Catalysis Science & Technology

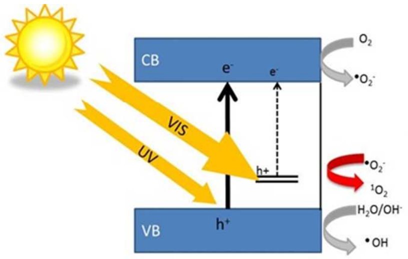
Accepted Manuscript

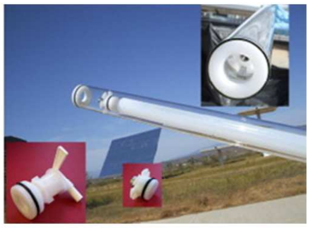
ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/catalysis

Solar photocatalysis for water disinfection: Materials and reactor design

*Donal A. Keane, Kevin G. McGuigan, Pilar Fernández Ibáñez, M. Inmaculada Polo-López, Anthony J. Byrne, Patrick S.M. Dunlop, Kevin O'Shea, Dionysios D. Dionysiou and Suresh C. Pillai**





This comprehensive review addresses the fundamentals of photocatalytic mechanism, recent developments in materials synthesis and reactor design.

Catalysis Science & Technology

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

REVIEW

Solar photocatalysis for water disinfection: Materials and reactor design

Donal A. Keane,[a] Kevin G. McGuigan,[b] Pilar Fernández Ibáñez,[c] M. Inmaculada Polo-López,[c] Anthony J. Byrne,[d] Patrick S.M. Dunlop,[d] Kevin O'Shea,[e] Dionysios D. Dionysiou[f,g] and Suresh C. Pillai[h,i]*

[a] *Chemistry Department and Environmental Research Institute, University College Cork, Cork, Ireland.*

[b] *Department of Physiology & Medical Physics, Royal College of Surgeons in Ireland, 123 St Stephens Green, Dublin 2, Ireland.*

[c] *Plataforma Solar de Almería – CIEMAT, PO Box 22, 04200 Tabernas, Almería, Spain.*

[d] *Nanotechnology and Integrated Bio-Engineering Centre, School of Engineering, Faculty of Computing and Engineering, University of Ulster, Newtownabbey, Northern Ireland, United Kingdom.*

[e] *Department of Chemistry and Biochemistry, Florida International University, Miami, FL 33199, USA.*

[f] *Environmental Engineering and Science Program, Department of Biomedical, Chemical and Environmental Engineering, University of Cincinnati, Cincinnati, Ohio 45221-0071, USA.*

[g] *Nireas-International Water Research Centre, University of Cyprus, 20537 Nicosia, Cyprus.*

[h] *Department of Environmental Science, School of Science, Institute of Technology Sligo, Ash Lane, Sligo, Ireland.*

[i] *Centre for Precision Engineering and Manufacturing (PEM), Institute of Technology Sligo, Ash Lane, Sligo, Ireland.* pillai.suresh@itsligo.ie

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

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 microroganisms from drinking water. The time taken for the conventional SODIS process can be greatly reduced by semiconductor (e.g. TiO_2, 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 TiO_2 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]

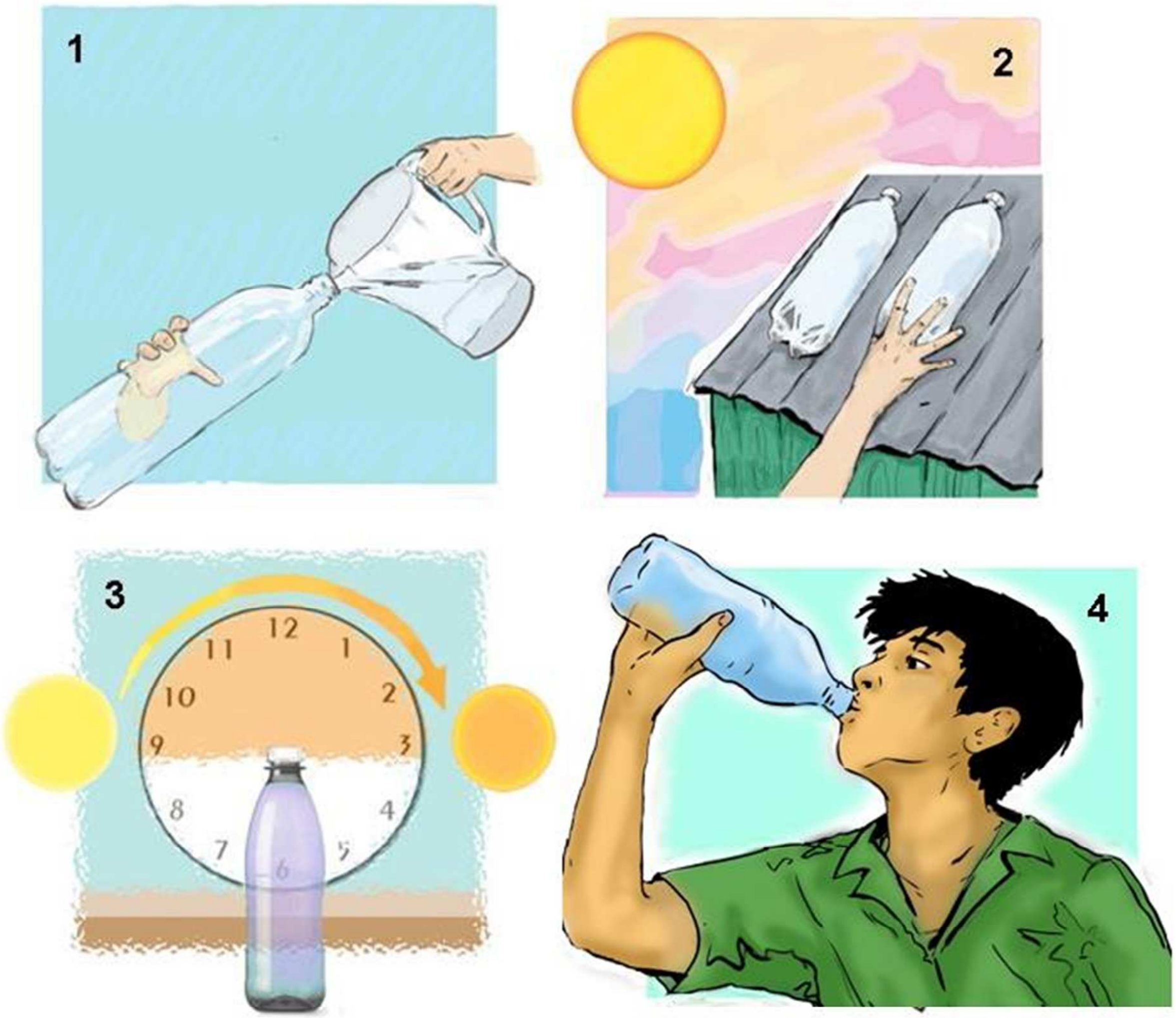


Fig. 1 A graphical description of the solar disinfection (SODIS) technique. (1) Fill the bottle. (2) Place the bottle in direct sunlight. (3) Wait a minimum of 6 hours. (4) The water is safe to drink. Reprinted from Journal of Hazardous Materials, Vol. 235-236, McGuigan *et al.*, Solar water disinfection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

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 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 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 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 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 'transferrable' 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]

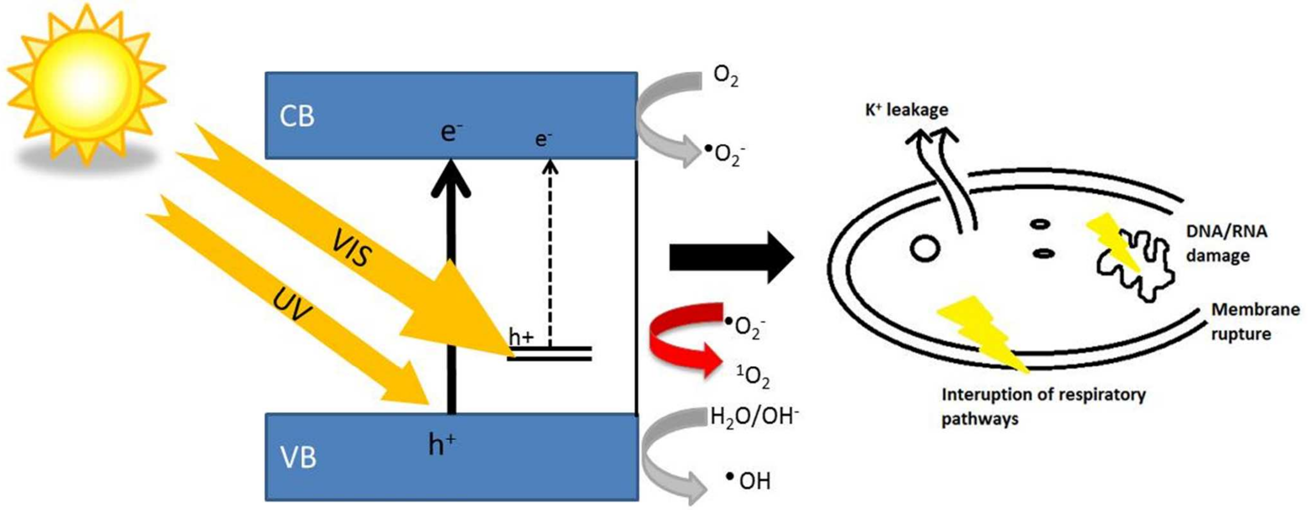


Fig. 2 Schematic diagram of bacterial disinfection using visible light active catalyst. Reprinted from *Applied Catalysis B: Environmental*, Vol. 130-131, Fisher *et al*., Nitrogen and copper doped solar light active TiO_2 photocatalysts for water decontamination, pp. 8-13., Copyright (2013), with permission from Elsevier.

However, SODIS technology has a number of disadvantages that hinder its widespread application. The major challenge remains 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 (TiO_2), into the process.

Thus, this review describes the use of both TiO_2 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 TiO_2 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]

$$TiO_2 + h\nu \rightarrow h^+_{VB} + e^-_{CB} \qquad (1)$$

$$H_2O + h^+_{VB} \rightarrow {}^{\bullet}OH + H^+ \qquad (2)$$

$$O_2 + e^-_{CB} \rightarrow O_2^{\bullet -} \qquad (3)$$

The H_2O becomes oxidized by h^+_{VB} producing H^+ and ${}^{\bullet}OH$ radicals (Eq. 2). Positive holes generated by light become trapped by surface adsorbed H_2O. The hydroxyl radicals can subsequently oxidize organic species to CO_2, H_2O 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.

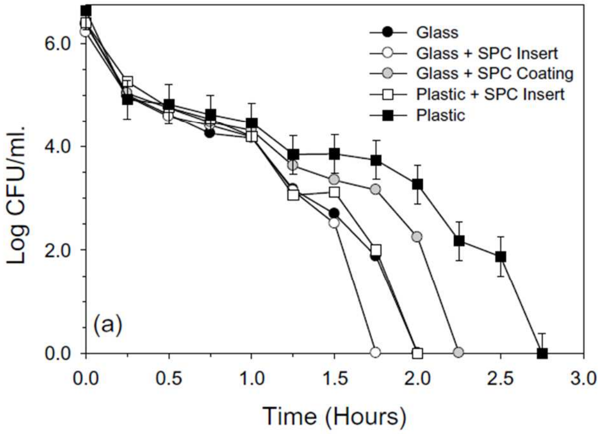


Fig. 3 Inactivation of *E. coli* K12 using glass and plastic bottles. Solar photocatalytic (SPC) inserts were employed in both glass and plastic bottles. The interior wall of the glass bottle was also coated. Reprinted from Solar Energy, Vol. 77, Duffy *et al*., A novel TiO_2-assisted solar photocatalytic 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). TiO_2 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 TiO_2 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 photocatalysis[30] and proposed mechanisms and modeling.[31] The majority of photocatalytic studies cite the hydroxyl radical ($^{\bullet}OH$) as the reactive oxygen species (ROS) responsible for microorganism inactivation, although other ROS such as hydrogen peroxide (H_2O_2) and the superoxide anion radical ($O_2^{\bullet-}$) have also been reported to be involved in the process. Proposed mechanisms of cell death include, DNA/RNA damage[28], membrane rupture[28], interruption of respiratory pathways[32] 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 TiO_2 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 TiO_2 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 the 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 TiO_2 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 TiO_2 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 TiO_2 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 TiO_2 coated on small pyrex glass cylinders loaded inside PET SODIS bottles.

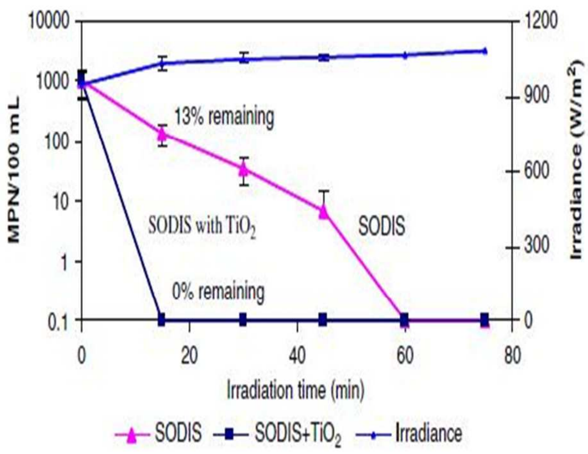


Fig. 4 Decrease of total coliforms during the treatment of SODIS plus TiO_2 disinfection. Reprinted from Water Research, Vol. 40, Gelover *et al*., A practical demonstration of water disinfection using TiO_2 films and sunlight, pp. 3274-3280, Copyright (2006), with permission from Elsevier.

Glass cylinders were coated with TiO_2 using a previously characterised sol-gel method[39] 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 TiO_2 in suspension. This led the research group to investigate the use of the coated TiO_2 cylinders in SODIS bottles. This is probably the first systematic report utilising a transparent uniform photocatalytic TiO_2 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 TiO_2 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 photocatlytic bottles are 'bactericidal' whereas standard SODIS bottles can sometimes be 'bacterio-static'. 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 TiO_2 photocatalysis) of this field study showed the TiO_2 coated cylinders to be a promising material for SODIS application.

Recently, Fisher *et al.*[6] investigated the use of doped, visible light active TiO_2 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 TiO_2 coated bottles showed no increase in MB degradation over undoped TiO_2. By contrast copper and copper/nitrogen co-doped TiO_2 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 TiO_2-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

Catalysis Science & Technology

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

REVIEW

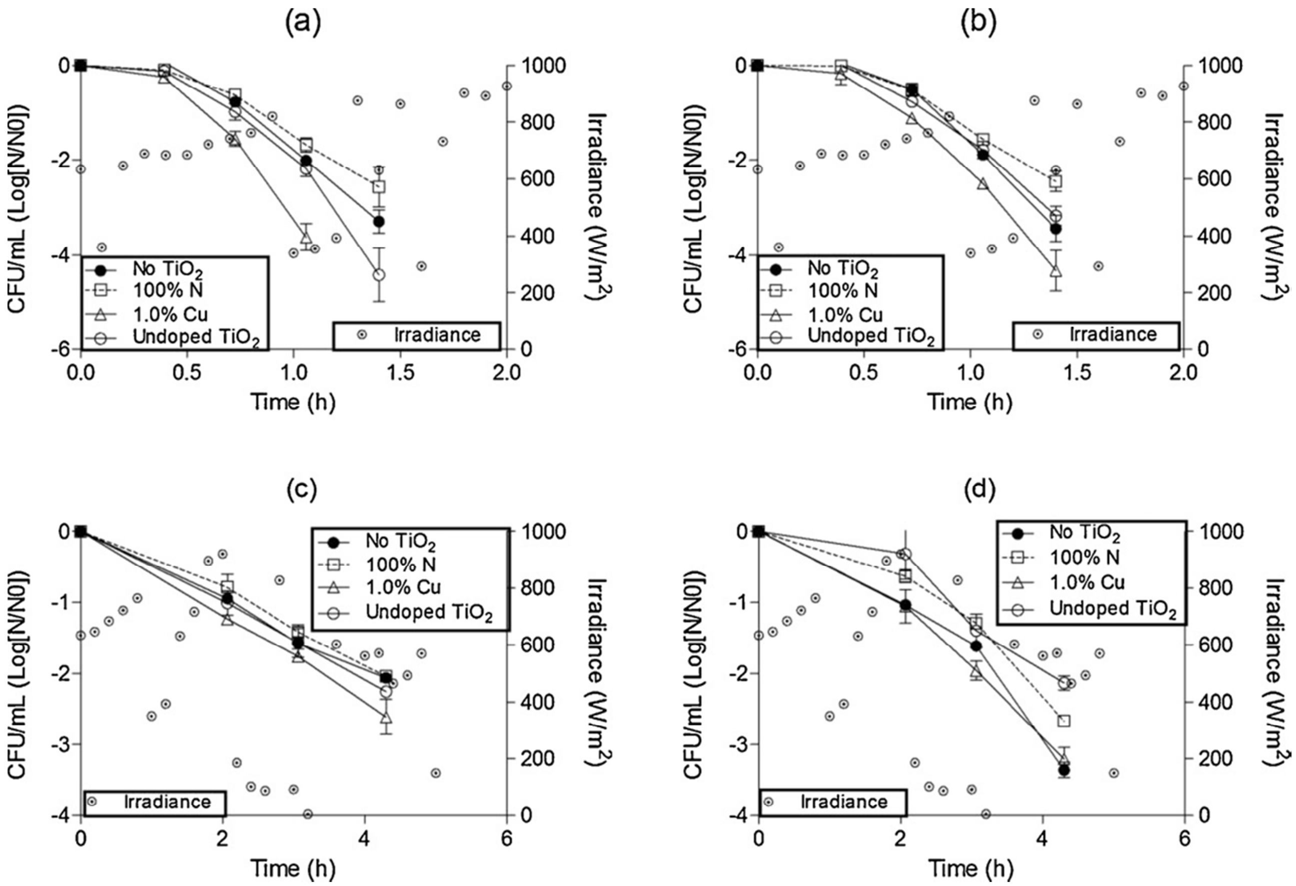


Fig. 5 Inactivation of *E. coli* and *Enterococcus faecalis* by solar light with or without UV-blocking film in the presence and absence of 3-mm glass beads coated with undoped TiO_2 thin films and films doped with 1% Cu/3.5% N. (a) E. coli, sunlight (b) Enterococcus, sunlight (c) E. coli, no UV (d) Enterococcus, no UV. Reprinted from *Applied Catalysis B: Environmental*, Vol. 130-131, Fisher *et al*., Nitrogen and copper doped solar light active TiO_2 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 TiO_2 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 TiO_2 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.

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.

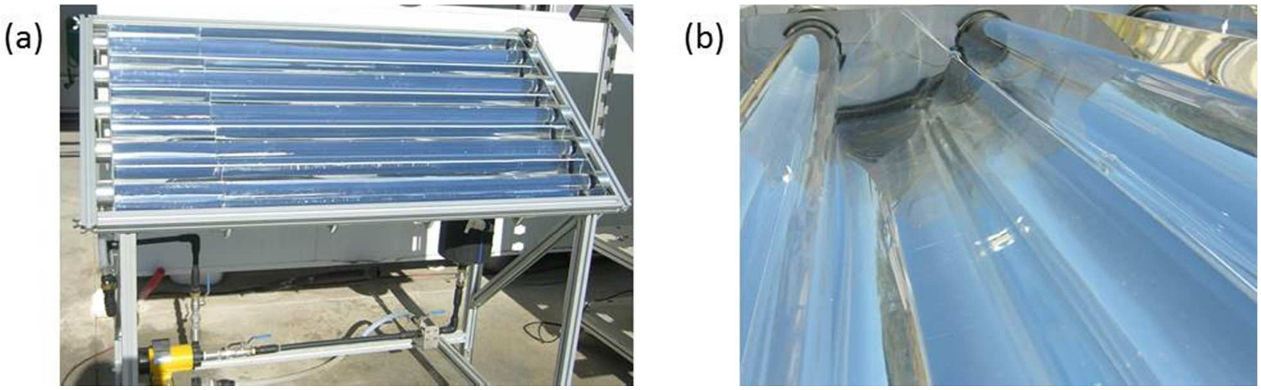


Fig. 6 CPC photo-reactor for water disinfection (a) CPC mirrors with (b) glass tubes

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 reactors[5] 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.

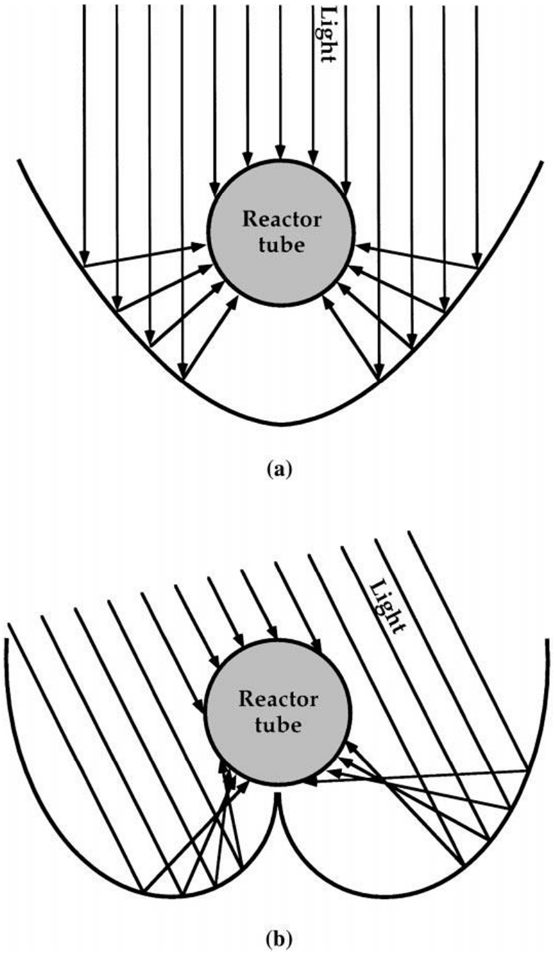
The CPC reactor mirrors are usually manufactured from anodized aluminium because they have high reflectivity in the UV range (87%–90%) and are highly resistant to the environmental conditions. Pipes and valves are made from polyethylene due to the robust nature of these materials. Water flows along the 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 titled 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 in is 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 Beckman[43] 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 (37º) 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 m^3 of contaminated water. The solar collector area is 98 m^2 with 975 L of total plant volume. The solar treatment method used in this plant is photocatalysis with 200 mg/L of suspended TiO_2. The estimated average treatment capacity of the solar plant is around 400 L/h. A preliminary study estimated the cost per m^3 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 house-hold users in developing countries. Ubomba-Jaswa and co-workers[48] 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-workers[49] 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 0.75 [51]. The 60L-CPC reactor showed enhanced inactivation results using photocatalysis with TiO_2 and solar photo-degradation[51]. 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 Pulgarín[52] 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-workers[50] reported that to achieve complete bacterial inactivation, an uninterrupted, 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 ~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.

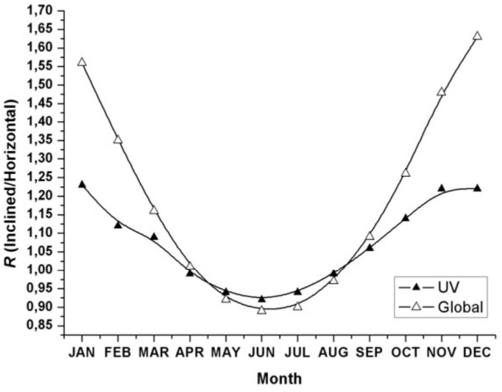


Fig. 8 Monthly mean irradiance in the PSA: relationship between extent inclined plane and horizontal (global and UV spectrum). Reprinted from Solar Energy, Vol. 86, Navntoft *et al.*, UV solar radiation on a tilted and horizontal plane: Analysis and comparison of 4 years of measurements, pp. 307-318.,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

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 Pulgarín[54] 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

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

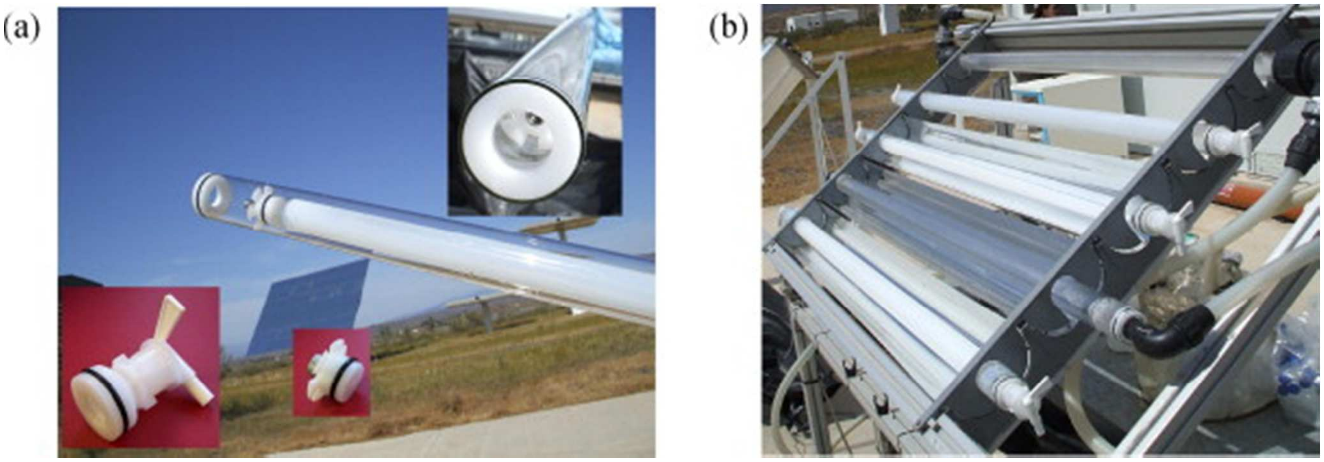


Fig. 9 Photographs showing the double tube configuration with internal tube cap and the valve for external tube (a); and the solar photocatalytic reactor with and without CPC during disinfection tests (b). Reprinted from Applied Catalysis B: Environmental, Vol. 128, Alrousan *et al.*, Solar photocatalytic 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 TiO_2catalyst 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 .**

TiO_2 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 TiO_2 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 TiO_2 (2) uncoated 50mm-borosilicate glass tubes, (3) 32mm-borosilicate glass tube externally dip coated with TiO_2 (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-workers[60] studied the photocatalytic inactivation of *E. coli* with immobilized TiO_2 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 TiO_2 immobilized onto a packing material of 10 mm glass Raschig rings. TiO_2 wall reactors consisted of TiO_2 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 TiO_2.

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 TiO_2 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 glass[62] but have the disadvantage that they require laboratory preparation. However, glass manufacturers have mass produced TiO_2 thin films on glass by a sol-gel method[63] and chemical vapour deposition[64], 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 Gelover[39] and Fisher[6]. 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] TiO_2 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 TiO_2 (powders) proven in the laboratory[66], 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 TiO_2 (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 TiO_2 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 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 route[6], 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.

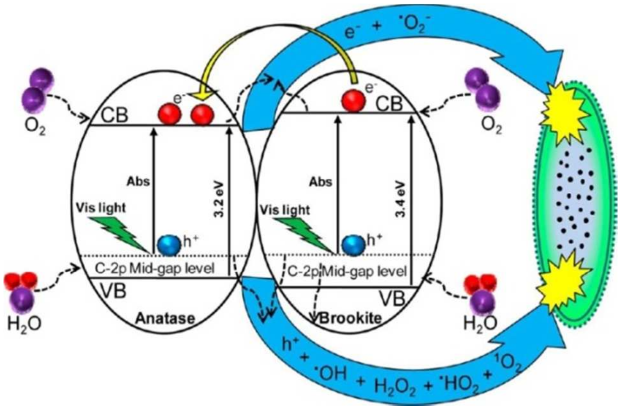


Fig. 10 Mechanism of visible-light induced photocatalytic bacterial killing using carbon-doped anatase-brookite heterojunctions. Reprinted with permission from *ACS Applied Materials & Interfaces*, Vol 5, Etacheri *et al.*, A Highly Efficient TiO_2–xC_x Nano-heterojunction Photocatalyst for Visible Light Induced Antibacterial Applications, pp. 1663-1672. Copyright (2013) American Chemical Society.

4.4.2 New nanoscale materials, nanocomposites and hetero-junctions for photocatalysis

An emerging area of research to increase the photocatalytic efficiency, is the use of 'nanoscale' TiO_2 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" TiO_2 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 TiO_2 on some materials[9]. Nano-assembled materials (such as nanoparticles, nanotubes, nanofibres, nanocages, nanorods etc.) have been shown to enhance the photoactivity of TiO_2, with the key contributing factor being the specific surface area of the structure.

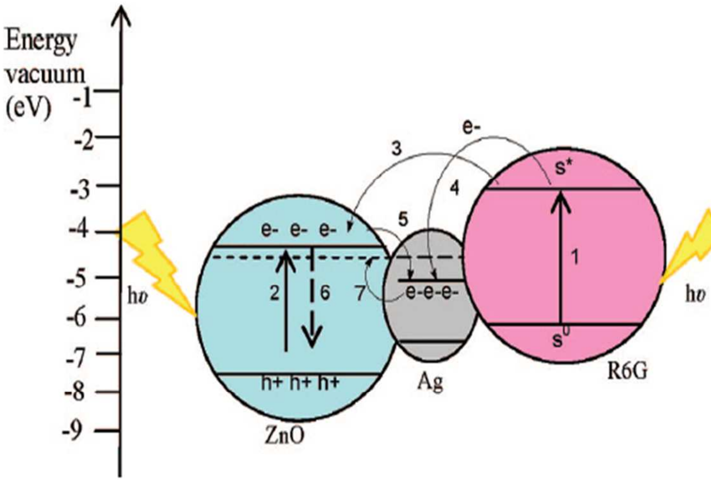


Fig. 11 A highly efficient Ag-ZnO photocatalyst; electron transfer events of Ag-ZnO photocatalysts in presence of a dye molecule (Rhodamine 6G). (1) S0 to S*; (2) VB to CB in ZnO charge carrier generation ; (3) S* to CB of ZnO; (4) S* to Ag; (5) CB of ZnO to Ag; and (6) CB to VB of ZnO (charge carrier recombination); (7) shifting of Fermi level of silver. The high reduction potential of S*, CB of ZnO (-0.8 V vs NHE) and of Ag (0.15 V) drives its electron injection reactions. 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 nanotubes[9]; as a nanostructured catalyst support material it has also been employed to utilize enhanced photoactivity at this scale. In addition to mproved 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-TiO_2 nanocomposites.[71] Akhavan and Ghaderi[72] reported that such TiO_2-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 TiO_2 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–TiO_2 nanorod composites. After combining with graphene oxide (GO), the GO–TiO_2 composites showed higher photocatalytic activities than that of TiO_2 nanorods alone for the inactivation of *E. coli* under solar simulated light. Pillai and co-workers[7] 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 TiO_2, in supported (composite) or unsupported form, could increase water disinfection efficiency in solar photocatalytic reactors. Further optimization could be achieved by doping of the TiO_2 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 spectrophotometery. Hermann and co-workers[87] reported the photocatalytic bleaching of methylene blue leads to the conversion of organic carbon into harmless formation of gaseous CO_2 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.

$$C_{16}H_{18}N_3SCl + 25.5\ O_2 \xrightarrow{TiO2} 16\ CO_2 + 6\ H_2O + HCl + H_2SO_4 + 3\ HNO_3 \qquad (4)$$

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 TiO_2 semiconductor, in addition to the $^{\bullet}OH$ and $O_2^{\bullet-}$, singlet oxygen ($^1O_2$) 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 that 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 indicators[90], 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 helmith 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 it’s 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 TiO_2 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.

Acknowledgements

S.C. Pillai, D. A. Keane and K.G. McGuigan would like to thank Enterprise Ireland (Grant Number PC/2009/0014) for research funding. Financial support by the Access to Research Infrastructures (to PSA facilities, Almeria) activity FP7-SFERA Grant No 228296) is also gratefully acknowledged. S. C. Pillai, D. D. Dionysiou, J. A. Byrne, P. S. M. Dunlop, and K. O'Shea wish to acknowledge financial support under the US-Ireland R&D Partnership Initiative from the Science Foundation Ireland (SFI-grant number 10/US/I1822), Department of Employment and Learning Northern Ireland (DELNI), and the US National Science Foundation-CBET (Award 1033317). D. D. Dionysiou also acknowledges support from the University of Cincinnati through a UNESCO co-Chair Professor position on "Water Access and Sustainability".

Notes and references

1. *Resolution A/RES/64/292. The human right to water and sanitation. United Nations General Assembly*, 2010.
2. *'On the right track. Good practices in realising the rights to water and sanitation' UN Special Rapporteur on the human right to safe drinking water and sanitation*, 2012, **ISBN 978-989-8360-09-0**.
3. K. G. McGuigan, R. M. Conroy, H.-J. Mosler, M. d. Preez, E. Ubomba-Jaswa and P. Fernandez-Ibañez, *Journal of Hazardous Materials*, 2012, **235–236**, 29-46.
4. J. A. Byrne, P. A. Fernandez-Ibanez, P. S. M. Dunlop, D. M. A. Alrousan and J. W. J. Hamilton, *International Journal of Photoenergy*, 2011.
5. S. Malato, P. Fernandez-Ibanez, M. I. Maldonado, J. Blanco and W. Gernjak, *Catal. Today*, 2009, **147**, 1-59.
6. M. B. Fisher, D. A. Keane, P. Fernández-Ibáñez, J. Colreavy, S. J. Hinder, K. G. McGuigan and S. C. Pillai, *Applied Catalysis B: Environmental*, 2013, **130–131**, 8-13.
7. M. Pelaez, N. T. Nolan, S. C. Pillai, M. K. Seery, P. Falaras, A. G. Kontos, P. S. M. Dunlop, J. W. J. Hamilton, J. A. Byrne, K. O'Shea, M. H. Entezari and D. D. Dionysiou, *Applied Catalysis B: Environmental*, 2012, **125**, 331-349.
8. N. Serpone, A. V. Emeline, S. Horikoshi, V. N. Kuznetsov and V. K. Ryabchuk, *Photochemical & Photobiological Sciences*, 2012, **11**, 1121-1150.
9. A. Di Paola, E. García-López, G. Marcì and L. Palmisano, *Journal of Hazardous Materials*, 2012, **211–212**, 3-29.
10. G. Palmisano, E. Garcia-Lopez, G. Marci, V. Loddo, S. Yurdakal, V. Augugliaro and L. Palmisano, *Chemical Communications*, 2010, **46**, 7074-7089.
11. R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki and Y. Taga, *Science*, 2001, **293**, 269-271.
12. V. Etacheri, M. K. Seery, S. J. Hinder and S. C. Pillai, *Inorganic Chemistry*, 2012, **51**, 7164-7173.
13. N. T. Nolan, D. W. Synnott, M. K. Seery, S. J. Hinder, A. Van Wassenhoven and S. C. Pillai, *Journal of Hazardous Materials*, 2012, **211–212**, 88-94.
14. D. W. Synnott, M. K. Seery, S. J. Hinder, G. Michlits and S. C. Pillai, *Applied Catalysis B: Environmental*, 2013, **130–131**, 106-111.
15. D. W. Synnott, M. K. Seery, S. J. Hinder, J. Colreavy and S. C. Pillai, *Nanotechnology*, 2013, **24**.
16. S. C. Pillai, P. Periyat, R. George, D. E. McCormack, M. K. Seery, H. Hayden, J. Colreavy, D. Corr and S. J. Hinder, *The Journal of Physical Chemistry C*, 2007, **111**, 1605-1611.
17. V. Etacheri, M. K. Seery, S. J. Hinder and S. C. Pillai, *Advanced Functional Materials*, 2011, **21**, 3744-3752.
18. N. T. Nolan, M. K. Seery and S. C. Pillai, *The Journal of Physical Chemistry C*, 2009, **113**, 16151-16157.
19. N. T. Nolan, M. K. Seery, S. J. Hinder, L. F. Healy and S. C. Pillai, *The Journal of Physical Chemistry C*, 2010, **114**, 13026-13034.
20. P. Periyat, D. E. McCormack, S. J. Hinder and S. C. Pillai, *The Journal of Physical Chemistry C*, 2009, **113**, 3246-3253.
21. T. Ihara, M. Miyoshi, Y. Iriyama, O. Matsumoto and S. Sugihara, *Applied Catalysis B: Environmental*, 2003, **42**, 403-409.
22. J. A. Rengifo-Herrera, E. Mielczarski, J. Mielczarski, N. C. Castillo, J. Kiwi and C. Pulgarin, *Applied Catalysis B: Environmental*, 2008, **84**, 448-456.
23. J. A. Rengifo-Herrera, J. Kiwi and C. Pulgarin, *Journal of Photochemistry and Photobiology A: Chemistry*, 2009, **205**, 109-115.
24. J. A. Rengifo-Herrera, K. Pierzchała, A. Sienkiewicz, L. Forró, J. Kiwi and C. Pulgarin, *Applied Catalysis B: Environmental*, 2009, **88**, 398-406.
25. J. A. Rengifo-Herrera, K. Pierzchała, A. Sienkiewicz, L. Forró, J. Kiwi, J. E. Moser and C. Pulgarin, *The Journal of Physical Chemistry C*, 2010, **114**, 2717-2723.
26. J. A. Rengifo-Herrera and C. Pulgarin, *Solar Energy*, 2010, **84**, 37-43.
27. T. Matsunaga, R. Tomoda, T. Nakajima and H. Wake, *FEMS Microbiol. Lett.*, 1985, **29**, 211-214.
28. D. M. Blake, P. C. Maness, Z. Huang, E. J. Wolfrum, J. Huang and W. A. Jacoby, *Sep. Purif. Methods*, 1999, **28**, 1-50.
29. C. McCullagh, J. M. C. Robertson, D. W. Bahnemann and P. K. J. Robertson, *Research on Chemical Intermediates*, 2007, **33**, 359-375.
30. J. Blanco-Galvez, P. Fernandez-Ibanez and S. Malato-Rodriguez, *J. Sol. Energy Eng. Trans.-ASME*, 2007, **129**, 4-15.
31. O. K. Dalrymple, E. Stefanakos, M. A. Trotz and D. Y. Goswami, *Appl. Catal. B-Environ.*, 2010, **98**, 27-38.
32. A. G. Rincon, C. Pulgarin, N. Adler and P. Peringer, *Journal of Photochemistry and Photobiology a-Chemistry*, 2001, **139**, 233-241.
33. K. Sunada, T. Watanabe and K. Hashimoto, *Journal of Photochemistry and Photobiology a-Chemistry*, 2003, **156**, 227-233.

34. E. F. Duffy, F. Al Touati, S. C. Kehoe, O. A. McLoughlin, L. W. Gill, W. Gernjak, I. Oller, M. I. Maldonado, S. Malato, J. Cassidy, R. H. Reed and K. G. McGuigan, *Solar Energy*, 2004, **77**, 649-655.
35. J. M. Meichtry, H. J. Lin, L. de la Fuente, I. K. Levy, E. A. Gautier, M. A. Blesa and M. I. Litter, *J. Sol. Energy Eng. Trans.-ASME*, 2007, **129**, 119-126.
36. J. M. Carey, T. M. Perez, E. G. Arsiaga, L. H. Loetscher and J. E. Boyd, *Water Science and Technology*, 2011, **63**, 1130-1136.
37. P. J. Carlson, L. A. Pretzer and J. E. Boyd, *Ind. Eng. Chem. Res.*, 2007, **46**, 7970-7976.
38. S. Gelover, L. A. Gomez, K. Reyes and M. T. Leal, *Water Research*, 2006, **40**, 3274-3280.
39. S. Gelover, P. Mondragon and A. Jimenez, *Journal of Photochemistry and Photobiology A-Chemistry*, 2004, **165**, 241-246.
40. O. M. Alfano, D. Bahnemann, A. E. Cassano, R. Dillert and R. Goslich, *Catal. Today*, 2000, **58**, 199-230.
41. J. I. Ajona and A. Vidal, *Solar Energy*, 2000, **68**, 109-120.
42. S. Malato Rodríguez, J. Blanco Gálvez, M. I. Maldonado Rubio, P. Fernández Ibáñez, D. Alarcón Padilla, M. Collares Pereira, J. Farinha Mendes and J. Correia de Oliveira, *Solar Energy*, 2004, **77**, 513-524.
43. J. A. Duffie and W. A. Beckman, *Wiley*, 2006, 928.
44. L. C. Navntoft, P. Fernandez-Ibañez and F. Garreta, *Solar Energy*, 2012, **86**, 307-318.
45. M. N. Chong, B. Jin, C. W.K. Chow, C. Saint, *Water Research*, *2010, 44, 2997-3027*
46. D. Bahnemann, *Solar Energy*, 2004, **77**, 445-459.
47. M. N. Chong, B. Jin, C. W. K. Chow and C. Saint, *Water Research*, 2010, **44**, 2997-3027.
48. E. Ubomba-Jaswa, P. Fernández-Ibáñez, C. Navntoft, M. I. Polo-López and K. G. McGuigan, *Journal of Chemical Technology & Biotechnology*, 2010, **85**, 1028-1037.
49. M. I. Polo-López, P. Fernández-Ibáñez, E. Ubomba-Jaswa, C. Navntoft, I. García-Fernández, P. S. M. Dunlop, M. Schmid, J. A. Byrne and K. G. McGuigan, *Journal of Hazardous Materials*, 2011, **196**, 16-21.
50. E. Ubomba-Jaswa, C. Navntoft, M. I. Polo-Lopez, P. Fernandez-Ibanez and K. G. McGuigan, *Photochemical & Photobiological Sciences*, 2009, **8**, 587-595.
51. M. I. Polo-López, P. Fernández-Ibáñez, I. García-Fernández, I. Oller, I. Salgado-Tránsito and C. Sichel, *Journal of Chemical Technology & Biotechnology*, 2010, **85**, 1038-1048.
52. A.-G. Rincón and C. Pulgarin, *Applied Catalysis B: Environmental*, 2004, **49**, 99-112.
53. P. Fernández-Ibáñez, C. Sichel, M. I. Polo-López, M. de Cara-García and J. C. Tello, *Catal. Today*, 2009, **144**, 62-68.
54. A.-G. Rincón and C. Pulgarin, *Applied Catalysis B: Environmental*, 2006, **63**, 222-231.
55. L. Prieto-Rodriguez, S. Miralles-Cuevas, I. Oller, A. Aguera, G. L. Puma and S. Malato, *Journal of Hazardous Materials*, 2012, **211**, 131-137.
56. R. van Grieken, J. Marugán, C. Sordo and C. Pablos, *Catal. Today*, 2009, **144**, 48-54.
57. D. M. A. Alrousan, M. I. Polo-López, P. S. M. Dunlop, P. Fernández-Ibáñez and J. A. Byrne, *Applied Catalysis B: Environmental*, 2012, **128**, 126-134.
58. R. van Grieken, J. Marugán, C. Sordo, P. Martínez and C. Pablos, *Applied Catalysis B: Environmental*, 2009, **93**, 112-118.
59. S. Khan, R. Reed and M. Rasul, *BMC Microbiol*, 2012, **12**, 1-11.
60. C. Sordo, R. Van Grieken, J. Marugan and P. Fernandez-Ibanez, *Water Science and Technology*, 2010, **61**, 507-512.
61. R. Meierhofer and G. Landolt, *Desalination*, 2009, **248**, 144-151.
62. R. L. Pozzo, M. A. Baltanas and A. E. Cassano, *Catal. Today*, 1997, **39**, 219-231.
63. H. Bach and D. Krause, Thin Solid Fims on Glass, 1997, Springer.
64. A. Mills, A. Lepre, N. Elliott, S. Bhopal, I. P. Parkin and S. A. O'Neill, *Journal of Photochemistry and Photobiology a-Chemistry*, 2003, **160**, 213-224.
65. J. Brinker and G. Scherer, *ol-Gel Science: The Physics and Chemistry of Sol-Gel Processing,* 1990, Academic Press.
66. J. C. Yu, W. K. Ho, J. G. Yu, H. Yip, P. K. Wong and J. C. Zhao, *Environ. Sci. Technol.*, 2005, **39**, 1175-1179.
67. J. W. J. Hamilton, J. A. Byrne, C. McCullagh and P. S. M. Dunlop, *International Journal of Photoenergy*, 2008.
68. V. Etacheri, G. Michlits, M. K. Seery, S. J. Hinder and S. C. Pillai, *Acs Applied Materials & Interfaces*, 2013, **5**, 1663-1672.
69. G. Li and K. A. Gray, *Chemical Physics*, 2007, **339**, 173-187.
70. Q. Li, M. A. Page, B. J. Marinas and J. K. Shang, *Environ. Sci. Technol.*, 2008, **42**, 6148-6153.
71. X. An and J. C. Yu, *Rsc Advances*, 2011, **1**, 1426-1434.
72. O. Akhavan and E. Ghaderi, *The Journal of Physical Chemistry C*, 2009, **113**, 20214-20220.
73. J. Liu, L. Liu, H. Bai, Y. Wang and D. D. Sun, *Applied Catalysis B: Environmental*, 2011, **106**, 76-82.
74. R. Georgekutty, M. K. Seery and S. C. Pillai, *J. Phys. Chem. C*, 2008, **112**, 13563-13570.
75. H. Choi, A. C. Sofranko and D. D. Dionysiou, *Advanced Functional Materials*, 2006, **16**, 1067-1074.
76. H. Choi, E. Stathatos and D. D. Dionysiou, *Applied Catalysis B: Environmental*, 2006, **63**, 60-67.
77. Y. Liu, J. Li, X. Qiu and C. Burda, *Water Science and Technology*, 2006, **54**, 47-54.
78. Q. Li, R. Xie, Y. W. Li, E. A. Mintz and J. K. Shang, *Environ. Sci. Technol.*, 2007, **41**, 5050-5056.
79. C. W. Dunnill, Z. A. Aiken, A. Kafizas, J. Pratten, M. Wilson, D. J. Morgan and I. P. Parkin, *Journal of Materials Chemistry*, 2009, **19**, 8747-8754.
80. S. C. Padmanabhan, S. C. Pillai, J. Colreavy, S. Balakrishnan, D. E. McCormack, T. S. Perova, Y. Gun'ko, S. J. Hinder and J. M. Kelly, *Chem. Mat.*, 2007, **19**, 4474-4481.
81. V. Etacheri, M. K. Seery, S. J. Hinder and S. C. Pillai, *Chem. Mat.*, 2010, **22**, 3843-3853.
82. S. Swetha, S. M. Santhosh and R. Geetha Balakrishna, *Photochemistry and Photobiology*, 2010, **86**, 1127-1134.
83. C. Han, M. Pelaez, V. Likodimos, A. G. Kontos, P. Falaras, K. O'Shea and D. D. Dionysiou, *Applied Catalysis B: Environmental*, 2011, **107**, 77-87.
84. M. Pelaez, A. A. de la Cruz, E. Stathatos, P. Falaras and D. D. Dionysiou, *Catal. Today*, 2009, **144**, 19-25.
85. M. Pelaez, P. Falaras, V. Likodimos, A. G. Kontos, A. A. de la Cruz, K. O'Shea and D. D. Dionysiou, *Applied Catalysis B: Environmental*, 2010, **99**, 378-387.

86. M. K. Seery, R. George, P. Floris and S. C. Pillai, *Journal of Photochemistry and Photobiology a-Chemistry*, 2007, **189**, 258-263.
87. A. Houas, H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard and J.-M. Herrmann, *Applied Catalysis B: Environmental*, 2001, **31**, 145-157.
88. A. Mills, C. Hill and P. K. J. Robertson, *Journal of Photochemistry and Photobiology a-Chemistry*, 2012, **237**, 7-23.
89. M. Agulló-Barceló, M. I. Polo-López, F. Lucena, J. Jofre and P. Fernández-Ibáñez, *Applied Catalysis B: Environmental*, 2013, **136–137**, 341-350.
90. A. H. Havelaar, M. Butler, S. R. Farrah, J. Jofre, E. Marques, A. Ketratanakul, M. T. Martins, S. Ohgaki, M. D. Sobsey and U. Zaiss*Water Research*, 1991, **25**, 529-545.
91. J. Wu, S. C. Long, D. Das and S. M. Dorner, *J. Water Health*, 2011, **9**, 265-278.
92. E. R. Bandala, L. Gonzalez, F. de la Hoz, M. A. Pelaez, D. D. Dionysiou, P. S. M. Dunlop, J. A. Byrne and J. L. Sanchez, *Journal of Photochemistry and Photobiology a-Chemistry*, 2011, **218**, 185-191.
93. C. Sichel, J. Tello, M. de Cara and P. Fernández-Ibáñez, *Catal. Today*, 2007, **129**, 152-160.

Dr. Donal A. Keane obtained his BSc (2003) and PhD (2007) in Chemistry in University College Cork (UCC), Ireland. Following this he completed a fellowship in membrane technology funded by the Irish Environmental Protection Agency. Then he moved to Dublin Institute of Technology (DIT), to join Prof. Suresh Pillai's photocatalysis research group. Following a period working in industry (Akzo Nobel, United Kingdom) he has returned as a postdoctoral researcher in UCC. His research interests include sol-gel science, small particle technology and coatings for separation science and environmental applications.

Prof. Suresh C. Pillai obtained his PhD in the area of Materials Science from Trinity College (TCD), The University of Dublin, Ireland and then performed a postdoctoral research at California Institute of Technology (Caltech), USA. He is an elected fellow of the Royal Microscopical Society (FRMS) and the Institute of Materials, Minerals and Mining (FIMMM). He was responsible for acquiring more than €2.5 million direct R&D funding. Prof. Pillai is a recipient of a number of awards for research accomplishments including the 'Industrial Technologies Award 2011' from Enterprise Ireland for commercialising nanomaterials for industrial applications. He has worked at CREST in DIT as a senior R&D manager responsible for nanotechnology research before moving to Institute of Technology Sligo as a senior lecturer in environmental sciences.

Prof. Kevin G. McGuigan is an Associate Professor of Medical Physics in the Royal College of Surgeons in Ireland (RCSI) teaching on Medicine, Pharmacy and Physiotherapy degree programmes. He obtained his PhD in semiconductor spectroscopy from Dublin City University (DCU). He is the director of the RCSI Solar Disinfection Research Group which develops appropriate technology interventions against waterborne disease for use in developing countries and specializes in running field studies to evaluate these technologies. He has completed large scale field studies of point-of-use technologies in Uganda, Kenya, Zimbabwe, S. Africa and Cambodia. He is a Fellow of the Institute of Physics and was awarded a higher doctorate (DSc) from DCU in 2013 on the basis of his published work in the fields of materials science, water treatment and acoustics.

Dr. Pilar Fernández Ibáñez is Senior Researcher in the Plataforma Solar de Almería in the Centro de Investigaciones Energéticas Medioambientales y Tecnológicas and Head of the group of Solar Treatment of Water. She obtained her PhD in Physics from the University of Granada (2004). Since then she has been working in water treatment and disinfection using solar energy. She was involved in a number of projects, co-authored 4 books and 16 book chapters, 80 publications in indexed journals, 2 patents, and graduated 3 PhD students. She has been awarded the status of Visiting Professor at the University of Ulster (2012).

Prof. Dionysios D. Dionysiou is a Professor of Environmental Engineering at the University of Cincinnati where he teaches courses on drinking water quality and treatment, advanced unit operations for water treatment, advanced oxidation technologies, and physical-chemical processes for water quality control. His research interests include advanced technologies for water treatment, advanced oxidation technologies, transition metal-based chemical oxidation, and nanotechnology. Prof. Dionysiou is the author or co-author of over 150 refereed journal publications, 90 conference proceedings, 15 book chapter publications, 17 editorials, and more than 450 presentations. He has received funding from NSF, US EPA, NASA, NOAA/CICEET, USGS, USDA, Cyprus Research Foundation, and DuPont. He is currently one of the editors of *Chemical Engineering Journal* (Elsevier), Editor of the *Journal of Advanced Oxidation Technologies*, and Special Issue Editor and Associate Editor for the *Journal of Environmental Engineering* (ASCE).

Dr. María Inmaculada Polo López obtained her PhD in Chemical Engineering from the University of Almeria (2012), Spain and a degree in Biology from the University of Granada (2006), Spain. Her research interests include the use of solar processes for water disinfection, solar reactors and the polymerase chain reaction (PCR) technique for pathogen detection and enumeration in water. Dr. Polo currently researches water disinfection using solar energy at Plataforma solar de Almeria, Spain. She has worked in 2 EU and 2 Spanish R&D grants. She has co-authored 4 book chapters, 15 publications in indexed international journals and has 50 contributions to different International Congresses and Symposiums.

Prof. Kevin O'Shea is Professor of Chemistry and Biochemistry and the Senior Associate Dean of the University Graduate School at Florida International University. He earned an undergraduate degree with Honors from California State University, Sacramento (1984) and a Ph.D. in Chemistry from University of California, Los Angeles (1989). His current research interests are focused in the area of the reactions of reactive oxygen species with organic compounds of biological importance and/or environmental significance. The fundamental understanding of the reactions of ROS with natural toxins and pollutants is critical to the development and application of advanced oxidation technologies for water purification. Professor O'Shea's research projects have been funded from a variety of agencies, including the National Science Foundation, the National Institutes of Health, Petroleum Research Fund, Dreyfus foundation, and the US Environmental Protection Agency. He has published ~ 70 peer-reviewed articles and book chapters in the research areas of organic and environmental chemistry.

Dr. Patrick S.M. Dunlop obtained his PhD in Photocatalytic Disinfection from the University of Ulster, UK in 2001. He subsequently spent 10 years working as a Research Fellow at Ulster on a number of national and EU funded projects (FP5 PEBCAT; FP6 SODISWATER) scaling up photocatalytic reactors for solar disinfection. In 2011 Dr. Dunlop moved into a lecturing position at Ulster where he teaches at all levels on the Clean Technology programmes. His research interests include the application of advanced oxidation technologies, nanotechnology, and materials chemistry for the disinfection of water, air and surfaces across a range of industrial applications. Recently funded research includes the EU FP7 Aqua-Pulse project (€1.4 million) and the US-Ireland Collaborative Research Project ($1 million).

Prof. J. Anthony Byrne is a Professor of Photocatalysis in the School of Engineering in the University of Ulster and is a core member of the Engineering Research Institute and Head of Photocatalysis Research in the Nanotechnology and Integrated BioEngineering Centre (NIBEC). He obtained his PhD in chemistry from the University of Ulster in 1997 researching photocatalytic water treatment. Since then he has worked on a range of projects involving the photocatalytic treatment and purification of water, photoelectrolytic water splitting using solar energy, and the decontamination of surfaces. His main research interests lie in the fabrication, characterisation and application of photocatalytic materials.

Catalysis Science & Technology

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

REVIEW

Solar photocatalysis for water disinfection: Materials and reactor design

Donal A. Keane,[a] Kevin G. McGuigan,[b] Pilar Fernández Ibáñez,[c] M. Inmaculada Polo-López,[c] Anthony J. Byrne,[d] Patrick S.M. Dunlop,[d] Kevin O'Shea,[e] Dionysios D. Dionysiou[f,g] and Suresh C. Pillai[h,i]*

[a] Chemistry Department and Environmental Research Institute, University College Cork, Cork, Ireland.

[b] Department of Physiology & Medical Physics, Royal College of Surgeons in Ireland, 123 St Stephens Green, Dublin 2, Ireland.

[c] Plataforma Solar de Almería – CIEMAT, PO Box 22, 04200 Tabernas, Almería, Spain.

[d] Nanotechnology and Integrated Bio-Engineering Centre, School of Engineering, Faculty of Computing and Engineering, University of Ulster, Newtownabbey, Northern Ireland, United Kingdom.

[e] Department of Chemistry and Biochemistry, Florida International University, Miami, FL 33199, USA.

[f] Environmental Engineering and Science Program, Department of Biomedical, Chemical and Environmental Engineering, University of Cincinnati, Cincinnati, Ohio 45221-0071, USA.

[g] Nireas-International Water Research Centre, University of Cyprus, 20537 Nicosia, Cyprus.

[h] Department of Environmental Science, School of Science, Institute of Technology Sligo, Ash Lane, Sligo, Ireland.
[i] Centre for Precision Engineering and Manufacturing (PEM), Institute of Technology Sligo, Ash Lane, Sligo, Ireland. pillai.suresh@itsligo.ie

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

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 microroganisms from drinking water. The time taken for the conventional SODIS process can be greatly reduced by semiconductor (e.g. TiO_2, 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 TiO_2 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]

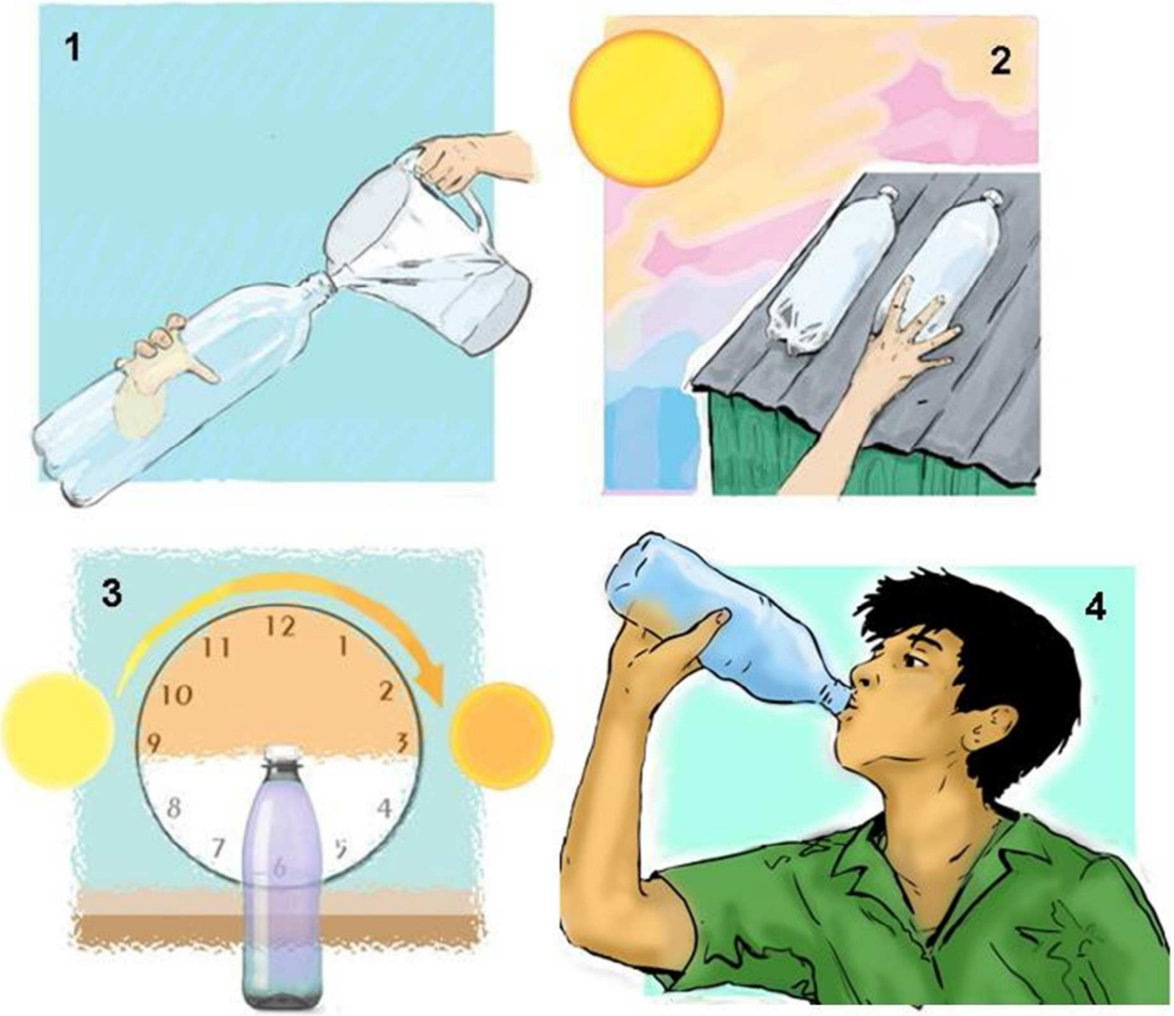


Fig. 1 A graphical description of the solar disinfection (SODIS) technique. (1) Fill the bottle. (2) Place the bottle in direct sunlight. (3) Wait a minimum of 6 hours. (4) The water is safe to drink. Reprinted from Journal of Hazardous Materials, Vol. 235-236, McGuigan *et al.*, Solar water disinfection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

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 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 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 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 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 'transferrable' 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 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.

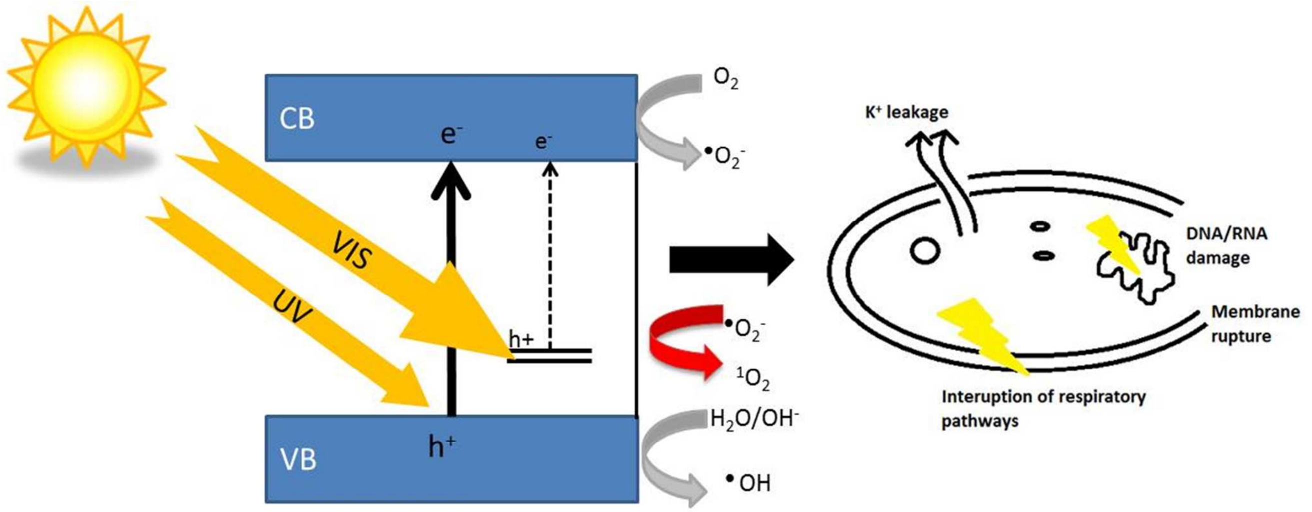


Fig. 2 Schematic diagram of bacterial disinfection using visible light active catalyst. Reprinted from *Applied Catalysis B: Environmental*, Vol. 130-131, Fisher *et al*., Nitrogen and copper doped solar light active TiO_2 photocatalysts for water decontamination, pp. 8-13., Copyright (2013), with permission from Elsevier.

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 (TiO_2), into the process.

Thus, this review describes the use of both TiO_2 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 TiO_2 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]

$$TiO_2 + h\nu \rightarrow h^+_{VB} + e^-_{CB} \qquad (1)$$

$$H_2O + h^+_{VB} \rightarrow {}^\bullet OH + H^+ \qquad (2)$$

$$O_2 + e^-_{CB} \rightarrow O_2^{\bullet -} \qquad (3)$$

The H_2O becomes oxidized by h^+_{VB} producing H^+ and $^\bullet OH$ radicals (Eq. 2). Positive holes generated by light become trapped by surface adsorbed H_2O. The hydroxyl radicals can subsequently oxidize organic species to CO_2, H_2O 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.

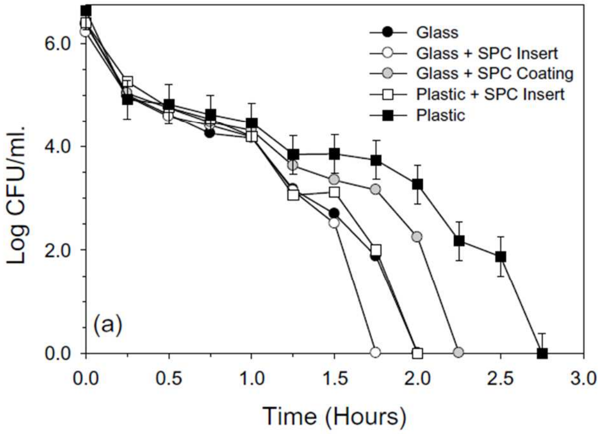


Fig. 3 Inactivation of *E. coli* K12 using glass and plastic bottles. Solar photocatalytic (SPC) inserts were employed in both glass and plastic bottles. The interior wall of the glass bottle was also coated. Reprinted from Solar Energy, Vol. 77, Duffy *et al*., A novel TiO_2-assisted solar photocatalytic 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). TiO_2 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 TiO_2 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 photocatalysis[30] and proposed mechanisms and modeling.[31] The majority of photocatalytic studies cite the hydroxyl radical ($^{\bullet}OH$) as the reactive oxygen species (ROS) responsible for microorganism inactivation, although other ROS such as hydrogen peroxide (H_2O_2) and the superoxide anion radical ($O_2^{\bullet-}$) have also been reported to be involved in the process. Proposed mechanisms of cell death include, DNA/RNA damage[28], membrane rupture[28], interruption of respiratory pathways[32] 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 TiO_2 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 TiO_2 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 the 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 TiO_2 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 TiO_2 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 TiO_2 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 TiO_2 coated on small pyrex glass cylinders loaded inside PET SODIS bottles.

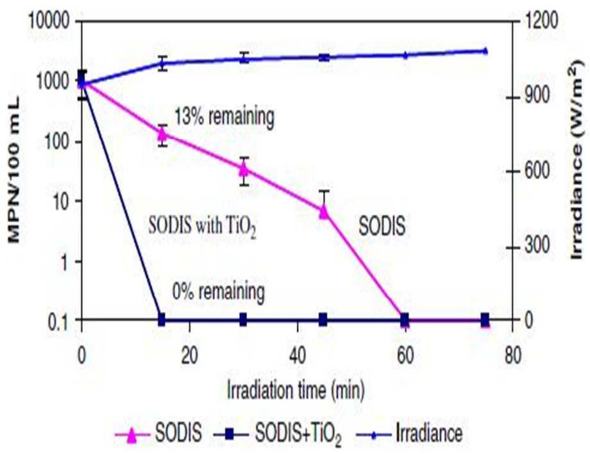


Fig. 4 Decrease of total coliforms during the treatment of SODIS plus TiO_2 disinfection. Reprinted from Water Research, Vol. 40, Gelover *et al*., A practical demonstration of water disinfection using TiO_2 films and sunlight, pp. 3274-3280, Copyright (2006), with permission from Elsevier.

Glass cylinders were coated with TiO_2 using a previously characterised sol-gel method[39] 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 TiO_2 in suspension. This led the research group to investigate the use of the coated TiO_2 cylinders in SODIS bottles. This is probably the first systematic report utilising a transparent uniform photocatalytic TiO_2 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 TiO_2 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 photocatlytic bottles are ‘bactericidal’ whereas standard SODIS bottles can sometimes be ‘bacterio-static’. 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 TiO_2 photocatalysis) of this field study showed the TiO_2 coated cylinders to be a promising material for SODIS application.

Recently, Fisher *et al.*[6] investigated the use of doped, visible light active TiO_2 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 TiO_2 coated bottles showed no increase in MB degradation over undoped TiO_2. By contrast copper and copper/nitrogen co-doped TiO_2 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 TiO_2-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

Catalysis Science & Technology

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

REVIEW

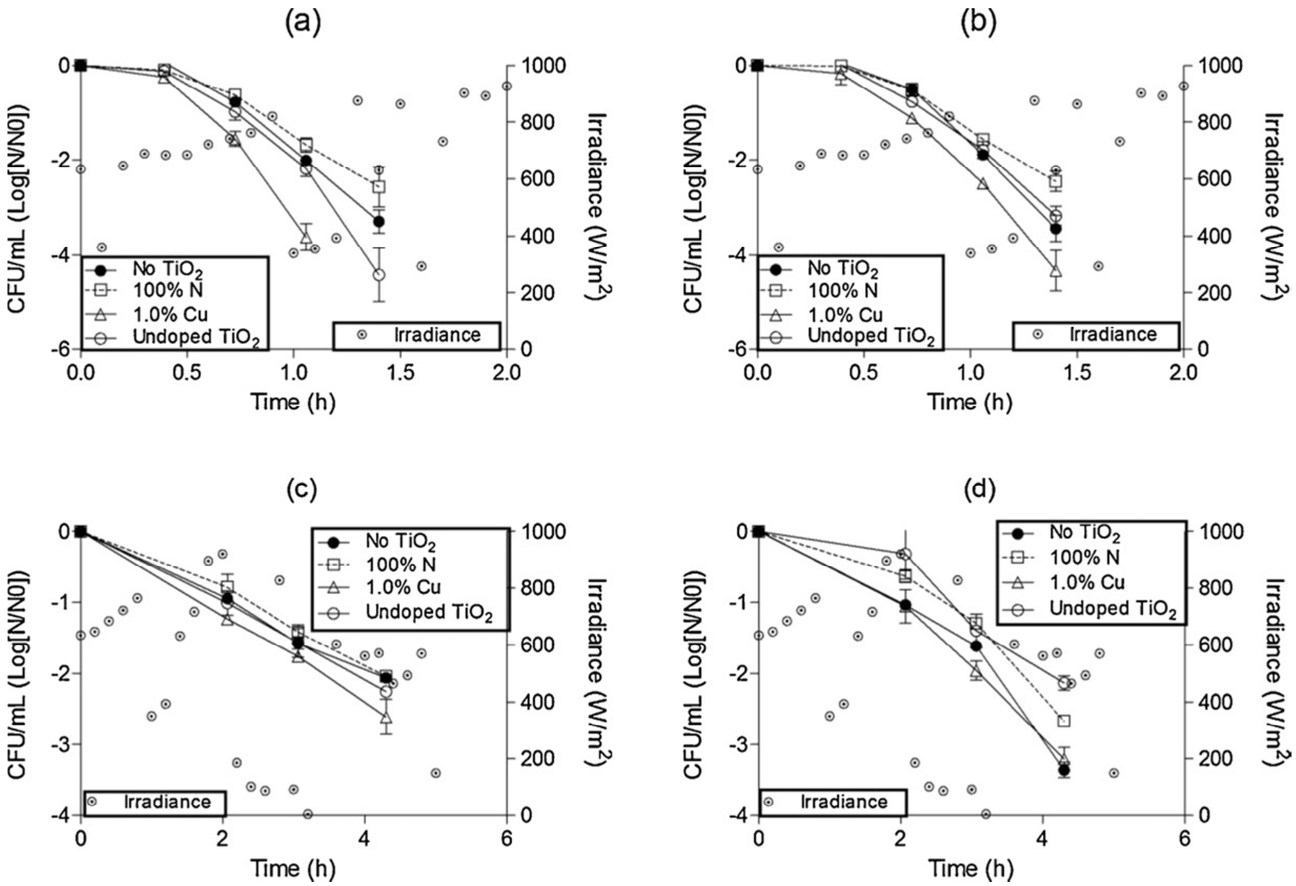


Fig. 5 Inactivation of *E. coli* and *Enterococcus faecalis* by solar light with or without UV-blocking film in the presence and absence of 3-mm glass beads coated with undoped TiO_2 thin films and films doped with 1% Cu/3.5% N. (a) E. coli, sunlight (b) Enterococcus, sunlight (c) E. coli, no UV (d) Enterococcus, no UV. Reprinted from *Applied Catalysis B: Environmental*, Vol. 130-131, Fisher *et al*., Nitrogen and copper doped solar light active TiO_2 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 TiO_2 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 TiO_2 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.

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.

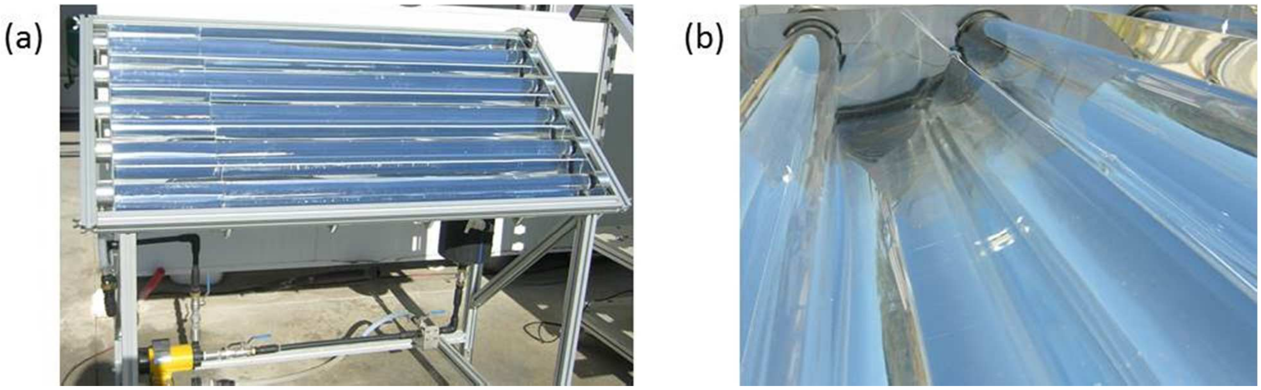


Fig. 6 CPC photo-reactor for water disinfection (a) CPC mirrors with (b) glass tubes

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 reactors[5] 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.

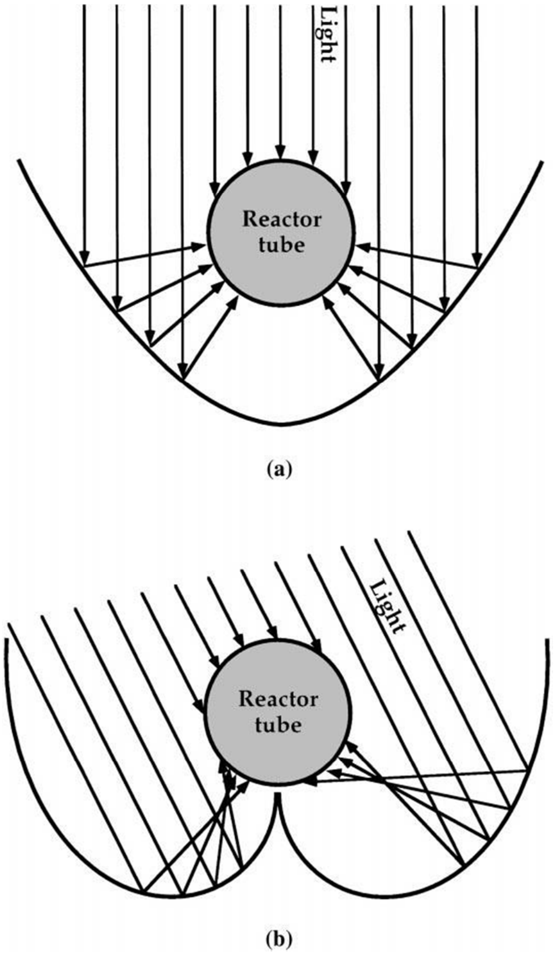
The CPC reactor mirrors are usually manufactured from anodized aluminium because they have high reflectivity in the UV range (87%–90%) and are highly resistant to the environmental conditions. Pipes and valves are made from polyethylene due to the robust nature of these materials. Water flows along the 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 titled 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 in is 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 Beckman[43] 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 (37º) 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 m^3 of contaminated water. The solar collector area is 98 m^2 with 975 L of total plant volume. The solar treatment method used in this plant is photocatalysis with 200 mg/L of suspended TiO_2. The estimated average treatment capacity of the solar plant is around 400 L/h. A preliminary study estimated the cost per m^3 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 house-hold users in developing countries. Ubomba-Jaswa and co-workers[48] 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-workers[49] 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.

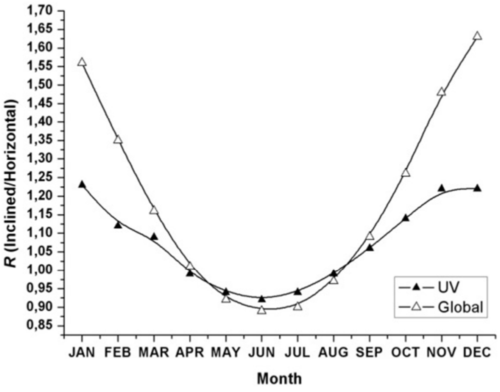


Fig. 8 Monthly mean irradiance in the PSA: relationship between extent inclined plane and horizontal (global and UV spectrum). Reprinted from Solar Energy, Vol. 86, Navntoft *et al.*, UV solar radiation on a tilted and horizontal plane: Analysis and comparison of 4 years of measurements, pp. 307-318.,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

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 0.75 [51]. The 60L-CPC reactor showed enhanced inactivation results using photocatalysis with TiO_2 and solar photo-degradation[51]. 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 Pulgarín[52] 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-workers[50] reported that to achieve complete bacterial inactivation, an uninterrupted, 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 ~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 Pulgarín[54] 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

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

REVIEW

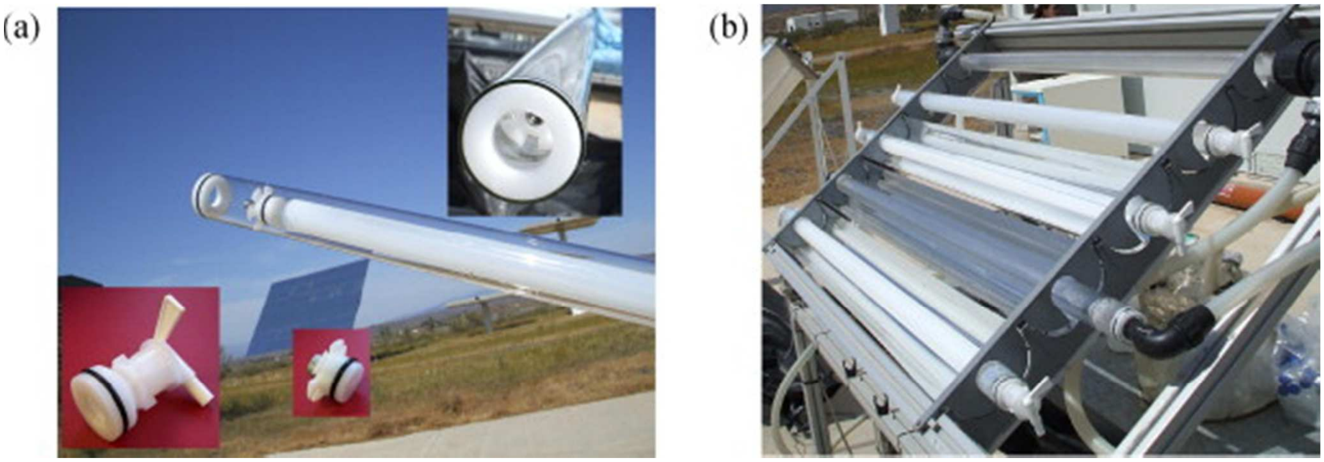


Fig. 9 Photographs showing the double tube configuration with internal tube cap and the valve for external tube (a); and the solar photocatalytic reactor with and without CPC during disinfection tests (b). Reprinted from Applied Catalysis B: Environmental, Vol. 128, Alrousan *et al.*, Solar photocatalytic 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 TiO_2catalyst 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 .**

TiO_2 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 TiO_2 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 TiO_2 (2) uncoated 50mm-borosilicate glass tubes, (3) 32mm-borosilicate glass tube externally dip coated with TiO_2 (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-workers[60] studied the photocatalytic inactivation of *E. coli* with immobilized TiO_2 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 TiO_2 immobilized onto a packing material of 10 mm glass Raschig rings. TiO_2 wall reactors consisted of TiO_2 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 TiO_2.

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 TiO_2 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 glass[62] but have the disadvantage that they require laboratory preparation. However, glass manufacturers have mass produced TiO_2 thin films on glass by a sol-gel method[63] and chemical vapour deposition[64], 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 Gelover[39] and Fisher[6]. 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] TiO_2 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 TiO_2 (powders) proven in the laboratory[66], 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 TiO_2 (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 TiO_2 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 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 route[6], 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.

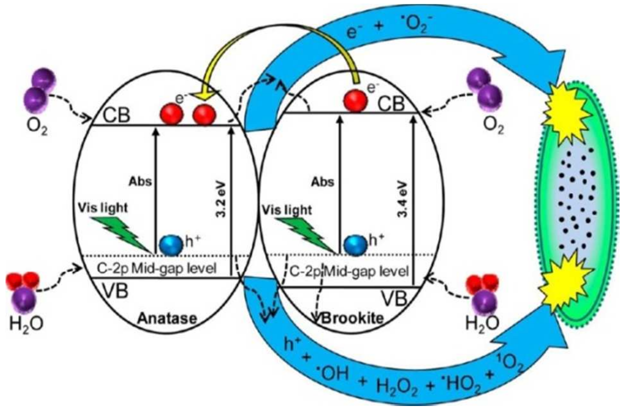


Fig. 10 Mechanism of visible-light induced photocatalytic bacterial killing using carbon-doped anatase-brookite heterojunctions. Reprinted with permission from *ACS Applied Materials & Interfaces*, Vol 5, Etacheri *et al.*, A Highly Efficient TiO_2–xC_x Nano-heterojunction Photocatalyst for Visible Light Induced Antibacterial Applications, pp. 1663-1672. Copyright (2013) American Chemical Society.

4.4.2 New nanoscale materials, nanocomposites and hetero-junctions for photocatalysis

An emerging area of research to increase the photocatalytic efficiency, is the use of 'nanoscale' TiO_2 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" TiO_2 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 TiO_2 on some materials[9]. Nano-assembled materials (such as nanoparticles, nanotubes, nanofibres, nanocages, nanorods etc.) have been shown to enhance the photoactivity of TiO_2, with the key contributing factor being the specific surface area of the structure.

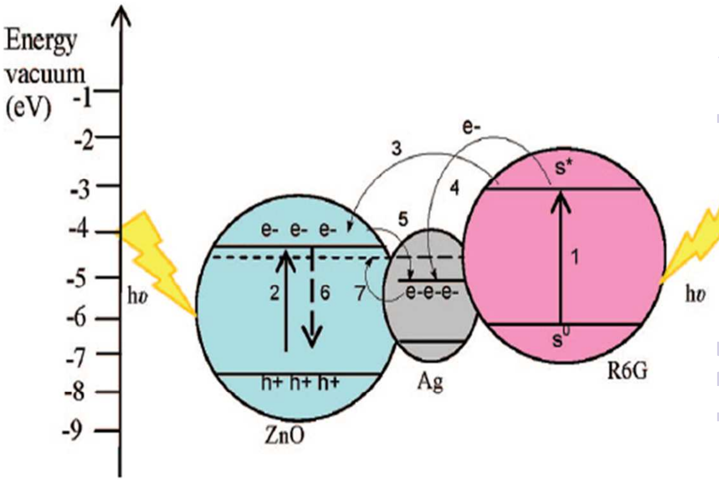


Figure 11. A highly efficient Ag-ZnO photocatalyst; electron transfer events of Ag-ZnO photocatalysts in presence of a dye molecule (Rhodamine 6G). (1) S0 to S*; (2) VB to CB in ZnO charge carrier generation ; (3) S* to CB of ZnO; (4) S* to Ag; (5) CB of ZnO to Ag; and (6) CB to VB of ZnO (charge carrier recombination); (7) shifting of Fermi level of silver. The high reduction potential of S*, CB of ZnO (-0.8 V vs NHE) and of Ag (0.15 V) drives its electron injection reactions. 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 nanotubes[9]; as a nanostructured catalyst support material it has also been employed to utilize enhanced photoactivity at this scale. In addition to mproved 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-TiO_2 nanocomposites.[71] Akhavan and Ghaderi[72] reported that such TiO_2-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 TiO_2 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–TiO_2 nanorod composites. After combining with graphene oxide (GO), the GO–TiO_2 composites showed higher photocatalytic activities than that of TiO_2 nanorods alone for the inactivation of *E. coli* under solar simulated light. Pillai and co-workers[7] 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 TiO_2, in supported (composite) or unsupported form, could increase water disinfection efficiency in solar photocatalytic reactors. Further optimization could be achieved by doping of the TiO_2 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 spectrophotometery. Hermann and co-workers[87] reported the photocatalytic bleaching of methylene blue leads to the conversion of organic carbon into harmless formation of gaseous CO_2 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.

$$C_{16}H_{18}N_3SCl + 25.5\ O_2 \xrightarrow{TiO2} 16\ CO_2 + 6\ H_2O + HCl + H_2SO_4 + 3\ HNO_3 \quad (4)$$

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 TiO_2 semiconductor, in addition to the $^{\bullet}OH$ and $O_2^{\bullet-}$, singlet oxygen ($^1O_2$) 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 that 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 indicators[90], 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 helmith 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 it's 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 TiO_2 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.

Acknowledgements

S.C. Pillai, D. A. Keane and K.G. McGuigan would like to thank Enterprise Ireland (Grant Number PC/2009/0014) for research funding. Financial support by the Access to Research Infrastructures (to PSA facilities, Almeria) activity FP7-SFERA Grant No 228296) is also gratefully acknowledged. S. C. Pillai, D. D. Dionysiou, J. A. Byrne, P. S. M. Dunlop, and K. O'Shea wish to acknowledge financial support under the US-Ireland R&D Partnership Initiative from the Science Foundation Ireland (SFI-grant number 10/US/I1822), Department of Employment and Learning Northern Ireland (DELNI), and the US National Science Foundation-CBET (Award 1033317). D. D. Dionysiou also acknowledges support from the University of Cincinnati through a UNESCO co-Chair Professor position on "Water Access and Sustainability".

Notes and references

1. *Resolution A/RES/64/292. The human right to water and sanitation. United Nations General Assembly*, 2010.
2. *'On the right track. Good practices in realising the rights to water and sanitation' UN Special Rapporteur on the human right to safe drinking water and sanitation*, 2012, **ISBN 978-989-8360-09-0**.
3. K. G. McGuigan, R. M. Conroy, H.-J. Mosler, M. d. Preez, E. Ubomba-Jaswa and P. Fernandez-Ibañez, *Journal of Hazardous Materials*, 2012, **235–236**, 29-46.
4. J. A. Byrne, P. A. Fernandez-Ibanez, P. S. M. Dunlop, D. M. A. Alrousan and J. W. J. Hamilton, *International Journal of Photoenergy*, 2011.
5. S. Malato, P. Fernandez-Ibanez, M. I. Maldonado, J. Blanco and W. Gernjak, *Catal. Today*, 2009, **147**, 1-59.
6. M. B. Fisher, D. A. Keane, P. Fernández-Ibáñez, J. Colreavy, S. J. Hinder, K. G. McGuigan and S. C. Pillai, *Applied Catalysis B: Environmental*, 2013, **130–131**, 8-13.
7. M. Pelaez, N. T. Nolan, S. C. Pillai, M. K. Seery, P. Falaras, A. G. Kontos, P. S. M. Dunlop, J. W. J. Hamilton, J. A. Byrne, K. O'Shea, M. H. Entezari and D. D. Dionysiou, *Applied Catalysis B: Environmental*, 2012, **125**, 331-349.
8. N. Serpone, A. V. Emeline, S. Horikoshi, V. N. Kuznetsov and V. K. Ryabchuk, *Photochemical & Photobiological Sciences*, 2012, **11**, 1121-1150.
9. A. Di Paola, E. García-López, G. Marcì and L. Palmisano, *Journal of Hazardous Materials*, 2012, **211–212**, 3-29.
10. G. Palmisano, E. Garcia-Lopez, G. Marci, V. Loddo, S. Yurdakal, V. Augugliaro and L. Palmisano, *Chemical Communications*, 2010, **46**, 7074-7089.
11. R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki and Y. Taga, *Science*, 2001, **293**, 269-271.
12. V. Etacheri, M. K. Seery, S. J. Hinder and S. C. Pillai, *Inorganic Chemistry*, 2012, **51**, 7164-7173.
13. N. T. Nolan, D. W. Synnott, M. K. Seery, S. J. Hinder, A. Van Wassenhoven and S. C. Pillai, *Journal of Hazardous Materials*, 2012, **211–212**, 88-94.
14. D. W. Synnott, M. K. Seery, S. J. Hinder, G. Michlits and S. C. Pillai, *Applied Catalysis B: Environmental*, 2013, **130–131**, 106-111.
15. D. W. Synnott, M. K. Seery, S. J. Hinder, J. Colreavy and S. C. Pillai, *Nanotechnology*, 2013, **24**.
16. S. C. Pillai, P. Periyat, R. George, D. E. McCormack, M. K. Seery, H. Hayden, J. Colreavy, D. Corr and S. J. Hinder, *The Journal of Physical Chemistry C*, 2007, **111**, 1605-1611.
17. V. Etacheri, M. K. Seery, S. J. Hinder and S. C. Pillai, *Advanced Functional Materials*, 2011, **21**, 3744-3752.
18. N. T. Nolan, M. K. Seery and S. C. Pillai, *The Journal of Physical Chemistry C*, 2009, **113**, 16151-16157.
19. N. T. Nolan, M. K. Seery, S. J. Hinder, L. F. Healy and S. C. Pillai, *The Journal of Physical Chemistry C*, 2010, **114**, 13026-13034.
20. P. Periyat, D. E. McCormack, S. J. Hinder and S. C. Pillai, *The Journal of Physical Chemistry C*, 2009, **113**, 3246-3253.
21. T. Ihara, M. Miyoshi, Y. Iriyama, O. Matsumoto and S. Sugihara, *Applied Catalysis B: Environmental*, 2003, **42**, 403-409.
22. J. A. Rengifo-Herrera, E. Mielczarski, J. Mielczarski, N. C. Castillo, J. Kiwi and C. Pulgarin, *Applied Catalysis B: Environmental*, 2008, **84**, 448-456.
23. J. A. Rengifo-Herrera, J. Kiwi and C. Pulgarin, *Journal of Photochemistry and Photobiology A: Chemistry*, 2009, **205**, 109-115.
24. J. A. Rengifo-Herrera, K. Pierzchała, A. Sienkiewicz, L. Forró, J. Kiwi and C. Pulgarin, *Applied Catalysis B: Environmental*, 2009, **88**, 398-406.
25. J. A. Rengifo-Herrera, K. Pierzchała, A. Sienkiewicz, L. Forró, J. Kiwi, J. E. Moser and C. Pulgarin, *The Journal of Physical Chemistry C*, 2010, **114**, 2717-2723.
26. J. A. Rengifo-Herrera and C. Pulgarin, *Solar Energy*, 2010, **84**, 37-43.
27. T. Matsunaga, R. Tomoda, T. Nakajima and H. Wake, *FEMS Microbiol. Lett.*, 1985, **29**, 211-214.
28. D. M. Blake, P. C. Maness, Z. Huang, E. J. Wolfrum, J. Huang and W. A. Jacoby, *Sep. Purif. Methods*, 1999, **28**, 1-50.
29. C. McCullagh, J. M. C. Robertson, D. W. Bahnemann and P. K. J. Robertson, *Research on Chemical Intermediates*, 2007, **33**, 359-375.
30. J. Blanco-Galvez, P. Fernandez-Ibanez and S. Malato-Rodriguez, *J. Sol. Energy Eng. Trans.-ASME*, 2007, **129**, 4-15.
31. O. K. Dalrymple, E. Stefanakos, M. A. Trotz and D. Y. Goswami, *Appl. Catal. B-Environ.*, 2010, **98**, 27-38.
32. A. G. Rincon, C. Pulgarin, N. Adler and P. Peringer, *Journal of Photochemistry and Photobiology a-Chemistry*, 2001, **139**, 233-241.
33. K. Sunada, T. Watanabe and K. Hashimoto, *Journal of Photochemistry and Photobiology a-Chemistry*, 2003, **156**, 227-233.

34. E. F. Duffy, F. Al Touati, S. C. Kehoe, O. A. McLoughlin, L. W. Gill, W. Gernjak, I. Oller, M. I. Maldonado, S. Malato, J. Cassidy, R. H. Reed and K. G. McGuigan, *Solar Energy*, 2004, **77**, 649-655.
35. J. M. Meichtry, H. J. Lin, L. de la Fuente, I. K. Levy, E. A. Gautier, M. A. Blesa and M. I. Litter, *J. Sol. Energy Eng. Trans.-ASME*, 2007, **129**, 119-126.
36. J. M. Carey, T. M. Perez, E. G. Arsiaga, L. H. Loetscher and J. E. Boyd, *Water Science and Technology*, 2011, **63**, 1130-1136.
37. P. J. Carlson, L. A. Pretzer and J. E. Boyd, *Ind. Eng. Chem. Res.*, 2007, **46**, 7970-7976.
38. S. Gelover, L. A. Gomez, K. Reyes and M. T. Leal, *Water Research*, 2006, **40**, 3274-3280.
39. S. Gelover, P. Mondragon and A. Jimenez, *Journal of Photochemistry and Photobiology A-Chemistry*, 2004, **165**, 241-246.
40. O. M. Alfano, D. Bahnemann, A. E. Cassano, R. Dillert and R. Goslich, *Catal. Today*, 2000, **58**, 199-230.
41. J. I. Ajona and A. Vidal, *Solar Energy*, 2000, **68**, 109-120.
42. S. Malato Rodríguez, J. Blanco Gálvez, M. I. Maldonado Rubio, P. Fernández Ibáñez, D. Alarcón Padilla, M. Collares Pereira, J. Farinha Mendes and J. Correia de Oliveira, *Solar Energy*, 2004, **77**, 513-524.
43. J. A. Duffie and W. A. Beckman, *Wiley*, 2006, 928.
44. L. C. Navntoft, P. Fernandez-Ibañez and F. Garreta, *Solar Energy*, 2012, **86**, 307-318.
45. M. N. Chong, B. Jin, C. W.K. Chow, C. Saint, *Water Research*, *2010, 44, 2997-3027*
46. D. Bahnemann, *Solar Energy*, 2004, **77**, 445-459.
47. M. N. Chong, B. Jin, C. W. K. Chow and C. Saint, *Water Research*, 2010, **44**, 2997-3027.
48. E. Ubomba-Jaswa, P. Fernández-Ibáñez, C. Navntoft, M. I. Polo-López and K. G. McGuigan, *Journal of Chemical Technology & Biotechnology*, 2010, **85**, 1028-1037.
49. M. I. Polo-López, P. Fernández-Ibáñez, E. Ubomba-Jaswa, C. Navntoft, I. García-Fernández, P. S. M. Dunlop, M. Schmid, J. A. Byrne and K. G. McGuigan, *Journal of Hazardous Materials*, 2011, **196**, 16-21.
50. E. Ubomba-Jaswa, C. Navntoft, M. I. Polo-Lopez, P. Fernandez-Ibanez and K. G. McGuigan, *Photochemical & Photobiological Sciences*, 2009, **8**, 587-595.
51. M. I. Polo-López, P. Fernández-Ibáñez, I. García-Fernández, I. Oller, I. Salgado-Tránsito and C. Sichel, *Journal of Chemical Technology & Biotechnology*, 2010, **85**, 1038-1048.
52. A.-G. Rincón and C. Pulgarin, *Applied Catalysis B: Environmental*, 2004, **49**, 99-112.
53. P. Fernández-Ibáñez, C. Sichel, M. I. Polo-López, M. de Cara-García and J. C. Tello, *Catal. Today*, 2009, **144**, 62-68.
54. A.-G. Rincón and C. Pulgarin, *Applied Catalysis B: Environmental*, 2006, **63**, 222-231.
55. L. Prieto-Rodriguez, S. Miralles-Cuevas, I. Oller, A. Aguera, G. L. Puma and S. Malato, *Journal of Hazardous Materials*, 2012, **211**, 131-137.
56. R. van Grieken, J. Marugán, C. Sordo and C. Pablos, *Catal. Today*, 2009, **144**, 48-54.
57. D. M. A. Alrousan, M. I. Polo-López, P. S. M. Dunlop, P. Fernández-Ibáñez and J. A. Byrne, *Applied Catalysis B: Environmental*, 2012, **128**, 126-134.
58. R. van Grieken, J. Marugán, C. Sordo, P. Martínez and C. Pablos, *Applied Catalysis B: Environmental*, 2009, **93**, 112-118.
59. S. Khan, R. Reed and M. Rasul, *BMC Microbiol*, 2012, **12**, 1-11.
60. C. Sordo, R. Van Grieken, J. Marugan and P. Fernandez-Ibanez, *Water Science and Technology*, 2010, **61**, 507-512.
61. R. Meierhofer and G. Landolt, *Desalination*, 2009, **248**, 144-151.
62. R. L. Pozzo, M. A. Baltanas and A. E. Cassano, *Catal. Today*, 1997, **39**, 219-231.
63. H. Bach and D. Krause, Thin Solid Fims on Glass, 1997, Springer.
64. A. Mills, A. Lepre, N. Elliott, S. Bhopal, I. P. Parkin and S. A. O'Neill, *Journal of Photochemistry and Photobiology a-Chemistry*, 2003, **160**, 213-224.
65. J. Brinker and G. Scherer, *ol-Gel Science: The Physics and Chemistry of Sol-Gel Processing,* 1990, Academic Press.
66. J. C. Yu, W. K. Ho, J. G. Yu, H. Yip, P. K. Wong and J. C. Zhao, *Environ. Sci. Technol.*, 2005, **39**, 1175-1179.
67. J. W. J. Hamilton, J. A. Byrne, C. McCullagh and P. S. M. Dunlop, *International Journal of Photoenergy*, 2008.
68. V. Etacheri, G. Michlits, M. K. Seery, S. J. Hinder and S. C. Pillai, *Acs Applied Materials & Interfaces*, 2013, **5**, 1663-1672.
69. G. Li and K. A. Gray, *Chemical Physics*, 2007, **339**, 173-187.
70. Q. Li, M. A. Page, B. J. Marinas and J. K. Shang, *Environ. Sci. Technol.*, 2008, **42**, 6148-6153.
71. X. An and J. C. Yu, *Rsc Advances*, 2011, **1**, 1426-1434.
72. O. Akhavan and E. Ghaderi, *The Journal of Physical Chemistry C*, 2009, **113**, 20214-20220.
73. J. Liu, L. Liu, H. Bai, Y. Wang and D. D. Sun, *Applied Catalysis B: Environmental*, 2011, **106**, 76-82.
74. R. Georgekutty, M. K. Seery and S. C. Pillai, *J. Phys. Chem. C*, 2008, **112**, 13563-13570.
75. H. Choi, A. C. Sofranko and D. D. Dionysiou, *Advanced Functional Materials*, 2006, **16**, 1067-1074.
76. H. Choi, E. Stathatos and D. D. Dionysiou, *Applied Catalysis B: Environmental*, 2006, **63**, 60-67.
77. Y. Liu, J. Li, X. Qiu and C. Burda, *Water Science and Technology*, 2006, **54**, 47-54.
78. Q. Li, R. Xie, Y. W. Li, E. A. Mintz and J. K. Shang, *Environ. Sci. Technol.*, 2007, **41**, 5050-5056.
79. C. W. Dunnill, Z. A. Aiken, A. Kafizas, J. Pratten, M. Wilson, D. J. Morgan and I. P. Parkin, *Journal of Materials Chemistry*, 2009, **19**, 8747-8754.
80. S. C. Padmanabhan, S. C. Pillai, J. Colreavy, S. Balakrishnan, D. E. McCormack, T. S. Perova, Y. Gun'ko, S. J. Hinder and J. M. Kelly, *Chem. Mat.*, 2007, **19**, 4474-4481.
81. V. Etacheri, M. K. Seery, S. J. Hinder and S. C. Pillai, *Chem. Mat.*, 2010, **22**, 3843-3853.
82. S. Swetha, S. M. Santhosh and R. Geetha Balakrishna, *Photochemistry and Photobiology*, 2010, **86**, 1127-1134.
83. C. Han, M. Pelaez, V. Likodimos, A. G. Kontos, P. Falaras, K. O'Shea and D. D. Dionysiou, *Applied Catalysis B: Environmental*, 2011, **107**, 77-87.
84. M. Pelaez, A. A. de la Cruz, E. Stathatos, P. Falaras and D. D. Dionysiou, *Catal. Today*, 2009, **144**, 19-25.
85. M. Pelaez, P. Falaras, V. Likodimos, A. G. Kontos, A. A. de la Cruz, K. O'Shea and D. D. Dionysiou, *Applied Catalysis B: Environmental*, 2010, **99**, 378-387.

86. M. K. Seery, R. George, P. Floris and S. C. Pillai, *Journal of Photochemistry and Photobiology a-Chemistry*, 2007, **189**, 258-263.
87. A. Houas, H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard and J.-M. Herrmann, *Applied Catalysis B: Environmental*, 2001, **31**, 145-157.
88. A. Mills, C. Hill and P. K. J. Robertson, *Journal of Photochemistry and Photobiology a-Chemistry*, 2012, **237**, 7-23.
89. M. Agulló-Barceló, M. I. Polo-López, F. Lucena, J. Jofre and P. Fernández-Ibáñez, *Applied Catalysis B: Environmental*, 2013, **136–137**, 341-350.
90. A. H. Havelaar, M. Butler, S. R. Farrah, J. Jofre, E. Marques, A. Ketratanakul, M. T. Martins, S. Ohgaki, M. D. Sobsey and U. Zaiss*Water Research*, 1991, **25**, 529-545.
91. J. Wu, S. C. Long, D. Das and S. M. Dorner, *J. Water Health*, 2011, **9**, 265-278.
92. E. R. Bandala, L. Gonzalez, F. de la Hoz, M. A. Pelaez, D. D. Dionysiou, P. S. M. Dunlop, J. A. Byrne and J. L. Sanchez, *Journal of Photochemistry and Photobiology a-Chemistry*, 2011, **218**, 185-191.
93. C. Sichel, J. Tello, M. de Cara and P. Fernández-Ibáñez, *Catal. Today*, 2007, **129**, 152-160.

Dr. Donal A. Keane obtained his BSc (2003) and PhD (2007) in Chemistry in University College Cork (UCC), Ireland. Following this he completed a fellowship in membrane technology funded by the Irish Environmental Protection Agency. Then he moved to Dublin Institute of Technology (DIT), to join Prof. Suresh Pillai's photocatalysis research group. Following a period working in industry (Akzo Nobel, United Kingdom) he has returned as a postdoctoral researcher in UCC. His research interests include sol-gel science, small particle technology and coatings for separation science and environmental applications.

Prof. Suresh C. Pillai obtained his PhD in the area of Materials Science from Trinity College (TCD), The University of Dublin, Ireland and then performed a postdoctoral research at California Institute of Technology (Caltech), USA. He is an elected fellow of the Royal Microscopical Society (FRMS) and the Institute of Materials, Minerals and Mining (FIMMM). He was responsible for acquiring more than €2.5 million direct R&D funding. Prof. Pillai is a recipient of a number of awards for research accomplishments including the 'Industrial Technologies Award 2011' from Enterprise Ireland for commercialising nanomaterials for industrial applications. He has worked at CREST in DIT as a senior R&D manager responsible for nanotechnology research before moving to Institute of Technology Sligo as a senior lecturer in environmental sciences.

Prof. Kevin G. McGuigan is an Associate Professor of Medical Physics in the Royal College of Surgeons in Ireland (RCSI) teaching on Medicine, Pharmacy and Physiotherapy degree programmes. He obtained his PhD in semiconductor spectroscopy from Dublin City University (DCU). He is the director of the RCSI Solar Disinfection Research Group which develops appropriate technology interventions against waterborne disease for use in developing countries and specializes in running field studies to evaluate these technologies. He has completed large scale field studies of point-of-use technologies in Uganda, Kenya, Zimbabwe, S. Africa and Cambodia. He is a Fellow of the Institute of Physics and was awarded a higher doctorate (DSc) from DCU in 2013 on the basis of his published work in the fields of materials science, water treatment and acoustics.

Dr. Pilar Fernández Ibáñez is Senior Researcher in the Plataforma Solar de Almería in the Centro de Investigaciones Energéticas Medioambientales y Tecnológicas and Head of the group of Solar Treatment of Water. She obtained her PhD in Physics from the University of Granada (2004). Since then she has been working in water treatment and disinfection using solar energy. She was involved in a number of projects, co-authored 4 books and 16 book chapters, 80 publications in indexed journals, 2 patents, and graduated 3 PhD students. She has been awarded the status of Visiting Professor at the University of Ulster (2012).

Prof. Dionysios D. Dionysiou is a Professor of Environmental Engineering at the University of Cincinnati where he teaches courses on drinking water quality and treatment, advanced unit operations for water treatment, advanced oxidation technologies, and physical-chemical processes for water quality control. His research interests include advanced technologies for water treatment, advanced oxidation technologies, transition metal-based chemical oxidation, and nanotechnology. Prof. Dionysiou is the author or co-author of over 150 refereed journal publications, 90 conference proceedings, 15 book chapter publications, 17 editorials, and more than 450 presentations. He has received funding from NSF, US EPA, NASA, NOAA/CICEET, USGS, USDA, Cyprus Research Foundation, and DuPont. He is currently one of the editors of *Chemical Engineering Journal* (Elsevier), Editor of the *Journal of Advanced Oxidation Technologies*, and Special Issue Editor and Associate Editor for the *Journal of Environmental Engineering* (ASCE).

Dr. María Inmaculada Polo López obtained her PhD in Chemical Engineering from the University of Almeria (2012), Spain and a degree in Biology from the University of Granada (2006), Spain. Her research interests include the use of solar processes for water disinfection, solar reactors and the polymerase chain reaction (PCR) technique for pathogen detection and enumeration in water. Dr. Polo currently researches water disinfection using solar energy at Plataforma solar de Almeria, Spain. She has worked in 2 EU and 2 Spanish R&D grants. She has co-authored 4 book chapters, 15 publications in indexed international journals and has 50 contributions to different International Congresses and Symposiums.

Prof. Kevin O'Shea is Professor of Chemistry and Biochemistry and the Senior Associate Dean of the University Graduate School at Florida International University. He earned an undergraduate degree with Honors from California State University, Sacramento (1984) and a Ph.D. in Chemistry from University of California, Los Angeles (1989). His current research interests are focused in the area of the reactions of reactive oxygen species with organic compounds of biological importance and/or environmental significance. The fundamental understanding of the reactions of ROS with natural toxins and pollutants is critical to the development and application of advanced oxidation technologies for water purification. Professor O'Shea's research projects have been funded from a variety of agencies, including the National Science Foundation, the National Institutes of Health, Petroleum Research Fund, Dreyfus foundation, and the US Environmental Protection Agency. He has published ~ 70 peer-reviewed articles and book chapters in the research areas of organic and environmental chemistry.

Dr. Patrick S.M. Dunlop obtained his PhD in Photocatalytic Disinfection from the University of Ulster, UK in 2001. He subsequently spent 10 years working as a Research Fellow at Ulster on a number of national and EU funded projects (FP5 PEBCAT; FP6 SODISWATER) scaling up photocatalytic reactors for solar disinfection. In 2011 Dr. Dunlop moved into a lecturing position at Ulster where he teaches at all levels on the Clean Technology programmes. His research interests include the application of advanced oxidation technologies, nanotechnology, and materials chemistry for the disinfection of water, air and surfaces across a range of industrial applications. Recently funded research includes the EU FP7 Aqua-Pulse project (€1.4 million) and the US-Ireland Collaborative Research Project ($1 million).

Prof. J. Anthony Byrne is a Professor of Photocatalysis in the School of Engineering in the University of Ulster and is a core member of the Engineering Research Institute and Head of Photocatalysis Research in the Nanotechnology and Integrated BioEngineering Centre (NIBEC). He obtained his PhD in chemistry from the University of Ulster in 1997 researching photocatalytic water treatment. Since then he has worked on a range of projects involving the photocatalytic treatment and purification of water, photoelectrolytic water splitting using solar energy, and the decontamination of surfaces. His main research interests lie in the fabrication, characterisation and application of photocatalytic materials.