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Review Article

Photocatalytic Enhancement for Solar Disinfection of Water: A Review

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It is estimated that 884 million people lack access to improved water supplies. Many more are forced to rely on supplies that are microbiologically unsafe, resulting in a higher risk of waterborne diseases, including typhoid, hepatitis, polio, and cholera. Due to poor sanitation and lack of clean drinking water, there are around 4 billion cases of diarrhea each year resulting in 2.2 million deaths, most of these are children under five. While conventional interventions to improve water supplies are effective, there is increasing interest in household-based interventions to produce safe drinking water at an affordable cost for developing regions. Solar disinfection (SODIS) is a simple and low cost technique used to disinfect drinking water, where water is placed in transparent containers and exposed to sunlight for 6 hours. There are a number of parameters which affect the efficacy of SODIS, including the solar irradiance, the quality of the water, and the nature of the contamination. One approach to SODIS enhancement is the use of semiconductor photocatalysis to produce highly reactive species that can destroy organic pollutants and inactivate water pathogens. This paper presents a critical review concerning semiconductor photocatalysis as a potential enhancement technology for solar disinfection of water.

1. Introduction

Water is the most important natural resource in the world and availability of safe drinking water is a high priority issue for human existence and quality of life. Unfortunately, water resources are coming under increasing pressure due to population growth, over-use and wastage. The World Health Organization (WHO) estimates that 884 million people lack access to improved water supplies. Many more are forced to rely on sources that are microbiologically unsafe, resulting in a higher risk of waterborne disease transmission, including typhoid, hepatitis and cholera [1–3].

As ever, the poor are the worst affected and, in developing countries, 50% of the population are exposed to polluted water sources which, along with inadequate supplies of water for personal hygiene and poor sanitation, are the main contributors to an estimated 4 billion cases of diarrhea each year. These factors result in an estimated 2.2 million deaths each year, the majority of which are children under the age of five [1].

The provision of piped-in water supplies is an important long-term goal; however, the WHO and the United Nations Children's Fund (UNICEF) acknowledge that we are unlikely to meet the Millennium Development Goal (MDG) target of halving the proportion of the people without sustainable access to safe drinking water and basic sanitation by 2015. While conventional interventions to improve water supplies at source (point of distribution) have long been recognized as effective in preventing diarrhoea, more recent reviews have shown household-based (point-of-use) interventions to be significantly more effective than those at the source. As a result, there is increasing interest in such household-based

interventions that deliver the health benefits associated with consumption of safe drinking water via low cost technologies [4].

In 2008, Clasen and Haller reported on the cost and cost effectiveness of house-hold based interventions to prevent diarrhoea [4]. They compared the following: chlorination using sodium hypochlorite following the "Safe Water System" (SWS) developed and promoted by the US Centers for Disease Control and Prevention (CDC), gravity filtration using either commercial "candle" style gravity filters or locally fabricated pot-style filters developed by Potters for Peace, solar disinfection following the "SODIS" method in which clear 2 L PET bottles are filled with raw water and then exposed to the sun for 6–48 h, and flocculation disinfection using Procter & Gambles PUR sachets, which combine an iron-based flocculant with a chlorine-based disinfectant and treat water in 10 L batches. They concluded that household-based chlorination was the most cost-effective. Solar disinfection (SODIS) was only slightly less cost-effective, owing to its almost identical cost but marginally lower overall effectiveness. Given that household-based chlorination requires the distribution of sodium hypochlorite, solar disinfection has a major advantage in terms of nonreliance on chemical distribution. Sunlight is widely and freely available on Earth and the combined effects of IR, visible and UV energy from the sun can inactivate pathogenic organisms present in water. There are a number of parameters which affect the efficacy of the SODIS process, including the solar irradiance, the quality of the water to be treated, and the nature of the contamination—as some pathogens are more resistant to SODIS than others. Furthermore, SODIS enhancement technologies may improve the process effectiveness without substantially increasing the cost. One such approach is the use of semiconductor photocatalysis.

Semiconductor photocatalysis uses light along with a semiconductor material to produce highly oxidative species that destroy organic pollutants in water and inactivate pathogenic microorganisms [5–10]. The process occurs at atmospheric pressure and ambient temperature, without the requirement for consumable chemicals (except for oxygen from the air). Photocatalysis may be able to provide a low cost and simple solution to the purification of water in developing regions where solar irradiation can be employed.

This paper presents a critical review concerning semiconductor photocatalysis as a potential enhancement technology for the solar disinfection of water. The purpose of this review is to inform the nonexpert with respect to solar disinfection, and photocatalytic disinfection. For more detailed information the reader is referred to the scientific papers cited.

2. Solar Disinfection of Water (SODIS)

SODIS is a simple and low cost technique used to disinfect contaminated drinking water. Transparent bottles (preferably PET) are filled with contaminated water and placed in direct sunlight for a minimum of 6 hours. Following exposure, the water is safe to drink as the viable pathogen load can be significantly decreased. Simple guidance for the use of SODIS is given in Figure 1. SODIS is used by an estimated 4.5 million regular users worldwide, predominately in Africa, Latin America, and Asia, and is recognised and promoted by the WHO [11, 12].

SODIS harnesses light and thermal energy to inactivate pathogens via a synergistic mechanism [13]. Around 4–6% of the solar spectrum reaching the surface of the Earth is in the UV domain, with maximum reported value of around 50 W/m^2 [14]. UV radiation (200–400 nm) can be classified as UVA (320–400 nm), UVB (280–320 nm), and UVC (200–280 nm). UVC is absorbed by the ozone layer along with a proportion of the UVB; therefore UVA represents the main fragment of solar ultraviolet radiation reaching the earth's surface.

Disinfection of water using solar energy has been carried out since Egyptian times. The process was first studied and reported in scientific literature by London-based scientists Downes and Blunt in the late 1870s [15] and was effectively rediscovered as a low-cost water disinfection method by Acra et al. in the late 1970s [16, 17]. The main findings of this work were that *Escherichia coli* was more resistant to SODIS than other organisms tested, and as such *E. coli* should be used as an indicator organism for SODIS efficiency, akin to the presence of viable faecal coliforms as an indicator of efficacy for conventional disinfection processes. Furthermore, it is the UV component of sunlight, and to a lesser extent the blue end of the visible spectrum, that is mainly responsible for the biocidal action observed during SODIS. Wegelin et al. from the Swiss Federal Institute of Aquatic Science and Technology (Eawag) reported on SODIS in terms of the scope of the process and the dose of radiation required [18]. They concurred with the conclusions of Acra et al. and reported that to obtain a 3-log reduction in the viable numbers of *E. coli* a cumulative exposure dose of 2000 kJ/m^2 (350–450 nm) was required. The same dose was found to inactivate bacteriophage f2 whereas picornavirus required twice this dose. Water temperatures above 50°C significantly increased the rate of bacterial inactivation. The research team at Eawag have significantly contributed to the scientific development, standardisation, and promotion of the SODIS process through the development of the online information network and the publication and distribution of the SODIS Manual and associated education resources [12].

Laboratory studies have demonstrated the effects of key operational parameters such as light intensity and wavelength, solar exposure time, availability of oxygen, turbidity, and temperature [19, 20]. The SODIS mechanism is understood to involve a number of biocidal pathways based upon absorption of UVA radiation and thermal inactivation. Direct UVA exposure can induce cellular membrane damage and delay microbial growth [21]. The biocidal action of UVA has also been attributed to the production of reactive oxygen species (ROS) which are generated from dissolved oxygen in water [22] and the photosensitisation of molecules in the cell, and/or any naturally occurring dissolved organic matter that can absorb photons of wavelengths between 320–400 nm, to induce photochemical reactions [23]. The thermal effect has been attributed to the high absorption of red and infrared photons by water. At temperatures below 40°C, the thermal effect is negligible with UVA inactivation

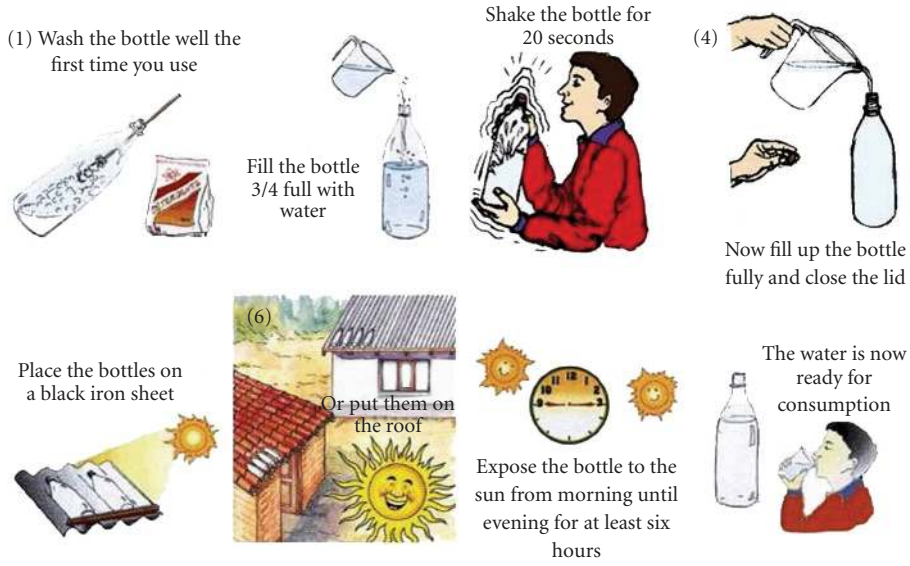

Figure 1: SODIS process—www.sodis.ch.

mechanisms dominating the inactivation process. Significant bactericidal action is evident at temperatures above 40–45°C with a synergistic SODIS process observed at temperatures above 45°C [13, 19, 23–25]. Detailed genetic assessment has also been used to probe the biocidal mechanism of SODIS [26, 27].

Researchers have shown SODIS to be effective against a wide range of microorganisms responsible for diarrheal illness [28–30]. The inactivation of resistant protozoa has also been reported [31–33]. Field trials have demonstrated a significant health benefits from consumption of SODIS treated water [34, 35]. The effectiveness of SODIS against cholera was also demonstrated in a Kenyan health impact assessment, where an 86% reduction cholera cases was observed in households regularly using SODIS [36].

Studies to improve the efficiency of the SODIS process using low-cost, commonly available materials have been conducted [37–40]; however, the simple approach of exposing a 2 L PET bottle to full sun for a minimum of 6 hours is the most commonly promoted and practiced method.

3. Enhancement Technologies for SODIS

There are several drawbacks of "conventional" SODIS technology. The use of PET bottles allows for only small volumes to be treated (2-3 L), and the process efficiency is dependent on a range of environmental parameters including the solar irradiance (which depends on the latitude, time of day, and atmospheric conditions), the initial water quality for example organic loading, turbidity, level, and nature of the bacterial contamination. The resistance that microorganisms display to solar disinfection leads to variation in treatment times. Malato et al. reviewed the reported inactivation time required for a range of microorganisms using SODIS under ca. 1 kW/m^2 global irradiance [10]. These vary enormously from 20 min for *Campylobacter jejuni* to 8 h for *Cryptosporidium parvum* oocysts. For *Bacillus subtilis* endospores, no inactivation was observed after 8 hours of SODIS treatment. SODIS is user dependent in that it requires the user to 'time' the exposure and as such there is no quality assurance in the process and as such, lack of compliance with the recommended protocol is a major issue.

There are a number of ways to improve or enhance the conventional SODIS process, including the design of SODIS bags where the solar dose per volume is increased, the use of UVA dosimetric sensors which indicate to the user when the desired dose has been received by the water, the design of customised SODIS treatment systems which maximise the solar dose using compound parabolic collectors (CPC) and may include UVA feedback sensors for automated control, and the use of semiconductor photocatalysis to enhance the treatment efficacy.

3.1. SODIS Bags. The SODIS method can be enhanced by use of a personal SODIS-reactor which would maximise the area for photon collection and minimise the path length for light penetration through the water to be treated. Furthermore, these SODIS bags could be deployed in emergency situations where access to drinking water is an immediate issue for example flooding or earthquake. The latter application can be limited due to the lack of PET bottles in disaster areas whereas bags have the advantage that they can easily be transported and stored in large quantities. Eawag has launched a project to develop specific SODIS bags, and several bag models are being developed in collaboration with partners from the private sector. A prototype is currently being field tested together with local organisations in Bolivia, DR Congo, Kenya, Nepal, and Nicaragua [41].

3.2. UV Dosimetric Indicators. Professor Mills' group at the University of Strathclyde has been investigating the use of photocatalytic systems as intelligent inks [42, 43]. As titanium dioxide (TiO_2) is excited by UVA light, these

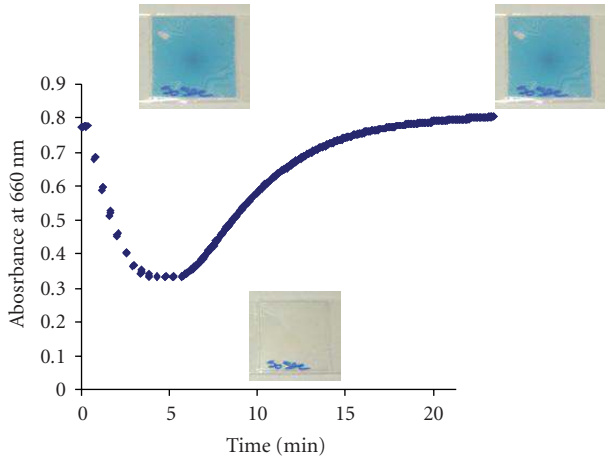

Figure 2: Colourimetric UVA dosimetric indicators—UVA exposure photo-reduced MB (blue) the LMB (white) (UVA dose = 9.0 kJ/m^2), MB subsequently reformed via oxidation in the dark.

systems may be used as UVA dosimetric indicators. At the University of Ulster, we have tested a simple prototype system to measure UVA dose utilising the photocatalytic reduction of methylene blue (MB) to leuco-Methylene Blue (LMB) (method adopted from Mills, Lee, and Sheridan [43]).

In the presence of the hole scavenger (glycerol), methylene blue is photocatalytically reduced to colorless leucomethylene blue, and the rate of decolouration is dependent on the UVA intensity (Figure 2). In the dark and in the presence of oxygen, the reduced form is reoxidised back to methylene blue. This results in a simple reversible UVA dosimetric indicator which could be utilised to provide some quality assurance for the SODIS user. There are a wide range of dyes or inks that could be utilised in these systems to provide simple dosimetric indicators for corresponding to UVA doses required for SODIS.

3.3. Compound Parabolic Collectors. Fernandez-Ibanez and Malato at the Plataforma Solar de Almeria (PSA) in Spain have focused on the use of nonconcentrating solar collectors for the enhancement of solar disinfection. Compound Parabolic Collectors (CPC's) are nonimaging systems which collect diffuse radiation. The collected energy is homogeneously distributed across the absorber surface. CPCs do not rely solely on direct solar radiation and are therefore effective even on cloudy days. In addition, they collect radiation independently of the direction of sunlight and do not require sun tracking.

The SODIS process relies heavily on the solar UVA which, as received at sea level, is composed of roughly similar portions of both direct and diffuse electromagnetic radiation. Given the diffuse nature of the UVA and the cylindrical shape of SODIS bottles, the use of sunlight collecting systems based on nonimaging optics has obvious potential. Navntoft et al. demonstrated the use of CPC technology to enhance the efficacy of SODIS on sunny and cloudy days [25]. The major advantage of CPC technology is that the concentration factor remains constant for all

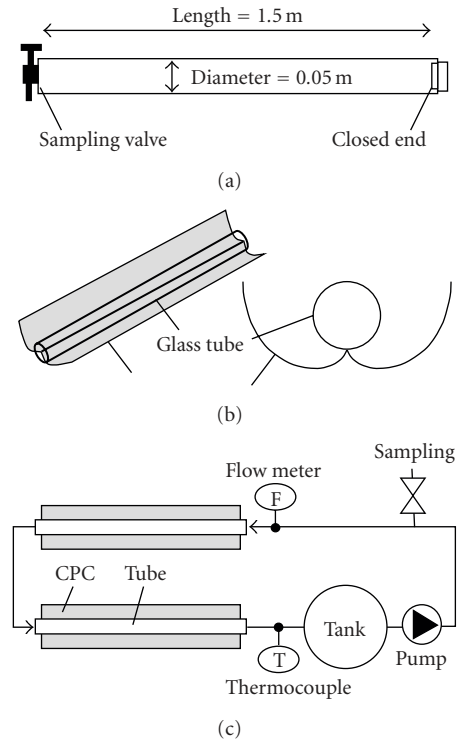

Figure 3: (a) Glass tube configuration. (b) Tube with CPC collector configuration. (c) Flow diagram of the solar CPC reactor (with permission from [48]).

values of sun zenith angle within the acceptance angle limit; therefore, it is theoretically possible to design larger volume SODIS systems. For example, recent work showed the effective inactivation of *E. coli* K12 in well water using a 25 L SODIS reactor with CPC [44]. Studies using CPC solar reactors including titanium dioxide as a photocatalyst have shown increased disinfection in comparison to SODIS alone [45–47].

Ubomba-Jaswa et al. investigated the effect of UVA dose on the inactivation efficiency of 3 types of SODIS reactors: borosilicate glass tubes (static batch), borosilicate glass tubes with compound parabolic collector (recirculating batch), and borosilicate glass tubes with CPC (recirculating batch) (Figures 3 and 4) [48]. They used *E. coli* K12 as the model microorganism suspended in natural well water and demonstrated inactivation of approximately 6-log colony forming units (CFU) mL^{-1} following receipt of a total uninterrupted minimum dose of >108 kJ/m^2 (295–385 nm).

4. Semiconductor Photocatalysis

4.1. Mechanism of Photocatalysis. When a semiconductor is irradiated with light of wavelength equal or greater than its band gap, energy is absorbed resulting in the promotion of electrons from the valence band to the conduction band, and the formation of electron-hole pairs (e^- and h^+) [5]. These charge carriers can recombine, with the energy being reemitted as light or heat, or they may migrate to the catalyst surface where they can participate in redox reactions at the

Figure 4: Borosilicate glass tubes with CPC.

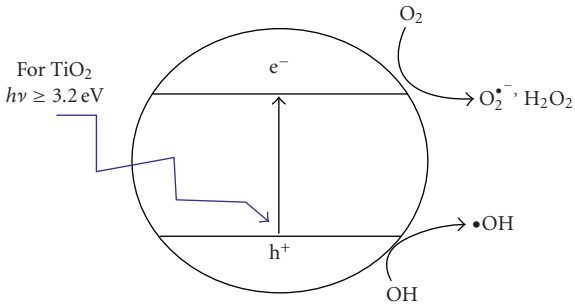

Figure 5: Schematic representation of the mechanism of photocatalysis on titanium dioxide particles.

particle-solution interface [8] (Figure 5). The reactive oxygen species (ROS) produced, including the hydroxyl radical, are very active, indiscriminate oxidants [49] destroying a large variety of chemical contaminants in water and also causing fatal damage to microorganisms [50]. The final products of the photocatalytic degradation of pollutants (given long enough treatment time) are CO_2, H_2O, and respective inorganic acids or salts.

For more detailed information on the mechanisms of semiconductor photocatalysis, the reader is referred to one of the many excellent reviews [5–10].

4.2. Photocatalytic Materials. Several compounds have been investigated as potential semiconductor photocatalysts, including metal oxides (TiO_2, ZnO, ZrO_2, V_2O_5, Fe_2O_3, SnO_2) and metal sulphides (CdS, ZnS) [51, 52]. Amongst these, the most popular photocatalyst for use in water treatment applications is titanium dioxide. TiO_2 is a wide band semiconductor (band gap = 3.2 eV for anatase); therefore, it requires UV excitation. To improve efficiency in solar applications, visible light active materials are desirable. However, while absorbing a greater number of solar photons, the smaller band gap gives a narrower voltage window to drive the redox reactions at the particle-solution interface. Metal sulphide semiconductors, which absorb in the visible region of the spectrum, tend to undergo photo-anodic corrosion [53]. Considering cost, chemical and photochemical stability, availability, and lack of toxicity, the most suitable catalyst reported to date for the treatment of water is TiO_2 [54].

4.3. Immobilised versus Suspended Photocatalyst. The photocatalyst can be utilised in aqueous suspension or it may be immobilised on a supporting solid substrate. Most studies have reported that suspension reactors are more efficient due to large surface area available for redox reactions [55], however; the main drawback of using nano or microparticles in suspension is the requirement for posttreatment separation and recycling of the catalyst, potentially making the treatment more complex and expensive. Therefore, treatment reactors utilising immobilised TiO_2 have gained attention. There are a wide range of methodologies available for the preparation of immobilised photocatalyst films on a range of supporting substrates, and a careful reactor design is required to prevent efficiency loss due to a reduction in catalyst surface area and poor mass transfer of reactants to the photocatalyst surface [56].

4.4. Photocatalytic Disinfection of Water. Matsunaga et al. reported the first application of TiO_2 photocatalysis for the inactivation of bacteria in 1985 [57]. Since then, there have been a large number of research publications dealing with the inactivation of microorganisms including bacteria, viruses, protozoa, fungi, and algae. Blake et al. carried out an extensive review of the microorganisms reported to be inactivated by photocatalysis [51]. In 2007, McCullagh et al. reviewed the application of photocatalysis for the disinfection of water contaminated with pathogenic microorganisms [58]. In 2009, Malato et al. published an extensive review on the decontamination and disinfection of water by solar photocatalysis [10] and, in 2010, Dalrymple et al. reviewed the proposed mechanisms and kinetic models widely used in photocatalytic disinfection studies [59].

In most photocatalytic disinfection studies, the hydroxyl radical is suggested to be the primary species responsible for microorganism inactivation; however, some papers do report involvement of other ROS, such as H_2O_2, $O_2^{\bullet -}$ [60–63]. These reactive species can cause fatal damage to microorganisms by disruption of the cell membrane or by attacking DNA and RNA [51]. Other modes of action TiO_2 photocatalysis have been proposed, including damage to the respiratory system within the cells [64] and loss of fluidity and increased ion permeability in the cell membrane [62]. Detailed spectroscopy-based studies attributed cell death to lipid peroxidation of bacterial cell membrane [61–63]. The peroxidation of the unsaturated phospholipids contained in the bacterial cell membrane results in loss of respiratory activity [65] and/or leads to a loss of fluidity and increased ion permeability [62]. It has also been suggested that cell membrane damage can open the way for further oxidative attack of internal cellular components, ultimately resulting in cell death [65].

Research at the University of Ulster has been mainly concerned with the use of immobilised TiO_2 films prepared by the deposition of Evnoik (Degussa) P25 onto a range of supporting substrates, including borosilicate glass, ITO glass, and titanium metal. For example, Alrousan et al.

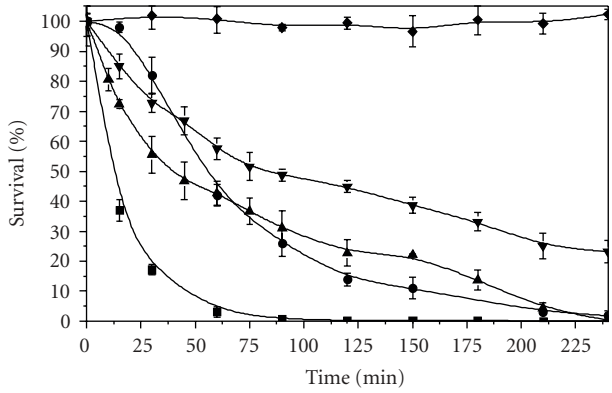

Figure 6: Comparison between photocatalytic and photolytic inactivation of *E. coli* in surface and distilled water (TiO_2, UV, Distilled water) ■, (TiO_2, UV, Surface water) •, (UV, Distilled water) ▲, (UV, Surface water) ▼, Dark control ♦ (with permission, from [66]).

reported on the photocatalytic inactivation of *E. coli* in surface water using immobilised nanoparticle TiO_2 films [66]. In this work, P25 was immobilized onto borosilicate glass using a dip coating method. The photoreactor was a custom-built stirred tank reactor which had excellent mixing and good mass transfer properties. The catalyst was irradiated in a back-face configuration that is, the light passed through the glass to excite the photocatalyst on the surface. It was found that the rate of photocatalytic inactivation of *E. coli* was more efficient with UVA-TiO_2 than direct photolytic inactivation with UVA alone, for *E. coli* suspended in both distilled water and surface water (Figure 6). The optimum catalyst loading for the inactivation was determined to be 0.5 mg/cm^2, approximately half that reported for photocatalytic degradation of formic acid and atrazine in the same reactor, under the same incident light intensity.

The organic and inorganic content of the surface water led to a reduction in the rate of photocatalytic disinfection in comparison to that observed in distilled water. The effect of selected individual constituents present in the surface water was examined to identify the main constituent responsible for the reduction in the rate of photocatalytic disinfection. The presence of inorganic ions, that is, sulphate and nitrate reduced the rate of photocatalytic inactivation, with sulphate having a more pronounced effect than nitrate. The presence of organic matter was found to be the dominating parameter responsible for the decrease in the rate of photocatalytic disinfection. The presence of inorganic ions will lead to a reduction in efficiency either by absorption of light, competing for ROS, or by adsorption to the catalyst surface. Organic matter will compete for ROS and may compete for photon absorption. The efficacy of photocatalytic disinfection will therefore be strongly dependent on the initial water quality. Where the water to be treated is of poor quality, a pretreatment stage, for example, simple filtration or settling, may be desirable prior to photocatalytic treatment.

Bacterial cells have been described as a rather easy target for disinfectants, with bacterial spores and protozoa suggested as more robust target organisms. *Clostridium perfringens* spores have been reported to be chlorine resistant at levels used in potable water supplies. Dunlop et al. reported on the photocatalytic inactivation of *Clostridium perfringens* spores on TiO_2 electrodes [67]. The TiO_2 electrodes were made using electrophoretic immobilisation of commercially available TiO_2 powders onto conducting supports, that is, indium-doped tin oxide-coated glass, titanium metal, and titanium alloy. The photocatalytic inactivation of *E. coli* and *C. perfringens* spores in water was observed on all immobilised TiO_2 films under UVA irradiation. The rate of photocatalytic inactivation of *E. coli* was found to be one order of magnitude greater than that of *C. perfringens* spores, demonstrating the greater resistance of the spores to environmental stress. In this work, it was shown that the application of an external electrical bias (electrochemically assisted photocatalysis) significantly increased the rate of photocatalytic disinfection of *C. perfringens* spores. The effect of incident light intensity and initial spore loading were investigated, and disinfection kinetics were determined to be pseudo-first order. This work demonstrated that UVA photocatalysis is effective against bacterial spores which are more resistant to environmental stress, including UVA irradiation, than bacterial cells.

Cryptosporidium species are waterborne, protozoan parasites that infect a wide range of vertebrates. The life cycle involves the production of an encysted stage (oocyst) which is discharged in the faeces of their host. The disease, Cryptosporidiosis, in humans usually results in self-limited watery diarrhoea but has far more devastating effects on immunocompromised patients (e.g., AIDS patients) and can be life-threatening as a result of dehydration caused by chronic diarrhoea. Owing to their tough outer walls, the oocysts are highly resistant to disinfection and can survive for several months in standing water. Cryptosporidium oocysts therefore present as an excellent challenge for disinfection technologies. Sunnotel et al. reported on the photocatalytic inactivation of *Cryptosporidium parvum* oocysts on nanostructured titanium dioxide films (Figure 7) [68].

The photocatalytic inactivation of the oocysts was shown to occur in Ringer's buffer solution (78.4% after 180 min) and surface water (73.7% after 180 min). Scanning electron microscopy (SEM) confirmed cleavage at the suture line of oocyst cell walls, revealing large numbers of empty (ghost) cells after exposure to photocatalytic treatment. No significant inactivation was observed in the oocysts exposed to UVA radiation alone demonstrating the substantial benefit in the addition of TiO_2 as a photocatalyst.

It is clear from the literature, that in lab scale reactors, photocatalysis under UVA irradiation is more efficient than UVA irradiation alone for the disinfection of water contaminated with pathogenic microorganisms. Therefore, it is essential that photocatalytic reactors are tested for disinfection under real sun conditions either on small scale batch (personal use) or at pilot scale (aimed at household or small community use), and using real water sources.

Gelover et al. studied small-scale batch disinfection in plastic bottles containing spring water naturally polluted with coliform bacteria, with and without the addition of

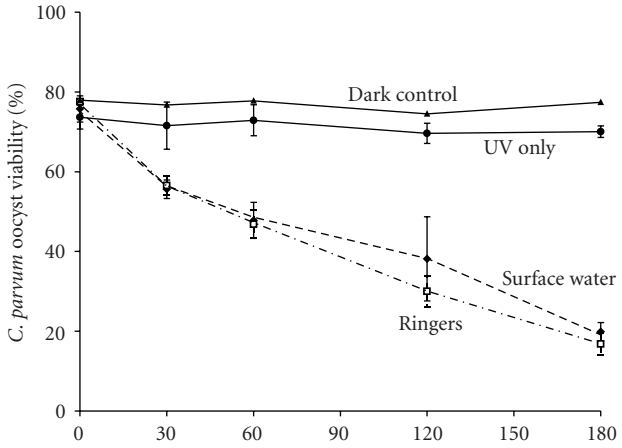

Figure 7: Photocatalytic inactivation of *C. parvum* oocysts suspended in Ringer's solution and surface water (with permission from [68]).

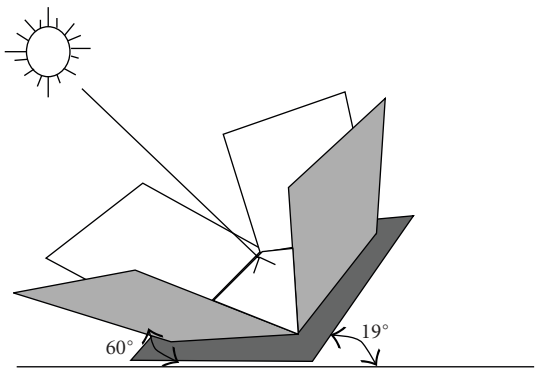

Figure 8: Simple solar collector made from 5 wooden sheets covered with aluminium foil (with permission from [69]).

TiO_2 [69]. The bottles were mounted in simple home-made solar collectors (Figure 8). Two litre PET bottles were filled with spring water and exposed to direct sunlight. The microbial loading was typically 2.5×10^3 MPN/100 mL (most probable number) of total coliforms and 9.0×10^2 MPN/100 mL of faecal coliforms.

TiO_2 was coated onto small Pyrex-glass cylinders, using a sol-gel method, and these were placed inside each bottle. It was found that photocatalytically enhanced SODIS was by far more effective than SODIS alone for the inactivation of both the total coliforms and the faecal coliforms (Figure 9). They measured bacterial regrowth following treatment and found that regrowth was observed with SODIS alone, but not with photocatalytically enhanced SODIS. This is an important finding, as bacteria have repair mechanisms which allow recovery following stress/injury and demonstrates the differences in the kill mechanisms involved in SODIS and photocatalytic disinfection.

With respect to larger-scale systems, Fernandez-Ibanez et al. reported on the pilot-scale photocatalytic disinfection of water under real sun conditions using a photoreactor with CPC [70]. The experiments were carried out under

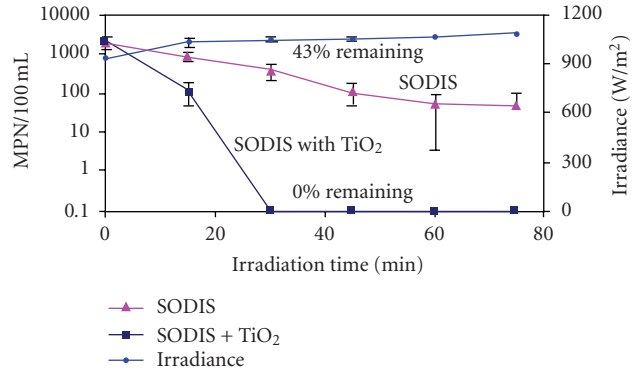

Figure 9: Decrease in faecal coliforms in natural spring water exposed to direct sunlight, comparing SODIS to TiO_2-enhanced SODIS (with permission from [69]).

sunlight at the Plataforma Solar de Almeria in southern Spain using compound parabolic collectors. The pilot plant consisted of three CPC collectors, each containing two Pyrex tubes (50 mm inner diameter, 1.5 m long), with a collector surface area of 0.25 m^2 and a total reactor volume treated of 11 L. Experiments were performed with suspended TiO_2 and, following modification to the reactor, with supported/immobilised TiO_2. In both cases, Degussa, P25 was employed as the photocatalyst. In the immobilised study, the catalyst was fixed onto glass fibre using SiO_2 as an inorganic binder. *E. coli* was used as the model microorganism suspended in distilled water. The photocatalytic suspension reactor was the most efficient, followed by the immobilised photocatalytic reactor, with SODIS being the least efficient treatment (Figure 10).

Further work undertaken by the group at Plataforma Solar de Almeria investigated the effect of UV intensity and dose on SODIS and photocatalytically enhanced SODIS [71]. The aim of the work was to study the dependence on solar irradiation conditions under natural sunlight using three microorganisms, *E. coli* K-12 culture and two wild strains *Fusarium solani* and *Fusarium anthophilum*. Photocatalytic disinfection experiments were carried out with TiO_2 supported on a paper matrix held concentrically within the CPC glass tube reactors described above, and with TiO_2 in the form of a slurry in Pyrex glass bottle reactors. The experiments were performed with different illuminated reactor surfaces, in different seasons of the year, and under changing weather conditions (i.e., cloudy and sunny days). Photocatalysis did not increase the rate of disinfection following receipt of the minimum solar dose; however, the solar-only disinfection was more susceptible to changes in solar irradiation than photocatalytic disinfection, that is, where light intensities were generally low or there was greater availability of diffuse UVA, the inclusion of the photocatalyst provided a significant benefit.

5. Issues to Be Addressed

5.1. Photoreactor Design. The SODIS process depends mainly on the UVA wavelengths present in sunlight. Solar

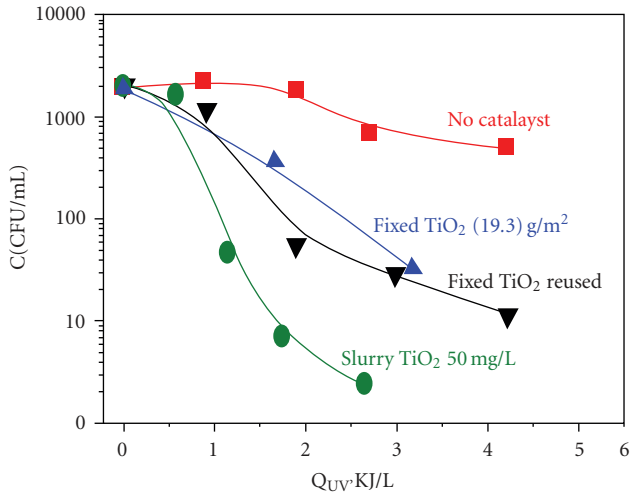

Figure 10: *E. coli* inactivation ($C_0 = 1 \times 10^4$ CFU/mL) versus Q_{UV} (energy per unit of volume, kJ/L) in the CPC solar photoreactor. Comparison of TiO_2 slurry (50 mg/L), with supported photocatalyst KN47 (19.3 g $TiO_2 m^{-2}$) and SODIS. With permission from [70].

UV at sea level is composed of roughly similar portions of both direct and diffuse electromagnetic radiation. Without cloud cover, the solar UVA spectrum is ca. 60% direct and ca. 40% diffuse. Therefore, the use of collecting systems based on nonimaging optics has a clear potential, compared to expensive imaging/concentrating optic-based systems. The major advantage with compound parabolic collectors is that collection factor remains constant for all values of sun zenith angle within the acceptance angle limit. Therefore, CPC enhancement can be utilised in the design of larger-scale solar disinfection systems which can be used for household or small community use. A photoreactor for use in developing countries should have the following attributes; high illuminated volume to total volume ratio; ability to operate under a low flow rate when utilising immobilised photocatalyst to maximise the residence time in flow systems; UVA dosimetric indicator (as both SODIS and photocatalytic disinfection are dose dependant); CPC of good quality that is, high UVA reflectivity (for aluminium this is typically 87–90%); reaction vessel with high (90%) UVA transmission (e.g., borosilicate glass); robust under potentially harsh environmental conditions; minimal life-cycle cost; low environmental impact; low maintenance requirements and ease of access to replacement parts; and minimal external power requirement.

If the system is to include a photocatalyst, the reactor design must also ensure the sufficient supply of an electron acceptor, typically dissolved oxygen from the air. In static batch systems, the concentration of dissolved oxygen will be rapidly consumed in the initial stages of the reaction and as water temperature increases the solubility of oxygen in water will be further reduced. For applications in developing countries, this is of paramount importance as the temperature within SODIS reactors can reach 55°C. An alternative may be to introduce other oxidants for example, H_2O_2; however, this would give rise to a dependence on consumable chemicals which is undesirable.

5.2. Photocatalyst Longevity. For application in remote locations and developing regions, the treatment system must be robust, noncomplex, and require only low-level maintenance. Therefore, photocatalyst regeneration is undesirable and more research is required to understand and predict photocatalyst longevity under typical working conditions. To reduce the complexity of the treatment system, immobilised photocatalyst systems are preferred; however, catalyst stripping may be a problem if the immobilisation protocol does not produce a robust hard wearing coating. Also, catalyst fouling by inorganic species present in the water can lead to a reduction in the photocatalytic efficiency over time. Miranda-García et al. investigated the degradation of 15 emerging contaminants (ECs) in a photocatalytic pilot plant utilising TiO_2 immobilised onto glass beads [72]. The CPC plant consisted of two modules of 12 Pyrex glass tubes mounted on a fixed platform tilted 37° (local latitude). Two of the glass tubes were packed with TiO_2-coated glass spheres (coated with a titania sol–gel). The total illuminated area was 0.30 m^2 and total volume was 10 L, of which 0.96 L was constantly irradiated. The system operated in recirculating batch mode with a flow rate of 3.65 $Lmin^{-1}$. They found that the degradation of the organic pollutants in distilled water was achieved under solar irradiation, and importantly, after 5 cycles of photocatalysis, the photocatalyst activity was not decreased significantly. Experiments using real water may present catalyst fouling problems.

5.3. Visible Light Active Photocatalyst Materials. The overall efficiency of TiO_2 under natural sunlight is limited to the UV-driven activity (for anatase $\lambda \leq 400$ nm), accounting only to ca. 4% of the incoming solar energy on the Earth's surface. Therefore, there has been substantial research effort towards shifting the absorption spectrum of TiO_2 towards the visible region of the electromagnetic spectrum. Different approaches have been attempted including doping the TiO_2 with metal ions [73]. According to the literature, one of the more promising approaches to achieve visible light activity is doping with nonmetal elements including N and S. Since Asahi et al. [74] reported the visible-light photo-activity of TiO_2 with nitrogen doping, many groups have demonstrated that anion doping of TiO_2 extends the optical absorbance of TiO_2 into the visible-light region. However, the number of publications concerning the photocatalytic activity of these materials for the inactivation of microorganisms is limited. Li et al. reported the inactivation of MS2 phage under visible light irradiation using a palladium-modified nitrogen-doped titanium oxide (TiON/PdO) photocatalytic fiber, synthesized on a mesoporous-activated carbon fiber template by a sol-gel process [75]. Dark adsorption led to virus removal, and subsequent visible light illumination (wavelengths greater than 400 nm and average intensity of 40 mW/cm^2) resulted in additional virus removal of 94.5–98.2% within 1 h of additional contact time. By combining adsorption and visible-light photocatalysis, TiON/PdO fibers reached final virus removal rates of 99.75–99.94%. EPR

measurements confirmed the production of •OH radicals by TiON/PdO under visible light illumination. Wu et al. also reported visible-light-induced photocatalytic inactivation of bacteria by composite photocatalysts of palladium oxide and nitrogen-doped TiO_2 [76]. The PdO/TiON catalysts were tested for visible-light-activated photocatalysis using gram-negative organisms that is, *E. coli* and *Pseudomonas aeruginosa* and the gram-positive organism *Staphylococcus aureus.* Their disinfection data showed that the PdO/TiON photocatalysts had a much better visible photocatalytic activity than either palladium-doped (PdO/TiO_2) or nitrogen-doped titanium oxide (TiON). The light source used in this work was a metal halogen desk lamp with a low UV output ($<0.01\,mW/cm^2$ for $\lambda \leq 400\,nm$). While these photocatalysts show promise, there was no comparison with undoped TiO_2 and solar-simulated light (which has around 5% UV) was not used.

In many cases, the UV activity of undoped TiO_2 is much greater than the visible light activity of the doped material. Therefore, for solar applications, the photocatalysts should be tested under simulated solar irradiation or under real sun conditions. Indeed, Rengifo-Herrera and Pulgarin recently reported on the photocatalytic activity of N, S codoped and N-doped commercial anatase (Tayca TKP 102) TiO_2 powders towards phenol oxidation and *E. coli* inactivation under simulated solar light irradiation [77]. However, these novel materials did not present an enhancement for the photocatalytic degradation of phenol or the photocatalytic inactivation of *E. coli* under simulated solar light, as compared to Degussa P25. They suggest that while the N, or N-S co-doped TiO_2, may show a visible light response, the localized states responsible for the visible light absorption do not play an important role in the photocatalytic activity.

More research is required to determine if visible light active materials can deliver an increase in the efficiency of photocatalysis under solar irradiation.

6. Conclusions

SODIS is a simple and low cost technique used to disinfect contaminated drinking water. Transparent bottles (preferably PET) are filled with contaminated water and placed in direct sunlight for a minimum of 6 hours. Following exposure, the water is safe to drink as the viable pathogen load can be significantly decreased. The process has approximately 4.5 million regular users, predominately in Africa, Latin America, and Asia and is recognised and promoted by the WHO. However, there are several drawbacks with "conventional" SODIS technology. The use of PET bottles allows for only small volumes to be treated (2-3 L) and the process efficiency is dependent on a range of environmental parameters including the solar irradiance (which depends on the latitude, time of day, and atmospheric conditions), the initial water quality for example, organic loading, turbidity, and level and nature of the bacterial contamination. There are a number of ways to improve or enhance the conventional SODIS process and these include the design of SODIS bags where the solar dose per volume is increased, the use of UV dosimetric indicators which measure the UV dose and indicate to the user when the desired dose has been received by the water, design of customised SODIS treatment systems which maximise the solar dose and the inclusion of UV feedback sensors for automated control, and the use of semiconductor photocatalysis to enhance the treatment efficacy. Semiconductor photocatalysis has been shown to be effective for the inactivation of a wide range of microorganisms at lab scale and under real sun conditions for both small-scale and large-scale applications. The use of CPC reactors enhances the efficiency of solar disinfection and photocatalytically enhanced solar disinfection. Nevertheless, there are a number of issues to be addressed before photocatalytically enhanced solar disinfection can be effectively deployed in developing regions. These include improvements in photoreactor design and the assessment of photocatalyst longevity under real operating conditions. Future developments in relation to visible light active photocatalytic materials may lead to more efficient solar photocatalysis for the disinfection of water.

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