Improving Solar Water Disinfection (SODIS) with a Photoreactive TiO$_2$/SWCNT Composite on Plastic PET Bottles

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Abstract

Approximately 1.1 billion people in the world lack access to safe drinking water, an issue that causes two million deaths a year due to waterborne diarrheal diseases. Solar disinfection (SODIS), a point-of-use water treatment method that uses UV radiation in sunlight to kill pathogenic organisms, was discovered by Professor Aftim Acra in the early 1980’s. Because SODIS relies largely on weather conditions, its efficiency varies greatly. The purpose of this study was to improve SODIS by coating plastic PET bottles with a TiO$_2$ and a TiO$_2$/SWCNT composite, a photocatalytic nanomaterial that exhibits strong antibacterial activity. Water samples were collected from the Quinnipiac River in Wallingford, CT and transferred into the bottles to be tested for bacteria at time intervals of 0 min., 180 min., and 360 min. of sun exposure. Two trials were performed with the same bottles to test for bottle reusability, and bacterial concentrations were determined through serial dilutions and plate counting. Results show that the TiO$_2$/SWCNT composite coating was the most effective in meeting EPA standards, preventing bacterial growth in optimal temperatures, and producing strong coatings. The TiO$_2$/SWCNT composite coating did kill more bacteria as hypothesized, but the full 360 min. of sun exposure was required.

Introduction

Water is essential for life, yet an inadequate supply of clean drinking water plagues an estimated 1.1 billion people worldwide. In the 1980’s, Professor Aftim Acra discovered solar disinfection (SODIS), which uses UV radiation in natural sunlight to kill pathogenic organisms. SODIS requires filling water into plastic polyethylene terephthalate (PET) bottles and leaving them in the sun, making it a simple, environmentally sustainable, and virtually costless technology. But despite its advantages, SODIS alone still faces certain challenges. Because it relies largely on specific weather conditions, its efficiency varies greatly. Due to widespread poverty and varying weather conditions around the world, many countries that lack clean water are located outside of the boundaries where SODIS is most effective. SODIS alone also does not provide residual protection against bacterial regrowth, as bacteria quickly grow back if disinfected water is stored for a long time and not immediately consumed.

To improve SODIS, this study utilizes titanium dioxide (TiO$_2$) as a coating on plastic PET bottles. TiO$_2$ is a metal oxide with many unique properties, including high photocatalytic activity, biological and chemical stability, lack of toxicity, strong oxidizing activity, and low price. Single-walled carbon nanotubes (SWCNTs) are also used; when combined with TiO$_2$ in a composite, SWCNTs not only provide a larger surface area but also trap electrons transferred from TiO$_2$, further enhancing oxidation and antibacterial potential.

The independent variable in this study is the type of coating, while the dependent variable is the concentration of bacteria found in the water. It is hypothesized that the TiO$_2$/SWCNT composite coating will enhance the SODIS process by killing more bacteria and decreasing the required sun exposure time. The results from this study will be valuable in the development and application of low-cost, energy-efficient, and environmentally-friendly methods of water purification for developing countries.

Materials and Methods

Synthesis of TiO$_2$ and Composite Suspensions: The bottles were coated using a 10% w/v suspension. The TiO$_2$ suspension consisted of 1g Acros Organics titanium (IV) oxide anatase powder and 10mL deionized water; the composite suspension consisted of 50mg Strem Chemical Inc. single-walled carbon nanotubes (SWCNTs) and 200mL water. 950mg TiO$_2$ powder was then added. The suspension was sonicated and heated until the water evaporated. One gram of dried composite was added to 10mL deionized water and sonicated for 30 min. Bottle Preparation and Coating: The bottles were rinsed, filled with river water, sonicated for 1 hour, and dried for 48 hours at room temp. The suspensions were introduced into the bottles and shaken to obtain a homogenous film over the bottle wall. The bottles dried after 24 hours at room temp, and then they were half-filled with water and shaken for 30 sec. to ensure no coating detached before use. Exposure to Sun: Nine bottles were tested: 3 blank controls, 3 TiO$_2$ coating, and 3 TiO$_2$/SWCNT composite. The bottles were filled with river water, placed inside an aluminum foil-covered solar reflector box, and left in the sun. Water samples were collected aseptically at 0, 180, and 360 min. The irradiation test was then repeated using fresh river water. Dilutions and Plate Counting: Water samples of 1.5mL were collected aseptically in micro-centrifuge tubes. This was the 0x dilution (original sample). 100µL of this 0x sample were plated onto an agar plate with micropipette, and the cells were spread evenly using a metal cell spreader. Successive dilutions of 900mL sterilized water and 100µL of the previous dilution were also plated. Plates were incubated for 3 days and colony-forming units were counted. Absorbance Measurements: Samples were analyzed for absorbance and transmittance with a Vernier LabQuest probe and Red Tide Spectrometer. Spectrometer cuvettes were filled ¼ and light was shined on the samples. Absorbance was converted into % transmission using an absorbance-%transmittance chart. 

Statistics: Two-sample t-tests were performed on a TI-83 graphing calculator to compare the bacterial concentrations remaining in the bottles after the 360 min. irradiation test. The t-statistic, p-values, and degrees of freedom are reported.
**Results**

In trial 1, bacterial concentrations decreased substantially throughout the irradiation test. The blank control, the TiO$_2$, and the composite started with average concentrations of 8500 cfu/mL, 34000 cfu/mL, and 13333 cfu/mL, respectively (Figure 1). At 180 min., the TiO$_2$ and composite bottles decreased to below half of the initial concentration, but the blank control still had roughly 63% of its initial bacterial concentration (Figure 2). At the end of the test, both TiO$_2$ and the composite had less than 6% of their original concentrations (Figure 2). The control, however, still had roughly 30% of the initial bacteria remaining, demonstrating the benefits of the photocatalysts (Figure 2). Only the composite met the Environmental Protection Agency (EPA) standard of 500 cfu/mL of coliform bacteria in water (Figure 1).

In the second trial there was no continuous decrease in bacterial concentration. The control, the TiO$_2$, and the composite bottles started with an average of 3000 cfu/mL, 5500 cfu/mL, and 1800 cfu/mL, respectively (Figure 3). At 180 min., the blank control and TiO$_2$ reached 250% and 150% of the initial concentration, respectively (Figure 4). The cause of the increase is believed to be the increase in water temperature. The composite bottles, however, prevented growth, averaging just 33% of its original concentration at 180 min. (Figure 4). After 360 min., the blank control bottles still had 93% of its initial concentration, ending essentially where it began (Figure 4). The TiO$_2$ performed slightly better, but the benefits of the composite were evident as it ended with just 8% of its original concentration (Figure 4). The average bacterial concentration in each type of bottle at the end of 360 min. is graphed in Figure 5. The error bars represent standard error, calculated by dividing the standard deviation by the square root of the number of measurements. Again, only 2-3 measurements were available for the calculation of standard deviation and standard error.

![Figure 1. Average bacterial concentrations in all bottles from 0-360 min. during trial 1.](image1)

![Figure 2. Normalized ratio of bacterial concentrations in all bottles from 0-360 min. during trial 1.](image2)

![Figure 3. Average bacterial concentrations in all bottles from 0-360 min. on 9/19/10.](image3)

![Figure 4. Normalized ratio of bacterial concentrations in all bottles from 0-360 min. on 9/19/10.](image4)
Discussion

The purpose of this study was to improve the SODIS method of water treatment by testing the antibacterial activity of two types of photocatalyst coatings, one of TiO$_2$ and the other of a TiO$_2$/SWCNT composite, on plastic PET bottles. Analysis of the bacterial concentrations of river water contained in the coated bottles throughout two trials of a 360 min. irradiation test yielded the conclusion that both the TiO$_2$ and the TiO$_2$/SWCNT composite coatings were able to kill more bacteria than the blank control bottles alone, but the full 360 min. of sun exposure was needed. Complete sun is not necessary, as there was evidence that the photocatalyst-covered bottles were able to reduce bacterial concentrations even in partly cloudy weather. Generally, higher temperatures aid the disinfection process, but results from the second trial demonstrated that high temperatures may also serve to incubate the bacteria and increase concentrations.

There were many benefits to the TiO$_2$/SWCNT composite coating, as opposed to the blank or the TiO$_2$ coatings. First, only the composite was able to reduce concentrations to below the EPA standard of 500 cfu/mL$^6$. Additionally, the TiO$_2$/SWCNT composite coating was able to prevent incubation and increases in bacterial concentration, continually killing bacteria even in temperatures optimal for bacterial growth. Finally, the TiO$_2$/SWCNT composite produced a more durable coating than the TiO$_2$ with Pluronic sulfactant, experiencing little to no coating loss after 360 min. the irradiation test.

In conclusion, the TiO$_2$/SWCNT composite coating seems to be the best option in terms of meeting EPA standards, preventing growth in optimal temperatures, and producing a strong coating. More trials are needed to confirm reliability and consistency of data through meaningful statistical analyses. Further investigation is necessary to determine the feasibility of the material in terms of cost and potential toxicity.

Sources of Error/Improvements

The most significant source of error is evident in the wide variation of initial bacterial concentrations in the different types of bottles. One possible explanation is that the nanomaterials themselves, particularly the TiO$_2$, were contaminated prior to the irradiation rest. In the future, this could be avoided by heat or pressure sterilizing the nanomaterials in an autoclave. However, the sterilization conditions would have to be examined to ensure that the structures of the chemicals were not altered in the sterilization process. It is important to note that despite generally higher starting points, the photocatalyst-coated bottles still killed more bacteria and ended with lower bacterial concentrations than the blank control bottles, demonstrating the effectiveness of such materials. The cost effectiveness as well as the availability of resources for mass production are important considerations for the implementation of the nanomaterials.

It was also difficult to position the bottles within the solar reflector box so that each bottle received the same sun coverage. Air and water temperature could have varied in different parts of the box, suggesting slightly different amounts of sun exposure depending on where in the box each bottle is placed. This inconsistency can be corrected by rotating the bottles within the box at specific time intervals so that each bottle is not always located in the same spot.
Further improvements can be made by testing additional time intervals instead of just 0 min., 180 min., and 360 min. Taking samples more frequently would provide a better comprehensive picture of bacterial concentrations in the water during the 360 min. irradiation test. As always, additional trials would be helpful to gain a better understanding of the mechanisms behind the SODIS process.

**Directions for Future Research**

There are many materials with antibacterial potential to improve SODIS. Investigation into additional nanomaterials such as antimicrobial peptides, chitosan particles, nano-silver compounds, zinc oxide, and fullerenes could yield promising alternatives for point-of-use water disinfection. Metal doping of titanium has also shown potential in past studies.

It would be helpful in future studies to identify the species of bacteria present in the river water at the start of the irradiation test and the species remaining at the end of the test. Besides certain species of indicator bacteria, perhaps there are certain types of bacteria against which SODIS and the TiO₂/SWCNT composite are more or less effective. One test for bacterial identification is the API 20E, an 18-24 hour identification test kit that distinguishes between certain Enterobacteriaceae and other gram negative bacteria.

Much is still unknown about the toxicity of these nanomaterials. Research into the effects of these materials on lab animals and ultimately humans is needed before consumption of these materials can be risked. TiO₂ and SWCNTs have shown exciting antibacterial activity, but many steps remain before they can be implemented into SODIS or other methods of water disinfection.

**References**


