provided by a solar panel and the total volume in the feed tank plus tubes is 20 L. Water was recirculated using a centrifugal pump powered by a battery connected to the solar panel.

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