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Development of a field enhanced photocatalytic device for biocide of coliform bacteria

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ABSTRACT

A field enhanced flow reactor using bias assisted photocatalysis was developed for bacterial disinfection in lab-synthesized and natural waters. The reactor provided complete inactivation of contaminated waters with flow rates of 50 mL/min. The device consisted of titanium dioxide nanotube arrays, with an externally applied bias of up to 6 V. Light intensity, applied voltage, background electrolytes and bacteria concentration were all found to impact the device performance. Complete inactivation of *Escherichia coli* W3110 (~8×10^3 CFU/mL) occurred in 15 sec in the reactor irradiated at 25 mW/cm^2 with an applied voltage of 4 V in a 100 ppm NaCl solution. Real world testing was conducted using source water from Emigration Creek in Salt Lake City, Utah. Disinfection of natural creek water proved more challenging, providing complete bacterial inactivation after 25 sec at 6 V. A reduction in bactericidal efficacy was attributed to the presence of inorganic and organic species, as well as the increase in robustness of natural bacteria.

Introduction

According to the Outdoor Industry Association, more than 140 million Americans make outdoor recreation a priority in their daily lives, including 82% of Utah residents (~2.4 million people) (Outdoor Industry Association, 2012). Much of Utah's outdoor recreation takes place in remote locations, making the consumption of water from natural sources more desirable than carrying excessive amounts of water; however, natural sources have the potential to contain bacteriological contaminants such as *Escherichia coli*, harmful itself and an indicator of the presence of other disease-causing bacteria. Although there are a variety of point-of-use alternatives for purifying source water, they have their disadvantages. The technology described herein utilizes a solar-driven oxidation reaction to inactivate bacteria rather than chemical oxidation (extended treatment times and unpleasant taste), physical filtration (costly pumping, need to replace filters), or ultraviolet disinfection (expensive parts) in currently available commercial products. Table 1 shows the characteristics of the most popular treatment methods currently on the market, along with the SolaPur device. The photocatalytic titania used for the reaction is non-toxic and non-consumable. The device used in this study treated over 380 L without a decrease in performance indicating that the photocatalytic titania substrate will not likely require frequent replacement.

Titanium dioxide (TiO_2) is a solid-state photocatalyst that produces reactive oxygen species (ROS) when exposed to ultraviolet radiation (<387 nm) (Fujishima and Honda, 1972). When TiO_2 is irradiated with sunlight, the UV portion of the

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Table 1 – Comparison of water disinfection systems.

	Filters	Ultraviolet (UV)	Iodine/chlorine	SolaPur
Mechanism	Physically blocks agents	Alters cellular components	Chemical sterilization	Photocatalysis/ photoelectrocatalysis
Effective against	Bacteria, protozoa	Bacteria, protozoa, viruses	Bacteria, protozoa (some), viruses	Bacteria, chemicals
Treatment time (per liter)	<1 min	1.5 min	5 min to 4 hr	~1.5 hr
Investment/volume treated	>$60/1000–5000 L	>$90/4000 L	<$0.50/1 L	< $0.50/1 L
Weight	>10 oz	>5 oz	<1 oz	< 10 oz
Disadvantages	Breakable components; replacement parts requirement.	Easily breakable; batteries requirement.	Poor taste; chemical expiration; consumed.	Slow treatment time

spectrum causes the formation of electron–hole pairs. The photogenerated charges can react with water molecules, forming ROS, such as •OH radicals, leading to bacterial inactivation via physical destruction of the cell membrane (Matsunaga et al., 1985; Pelaez et al., 2012). TiO_2 induced photocatalytic (PC) inactivation has been studied with both suspended and immobilized nanoparticles (Alrousan et al., 2009; Kim et al., 2013; Matsunaga and Okochi, 1995; Rincón and Pulgarin, 2003; Sunada et al., 2003; Wei et al., 1994; Wolfrum et al., 2002; Wu et al., 2008). Rincón and Pulgarin (2003) found that suspended TiO_2 nanoparticles (TNPs) had slightly higher biocidal activity rates than Nafion® supported TNP coated membranes. It was suggested that the support structure could have played a role in the recombination of the electron–hole pairs, which would lead to lower radical formation and biocidal activity (Rincón and Pulgarin, 2003). However, immobilization of TiO_2 is typically preferred if the material is to be reused, as TNP suspensions can be difficult to implement into devices where separation of the material from the water is needed before consumption.

Inherently immobilized TiO_2 nanotubes can be easily formed through the anodization of titanium metal. Anodically formed TiO_2 nanotube arrays (TNAs) are also beneficial as they can be created on any titanium morphology, which also provides better connectivity to the metal substrate (Butterfield et al., 1997; Nie et al., 2014; Smith et al., 2013). Connectivity is especially important in a photoelectrocatalytic (PEC) cell, where an anodic bias is applied to the titanium substrate of the TNA for improved efficiency. Driving photogenerated electrons away from the surface reduces electron–hole pair recombination, increasing the time and concentration of holes that can react with water molecules to form radicals or directly oxidize bacteria. It also prevents the TNA from becoming negatively charged, eliminating any electrostatic repulsion that the negatively charged bacteria would have to overcome (Gerischer, 1993).

Consumer devices using this technology have not yet been established due to long treatment times (typically observed in batch reactors) or low throughput (i.e. microfluidic chambers). This research has led to the development of an economical device that is ideal for portable, point-of-use applications, such as backpacking. The following reports the study on a flow reactor that combines PEC inactivation with electroporation for the inactivation of *E. coli* W3110. Parameters such as contact time, lighting conditions, applied voltage and NaCl concentrations were investigated. Additionally, in-situ testing was conducted at Emigration Creek at Rotary Glen Park in Salt Lake City, Utah to evaluate the efficacy of the system in a real-world setting with natural surface water.

1. Materials and methods

1.1. *Device formation*

The flow reactor, shown in Fig. 1, contains polylactic acid (PLA) channels (4 mm width and 4 mm height spaced approximately 8 mm apart) with a stainless steel back plate and a UV transparent polystyrene faceplate. The anodically formed photocatalytic TNAs wire (0.28 mm diameter, 1 m long) was placed within the PLA channel at a distance 0.2 mm from the back plate, with a portion exposed to allow for connection to the power supply. The titanium wire (ESPI metals, 99.7% Ti) was cut to size, ultrasonically cleaned in a 1/1 (V/V) methanol/isopropanol solution and then chemically polished in an acetic acid solution. Anodization was performed at 30 V for 60 m in 96.5 wt.% ethylene glycol, 0.5 wt.% ammonium fluoride, and 3 wt.% deionized water using mechanical stirring and a Pt gauze (52 mesh) cathode. After anodization, samples were rinsed with methanol and ultrasonicated in deionized (DI) water. The amorphously formed nanotubes (NTs) were crystallized at 500°C for 2 hr in a reducing nitrogen and hydrogen atmosphere. The nanotubes used in the device were designed to incorporate a large overpotential, so that water splitting was not visually observed on the TNA anode with a 50 mL/min flow at 6 V. The TNA surface was examined after annealing using a scanning electron microscope (S-4800, Hitachi, Japan).

1.2. *E. coli preparation*

E. coli W3110 was selected as the model bacteria to evaluate inactivation efficiencies under varying parameters and conditions. Bacterial strains were pre-cultured in Luria Bertani (LB) broth at 40°C for approximately 3 hr while shaking at 200 r/min. The culture was ready when the absorbance indicated that the bacteria were near the peak of the logarithmic growth phase, or an absorbance of ~1.1 (optical density (OD_{600})). The culture was diluted in the appropriate NaCl solution (10, 100, or 1000 ppm) until the