The photocatalytic enhancement of acrylic and PET solar water disinfection (SODIS) bottles

J. M. Carey, T. M. Perez, E. G. Arsiaga, L. H. Loetscher and J. E. Boyd

ABSTRACT

The solar water disinfection method (SODIS) was modified by the addition of a photocatalytic layer of titania on the interior surface of polyethylene terephthalate (PET) and acrylic bottles. Titania was solvent deposited on the interior of commercially available PET bottles, as well as bottles that were constructed from acrylic. Uncoated and titania-coated acrylic bottles removed 3,000,000–5,000,000 colony forming units per milliliter of K12 E. coli from 670 mL of contaminated water in 40 min of solar irradiance. After five hours of sunlight exposure, the concentration of 10 ppm methyl orange (a representative organic water contaminant), was reduced by 61% using the titania-coated acrylic bottles. The concentration of 87 ppb microcystin-LR (a representative algal toxin) was reduced by 70% after 7 hours of sunlight exposure in the titania-coated acrylic bottles. Acrylic is an effective alternative to PET for use in the SODIS method due to its greater UV transparency. The addition of titania to PET and acrylic bottles confers the ability to remove chemical contaminants in addition to inactivating microbiological contaminants.

Key words | bacteria, chemical contamination, photocatalysis, SODIS, titania

INTRODUCTION

Poor drinking water quality is a major global issue, particularly in developing nations. One commonly used method for drinking water treatment is known as solar water disinfection (SODIS). In this approach, microbiologically contaminated water is placed inside common polyethylene terephthalate (PET) bottles, which are then exposed to sunlight for a period of several hours. The UV-A radiation from the sun, in conjunction with direct solar heating, results in the inactivation of pathogens in the water. Despite its disinfection capabilities, SODIS is unable to treat chemically-contaminated water (Meichtry et al. 2007). Another limitation to the conventional SODIS method is the relatively modest ultraviolet transparency of PET. Glass has also been utilized as a SODIS bottle material, but the fragility and weight of glass bottles as compared to PET bottles make them less desirable despite the generally good UV transparency of borosilicate glass (Duffy et al. 2004). The SODIS method is highly dependent upon the UV transparency of the bottle material and further investigation into the optimal bottle composition is warranted.

Titania photocatalysis is an alternative water purification method that is capable of inactivating microbiological agents, as well as removing chemical contaminants from water. Titania is a photocatalyst that is often investigated for water purification purposes because it is cheap, nontoxic, stable, and widely available. Titania is activated by the absorption of UV light (λ < 400 nm), generating excited electron-hole pairs which drive redox reactions in aqueous media. Degussa P-25 is widely considered to be the benchmark titania photocatalyst and is 80% anatase and 20% rutile, with an average particle size of 30 nm (Carlson et al. 2007).

Due to the nanoscale nature of the photocatalyst, post-use filtration to remove titania is not a trivial or practical process for most applications. A more practical approach is to deposit the photocatalyst on a fixed surface, such as glass (Sobczyński & Dobosz 2001), acrylic (Carlson et al. 2007) or PET.
(Meichtry et al. 2007) prior to use. This approach eliminates the need for post-irradiation treatment.

Previous efforts have been made to combine the SODIS method with titania photocatalysis, a technique known as solar photocatalytic disinfection. Duffy et al. (2004) and Lonnen et al. (2005) coated acetate sheets with titania for insertion into borosilicate glass and PET bottles. Duffy et al. reported significantly better performance from titania modified glass bottles than from titania modified PET bottles and attributed this to the greater UV transparency of the borosilicate glass materials. Meichtry et al. (2007) applied titania to various materials (glass rings, glass rods, and porcelain beads) that were then placed inside PET bottles. Titania suspensions were also dispersed over the interior walls of PET bottles and allowed to dry, leading to uniform titania coatings on the inside walls of the bottles. That study showed that the direct application of titania onto the interior walls of PET bottles was greatly superior to the utilization of glass supports within the bottles. Ongoing efforts at optimizing the plastic material used, and comparing half-impregnated bottles with fully coated bottles were also noted (Meichtry et al. 2007).

The SODIS method uses PET for several reasons, not the least of which is its widespread commercial availability. It is moderately UVA-transparent, chemically stable, lightweight, and durable. Acrylic exhibits these same characteristics, albeit with better UVA transparency, and serves well as a support material for titania photocatalysis (Carlson et al. 2007). In the study described here, titania-coated bottles, both PET and acrylic, were tested in order to assess their ability to remove microbiological and chemical contaminants from water with solar illumination.

**EXPERIMENTAL**

**Materials**

Titania (P-25) was supplied by Degussa Inc. Square (7.5 × 7.5 × 14 cm) PET bottles (Nalgene) were purchased from Fisher Scientific. Acrylic (poly(methyl methacrylate)) bottles were constructed from Acrylite OP-4 acrylic (Cyro Industries) with a thickness of 4.76 mm. Trichloroethylene (Spectrum), 89% aqueous phenol (Mallinckrodt), sodium hydroxide (Fisher), dichloromethane (Spectrum), methanol (Spectrum), and methyl orange (Amend) were all used as received. K12 *Escherichia coli* was obtained from Carolina Biological Supply as were the nutrient broth used for culturing bacteria suspensions and the agar used to plate bacteria samples. Microcystin-LR was purchased from Calbiochem.

A Millipore MilliQ A-10 system was utilized to purify the water used in all experiments (18.6 MΩ·cm).

**Methods**

**UV-transparency of support materials**

The UV-visible absorbance spectra of the PET and OP-4 acrylic were collected using a StellarNet EPP2000 fiber optic spectrometer.

**Titania deposition on PET bottles**

Titania was solvent deposited onto two of the four “vertical” interior faces of the PET bottles. The solvent mixture consisted of 5 mL of 89% aqueous phenol and 3 mL of trichloroethylene. This mixture was poured inside each bottle, which was then rotated until the solvent had been dispersed over the desired half of the interior. The excess solvent was poured from the bottle, and 0.5 g of titania was placed in the bottle. With vigorous shaking, a uniform coating of titania was achieved on the half of the bottle that had come in contact with the solvent. Titania did not adhere to the half of the bottle that was not exposed to the solvent. All bottles prepared in this manner were then vigorously washed several times with water to remove loose titania. Following the deposition of the titania, the interior of the bottles retained a strong, pungent phenolic odor, and the titania layer was yellow. In order to remove the residual phenol, a 1% aqueous NaOH solution was placed inside each titania-coated bottle and allowed to stand until the color of the titania had changed from yellow to white. The NaOH was then poured out, and the bottles were thoroughly rinsed with water. The bottles (with the lids removed) were subsequently placed between two 400-W Hg-vapor lamps situated 80 cm apart. The bottles were alternately exposed to the light while filled with water and while empty. These steps were taken in order to allow the titania to photocatalytically degrade the excess phenol. This process, which lasted a total of 150 h, was continued until the phenol odor had subsided. The final mass of deposited titania on each bottle averaged 0.30 g, providing an average titania thickness of 1.4 mg/cm².

**Construction of acrylic bottles**

Each acrylic bottle was constructed from a 31.8 cm × 12.1 cm sheet of acrylic. For the construction of titania-coated acrylic bottles, half of one side of the sheet of acrylic was masked off, and the other half was sandblasted.
This sandblasted surface was then thoroughly cleaned with water and methanol. As described by Carlson et al. (2007), titania was solvent deposited onto the sandblasted region of the acrylic using a mixture of dichloromethane and methanol as the solvent. An average of 0.24 mg of titania was deposited on three acrylic bottles for a film thickness of 1.1 mg/cm². The titania-coated portion of the acrylic sheet would later become the interior surface of the acrylic bottle.

The interior of a PET bottle was used to form a solid concrete casting that was utilized as the template for forming the acrylic bottles. After the PET had been cut away from the cured concrete casting, the acrylic sheets were warmed with a heat gun in order to thermoform them to the surface of the concrete mold. The ends of the sheet were then solvent welded together using dichloromethane. Two flat plates of acrylic were solvent welded to the top and bottom of the bottle to serve as the base and the lid. A hole was drilled through the top plate and fitted with a rubber stopper. In this way acrylic bottles were formed with geometries that effectively matched that of the original PET bottles.

Solar illumination studies

All solar experiments were conducted on the rooftop of the laboratory facility on essentially cloudless days during June, 2009 in Plainview, Texas (latitude 34° 11’ 50” N, longitude 101° 43’ 31” W, altitude 1,052 m). Solar spectra were collected using a calibrated cosine receptor (model CR2) with the StellarNet spectrometer. The UV irradiance, integrated from 300 to 400 nm, averaged 144 W/m² during the solar exposure experiments. The ambient outside temperatures during the experiments ranged from 30 to 53 °C. The solution temperatures started at 22 °C and ended at 53 °C. A 2.5 cm wide vertical black stripe was painted on the exterior edge of each bottle to facilitate thermal convection within the bottles due to localized solar heating. For control purposes, even the unmodified bottles were constructed with the black thermal stripe. Meera & Ahammed (2008) have previously shown that black-backed bottles have superior SODIS performance. Simple reflectors, designed to mimic the metallic roofing materials often used in SODIS applications, were constructed from wooden frames covered in aluminum foil. These L-shaped wooden frames, used for all solar experiments, were 41 cm long, 32 cm tall, and 17 cm deep. Each reflector was large enough to provide a reflective background for three bottles. For each experiment, the reflectors and bottles were oriented perpendicular to the solar illumination, and were reoriented at each sampling interval to maintain that orientation. Titania-coated bottles were positioned so that the uncoated halves were facing the sun and the coated halves were facing the reflectors. The black stripes were facing toward the reflectors, and thus the black stripe could absorb only the light that either was transmitted through the bottles, or was directed onto the back of the bottle by the reflective background. Three separate bottles of each type were used in each experiment except for the experiments involving microcystin-LR (MLR). The high cost of this toxin necessitated the use of a single bottle with triplicate sampling rather than three distinct bottles of each type. Each series of experiments (bacteria, methyl orange (MO), and MLR) was performed so that the acrylic and PET bottles, both modified and unmodified, were studied simultaneously under identical illumination and thermal conditions. However, the E. coli, MO, and MLR experiments, were each performed on different days. Solar experimentation began at 10:00 AM for each data series.

For each experiment, the bottles were filled with 670 mL of solution. This left a 2 cm air gap at the top of each bottle after the bottles were sealed. In order to mimic typical SODIS applications, the bottles were not stirred or shaken during each sampling procedure, and agitation was minimized as much as possible.

Microbiological study

E. coli cells were cultured in nutrient broth at 37 °C for 15 h. Cells were then washed three times with centrifugation for 15 min at 3,200 rpm. Cells were resuspended in 0.9% (w/v) aqueous NaCl solution to achieve final concentrations of 3 × 10⁶ – 5 × 10⁶ colony forming units per milliliter (CFU/mL). These suspensions were introduced into the PET and acrylic bottles prior to solar illumination. Due to the large initial bacteria concentrations, it was necessary to dilute the samples taken directly from the bottles prior to agar plating. For the first three sampling periods (0 min, 10 min, and 20 min) a 1:2,500 dilution was made. At 40 min and 60 min, a 1:1,250 dilution was made. At the 90 min, 120 min, and 180 min periods, 1:750, 1:500, and 1:250 dilutions were made, respectively. Subsequently, 0.1 mL samples were taken from each diluted sample and spread on agar plates. All samples taken from the dark controls were diluted 1:2,500. These plates were incubated at 37 °C for 20 h, and the bacteria colonies were manually counted. The detection limit for the microbiological analysis was 10 CFU/mL for undiluted samples.

Organic dye degradation

Aqueous solutions of 10 ppm MO were introduced into the PET and acrylic bottles. After placement of the bottles in
direct sunlight, samples were collected each hour for five hours. These samples were placed in 1 cm cuvettes, and the optical density at 463 nm was used to determine the MO concentration.

Algal toxin degradation

The PET and acrylic bottles were filled with 90 ppb aqueous solutions of MLR. During the solar experiment, samples were collected every hour for 7 hours. The samples were analyzed using a Shimadzu Prominence HPLC. The analyses utilized an isocratic mobile phase that was 65% 7 mM ammonium acetate buffer solution, and 35% acetonitrile. The flow rate was 1.5 mL/min, and the injection volume was 200 µL. Analysis was performed with a diode array detector at 240 nm. The detection limit and limit of quantitation were estimated to be 1 ppb and 3 ppb respectively.

RESULTS AND DISCUSSION

Characterization of support materials

The UV transparency of the bottle walls is very important for SODIS applications (Meichtry et al. 2007), and for photocatalytic support materials (Carlson et al. 2007). Whether the chemical or microbiological degradation occurs photolytically or photocatalytically, the UV irradiance available will affect the reaction rate. The UV-visible spectra of the PET and acrylic materials are shown in Figure 1. OP-4 acrylic is transparent down to 260 nm, whereas PET begins to strongly absorb at around 350 nm. This is of great importance since titania is only capable of utilizing light with λ < 400 nm. There is thus a significant amount of solar UVA radiation available for photolysis and/or photocatalysis which is absorbed by the PET bottles but transmitted through the acrylic bottles. Although the solar spectrum has negligible intensity below 300 nm, acrylic bottles allow the transmission of solar illumination in between 300 and 350 nm that would be absorbed by a PET bottle. It would thus be expected that the acrylic bottles would outperform PET bottles in pure SODIS applications as well as when modified with a photocatalyst.

The solvent deposition technique used to adhere the titania to polymeric surfaces has been shown to result in very durable and photocatalytically active surfaces, and the highly crosslinked nature of the acrylic used is additionally beneficial in minimizing photocatalytic attack of the acrylic surface with prolonged application (Carlson et al. 2007). As noted by Meichtry et al. (2007), the use of half-coated titania bottles allows for enhanced collection of solar light, and thus half-coated bottles were used in this study after preliminary tests showed greater photocatalytic success with half-coated bottles than with fully coated bottles (data not shown). Half-coated bottles also allow for much thicker titania films which is advantageous for complete utilization of the incident illumination. The film thicknesses reported herein (1.1–1.4 mg/cm²) thus are much greater than those used by Meichtry et al. (0.009–0.010 mg/cm²) in their fully coated bottles. The use of organic solvents in the titania deposition process is certainly a potential environmental and toxicological concern for SODIS applications. However, the remarkable adhesion strength of the solvent deposited titania layers (Carlson et al. 2007) could at least partially offset that negative aspect of this deposition strategy through bottles with longer usable lifetimes. It is clear that prior to actual field testing of acrylic SODIS or acrylic-titania bottles with human consumers, potential health risks of using these materials would need to be performed analogous to the work done previously with PET SODIS bottles (Schmid et al. 2008).

Microbiological study

The results of the E. coli study are shown in Figure 2. The acrylic SODIS bottles significantly outperformed their PET counterparts. For both the acrylic SODIS and acrylic-titania bottles, the bacterial concentration dropped below the detection limits after 20–40 min of solar illumination. The bacterial concentration in the dark control was unchanged during the experiment indicating that there was no direct toxicity from residual phenol, a known antimicrobial agent, in the PET SODIS bottles. In the illuminated PET SODIS and PET-titania bottles, inactivation occurred after 40–60 min of
solar exposure. Figure 2 also shows that the addition of titania to the bottles does not increase the rate of *E. coli* inactivation. This is an indication of the marked susceptibility of this bacterial strain to UV attack. It is not clear that this would be true for all microbiological species such as cyst-forming parasites. Furthermore, the solar experiments reported herein were performed with temperature conditions (final temperature of 53°C) which are known to drastically increase SODIS rates. Further investigations are required to determine if photocatalytic modification of these bottles confers enhanced antimicrobial activity with other microbiological species or at other temperatures. It is clear, however, that with *E. coli* K12 under the conditions tested, that the SODIS bottle composition itself is far more important to the bacterial inactivation rates than the addition of the photocatalytic titania layer.

**Organic dye degradation**

MO was chosen for this study due to its ubiquity in the photocatalytic literature and because its substantial UVA absorbance makes it a fairly recalcitrant target for photocatalytic degradation when the illumination is supplied to the photocatalyst through the reactor solution (Loetscher et al. 2009).

The degradation of 10 ppm MO utilizing the PET and acrylic bottles is shown in Figure 3. No substantial decline in the concentration is evident in the unmodified SODIS bottles, indicating the resistance of MO to direct UV photolysis. Minimal adsorption onto the titania or plastic surfaces was indicated by the dark control experiment. However, significant levels of degradation were observed in the illuminated titania-coated bottles. The extent of degradation was greater in the acrylic-titania bottles than in the PET-titania bottles. This result can be attributed to the greater UV-transparency of the acrylic. Table 1 provides first order rate constants for the degradation of MO in each illuminated sample calculated from the data in Figure 3. The importance of the photocatalytic titania film within the bottle, as well as the significance of the bottle-wall composition are both highlighted by the comparison of these rate constants.

**Algal toxin degradation**

Although MO is a commonly used species for photocatalytic degradation studies, it is perhaps not the ideal model for SODIS bottle drinking water purification since it is highly unlikely to be present in field applications where the SODIS

![Figure 2](https://iwaponline.com/wst/article-pdf/63/6/1130/445565/1130.pdf)

**Figure 2** Inactivation of *E. coli*. Each data point represents the average of three samples from three separate bottles. Error bars represent one standard deviation. The data is truncated at 90 min for clarity. No bacterial concentration changes occurred after 90 min.

![Figure 3](https://iwaponline.com/wst/article-pdf/63/6/1130/445565/1130.pdf)

**Figure 3** Degradation of methyl orange. Each data point represents the average of three samples from three separate bottles. Error bars represent one standard deviation.

**Table 1** Pseudo first order rate constants for the degradation of methyl orange and microcystin-LR

<table>
<thead>
<tr>
<th>Rate Constants (h⁻¹)</th>
<th>Methyl Orange</th>
<th>Microcystin-LR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylic – SODIS</td>
<td>0.0156</td>
<td>0.0167</td>
</tr>
<tr>
<td>Acrylic – Titania</td>
<td>0.175</td>
<td>0.170</td>
</tr>
<tr>
<td>PET – SODIS</td>
<td>0.00947</td>
<td>0.00530</td>
</tr>
<tr>
<td>PET – Titania</td>
<td>0.101</td>
<td>0.132</td>
</tr>
</tbody>
</table>
technique is most likely to be used. The algal toxin microcystin-LR is produced by many strains of algae including Microcystis, Anabaena, and Nostoc (Sangolkar et al. 2006). MLR is present in many surface drinking water sources, is a known hepatotoxin, and has been the focus of many water purification studies including chlorination (Acero et al. 2005; Rodríguez et al. 2008), oxidation with KMnO₄ (Bourne et al. 2006; Rodríguez et al. 2008), and photocatalysis (Cornish et al. 2000; Liu et al. 2002; Shephard et al. 2002; Lawton et al. 2003; Antoniou et al. 2008). In order to evaluate the ability of the modified and unmodified SODIS bottles to degrade a relevant drinking water contaminant, MLR was also utilized for the characterization of these bottles.

Figure 4 shows the photocatalytic degradation of 87 ppb MLR using the PET and acrylic bottles. No decline in the toxin concentration was observed in the absence of illumination. The PET SODIS bottles also demonstrated negligible MLR degradation, while the acrylic SODIS bottle did show a very small amount of photolytic degradation. Significant degradation was seen in both PET and acrylic titania-modified bottles. As with the MO, the extent of this degradation was greater in the acrylic-titania bottles than in the PET-titania bottles. Table 1 also summarizes the first order rate constants for the degradation of MLR in each illuminated sample calculated from the data in Figure 4. The faster degradation rate using the acrylic-titania bottles can again be attributed to the higher level of UV-transparency in the acrylic bottles. MLR was markedly degraded using the titania-modified SODIS method, whereas the unmodified SODIS bottles were incapable of doing so regardless of bottle composition.

CONCLUSIONS

SODIS has proven to be an effective, low-tech solution to providing improved drinking water in places where more cumbersome, technologically advanced, and energy consumptive approaches are just not practical. However, it is not capable of degrading most chemical contaminants and is also limited in its effectiveness by the UV-transparency of the bottle walls. In this report we have shown that the photocatalytic enhancement of the SODIS method does provide the capacity for degradation of chemical contaminants even though it may not accelerate the inactivation of microbiological contaminants. Furthermore, substantial benefits can be gained by using highly UV transparent polymeric bottle materials in both SODIS and photocatalytically enhanced SODIS applications.

The solvent deposition of titania films on the interior walls of acrylic and PET bottles come with the likely disadvantage that such bottles could not easily be prepared by indigenous people groups lacking technological sophistication. The ease and cost-effectiveness with which the conventional SODIS approach can be implemented is admittedly central to the success of the SODIS method in field applications. Unlike the nearly ubiquitous PET bottles, acrylic bottles are not widely available to consumers in economically developing countries. The current study does, however, indicate substantial benefits to using both more transparent SODIS materials, and photocatalytically enhanced bottles as well. The photocatalytic modification described herein and the utilization of more UV-transparent materials as opposed to conventional PET bottles combine to make a more expensive and complex process, but the benefits described herein warrant further investigation and consideration of titania-modified acrylic bottles for drinking water sterilization and purification.

ACKNOWLEDGEMENTS

We thank Degussa for the donation of the P-25 titania used for this study. This research was funded in part by a Departmental Research Grant from the Welch Foundation (Grant No. BW-0044).

REFERENCES


