

Review: Solar photocatalysis for water disinfection: Materials and reactor design

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As of 2010, access to clean drinking water is a human right according to UN regulations. Nevertheless, the number of people living in areas without safe drinking water is predicted to increase by three billion by the end of this decade. Several recent cases of *E. coli* and *Cryptosporidium* contamination in drinking water are also reported in a number of advanced countries. Therefore ensuring the potability of drinking water is urgent, but highly challenging to both the developing and developed world in the future. A combination of solar disinfection and photocatalysis technology offers real possibilities for removing lethal pathogenic microorganisms from drinking water. The time taken for the conventional SODIS process can be greatly reduced by semiconductor (e.g. TiO₂, ZnO, nano-heterojunctions) based photocatalysis. This review addresses the fundamental reaction mechanism, advances in materials synthesis and selection and recent developments in the reactor design for solar energy driven photocatalysis using titanium dioxide. The major advantage of using photo-reactors is that they enhance disinfection by increasing photon flux into the photocatalyst. Other major factors affecting such efficiency of solar-based photocatalysis such as the illuminated volume/total volume ratio, catalyst load and flow rate, are discussed in detail. The significance of using immobilised catalysts over the catalyst powder in slurries is also highlighted. It is noted that, despite encouraging early field studies, the commercialisation and mass production of solar photocatalysis systems remains highly challenging. Recommendations for future directions for addressing issues such as mass transfer, requirement of a standard test method, photo-reactors design and visible light absorption by TiO₂ coatings are also discussed.

1. Introduction

In 2010, of historic significance, 'the human right to water and sanitation' was resolved by the General Assembly of the United Nations.¹ A decade earlier, in 2000, following the United Nations Millennium Declaration, one of the targets of the seventh

Millennium Development Goal (Ensure Environmental Sustainability) was established; to halve the proportion of the population without sustainable access to safe drinking water and basic sanitation by 2015.

In 2012, the UN published a strategic document on good practices in the realization of the 'right to water and sanitation'.²

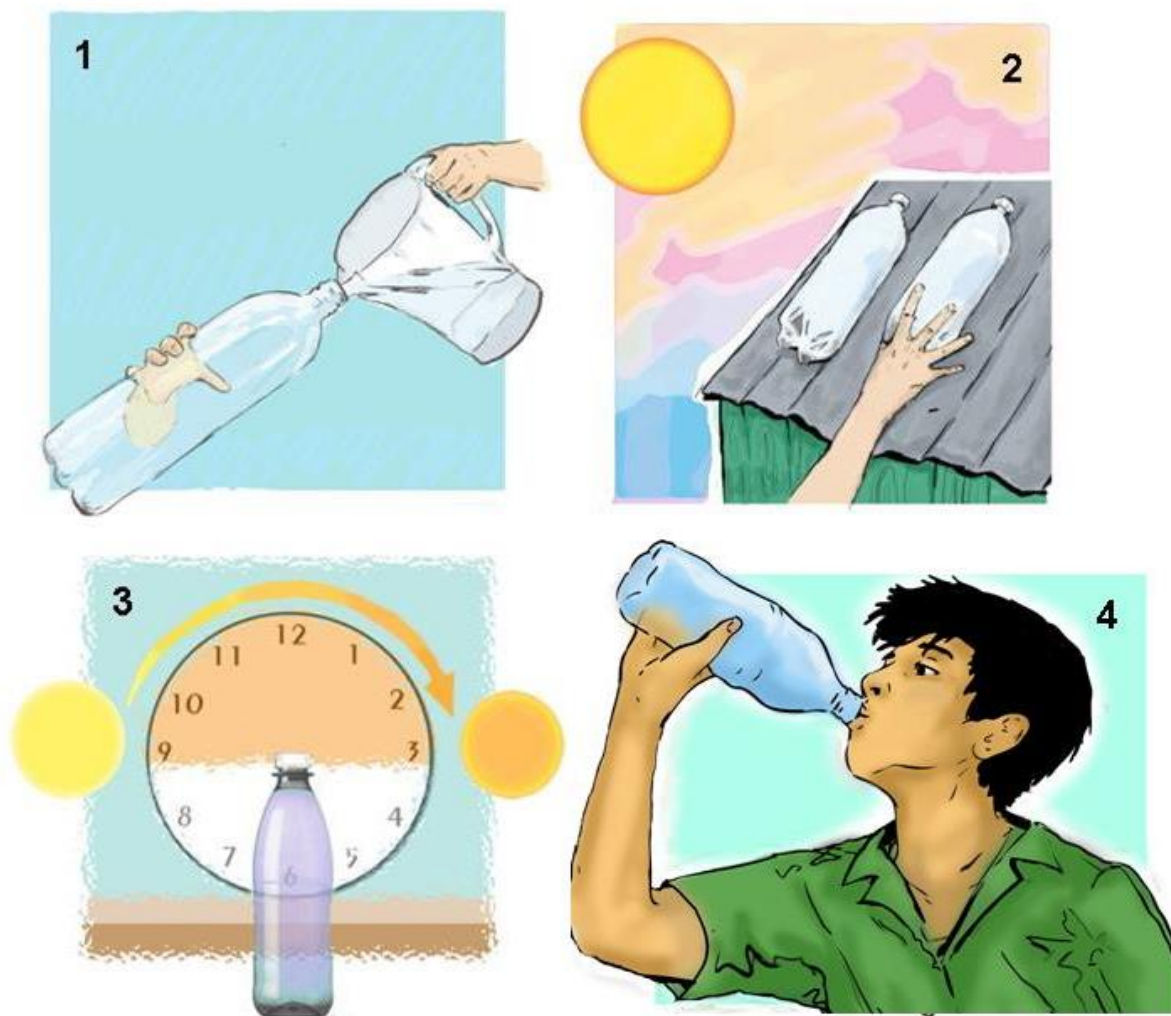


Fig. 1 A graphical description of the solar disinfection (SODIS) technique. (1) Fill the bottle. (2) Place the bottle in direct sunlight. (3) Wait a minimum of 6 hours. (4) The water is safe to drink. Reprinted from *Journal of Hazardous Materials*, Vol. 235-236, McGuigan *et al.*, Solar water disinfection (SODIS): A review from bench-top to roof-top, pp. 29-46., Copyright (2012), with permission from Elsevier.

5 The report highlighted three important points: a) Boiling and chlorination is impractical and expensive when chlorine tablets and fuel are not readily available, b) Solar disinfection (SODIS) and bio-sand filters are cheap and feasible alternatives, only when used properly, and c) Successful water treatment depends on
10 choosing the appropriate method which is dependent on a number of factors such as location, culture, existing water quality and implementation.

Disinfection of drinking water using solar energy is not a recent
15 development and has been practiced in ancient cultures for centuries. McGuigan *et al.*³ has recently traced the historical development of solar water disinfection. SODIS, more

specifically, is a procedure which uses only sunlight and plastic
bottles, designed for drinking water purification in remote regions
in which sunlight is plentiful. The simple steps involved are best
20 described schematically as presented in Figure 1. As a 'good practice' the UN cites the advantages of being easy to understand and use and unchanged water taste. McGuigan *et al.*³ also emphasize the importance of low cost of any employed method, pointing out the poorest are the most likely to have worst access
25 to clean drinking water. Furthermore, taking into account that the regions of the world most affected are those with large annual sunfall, it can be concluded that SODIS is a 'geographically' attractive method for the water quality assurance. Successful use

of SODIS projects in Uganda and Vietnam have led to the UN description of SODIS as a 'sustainable' and 'transferable' technology.²

A number of extra steps have been employed to increase the efficiency of the SODIS method such as use of reflective or

black surfaces, shaking the bottle to increase dissolved oxygen and filtering prior to filling the bottle.³

However, SODIS technology has a number of disadvantages that hinder its widespread application. The major challenge remains

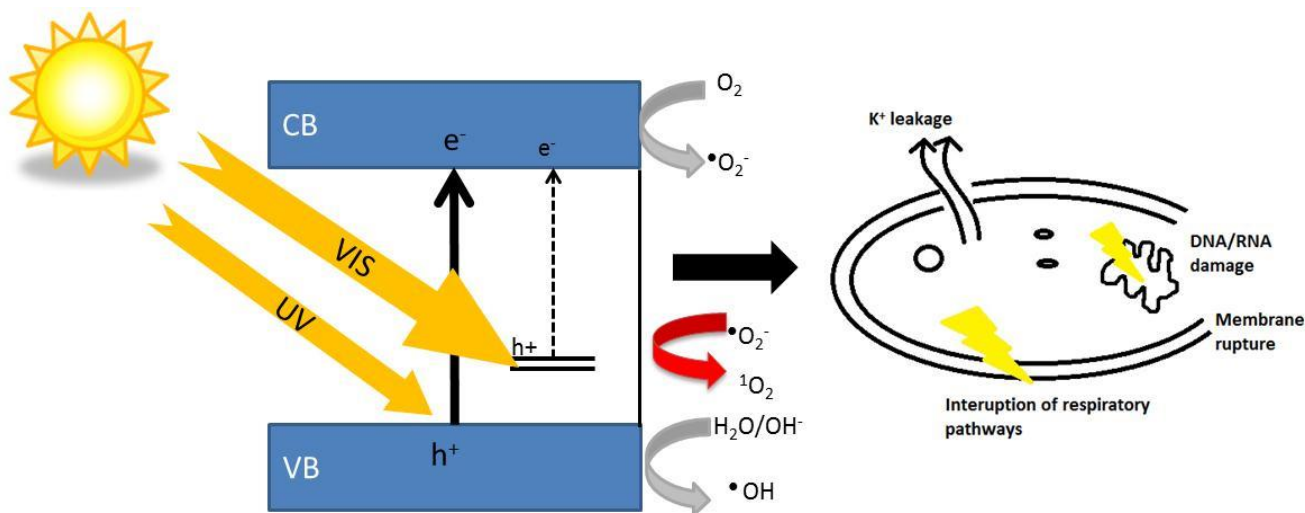


Fig. 2 Schematic diagram of bacterial disinfection using visible light active catalyst. Reprinted from *Applied Catalysis B: Environmental*, Vol. 130-131, Fisher *et al.*, Nitrogen and copper doped solar light active TiO₂ photocatalysts for water decontamination, pp. 8-13., Copyright (2013), with permission from Elsevier.

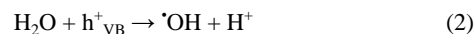
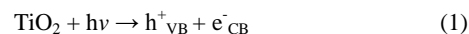
the significant time (up to 6 hours) taken to fully inactivate the pathogens in water. Furthermore, only small bottle-sized volumes of water can be treated in the SODIS protocol, described above. Another disadvantage is the variation in treatment time recently highlighted by Byrne *et al.*⁴ The treatment time is dependent on a number of variable factors such as solar irradiance and starting water quality.

Although not currently recognized as good practice, another method of water disinfection in remote locations is use of a solar water disinfection system or plant. These systems may be distinguished from the bottles used in the SODIS protocol in that they are *immobile* and are typically continuous flow, engineered, point of use reactors. Malato *et al.*⁵ have reviewed the state of the art of such solar reactors. Such reactors are an engineered advancement of the SODIS protocol, applicable to treating greater volumes of water for household use. Hereafter, in this review, the two different configurations will be labeled as 'bottles' and 'reactors'.

The other key development of SODIS bottles and reactors is the increase in disinfection efficacy by incorporation of a photocatalyst, typically titanium dioxide (TiO₂), into the process. Thus, this review describes the use of both TiO₂ photocatalysis and bottle/reactor design as further technological advancements to the simple SODIS protocol. Bearing in mind the recent human right to access drinking water, this review focusses on field studies in which TiO₂ is employed in both SODIS bottles and solar disinfection reactors, relevant to real-world use in developing regions.

2. Photocatalytic disinfection of water

The total time taken for the SODIS based disinfection process can be significantly reduced by the addition of semiconductor based photocatalysts, which offers real possibilities for enhanced killing of micro-organisms and photo-mineralisation of organic contaminants from water.⁶ Contrary to solar-thermal reactions, which collect photons at a low-energy high-wavelength to achieve the thermal effect, solar photocatalysis uses only the photons of short-wavelength to initiate a photochemical process. The mechanism (Figure 2) of photocatalytic disinfection^{4, 5, 7-10} is as follows: The absorption of a photon from the solar energy excites an electron (e^-_{CB}) to the conduction band generating a positive hole (h^+_{VB}) in the valence band (Eq. 1.1) of semiconductors such as titanium dioxide.⁷



The H₂O becomes oxidized by h^+_{VB} producing H⁺ and $\cdot\text{OH}$ radicals (Eq. 2). Positive holes generated by light become trapped by surface adsorbed H₂O. The hydroxyl radicals can subsequently oxidize organic species to CO₂, H₂O or other simpler molecules. Titanium dioxide based photocatalysts (band gap of 3.2 eV) on which most of the research has focused until now, possesses a relatively high self-sterilisation under ultraviolet (UV) light (wavelength <390 nm). However, introduction of artificial UV light sources is not practical in remote areas where there is a lack of power supplies. Utilisation of the main part of the solar spectrum by the development of photocatalysts (Figure 2) that can yield high photocatalytic activity under visible light^{7, 11-21} would be highly beneficial in remote regions.

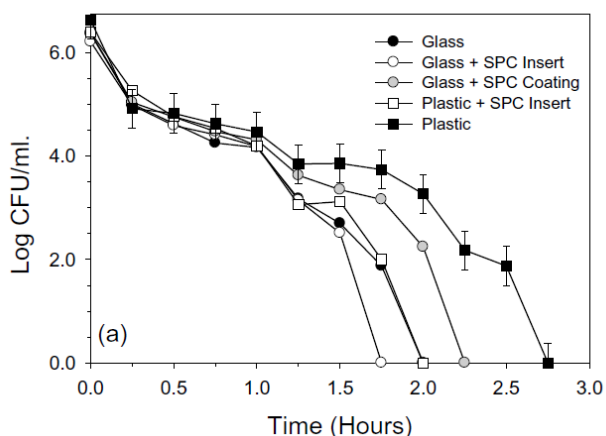


Fig. 3 Inactivation of *E. coli* K12 using glass and plastic bottles. Solar photocatalytic (SPC) inserts were employed in both glass and plastic bottles. The interior wall of the glass bottle was also coated. Reprinted from Solar Energy, Vol. 77, Duffy *et al.*, A novel TiO₂-assisted solar photocatalytic batch-process disinfection reactor for the treatment of biological and chemical contaminants in domestic drinking water in developing countries, pp. 649-655., Copyright (2004), with permission from Elsevier.

Hydroxyl radicals have the most positive electrochemical reduction potential (+2.8 V vs. normal hydrogen electrode (NHE)) among other substances generally employed for water disinfection, *e.g.* chlorine (+1.36 V). TiO₂ photocatalysis, therefore, has real potential for disinfection of resistant microorganisms.^{7, 22-26} In addition to the hydroxyl radicals, other oxidative species such as superoxide anions and singlet oxygen can also be created (Figure 2).

The first report of TiO₂ photocatalytic inactivation of bacteria was in 1985 by Matsunaga *et al.*²⁷, and since then a large number of microorganisms have been reported to be photocatalytically inactivated. A number of reviews address different aspects of the process such as application of photocatalysis for disinfection of water contaminated with pathogenic micro-organisms^{28,29}, decontamination of water by solar photocatalysis³⁰ and proposed mechanisms and modeling.³¹ The majority of photocatalytic studies cite the hydroxyl radical ([•]OH) as the reactive oxygen species (ROS) responsible for microorganism inactivation, although other ROS such as hydrogen peroxide (H₂O₂) and the superoxide anion radical (O₂^{•-}) have also been reported to be involved in the process. Proposed mechanisms of cell death include, DNA/RNA damage²⁸, membrane rupture²⁸, interruption of respiratory pathways³² and increased ion permeability.³³ These mechanisms are summarized schematically in Figure 2.

2.1 Solar photocatalytic disinfection of water; selected field studies

A number of researchers have investigated the effect of solar photocatalytic (SPC) disinfection using titanium dioxide. Numerous lab-scale studies on inactivation of microorganisms by photocatalysis with TiO₂ have been reported but few studies have attempted to scale-up the process in bottles or solar pilot plants, using sunlight in real-life conditions.

Duffy *et al.*³⁴ were one of the first groups to investigate

systematically if TiO₂ coatings could be used to accelerate bacteria inactivation in SODIS bottles. The coating materials and methods used were selected so that they could be easily replicated in an urban setting in a developing country. A plastic acetate sheet was coated with the commercial catalyst Degussa Evonik P25 (referring to as P25 from now on) powder and used as an insert to cover the bottom half of PET and borosilicate glass bottles. The bottom half of glass bottles (inner wall) was also coated successively (10 times) with P25. The inactivation of *E. coli* K12 was carried out to investigate the disinfection properties of these coatings. The PET bottles fitted with solar photocatalytic (SPC) inserts achieved inactivation in approximately 75% the length of time it took for standard PET SODIS bottles as shown in Figure 3. The coated glass bottle took approximately 20% longer time period to achieve inactivation compared to the uncoated bottle. Other interesting findings were that inactivation in borosilicate glass bottles was superior (20%) to that in PET bottles and that smaller volume bottles exhibited much superior performance to than in larger volume bottles. The superiority of borosilicate glass to plastic is due to greater solar light transmittance, as discussed recently by McGuigan *et al.*³

In a similar approach, Meichtry *et al.*³⁵ coated a range of substrates such as glass rings, glass rods and porcelain beads with P25 powder. The inside of PET bottles was also coated. Photocatalytic activity was evaluated by measuring degradation of the model compounds 4-chlorophenol and 2,4-dichlorophenoxyacetic acid. In all cases the coated surfaces resulted in a large degree of degradation of the model chemicals in the measured time period whereas no photodegradation was observed in uncoated bottles. The coated beads and rings performed better than the bottles, however TiO₂ was observed to delaminate from the beads. Smaller volume bottles were also found to perform better than larger volume bottles. Despite the superiority of the coated inserts, the study concluded that the coated bottles are more suitable for photocatalytic application as they do not contain fragile fillings and can be fabricated on site, which is not the case for coated inserts.

In a recent study by Carey *et al.*³⁶, the inside of the PET (Poly Ethylene Terephthalate) and homemade acrylic (Poly(methyl methacrylate)) square bottles were coated with P25. Two out of the four sides of the square bottles were coated. Acrylic bottles were chosen as an alternative to PET bottles due to its greater UV transparency. The photocatalytic activity of the coated and uncoated bottles were evaluated by inactivation of *E. coli* and the degradation of microcystin-LR and methyl orange. The addition of TiO₂ to the bottles did not increase the rate of *E. coli* inactivation, which may be due to the high temperature (53° C), which is known to increase SODIS rates. The TiO₂ coatings did however result in an increased degradation rate of both methyl orange and microcystin-LR. The acrylic bottles were superior to PET bottles in all tests.

Acrylic material allows the transmission of solar illumination between 300 and 350 nm. A greater amount of solar UVA radiation is available for photolysis and/or photocatalysis resulting in the acrylic bottles out performing PET bottles in pure SODIS application as well as when modified with a photocatalyst. Thus, acrylic material is a viable alternative to PET for SODIS bottles. In fact, Carlson *et al.*³⁷ previously reported

that the P25 coatings on acrylic showed greater durability and comparable UV photocatalytic degradation of methyl orange to P25 coatings on glass. In a significant field study, Gelover *et al.*³⁸ assessed the photocatalytic efficacy of immobilised TiO₂ coated on small pyrex glass cylinders loaded inside PET SODIS bottles.

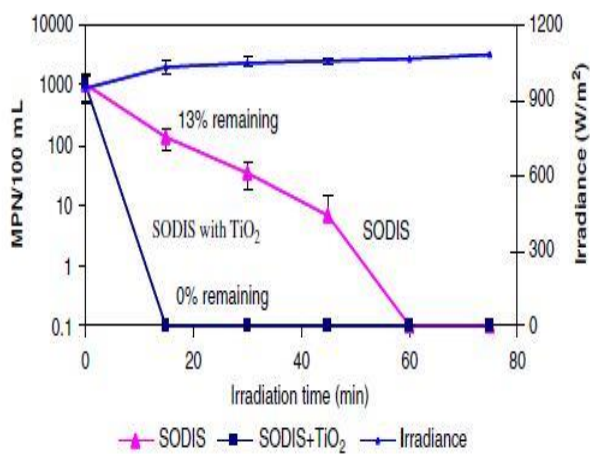


Fig. 4 Decrease of total coliforms during the treatment of SODIS plus TiO₂ disinfection. Reprinted from Water Research, Vol. 40, Gelover *et al.*, A practical demonstration of water disinfection using TiO₂ films and sunlight, pp. 3274-3280, Copyright (2006), with permission from Elsevier.

Glass cylinders were coated with TiO₂ using a previously characterised sol-gel method³⁹ and annealed at 500 °C. This cycle was repeated three times resulting in a thin film of average thickness of 600 nm crystallized in the anatase phase. Photodegradation of 4-chlorophenol and carbaryl under solar irradiation in a parabolic solar collector was found to be comparable to P25 TiO₂ in suspension. This led the research group to investigate the use of the coated TiO₂ cylinders in SODIS bottles. This is probably the first systematic report utilising a transparent uniform photocatalytic TiO₂ film in SODIS bottles. The performance of the photocatalytic SODIS bottles was significantly better than standard SODIS bottles for total and faecal coliform deactivation. Total coliform inactivation in the photocatalytic bottles took less than 20 minutes in comparison to 60 minutes in standard bottles as shown in Figure 4. Faecal coliforms achieved inactivation in 30 minutes in photocatalytic bottles whereas standard bottles did not achieve

inactivation in the measured time period (80 minutes). Another remarkable finding is that both total and faecal coliforms were incapable of regrowth in the photocatalytic bottles. After SODIS treatment, the closed bottles were stored for seven days in ambient light at room temperature. Standard SODIS bottles showed an oscillating increasing-decreasing total coliform population pattern, whereas no coliform was detected in TiO₂ photocatalytic SODIS bottles.

The significance of this result is two-fold. Firstly, it shows another advantage in the application of photocatalytic coatings in SODIS bottles, namely that photocatalytic bottles are 'bactericidal' whereas standard SODIS bottles can sometimes be 'bacteriostatic'. Although coliforms were not detected after 7 days, the phenomenon of bacterial regrowth immediately after treatment in SODIS bottles would have negative implications for storage of treated drinking water. Secondly, as noted by Byrne *et al.*⁴, the result points towards a difference in bacteria 'kill' mechanism between SODIS and photocatalytic SODIS disinfection. The cellular repair mechanism in the SODIS bottles was beyond the scope of the field study, but is worthy of further discussion in light of the differences shown with SPC SODIS bottles. Overall the reproducibility (replication over a 6 month time period) and consistency (agreement with kinetic data of bactericidal mechanism of TiO₂ photocatalysis) of this field study showed the TiO₂ coated cylinders to be a promising material for SODIS application.

Recently, Fisher *et al.*⁶ investigated the use of doped, visible light active TiO₂ coated borosilicate glass bottles and glass beads. Transparent coatings were prepared by a sol-gel method and doped with nitrogen and copper to achieve visible light activity. The photocatalytic efficacy was evaluated by degradation of methylene blue (MB) and *E. coli*. The coated bottles produced increased degradation of the dye compared to the uncoated bottles with complete decolouration after 6 hours.⁶ The doped TiO₂ coated bottles showed no increase in MB degradation over undoped TiO₂. By contrast copper and copper/nitrogen co-doped TiO₂ thin films showed potential for the degradation of *E. coli*. The former appeared to accelerate the inactivation of indicator bacteria when coated on the interior of bottles, while the latter only showed effectiveness when coated on spherical glass-beads. The increased disinfection of *E. coli* in the presence of TiO₂-coated beads may be due to the fact that, unlike in coated bottles, light absorption occurred on the surface of the catalyst in contact with the media. It should also be noted that the increased surface-to-volume ratio of the glass beads relative to bottles, and also the

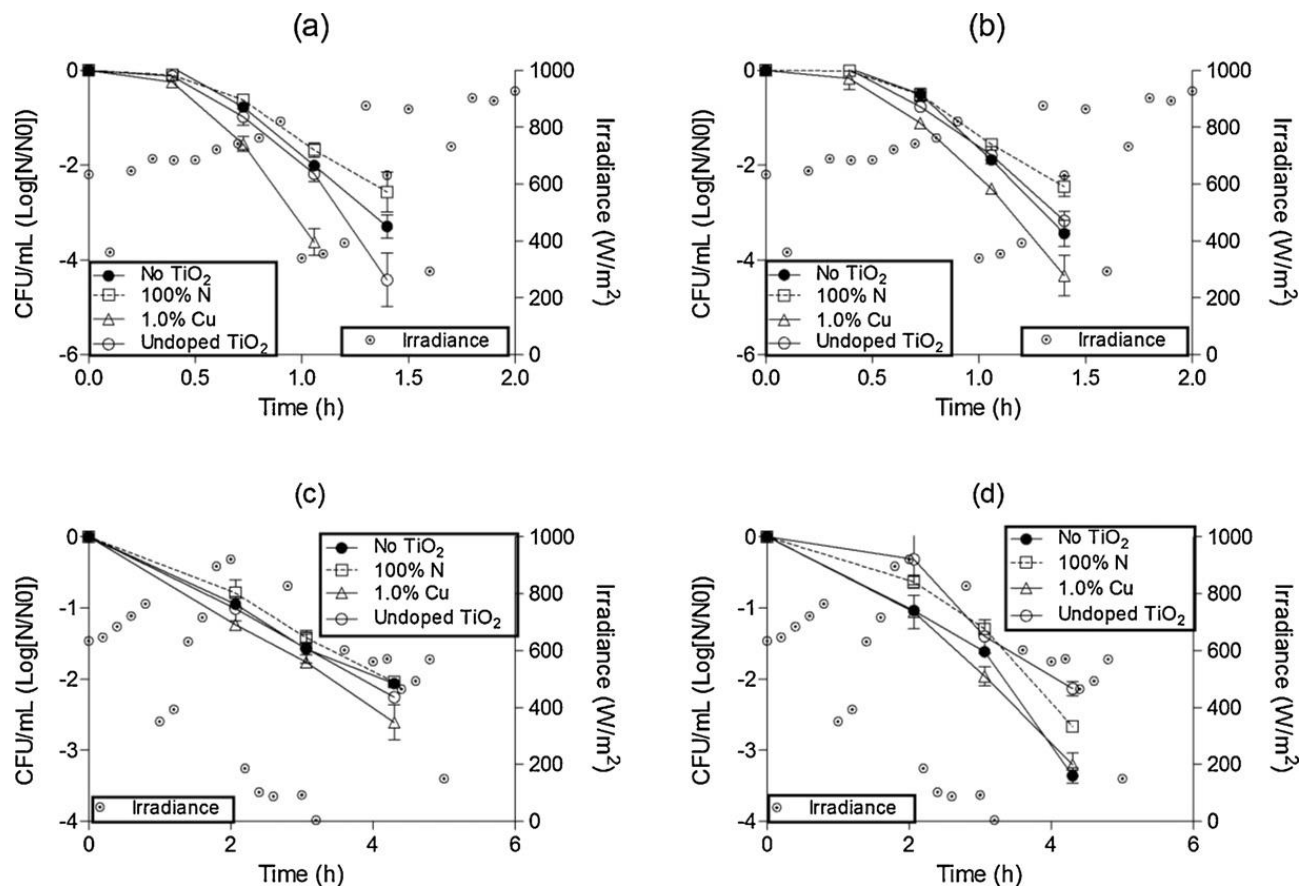


Fig. 5 Inactivation of *E. coli* and *Enterococcus faecalis* by solar light with or without UV-blocking film in the presence and absence of 3-mm glass beads coated with undoped TiO₂ thin films and films doped with 1% Cu/3.5% N. (a) *E. coli*, sunlight (b) *Enterococcus*, sunlight (c) *E. coli*, no UV (d) *Enterococcus*, no UV. Reprinted from *Applied Catalysis B: Environmental*, Vol. 130-131, Fisher *et al.*, Nitrogen and copper doped solar light active TiO₂ photocatalysts for water decontamination, pp. 8-13., Copyright (2013), with permission from Elsevier.

shorter mean distance between target micro-organisms and illuminated photocatalytic surfaces also contributed to the enhanced inactivation. Fisher *et al.* also observed that copper and nitrogen doped TiO₂ accelerated anti-bacterial action when coated on glass beads but not when coated on the interior surface of glass bottles indicating that any reactive species produced at Cu and N-doped photocatalytic surfaces are short-time lived and can only diffuse short distances and that bacterial disinfection by such species might be transport-limited. Cu- and N-doped TiO₂ immobilised coatings showed potential for the degradation of biological contaminants in the presence of solar light in these experiments (Figure 5). Applications of these types of immobilised doped photocatalytic coatings for the treatment of contaminated drinking water and wastewater appear to merit future investigation.

25 3.Improving solar photocatalytic process by suitable reactor design

Photo-degradation or photocatalytic inactivation of microorganisms in water via solar irradiation can be enhanced using photo-reactors. The first photoreactors for solar photocatalytic applications designed at the end of the 1980s were based on parabolic-trough collectors. One of the main advantages of photo-reactors is that they enhance disinfection by increasing photon flux into the sample.^{4,30} Nevertheless, for optimising the photo-reactor efficiency, other system factors must also be taken into account such as the total volume of treated water, reduction of the user dependence of the process and use of cheap and robust materials.

A wide range of reactor configurations have been used in photocatalysis for water disinfection. Many researches have carried out experimental works at lab-scale (10 mL – 2 L) to test the efficiency of catalyst while other investigations have been conducted using pilot-scale photo-reactors (>10L). Among the

most promising large-scale reactors are the so-called Compound Parabolic Collectors (CPC) reactors (Figure 6), which have

proven successful for both water disinfection and detoxification.

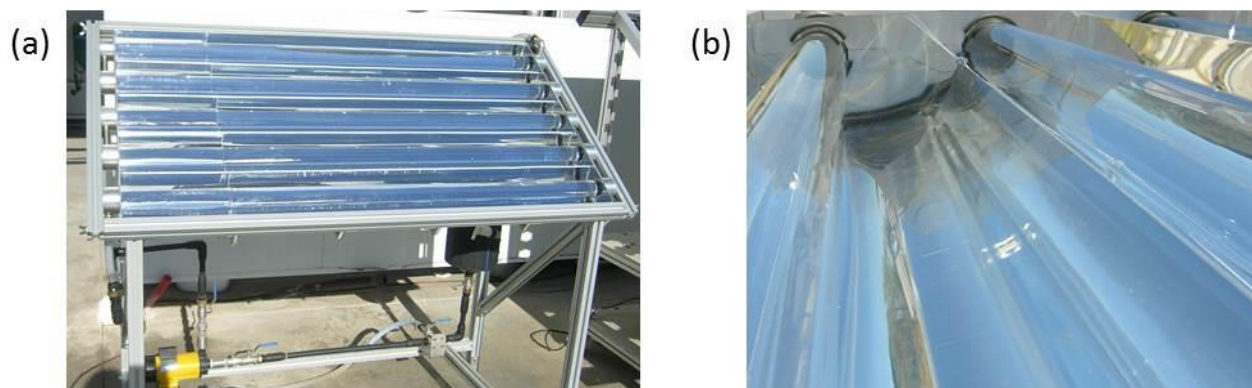


Fig. 6 CPC photo-reactor for water disinfection (a) CPC mirrors with (b) glass tubes

The parabolic trough reactors have a parabolic profile with the reactor pipe in the focal path as shown geometrically in Figure 7.⁴⁰ Compound parabolic collectors (CPC), a type of low-concentration collector used in thermal applications, combine some characteristics of parabolic concentrators and flat stationary systems. They collect solar radiation in static conditions with a high collection rate of the solar diffuse-radiation.⁴¹ The main advantages of these reactors⁵ are: (1) Use of non-imaging concentration with diffuse focus. (2) Highly efficient use of the solar photon flux due to the homogeneous distribution of radiation into the absorber. (3) Utilization of both diffuse and direct solar radiation, having high efficiency even on cloudy days. (4) Maintaining a constant concentration factor ($CF = 1$) for all values of sun zenith angle within the acceptance angle limit.

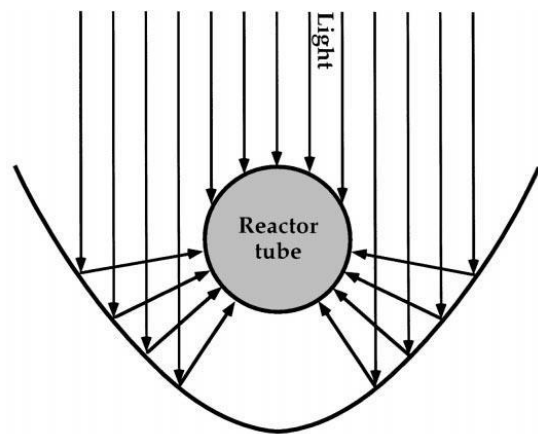
The CPC reactor mirrors are usually manufactured from anodized aluminium because they have high reflectivity in the UV range (87%–90%) and are highly resistant to the environmental conditions. Pipes and valves are made from polyethylene due to the robust nature of these materials. Water flows along the tubes to a tank using a centrifugal pump which is selected depending on the reactor dimensions, permitting a turbulent regime inside the photo-reactor. The photo-reactor tube should be made of borosilicate 25 glass because of its high transmission in the UV range (90%). CPC mirrors and borosilicate tubes are placed on a frame tilted at the same angle than the local latitude facing the south if the location is in the north hemisphere or facing the north if the location is in south hemisphere.⁴²

The inclination of the CPC reactors enhances the collection of direct solar radiation to the detriment of diffuse. According to Duffie and Beckman⁴³ the annual solar radiation global gain means 10 % in the inclined plane to the horizontal. This value depends on several factors such as climatology, inclination, orientation and the direct and diffuse solar radiation in a determined location. Navntoft *et al.*⁴⁴ collected solar radiation data of global and UV-A radiation for four consecutive years (2008-2011) at PSA in horizontal and inclined (37°) planes. This study demonstrated that during the months of August to April, the solar radiation gain varies between 1 and 1.25 in the UV range and 1 to 1.55 in the global solar spectrum at PSA. However, for the months of May to July this ratio reduces to 0.95 (UV) and 0.85 (global) (Figure 8).

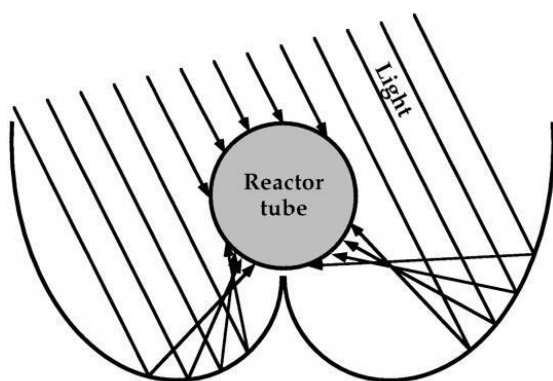
On the other hand, the CPC reactors have low environmental impact, are easy to construct and maintain, and have low power requirements.⁵ Furthermore, CPC reactor technology is much more affordable compared with highly concentrating systems (e.g., parabolic concentrator). The solar CPC pilot plants designed and built today are mostly at laboratory scale for water disinfection while some examples have been reported in literature at large scale (thousands of liters) for water decontamination. This is the case for a commercial non-concentrating solar CPC detoxification system built to treat 1 m³ of contaminated water. The solar collector area is 98 m² with 975 L of total plant volume. The solar treatment method used in this plant is photocatalysis with 200 mg/L of suspended TiO₂. The estimated average treatment capacity of the solar plant is around 400 L/h. A preliminary study estimated the cost per m³ of effluent treated between 7 and 10 € (30 and 70% capital and operational costs, respectively).⁵ Since 2000, other demonstration level photocatalytic plants have been installed for the treatment of industrial wastewater contaminated with pesticides, pharmaceuticals etc.^{5, 45, 46, 47}

Some authors have investigated the cost of solar water disinfection (SODIS), using small scale CPC reactors for household users in developing countries. Ubomba-Jaswa and co-workers⁴⁸ reported that a 25L-CPC batch reactor could provide solar disinfected water at a total treatment cost of \$0.2 per 100L, taking into account that the estimated photo-reactor built cost is \$200 with 10 years of operational life. An advantage of the CPC system is the modular system, and Polo-López and co-workers⁴⁹ reported that a 6-tube automated sequential CPC batch reactor could provide solar disinfected water with a total cost of \$0.23 per 100L. Much research has been carried out studying various reactor configurations with the objective of enhancing the efficiency of the photocatalytic treatment. Some of the main factors affecting such efficiency are summarized below:

i) **The illuminated volume/total volume ratio.** In a flow system, the solar radiation dose is delivered in an interrupted manner



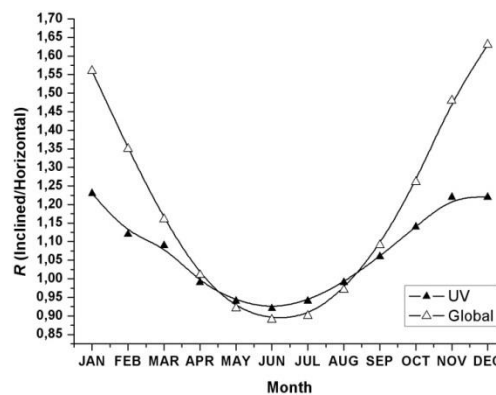
(a)



(b)

Fig. 7 Geometric profile of: (a) a Parabolic trough reactor (PTR) and (b) a compound parabolic collecting reactor. Reprinted from *Catalysis Today*, Vol. 58, Alfano *et al.*, Photocatalysis in water environments using artificial and solar light, pp. 199-230, Copyright (2000), with permission from Elsevier.

since the system contains dark parts where the water is not illuminated such as pipes and storage tanks. An important issue in solar reactors is to minimize these dark areas in favour of illuminated volume. This aspect has been notified in literature, in which two different CPC reactors were compared with respect to their performances to inactivate 10^3 CFU/mL of *Fusarium solani* spores. A 14L-CPC reactor with ratio of 0.3 (14 L of total volume and 4.7 L of illuminated volume)⁵⁰ was compared to a 60L-CPC reactor with a ratio of 0.75⁵¹. The 60L-CPC reactor showed enhanced inactivation results using photocatalysis with TiO_2 and solar photo-degradation⁵¹. On the other hand, the interrupted illumination can affect the inactivation results depending on the microbial target. This effect is due to the presence of dark areas which permit bacterial recovery. Rincón and Pulgarín⁵² observed that an effective disinfection time (EDT) was necessary to ensure no bacterial regrowth after solar treatment and before water consumption. Ubomba-Jaswa and co-workers⁵⁰ reported that to achieve complete bacterial inactivation, an uninterrupted,



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Fig. 8 Monthly mean irradiance in the PSA: relationship between extent inclined plane and horizontal (global and UV spectrum). Reprinted from *Solar Energy*, Vol. 86, Navntoft *et al.*, UV solar radiation on a tilted and horizontal plane: Analysis and comparison of 4 years of measurements, pp. 307-318., Copyright (2012), with permission from Elsevier.

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continuous accumulated UVA dose independent of the incident solar UV intensity was required. These authors used a continuous flow system where a residual viable concentration $\sim 10^2$ CFU/mL remained after 5 h of exposure to strong sunlight and a cumulative dose of >108 kJ m^{-2} . Therefore, this aspect plays a main role both in solar photo-degradation and solar photocatalysis through the use of re-circulatory continuous flow reactors.

ii) **Catalyst load in slurry reactors.** Controversial results regarding the catalyst load using suspended TiO_2 have been observed in recent literature. However, this aspect may be due to the different reactor configurations used to conduct solar photocatalytic tests using target micro-organisms. Examples of this difference are reported in the work performed by Fernández-Ibáñez and co-workers.⁵³ They reported the efficiency of photocatalysis with several TiO_2 concentrations (10, 20, 35, 50, 100, 250, 500 mg L^{-1}) to inactivate spores of *Fusarium solani* in water using two different solar reactors, 200mL-solar stirred tank (bottle) reactors and 14L-CPC flow-through reactor. Maximum *Fusarium sp* spore inactivation was achieved at different catalyst load i.e. 35 mg L^{-1} and 100 mg L^{-1} for bottle and CPC reactor, respectively. This behaviour was attributed to optical phenomena generated by the light traveling through the reactor wall, revealing the importance of photo-reactor diameter and optical path length. Nevertheless, optimum catalyst load to inactivate bacteria differ from earlier studies. Rincón and Pulgarín⁵⁴ tested several TiO_2 concentrations (50, 100, 250, 500 mg/L) in Pyrex glass bottle of 50 ml using solar simulator. They reported that the catalyst concentration reaching best *E. coli* inactivation efficiency is 500 mg/L . On the other hand, in CPC systems optimum catalyst concentration was found to be 200 mg/L to remove chemical compounds.^{8,10,39,46,47,53,55} This highlights that although optical phenomena inside the photo-reactor play an important role to determine the optimal catalyst concentration, the type of target micro-organism can also influence the final results. Chemical and microbial processes have different photo-degradation behaviors and significantly different inactivation kinetics have been observed between strains of the same pathogen. These

controversial results mark the importance of knowledge of the

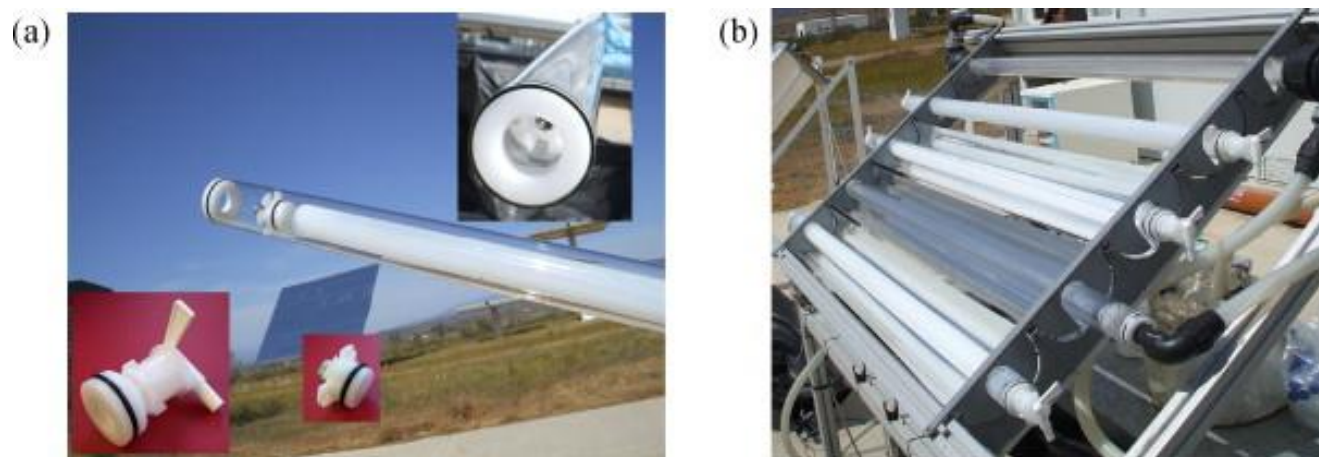


Fig. 9 Photographs showing the double tube configuration with internal tube cap and the valve for external tube (a); and the solar photocatalytic reactor with and without CPC during disinfection tests (b). Reprinted from Applied Catalysis B: Environmental, Vol. 128, Alrousan *et al.*, Solar photocatalytic disinfection of water with immobilised titanium dioxide in re-circulating flow CPC reactors, pp. 126-134, Copyright (2012), with permission from Elsevier.

target and of their baseline behavior before introducing such water treatment systems in the field. At this point it is also worth mentioning the research carried out by Prieto-Rodriguez *et al.*⁵⁵ which describes a methodology for determining the optimal P25 TiO₂ catalyst load for solar photocatalytic destruction of emerging contaminants, EC's, (e.g. pharmaceuticals, xenobiotics, pesticides etc.). Although a direct empirical comparison of optimal catalyst load and reactor design for photocatalytic destruction of microorganisms and EC's cannot be made for the mechanistic reasons pointed out above, interesting parallels exist in terms of findings and methodology, which fall under the overall umbrella of solar photocatalytic water treatment. For such an overview, the reader is referred to the extensive review of Malato *et al.*⁵ which covers both water decontamination and disinfection by solar photocatalysis.

iii) **Immobilized versus suspended photocatalyst.** One of the disadvantages often highlighted with photocatalytic disinfection is the need to remove suspended photocatalyst particles from the water after solar treatment. This post-treatment could be avoided if the catalyst is immobilized onto surfaces. Intense research interest has focused on the development of methodologies and materials to immobilize the catalyst onto surfaces such as glass, fibre and different configurations such as rings, dipping the photo-reactor inner wall^{56, 57} packing of a fixed-bed,⁵⁸ and glass plate (thin-film fixed bed reactor)⁵⁹. Nevertheless, in none of the above cases has the inactivation efficiency for an immobilized system outperformed a suspended photocatalyst system.

iv) **Flow rate .**

TiO₂ efficiency may be limited by the amount of dissolved oxygen in the water matrix since oxygen acts as the electron acceptor. It is well known that dissolved oxygen deficiencies reduce hydroxyl radical generation. In a re-circulatory continuous flow reactor it is important to work in the turbulent regime to ensure that oxygen dissolves effectively in the aqueous solution. Moreover, it is important to use the appropriate flow rate to guarantee that catalysts do not aggregate too much during solar treatment.⁵¹ On the contrary, the use of immobilized

photocatalysts usually introduces mass transport limitations that reduce the overall efficiency of the process, a feature that could be particularly significant in disinfection processes due to the high size of microorganisms.³⁰ Therefore, systems using immobilized photocatalysts should be operating in different ways to those using suspended photocatalysts. Due to the low contact between catalyst and target micro-organism, it is recommended that low flow rates are used to maximize the residence time which in turn will maximize the opportunities for contact with the micro-organism.

Alrousan *et al.*⁵⁷ examined the use of compound parabolic collectors (CPC) and immobilised titanium dioxide for photocatalysts for solar disinfection. Solar photocatalytic disinfection of water using P25 immobilised on borosilicate glass tubes was carried out (Figure 9). The photocatalytic efficiency of immobilized P25 TiO₂ to inactivate *E. coli* using a 7L-CPC flow reactor was evaluated under real sunlight. Several photo-reactors configurations were tested: (1) borosilicate glass tubes (1.5 m in length) of diameter 50 mm dip coated with P25 TiO₂ (2) uncoated 50mm-borosilicate glass tubes, (3) 32mm-borosilicate glass tube externally dip coated with TiO₂ (which was placed inside the 50 mm glass tube), and (4) uncoated 32mm-borosilicate glass tube.

It was found that the use of CPCs improved the SODIS and solar photocatalytic disinfection. The authors showed that not all configurations were efficient to inactivate *E. coli*. The concentric tube arrangement (a tube within a tube) with CPC was the most effective configuration. Photocatalysis has advantages in terms of the non-recovery of inactivated organisms and the inactivation of SODIS resistant organisms.⁵⁷

Sordo and co-workers⁶⁰ studied the photocatalytic inactivation of *E. coli* with immobilized TiO₂ in two different configurations (a wall and a fixed-bed reactor) in a solar 10L-CPC pilot plant, comparing the use of a slurry reactor and the solar disinfection without catalyst. The fixed-bed reactor consisted of TiO₂ immobilized onto a packing material of 10 mm glass Raschig rings. TiO₂ wall reactors consisted of TiO₂ immobilized on a glass tube placed in the axis of the photoreactor with the help of a

tubular support (external diameter of inner tube: 32 mm; inner diameter of external tube: 46.4 mm).⁶⁰ They observed that higher efficiency was reached with slurry TiO₂.

It should finally be noted that no study has ever set out to specifically design an efficient solar photocatalytic disinfection reactor – research groups have modified existing reactors widely used for chemical treatment. In this respect there is a need for a chemical engineering approach to try and design an efficient reactor for SPC disinfection from first principles. The existing light modelling and CPC design are relevant, but the oxygen transfer kinetics, mass transfer of bacteria to the catalyst, and the catalyst support configuration need to be specifically designed for disinfection purposes.

4. Recommendations for future directions

Although there have been numerous publications in the area of solar photocatalytic disinfection, the number of field studies in photocatalytic TiO₂ in SODIS bottles is remarkably low. This is surprising considering that in 2009, two million users were practising SODIS in 33 countries.⁶¹ However, despite the promising early field studies, the technical application of SPC in SODIS bottles remains a barrier for realisation of a working prototype ready for large scale manufacture and application. Examination of the field studies described above raises a number of issues which we suggest is preventing this application and provides some potential research directions for future realisation.

4.1 Mass transfer. Mass transfer has long been identified as the major limitation in applying the intrinsic advantage of photocatalytic water decontamination.⁶² The mass transfer of bacteria in a static bottle to the surface of the catalyst in a coating will always be lower than that of a dispersed powder. In SODIS field studies this is manifested in simple observations that smaller coated bottles perform better than larger ones and higher surface area coated inserts such as glass beads perform better than coated walls of the bottle. In this respect, it remains questionable whether the ideal configuration of a bottle with coated walls, will have a sufficient bactericidal effect to find application.

4.2 Bottle reactor design. One of the greatest difficulties in applying photocatalytic materials in SODIS bottles is that the design must be simple and inexpensive. Whereas the catalyst in photoreactors can be engineered with complexity to achieve greater efficiency, the bottles are limited to either a coated wall or coated insert(s). Furthermore the material must be inexpensive to manufacture and almost disposable. Researchers have designed powdered coatings so that bottles can be potentially prepared in communities in developing countries. The salient issue with powder coatings is delamination of the coating which has been observed in a number of studies. On the other hand, sol-gel

coatings have been shown to have excellent adhesion to glass⁶² but have the disadvantage that they require laboratory preparation. However, glass manufacturers have mass produced TiO₂ thin films on glass by a sol-gel method⁶³ and chemical vapour deposition⁶⁴, and could potentially do likewise for photocatalytic glass bottles. Sol-gel coatings at present are the most viable way of mass production of coatings. Firstly they have been well characterised for SODIS application as shown by Gelover³⁹ and Fisher⁶. Secondly, submicron thin films and coatings (especially optical) represent one of the earliest commercial successes of sol-gel technology, overcoming disadvantages such as economy, processing time and cracking.⁶⁵ TiO₂ thin films have similarly shown excellent adhesion to glass, with a sol shelf life and material economy (multiple coating from single sol) suitable for inexpensive manufacturing. Furthermore it is relatively easy to coat large substrates or axially symmetric substrates such as pipes, tubes, rods and fibres not easily coated by conventional methods.⁶⁵ In this respect sol-gel coatings are particularly well suited for photocatalytic SODIS bottle design considering the substrates employed to date in field studies such as glass bottle wall, glass or ceramic rings, cylinders and beads. A final point is that considering the use of glass bottles in SODIS has proved troublesome due to breakage in transit to remote locations, the use of brittle coated inserts could prove too cumbersome to find application in specific regions.

4.3 Light absorption by photocatalyst coatings. Despite the strong visible light induced antibacterial effect of doped TiO₂ (powders) proven in the laboratory⁶⁶, the societal and commercial application of such material in SODIS bottles is found to be difficult. The visible light activity of a coating on the inner wall will in fact decrease the light transmittance through to the active side of the catalyst, through absorption, reflection and scattering resulting in decreased photocatalytic activity of coated bottles compared to uncoated ones, in the same way glass is superior to PET as a SODIS bottle. The configuration of a “half coated” square bottle may prove the most efficient way of solar light accessing the active side of the catalyst coating.³⁶

4.4 Development of a highly efficient solar photocatalyst
The major issue facing the commercialisation of semiconductor photocatalysis is the wide band gap of TiO₂ (3.2 eV), meaning that only UV light ($h\nu < 390$ nm) can activate the photo-induced catalytic process, therefore limiting the application of titania to approximately 5% of the UV light of the solar spectrum. It is therefore vital to reduce the band gap of titania so that both the UV and visible regions of the electromagnetic spectrum can be used for the photocatalytic and disinfection reactions.

4.4.1 Development of doped photocatalysts

One approach investigated is doping the TiO₂ with metal ions.⁶⁷ Non-metal doping is another popular approach; Asahi *et al.*¹¹ investigated the visible light absorption of anatase titania through nitrogen doping and they concluded that the substitutional N doping (TiO_{2-x}N_x) causes the narrowing of band gap by mixing N 2p orbitals of the dopant with O 2p orbitals of titanium dioxide.¹¹ This study was considered as a significant development in the area of visible light photocatalysts and a number of investigations have concentrated on N-doping since then. However, the number

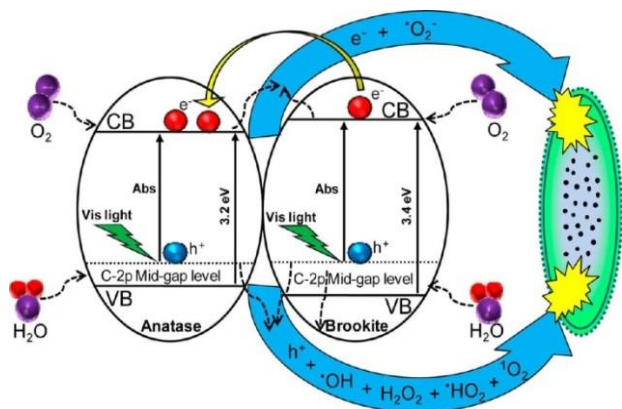
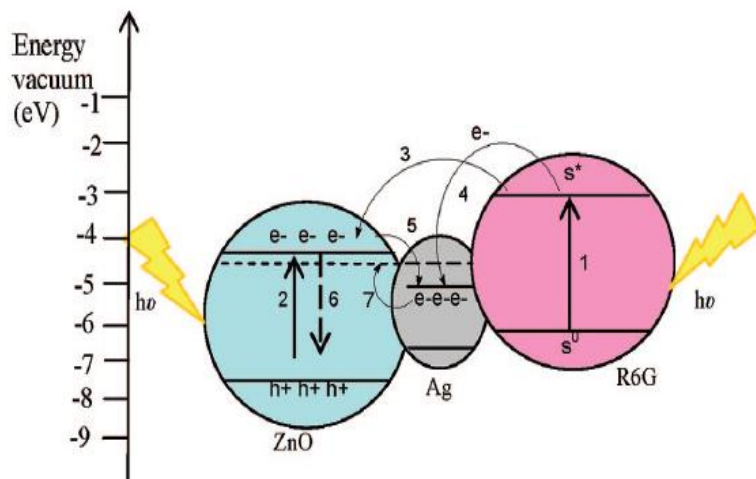


Fig. 10 Mechanism of visible-light induced photocatalytic bacterial killing using carbon-doped anatase-brookite heterojunctions. Reprinted with permission from *ACS Applied Materials & Interfaces*, Vol 5, Etacheri *et al.*, A Highly Efficient TiO₂-xC_x Nano-heterojunction Photocatalyst for Visible Light Induced Antibacterial Applications, pp. 1663-1672. Copyright (2013) American Chemical Society.

of publications concerning the photocatalytic activity of these doped visible light active materials for the inactivation of microorganisms in solar field studies is very low. In an effort to address this, transparent N-doped titania thin films were applied by a sol-gel route⁶, in solar disinfection field studies which is described in detail in section 2.1. Glass bottles coated with these sols and annealed at 600 °C were found to degrade the model pollutant methylene blue faster than uncoated bottles. However, contrary to the expectations, N-doped titania photocatalytic coatings did not show any significant increase in water pollutant degradation rates compared to undoped titania.⁶ By contrast, Cu and N-doped photocatalyst-coated bottles appeared to demonstrate improved bacterial photoinactivation relative to undoped titania, and these effects appeared to persist in the absence of UV wavelengths.⁶ There are a number of recent reports present in the literature on the visible light inactivation of bacteria^{22-26, 68}, but the effective and consistent use of these materials for long term solar disinfection is yet to be developed.

4.4.2 New nanoscale materials, nanocomposites and heterojunctions for photocatalysis

An emerging area of research to increase the photocatalytic efficiency, is the use of 'nanoscale' TiO₂ which has been subject to reviews by Li *et al.*⁶⁹ and more recently Di Paolo *et al.*⁹ In addition to the salient issue of the small amount of photons absorbed in the visible region discussed above, the authors identify other drawbacks of "bare" TiO₂ such as high recombination rate for the photo produced electron-hole pairs,



difficulty in significantly improving performance by loading or doping with foreign species that often work as recombination centres, and difficulty in supporting powdered TiO₂ on some materials⁹. Nano-assembled materials (such as nanoparticles, nanotubes, nanofibres, nanocages, nanorods etc.) have been shown to enhance the photoactivity of TiO₂, with the key contributing factor being the specific surface area of the structure.

Fig. 11 Mechanism of visible-light induced photocatalytic bacterial killing using carbon-doped anatase-brookite heterojunctions. Reprinted with permission from R. Georgekutty, et al, A highly efficient Ag-ZnO photocatalyst, Synthesis, properties and mechanism *J. Phys. Chem. C*, 2008, **112**, 13563-13570 . Copyright (2013) American Chemical Society.

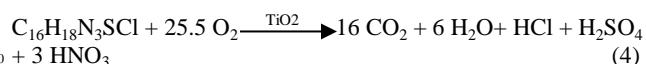
A good example is carbon nanotubes⁹; as a nanostructured catalyst support material it has also been employed to utilize enhanced photoactivity at this scale. In addition to improved surface area, an increase in carrier lifetime, due to charge transfer into the support, is suggested as a reason for greater photocatalytic activity. Another example is palladium-modified nitrogen-doped titanium oxide (TiON/PdO) supported on a mesoporous-activated carbon fiber templated by a sol-gel process.⁷⁰ A combination of adsorption and visible-light photocatalysis resulted in highly efficient virus deactivation. A further example, is the use of graphene-TiO₂ nanocomposites.⁷¹ Akhavan and Ghaderi⁷² reported that such TiO₂-reduced graphene oxide (RGO) nano-composites could improve the efficiency for the killing of *E. coli* bacteria under solar irradiation. This was found to be due to the reduced graphene oxide platelets acting as electron sinks, accepting conduction band electrons from the UV excited TiO₂ and effectively decreasing the rate of recombination of charge carriers. The optical absorption was not significantly different following the deposition of the RGO. In 2011 Liu *et al.*⁷³ reported a simple two-phase assembling method to produce graphene oxide-TiO₂ nanorod composites. After combining with graphene oxide (GO), the GO-TiO₂ composites showed higher photocatalytic activities than that of TiO₂ nanorods alone for the inactivation of *E. coli* under solar simulated light. Pillai and co-workers⁷ have

highlighted recombination of photogenerated charge carriers is the major limitation in semiconductor photocatalysis as it reduces the over-all quantum efficiency (Figure 10). Both hetero-junction semiconductor coupling and nanosized crystals (Figure 11) have been reported to reduce such carrier recombination and thereby an increased the photocatalytic efficiency in the visible region.^{12-20, 68 74-86}

The use of nanoscale TiO₂, in supported (composite) or unsupported form, could increase water disinfection efficiency in solar photocatalytic reactors. Further optimization could be achieved by doping of the TiO₂ phase to increase visible light activity and could be incorporated in the catalyst preparation procedure, a good example of which is shown by Li *et al.*⁷⁰

4.5 Requirement of a standard test method for water disinfection

The standard ISO 10678; 2010, the 'determination of photocatalytic activity of surfaces in an aqueous medium by degradation of methylene blue' is a popular test pollutant in photocatalysis because of simplicity as this involves the assessment of the rate of photocatalytic reaction of the dye molecules in aqueous solution via UV/vis spectrophotometry. Hermann and co-workers⁸⁷ reported the photocatalytic bleaching of methylene blue leads to the conversion of organic carbon into harmless formation of gaseous CO₂ and that of nitrogen and sulfur heteroatoms into inorganic ions. For example the proposed full degradation of methylene blue can be explained as in equation 4.



In a recent review, Mills *et al.*⁸⁸ showed that this mineralisation process occurs on a longer timescale than the 'photo-bleaching' reaction of the dye. Therefore it is worth noting that the measurement of the rate of 'photo-bleaching' of the dye molecule is not equal to the rate of mineralisation of the dye, which is found to be a much slower process. During the solar irradiation on the TiO₂ semiconductor, in addition to the 'OH and O₂⁻, singlet oxygen (¹O₂) can also be produced. The photocatalytic inactivation of *E. coli* does not always involve hydroxyl radical production (mainly for solar or visible light activated catalysts). In some cases, the formation of singlet oxygen, a less oxidative, reactive oxygen species was reported to be responsible for the bacterial inactivation.²⁰⁻²² The hole, produced by the visible light irradiation, in the mid-gap or isolated energy levels (as a result of doping) would not have the adequate redox potential to oxidise organic molecules of the pollutant. Therefore the methylene blue degradation is not always a good reaction system to determine the photocatalytic properties of solar or visible light activated materials. It was also noted that the standard ISO 27447: 2009, 'test method for antibacterial activity of semiconducting photocatalytic materials' focuses mainly on the photocatalytic disinfection of surfaces (e.g., construction materials and fabrics) and it does not cover the disinfection of water. The ISO standard 10676 2010, 'describe a method for water purification of semiconducting photocatalytic materials by measurement of forming ability of active oxygen using DMSO. A new standard is therefore required to analyse the water disinfection properties of

photocatalysts.⁸⁸ Current photocatalytic test methods based on various applications are given in Table 1

Table 1 Current recommended ISO standards for various photocatalysis tests

Photocatalytic Test	ISO standard
Anti-bacterial activity	ISO 27447: 2009
Surface photocatalytic activity	ISO 10678: 2010
Air purification	ISO 22197-1: 2007
	ISO 22197-2:2011
	ISO 22197-3: 2011
Self-cleaning performance	ISO 27448: 2009
Water purification (DMSO method)	ISO 10676 2010

The use of *E. coli* as indicator of microbiological contamination for research studies is not the best choice, as this bacterium is much more sensitive to any disinfecting method than other faecal bacteria.⁸⁹ The indicators selected to do studies on water disinfection should represent both the potential occurrence and the response of pathogens to water disinfection, and faecal bacteria (faecal coliforms, *E. coli*, enterococci) are commonly used for this purpose. However, these indicators do not provide information on the occurrence and behaviour of viruses and protozoa. Hence, alternative indicators are used to evaluate water treatments: somatic coliphages (SOMCPH), F-specific RNA phages (FRNA) and bacteriophages infecting Bacteroides are used as viral indicators⁹⁰, and spores of sulphite-reducing clostridia (SRC) are used as indicators of oocysts of *Cryptosporidium* sp.⁹¹ Bandala *et al.*⁹² have recently used an azo dye, Acid orange 24 (AO24), as a visual dosimetric indicator to measure the solar radiation dose required to inactivate helminth ova in a homogeneous photocatalytic system (photo-Fenton process). It was found that the solar radiation dose required for complete dye degradation, in which there is a visual change in colour from red to colourless, was comparable to that required for helminth ova inactivation. In respect to SODIS, this result is significant for two reasons. Firstly, helminth ova can be considered an appropriate index for microbiologically safe drinking water as it is very resistant pathogen found in developing countries. Secondly, the visual colour change of the dye and its ease of use is compatible with the goals of SODIS. It is also worth pointing out that in the study, the authors define the process as enhanced photocatalytic solar disinfection (ENPHOSODIS), which describes the application of any advanced oxidation technology to water disinfection using solar radiation. On the other hand, Agulló *et al.* suggest that a single microbial indicator may not be enough to guarantee a low risk of infection.⁸⁹ Depending on the final application of the disinfection method and which type of use of disinfected water will be done, the selection of the indicator or microbial contamination may change. For example, if the final application is wastewater reuse

for industrial or agricultural uses, the microbial quality will be assessed looking at other bacteria (*Legionella*, *Salmonella*, etc.) or resistant forms like spores or cysts, which are more robust against disinfection methods due to their structure and chemical composition. The photocatalytic disinfection results will depend very much on the microorganism used in the study. For example, *Enterococcus faecalis* is well known to be more resistant to solar disinfection and TiO₂ mediated photocatalysis than *E. coli*, while spores of *Fusarium* are much more resistant than the above mentioned bacteria.⁹³ However, the choice/s of organism/s must be general enough to allow easy cultivation and therefore widespread use of a new standard.

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