A Novel TiQ2-Assisted Solar Photocatalytic Batch-Process Disinfection Reactor for the Treatment of Biological and Chemical Contaminants in Domestic Drinking Water in Developing Countries

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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

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Abstract

The technical feasibility and performance of photocatalytic TiO$_2$ coatings in batch-process solar disinfection (SODIS) reactors to improve potability of drinking water in developing countries have been studied. Borosilicate glass and PET plastic SODIS reactors fitted with flexible plastic inserts coated with TiO$_2$ powder were shown to be 20% and 25% more effective, respectively, than standard SODIS reactors for the inactivation of E. coli K12. Isopropanol at 100 ppm concentration levels was observed to be completely photodegraded after 24 h continuous exposure to 100 mW/cm$^2$ simulated sunlight in a similar solar photocatalytic disinfecter (SPC-DIS) reactor. The technique for producing the TiO$_2$-coated plastic inserts is described and demonstrated to be an appropriate and affordable technology for developing countries.

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1. Introduction

Batch-process solar disinfection (SODIS) is an exciting technique for improving the quality of biologically contaminated drinking water in developing countries. The technique involves storing contaminated drinking water in transparent containers (plastic bags, plastic bottles or glass bottles) that are placed in direct sunlight for periods of up to 8 h, before consumption (Conroy et al., 1996). This technique has been shown to be highly effective against a broad range of bacterial pathogens such as E. coli (McGuigan et al., 1999), Vibrio cholerae (Conroy et al., 2001), Salmonella typhimurium (Smith et al., 2000) and Shigella dysenteriae Type I (Kehoe et al., 2004). Crucially, however, SODIS has been shown to be ineffective against chemically contaminated drinking water (SANDEC, 2003) and is, as
yet, untested against the more resistant pathogens such as protozoa. Suspensions of the non-toxic photocatalyst TiO₂ have been shown to photodegrade chemical contaminants in water using solar UV (Blake et al., 1992; Goswami et al., 1993; Giménez, 1996; Fujishima et al., 2000; Malato et al., 2002) and have also been used with batch process and continuous flow SODIS reactors to enhance and accelerate the inactivation rate of bacterial pathogens (Matsunaga et al., 1985; Morioka et al., 1988; Saito et al., 1991; Ireland et al., 1993; Block et al., 1997; Salih, 2002; Rincón and Pulgarin, 2003) in a process dubbed solar photocatalytic disinfection (SODIS).

The use of photocatalyst suspensions as part of a routine intervention for improving the potability of water at the household level (point-of-use water treatment) is not feasible since the TiO₂ particles would have to be recovered by filtration after solar exposure and before consumption (Pozzo et al., 1997). An additional step such as this in the solar disinfection protocol is likely to have a negative impact on the probability of compliance within communities in developing countries. A more acceptable alternative would be to isolate the photocatalyst onto some form of coated flexible insert, which would reside permanently within the batch-process SODIS reactor, or to attach it to the walls of the vessel.

The aims of this study were:

1. To determine if TiO₂ coatings can be used to accelerate the rate of SODIS inactivation.
2. To determine if TiO₂ coatings can be used in conjunction with SODIS technology to reduce levels of chemical contamination in drinking water.
3. To confirm that effective TiO₂ coatings can be produced without any specialised equipment using materials that can be obtained easily in any urban community in a developing country.

2. Experimental

2.1. Immobilisation of TiO₂ onto glass

A 100 ml Pyrex® Duran bottle was rinsed with distilled water, filled with a 1% detergent solution and sonicated for 15 min, after which it was rinsed with distilled water and sonicated for a further 15 min. This step was repeated 3 times. The bottle was then dried in an oven at 105 °C for 1 h before being weighed. Degussa P-25 TiO₂ was obtained from a local builder's supplier, where it was on sale as an all-weather additive and pigment for exterior wall plaster. A 1% w/v solution of TiO₂ in distilled water was prepared and sonicated for 15 min. The Duran bottle was laid on its side on a horizontal surface and 20 ml of the TiO₂ suspension was placed inside the bottle using a pipette. The bottle was rolled so that the suspension coated the lower half of the bottle but the upper half was left uncoated, at which point excess suspension was carefully removed. The bottle was placed on its side in a domestic oven at 105 °C for 20 min until the layer of TiO₂ was dried. This "half-coating" step was repeated 10 times. The bottle was finally annealed at 250 °C in a domestic oven for at least 12 h. This anneal temperature was chosen because it is the highest that one might expect a domestic oven to achieve. TiO₂ SPC coatings onto PET (polyethylene terephthalate) plastic bottles were not attempted because they would not survive the annealing stage.

2.2. Immobilisation of TiO₂ onto plastic sheets

A 5 mm diameter cylindrical line of black silicone adhesive bathroom sealant (Evo-Stick, Evode Industries, Dublin, Ireland) was laid down one side of an A4-size overhead projector (OHP) acetate transparency sheet (5star Ltd. Cambridge, UK). A reasonably reproducible coating of adhesive was accomplished by using a rectangular-tooth edged tiling trowel to spread the adhesive across the flexible plastic sheet in straight, parallel lines. Each sheet was then completely covered with TiO₂ powder and allowed to dry for 24 h. Any excess TiO₂ powder was shaken off and retrieved, before the coated sheet was washed with distilled water and left to dry overnight. The finished sheet was cut into the correct dimensions so that it covered the lower half of the internal surface of a 100 ml Duran bottle. The coated acetate insert was then rolled up and inserted through the neck opening of the bottle before being unfolded such that the TiO₂ coating faced the bottle’s central axis. The bottles used were either 1000 ml plastic (polyethylene terephthalate (PET)) coca-cola bottles or autoclavable borosilicate Pyrex® Duran Bottles (Schott Corp., New York, USA) of volume 250, 500 or 1000 ml. For simulated chemical photodegradation experiments 30 ml universal containers were used.

2.3. Optical experiments

Bacterial samples were irradiated using natural sunlight at the Plataforma Solar de Almería (PSA) solar research facility in Almería, Spain (Latitude 37° 05' 54", Longitude 2° 21' 32") in June/July 2003. Measurements of solar dose were made using a 300-400 nm broadband UV radiometer (CUV3, Kipp & Zonen, Netherlands). Chemical photodegradation measurements were carried out using simulated solar irradiation from a commercial 150 W diverging beam, xenon arc solar simulating lamp (Oriel Corp. Stratford, CT, USA) fitted with an air mass M = 1.0 solar filter (Oriel Corp. Stratford, CT, USA). Optical irradiances were monitored using a calibrated
optical power meter (Coherent, Cambridge, UK, model 200/10+). Sample bottles were laid on their sides on a horizontal surface such that the TiO$_2$ coating within the bottle was facing upwards towards the light. Chemical samples in the photodegradation experiments were exposed to optical irradiances of 100 mW/cm$^2$, which corresponds to strong equatorial sunshine.

2.4. Bacterial preparations

*Escherichia coli* K12 (ATCC, 10798) was used as the test organism in these studies, due to its widespread use as a faecal indicator. A single colony was inoculated in 100 ml of sterile Luria broth (Sigma; L 3522) and incubated at 37 °C for 18 h to obtain a stationary phase culture. Cells were harvested by centrifugation at 855 x g for 14 min and washed three times with pre-distilled Milli Q filtered water. Finally, the pellet was resuspended in sterile pre-distilled Milli Q filtered water and the CFU/ml were calculated by the method of Ho and Somasegeram (1982) following incubation at 37 °C for 18 h to obtain a stationary phase culture. The samples were incubated at 37 °C for 14 min and washed three times with pre-distilled Milli Q filtered water. Finally, the pellet was resuspended in sterile pre-distilled Milli Q filtered water and the CFU/ml were calculated by the method of Ho and Somasegeram (1982) following incubation at 37 °C for 18 h. Where less than 10 colonies/plate were observed, the data were expressed as a function of time.

2.5. Photodegradation of isopropanol

Isopropanol was used as a test chemical contaminant because it has been reported to photodegrade to acetone readily in a reaction that is amenable to gas chromatography analysis (Fujishima et al., 2000). Isopropanol and 1-butanol (Sigma Aldrich), were used as received. A solution of stock isopropanol (1000 ppm) was made using deionised water. This was diluted down to 100 ppm for photodegradation purposes and 30 ml of this solution was transferred to a bottle of the control and irradiated groups at the beginning of each experiment and at each sampling interval. These volumes were diluted in a series of 10-fold dilutions and plated on Luria agar (Sigma; L 3147) and the CFU/ml were calculated by the method of Ho and Somasegeram (1982) following incubation at 37 °C for 18 h. Where less than 10 colonies/plate were observed, 250 μl of the neat sample was transferred to a plate using the spread plate technique. The colonies were then counted and multiplied by four to convert to CFU/ml. The limit of detection of this method is approximately 4 CFU/ml.

3. Results

3.1. Inactivation of *E. coli* K12

Representative data for the variation of bacterial population within a variety of 1000 ml SODIS and SPC-DIS reactor configurations during solar exposure is shown as a function of time (Fig. 1(a)) and solar UV (300–400 nm) dose (Fig. 1(b)).

![Fig. 1. Comparison of inactivation of *E. coli* K12 samples for 1000 ml batch-process SPC-DIS and SODIS reactors exposed simultaneously to natural sunlight at the Solar Platform in Almeria, Spain as a function of time. (b) The same data expressed in terms of UV dose (300–400 nm) received. To avoid confusion, representative error bars are displayed on only one plot in each graph.]
Several consistent trends were observed throughout this series of comparisons:

1. SPC-DIS reactors fitted with the flexible TiO₂ acetate inserts achieved complete bacterial inactivation (i.e. below the limit of detection = 4 CFU/ml) in approximately 75% (77.3% ± 3.3%) of the time required for the corresponding identical SODIS reactor to achieve the same level of inactivation. Similarly the cumulative UV dose (kJ) required to achieve complete inactivation in the SPC-DIS reactor was approximately 75% (74.4%±4.1%) of that required for the corresponding SODIS container. These results were obtained for both Pyrex® borosilicate glass and PET plastic containers and for reactor volumes of 1000, 500 and 250 ml.

2. The annealed TiO₂ SPC coating on glass was not effective. The times and doses required for complete inactivation were approximately 20% larger (18%±8.8% and 21%±8.4%, respectively) for the SPC coated reactors than their corresponding uncoated SODIS counterparts.

3. Borosilicate glass SPC-DIS or SODIS reactors achieved complete inactivation in 80% (±7%) of the time required for PET plastic reactors. Although the glass and plastic bottles hold identical fluid volumes (1000 ml) they have different dimensions and therefore each bottle presented different effective surface areas to the sun (145 and 176 cm², respectively). Consequently, despite being exposed simultaneously, the glass and plastic bottles received slightly different cumulative doses of solar UV within the same time period. Nevertheless, having compensated for this (Fig. 1b), borosilicate glass reactors achieved complete bacterial inactivation in only 83% (±7%) of the dose required to achieve similar inactivation in the corresponding PET reactor.

Having identified the optimum SPC-DIS reactor configuration from Fig. 1 as being a flexible TiO₂-coated acetate insert fitted into a borosilicate glass bottle, the effect of SPC-DIS reactor volume on inactivation rate was investigated and the results are shown in Fig. 2.

Inactivation within the 250 ml SPC-DIS reactor was much faster than for the larger volumes (Fig. 2(a)). The bacterial population dynamics of the 1000 and 500 ml SPC-DIS reactor samples are identical within experimental error.

However, if the inactivation is plotted against solar UV dose expressed in Joules, a consistent trend is apparent (Fig. 2(b)) with the dose required for complete inactivation increasing as reactor volume increases. This trend can be more clearly observed in Fig. 2(c) where the volume of the SPC-DIS reactor has been considered by plotting the inactivation against Solar UV dose per litre.

The data is fitted to a first order regression line of slope -1.84 x 10⁻³ log-units per joule per litre (correla-

2.65-2.76)

3.2. Photodegradation of propanol

No photodegradation was observed for 100 ppm isopropanol samples that were exposed in standard
Table 1
Comparison of 130 W UV values as a function of SPC-DIS reactor volume for borosilicate Schott glass Duran bottles

<table>
<thead>
<tr>
<th>Volume (ml)</th>
<th>Diameter (cm)</th>
<th>Height (cm)</th>
<th>Inactivation rate (log units/kJ)</th>
<th>130 W UV (min/log unit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>7.0</td>
<td>8.0</td>
<td>7.3</td>
<td>13.6</td>
</tr>
<tr>
<td>300</td>
<td>9.0</td>
<td>10.0</td>
<td>5.6</td>
<td>17.0</td>
</tr>
<tr>
<td>1000</td>
<td>10.0</td>
<td>14.5</td>
<td>1.8</td>
<td>21.1</td>
</tr>
</tbody>
</table>

4. Discussion

The observed ~25% reduction in inactivation time and UV dose suggests that the advanced oxidative processes (AOPs) caused within the SPC-DIS reactors by the solar UV activated TiO$_2$ creates a hostile environment that accelerates the bactericidal processes. In light of this result studies are currently underway to examine the possibility that SPC-DIS reactors could be used to inactivate biological pathogens that are highly resistant to solar disinfection such as bacterial spores or protozoa (Kilvington, 2003).

The observed photodegradation of isopropanol demonstrates proof of principle regarding the use of batch-process SPC-DIS reactors for the domestic treatment of chemically contaminated drinking water. The mechanism whereby isopropanol is photodegraded to acetone has been described in detail by Hermann (1994). Typically organic chemical contaminant concentrations of ppb would be expected in surface waters in developing world however the kinetics of the conversion to acetone would not be expected to differ significantly from that reported here in the ppm range. Isopropanol was used because its absorption spectrum does not overlap with sunlight (no direct photolysis) and its complete conversion to acetone. This could permit closing the mass balance and avoiding interpretation errors. Furthermore, both isopropanol and its photoproduct acetone are amenable to GC analysis. It is more likely that the chemical contaminants in developing countries would be organic pesticides. Malato et al. (2002) report complete mineralisation of water contaminated with commonly used agricultural pesticides using TiO$_2$ suspensions and compound parabolic solar collectors although these facilitate much better irradiance levels than could be expected using basic batch-process technology. Further studies to examine the kinetics of batch-process SPC photodegradation of organic pesticides, and their photoproducts, are planned. It should be noted that 24 h of continuous simulated radiation was required to achieve the observed reduction in contaminant concentration. It is likely therefore that if natural sunlight is used for treating real waters, samples may have to be exposed over several days to ensure adequate photodegradation. The time required for this would obviously vary with the chemical identity of the contaminant and the local sunshine conditions, but most developing countries in Africa, the Middle East and South America experience excellent sunshine conditions.

SODIS containers. Similarly 100 ppm samples of the photoproduct acetone were unaffected by exposure to simulated sunlight.

The concentration profile for 100 ppm isopropanol samples is shown in Fig. 3 as a function of both exposure time and cumulative UV (300-400 nm) dose. The rate of photodegradation was calculated by linear regression to be 3.9 ppm/h (correlation coefficient $R^2 = 0.987$). This corresponds to 2.1 ppm/kJ of UV in the 300-400 nm range. The rate of photodestruction of acetone was similarly calculated to be 2.3 ppm/h (correlation coefficient $R^2 = 0.864$), which corresponds to 1.3 ppm/kJ of UV 300-400 nm range. The disparity between the rate of decrease of isopropanol and rate of production of acetone suggests some sort of side-reaction or incomplete oxidation.

![Graph of isopropanol and acetone concentration as a function of exposure time and UV (300-400 nm) dose for a 100 ppm isopropanol solution exposed to 100 mW/cm$^2$ of simulated solar radiation in a SPC-DIS reactor fitted with TiO$_2$-coated OHP insert.](image-url)
This has further implications with regard to the number of SPC-DIS reactors required by each user to meet their water demands.

The effect that solar UV induced AOPs, generated at the photocatalyst surface, might have on the PET bottle and acetate support material is not known. Long-term (over 12 months) use of PET SODIS bottles has been shown to give rise to a gradual deterioration of the optical transmission properties of the container material and some degree of photodegradation of the plastic itself (Wegelin et al., 2001). However the photoproducts that were observed in this study were found to reside solely on the outside of the bottle and no photoproducts were detected within the water samples. Nevertheless studies are underway to repeat this work using SPC batch-process reactors fitted with flexible TiO$_2$ coated plastic sheets acetates to evaluate the effect of TiO$_2$ photocatalysis on synthetic plastics (Horikoshi et al., 1998, 1999).

Borosilicate glass SODIS and SPC-DIS reactors require approximately 20% less time and UV energy to completely inactivate the E. coli K12 compared to PET containers. This is likely to result from the more favourable UV transmission properties of the glass compared to PET (Kehoe, 2002). However other factors must be considered before deciding which reactor material should be used. Previous field trials of the SODIS reactors carried out by the authors in Kenya (Conroy et al., 1996, 2001) used plastic bottles only. The main reason for this was that there was no reliable road network connecting the communities participating in the trials and fragile glass SODIS bottles were unlikely to survive the cross-country, off-road journey to the villages.

Whether flexible TiO$_2$ coated plastic inserts could be used in developing countries as a point-of-use intervention is predicated on whether it is possible to produce them using locally available material. It is unlikely that a small rural community in a developing country would have easy access to OHP transparencies, silicone adhesive or TiO$_2$ powder, but these materials would be available in larger nearby towns. There is a strong possibility that SPC-DIS inserts could be manufactured on a "cottage industry" basis and then distributed throughout the rural communities by local aid agencies.

5. Conclusions

Addition of TiO$_2$-coated OHP acetate inserts to standard batch process solar disinfection bottles improves the efficiency of bacterial inactivation by 20-25%. In addition, SPC-DIS-reactors achieve photodegradation of isopropanol and so may be an appropriate technology for the degradation of other chemical contaminants. Flexible TiO$_2$-coated OHP acetate inserts are an affordable and simple technology for use in urban and semi-urban areas within developing countries and warrant further study.

6. Uncited references

Nagame et al. (1989).

Acknowledgements

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References


