

*ule2009 International Workshop on Urbanisation, Land Use, Land Degradation, and Environment
28 September-01 October 2009, Denizli Turkey*

Photocatalytic enhancement of solar water disinfection for application in developing regions.

Dunlop P.S.M.^{1*}, Alrousan D.M.¹, Polo-López M.I.², Fernández-Ibáñez P.², Byrne J.A.¹

1 Photocatalysis Research Group, Nanotechnology and Integrated BioEngineering Centre, University of Ulster, Shore Road, Newtownabbey, Northern Ireland, BT37 0QB.

2 Plataforma Solar de Almería - CIEMAT, PO Box 22, 04200 Tabernas, Almería, Spain.

* Email: psm.dunlop@ulster.ac.uk Telephone: +44 2890368942

Abstract

Solar water disinfection (SODIS) is an effective, simple, household level, point-of-use technology suitable for application in developing countries. Contaminated water is placed in a plastic container (typically a 2L PET bottle) and exposed to sunlight for at least 6 hours. Laboratory and field trials have demonstrated SODIS to be effective against a wide range of waterborne pathogens with health impact assessments demonstrating significant benefits from consumption of SODIS treated water. Photocatalytic (PC) enhancement of the SODIS process could provide larger volumes of safe drinking water and reduce the sunlight exposure time.

Pilot scale, modular PC-SODIS reactors were designed and constructed from low-cost materials and tested, under real sunlight the south of Spain, for their efficiency to disinfect water containing $\sim 1 \times 10^6$ *Escherichia coli* cells/mL. The inclusion of an immobilised nanostructured titanium dioxide coating within 1.25 L static batch and 7 L re-circulating reactors accelerated the rate of disinfection with 6-log kill observed in 3 hours. Complete disinfection was not observed in re-circulating SODIS reactors. Photocatalytic enhancement was observed during full sun and cloudy weather conditions.

Keywords: Solar disinfection, SODIS, photocatalysis, titanium dioxide, water

Introduction

The provision of safe, clean drinking water is of paramount importance for human health; however, in developing countries the quality of potable water is typically very poor and effective water treatment processes are generally not available. The World Health Organisation estimate that 1.1 billion people across the world lack access to improved water supplies [1]. In Sub-Saharan Africa 769,000 children under 5 years of age, died annually from diarrhoeal diseases in 2000-2003 [1]. In order to meet the Millennium Development Goal, which aims to reduce by half the number of people without access to improved water and sanitation by 2015 [2], the WHO now recommends implementation of point-of-use drinking water treatment methods [3]. The cost of point-of-use water purification devices (e.g. sedimentation, boiling, ceramic filters, chlorine tablets/solutions etc.) generally prohibits widespread uptake of these technologies within the communities most at risk of waterborne disease.

Solar disinfection (SODIS) is an alternative point-of-use water treatment process which has been demonstrated to be practical at household level [4]. SODIS was first described in detail by Acra *et al* [5] and has recently been promoted by Swiss organisation EAWAG/SANDEC across Latin America and African countries. SODIS is a simple, effective, inexpensive and environmentally stable water treatment method [6]. The SODIS process consists of filling plastic bottle (typically made from polyethylene terephthalate (PET)) with contaminated

water and exposing the container to sunlight for at least 6 hours. A synergistic disinfection mechanism has been proposed whereby absorption of UVA radiation and heat (visible/IR absorption) result in the inactivation of a wide range of waterborne pathogens. For effective SODIS water with a turbidity less than 30 nephelometric turbidity units (NTU) is required [6].

SODIS is currently used for drinking water purification by approximately two million users in thirty-one countries [7]. The health benefits associated with consumption of SODIS treated water have been demonstrated in a number of studies. Conroy *et al.* conducted a study on children living in Kajiado, Kenya, reporting a 10% reduction in incidence of diarrhoea and a 24% decrease in severe diarrhoea within children under five [8]. The effectiveness of SODIS against cholera was also demonstrated in a Kenyan health impact assessment where Conroy *et al.* reported an 86% reduction in the cases of cholera among SODIS users [9].

Although SODIS is a viable and proven water purification process there are a number of problems associated with the technology which prevent widespread use. Practical application on a large scale is limited by the small volumes of water treated and the long treatment time, e.g. the time taken to disinfect a 2L bottle of water is in excess of 6 hours. Research into low cost SODIS enhancements which increase the volume of treated water and decreases the solar exposure time could significantly improve the acceptability and use of SODIS as a household level point-of-use water purification technology.

The addition of a catalyst could increase the rate of disinfection observed in SODIS reactors. Photocatalysis, defined as the acceleration of a reaction using a light driven catalyst [10], has been reported to be an efficient water disinfection process [11]. Titanium dioxide (TiO_2) is generally the photocatalyst of choice as it is inexpensive, non toxic and photo-stable. Photoreactors based upon immobilised catalyst surfaces are more practical than slurry based reactors where the small titanium dioxide particles (ranging from nanometers to microns in diameter) must be removed before consumption. TiO_2 is activated upon excitation of UVA radiation (band-gap of 3.0 - 3.2 eV). Photocatalytic experiments are generally carried out in laboratories employing UVA lamps, however, photocatalysis using solar radiation (5% UVA) has also been reported [12].

In this paper we discuss the photocatalytic enhancement of the SODIS process with the aim of a) increasing the volume of water which can be treated and b) increasing the speed and efficacy of the disinfection process using immobilised nanostructured TiO_2 coatings.

Methods and Materials

Pilot scale solar photoreactor

Modular systems comprising Pyrex glass tubes (1500 mm long, 50 mm outer diameter; Schott, Germany) were positioned at the focus of an aluminium compound parabolic collector (0.5 mm thickness; Alanod Aluminium GmbH, Germany). The reflectivity of the CPC mirror in the UV region was 82%, as reported by the manufacturer. For a static batch reactor, the glass tubes were fitted with polyethylene end stoppers (reactor volume 2.5 L per tube). For re-circulating reactors the glass tubes were fitted with polyethylene end pieces and connected in series with a centrifugal pump (flow rate 2 L/min; Pan World Co. Ltd.) and a 7 L glass reservoir. A schematic of both batch and re-circulating systems is shown in figure 1.

Pilot scale photocatalytic reactor

Degussa P25 (5% wt/vol in methanol) was immobilised onto Pyrex glass tubes (1500 mm long, 32 mm and 50 mm external diameter; Schott, Germany) using in-house dip coating

apparatus. Following immobilisation of 0.5 mg/cm^2 , tubes were annealed in a furnace at 400°C in air for 1 hour [13]. A range of glass tube combinations were produced with TiO_2 immobilised onto the inside of the large tube and to the outside of the small tube. To provide the maximum coated area to reactor volume ratio, a small coated tube was concentrically fixed inside a large coated tube, providing immobilised TiO_2 on both surfaces in contact with water (i.e. inside face of large external tube and outside face of small internal tube; referred to as “coated internal; coated external”).

Bacterial preparation

A single colony of *Escherichia coli* K12 (ATCC 23631) was taken from refrigerated stock, subcultured in Luria Broth nutrient medium (Sigma-Aldrich, USA) and incubated at 37°C with constant agitation on a rotary shaker at 100 rpm for 24 hours to produce stationary phase cells at a concentration of 10^9 CFU/mL. *E. coli* suspensions were centrifuged at 300 rpm for 10 min and re-suspended in sterile PBS (phosphate buffer saline). Inoculation ratios of 1 mL stock to 1 L reactor solution were used to achieve a final bacterial cell density of $\sim 10^6$ CFU/mL. The detection of *E. coli* cells in samples taken from the reactor was carried out by serial dilution in sterile PBS solution and plating an appropriate volume onto Luria agar (Sigma–Aldrich, USA). Following overnight incubation at 37°C , colonies were visually identified and counted.

Experimentation

Experiments were carried out under real sun conditions at the Plataforma Solar de Almería, Spain (latitude 37°N , longitude 2.4°W) using the above described photoreactors tilted to 37°N (local altitude) and facing the south. Batch reactors were filled with distilled water (1.25 L for double tubes). Re-circulating reactors were filled with 7 L of saline water (0.9% NaCl in distilled water). *E. coli* cells were inoculated 15 min prior the beginning of the experiment and the reactor was covered with black plastic cover (dark equilibration). At time zero the cover was removed and the first sample taken. Samples were taken at subsequent intervals and bacterial cell density determined as described above. The water temperature and ambient UVA radiation were monitored at regular intervals during the experiment.

Results and Discussion

Static batch reactors

In the batch reactor, a 6-log kill was observed using all catalyst coating configurations examined (figure 2). Control experiments, where the reactor was maintained in the dark, did not show significant disinfection. Maximum disinfection was observed using the catalyst immobilised on the external surface of the inner tube (coated internal; uncoated external) with complete disinfection observed within 3 hours. Diffuse reflectance experiments (results not shown) confirmed loss of incident photons, via absorption or reflection by the catalyst on the internal surface on the external glass tube, preventing optimal SODIS and/or photocatalysis. Poor mass transfer of the pollutants to the catalyst surface in the static batch system, coupled with the dissolution of dissolved oxygen as water temperature increased to $>35^\circ\text{C}$, decreased the photocatalytic disinfection efficiency. SODIS and solar activated photocatalytic disinfection experiments have been widely reported [14], however, research on the use of immobilised photocatalysts within these systems is limited.

Effect of weather on PC-SODIS

Experiments examining the effect of UVA intensity, as a function of weather conditions, were undertaken using the coated internal; uncoated external tube configuration in a static batch reactor (figure 3). As expected, optimal disinfection was observed in full sun conditions

where the incident UVA photon flux is uninterrupted. The proposed “minimal lethal UVA dose” theory governing SODIS [15] is relevant to photocatalytic experiments, however, further work is required to develop the theory to fit photocatalytic applications. Photocatalytic enhancement was evident under cloudy conditions but complete disinfection was not observed during very cloudy/wet weather.

Re-circulating reactors

Photocatalytic coatings enhanced the rate of disinfection under all re-circulating batch conditions examined, in comparison to SODIS alone where complete disinfection was not observed (figure 4). Control experiments, where the bacterial suspension was re-circulated in the dark, did not show significant disinfection (results not shown to ensure clarity in figure 4). Experiments using immobilised titanium dioxide on both the internal surface of the external tube and the external surface of the internal tube (coated external; coated internal) resulted in a 6-log kill of the 7 L volume in 3.25 hours. The increased mass transfer of pollutants to the catalyst surface, and higher dissolved oxygen levels, resulting from the fluid flow significantly increased the rate of photocatalytic disinfection, however, the rate of SODIS was significantly decreased. Photocatalytic disinfection of water has been widely studied in both laboratory and field conditions. The range of microorganisms, diversity of reactor configurations and effect of operational parameters has been recently reviewed [16].

Conclusion

The use of immobilised photocatalytic coatings has been shown to enhance SODIS for the inactivation of *E. coli* in both static batch and re-circulating reactor configurations. 6-log disinfection of 7 L of water was demonstrated in a re-circulating reactor following 3.25 hours exposure to strong sunlight in the South of Spain. PC-SODIS is a suitable process for implementation in developing countries given the modular nature of the reactors, the low reactor cost, lack of required maintenance and low operating cost, however, further work is required to elucidate the effect of turbidity on the efficiency of disinfection and catalyst lifetime.

Acknowledgements

The authors acknowledge the funding received through the EU SODISWATER project (INCO-CT-2006-031650).

References

- [1] World Health Organisation Report, (1997), (<http://whqlibdoc.who.int/publications/1997/9241545038.pdf>, (accessed 2009-01-25))
- [2] United Nations, Water for Life Report, (2005), (<http://www.un.org/waterforlifedecade/pdf/waterforlifebklt-e.pdf>, (accessed 2008-11-05)).
- [3] World Health Organisation and UNICEF Report, (2005), (http://www.who.int/water_sanitation_health/waterforlife.pdf (accessed 2008-11-05)).
- [4] M. Wegelin, S. Canonica, K. Mechsner, T. Fleischmann, F. Pesaro, A. Metzler, J Water SRT, Aqua. 43 (1994)154 – 169.
- [5] A. Acra, M. Jurdi, H.M. Allen, Y. Karahagopian, Z. Raffoul, Lancet 1 (1989)280-280.
- [6] R. Meierhofer, M. Wegelin, (2002), (http://www.sodis.ch/files/SODIS_Manual_english.pdf (accessed 2008-12-05)).
- [7] P. Schmid, M. Kohler, R. Meierhofer, S. Luzi, M. Wegelin, Wat. Res. 42 (2008)5054-5060.
- [8] R.M Conroy, M.E. Meegan, T. Joyce, K.G. McGuigan, J. Barnes, Lancet 348 (1996) 1695-1697.

- [9] R.M Conroy, M.E. Meegan, T. Joyce, K.G. McGuigan, J. Barnes, Arch. Dis. Child. 85 (2001)293-295.
- [10] A. Mills, S. LeHunte, J. Photochem Photobiol A: Chem 108 (1997)1-35.
- [11] P.S.M. Dunlop, J.A. Byrne, N. Manga, B.R. Eggins, J. Photochem Photobiol A: Chem 148 (2002)355-363.
- [12] S. Malato, J. Blanco, D.C. Alarcon, M.I. Maldonado, P. Fernandez-Ibanez, W. Gernjak, Catal. Today. 122 (2007)137-149.
- [13] J.A. Byrne, B.R. Eggins, NMD Brown, B. McKinney, M. Rouse NMD, App. Catal. B: Environ. 17 (1998)25-36.
- [14] A.G. Rincon, C. Pulgarin, J. Sol. Energ.-T ASME. 129 (2007)100-110.
- [15] E. Ubomba-Jaswa, C. Navntoft, I.M. Polo-Lopez, P. Fernandez-Ibanez, K.G. McGuigan, Photochem. Photobiol. Sci. 8 (2009)587-595.
- [16] C. McCullagh, J.M.C. Robertson, D.W. Bahnemann, P.K.J. Robertson, Res. Chem. Intermed. 33 (2007).

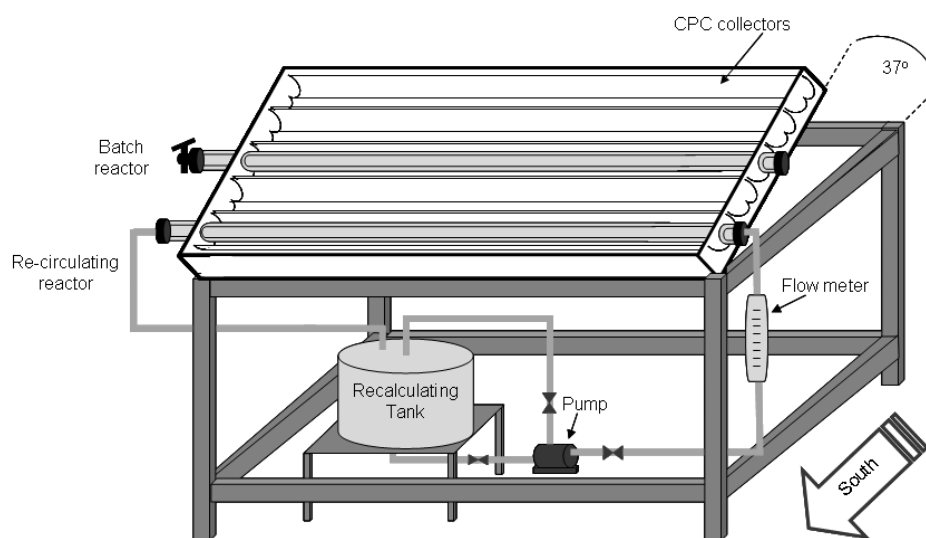


Figure 1: Schematic batch and re-circulating solar photoreactor.

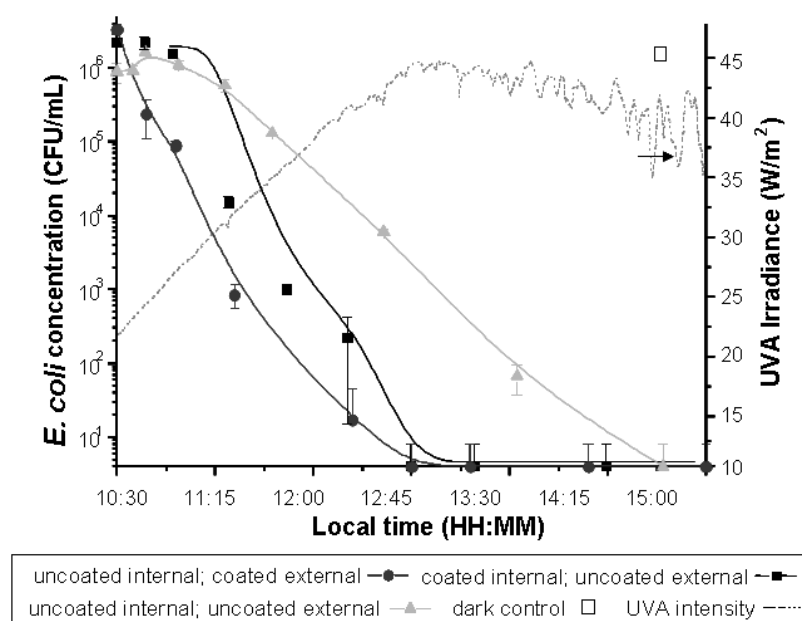


Figure 2: Solar photocatalytic disinfection in 1.25 L batch reactor.

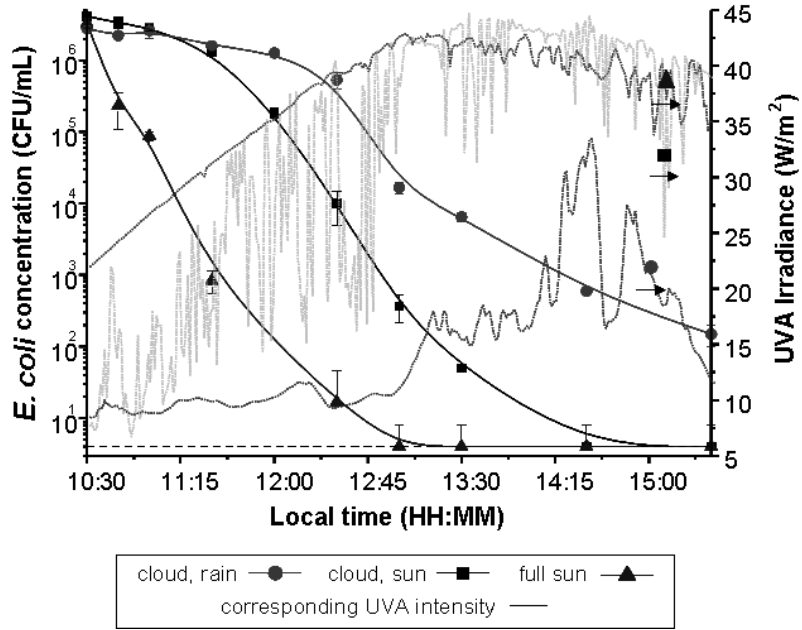


Figure 3: Effect of weather conditions during PC-SODIS in a static batch reactor (using coated internal; uncoated external tube configuration).

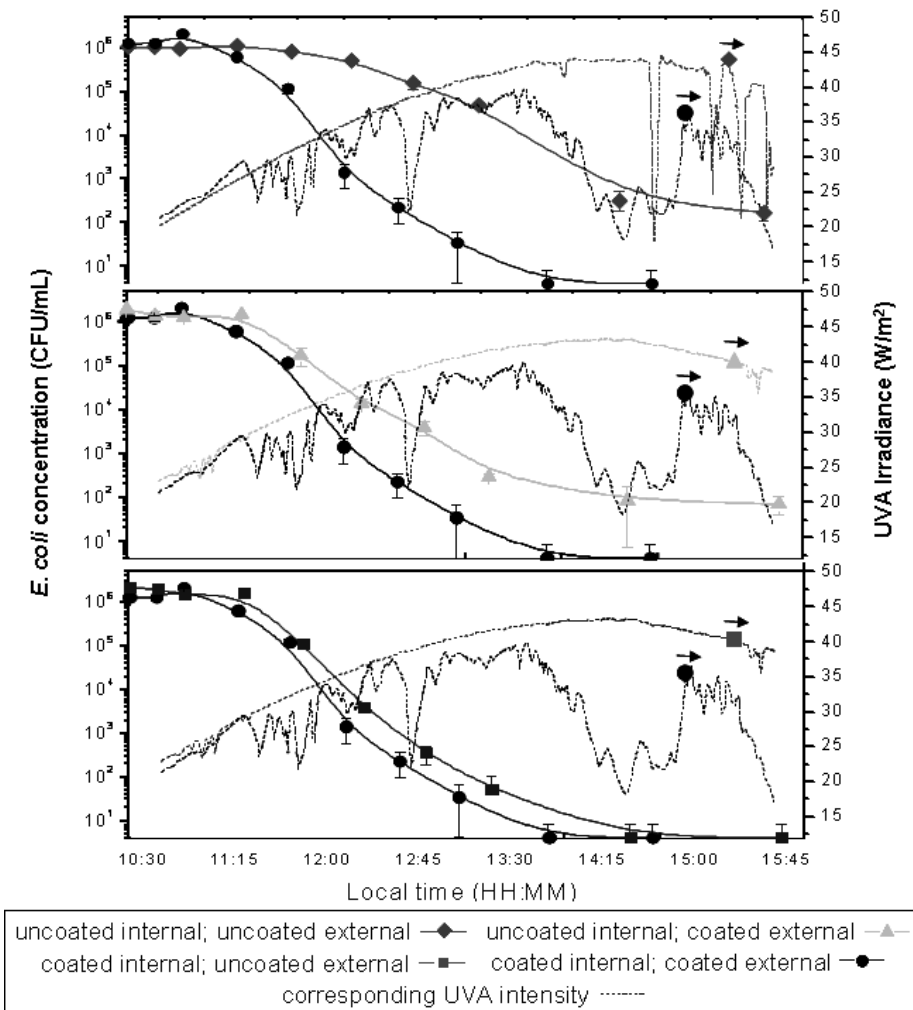


Figure 4: Solar photocatalytic disinfection in 7 L re-circulating reactor.