University of Nevada, Reno

# Examining Tantalum-Based Photocatalysts for Photoinactivation of *E. coli*

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by

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We recommend that the thesis
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**Raghavi Anand**

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**Abstract**

*Escherichia coli* (*E. coli*) is a bacterium that contaminates potable water sources, and can cause a host of gastrointestinal infections. It is valuable to explore alternative cost-effective, efficient ways to reclaim wastewater and sterilize potable water outside of the current methods. Solar power is a renewable energy source, which can be harnessed for light-driven processes, applicable in this scenario. Photocatalysts, compounds that are active when illuminated with light, can be used in combination with solar light for photoinactivation of *E. coli*. This work helped to determine if tantalum pentoxide ($Ta_2O_5$) and tantalum oxynitride (TaON) can photoinactivate *E. coli* (DH5-Alpha). The results support the extrapolation that these two tantalum-based oxides have the ability to photoinactivate *E. coli,* but quantification is arduous and challenging. Current laboratory constraints including access to better analytical tools made it difficult to evaluate the hypothesis effectively. Further experiments must be conducted in a controlled manner to verify the results seen in preliminary experiments.

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# Table of Contents

**Abstract** ..... **i**

**Acknowledgements** ..... **v**

**Table of Contents** ..... **iv**

**List of Tables** ..... **vv**

**List of Figures** ..... **vi**

**Introduction** ..... **vi**

**Methods** ..... **5**

Preliminary Analysis & Investigation ..... 5

Reagent Preparation ..... 5

E. coli Sample Preparation & Initial Analysis ..... 6

Tantalum-based Photocatalyst Preparation ..... 6

Photoinactivation Trials ..... 7

E. coli Sample Analysis: Post-Treatment ..... 7

**Results** ..... **7**

**Discussion** ..... **11**

**References** ..... **13**

## List of Tables

Table 1: *CFU Count Following Photoinactivation Treatment*……..…10

## List of Figures

Figure 1: *Excitation of electrons from valence to conduction band*……..3

Figure 2: *XRD of Tantalum Pentoxide and Tantalum Oxynitride*……..8

Figure 3: *SEM Image of $Ta_2O_5$ and TaON*……9

## Introduction

Water sources are often contaminated with various components, like fecal matter and other environmental pollutants (Kaspar et. al. 1990; Smith et. al. 2000; Probert et. al. 2017). This is problematic for groundwater or drinking water sources, especially with the increasing: population, water pollution, natural disasters, and shortage of clean water sources. Photoinactivation is a technique growing in popularity for the disinfection and sterilization of potable water and reclamation of wastewater. This technique is appealing due to its efficiency and cost-effectiveness, especially as it utilizes solar energy, a renewable energy source (Lee et. al. 2012). The photocatalytic sterilization method has garnered much attention in lieu of techniques like heat treatment, ultraviolet ray irradiation, and chemical disinfectant dosage (Horie et. al. 1996). Photoinactivation is an inactivation mechanism consisting of hydrogen peroxide ($H_2O_2$) and oxygen radicals ($O_2\bullet^-$) entering the inner cell by diffusion, and subsequently generating the hydroxyl (OH) radical. This radical causes cell wall damage and then peroxidation of the polyunsaturated phospholipid component of the lipid membrane (Cho et. al. 2004) by reactive oxygen species (ROS). Upon irradiation by ultraviolet (UV) light, the beginning step of photocatalytic bacterial destruction is the excitation of electrons from the valence band to the conduction band of the photocatalyst, followed by the formation of hydroxyl radicals (Christensen et. al. 2003). Previous work in the field has led to the conclusion that OH radicals are crucial for *E. coli* inactivation; in fact, the hydroxyl radical is the primary species involved with inactivation (Horie et. al. 1996; Cho et. al. 2004; Di Paola et. al. 2012). This mechanism is not understood fully, but Singh et al. (2016) recently reported that photocatalysts absorb visible light and adopt an excited state so that they

can affect an electron transfer reaction (also known as a redox reaction). Photocatalysts can also direct the transfer of energy to ground state oxygen to form singlet oxygen, which is responsible for bacterial inactivation.

This project focuses on evaluating the photoactivity of tantalum pentoxide ($Ta_2O_5$) and tantalum oxynitride (TaON). Similar photoinactivation experiments have been conducted numerous times with the photocatalytic material titanium dioxide ($TiO_2$) (Fujishima et. al. 2000; Christensen et. al. 2003; Cho et. al. 2004). In fact, about 75% of the articles published in the last 3 years are related to titanium dioxide ($TiO_2$) (Di Paola et. al. 2012), but tantalum-based materials (specifically $Ta_2O_5$ and TaON) have not been explored further in studies. While titanium dioxide is a non-toxic, cost-effective, and environmentally-friendly material (it's found in powdered donuts and in sunscreen!), there are some drawbacks that exist with the use of this material. That is, $TiO_2$ shows limitations such as photoactivity confined to the ultra-violet (UV) spectrum (Selvaraj et. al. 2015). This photocatalyst also faces difficulty with commercialization due to its lack of photocatalytic activity in the visible light region, capacity for adsorption, stability, uniformity, and separability (Dong et. al. 2015).

Basic information regarding the band model of insulators is necessary to fully understand the background of this project. The energy difference between the valence band and the conduction band is known as the band gap. Most oxide semiconductors, or photocatalysts, generally have a band gap (Fig. 1), which is not too large like that of an insulator, but not too small like that of a conductor.

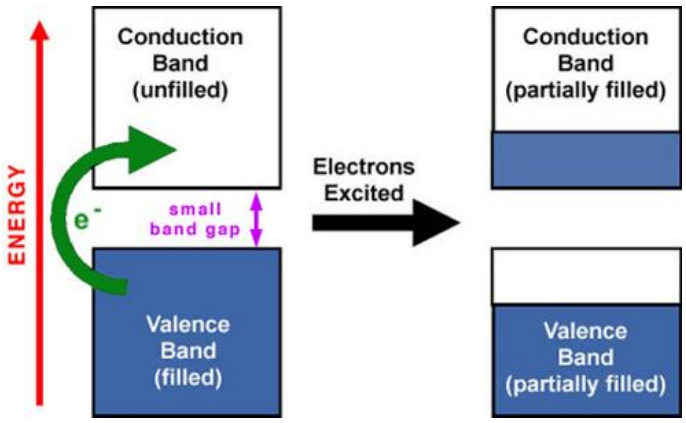


**Figure 1. Excitation of electrons from valence to conduction band**. This figure shows the first step required for photocatalytic bacterial destructions (Frey & Cassiday 2010).

The valence band is the band of lower energy, while the conduction band is that of higher energy; a gap between the two signifies that electrons can be set free only if energy is added to the system. This energy can be in the form of light. Often, researchers will ensure that appropriate elements are chosen to finetune the optical band gap such that it can absorb visible light and increase photocatalytic activity in the system (Selvaraj et. al. 2015). As reported by Cho et. al. (2004), an important step in the generation of an electron-hole pair in the conduction band and the valence band, respectively, involves light absorption. Semiconductors are characterized by a filled valence band and an empty conduction band, where the absorption of a photon of energy larger than that of the bandgap leads to the formation of an electron-hole pair. (Bahnemann 2004). Because of this, it is notable that the edges of the valence bands for the tantalum-based oxides are found to be shifted to higher potential energies on the order of $Ta_2O_5$ < TaON, and thus it is concluded that TaON is a promising catalyst for the oxidation of water (Chun et. al. 2003). This means it has applications in water treatment via light irradiation.

This work aims to determine if the tantalum-based photocatalysts, specifically tantalum pentoxide ($Ta_2O_5$) or tantalum oxynitride (TaON), have the ability to photoinactivate *E. coli*. If so, which one is better at photoinactivation of this bacterium: $Ta_2O_5$ or TaON? The hypothesis is that TaON will perform better due to its smaller bandgap and higher promise in photocatalytic ability. This hypothesis is rooted in calculations for photon energy E (hv) and the excitability of TaON within the visible solar spectrum. Equation (1) (Zhenghua et. al. 2016) allows for the calculation of the wavelength that corresponds to the appropriate band gap energy, where E is measured in electron volts (eV), and λ signifies wavelength of light measured in nanometers (nm). The energy (eV) is the energy that has the potential to excite to the photocatalyst, which is a semiconductor.

(1) $E = 1240 / \lambda$

Recall that the smaller the band gap, the greater the likelihood that the electrons can be excited from the conduction band to the valence band. $Ta_2O_5$ has a band gap of 3.9 eV and TaON has a band gap of 2.54 eV (Wang-Jae et. al. 2003). These values have been verified in the lab with the use of Tauc's plots to obtain the following: $Ta_2O_5$ has a band gap of 3.92 eV and TaON has a band gap of 2.54 eV (Khanal, 2018, personal communication). Thus, the maximum wavelength, or minimum photonic energy that can excite $Ta_2O_5$, is about 318 nm. which falls in the UV region of the electromagnetic spectrum. The maximum wavelength, or minimum photonic energy that can excite TaON, is 488 nm. which lies in the visible light region of the electromagnetic spectrum. Considering the fact that the spectrum of solar radiation is largely composed of visible light (~50%) and not UV light (~3%) (Fondriest Environmental Inc. 2014), it would be

preferred that the photocatalyst be excited by visible light rather than UV light. Although $Ta_2O_5$ is not active in the visible light region, the solar radiation still has some UV light so it is worthwhile to test the effect of this photocatalyst as well. The hypothesis and ideal outcome is that TaON electrons can be excited with just sunlight. This reasoning also provides a good justification as to why titanium dioxide is not the photocatalyst of choice. Titanium dioxide ($TiO_2$) has a band gap of about 3.2 eV (Dette et. al. 2014), which corresponds to a wavelength of about 388 nm. This falls in the UV-Vis region of the electromagnetic spectrum. $TiO_2$ has a higher band gap energy than that of TaON.

## Methods

### *Preliminary Analysis & Investigation*

A few trial plates of *E. coli* (DH5-Alpha cells) were grown for familiarization purposes. The main goal of this step is to determine internal contamination levels, if any, and become familiar with the behavior of the bacteria type.

### *Reagent Preparation*

900 mL of liquid Luria broth (LB) was prepared in the autoclave to store for future use. One sleeve of LB-agar plates were prepared for the duration of the experiment. Glassware was sterilized for future experimental use to eliminate any potential sources of contamination. Then, 500 mL of deionized water was sterilized in the autoclave and stored in a glass bottle for further use.

*E. coli Sample Preparation & Initial Analysis*

Wild-type *E. coli* (DH5-Alpha cells) were grown overnight at 37°C in LB broth (Sigma-Aldrich, USA) in a shaker incubator. Liquid LB was inoculated aerobically and anaerobically to test any difference in final results. To determine the bacterial concentration, the solution was spread uniformly on agar plates in duplicate to verify reproducibility. Plates were incubated overnight at 37°C and colony-forming units (CFUs) were counted. These were the control plates.

*Tantalum-based Photocatalyst Preparation*

Tantalum ethoxide was used as a precursor (Sigma-Aldrich, USA) of tantalum ions for the synthesis of both the tantalum-based materials: tantalum pentoxide ($Ta_2O_5$) and tantalum oxynitride (TaON). TaON was obtained after ammonolysis of as-synthesized $Ta_2O_5$ crystals following the unique nitridation technique developed in Dr. Subramanian's SOLAR lab. The materials were synthesized by the graduate student, Vijay Khanal, and the powders were sent for XRD and SEM imaging. Varying concentrations of the two materials were used (0.01 wt%, 0.1 wt%, 1 wt%).

*Photoinactivation Trials*

Trials were conducted in a solar simulator (Oriel Sol1A, Class AAA) fitted with a xenon (Xe) lamp (400 W - 800 W), with an intensity that can be controlled and varied. Four sets of experiments were conducted in duplicate for both $Ta_2O_5$ and TaON, with two varying parameters: photocatalyst concentration and light intensity. 10 mL glass beakers (Fisher Scientific, USA) were used instead of a traditional photoreactor vessel

for simplicity and ability to run multiple trials simultaneously. The beakers were used instead of test tubes due to the increased surface area that the solar light can irradiate. The $Ta_2O_5$/*E. coli* slurry and the TaON/*E. coli* slurry were mixed inside separate test tubes at varying concentrations (wt%). A pipette was used to thoroughly mix contents. The "reactors" were then left open to the air environment inside the solar simulator because the photoinactivation mechanism only proceeds in the presence of oxygen. The "reactors" were then illuminated by the Xe-lamp at desired wattage. Photoinactivation progress was monitored by sampling reactors' contents after an interval of 8-12 hrs.

*E. coli Sample Analysis: Post-Treatment*

Bacterial concentration was calculated by taking into account the amount of solution plated and the amount of photocatalysts present in the solution. The solution of bacteria and photocatalyst was spread uniformly on agar plates in triplicate to verify reproducibility. Plates were incubated overnight at 37°C and colony count was determined by counting CFUs. Results were compiled into a table to determine if colony count had decreased in comparison to the control plates. Results were analyzed for statistical significance and a significant decrease in colony count post-treatment.

## Results

To determine the phase of the crystal structures of tantalum pentoxide ($Ta_2O_5$) and tantalum oxynitride (TaON), an analytical method known as X-ray powder diffraction (XRD) was utilized. XRD provides a "unique fingerprint for each compound"

(Khanal, 2018, personal communication). The graduate student from Dr. Subramanian's lab, Vijay Khanal, was able to provide this data for the project. The XRD (Fig. 2) shows that tantalum pentoxide has a unique crystal structure compared to tantalum oxynitride as evidenced by the intensity (counts), indicating that the photocatalysts will respond to light differently due to their composition.

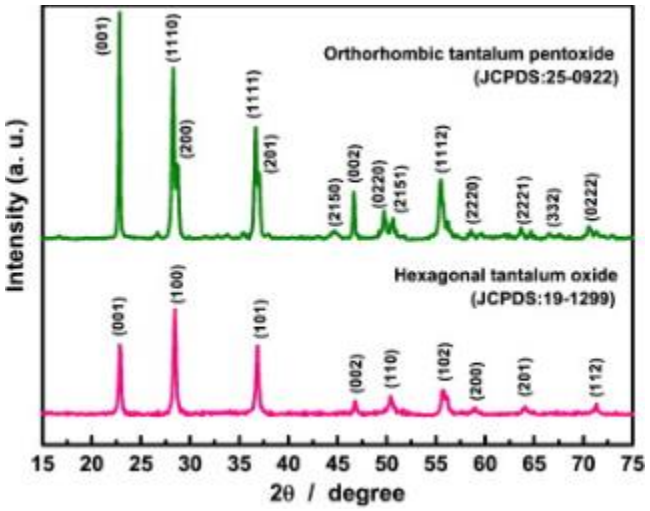


**Figure 2. XRD of Tantalum Pentoxide and Tantalum Oxynitride**. X-ray diffraction of $Ta_2O_5$ powder (green) and TaON powder (pink) are displayed. The intensity, counts, indicates the unique crystalline structure of the two photocatalysts.

Tantalum pentoxide is a white powder and tantalum oxynitride is a yellow powder. The color provides general information about the range of spectra that the photocatalysts are excited by. The color difference demonstrates that the two tantalum-based photocatalysts are excited by different wavelengths (Khanal, 2018, personal communication).

Scanning electron microscopy (SEM) was used to produces microscopic images of the sample to more closely examine the surface topography and composition of both photocatalysts. Figure 3 shows the surface topography of the photocatalysts that were utilized in this experiment. As evidenced by the figure, the surface topography of either

photocatalyst varies greatly, which could lend to its performance in this experimental application.

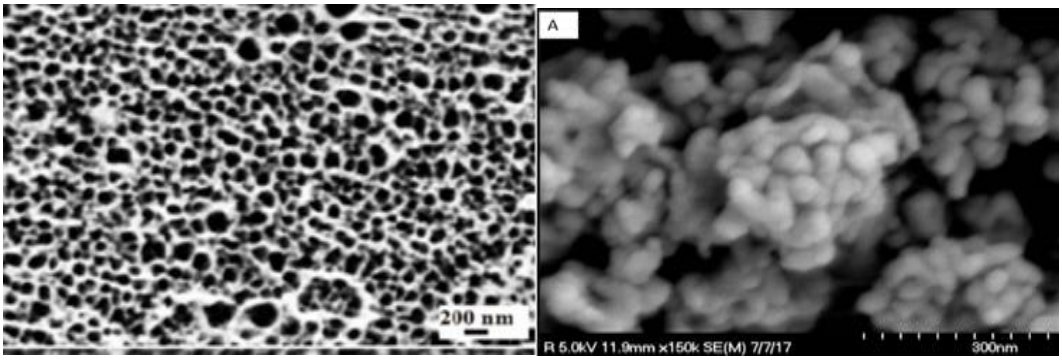


**Figure 3. SEM Image of $Ta_2O_5$ and TaON.** The images above show the surface topography of tantalum pentoxide (left) (Minagar et. al. 2015) and tantalum oxynitride (right).

Several preliminary trials were performed to determine the optimization parameters for the photoinactivation trials. Evidence from 7 trials supports that the optimized concentration of the photocatalyst in sterile water was around 0.01 g/10 mL (or 0.01 wt%), the optimal intensity for the solar simulator was 500 W, and the optimal run time for the photoinactivation trials was 7 - 8 hours. The photocatalysts sediment to the bottom of the beaker at higher concentrations and longer run times, to the point where there is no predicted useful interaction between *E. coli* and the photocatalyst. At intensities greater than 500 W, the solar simulator chamber tends to heat up leading to an unfavorable environment for bacterial survival.

Anaerobically grown *E. coli* were used in the first set of photoinactivation trials. Plating of these bacteria following the 7.5 hour trial run time showed that TaON produced a positive result. Compared to the control plate that underwent the same treatment as $Ta_2O_5$ and TaON, it is evident that there are fewer bacterial colonies after treated with TaON in the photoinactivation trial. The $Ta_2O_5$ plate looked similar to the control plate and did not seem to show any noticeable reduction of *E. coli* bacterial

colonies. While anaerobically grown bacterial cultures yielded sufficient colonies, it proved important to cultivate aerobically grown bacterial colonies, as *E. coli* survives best in aerobic environments. Moreover, the photoinactivation mechanism only proceeded in the presence of oxygen.

Table 1 shows the number of colony-forming units (CFUs) following the treatment of the photocatalyst added, suggesting that $Ta_2O_5$ works as a photoinactivator.

**Table 1. CFU Count Following Photoinactivation Treatment.** The table below shows the average number of CFUs across trials following treatment of the photocatalyst, in which the first row is the control.

| Photocatalyst Added | Concentration (in mg/mL) | Avg. Count of CFUs |
|---|---|---|
| None | 0 | 1132 |
| Tantalum oxynitride (TaON) | 0.1 | 1888 |
| Tantalum pentoxide ($Ta_2O_5$) | 0.11 | 228 |

All the colonies formed on the control plate were medium-sized and easy to distinguish from one another. The colonies formed on the plate following the TaON treatment were incredibly small, approximately ¼ of the size of a control colony, and more difficult to count. The colonies formed on the plate following the $Ta_2O_5$ treatment were much larger and spaced farther apart.

**Discussion**

Overall, it can be extrapolated from the results in this experiment to say that tantalum-based oxides certainly have the ability to photoinactivate *E. coli*, but quantification is arduous and challenging. Tantalum oxynitride shows promise as a photocatalyst that can be applied for photoinactivation of *E. coli*. Tantalum pentoxide does not seem to produce the same response as tantalum oxynitride, as initially predicted. This has potential applications in reclamation of wastewater and sterilization of potable water. However, more controlled experimentation is essential. Current laboratory constraints, including access to better analytical tools, have made it difficult to evaluate the hypothesis effectively.

There was significantly less initial starter culture (of liquid LB inoculated with *E. coli*) for the photoinactivation trials conducted with $Ta_2O_5$, which could have lent to the significantly fewer number of colony forming units associated with those trials. In other words, $Ta_2O_5$ might have the potential to photoinactivate *E. coli*.

Future experiments can investigate the addition of additives and explore the results of compound functionalization. Additives include quantum dots (e.g. CdS or CdSe) (Robel et. al. 2006), graphene (e.g. graphene oxide or GO, reduced graphene oxide or rGO, etc.), a combination of both quantum dots and graphene (Lin et. al. 2010), or addition of other metal nanoparticles (Merka et. al. 2014, Subramanian et. al. 2001), which have been shown to increase the photoresponse of a compound or system. For example, the incorporation of graphene oxide (GO), a single layer of graphite, or reduced graphene oxide (rGO), a reduced form of GO, into a photocatalyst increases the photo-response of the system (Selvaraj et. al. 2014). In this case, GO or rGO, could

produce a greater reduction in colonies post-treatment. Functionalization, on the other hand, allows for the photocatalyst to be chemically modified (also known as doping) (Aroutiounian et. al. 2005) with various functional groups, like amines, phosphorus, or bismuth to ultimately enhance its photoactivity.

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