NANOSTRUCTURED PHOTOCATALYSIS
FOR WATER PURIFICATION

by

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A thesis submitted in conformity with the requirements
for the degree of Masters of Applied Science
Graduate Department of Civil Engineering
University of Toronto

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Nanostructured Photocatalysis for Water Purification

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Degree of Masters of Applied Science
Convocation 2013

ABSTRACT

The integration of photocatalytic advanced oxidation into solar disinfection is a robust method of improving the microbial and chemical quality of treated water. This study evaluates the performance of photocatalytic solar irradiated batch reactors through an analytical model that reduces treatment parameters by simplifying photoreactor geometry and relating performance to reactor configuration. Accompanying experiments compare the performance of titanium dioxide coated foams of varying pore size to suspended and fixed film configurations through degradation of organic dyes (acid orange 24 and methylene blue), Escherichia coli, and 1,4-dioxane. Results indicate that a catalyst immobilized on a foam support can match the performance of a suspension due to effective mass transport and association between analyte and foam. Additionally, the potential treatment capacity of solar photocatalysis was compared to conventional treatment methods. Results of this comparison stress the fundamental limitation of solar photocatalysis if visible light wavelengths are not harnessed.
ACKNOWLEDGMENTS

The thesis presented here is a culmination of two years work involving the efforts of many supportive and talented individuals. Funding for the work was generously provided by the National Sciences and Engineering Research Council Chair in Drinking Water Research, the Southern Ontario Water Consortium, and the Ontario Graduate Scholarship program.

Foremost, I would like to acknowledge my supervisors, Dr. Ron Hofmann and Dr. Susan Andrews, for their enduring support and guidance. The diversity and comprehensiveness of your combined knowledge in the areas of chemistry, biology and engineering was an invaluable asset throughout this process. The complementary nature of your supervision styles, as well as your seamless teamwork and communication, made this a wonderful experience. I cannot thank both you enough for your advice, support, accessibility and kindness. I’d also like to thank Dr. Bob Andrews for introducing me to the Drinking Water Research Group and for your enthusiasm in all things water.

Thank you to all my colleagues in the Drinking Water Research Group for being such truly excellent, fun, smart and supportive people. I’d like to particularly acknowledge Jim Wang and Jules Carlson for their help developing GC-MS methods; Tania Lungo, Jennifer Lee and Sabrina Diemert for their fantastic technical and administrative support; and Lizbeth Taylor Edmonds for all things biology. You succeeded against all odds in convincing me that microbiology is more than just “goo” and have instilled in me a true curiosity and admiration for this field. Additional thanks to my officemates and conference teammates, Heather, Jacque-Ann, Nick, Sara, Chunkei, Steph, Clare and Ola for your encouragement, sage advice, pep talks and general positive vibes.

The support of my family and friends has been integral to this work. Thanks to my brother Matt for his unique and inspirational words; and to my Howland homes for feeding me and really understanding the concept of a good study jam. Finally, I’d like to dedicate this thesis to my parents. You are both wonderful, incredibly supportive, intelligent, and caring. If I keep working hard, maybe one day I’ll be able to beat you at Scrabble.
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<table>
<thead>
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<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>Al₂O₃</td>
<td>alumina or aluminum oxide</td>
</tr>
<tr>
<td>AOP</td>
<td>advanced oxidation process</td>
</tr>
<tr>
<td>AO24</td>
<td>acid orange 24</td>
</tr>
<tr>
<td>°C</td>
<td>degrees Celsius</td>
</tr>
<tr>
<td>CaFe₂O₄</td>
<td>calcium iron oxide</td>
</tr>
<tr>
<td>CdS</td>
<td>cadmium sulphide</td>
</tr>
<tr>
<td>CO₂</td>
<td>carbon dioxide</td>
</tr>
<tr>
<td>CT</td>
<td>contact time</td>
</tr>
<tr>
<td>D</td>
<td>barrier/wall thickness</td>
</tr>
<tr>
<td>DBP</td>
<td>dibutyl phthalate</td>
</tr>
<tr>
<td>e⁻</td>
<td>photogenerated electron</td>
</tr>
<tr>
<td>EDC</td>
<td>endocrine disrupting compound</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protection Agency</td>
</tr>
<tr>
<td>eV</td>
<td>electron volt; 1 eV = 1.602 × 10⁻¹⁹ J</td>
</tr>
<tr>
<td>F</td>
<td>solar flux</td>
</tr>
<tr>
<td>GC-MS</td>
<td>gas chromatography-mass spectrometry</td>
</tr>
<tr>
<td>h⁺</td>
<td>photogenerated electron hole</td>
</tr>
<tr>
<td>H</td>
<td>hour angle</td>
</tr>
<tr>
<td>H·</td>
<td>hydrogen radical</td>
</tr>
<tr>
<td>H⁺</td>
<td>hydrogen ion</td>
</tr>
<tr>
<td>H₂</td>
<td>diatomic hydrogen</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>hydrogen peroxide</td>
</tr>
<tr>
<td>Hv</td>
<td>photon of light energy</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>J</td>
<td>joules</td>
</tr>
<tr>
<td>K</td>
<td>thermal conductivity</td>
</tr>
<tr>
<td>k_f</td>
<td>formation rate constant</td>
</tr>
<tr>
<td>k_o</td>
<td>oxidation rate constant</td>
</tr>
<tr>
<td>k_r</td>
<td>recombination rate constant</td>
</tr>
</tbody>
</table>
K
Kelvin

kg
kilograms

kJ/m²
kilojoules per square meter

L
liter

LED
light emitting diode

m
mass

MB
methylene blue

MgFe₂O₄
magnesium iron oxide

Nₐ
Avogadro’s number; \( Nₐ = 6.02 \times 10^{23} \)

nm
nanometer

NOM
natural organic matter

NTU
Nephelometric Turbidity Unit

O₂
diatomic oxygen

O₂⁻
oxygen radical/superoxide

OH⁻
hydroxide ion

OH⁻
hydroxyl radical

OOH⁻
hydroperoxide radical

PAE
phthalate ester

PPI
pores per inch

PCP
personal care products

PET
polyethylene terephthalate

PhAC
pharmaceutically active compounds

Pr³⁺:Y₂SiO₅
praseodymium activated yttrium silicon oxide crystal

PV
photovoltaic

PVC-UV
photovoltaic powered ultra-violet light

PVC-Cl₂
photovoltaic powered chlorine generator

Q
energy flow rate

R
reactant

S₀
solar constant

SA
surface area

SEM
scanning electron microscope
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>silica or silicon oxide</td>
</tr>
<tr>
<td>SiO₂/CrOₓ</td>
<td>silica-chromium oxide composite</td>
</tr>
<tr>
<td>SODIS</td>
<td>solar disinfection</td>
</tr>
<tr>
<td>T</td>
<td>time</td>
</tr>
<tr>
<td>T</td>
<td>temperature</td>
</tr>
<tr>
<td>TiO₂</td>
<td>titania or titanium dioxide</td>
</tr>
<tr>
<td>TiO₂/PdO</td>
<td>palladium-modified nitrogen-doped titanium dioxide</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>UV-A</td>
<td>low energy UV light (315 to 400 nm)</td>
</tr>
<tr>
<td>UV-C</td>
<td>high energy germicidal UV light (200 to 280 nm)</td>
</tr>
<tr>
<td>W</td>
<td>watts</td>
</tr>
<tr>
<td>W/m²</td>
<td>watts per square meter</td>
</tr>
<tr>
<td>WHO</td>
<td>World Health Organization</td>
</tr>
<tr>
<td>WO₃</td>
<td>tungsten trioxide</td>
</tr>
<tr>
<td>Xe</td>
<td>xenon</td>
</tr>
<tr>
<td>ZnFe₂O₄</td>
<td>zinc iron oxide</td>
</tr>
<tr>
<td>Δ</td>
<td>declination</td>
</tr>
<tr>
<td>Θ</td>
<td>solar zenith angle</td>
</tr>
<tr>
<td>T</td>
<td>transmittance</td>
</tr>
<tr>
<td>Φ</td>
<td>latitude</td>
</tr>
<tr>
<td>Δ</td>
<td>change in</td>
</tr>
<tr>
<td>Φ</td>
<td>radiant flux</td>
</tr>
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1 INTRODUCTION AND RESEARCH OBJECTIVES

The global distribution of safe drinking water is insufficient and the lack of clean water can have far reaching debilitating effects on a community. Limited access to water and contaminated water sources result in an overall decrease in quality of life related to the uncontrolled spread of disease and chronic illness (WHO 2011). These consequences of living without water security have become evident in developing rural and urban communities where centralized public water supply systems have not been implemented or have failed to produce water safe for consumption. In these areas, point-of-use or household treatment options may be the most reliable solutions as they simplify the overall treatment process and reduce the risk of recontamination (EAWAG & SANDEC 2002). Solar Disinfection (SODIS), the process of disinfecting contaminated waters through the exposure of polyethylene terephthalate (PET) bottles to direct solar radiation, has been widely implemented as a household water treatment solution. SODIS has been a valuable and successful concept owing to its ease and simplicity of application; however, the process is sensitive to turbidity and solar flux conditions, and does not improve the chemical quality of water (Byrne et al. 2012). Therefore, an ideal enhancement to the SODIS method would be a process which could improve its resiliency to source water quality and environmental conditions without hindering its accessibility.

The integration of photocatalytic advanced oxidation into the SODIS method has been proposed as a comparatively robust method for improving both the microbial and chemical quality of SODIS treated water (Byrne et al. 2012, Blanco et al. 2009, Shannon et al. 2008, Lonnen et al. 2005). The insertion of a powdered suspension of TiO₂ photocatalyst in SODIS bottles has been shown to increase the rate of microbial inactivation and improve the chemical quality of the water (Dunlop et al. 2011, Lonnen et al. 2005, Pelaez et al. 2012, Zhang et al. 2010). Although suspended systems are an efficient configuration for employing the photocatalyst, due to concerns regarding re-use, ascetics and health, the catalyst must be removed before consumption which may require the application of a chemical treatment or fine filter which are unlikely to be cheaply available and complicate the purification process (Gumy et al. 2006, Plantard et al. 2011). Therefore, the simplicity required for the effective implementation of point-of-use water treatment for rural and impoverished communities is most practically achieved for photocatalysis enhanced SODIS by integrating the catalyst in an immobilized configuration.
The efficiency of photocatalytic advanced oxidation is affected by factors that are highly divergent at the nanoscale (surface area, number of reaction sites, absorption energy and interaction with light) leading to new opportunities for improving and optimizing this application through nanostructured materials (Liu et al. 2011; Li et al. 2012; Li & Shang 2008). Immobilization of photocatalytic nanoparticles on foam supports is considered attractive because the porosity, high surface area, low density, high permeability and translucency of these materials promote higher efficiency photocatalytic reactions.

Our study focuses on comparing the water purification performance of solar irradiated batch reactors with photocatalyst configurations in suspension, fixed films and immobilized on foam supports. Configurations are compared through both modeling and experimentation. The analytical model developed reduced the parameters involved in photocatalytic treatment by simplifying the reactor geometry and developing a set of equations that relate treatment performance with reactor configuration. To accompany this model, experiments were conducted that compared the performance of titanium dioxide coated foams of varying pore size to suspended and thin film configurations. Performance was evaluated by measuring the degradation of a wide range of pollutants including organic dyes (acid orange 24 and methylene blue), \textit{Escherichia coli}, and 1,4-dioxane in a batch reactor under simulated solar radiation.

Although solar photocatalysis has been heavily researched for its application in low cost and low energy production of clean water, it is a fairly new technology and therefore has often been overlooked in past investigations comparing point-of-use treatment options (Burch & Thomas et al. 1998, Ibeto et al. 2010, Mintz et al. 2001). When photocatalysis has been considered, it was generally agreed to be too cost prohibitive in its current state, but that more research is needed to bring the technology to fruition (Furqua 2010, Malato et al. 2009, Shannon et al. 2008, Byrne et al. 2012, Blanco et al. 2009). Characterizing this potential, which is currently poorly defined, is relevant in order to fundamentally compare photocatalysis to other solar disinfection methods. Therefore, a comparative model has been employed to compare photocatalytic treatment under optimal conditions to various other solar-powered purification methods including photovoltaic powered UV-C lamps, chlorine generators, heat treatment and SODIS. The comparison aims to give perspective to the relevance of research on photocatalytic water treatment and its potential to become economically viable.
1.1 Research Objectives

Analytical theoretical models and bench-scale studies will be undertaken to determine the following research objectives:

1. Develop an analytical model to evaluate the optimal configuration for an immobilized photocatalyst in a semiconductor photocatalyst enhanced SODIS system

2. Evaluate the comparative performance of foams coated with nanoparticles of TiO$_2$, nanoparticle suspensions and fixed film photocatalyst configurations in terms of the degradation of organic dyes (methylene blue and acid orange 24), *Escherichia coli* and 1,4-dioxane in a solar irradiated batch reactor.

3. Create a fundamental framework to compare the theoretical potential of solar photocatalytic purification systems to other various solar powered purification mechanisms including photovoltaic (PV) powered UV-lamps, PV powered chlorinators, water boiling and polyethylene terephthalate (PET) bottle solar disinfection (SODIS).

1.2 Description of Chapters

- *Chapter 2* provides a summary of related background information through a review of literature featuring the following key areas: theory and mechanism of photocatalytic advanced oxidation, various photocatalytic materials and their properties, proposed mechanisms and empirical efficiencies of solar driven disinfection mechanisms, current research in the area of photocatalytic water purification and health concerns related to its applications.

- *Chapter 3* presents an analytical model for characterizing the performance of immobilized photocatalytic materials and comparing it to the performance of suspension and fixed film configurations.

- *Chapter 4* presents an experimental investigation on the potential of nano-titanium dioxide coated foams of various pore sizes to degrade organic dyes, 1-4 dioxane and *Escherichia coli* in small-scale batch reactors under simulated solar radiation.
Chapter 5 presents a model comparing the purification potential of solar photocatalytic systems to conventional small-scale solar water treatment methods.

Chapter 6 summarizes the significant findings of this research and provides recommendations for future work.

1.3 REFERENCES


Swiss Federal Institute of Environmental Science and Technology (EAWAG) and Department of Water and Sanitation in Developing Countries (SANDEC) (2002) Solar Water Disinfection: A Guide for the Application of SODIS.


2 LITERATURE REVIEW

2.1 FUNDAMENTALS AND THEORY

2.1.1 Introduction
Nanostructured photocatalytic materials are part of a series of new water purification technologies known as advanced oxidation processes (AOPs) which are characterized by the production of highly oxidizing radical species. These technologies have attracted increasing attention for their application as a method for the oxidation of organic pollutants in the environment, particularly in water systems (Likodimos et al. 2010). The photocatalytic process harnesses light energy to produce oxidizing hydroxyl radicals (OH·) that then react to degrade organic contaminants. This degradation mechanism is associated with a fewer number of toxic byproducts than conventional chemical disinfection and if complete mineralization is achieved can greatly reduce the need for sludge and waste removal (Casbeer et al. 2012; Fujishima & Zhang 2006). The efficiency of a photocatalytic reaction is largely dependent on the surface area and the absorption energy range of the catalyst. Recent studies have shown that these properties are divergent in the nanoscale counterparts of many semiconductor catalysts, therefore, nanostructured materials offer new opportunities for optimizing reaction efficiency and production of oxidative radical species (Liu et al. 2011; Li and Shang 2008; Li et al. 2012).

The application of advanced oxidation by nanostructured photocatalysis for water purification is as an innovative technique for eliminating pollutants in drinking water and waste water because of its ability to quickly and effectively degrade a wide range of contaminants including both conventional and emerging contaminants. This review of the literature will discuss the discovery and development of photocatalysis for water purification including a detailed description of the reaction mechanism, the various materials employed as photocatalysts and their proposed applications. Key areas of current research will be highlighted and mention will be given to environmental and health concerns involved in incorporating nanomaterials and photocatalysis into the water treatment process.
2.1.2 Development of Photocatalytic Materials

It is well known that light can play an important role in the chemical reactions that occur in water systems. Pure water is transparent to visible light and translucent to ultraviolet light, therefore, chemical species and solids suspended in water can interact with photons of these wavelengths. Photocatalytic reactions at the surface of a semiconductor immersed in water were first demonstrated by Fujishima and Honda (1972) using a titanium dioxide (TiO$_2$) electrode. When the TiO$_2$ electrode was connected to a platinum electrode, the hydrolysis of water was discovered on the TiO$_2$ surface and attributed to the following photochemical reaction:

$$\text{TiO}_2 + 2 \text{hv} \rightarrow 2 \text{e}^- + 2 \text{h}^+ \quad \text{Excitation of TiO}_2 \text{ by photons (2.1)}$$

$$2 \text{h}^+ + \text{H}_2\text{O} \rightarrow \frac{1}{2} \text{O}_2 + 2 \text{H}^+ \quad \text{Oxidation at TiO}_2\text{ electrode (2.2)}$$

$$2 \text{e}^- + 2 \text{H}^+ \rightarrow \text{H}_2 \quad \text{Reduction at platinum electrode (2.3)}$$

This reaction scheme was of initial interest for its potential to produce hydrogen gas from water and light in the solar spectrum range (visible and near visible UV) as an alternative energy source to fossil fuels (Li et al. 2011; Fujita et al. 2011). When it later became apparent that the intermediate reactions involved resulted in the production OH radicals, photocatalysis emerged as a popular field for investigating the degradation of pollutants in water (Herrmann 2010; Fujishima & Zhang 2006). TiO$_2$ remains the predominant material of interest for photocatalytic reactions, particularly in water purification applications. Much of the research has focused on altering the material composition or structure in order to improve its efficiency at absorbing visible light photons and thus maximize energy uptake in the solar spectrum (Kisch & Macyk 2002).

As advanced techniques for nanoscale synthesis and imaging began to emerge, nanostructured materials became increasingly popular in photocatalysis research due to the high reactivity attributed to catalytic materials with high surface area to volume ratios. It has also been discovered that decreasing the size of the semiconductor can alter the range of energy wavelengths it absorbs and improve the efficiency of electron hole pair production by preventing recombination within the bulk of the material (Zhang 2012). Discoveries such as these have helped nanostructured photocatalysts gain popularity for potential applications in water purification.
2.1.3 The Photocatalytic Mechanism

2.1.3.1 Electronic Band Structure Theory

The detailed mechanism for photocatalytic oxidation is a complex process that is currently under investigation by many research groups. Presented here is the current best understanding of the reaction mechanism as it can be used to degrade pollutants in water. The basis of the mechanism is related to the electronic band structure theory of solids which describes the electrical conductance of a material. All materials have two energy bands: a lower energy valence band, consisting of the range of energy levels where unexcited electrons exist, and a higher energy conduction band, consisting of the range of energies where promoted electrons can move freely within the atomic lattice. The amount of energy required for an electron to transition between these levels is most conveniently expressed in electron volts, a unit of energy derived by normalizing the potential difference by the charge of a single electron.

The energy band gap of a material is defined as the difference between the highest energy level in the valence band and the lowest energy level in the conduction band. In this gap between energy regions, no electron energy states can exist. The energy that can be absorbed from a photon is related to the wavelength of light by Planck’s relation:

\[
\text{Energy (eV)} = \frac{\text{Plank's constant (eVs)} \cdot \text{speed of light (m/s)}}{\text{wavelength of light (nm)} \cdot 10^9}
\]  

Figure 2-1: Energies of ultraviolet and visible light in the electromagnetic spectrum

The energy band gap of a material is defined as the difference between the highest energy level in the valence band and the lowest energy level in the conduction band. In this gap between energy regions, no electron energy states can exist. The energy that can be absorbed from a photon is related to the wavelength of light by Planck’s relation:
This is an inverse relationship, therefore the shorter the wavelength of light, the more energy it can impart to a material. This relationship is depicted in Figure 2-1 where it can be seen that the wavelength of light decreases from the visible as it moves into the ultraviolet region.

When a photon of energy equal to or greater than the material band gap is absorbed it can excite electrons from the valence band into the conduction band. Figure 2-2 shows the relative size of the energy band gap for conductors, semiconductors and insulators.

**Figure 2-2:** Illustration of the band gap of various materials at room temperature. Band gaps for semiconductors are within the range of 0 to 7 eV, which overlaps with energy of visible light photons and allows a few electrons to exist within the conduction band at room temperature.

The band gap of an insulator is too large to allow electrons to be promoted into the valence band and in a conductor the two bands inherently overlap creating a constant transient flow of electrons in the material. At room temperature an insulator has no electrons that have enough energy to exist in the conduction band, therefore the conduction band is completely full, the valence band is completely empty and no current will arise if an electric field is applied. For semiconductors, the band gap is small enough that at room temperature some electrons will have enough kinetic energy to exist within the conduction band, allowing a small current to flow with an applied electric field (Neamen 1992). Semiconducting materials usually have band gaps in the range of 0 to 7 eV, directly bounding accessible energy levels in the visible and UV light range (Malato *et al.* 2009). For this reason, visible and UV light energy can be used to excite valence band electrons in many types of semiconducting materials.
2.1.3.2 Electron-Hole Pair Production and Migration

When a semiconductor is illuminated with photons of equal or greater energy wavelengths than its band gap, the light is absorbed causing the promotion of excited electrons into the conduction band. When an excited electron jumps from the valence band, it leaves behind an electron hole, which is the positive complement to an excited electron. The photogenerated hole will have an oxidation potential corresponding to the highest point in the valence band and the electron will have a reduction potential corresponding to the lowest point in the conduction band (Yerga et al. 2009). In most cases, these pairs recombine and the photon energy is lost to heat dissipation. However, if the electron or hole becomes trapped by a suitable scavenger or surface defect, the pair can be spatially separated allowing the photogenerated hole to reach the semiconductor surface and react to produce highly oxidizing radical species (Fujishima & Zhang 2006; Malato et al. 2009). These species can then react to oxidize organic pollutants, disinfect microorganisms, and degrade disinfection byproducts (Li et al. 2008). In the specific case of semiconductor photocatalytic degradation of organic pollutants in water, the following reaction scheme has been generally supported (Malato et al. 2009; Casbeer et al. 2012; Likodimos et al. 2010; Vereb et al. 2012; Kaneco et al. 2006):

\[
\text{Photocatalyst} + h\nu \rightarrow e^- + h^+ \quad (2.5)
\]

\[
\text{OH}^- \text{ or } H_2O(\text{surface}) + h^+ \rightarrow \text{OH}^- (+H^+) \quad (2.6)
\]

\[
O_2 + e^- \rightarrow O_2^- + H^+ \rightarrow \text{OOH}^- \quad (2.7)
\]

\[
\text{OH}^- (\text{or } \text{OOH}^-) + \text{organic pollutant} \rightarrow \rightarrow \text{oxidative products} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad (2.8)
\]

The highly reactive radical species, OH\(^-\) (and OOH\(^-\)), which are formed from the excited electron and photogenerated hole, then react as strong oxidizers degrading the pollutant. This reaction mechanism is illustrated in the schematic shown in Figure 2-3. The electron hole can also react directly with the pollutant, however, due to the relatively small concentration of contaminant and the necessity that the pollutant be adjacent to the photocatalyst surface, the reaction scheme involving the production of intermediate radicals is considered to be the far more dominant degradation mechanism (Malato et al. 2009).
Figure 2-3: Schematic for the degradation of contaminants in water by oxidation with radical hydroxyl species. The light energy creates an electron hole pair, which can become spatially separated in the material and form intermediate radicals.

2.1.3.3 Photocatalytic Reaction Kinetics

The reaction kinetics for photocatalytic systems are complex and can vary widely between contaminants, particularly if the water contains mixtures of pollutants. However, empirically the degradation of single pollutants in photocatalytic reactions has been shown to obey first order kinetics following a Langmuir-Hinshelwood (L-H) kinetic scheme (Jing et al. 2011; Malato et al. 2009; Kaneco et al. 2006):

\[
\frac{dC}{dt} = k_r \theta_x = \frac{k_r K C_o}{1 + K C_o}
\]

\( r_o \) = reaction rate
\( k_r \) = reaction rate constant
\( \theta_x \) = fraction of surface covered by the substance
\( C_o \) = concentration of pollutant
\( K \) = reactant adsorption constant
It should be noted that although some of these rate constants in related reaction schemes are known to have physical meaning concerning surface interactions, it has not been verified that the rate constant values for photocatalytic reactions have direct physical meaning. Consequently, the constant $K$ and $k_r$ have to be derived experimentally even though they have been used to model data with correlations > 0.98 (Kaneco et al. 2006; Malato et al. 2008; Yang et al. 2006). Values, such as $\theta_{x}$, have not been proven to be associated with a physical aspect of the photocatalytic reaction mechanism. Empirically applicable rate constants can be found by linearizing the L-H kinetic scheme and plotting the inverse of Equation 2.9 (Kaneco et al. 2006; Malato et al. 2008; Yang & Lee 2006; Son et al. 2009):

$$\frac{1}{r_o} = \frac{1}{k_r} + \frac{1}{k_rKC_o}$$

(2.10)

Each set of rate constants can be determined for a specific photocatalytic reaction. The determined values are expected to predict the degradation of various initial concentrations of contaminants in only the exact conditions in which they are determined; therefore, altering the pH, temperature, radiant flux or catalyst loading of the system will likely result in different kinetic constants.

It seems intuitive that radiant flux ($\Phi$) would be related to the reaction rate and indeed this is observed to be the case in all types of photocatalytic reactions, affirming the key role of photon induced electron-hole pair production. However, empirical studies have found that the order of proportionality will vary, displaying first order linearity ($r \propto \Phi$) at low flux values and then reducing to an order of $\frac{1}{2}$ ($r \propto \Phi^{0.5}$) as the radiant flux increases. This alteration is generally abrupt and is attributed to an excess of photogenerated species, although the exact transition point is poorly defined (Malato et al. 2009).

Simple models have been developed to predict the effect of varying flux on photocatalytic water purification kinetics. Malato et al. (2009) related radiant flux to the production of hydroxyl radicals by analyzing the competitive rate of each reaction involved in the absorption of a photon by the photocatalyst leading to the release of a free electron hole. The three reactions considered are shown below using TiO$_2$ as an example photocatalyst:
Basic assumptions of this model are that the electron hole is the limiting species in the reaction and that every electron hole which does not undergo recombination will form a hydroxyl radical. Considering the mechanism, the instantaneous concentration of electrons and holes will likely be the same, such that $[e^-][h^+] = [h^+]^2$. Therefore, if holes are the limiting species, than according to the above reaction mechanism at any one instant:

$$\frac{dh^+}{dt} = k_f \Phi - k_o [e^-][h^+] R = 0$$

$$[e^-][h^+] = [h^+]^2 \quad \Rightarrow \quad k_f \Phi = k_i [h^+]^2 + k_o [h^+] R \quad (2.15)$$

Radiant flux can be considered in two regimes: a high regime in which an overabundance of electron-hole pairs are produced and a low regime in which each pair produced has readily available reactant. This can be used to simplify the above reaction in two cases:

**High $\Phi$**

$$k_i [h^+]^2 > k_o [h^+] R \quad \Rightarrow \quad [OH^-] = [h^+] \approx k_{high} \cdot \Phi^{1/2} \quad (2.16)$$

**Low $\Phi$**

$$k_i [h^+]^2 < k_o [h^+] R \quad \Rightarrow \quad [OH^-] = [h^+] \approx k_{low} \cdot \Phi \quad (2.17)$$

This scheme is corroborated by the existence of a further regime at the highest intensities in which the reaction is no longer dependent on the radiant flux. In this regime the reaction rate becomes predominantly dependent on the mass transfer within the system (Malato et al. 2009).

### 2.1.4 Benefits of Nanostructured Catalytic Materials

At the nanoscale, reactions begin to occur differently as the size of the material and the wavelengths of light energy begin to converge. In terms of photocatalyst efficiency, the efficiency of the photocatalytic mechanism is aided by the nanostructure of a material in predominantly four ways:

1. Nanomaterials have greatly reduced volume to surface area ratios. Reducing the interior volume of the material decreases the likelihood of reactive electron-hole pairs
recombining within the material by creating more surface defects. This increases the number of oxidizing holes available for reactions with pollutants. Some nanoscale textures, such as organized pores or honeycomb lattices, have also been shown to be able to scavenge and collect released electrons by creating low energy pathways or attractive charge centers, further reducing the risk of recombination (Li & Shang 2008).

2. Increasing the surface area of the material improves photocatalytic activity by increasing the number of available reaction sites. Novel nanostructures such as nanopores can offer more active adsorption sites and photocatalytic centers (Liu et al. 2011; Li et al. 2012).

3. The energy levels in a nanomaterial become more discrete due to the convergence of the material size with the corresponding photon energy wavelength absorbed by the band gap. This means that the range of energies that the material can uptake is widened, and the band gap of the material can be altered by changing its size. When the diameter of the material is on the same order of magnitude as the wavelength of light which can be absorbed by its band gap, the result is an effect known as quantum confinement. Quantum confinement occurs in particles where the number of atoms is small enough that the discrete energy levels within the bands become apparent. This occurs because there are not enough electrons to form a continuous valence or conduction band. Smaller gaps form within the bands, creating an overall widening of the band gap. When the band gap is widened, higher energy photons are required to promote electrons to the conduction band, therefore the range of light energies which are most ideally absorbed by the material is shifted towards the higher energy end of the electromagnetic spectrum (Reddy et al. 2003). This means that the band gap of a nanoscale semiconductor can be altered by varying the size of the particle.

4. Some materials with unique nanostructure have been shown to improve the efficiency of the interactions with light by lengthening the optical pathway, increasing scattering and improving the uptake of slowed photons (Li & Shang 2008).
2.2 CONVENTIONAL PHOTOCATALYTIC MATERIALS

2.2.1 Titanium Dioxide

2.2.1.1 Homogenous Titanium Dioxide

Continuing from the discovery of photochemical splitting of water at the titanium dioxide electrode, TiO₂ has been at the forefront of materials developed for photocatalytic purification processes. TiO₂ is often considered to be a near ideal catalyst due its low cost, chemical stability, good photocatalytic capability and apparent non-toxicity (Hoffmann et al. 1995). Photocatalysts must be able to reverse their valence state to accommodate an electron hole without causing its decomposition; titanium dioxide achieves this through a non-stiochiometric Ti³⁺ → Ti⁴⁺ reaction (Mohamed et al. 2012). TiO₂ crystallizes in three forms: rutile, anatase and brookite. The brookite form is an orthorhombic crystal consisting of TiO₆ octahedra interconnected along three common edges (Osterloh, 2008; Pelaez et al. 2012). The brookite crystal form is stable at only very low temperature and is by far the least common structure, for these reasons it is not considered a useful photocatalyst (Reddy et al. 2002). The far more common rutile and anatase phases both form tetragonal crystal structures with connections at two and four common edges, respectively (Osterloh, 2008; Pelaez et al. 2012).

Figure 2-4: Anatase TiO₂ crystal structure: each TiO₆ octahedron is shared at the four vertices forming [0 0 1] planes
Due to these lattice variations, the rutile and anatase phases differ in their electronic band structure. Their band gap sizes and locations vary slightly with rutile exhibiting a band gap of 3.0 eV and anatase exhibiting a band gap of 3.15 eV. The anatase structure, which is shown above in Figure 2-4, is considered to be the most photoactive phase because the band gap for anatase is ~0.15 eV more negative than for rutile, providing it with a higher reducing power and increasing its ability to produce radical species from oxygen (Han et al. 2011; Osterloh 2008).

For these reasons, the well-known industrial catalyst Aeroxide P-25® (Evonik, Germany) is made predominantly of anatase phase TiO$_2$ (80%) with the remainder comprising of rutile phase TiO$_2$ (~20%). The high photoactivity of this catalyst has been attributed to the particular proportionality of these two phases. The rutile phase, which has a more positive conduction band energy level, can act in conjunction with the anatase phase by trapping the photogenerated electrons produced from the anatase conduction band. This multi-crystal phase interaction can work to reduced recombination by enhancing the separation of photogenerated electrons and holes (Palaez et al. 2012).

Several studies have shown that TiO$_2$ under UV light illumination has been very effective at oxidizing organic pollutants such as pharmaceuticals and endocrine disrupting compounds (Kaneco et al. 2006; Kisch et al. 2002; Fujishima & Zhang 2006; Vereb et al. 2012). As an advanced oxidation process, combination UV/TiO$_2$ has been shown to achieve the same log-inactivation of *E. coli* in a shorter contact time compared to other common methods employing UV and H$_2$O$_2$ (Paleologou et al. 2007). Despite its inherent advantages, there have been two significant drawbacks to employing TiO$_2$ as the catalytic material in water purification applications. The first drawback is the non-optimal band gap of TiO$_2$ for solar applications. The second drawback is the high rate of recombination between photogenerated electron-hole pairs within the bulk of the material (Zhang 2012; Malato et al. 2009). Tackling issues related to photocatalyst efficiency and suppression of electron hole pair recombination is an emerging field which employs various physical modifications to increase surface area, create longer pathways for light, increase reaction sites for the catalytic process and promote reactant transport (Li et al. 2011; Li et al. 2012; Liu et al. 2011).
TiO$_2$ has a non-optimal band gap for solar energy applications (Zhang 2012; Malato et al. 2009). The band gap of unmodified TiO$_2$ has a median value of 3.2 eV, placing its optimum absorption range just outside the visible spectrum (Daude et al. 1977; Fujishima & Zhang 2006; Casbeer et al. 2012, Malato et al. 2009). The overlap between the range of energies absorbed by TiO$_2$ and those emitted within the solar spectrum is depicted in Figure 2-5. Although there is a reasonable overlap, it is clear that TiO$_2$ does not have an ideal band gap for catalyzing photochemical reactions with sunlight. In practice, TiO$_2$ photocatalytic activity is limited to light of wavelength less than 400 nm (more than 3.1 eV) (Li et al. 2008). Due to this inefficient absorption, research has focused on modifying the material to alter the band gap. Several variations, dopants, and nanostructures of TiO$_2$ have been investigated to narrow the band gap and enhance its photocatalytic activity into the visible light range.

![Figure 2-5: Overlap between TiO$_2$ light absorption range and the solar spectrum](image)

**2.2.1.2 Heterogeneous Titanium Dioxide**

The synthesis of metal ion doped TiO$_2$ and nonmetal composite TiO$_2$ structures are the most common alternations made to the catalyst, both with the goal of altering the material band gap. Doping with metal ions creates local energy levels within the band gap of the photocatalyst that allow for electrons to be promoted through intermediate transitions between the valence and conduction bands of the semiconductor. These intermediate energy transitions can have
absorption bands within the visible light range (Fujishima & Zhang 2006). As illustrated in Figure 2-6, the transitions facilitate the generation of electron hole pairs from lower energy wavelengths of light. However, metal ion doping has been shown to be very sensitive to the method of synthesis, with some methods resulting in materials which display negligible photocatalytic activity under visible light and reduced activity under UV illumination. It is hypothesized that in these cases the impurities fill the band gap and create a material that behaves similar to a conductor where there does not exist adequate spatial separation between energy states to prevent recombination (Fujishima & Zhang 2006).

![Figure 2-6: Transition scheme for band gap alterations in modified heterogeneous TiO₂ materials.](image)

Alternatively, doping or forming composites with nonmetals has reported to result in a red shift in the energies that can be absorbed by the photocatalyst (Malato et al. 2009). The red shift, which is a shift towards the red/IR range of the electromagnetic spectrum, is a result of a specific method of band gap narrowing in which the energy level of the highest occupied state in the valence band is raised without alteration to the available promotion states in the conduction band as depicted in Figure 2-6. This shift has been interpreted to occur when the nonmetal acts as a p-type dopant, adding more electron holes and combining its p-type valence molecular orbitals with that of the photocatalyst (Fujishima & Zhang 2006; Kisibi et al. 2008).
2.2.2 Alternative Semi-Conductors

Although there remains a strong potential for effective and environmentally sensible photocatalytic technology to develop from TiO$_2$ derived materials, the challenges of photo-efficiency and non-optimal band gap have prompted exploration into other semiconductors that may have inherent properties more suitable for solar initiated photocatalysis. There exist many semiconductors, mostly complex oxides that have band gaps within the visible light range and maintain the capability to drive advanced oxidation reactions for degradation of organic compounds in water (Song et al. 2008). Figure 2-7 shows a comparison of the band gaps of several semiconductors that have been investigated for their potential as photocatalysts. It can be seen that TiO$_2$ and Zinc derived materials are effective under UV irradiation due to their high energy band gaps, while complex oxides and iron containing compounds such CaFe$_2$O$_4$, MgFe$_2$O$_4$, ZnFe$_2$O$_4$, CdS and WO$_3$ have more narrowed lower energy band gaps that can effectively absorb energy within the visible range (Casbeer et al. 2012).

![Figure 2-7: Band gap of selected semiconductors. (Adapted from Casbeer et al. 2012)](image_url)

When research into photocatalytic materials first developed and the limitations of TiO$_2$ became evident, many of the materials presented here were considered as early stage alternatives. Unfortunately, most early attempts to develop photocatalysts from these materials were failures, many being chemically unstable and others displaying little or no catalytic activity. Consequently, it became generally agreed that no alternative semiconductor could meet the
requirements of efficiency, band gap, chemical stability and photoactivity required to surpass the performance of TiO$_2$ derived materials (Fujishima & Zhang 2006). However, more recent work has shown that the photocatalytic activity of a catalyst can be strongly influenced by a series of previously unconsidered factors such as crystal structure, particle size, dispensability, and hydroxyl surface density (Fu et al. 2012). Encouraged by these insights, previously disregarded materials such as ZnO, NiO, ferrites and cadmium derived materials are being revisited for their photocatalytic potential in various novel crystal forms, composites and nanostructures (Song et al. 2008; Fu et al. 2012; Casbeer et al. 2012; Ouyang et al. 2012). Consequently, alternative materials have re-emerged as a popular research area and the number of promising catalytic semiconductors and complex oxide materials reported in the literature is continuing to expand.

### 2.3 Novel Material Systems

#### 2.3.1 General Considerations

New realizations concerning the structural sensitivities of photocatalytically active materials has spurred additional research aiming to find the optimal material for degrading pollutants in water. When considering the development of new photocatalyst materials, there are several factors that need to be taken into consideration. Some factors commonly identified include: suitable band edge potentials for redox applications, ability to maintain separation of photoexcited electron holes pairs through migration to catalyst surface, energy loss of charge carriers related to transport and recombination, environmental and chemical stability, and toxicity (Yerga et al. 2009; Mohamed et al. 2012). Semiconductors employed in photocatalytic applications must possess certain chemical and physical characteristics to accommodate these considerations. To produce separated electron-hole pairs, the semiconductor’s metallic element must have more than one stable valence state and the catalyst should be able to reverse its valence state to accommodate the introduction of a positive hole without decomposing (Mohamed et al. 2012). Although the size of the band gap must be appropriate to allow excitation from the given light source, it is also known that materials with larger band gaps are more effective because they reflect an increased thermodynamic driving force (Osterloh 2008). Larger band gap materials require higher energy illumination and therefore most new materials attempt to achieve a balance between efficiency and energy requirements.
All wavelengths of light with energies higher than the material band gap can be used to photoexcite an electron, however, the electron’s resultant kinetic energy remains proportional to the band gap (even if promoted by a photon with greater energy) as this additional energy is quickly dissipated (Eisberg & Resnick 1985). Therefore, wider band gap materials intrinsically produce higher energy electron-hole pairs that have a stronger oxidative capacity (Osterloh 2008). In addition, the greater thermodynamic driving force between the electron and the hole, which imparts to them a greater kinetic energy, reduces the likelihood of recombination (Eisberg & Resnick 1985).

The efficiency of smaller band gap materials can be enhanced by improvements to catalyst configuration, crystalline structure or the addition of one-dimensional nanostructures (Peng & Ichinose 2011). It has been determined that crystal structure has a significant impact on photoactivity. The crystal structure of a photocatalytic material must be arranged such that there is an efficient charge transport pathway connecting the interior with the surface to facilitate the separate migration of the electron hole pair (Osterloh 2008). Unique material structures and textures have been increasingly employed to increase photo efficiency. Figure 2-8 shows several scanning electron microscopy (SEM) images of novel nanostructure TiO$_2$ materials that have recently been developed. The high surface area of the porous structures shown in Figure 2-8a-d can offer more active adsorption sites and photocatalytic centers (Liu et al. 2011; Li et al. 2012). The inverse opal structure shown in Figure 2-8e acts to increase the surface area of the material while also providing multiple scattering pathways and harvesting the slow photons that can linger near the edges of its photonic gaps (Li & Shang 2008). These images represent a few examples of novel material structures that have been designed to improve photocatalytic activity. Studies have shown a strong link between catalyst structure and photoactivity that is attributed to variation in surface area, pore volume, reactant/medium diffusivity, transparency to illumination and mass transfer rates from the medium to the photocatalyst (Dagan & Tomkiewicz 1993, Alfano et al. 2000). Research related to determining the optimum catalyst configuration is ongoing.
2.3.1 Visible Light Photocatalysts

Despite the inherent inefficiency of a narrow band gap photocatalyst, the potential to be able to use solar energy as the illumination source is attractive enough that investigating materials for visible light photocatalysis remains a research priority. Investigations are currently underway
that aim to produce new complex oxides, alloys and combination materials that may have enhanced visible light photoactivity. Successes have been achieved with nonmetal dopants to TiO$_2$, particularly with nitrogen, sulfur and carbon (Ksibi et al. 2008, Pelaez et al. 2008, Han et al. 2011, Liu et al. 2012). The most successful metal dopants have been gold and iron (Casbeer et al. 2012; Vereb et al. 2012; Zhang 2011). Investigation of materials doped with heavy metal oxides such as bismuth, tungsten and cadmium have recently been shown to produce effective visible light photocatalysts (Li et al. 2011; Zhang et al. 2011; Ouyang et al. 2012). However, these investigations are tempered by theories relating to the effect of released metal ions into the water that may be causing uncertainties in reported photocatalytic activity as well as potential concerns about the toxic effects of heavy metals in drinking water (Xiong et al. 2011). A new trend in visible light activated novel material composites has been to create materials combining semiconductors and nanostructured carbon such as carbon nanotubes, fullerenes and graphene. In these materials, the carbon acts as a nonmetallic dopant, improving visible light photoactivity. Both graphene and carbon nanotubes are good conductors with high surface areas and high adsorption capacities which makes them excellent dopants and surface supports for semimetal catalysts (Akhavan et al. 2008; Fu et al. 2012).

### 2.3.2 Photocatalytic Foams and Aerogels

Photocatalytic foams and aerogels are two types of catalyst configurations that have been investigated for their application as photocatalytic materials for water purification. These materials are characterized by their very high surface area, high pore volume, very low densities, translucency, complex microstructure and high permeability (Dagan & Tomkiewicz 1993, Plesch et al. 2009). There exist several distinctions between foams and aerogels, but the key variation is the fineness and intricacy of the microstructure, which is far greater for aerogels than foams. Aerogels have a smaller pore size and greater surface area to volume/mass ratio (Dagan 1993). Unsurprisingly, the synonymous porous nature of these materials lends itself to photocatalytic applications as the configuration is able to simultaneously increase reactive sites while providing effective transport channels for the reactant to move through the material. Coupled with a high translucency to visible and low UV-light, these materials present an opportunity to produce photocatalysts with higher quantum efficiency due to improvements in light capture and molecular transport capabilities (Zhao et al. 2008).
At present, TiO$_2$ photocatalytic foams have been synthesized in two ways: an unsupported configuration where foam material is fabricated directly from the semiconductor, and coated on a foam support made of an alternate material. Unsupported TiO$_2$ foams when directly compared to suspended configurations have shown a 120% increase in photocatalytic activity using acetaldehyde as a probe compound (Zhao et al. 2008). However, these materials often lack stability in water which limits the extent to which they can be effectively immobilized. Alternatively, composite materials have been synthesized by depositing the catalyst as a coating on stable foams of complimentary composition. TiO$_2$ has been supported on silicon carbide foams (Kouame et al. 2011) and on ceramic foam supports, as depicted in Figure 2-9, by a sol-gel method (Plesch et al. 2009). Along with the structural advantages previously discussed, the immobilization of the catalyst on an absorbing material such as silica can also prevent catalyst particle agglomeration, improving the proximity of the catalyst to the contaminant (Wang et al. 2011). Metallic foams can also be used as supports for photocatalysts. Composite materials formed through electrodeposition or nanocrystalline electrodeposition of TiO$_2$ on aluminum metallic foams have been reported in literature as effective photocatalysts for the degradation of simple organics (Ishikawa & Matsumoto 2001, Guiang et al. 2008). The effect of varying the base material on the efficiency of the photocatalytic coating in terms of light penetration and pollutant absorption has not been thoroughly investigated and is poorly characterized in the literature.

Figure 2-9: Photocatalytic alumina (Al$_2$O$_3$) foams coated with P25 Degussa TiO$_2$ slurry (Adapted from Plesch et al. 2009)
Aerogels, a finer analogy to foam materials, are well known for catalytic applications because of their unusually large surface area (Pajonk 1997, Wang et al. 2007). Photocatalytic composites with silica aerogels have been developed from both TiO$_2$ and other transition metal oxides. The most successful of these, a SiO$_2$/CrO$_x$ composite, has been able to reproduce the same photoactivity of suspended TiO$_2$ under UV-light with only visible light illumination (Wang et al. 2011, Wang et al. 2004). Aerogels are as a more advanced and intricate material system, however, they are currently limited in photocatalytic applications by the laborious and expensive synthesis process as well as the potential for high pressure build-up in flow-through systems with increasingly fine pore size.

### 2.3.3 Anti-Stokes Fluorescent Materials

Fluorescence, the passive emission of light from a material that has absorbed electromagnetic radiation, is a common phenomenon in solid materials. The vast majority of fluorescent materials emit energy at wavelengths slightly longer than the corresponding wavelengths of energy absorbed. This energy conversion, known as a Stokes-shift, mechanistically occurs when a small amount of the incident light energy is transformed within the material into discrete packets of lattice vibrational energy known as phonons (Rakovich & Donegan 2008). This transition from photon to phonon energy allows for the emission energy of the light to change without altering the overall energy of the system. A small portion of fluorescent materials possess the capability of emitting light at wavelengths shorter than the radiation absorbed, which is accordingly referred to as an anti-Stokes shift. Anti-Stokes fluorescence can occur through a reverse of the Stokes emission process in which phonons are absorbed from the vibrating lattice, however, it is also possible to fluoresce anti-Stokes through a subsequent photon absorption process in which energy from more than one photon is absorbed before a single photon is emitted (Cates et al. 2011). Anti-Stokes emission processes traditionally require excitation by a coherent high density electromagnetic field (i.e., laser excitation) and are most commonly observed with lower energy transitions, such as from infrared to visible light (Rakovich & Donegan 2008, Cates et al. 2011). However, a recent new approach for the up-conversion of visible into UV-light with low density excitation has been achieved through a triplet-triplet annihilation mechanism in which two molecules in a highly excited state interact upon collision to produce a ground state molecule and a lower excited state molecule (Tanaka et al. 2010, Singh-Rachford & Castellano 2010).
simultaneous transition of states is accompanied by the release of a high energy photon. For some materials, this process can facilitate the up-conversion to UV wavelengths using natural solar illumination as the excitation source (Singh-Rachford & Castellano 2009).

There exist a very restricted number of materials that are capable of undergoing this type of energy conversion process because of the specific energy level transitions that must be achievable. The most extensively studied materials have been rare earth metal ion-doped crystals and fibres (Hu et al. 2006). In the current state of development, the quantum efficiency for up-conversion reaction of this nature, as defined by the ratio reduction in incident to emitted light power density, are on the order of $10^{-3}$ (Cates et al. 2011, Merkel & Dinnocenzo 2009, Tanaka et al. 2010). A strictly photolysis based disinfection mechanism has been presented by Cates et al. (2011) in which a Y$_2$SiO$_5$ microcrystalline material with a Pr$^{3+}$ activator was able to achieve visible to germicidal UV-C conversion in order to effect some surface microbial inactivation. A system for the coupling of a visible-light to UV-A light up-converting material with a photocatalytic process has not been attempted. This elegant concept of passive light manipulation for water purification is a theoretically achievable means of improving the efficiency of the photocatalytic system; however, at present it is unclear if the intensity of up-converted light would be sufficient to have more than a negligible impact on the overall photocatalytic process.

**2.4 Designing and Evaluating Photoreactors**

**2.4.1 General Considerations**

Photocatalysis remains a popular field of investigation and with advances in the capabilities of synthesis and characterization techniques, the range of materials and composites that can be created and studied is continually expanding. As previously discussed, current materials research in the field is generally concentrated in two areas: developing the optimum photocatalytic material and altering existing materials to improve visible light performance. Although research aiming to find an optimal photocatalytic material continues, prominent applied research is being simultaneously conducted to characterize the potential for photocatalytic oxidation to remove specific contaminants and design technologies for the integration of advanced oxidation by nanostructured photocatalysis into the water treatment process. Successful implementation is
dependent on the design of practical and functional reactors that can accommodate this photocatalytic mechanism. When designing these photoreactors there are three key considerations: type of photocatalytic material, reactor geometry and illumination source. Most systems being currently investigated rely on a form of TiO\textsubscript{2} photocatalyst, although the material size and structure vary greatly. Applied research has been more generally focused on the remaining consideration of reactor geometry and illumination source. Although reactor geometry is a familiar parameter for consideration in conventional reactors, in photoreactors the additional factor of supporting uniform illumination of photocatalyst surface creates unique challenges. Illumination source is a parameter unique to photoreactors, and several interesting options are being investigated.

In addition to the relative photoactivity of the semiconductor catalyst material employed, the comparative performance of these photoreactors must likewise be evaluated. The number of variables to consider when evaluating reactor performance can be minimized through the use of a test compound on which the comparative performances of the reactors can be judged. Advanced oxidation processes are advantageous for their indiscriminate removal and inactivation of contaminants in water by oxidation with radical species. Photocatalytic advanced oxidation has demonstrated the ability to simultaneously remove organic compounds and heavy metals while also transforming nonbiodegradable organics into biodegradable compounds (Yang & Lee 2006). Although there is a high potential that photocatalytic purification will be effective on a particular compound, removal must first be characterized in order to quantify the kinetics and thermodynamics of each degradation mechanism. Due to the multitude of parameters considered when designing a photocatalytic purification system, contaminant degradation characterization is essential for determining the reactor configuration, dose, illumination time, temperature, pH and other water quality parameters that would have to be attained for successful implementation. Evaluation and characterization of specific contaminant removal by photocatalysis in different photoreactor systems is useful both as a method for comparing performance as well as evaluating the range of potential applications for the system.

### 2.4.2 Photoreactor Geometry

The most significant impediment to successful implementation of photocatalytic technologies is the establishment of effective reactor designs for large-scale use with the central issue of
achieving uniform light distribution to a large surface area of catalyst (Ray 2009). In general, there are two basic photoreactor configurations: reactors with suspended photocatalyst in solution and reactors with the catalyst immobilized onto an inert substrate. Although suspension reactors display greater degradation efficiency due to idealized electron-hole transfer to solution and the relative ease of achieving a high ratio of illuminated catalyst surface area, it creates practical issues when the catalyst must be filtered, precipitated or otherwise removed from the effluent (Daniel & Gutz 2007).

Reflecting these considerations, reactor design aims to create a balance between the strong oxidative potential achieved when the catalyst is in suspension and the ease of separation that is facilitated by an immobilized catalyst configuration (Zhang et al. 2012). One solution to this issue has been to create low flow reactor systems in which the catalysts is first suspended and then removed later in the process. Methods for removal that have been investigated include coagulation, ultrasonic irradiation, cross-flow microfiltration, foam flotation and agglomeration through pH adjustment (Hasegawa et al. 2003). Although each of these techniques can successfully remove the catalyst, they can be time consuming, energy intensive and they reduce the ease of catalyst re-use. At present, immobilized reactors have been unable to reproduce the efficiency of suspended systems; however, they maintain the inherent advantage of avoiding a separation procedure. Combination photocatalytic disinfection and filtration has been performed with TiO$_2$ immobilized on flat sheet polymeric membranes (Chong et al. 2010). Although this reactor design was able to degrade organics and produce a high quality effluent, the system retained only half the photocatalytic activity of the comparative dose in suspension (Molinari et al. 2000). Likodimos et al. (2010) have proposed a system in which nanostructured TiO$_2$ with high UV–visible response is stabilized on nanotubular membranes in order to achieve photocatalytically active nanocomposite membranes. Novel photoreactor systems that maintain immobilization of the catalyst in very small scale capillaries (Zhang et al. 2012) or on activated carbon (Dong et al. 2012) have also been reported to retain high photoactivity while avoiding the need to separate catalysts in suspension after disinfection.
2.4.3 Illumination Source

2.4.3.1 Artificial Light Sources

For efficient energy transfer from light radiation to the catalyst, the light source for a photoreactor will ideally emit a high intensity light with a narrow emission spectrum at the same wavelengths as the material band gap. Conventional artificial light sources include both incandescent and gas discharge lamps. Incandescent bulbs require very high heat, are extremely inefficient, and impractical for producing the short wavelengths of light required for photocatalyst excitation (Chen et al. 2005). Gas discharge lamps produce light through energy intensive excitation of low ionization filling gas and are the current standard UV-light for water treatment applications (Vilhunen et al. 2009). The filling gas must be relatively inert, have a sufficient vapour pressure, and have its lowest excited state at a level that resonance radiation can appear in the UV-visible range. Currently, these constraints are met only by mercury- an unfavourable component due to its notable toxicity (Chen et al. 2005; Vilhunen et al. 2009).

![Diagram of charge flow in an LED with a semiconducting p-n junction](image)

**Figure 2-10:** Schematic of the charge flow in an LED with a semiconducting p-n junction

An alternative to conventional lamps is the light emitting diode (LED). An LED is a solid state light source that emits radiation by combining electrons and holes across a semiconductor heterojunction (Chen et al. 2005; Vilhunen et al. 2009). This junction, as depicted in Figure
is a p-n type junction, which describes a material that has been doped to be rich in positive charge carriers on one side and negative charge carriers on the other. When a potential is set across the junction, the charge carries flow, causing the electrons and holes to recombine which drops the electrons into the valence band and lowers its energy state. This transition releases energy in the form of a photon with the same energy as the junction band gap. LEDs are efficient emitters of nearly monochromatic light with spectral peaks that can be tailored to match the application (Ghosh et al. 2008). For photocatalytic applications, this is beneficial since the LED can be tuned to match the specific spectral peak equal to the energy band gap of the catalyst. In addition, short wavelength LEDs have been produced from low toxicity gallium nitride, indium and aluminum materials, making them a more benign alternative to the use of mercury lamps (Vilhunen & Sillanpaa 2010; Wang et al. 2012). Novel UV-LED/TiO₂ photoreactors have been designed with immobilized and suspended geometries, both of which have been successful at degrading organic dyes (Natarajan et al. 2011b; Wang & Ku 2006). LEDs have also been shown to operate well with a variety of photocatalytic materials including metal doped TiO₂, TiO₂ nanoparticles and TiO₂ nanofibres (Ghosh et al. 2009).

2.4.3.2 Solar Light-Driven Photoreactors
From both an environmental and economic view point, directly harnessing solar light to drive the photocatalytic reaction is an attractive option. Solar energy is freely abundant, renewable, regionally reliable and environmentally sustainable. Solar light treatment systems have been proposed for both small scale point-of-use applications, as well as for larger industrial water treatment facilities. With continued research and development, the technology is considered to have the potential to be effective in both contexts (Byrne et al. 2012, Blanco et al. 2009, Shannon et al. 2008, Lonnen et al. 2005, Rocha et al. 2011). For these reasons, developing photoreactors that operate using solar radiation as the illumination source is a prominent area of research. Table 2-1 shows a sample of recent solar photocatalytic reactor research installations. Although this topic has been thoroughly investigated, there remain a number of fundamental disadvantages preventing the successful establishment of solar photocatalytic water purification technologies.
Table 2-1: Selection of recent solar photocatalytic reactor research installations

<table>
<thead>
<tr>
<th>Research Group or Installation</th>
<th>Details of Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plataforma Solar de Almeria</td>
<td>Multiple TiO₂ installations</td>
</tr>
<tr>
<td>Almeria, Spain</td>
<td>Large scale compound parabolic collector reactor</td>
</tr>
<tr>
<td></td>
<td>SOLWATER project for rural areas of developing countries</td>
</tr>
<tr>
<td>Sandia National Laboratories</td>
<td>Multiple installation with varying catalysts</td>
</tr>
<tr>
<td>Albuquerque</td>
<td>Solar detoxification loops in a parabolic trough reactor</td>
</tr>
<tr>
<td>University of Lyon</td>
<td>Flow through TiO₂ based series of compound parabolic reactors</td>
</tr>
<tr>
<td>AQUACAT Project</td>
<td></td>
</tr>
<tr>
<td>Textile Factory</td>
<td>Series of TiO₂ based thin film fixed bed reactors</td>
</tr>
<tr>
<td>Menzel Temime, Tunisia</td>
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The most conspicuous inefficiency related to solar energy applications is the non-optimal band gap of common photocatalysts for solar photocatalytic applications. The sun’s emission pattern is mainly in the visible spectrum with some low UV light, a disparity that is exaggerated by the Earth’s atmosphere which strongly attenuates UV wavelengths, but is completely transparent to visible light (Marshal & Plumb 2008). The result is broad spectrum radiation that consists of no more than 2-4% UV-A radiation (the range of wavelengths most suitable for photoexcitation in TiO₂) by the time it reaches the Earth’s surface (Bahnemann 2004, Malato et al. 2009). Therefore, unlike artificial light sources that can be tailored to emit light in the range absorbed by the catalyst, only a narrow band of the total solar radiation emitted is captured as energy by the system.

To improve overall efficiency, some solar systems are designed with a light concentrating apparatus that uses a reflective surface to concentrate light into the photoreactor (Ray 2009, Byrne et al. 2012). The decision of whether or not to employ a solar concentrator is one of the key design decisions involved in developing solar photocatalytic reactors. Photoreactors that employ solar concentrators have the important advantage that a greater volume of water can be treated for the same light harvesting area. However, the use of a reflective surface increases optical losses and can only operate with direct solar beams, wasting the diffuse UV-light range of solar radiation, which makes up the large majority of light that is available on cloud-covered days (Alfano et al. 2000). Therefore, systems that do not employ solar concentrations are able to
more reliably harvest solar energy in varying atmospheric conditions. Photoreactors designed for cost-effective point-of-use applications are more limited in their design variations due to limitations of complexity and scale. Mechanisms have been developed that aim to augment Solar Disinfection (SODIS) methods in small point-of-use photocatalytic reactors by the integration of an immobilized photocatalyst. The particulars of this approach will be further discussed in Section 2.5.3 on semiconductor photocatalysis enhanced solar disinfection.

2.4.4 Characterizing the Removal of Specific Contaminants

2.4.4.1 Organic Dyes

Organic dyes are often employed as a preliminary test compound to ensure that a process or photoreactor configuration has the potential to apply to real systems. Common dyes for these experiments include methylene blue, malachite green, rhodamine B and reactive red 22 (Natajaran et al. 2012; Wang & Ku 2006; Sahoo & Gupta 2012). These degradation results are used to show comparative reactor performance and can be applied as surrogates to predict how various factors will affect the degradation of contaminants within the same photocatalytic system. While dyes are rarely the target analyte in drinking water systems, the degradation of organic dyes is an common goal for discharged industrial waste streams, particularly from textile plants where colouring can have detrimental effects on the aquatic ecosystems. Using a thin film TiO$_2$ catalyst configuration, Damodar et al. (2007) demonstrated 85-95% removal of four different reactive dyes using solar radiation. Degradation of these dyes can be quickly and easily monitored using spectrophotometric methods. Although each of the dyes investigated has shown the potential to be completely removed, factors such as catalytic dose, initial concentration of dye and pH of the reaction mixture have been found to influence the degradation process (Sahoo & Gupta 2012).

Largely due to their low-cost and ease of detection, coloured organic dyes have been investigated for applications as dosimetric indicators in photocatalytic reactions. The goal of such applications is to correlate the required fluence for the inactivation of disease causing organisms to the discolouration of the organic dye in a separate simultaneous reactor. Bandala et al. (2011) investigated the correlation between the degradation of Acid Orange 24 to the inactivation of three waterborne pathogens: *Ascaris ova*, *E. coli*, and *Pseudomonas aeruginosa*. It was found
that complete discolouration of the dye is associated with a similar fluence to the complete inactivation of Ascaris ova. The photocatalytic reduction of methylene blue has also been used in a similar context as a method for cheaply quantifying UV-A dose (Byrne et al. 2012).

2.4.4.2 Disease-Causing Organisms

Disease-causing organisms are conventional contaminants that are the essential targets for removal in any disinfection system. Photocatalytic processes can inactivate both bacterial and viral pathogens as well as fungi, protozoa, and spores (Pigeot-Rémy et al. 2011; Li et al. 2008; Robertson et al. 2012). Although a number of studies have been performed to investigate the mechanism of photocatalytic disinfection, the details of the process are still unknown. The current agreed mode of action involves persistent cell wall damage followed by direct intracellular attack by hydroxyl radicals and occasionally other reactive oxygen species (McCullagh et al. 2007). Gel electrophoresis studies have shown that the radicals attack intracellular proteins indiscriminately which suggests that it would be nearly impossible for bacteria to develop resistance to photocatalytic treatment (Robertson et al. 2012).

The exposure of bacteria to TiO$_2$ nanoparticles even in the absence of a light source has a detrimental effect on membrane permeability. Therefore, when irradiated under UV-A light this predisposition can help lead to the total loss of bacterial cultivability for E. coli. The contact of TiO$_2$ particles with bacteria in the dark increased the bacterial sensitivity to membrane-perturbing agents, suggesting an increase in outer membrane permeability (Pigeot-Rémy et al. 2011). The removal of viruses has also been proven using modified TiO$_2$ suspensions by the near complete inactivation of MS2 coliphage by irradiation with near UV visible light (Li et al. 2008). The details of this research are described in further detail in Case Study 1.

2.4.4.3 Algae, Cyanobacteria and Cyanotoxins

Algae are a diverse group of photosynthetic aquatic organisms. In its broadest classification, this group can include multi-cellular and unicellular eukaryotic unstructured plants as well as prokaryotic cyanobacteria. Algal blooms and the growth of algae on exposed sunlight surfaces can create aesthetic, economic, environmental, and health consequences. The uncontrolled growth of algae leads to an unbalanced trophic energy distribution which is deleterious to aquatic ecosystems. Large algal blooms such as these, or even more moderate fluctuations in algal
growth, can contaminate drinking water supplies through the release of cyanotoxins, a secondary metabolite of algal cyanobacteria (Metzler et al. 2011; Antoniou et al. 2009). Large blooms can create biofouling of drainage pipes and cause disturbances in other parts of the distribution system (Linkous et al. 2000). Traditional methods of controlling algal growth, such as copper based algaecides, are associated with high cost and high risk of damaging environmental after-effects (Gamage & Zhang 2010; Ochiai et al. 2010). In general, algae are more resistant to common chemical oxidants than bacterium, which creates a challenge for photocatalytic treatment. However, it is noteworthy that photosynthetic algae can only grow in areas with sufficient sunlight and this makes a light-driven control mechanism an elegant approach (Linkous et al. 2000).

Suspensions of photocatalytic particles and surface immobilized films have each been investigated for their ability to control algal growth. Both configurations were successful at completely inhibiting algal growth in regions nearest the catalyst. Although the surface configuration has many advantages and is far simpler to employ, it has the potential to be biofouled in the presence of large concentrations of algae that obscure light from reaching the semi-conductor and halt the generation of radical species (Linkous et al. 2000; Metzler et al. 2011). In the case of suspended configurations, complimentary mechanisms such as entrapment by nano-TiO₂ particles and energy interferences in the photosynthesis process were acknowledged as contributing to the inhibitory effect (Metzler et al. 2011). Investigators of photocatalytic algae inhibition used spin-trapping radical measurements and correlated degradation with other organics to indicate that the stress caused by the non-specific attack of the hydroxyl radicals and other strong oxidative species was the primary mechanism of growth inhibition (Ochiai et al. 2012; Linkous et al. 2000).

Drinking water treatment methods such as coagulation and filtration have been shown to induce cyanobacteria cell lysis, thereby releasing cyanotoxins into the effluent. These cyanotoxins are the primary concern from a drinking water health perspective. In addition to the possibility of controlling the bacteria growth, photocatalysis has been considered as an end of line advanced oxidation method for controlling cyanotoxin levels in the final effluent (Antoniou et al. 2009).
2.4.4.4 Emerging Contaminants

AOPs are largely concerned with producing water of a higher quality than possible with conventional methods and for that reason the characterization of removing emerging contaminants such as personal care products (PCPs), pharmaceutically active compounds (PhACs) and endocrine disrupting compounds (EDCs) is a high priority for photocatalytic oxidative degradation processes. PhACs such as triclosan, tamoxifen and gemfibrozil have been shown to be successfully degraded by TiO$_2$ under UVA irradiation (Son et al. 2009; Yurdakal et al. 2007). In addition, these contaminants have all been modeled to fit the same Langmuir-Hinshelwood kinetics scheme (Son et al. 2009; Yurdakal et al. 2007). A common group of EDCs known as phthalate esters have been shown to be degraded by TiO$_2$/UV-A following this same kinetic scheme (Jing et al. 2012; Kaneco et al. 2006). Many of these compounds are stable and can bioaccumulate in the environment; therefore their accelerated degradation by photocatalysis is an attractive alternative to conventional methods for handling the removal of emerging contaminants.

2.5 Solar Photocatalytic Disinfection

2.5.1 Introduction

Solar Disinfection (SODIS) is a well-known cost-effective mechanism for the inactivation of disease causing organisms in water. The SODIS process, as depicted in Figure 2-11, involves the exposure of polyethylene terephthalate (PET) bottles to direct solar radiation for a minimum of six hours after which the pathogen load is decreased and the quality of the water substantially improved. The inactivation caused by SODIS treatment is understood to involve several modes of action resulting from the absorption of short wavelength UV radiation and long wavelength infrared thermal radiation (Blanco et al. 2009, EAWAG & SANDEC 2002, Bryne et al. 2012). These two types of radiation have been shown to act synergistically and under ideal conditions can provide enough inactivation to create safe drinking water levels in a variety of pathogens including Escherichia coli, Vibrio cholera, Salmonella typhimurium, Shigella dysenteriae Type I, Pseudomonas aeruginosa, Candida albicans, Fusarium solani, and the trophozoite stage of Acanthamoeba polyphaga (Blanco et al. 2009).
SODIS has many attractive qualities; nevertheless, it has several serious intrinsic disadvantages. SODIS requires strong direct solar radiation and clear water, and is therefore dependent on both climatic conditions and source water quality. Additionally, SODIS is purely a disinfection mechanism and does not improve the chemical quality of water (EAWAG & SANDEC 2002). In many regions where SODIS is applied, infections organisms are the most conspicuous water quality issue; however, the potential for long term, chronic or developmental health problems associated with the exposure to organic pollutants or heavy metals should not be overlooked. Chemical water quality issues such as these can have neurotoxic, teratogenic and developmental effects that can be particularly harmful to young children, breast feeding mothers and other vulnerable members of the population (Guilette et al. 1998, Younes & Gala-Gorchev 2000). The integration of solar photocatalytic advanced oxidation with the SODIS method has been proposed as a method for improving both the microbial inactivation and chemical purification of the process (Byrne et al. 2012, Blanco et al. 2009, Shannon et al. 2008, Lonnen et al. 2005). Building from this established motivation for the implementation of effective enhanced solar disinfection, the remainder of this section will be dedicated to outlining the best understanding of the SODIS inactivation mechanism, as well as evaluating the literature related to enhancing the process by the introduction of a semiconductor photocatalytic component.
2.5.2 The Solar Disinfection Mechanism

2.5.2.1 Optical Effects: Short Wavelength Inactivation

In SODIS, the key parameter for inactivation has been determined to be short wavelength UV-A radiation in the range of 320-400 nm. All solar light with wavelengths shorter than 400 nm has a biocidal effect, however, the atmosphere so strongly attenuates wavelengths shorter than 320 nm, only the UV-A is left as an effective range (Blanco et al. 2009, EAWAG & SANDEC 2002). Pathogenic organisms thrive preferentially in conditions similar to those in the human intestines and are therefore susceptible to harsh environmental conditions. When pathogenic microorganisms are exposed to high enough levels of UV-A radiation it can directly interact with DNA, nucleic acids and enzymes adversely affecting processes and causing cell death. In addition, UV-A radiation can indirectly result in activation by interacting with dissolved oxygen in the water to produce highly reactive oxygen species (EAWAG & SANDEC 2002). This mechanism is reflected in the recommendation to aerate the water by shaking it, as depicted in Figure 2-11, which has the goal of increasing the dissolved oxygen content in the water. The extent of UV-A fluence required to achieve sufficient water quality is observed to be highly variable with strong dependence on source water turbidity and water temperature. At a temperature of 30°C, a fluence of 2000 kJ/m² (corresponding to approximately 6 hours of near ideal sun exposure) is required to achieve a 3-log reduction of E. coli (EAWAG & SANDEC 2002). The incidence of suspended particles in the water deters the transmission of light and reduces the interaction between the radiation and the microorganism. Water with turbidity higher than 30 NTU cannot be effectively treated by the SODIS method without pre-treatment (EAWAG & SANDEC 2002).

2.5.2.2 Thermal Effects: Long Wavelength Inactivation

Long wavelength infrared radiation, with wavelengths above 700 nm, influences the temperature of the water and can both support optical inactivation and perform direct inactivation of pathogenic microbes in the water, the latter process commonly referred to as pasteurization. Most pathogenic microbes including E. coli, V. cholera, and Giardia cysts are sensitive to heat and can be inactivated by 60 minutes of exposure to water at temperatures above 50-60 °C (EAWAG & SANDEC 2002). However, field research has shown that under usual conditions, waters being treated by SODIS very rarely reaches temperatures greater than 50°C, therefore
pasteurization from direct sunlight is impractical without the support of an alternate heating mechanism (Byrne et al. 2012, Ricon & Pulgarin 2004). The extent to which each of the three mechanisms of direct UV-A exposure, interaction with reactive oxygen species and thermal inactivation is responsible for the overall quality of water produced by the SODIS method is poorly characterized; nevertheless, studies have empirically shown the beneficial synergistic effect of these mechanisms. At a temperature of 50°C, a 3-log reduction of E. coli can be achieved with 25% of the fleunce required at 30°C (EAWAG & SANDEC 2002).

### 2.5.3 Semiconductor Photocatalysis-Enhanced Solar Disinfection

The goal of integrating a photocatalytic component into the SODIS method is to develop a small and inexpensive point-of-use photoreactor that can improve overall water quality by enhancing the inactivation of microbes and contributing additional oxidative degradation of organic pollutants and/or sorption of heavy metal contaminants to the catalyst. Comparative studies have been performed with several indicator pathogenic species including protozoa, viruses, E. coli and other coliform bacteria, fungi and spores. Employing thin film immobilized TiO$_2$ on acetate sheets, Lonnen et al. (2005) found consistently improved inactivation rates. When treating bacteria, viruses, and spores, many species displayed the same log-reduction in approximately half the irradiance time required for SODIS alone (Lonnen et al. 2005). Gelover et al. (2006) performed a similar investigation in which pyrex-glass cylinders were coated with TiO$_2$ by a sol-gel method and exposed to direct sunlight. They found that the photocatalytically enhanced system was far more effective, as shown in Figure 2-12, resulting in both a higher inactivation rate and greater final achieved inactivation level of faecal coliforms (Byrne et al. 2012).

Nonetheless, for this integrated system to be implemented, there remain several issues of optimization that need to be addressed. For simplicity of application, an immobilized photocatalyst is favourable in SODIS configurations (Dunlop et al. 2011). The most commonly investigated configuration has been thin films, which suffer from reduced mass transfer and therefore remain less efficient than suspended catalysts applications (Byrne et al. 2012). The persistent problem of the non-optimal band gap of TiO$_2$ for solar applications and the poorly characterized longevity and reusability under typical SODIS conditions are additional parameters requiring attention. Further investigation of these optimization parameters is required for the production of the optimal water purification system based on photocatalysis enhanced SODIS.
Figure 2-12: Decrease in faecal coliforms in natural spring water exposed to direct sunlight, comparing SODIS to TiO$_2$ photocatalyst enhanced SODIS (Adapted from Byrne et al. 2012).

2.6 CASE STUDIES

Since the photocatalytic splitting of water was demonstrated, there has been an abundance of research asserting potential applications in water purification. However, each system is complex and is affected by a number of factors including photocatalytic material, water quality conditions and light source. This section will introduce four case studies carried out by different research groups using photocatalysis. These studies will discuss the application of UV and visible light photocatalysis for the treatment of target contaminants such as viral surrogates and endocrine disrupting compounds. Based on these cases, this section will clarify some of the possible applications in the water treatment process by detailing how photocatalytic materials have been accessed for potential as a purification method in water systems.

2.6.1 Case 1

“Treatment of coliphage MS2 with palladium-modified nitrogen-doped titanium dioxide photocatalyst illuminated by visible-light”

In 2008, Li et al. were the first research group to display the potential for photocatalytic inactivation of viruses under visible light illumination. A palladium modified nitrogen-doped titanium oxide (TiON/PdO) nanoparticle photocatalyst was synthesized by a sol-gel method and shown to have superior photocatalytic activity compared to nitrogen-doped TiO$_2$ under visible light (Li et al. 2008). The sol-gel technique was then combined with a template technique to immobilize the catalyst and create a photocatalytic fiber. These fibers were then illuminated with
a 400 nm wavelength light source in a batch reactor containing an MS2 coliphage suspension. MS2 coliphage is a virus that infects *E. coli* bacteria. Virus removal was characterized in the absence of illumination and it was found that a 95.4-96.7% reduction in viable virus concentration could be observed in a dark room equilibrated solution. However, upon illumination an additional 94.5-98.2% removal was detected. This resulted in an overall average of 3-log removal of MS2 coliphage from the solution after 20 minutes of illumination (Li et al. 2008). Spin trapping electron paramagnetic resonance (EPR) experiments were performed to verify the presence of reactive radicals. Radical species were only detected when samples were illuminated, supporting that the additional removal of virus upon illumination was a result of an advanced oxidation mechanism. The results of this study indicate that TiON/PdO can remove viruses from water under dark conditions and that illuminating this material enhances the extent of virus removal.

### 2.6.2 Case 2

**“Comparative study on UV and visible light sensitive bare and doped titanium dioxide photocatalysts for the decomposition of environmental pollutants in water”**

As previously discussed, many materials have been developed with potential applications in visible and UV light photocatalysis. A recent review by Vereb et al. (2012) performed a comparative analysis of the various types of bare, doped and composite TiO$_2$ photocatalytic materials under UV and visible light irradiation to determine the relative performance of each catalyst. Materials were selected to elucidate the effect of varying the dopant and the synthesis method of the photocatalyst. Varying the dopant affects the material band gap and varying the synthesis method has been shown to have an effect on the crystal structure and therefore the efficiency of the photoactivity. Various doped materials considered included iodine (TiO$_2$-I), nitrogen (TiO$_2$-N), silver (TiO$_2$-P25-Ag), gold (TiO$_2$-P25-Au) and iron (TiO$_2$-Fe) samples. Bare nano-TiO$_2$ prepared by a sol-gel method (TiO$_2$-RHSE), a flame method (TiO$_2$-FH) and commercially available anatase phase (TiO$_2$-AA) were considered in comparison to nano-aeroxide (TiO$_2$-P25) TiO$_2$ as a reference. The results for the degradation of two common organics, phenol and oxalic acid, under UV and visible light illumination are shown in Figure 2-13. These organics were selected as probe compounds because of their frequent appearance in the oxidative degradation pathways of common pollutants and due to their varying characteristics.
in terms of absorbance and electron affinity. The evident variation in photocatalyst performance between the two compounds is attributed to these differences which create fundamental deviations in their interaction with the catalyst and with the radicals (Vereb et al. 2012).

**Figure 2-13:** Photocatalytic degradation of (a) phenol and (b) oxalic acid under UV and visible light illumination employing iodine (TiO\(_2\)-I), nitrogen (TiO\(_2\)-N), silver (TiO\(_2\).P25-Ag), gold (TiO\(_2\).P25-Au) and iron (TiO\(_2\)-Fe) doped titanium and bare nano-TiO\(_2\) prepared by a sol-gel method (TiO\(_2\).RHSE), a flame method (TiO\(_2\)-FH) and a commercial available nano-aeroxide (TiO\(_2\).P25) and anatase phase (TiO\(_2\)-AA). (Adapted from Vereb et al. 2012)
These results concluded that under visible light illumination, iron and nitrogen doped TiO$_2$ have the greatest oxidative potential of the currently developed doped and bare TiO$_2$ catalysts (Vereb et al. 2012). The results also show that significant influence of catalyst synthesis method on the degradation of both organics. Varying synthesis method can lead to serious defects in the crystal structure which need to be considered when comparing the photoactivity of catalysts made from varying materials. Results also show the variable results with different probe compounds since the comparative performance of the catalysts varied greatly between phenol and oxalic acid.

2.6.3 Case 3

“Titanium dioxide mediated photocatalytic degradation of dibutyl phthalate in aqueous solution”

Phthalate esters (PAEs) are a class of compound commonly used as plasticizers for resins, in adhesive applications, in cosmetics and in polyvinyl chloride plastics (Huang & Chen 2010). PAEs are released into waterways during the manufacturing, use and disposal of these products. Many PAEs are known to have deleterious health effects. Dibutyl phthalate (DBP) is a particularly stable PAE that is found ubiquitously in waterways due to its long hydrolysis half-life, which is estimated to be around 20 years (Bajt et al. 2008). DBP is a known endocrine disrupting compound (EDC) and teratogenic compound. It has also been routinely used as an indicator ECD since high concentrations of DBP are often correlated with high concentrations of other ECDs (Yoshida et al. 2003) Therefore, determining an efficient and effective method for removing PAEs such as DBP from waterways and water that may be used for human consumption is an important environmental issue.

Accelerated degradation of micro-pollutants using semiconductor photocatalysis is a heavily researched emerging technology for the elimination of EDCs because it has shown the ability to perform complete mineralization and has the potential to be executed far more quickly and cheaply than conventional biological treatment mechanisms, which can require several days to months for effective treatment (Kuol, 2006). The following reaction scheme for the TiO$_2$ photocatalytic degradation of DBP has been generally supported (Hasegawa et al. 2003; Huang & Chen 2010; Kaneco et al. 2006; Malato et al. 2009):
\[
\begin{align*}
\text{TiO}_2 + \text{hv} & \rightarrow \text{e}^- + \text{h}^+ \quad (2.18) \\
\text{OH}^- \text{ or H}_2\text{O(surface)} + \text{h}^+ & \rightarrow \text{OH}^{-}\text{(+H}^+\text{)} \quad (2.19) \\
\text{O}_2 + \text{e}^- & \rightarrow \text{O}_2^{-} + \text{H}^+ \rightarrow \text{OOH}^- \quad (2.20) \\
\text{OH}^{-} \text{ (or OOH}) + \text{DBP} & \rightarrow \text{oxidative products} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad (2.21)
\end{align*}
\]

It has been shown that DBP can be completely removed from solutions with initial contaminant concentrations of 5 mg/L by illuminating the suspension in the presence of TiO\(_2\) for less than 3 hours with a Xe lamp which emits a broad range of wavelengths extending across the UV and visible light spectrum. This degradation over time matched well to the empirically derived Langmuir-Hinshelwood kinetics scheme which is commonly applied to multistep catalytic reactions (Kaneco et al. 2006). Although novel techniques such as immobilized catalyst geometries and visible light photocatalysis have not yet been employed for the quantitative characterization of DBP removal, it is clear that the photocatalytic mechanism is capable of degrading the indicator EDC.

2.6.4 Case 4

“Photocatalytic reactor based on UV-LED/TiO\(_2\) coated quartz tube for degradation of dyes”

Natajaran et al. (2011a) have developed a photocatalytic reactor using a UV-LED source in conjunction with a TiO\(_2\) coated quartz tube. This system, shown in Figure 2-14, has been successfully applied for the degradation of organic dyes including malachite green, methylene blue and rhodamine B. The reactor consists of three passes of tubing irradiated by 15 UV-LED p–n junction devices made of indium gallium nitride with irradiation wavelengths in the range of 390-410 nm mounted inside a cylindrical pipe. A solution containing the dyes was continuously circulated through the reactor at a flow rate of 3 mL/min. After 5 hours of circulation, 100% degradation of malachite green and near 60% degradation of methylene blue and rhodamine B were achieved. The photocatalytic degradation of dyes were also confirmed by kinetic studies and observed to follow the Langmuir–Hinshelwood kinetics (Natajaran et al. 2011a).
Figure 2-14: Schematic representation of photocatalytic reactor (Adapted from Natajaran et al. 2011a)

2.7 HEALTH PRECAUTIONS AND REGULATIONS

2.7.1 Health and Environmental Concerns

Although nanomaterials have been shown to have great potential for improving water quality and energy efficiency, the unknown nature of the technology has concern over its potential to cause unforeseen deleterious effects on human health and the physical environment. An increase in the ratio of surface atoms to inner atoms causes an increase in reactivity, and because of this, nanomaterials have been shown to have substantially different toxicological characteristics compared with their bulk counterparts (Savolainen et al. 2010). These variations in material properties mandate separate evaluation of their toxicity and potential health risks.

Currently nanomaterials are already accumulating in the environment as applications of nanotechnology increase in commercial products, industrial process and medical applications (Tucillo et al. 2011). These materials, which are frequently discharged into source waters that enter drinking water treatment plants, are generally thought to be found at very low concentrations, although their relevance as emerging contaminants is growing. Nanomaterials in
water systems can affect health through direct applications in the treatment process and accumulation in the physical environment. These concerns are compounded by the fact that once released into the environment, there are no current methods of tracking or detecting nanomaterials. The main material of interest for photocatalytic applications, nano-TiO$_2$, has been associated with fibrosis and pulmonary damage in mice when inhaled sub-acutely with a total dose in the range of 154 µg TiO$_2$ per mouse (Grassian et al. 2007). Although studies have been performed on oral exposure to titanium dioxide and other common nanoparticles, evaluation of oral toxicity is complicated by speciation chemistry, and few studies have been able to adequately access toxicity (Tucillo et al. 2011). Recent reviews have reported nanoparticle absorption in the gut and pervasive dispersion throughout the body; however, data limitations have prevented conclusions about toxicological consequences of this uptake (Card et al. 2011). Although very little concrete results have been obtained, the United State Environmental Protection Agency (EPA) currently anticipates that released nanomaterials may have detrimental effects on ecosystem health. Further characterizing these effects is currently a key science question in the EPA’s Nanomaterials Research Strategy (2009). Therefore, a key priority in employing nanotechnology in the drinking water treatment process is to prevent the leeching of these materials from the purification process into the effluent water stream. An additional concern is the health and safety of workers in treatment plants. Although inhalation is an unlikely route of exposure for the general public who will drink the water purified by nanomaterial photocatalysis, it could be a potential hazard for workers in the drinking water treatment plant. Developing and adopting appropriate methods of analysis, categorization, characterization, and environmental risk assessment for nanomaterials and their effects on human health are needed to combat the uncertainties in this currently expanding industry. Nanotechnologies have the potential for great future strides in drinking water treatment processes, but these ambitions need to be weighed against the potential risks of environmental contamination and unintentional deleterious health effects.

2.7.2 Summary of Regulations
Under the Canadian Environmental Protection Act, environmental and human health risk assessments are required for any new chemical substances entering industry in Canada (Environment Canada 2007b). Unfortunately, nanomaterials fall into a gap in current
categorization, dividing its regulation amongst individual sectors. This gap is common in the policies of several nations and creates problems for the regulating the use of nanomaterials. A report from The Royal Society (2004) recommends prohibiting the release of free nanomaterials into the environment until more research is conducted on potential deleterious effects. The EPA has expressed concern over the possibility that nanomaterials will be biomagnified if released into the environment (Karn et al. 2009). Because of these concerns, applications for nanotechnology in drinking water treatment should be designed to limit the release of the material into the effluent water stream.

Environment Canada has recently recognized endocrine disrupting compounds (EDCs) and, pharmaceuticals and personal care products (PPCPs) as major threats to aquatic ecosystem health (Environment Canada 2007a; Environment Canada 2011). Accelerated degradation of micropollutants using semiconductor photocatalysis is a popular emerging technology for the elimination of EDCs and PPCPs in wastewater because it has shown high efficiency of mineralization and has the potential to be executed far more quickly and cheaply than conventional biological treatment mechanisms which can require several days to months for effective treatment (Kuol & Chen 2006). Therefore, when careful application and concern for potential leaching is considered, photocatalytic oxidation has the potential to become a fast and cost effective mechanism for the removal of emerging contaminants which have a high potential to be regulated in the future.

2.8 REFERENCES


Swiss Federal Institute of Environmental Science and Technology (EAWAG) and Department of Water and Sanitation in Developing Countries (SANDEC) (2002) Solar Water Disinfection: A Guide for the Application of SODIS.


3  MODELING THE PERFORMANCE OF IMMOBILIZED PHOTOCATALYSTS FOR WATER PURIFICATION

ABSTRACT

The analytical model we have developed employs a simplified geometric configuration to reduce the number of parameters influencing photocatalytic treatment efficiency. Reactor performance is modeled by characterizing two factors: the fraction of the total water volume that is in direct contact with catalyst and the fraction of catalyst that is exposed to light. Through this approach, the model compares photoreactors with catalyst configured as suspensions, thin-films and immobilized on foam supports of varying density. Results indicate the best configuration in terms of efficiency and treated volume is the thin film when the application of the catalyst is not restricted by the area of the reactor. For small reactors with restricted surface area, a suspension configuration is preferred over a thin film configuration. Furthermore, when adhered to a foam support, the performance of an immobilized catalyst can approach that of a suspension and the performance is most similar in smaller systems.

3.1 INTRODUCTION

The shape or configuration of a photocatalyst within its reactor is a key factor affecting the water purification process efficiency. The configuration affects the number of available surface reactions sites, the catalyst area exposed to light and the penetration of light through the reactor (Pelaez et al. 2012, Plantard et al. 2011). By optimizing the configuration, a photoreactor aims to create a balance between the surface area of the catalyst exposed to light and the uniform distribution of the catalyst throughout the volume of the reactor. Additionally, immobilized catalyst reactors are preferred over suspended configurations because they can be reused more readily and obviate the need to remove the catalyst after treatment (Daniel & Gutz 2007; Zhang et al. 2012). Due to their ease of preparation and application, thin films have been commonly employed; however, in large volumes of water films exhibit decreased efficiency due to limited...
mass transfer rates, small number of active sites and incomplete photon absorption (Chen et al. 2006, Antoniou et al. 2009, Plantard et al. 2011).

These concerns have spurred investigation into alternative immobilized structures such as three dimensional porous films and foams. Antoniou et al. (2009) investigated the effects of increasing the thickness of porous thin films on the degradation of microcystin-LR and methylene blue. As the film thickness increased, contaminant degradation improved until it reached a plateau. This plateau was higher for smaller compounds, indicating that the limits to thickness are a function of contaminant size, with the smaller compounds more easily able to penetrate into the pores of the film (Antoniou et al. 2009). In order to improve mass transfer rates, an intuitive extension of this research is to three dimensionally expand the porous film into a foam with larger pores that could be evenly distributed throughout the volume of water. A foam configuration mimics a suspension reactor while maintaining catalyst immobilization. Such a configuration would have the advantage of increasing the contact area between the catalyst and the contaminant, a parameter known to limit the efficiency of catalytic reactions (Antoniou et al. 2009, Palaez et al. 2012).

Plantard et al. (2011) performed a study on the comparative photocatalytic activity of aluminum foams of varying mesh density coated with TiO$_2$ by a sol-gel method for the degradation of organic probe compound 2,4-dichlorophenol. It was found that degradation efficiency increased with finer pore size as it approached both the configuration and activity of its suspended counterpart (Plantard et al. 2011). Conversely, Plesch et al. (2009) conducted a study on TiO$_2$ coated alumina foams for the degradation of phenol and found that photocatalytic efficiency improved with increasing pore size. However, the pore sizes employed in this study were all smaller than those in the study by Plantard et al. (2011). This relationship is further illustrated in Table 3-1. These results allude to the possibility of an optimum pore size which would balance permeability with contact area and would be correlated to the size of the target compound. These trends in reactor performance have been empirically quantified, but a theory has not been developed to describe the relationship between photocatalytic catalyst configuration and reactor performance. The goal of this study will be to develop an analytical model which describes such a theory.
Table 3-1: Comparison between foam pore size and degradation efficiency trend

<table>
<thead>
<tr>
<th>Data Source</th>
<th>Pore Size (mm)</th>
<th>Pores per inch</th>
<th>Degradation Efficiency Trend</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plantard et al. (2011)</td>
<td>3</td>
<td>8.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>Plesch et al. (2009)</td>
<td>1.7</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.3</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>25</td>
<td></td>
</tr>
</tbody>
</table>

3.2 **Objective**

The objective of this study is to produce a theoretical model to predict the optimal geometric configuration for distributing an immobilized photocatalyst within a solar irradiated batch reactor.

3.3 **Modeling Mechanics**

3.3.1 Introduction to Analytical Model Approach

3.3.1.1 Simplified Reactor Configuration

The analytical model presented here is an attempt to reduce the parameters involved in photocatalytic batch reactor water treatment in order to predict the optimal catalyst configuration. The approach adopted assumes a planar light source, such as a collimated beam or sunlight with a high solar zenith, and two simplified reactors: one in which the available reactor surface area is far greater than the volume of the catalyst (unrestricted surface area) and one in which the surface area of the reactor is far less than the volume of the catalyst (restricted surface area). This simplified geometry is shown as an example in Figure 3-1.

![Figure 3-1: Simplified geometry for theoretical model. A is the base area of the photoreactor, $\Phi$ is the incident flux, $N\delta_w$ is the thickness of the water layer and $N\delta_p$ is the thickness of the catalyst](image-url)
The available area for the reactor is shown by the distance A. The bulk of the reactor is comprised of two components: a known volume of catalyst and a known volume of water. The distribution of two components in the reactor is described by the stacking of thin layers represented by $\delta_w$ for water layers and $\delta_p$ for photocatalyst layers. Each single $\delta$ layer represents an indivisibly thin layer of material. (These layers are analogous to the theoretical plates used to describe the efficiency of a separation process in chromatography or the increasing layers of atmospheric thickness used to describe energy balance in the atmosphere). The incident light, indicated by the flux $\Phi$, then passes through some combination of catalyst and water across the photoreactor surface. In the reactor configuration shown in Figure 3-1 the light passes through $N$ layers of water and then $N$ layers of photocatalyst before reaching the base of the reactor. The volume of catalyst or water is enumerated by the addition of these infinitely thin layers, $\delta_w$ and $\delta_p$. The total volume of water, $V_T$, or the total volume of catalyst, $V_p$, is represented by the number, $N$, of thin layers as follows:

$$V_T = N \cdot \delta_w \cdot A \quad \text{and} \quad V_p = N \cdot \delta_p \cdot A$$ (3.1)

### 3.3.1.2 Defining Factors Affecting Reactor Performance

In this model, a method for predicting reactor performance is defined by characterizing the major influences on the system. If negligible mixing is assumed, then only water layers in direct physical contact with catalyst layers exposed to light can be considered in treatment range. Investigations show that some mixing due to convective heating occurs during solar water disinfection; however, the extent of this mixing has not well known (EAWAG & SANDEC 2002). Studies of natural water systems have shown that solar driven convective mixing in shallow pools of 30 cm depth leaves water largely stratified (Jacobs et al. 1994). Additionally, laboratory experiment indicate that when water is illuminated with constant intensity light, it passes through a period of mixing before reaching a new isothermal steady state in a few minutes (Lei & Patterson, 2002). Although variations in radiation occur during the daytime, there are also significantly long periods of time where the solar radiation is approximately constant (Lei & Patterson, 2002). Based on these observations, it is supposed that although convective mixing occurs, a solar illuminated photoreactor would still undergo substantial periods of time where the
mixing was negligible and, for the purpose of this model, a simplified steady-state assumption can be made.

If mixing is considered negligible, then close proximity of contaminant to catalyst is requisite for treatment as the radical species produced in photocatalytic advanced oxidation processes have a half-life on the order of nanoseconds. This direct contact between light activated catalyst and water is dependent on two factors: the surface area of the catalyst exposed to light and the distribution of catalyst within the volume of water. The model accounts for these factors using the follow fractional variable between 0 and 1:

\[ C_f = \text{the fraction of the total volume of water directly contacting the catalyst} \quad (3.2) \]
\[ I_f = \text{the fraction of catalyst exposed to the incoming radiation} \quad (3.3) \]

For example, a \( C_f \) value of 1 would represent a suspension configuration in which every layer of water is in direct contact with photocatalyst. Likewise, an \( I_f \) value of 1 would mean that the entire volume of catalyst is being exposed to light radiation, such as a configuration with the entire volume of catalyst was spread out in a single thin layer with a single layer of water on top.

In order to quantify reactor performance, these factors are used to define a parameter representing the volume of water that is in direct contact with catalyst exposed to light. This is called \( V_E \), the effective treated volume, and is calculated as follows, where \( V_T \) is the total volume of water in the photoreactor:

\[ V_E = C_f \cdot I_f \cdot V_T \quad (3.4) \]

The effective treated volume is the volume that is exposed to photocatalytically produced radicals; therefore, the higher the value for \( V_E \), the better the reactor configuration. Clearly, water cannot be practically defined as treated or untreated; rather there is always a degree of treatment which is typically expressed as percent or log removal of contaminants. Consequently, the value for \( V_E \) does not offer any direct physical meaning, but is a theoretical value for comparing reactor performance. It can be seen from Equation 3.4 that for the entire volume of water to be treated (i.e. \( V_E = V_T \)), we must have \( C_f = I_f = 1 \). This follows directly from the definitions of \( C_f \) and \( I_f \). The best configuration will therefore be quantified in terms of the
effective treated volume of water and the efficiency of the configuration as determined by the ratio of total water volume to effective treated volume:

\[ \eta = \frac{V_E}{V_T} = C_f \cdot I_f \]  

### 3.3.1.3 Basic Model Framework

This model will use the theory described above to compare the efficiency of reactors by simulating three configurations: catalyst suspended as a colloidal solution, catalyst immobilized on a thin-film, and catalyst immobilized on a 3-dimensional support. The basic framework for the model is presented here and will be developed with greater detail in sections to follow. The analytical approach will begin with a single \( \delta_w \) thin layer of water and a \( \delta_p \) thin layer of catalyst and then build up the system in both the volume of water and the three dimensional distribution. As the three dimensional nature of the catalyst develops, changes in the transmission of light through the material and the permeability of the reactant into the catalyst structure will be considered.

Light transmission through the reactor will cause variations in \( I_f \), the fraction of catalyst exposed to light. Light attenuation will affect \( I_f \) in both suspended and foam photocatalyst configurations. These variations will be modeled to decrease additively with increasing layers of photocatalyst. The relationship between increased layers and light transmittance is summative; this is because transmission through a deeper layer is dependent on the light transmitted through the layer preceding it. Transmission will be modeled by defining \( \tau \), the fraction of light transmitted through a single layer \( \delta_p \).

The permeability of the reactant into the catalyst structure will cause variations in \( C_f \), the fraction of the water volume coming into direct contact with catalyst. A suspended catalyst is a mobile particulate that can be displaced in order to allow the reactant to easily permeate into the body of the catalyst. Therefore, \( C_f \) is not reduced in suspension reactors. Conversely, immobilizations are a rigid structures and susceptible to reduced permeability, therefore, the permeability will affect the contact fraction in immobilized reactors. Variation in permeability will be modeled as a constant and can be physically inferred from pore size and/or mesh density. The relationship
between layers and permeability is independent of the number of layers above or below it. Permeability will be modeled by defining $\rho$, the permeability of a single layer $\delta_p$.

Furthermore, the model will be divided into two scenarios, each evaluated separately. The first case will investigate an unrestricted surface area reactor. In this case, the amount of photocatalyst will be the limiting factor in reactor design. The second case will investigate a restricted surface area reactor. In this second case, there is an abundance of photocatalyst and the surface area becomes the limiting factor in reactor design.

3.3.2 CASE 1: Unrestricted Surface Area

3.3.2.1 Introduction

As mentioned previously, this first section presents an analytical model for applying photocatalyst in a reactor with unlimited surface area. Plainly, the notion of an unlimited surface area photoreactor is not feasible; however, a reactor would mimic this condition in a scenario where the volume of photocatalyst was small when compared to the available surface area. In this case, there is enough area available to spread the catalyst in a thin layer $\delta_p$ such that the entire volume of photocatalyst, $V_p$, is equal to a single layer times the available area. In this manner, the amount of photocatalyst becomes the limiting factor in the structure of the reactor. Such a reactor could be practical for treating wastewater discharged over a large area.

3.3.2.2 Thin Film

A thin film reactor will be the first configuration considered, as it is the simplest geometrically. In order to apply the entire available catalyst as a thin film, there must be a much larger surface area available than volume of photocatalyst. In this case, the catalyst has no thickness and the total volume is spread in a single layer such that $V_p = \delta_p A$. To begin, a single layer of water is placed above the catalyst layer, as depicted in Figure 3-2. There is no impediment between the water and the catalyst or between the catalyst and the light source; therefore, $C_f = I_f = 1$. The total volume of water, $V_T$, is known by $V_T = \delta_w A$. From this the performance parameters can be calculated:

$$V_E = C_f \cdot I_f \cdot V_T = \delta_w A$$
This is summarized below alongside Figure 3-2. This configuration has an optimal efficiency because the entire volume of water is in direct contact with catalyst that has been exposed to light.

\[ \eta = \frac{V_E}{V_T} = C_I \cdot I_f = 1 \]

**Figure 3-2:** Single layer of water $\delta_w$ on top of a single layer of photocatalyst $\delta_p$.

It may seem intuitive that this is the best possible configuration and the results corroborate that assertion. Under the conditions stipulated in this model, the efficiency of thin-film reactors cannot be improved. However, only the smallest volume of water was applied in this configuration, so it is worthwhile to advance this model both for the completeness of the analysis as well as to investigate the possibility of improving the effective treated volume.

### 3.3.2.3 Progression: Building Layers

This model will now progress beyond the thin film configuration towards more complex structures. It is crucial to remember that the limiting factor for the unrestricted area condition is the volume of the photocatalyst. Therefore any modification to the reactor structure cannot include the addition of extra catalyst. Without increasing the volume of photocatalyst applied, the structure of the reactor can be adjusted in two ways: increasing the water volume and distributing the catalyst.
Figure 3-3: Double layer of water $2\delta_w$ on top of a single layer of photocatalyst $\delta_p$.

Let’s first begin by adding a single additional water layer. This increases $V_T$ such that $V_T = 2 \delta_w A$, doubling the water volume, as shown in Figure 3-3. Assuming that sunlight lost through the additional water layer is negligible, the irradiance fraction is unchanged. Therefore, $I_f = 1$, identical to the configuration in Figure 3-2. The contact fraction, however, is not identical because the top water layer does not come in contact with the catalyst. Only the first layer $\delta_w A$, which is half the total volume, comes in direct contact with the catalyst. Therefore, it lowers the contact fraction by half to $C_f = \frac{1}{2}$. From this, the performance parameters are determined:

$$V_E = C_f \cdot I_f \cdot V_T = \frac{1}{2} \cdot 2 \delta_w A = \delta_w A$$

$$\eta = C_f \cdot I_f = \frac{1}{2} \cdot 1 = \frac{1}{2}$$

Comparing these results to Figure 3-2, the effective treated volume is not increased but the overall efficiency of the reactor configuration is decreased by half. Although it was clear that adding additional layers of water could not improve efficiency it is now evident that the overall effective treatment volume will likewise not increase.
Figure 3-4: Layer of water $\delta_w$ on top of two layers of combined photocatalyst and water

Returning to our choices for adjusting the reactor configuration, the second option is to distribute the catalyst throughout the water volume. The catalyst can only be distributed as much as the reactor volume allows, thus greater catalyst distribution must occur in conjunction with the addition of water layers. Since the catalyst has no thickness a three dimensional distribution cannot completely cover the horizontal cross-section of the reactor in a single layer, as shown in Figure 3-4. Here the catalyst is distributed upwards one layer creating two layers each containing $\delta_p: A/2$ amount of catalyst and two layers $\delta_w: A/2$ of water followed by a single water layer. These layers are not fixed in place; therefore there is a certain probability that at any time catalyst from the top layer will be impeding light from reaching catalyst in the lower layer. The light must now travel through a combination of water and catalyst to reach lower reactor depths. Because of this distribution, we can no longer consider the light attenuation to be negligible and $I_r \neq 1$. In order to quantify attenuation due to increased catalyst distribution, we define $\tau$, a parameter relating the amount of light allowed through a layer of catalyst, such that $0 \leq \tau \leq 1$. If $\tau = 1$, the layer is completely transparent and all of the light passes through it. Likewise, if $\tau = 0$ the layer is completely opaque and the light will be blocked from reaching lower layers. Additionally, because as the number of layers increases, the amount of catalyst in each layer decreases, the light allowed past a single layer of catalyst is dependent on the number of layers. As such, the fraction of light removed from a layer will be described by $\tau/n$. Therefore, the fraction of the total initial light hitting a particular layer $n$ can be described by the following where $\tau/n$ is the fraction of light transmitted through a single layer $\delta_p$ and $n$ is the number of layers over which the catalyst is distributed:
\( I_{f_n} = I_f \) transmitted from the previous layer \((n - 1) \cdot \) fraction removed by current layer

\[
I_{f_n} = I_{f_{n-1}} \cdot \left( \frac{\tau}{n} \right)
\]

\[
I_{f_n} = I_{f_{n-1}} \cdot \frac{\tau}{n}
\] (3.6)

In this manner, the light transmitted through each layer of catalyst is dependent on the number of previous layers and the fraction of light transmitted will decrease with depth. The fraction of the incoming light radiation hitting each of the layers in the two layer system is therefore:

\[
I_{f_1} = 1
\]

\[
I_{f_2} = I_{f_1} \cdot \frac{\tau}{2} = \frac{\tau}{2}
\]

Since each layer is the same thickness, the overall irradiance fraction can be described as the average of the two layers:

\[
\bar{I}_{f} = \left( \frac{1 + \frac{\tau}{2}}{2} \right)
\]

\[
\bar{I}_{f} = \frac{\tau + 2}{2}
\]

Let’s now consider the effect of redistribution on contact fraction. Recall that the bottom two layers only contain half a water layer and half a catalyst layer, therefore the total water volume is

\[
V_T = \delta_w A + \frac{\delta_w}{2} A + \frac{\delta_w}{2} A = 2 \delta_w A.
\]

Since only the top surface of the catalyst is exposed to light, half of the top layer and the second layer are exposed, therefore the contact fraction is:

\[
C_f = \frac{\delta_w A}{2 \delta_w A} = \frac{1}{2}
\]

From this, the performance parameters are determined:

\[
V_E = C_f \cdot I_f \cdot V_T = \frac{1}{2} \cdot \frac{\tau + 2}{2} \cdot 2 \delta_w A = \frac{\tau + 2}{2} \delta_w A
\]

\[
\eta = C_f \cdot I_f = \frac{1}{2} \cdot \frac{\tau + 2}{2} = \frac{\tau + 2}{4}
\]

Comparing these results, summarized alongside Figure 3-4, to the previous configuration, Figure 3-3, the light attenuation has lowered both the effective volume and the efficiency by a
factor of \( \frac{(\tau + 2)}{2} \). In fact, if \( \tau = 1 \), then the performance parameters would exactly equal the previous configuration. It is evident that this trend will increase with increasing layers and the light will be further attenuated. In order to further characterize the trends in the performance parameters, the following section will generalize these equations to the \( n^{th} \) layer.

3.3.2.4 Generalization: Expansion to \( n \) Layers

The structure shown below in Figure 3-5 represents the most general unrestricted area configuration. The structure has been increased in total water volume and catalyst distribution to the \( n^{th} \) layer. This generalization allows us to analyze and graphically display trends. A summary of the \( n^{th} \) order performance parameters is depicted below alongside Figure 3-5.

![Figure 3-5: Layer of water \( \delta_w \) on top of \( n \) layers of combined photocatalyst and water](image)

At first glance the equations for these parameters may seem daunting, but the derivation is an extrapolation of the method shown for the one and two layer scenarios. To determine the irradiance fraction, consider any two layers: a and a-1

\[
I_{fa} = I_{fa-1} \cdot \frac{\tau}{n} \cdot n = I_{fa-2} \cdot \left( \frac{\tau}{n} \right)^2
\]

Again, since each layer is the same thickness, the overall irradiance fraction can be described as the average radiation in each layer. The average of \( n \) layers is calculated by summing the
Stephanie Loeb

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irradiance fraction for each layer 1 through n and dividing it by n layers. **Equation 3.7** expresses this in summation notation:

\[
\overline{I}_f = \frac{\sum_{i=1}^{n} \left( \frac{I}{n} \right)^{a_{i-1}}}{n}
\]  

(3.7)

Reviewing **Figure 3-5**, even though the catalyst has been distributed throughout the layers of water, it is unlikely that the contact fraction is improved. The total volume of water is

\[
V_T = \delta_w A + nA(\delta_w - \frac{\delta_w}{n}) = n\delta_w A,
\]

each layer containing only 1/nth of the total catalyst volume. Assuming that only the top face of the catalyst is exposed to light, it follows that:

\[
C_f = \frac{\delta_w A}{n \delta_w A} = \frac{1}{n}
\]  

(3.8)

From this, the performance parameters are determined:

\[
V_E = C_f \cdot I_f \cdot V_T = \frac{1}{n} \cdot \frac{\sum_{i=1}^{a=n} \left( \frac{I}{n} \right)^{a_{i-1}}}{n} \cdot n \delta_w A = \sum_{i=1}^{a=n} \left( \frac{I}{n} \right)^{a_{i-1}} \delta_w A
\]  

(3.9)

\[
\eta = C_f \cdot I_f = \frac{1}{n} \cdot \frac{\sum_{i=1}^{a=n} \left( \frac{I}{n} \right)^{a_{i-1}}}{n} = \sum_{i=1}^{a=n} \left( \frac{I}{n} \right)^{a_{i-1}} \frac{1}{n^2}
\]  

(3.10)

In order to quickly solve and analyze these equations for trends, the results were coded in MATLAB which was used to produce data arrays for \( C_f, I_f, V_E, \) and \( \eta \) for possible values of \( n \). The results of these calculations will be discussed below. MATLAB codes and preliminary graphical outputs are shown for reference in appendix section A.1.1.

### 3.3.2.5 Results and Discussion

For the purpose of comparing and characterizing the effects of varying reactor configurations, the model results were output and graphed. The results are shown as two lines, the first representing a thin-film reactor and the second a suspension. For the thin-film reactor, the catalyst is a single unit layer on the base of the reactor and theoretical layers are added as water layers on top of the catalyst. The suspension configuration is modeled by distributing the catalyst amongst the additional layers, as was described in **Figure 3-5** with **Equation 3.9** and 3.10. The thin film case is analogous to adding more water layers without distributing the catalyst. The
suspension involves the addition of water layers with the simultaneous increased division and distribution of the catalyst throughout the water volume.

**Figure 3-6** shows the trend in effective treated volume for a suspension and a thin film with increasing number of layers and **Figure 3-7** shows the trend for the efficiency. Examples values of $A=1$ and $\tau = 0.5$ were selected for illustrative purposes; a different choice of constant would not alter the overall trend displayed. Reflecting on **Figure 3-6**, it is clear that the thin-film reactor is the best configuration. When the mass of catalyst is restricted but the surface area is not, a single water layer is the maximum treated volume possible. This is expected, since it would be impossible to have a water volume in direct contact with catalyst that was greater than the total catalyst volume. Therefore, increasing the water volume beyond the catalyst volume has no impact on the actual portion of water in contact with catalyst which remains $\delta_w A$; although we will see in the next figure that the additional water added to the system greatly reduces the efficiency. In suspension, the effective volume is reduced due to the reduced light transmission through the reactor. The light attenuation reduces the irradiance fraction and results in effective treated volume values lower than $\delta_w A$.

**Figure 3-6**: Trend for the effective water volume with increasing number of theoretical layers $n$ with a surface area of $A=1$ and $\tau = 0.5$
Although the thin-film is the clear choice in terms of effective treated volume, the efficiency of the reactor is only marginally better, as shown in Figure 3-7. As the overall water volume increases, the effective volume is not increasing in either the thin-film or the suspension reaction, therefore each measure of efficiency is dropping off with 1/n. The additional loss due to $I_f$ is only a small contribution in comparison.

![Graph showing trend for efficiency with increasing number of theoretical layers](image)

**Figure 3-7:** Trend for the efficiency with increasing number of theoretical layer n with a surface area of $A=1$ and $\tau = 0.5$

### 3.3.3 CASE 2: Restricted Surface Area

#### 3.3.3.1 Introduction

From the unrestricted surface area model results, it is clear that the thin film configuration gives the best photoreactor performance. However, it is apparent that restricting the surface area will impact results obtained under a similar analysis. This section will present an analytical model for applying various limited surface area reactor configurations. Here the catalyst volume is large compared to the available area. There is not enough area available to spread out the entire volume of catalyst in a thin layer $\delta_p$. Therefore, any application of the catalyst will have a certain thickness which can be described as a series of $N$ stacked layers such that $V_p = N \delta_p A$. In this manner, the surface area becomes the limiting factor. Surface area would be restricted in any situation when space, funds or materials were constrained. This is likely to be the case with any...
photoreactor that is part of a treatment train or in point-of-use applications such as photocatalytically enhanced SODIS treatment.

### 3.3.3.2 Thick Film

Corresponding to thin films, this section will begin with a single layer configuration, as shown in Figure 3-8. This figure shows N stacked catalyst layers with a single water layer above. There is no impediment between water and catalyst or between catalyst and the light source; therefore, $C_f = I_f = 1$. The total volume of water, $V_T$, is $V_T = \delta_w A$, and from this the performance parameters can be calculated for this configuration:

$$V_E = C_f \cdot I_f \cdot V_T = \delta_w A$$
$$\eta = \frac{V_E}{V_T} = C_f \cdot I_f = 1$$

These results mimic those of the thin film reactor. However, as the following examples will display, it is possible to greatly increase the effective treated volume above $\delta_w A$ when $A$ is restricted. This is quite different from the unrestricted area case, where $\delta_w A$ was the maximum achievable volume. Note that the efficiency is calculated in terms of the water treated and not in terms of the catalyst volume employed in the reaction.

![Figure 3-8: Single layer of water $\delta_w$ on a layer of photocatalyst with thickness $N\delta_p$](image)

### 3.3.3.3 Progression: Building Layers

The model will now progress beyond the thick film configuration by increasing the number of layers, with the aim of increasing $V_E$. As before, the reactor configuration can be modified in two
ways: increasing the water volume and increasing the three dimensional distribution of the catalyst. Adding additional water layers to the system increases $V_T$ without effecting $V_E$ thereby causing a decrease in reactor efficiency. Proof of this was given in the discussion complimenting Figure 3-3 and thus will not be repeated here. For the restricted volume scenario, the catalyst has thickness, therefore, it can be three dimensionally distributed by spreading even thin layers throughout the volume of the water. If the catalyst is split into $n$ layers, then each layer is $1/n^{th}$ the thickness of entire volume. The thickness of each layer is described by:

$$\frac{N\delta_p}{n} \quad \text{with} \quad 1 < n < N$$

This catalyst slicing is depicted in Figure 3-9 where the catalyst is split into two layers, each with a thickness of $N \cdot \delta_p/2$. Between each catalyst layer, a water layer is included. This is the first configuration investigated that can increase the total water volume without decreasing the contact fraction. Since both water layers have a complete catalyst layer below them, it is clear that $C_r = 1$ in this reactor.

![Figure 3-9: Single layers of water $\delta_w$ between layers of photocatalyst with thickness $\frac{N\delta_p}{2}$](image)

In order to reach deeper water layers, the light must now travel through alternating layers of catalyst and water. The amount of light attenuated by a catalyst layer is dependent on the thickness of that layer; with thicker layers having a greater degree of opacity. The transmission $\tau$ is again defined as the transmittance through an infinitely thin layer of catalyst $\delta_p$. Therefore, the

**Performance Summary**

**Suspension**

$$V_E = \left(1 + \frac{N}{2}\right)\delta_w A$$

$$\eta = \frac{1 + \frac{N}{2}}{2}$$

**Immobilized Catalyst**

$$V_E = \rho \left(1 + \frac{N}{2}\right)\delta_w A$$

$$\eta = \frac{\rho \left(1 + \frac{N}{2}\right)}{2}$$
transmittance through a layer with thickness \( N \delta_p / n \) can be found by \( \tau^{N/n} \). This follows from the definition of \( \tau \) as the transmittance through a single layer: since \( N \) is the number of single layers, \( n = N \) describes single layer thickness which results in \( \tau^{N/n} = \tau^{N/N} = \tau \). The irradiance fraction through any layer out of a possible \( n \) layers of thickness \( N \cdot \delta_p / n \) is therefore given by:

\[
I_{f_a} = I_{f_{a-1}} \cdot \tau^{N/n}
\]  

(3.12)

The transmission of light is dependent on both the thickness and the number of layers preceding and is therefore modeled as a cumulative function with both these variables. For the two layer system shown in Figure 3-9, the mean irradiance fraction is solved by averaging the transmittance through each of the two layers as follows:

\[
I_{f_1} = 1
\]

\[
I_{f_2} = I_{f_1} \cdot \tau^{N/2} = \tau^{N/2}
\]

\[
\bar{I}_f = \frac{1 + \tau^{N/2}}{2}
\]

From this, the performance parameters are determined to be:

\[
V_E = C_f \cdot I_f \cdot V_T = 1 \cdot \frac{1 + \tau^{N/2}}{2} \cdot 2 \delta_w A = \left(1 + \tau^{N/2}\right) \delta_w A
\]

\[
\eta = C_f \cdot I_f = 1 \cdot \frac{1 + \tau^{N/2}}{2} = \frac{1 + \tau^{N/2}}{2}
\]

The results are summarized alongside Figure 3-9. Similar to the previous section, the light attenuation through the catalyst has lowered the efficiency by a factor equal to \( \bar{I}_f \), but in this case the effective volume has increased by a factor of \( 1 + \tau^{N/2} \). As progressively more layers are added, the trend continues and the effective volume increases as more layers are added since \( 1 + \tau^{N/2} > 1 \) for every \( n < N \).

These results assume that the catalyst has been suspended within the volume of the reactor; however, the catalyst can also be distributed, as a rigid immobilized structure. A suspension is a mobile particulate that can be displaced in order to allow the reactant to effectively permeate the suspension. However, if the three dimensional configuration is immobilized, the particulate is not mobile and small pores or a fine mesh density can impede the ability of a reactant to
permeate into the body of the catalyst causing a detrimental effect on the contact fraction. Since the permeability is not affected by previous layers it is constant, as opposed to summative, with increasing number of layers $n$. Here we define the permeability factor, $\rho$, as the permeability of an infinitely thin catalyst slice, $\delta_p$. In this case, a higher number of layers $n$, can be thought of as increasing the mesh density or lowering the pore size of the foam. An increase in $n$ causes a decrease in the contact fraction $C_f$ by the following, where $\rho$ is the permeability factor and $n$ is the number of theoretical layers:

$$C_f = \rho^{N/n}$$  \hspace{1cm} (4.13)

Now we can consider our two layer system in the context of an immobilized catalyst. Due to this rigidity, the permeability of the system is reduced and the new contact fraction is as follows:

$$C_f = \rho^{N/2}$$

The irradiance fraction is unchanged. From here, the updated performance parameters are:

$$V_E = C_f \cdot I_f \cdot V_T = \rho^{N/2} \cdot \frac{1 + \tau^{N/2}}{2} \cdot 2 \delta_w A = \rho^{N/2} \left(1 + \tau^{N/2}\right) \delta_w A$$

$$\eta = C_f \cdot I_f = \frac{\rho^{N/2} \left(1 + \tau^{N/2}\right)}{2}$$

These results are also summarized alongside Figure 3-9, under the immobilized catalyst subheading. Since the contact fraction is now less than one, the increase in the effective volume is further tempered. The overall trend in efficiency and effective volume is determined by the competing rates of increased volume and decreasing permeability and light transmittance. In order to further characterize these trends in performance parameters, the last section will expand these results to the $n^{th}$ layer.

### 3.3.3.4 Generalization: Expansion to N Layers

The structure shown below in Figure 3-10 represents the most general configuration for the restricted surface area reactor. The structure has been increased in total water volume and three dimensional catalyst distribution such that the reactor consists of $n$ water layers alternating with $n$ catalyst layers with a thickness $N/n$. This generalization allows us to analyze and graphically display trends. A summary of the $n^{th}$ order performance parameters for both the immobilized and suspended configurations is just below Figure 3-10.
Again, although the equations seem dense, the derivation is performed by extrapolating the one and two layer scenarios. To determine the general irradiance fraction, consider again any two layers \( a \) and \( a-1 \):

\[
I_{a-1} = I_{a-2} \cdot \frac{\tau^{N/n}}{\tau^{N/n}}
\]

\[
I_a = I_{a-1} \cdot \frac{\tau^{N/n}}{\tau^{N/n}} = I_{a-2} \cdot \frac{\tau^{N/n}}{\tau^{N/n}} = I_{a-2} \cdot \left( \frac{\tau^{N/n}}{\tau^{N/n}} \right)^2
\]

Since each layer is the same thickness, the overall irradiance fraction can be described as the average radiation in each layer. The average of \( n \) layers is calculated by summing the irradiance fraction for each layer 1 through \( n \) and dividing it by \( n \) layers. **Equation 3.14** expresses this in summation notation:

\[
\bar{I}_c = \frac{\sum_{i=1}^{a=n} \left( \frac{\tau^{N/n}}{\tau^{N/n}} \right)^{a_i-1}}{n}
\]  

(4.14)

For all suspension reactors, the contact fraction is \( C_f = 1 \), therefore for a suspended catalyst with total catalyst volume of \( V_p = N \delta_p A \) divided into \( n \) layers, the performance parameters are:

\[
V_E = C_f \cdot I_f \cdot V_T = 1 \cdot \frac{\sum_{i=1}^{a=n} \left( \frac{\tau^{N/n}}{\tau^{N/n}} \right)^{a_i-1}}{n} \cdot n \delta_w A = \left( \sum_{i=1}^{a=n} \left( \frac{\tau^{N/n}}{\tau^{N/n}} \right)^{(a_i-1)} \right) \delta_w A
\]

(3.15)

\[
\eta = C_f \cdot I_f = 1 \cdot \frac{\sum_{i=1}^{a=n} \left( \frac{\tau^{N/n}}{\tau^{N/n}} \right)^{a_i-1}}{n} = \frac{\sum_{i=1}^{a=n} \left( \frac{\tau^{N/n}}{\tau^{N/n}} \right)^{(a_i-1)}}{n}
\]

(3.16)

Combining the permeability model with the irradiance fraction defined for suspensions, a set of equations are developed to determine the effective treated volume and efficiency for immobilized catalyst reactors. Since the permeability model indicates that the relationship is not summative, **Equation 3.13** can be applied as an additional factor to the suspension equations. In this way, the performance parameters for \( n \) layers of immobilized catalyst are:

\[
V_E = C_f \cdot I_f \cdot V_T = \rho^{N/n} \cdot \frac{\sum_{i=1}^{a=n} \left( \frac{\tau^{N/n}}{\tau^{N/n}} \right)^{a_i-1}}{n} \cdot n \delta_w A
\]

\[
= \rho^{N/n} \left( \sum_{i=1}^{a=n} \left( \frac{\tau^{N/n}}{\tau^{N/n}} \right)^{(a_i-1)} \right) \delta_w A
\]

(3.17)
\[ \eta = C_{f} \cdot I_{f} = \rho^{N/n} \cdot \frac{\sum_{i=1}^{a=n} \left( \frac{N}{n} \right)^{a_i-1}}{n} \]

\[ = \frac{\rho^{N/n} \cdot \sum_{i=1}^{a=n} \left( \frac{N}{n} \right)^{(a_i-1)}}{n} \]  

(3.18)

**Performance Summary**

**Suspension**

\[ V_{E} = \left[ \sum_{i=1}^{a=n} \left( \frac{N}{n} \right)^{(a_i-1)} \right] \delta_{w} A \]

\[ \eta = \frac{\sum_{i=1}^{a=n} \left( \frac{N}{n} \right)^{(a_i-1)}}{n} \]

**Immobilized Catalyst**

\[ V_{E} = \left[ \rho^{N/n} \sum_{i=1}^{a=n} \left( \frac{N}{n} \right)^{(a_i-1)} \right] \delta_{w} A \]

\[ \eta = \left[ \rho^{N/n} \cdot \sum_{i=1}^{a=n} \left( \frac{N}{n} \right)^{(a_i-1)} \right] \frac{\delta_{w} A}{n} \]

Figure 3-10: Layer of water $\delta_{w}$ on top of $n$ layers of alternating photocatalyst and water

In order to quickly solve and analyze these equations for trends, the results were coded in MATLAB which was used to produce data arrays for $C_{f}, I_{f}, V_{E}$, and $\eta$ for possible values of $n$ and $N$. The results of these calculations will be discussed below. The MATLAB codes and preliminary graphical outputs are shown for reference in appendix section A.1.2.

### 3.3.3.5 Results and Discussion

For the purpose of comparing and characterizing the effects of varying reactor configurations, the model results were output and graphed. Example values of $N = 100$, $\tau = 0.95$, $\rho = 0.5$ and $A = 1$ were selected for illustrative purposes; a different choice of constant would not alter the overall trend displayed. The results are shown as three lines, the first representing a thick-film reactor, the second a suspension and the third an immobilized catalyst. For the thick-film reactor, the catalyst is a single unit layer on the base of the reactor and theoretical layers are added as water layers on top of the catalyst. The suspension configuration is modeled by distributing the catalyst amongst the additional layers, as was described in Figure 3-10 with Equation 3.15 and 3.16. The immobilized catalyst is modeled by also including the permeability
which is shown in Equation 3.17 and 3.18. All six equations are summarized in Table 3-2. Equations for thick films are determined by setting up the system as previously shown in Figure 3-8, with the catalyst packed into a thick layer. The additional water volume added decreases the contact fraction each time by $C_f = 1/n$ while the irradiance fraction remains unity. This results in a maximum volume of water treated at $V_E = \delta_w \cdot A$ and an overall efficiency which decreases quickly with increasing water volume.

Table 3-2: Summary of Analytical Model Equations

<table>
<thead>
<tr>
<th>PARAMETER</th>
<th>FLAT FILM</th>
<th>SUSPENSION</th>
<th>IMMOBILIZED CATALYST</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\bar{I}_f$</td>
<td>$\bar{I}_f = 1$</td>
<td>$\bar{I}<em>f = \frac{\sum</em>{i=1}^{a=n} \left( \frac{N}{n} \right)^{(a_i - 1)}}{n}$</td>
<td>$\bar{I}<em>f = \frac{\sum</em>{i=1}^{a=n} \left( \frac{N}{n} \right)^{(a_i - 1)}}{n}$</td>
</tr>
<tr>
<td>$C_f$</td>
<td>$C_f = \frac{1}{n}$</td>
<td>$C_f = 1$</td>
<td>$C_f = \rho \frac{N}{n}$</td>
</tr>
<tr>
<td>$V_E = C_f \cdot I_f \cdot V_T$</td>
<td>$V_E = \delta_w \cdot A$</td>
<td>$V_E = \delta_w \cdot A \cdot \sum_{i=1}^{a=n} \left( \frac{N}{n} \right)^{(a_i - 1)}$</td>
<td>$V_E = \delta_w \cdot A \cdot \left[ \rho \frac{N}{n} \right] \cdot \sum_{i=1}^{a=n} \left( \frac{N}{n} \right)^{(a_i - 1)}$</td>
</tr>
<tr>
<td>$\frac{V_E}{V_T} = C_f \cdot I_f$</td>
<td>$\frac{V_E}{V_T} = \frac{\sum_{i=1}^{a=n} \left( \frac{N}{n} \right)^{(a_i - 1)}}{n}$</td>
<td>$\frac{V_E}{V_T} = \left[ \rho \frac{N}{n} \right] \cdot \frac{\sum_{i=1}^{a=n} \left( \frac{N}{n} \right)^{(a_i - 1)}}{n}$</td>
<td></td>
</tr>
</tbody>
</table>

Figure 3-11 shows the trend in effective treated volume with increasing number of suspended layers for a catalyst thickness of $N = 100$ and Figure 3-12 shows the efficiency trend. This graph shows the effect of permeability curbing effective volume treated when using an immobilized photocatalyst configuration. The suspension increases smoothly with the increased distribution of the catalyst. Reflecting on Figure 3-11, it is clear that the thick film delivers the poorest performance. The volume of the catalyst is constrained and inaccessible to the water in the body of the reactor. The suspension offers the best performance, with the immobilized catalyst closely mirroring the suspension until they diverge at high values of $n$. The efficiency trends follow a
similar pattern. **Figure 3-12** shows suspending or immobilizing the catalyst in a three dimensional distribution moderates the drop in efficiency as more layers of water are added.

**Figure 3-11**: Trend in effective treated volume with increasing number of theoretical layers. $N = 100, \tau = 0.95, \rho = 0.5$ and $A = 1$.

**Figure 3-12**: Trend in efficiency with increasing number of theoretical layers. $N = 100, \tau = 0.95, \rho = 0.5$ and $A = 1$. 
The surface plots in Figure 3-13 and Figure 3-14 show the same equations plotted for increasing values of N and n. The catalyst volume N has no effect on the efficiency and acts as a coupled restraint with effective treated water volume following the number of layer n since $1 < n < N$. The effect of the permeability factor, $\rho$, results in less efficient and lower effective treated volume for the foams compared to the suspension.

**Figure 3-13:** Trends for increasing the number of theoretical layers and the volume of catalyst on the effective treated volume. The red curve is a thin film; blue is foam of increasing mesh density; and green is a suspension. $\tau = 0.95$, $\rho = 0.5$ and $A = 1$.

Comparing the results from both the restricted and unrestricted cases, it becomes clear that the best configuration in terms of efficiency and treated volume is the thin film when the application of the catalyst is not restricted by the area of the reactor. When the area of the reactor is restricted, a suspension performs best, but its performance can be closely approached by an immobilized catalyst which is evenly distributed throughout the body of the reactor such as a foam reactor configuration. The performance of the suspension and foam are most similar in
smaller systems with $n < 20$, where the performance of the two systems is predicted to be nearly identical.

**Figure 3-14:** Trends for increasing the number of theoretical layers and the volume of catalyst on the efficiency of the photocatalyst application. The red curve is a thin film; blue is foam of increasing mesh density; and green is a suspension. $\tau = 0.95$, $\rho = 0.5$ and $A = 1$.

Several assumptions were made in this model to reduce the parameters affecting the system including limited mixing, planar light source, and little temperature variation. Although these factors were not incorporated quantitatively, the effect they would have on the model can be qualitatively discussed.

A non-planar light source would allow light to enter the system from the sides. The suspension and immobilized configuration would be able to capture more of this light than the fixed film, likely causing a small decrease in the comparative performance for the film configuration. Low convective mixing, by far the largest assumption made in this model, would have the converse influence, increasing the comparative performance for the film. This is because the addition of
convective mixing will have no influence on the transmission of light, but will greatly improve the contact fraction, which is the detrimental factor in the poor performance of the fixed film. The comparative performance of the suspension to the immobilized catalyst would not be greatly affected, as the convective mixing would improve the contact fraction for both systems in a similar manner.

**3.4 SUMMARY AND CONCLUSIONS**

The model presented here has evaluated the effect of photoreactor configuration on the water purification process efficiency of the system. Model results were divided into two scenarios, each evaluated separately. The first case considers an unrestricted surface area reactor in which the amount of catalyst is the limiting factor in reactor design. In this scenario, the reactor would be very large allowing for the entire mass of catalyst to be spread out on the base of the reactor as a single indivisibly thin layer. The second case considers a restricted surface area in which the area is the limiting reactor design factor. In this scenario, the reactor size would be restricted so that the entire mass of the catalyst is divided into many layers.

Comparing the results from both cases, the best configuration in terms of efficiency and treated volume is the thin film when the application of the catalyst is not restricted by the area of the reactor. This configuration can be visualized as a reactor with a very large area covered in an infinitely thin layer of photocatalyst with the water covering the catalyst in a single similarly thin layer. The ideal performance of the reactor is attributed to the ideal contact fraction and zero light attenuation that can be achieved with the stacking of a single indivisibly thin layer of water and catalyst. As may be evident from this description, a reactor of this configuration is generally impractical for most applications, particularly small scale SODIS systems. When the area of the reactor is restricted, it was found that a suspension performs best in terms of efficiency and treated volume, but its performance can be closely approached by an immobilized catalyst which is evenly distributed throughout the body of the reactor such as when using a foam or aerogel configuration to support the catalyst. The performance of the suspension and foam are most similar in smaller systems with less than 20 theoretical layers, where the performance of the two systems is predicted to be nearly identical. Based on these model results, an immobilized catalyst should theoretically be able to practically match the performance of a suspension reactor.
3.5 References


4 NANOSTRUCTURED PHOTOCATALYTIC FOAMS FOR ENHANCED SOLAR DISINFECTION

ABSTRACT

The application of photocatalytic materials as an advanced oxidation process is an innovative technique for drinking water and waste water purification because of its ability to degrade a wide range of contaminants. For small-scale low energy production of clean water, immobilization of photocatalytic nanoparticles on foam supports is considered attractive because these materials can promote higher efficiency reactions and an immobilized material simplifies the separation of the catalyst from the water after treatment. Experiments were conducted to compare the performance of titanium dioxide coated foams of varying pore size to suspension and fixed film reactors. The degradation of organic dyes (acid orange 24 and methylene blue), 1,4-dioxane and Escherichia coli was characterized in a batch reactor designed to mimic an enhanced Solar Disinfection (SODIS) system with simulated solar light, limited mixing and significant water depth. These results examined the relationship between target contaminant degradation and reactor configuration. It was found that a catalyst immobilized on a foam support can match or surpass the efficiency of a suspension configuration due to effective mass transport and association between the analyte and the foam. Efficiency is related to pore size; however, the ideal pore size varied between target contaminants.

4.1 INTRODUCTION

The integration of solar photocatalytic advanced oxidation into the Solar Disinfection (SODIS) method has been proposed as a robust approach for improving the microbial and chemical quality of the treated water. The goal of this integration is to develop a small and inexpensive point-of-use photoreactor. A vital decision in photoreactor design is the photocatalyst configuration, which refers to the shape or form of the catalyst within the reactor. Variations include different sized particulate suspensions, immobilized thin films, and many different structures of substrate material with photocatalytic surface coatings (Akhavan et al. 2008,
Guiang et al. 2008, Han et al. 2011, Kisch et al. 2002, Li & Shang 2008, Zhang et al. 2012). Traditionally, configuration was viewed as a binary decision between suspending the catalyst in the water or to somehow immobilizing the catalyst to a substrate, often in the form of a fixed film (Ray 2009). Although suspended systems are an efficient configuration, the catalyst must be removed before consumption which can require the application of a chemical treatment or fine filter which may not be cheaply available and complicates the purification process (Gumy et al. 2006, Plantard et al. 2011). Therefore, the immobilization of the photocatalyst remains an attractive alternative, particularly for small scale point-of-use applications.

Immobilization of photocatalytic nanoparticles on foam supports is considered attractive because the porosity, high surface area, low density, high permeability and translucency of these materials can promote higher efficiency reactions. A suspended photocatalyst has been empirically demonstrated to be more efficient than a fixed film reactor. Therefore, foams and porous films have been investigated in an attempt to mimic the configuration of a suspension while maintaining immobilization (Antoniou et al. 2009, Plantard et al. 2011, Plesch et al. 2009). However, a broad comparison of catalyst configurations including a wide range of foam pore sizes, suspension and fixed film reactors has not been empirically undertaken. Furthermore, past investigations have been performed with probe compounds and the relationship between configuration performance and target compound has not been described, particularly for biological contaminants and common environmental pollutants. The study presented aims to predict the best configuration for an immobilized catalyst in an enhanced SODIS reactor and to examine the relationship between target contaminant degradation and reactor configuration.

### 4.2 Objective

The objective of this study is to evaluate the comparative performance of TiO$_2$ coated foams of varying pore size, a TiO$_2$ suspension and TiO$_2$ fixed film photocatalyst configurations in terms of the degradation of acid orange 24 azo dye as a probe compound, the degradation of *Escherichia coli* and the degradation of 1,4-dioxane for comparative analysis in a SODIS batch reactor under simulated solar spectrum light irradiation.
4.3 MATERIALS AND METHOD

4.3.1 Aluminum Foams

Aluminum foams, depicted in Figure 4-1, were purchased from ERG Materials and Aerospace. Foams had a relative density of 7.85% +/- 0.95% as determined by the manufacturer. The relative density is the mass of the foam material divided by the mass the material would be if it were a solid block of the same dimensions. All foam samples were cylindrical with a height of 2 cm and a diameter of 6 cm. Four pore sizes (5, 10, 20 and 40 pores per inch (PPI)) were selected in order to cover a wide range of mesh densities, in turn, increasing the likelihood of detecting a trend with an optimum pore size, if present. As the number of pores per inch increases, the mesh density of the foams increases creating a more intricate foam structure with a greater surface area to volume ratio. Although foams were designed to have a relatively density between 6 and 10%, it was found that the foams with greater number of pores per inch tended to weigh more by ~2 g and have relative density on the higher end of the indicated range.

![Figure 4-1: Aluminum foam with 5, 10, 20 and 40 PPI (pores per inch)](Image)

As the relative density and PPI increase, the specific surface area of a foam material also increases. Since the relative density of each sample is within a small range, the specific surface area increases as the number of pores per inch increases. ERG Aerospace (2011) characterizes the specific surface area of their foams based on geometric calculations which are then confirmed by multipoint BET (Brunauer-Emmett-Teller) analysis through the adsorption of krypton gas at cryogenic temperatures. For foams with a relative density near 8%, the specific surface area is 350, 790, 1200 and 1800 m²/m³ for 5, 10, 20 and 40 PPI foams, respectively.
4.3.2 Reagents and Equipment

The laboratory equipment, materials and chemical reagents used in the photocatalytic foam experiments are listed below in Table 4-1 and Table 4-2, respectively.

Table 4-1: Laboratory equipment

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Manufacturer</th>
<th>Product Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET Solar Simulator</td>
<td>Photoemission Tech (Camarillo, CA)</td>
<td>SS150AAA</td>
</tr>
<tr>
<td>Crystallizing Dishes</td>
<td>Fisher Scientific (Ottawa, ON)</td>
<td>08-762-4</td>
</tr>
<tr>
<td>Ultra-Sonicator</td>
<td>Laval Lab Inc. (Laval, QB)</td>
<td>Laborette 17</td>
</tr>
<tr>
<td>Muffle Furnace</td>
<td>Fischer Scientific (Ottawa, ON)</td>
<td>F-A1730</td>
</tr>
<tr>
<td>Scanning Electron Microscope</td>
<td>JEOL USA Inc. (Peabody, MA)</td>
<td>JSM6610-Lv</td>
</tr>
<tr>
<td>Dioide Array Spectrophotometer</td>
<td>Cecil Instruments (Cambridge, UK)</td>
<td>CE3055</td>
</tr>
<tr>
<td>Gas Chromatograph Mass Spectrometer (GC-MS)</td>
<td>Agilent Technologies (Mississauga, ON)</td>
<td>Varian 400 GC/MS</td>
</tr>
<tr>
<td>Analytical Balance</td>
<td>OHAUS (Florham Park, NJ)</td>
<td>AP2105</td>
</tr>
<tr>
<td>Acrodisc 0.45 µm syringe filters</td>
<td>PALL Corp. (Anne Arbour, MI)</td>
<td>PN 4614</td>
</tr>
<tr>
<td>Centrifuge</td>
<td>Thermo Scientific (Asheville, NC)</td>
<td>Sorvall RC-5C Plus</td>
</tr>
<tr>
<td>10 mL Centrifuge Tubes</td>
<td>Fischer Scientific (Ottawa, ON)</td>
<td>05-562-16C</td>
</tr>
<tr>
<td>50 mL Centrifuge Tubes</td>
<td>Fischer Scientific (Ottawa, ON)</td>
<td>05-562-16B</td>
</tr>
<tr>
<td>C_{18} SPE cartridges</td>
<td>Waters (Mississauga, ON)</td>
<td>WAT043395</td>
</tr>
<tr>
<td>GC-MS vials</td>
<td>VWR Scientific (Mississauga, ON)</td>
<td>C58002W</td>
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<td>Genie Vortex Mixer</td>
<td>Fischer Scientific (Ottawa, ON)</td>
<td>12-812</td>
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<tr>
<td>Bench Top Shaker/Incubator</td>
<td>Thermo Scientific (Asheville, NC)</td>
<td>3527</td>
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<tr>
<td>Biosafety Cabinet</td>
<td>Thermo Scientific (Asheville, NC)</td>
<td>SN:10909-B</td>
</tr>
<tr>
<td>Sterilmatic Autoclave</td>
<td>Market Forge Industries (Everet, MA)</td>
<td>120/208-240</td>
</tr>
<tr>
<td>-80 C Freezer</td>
<td>Caltec (Mississauga, ON)</td>
<td>8326</td>
</tr>
<tr>
<td>Cryogenic Vials</td>
<td>VWR Scientific (Mississauga, ON)</td>
<td>479-0821</td>
</tr>
<tr>
<td>Incubator</td>
<td>Fischer Scientific (Ottawa, ON)</td>
<td>11679304</td>
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Table 4-2: Materials and chemical reagents

<table>
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<tr>
<th>Material or Chemical</th>
<th>Manufacturer</th>
<th>Product Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum Foams</td>
<td>ERG Materials &amp; Aerospace Corp. (Oakland, CA)</td>
<td>Duocel 6101-T6</td>
</tr>
<tr>
<td>Aeroxide® TiO₂ P-25</td>
<td>Evonik Industries (Essen, Germany)</td>
<td>10007287</td>
</tr>
<tr>
<td>10% HNO₃</td>
<td>Sigma-Aldrich Corp. (Oakville, ON)</td>
<td>438073</td>
</tr>
<tr>
<td>Acetone</td>
<td>Sigma-Aldrich Corp. (Oakville, ON)</td>
<td>270725</td>
</tr>
<tr>
<td>Acid Orange 24</td>
<td>Sigma-Aldrich Corp. (Oakville, ON)</td>
<td>S468339</td>
</tr>
<tr>
<td>Methylene Blue</td>
<td>Fischer Scientific (Ottawa, ON)</td>
<td>792949</td>
</tr>
<tr>
<td>1,4-dioxane</td>
<td>Sigma-Aldrich Corp. (Oakville, ON)</td>
<td>34857</td>
</tr>
<tr>
<td>1,4-dioxane-d₈</td>
<td>Sigma-Aldrich Corp. (Oakville, ON)</td>
<td>269816</td>
</tr>
<tr>
<td>Hexane</td>
<td>Sigma-Aldrich Corp. (Oakville, ON)</td>
<td>650552</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>Sigma-Aldrich Corp. (Oakville, ON)</td>
<td>650463</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>Sigma-Aldrich Corp. (Oakville, ON)</td>
<td>34967</td>
</tr>
<tr>
<td>E. coli ATCC 23631</td>
<td>Cedar Lane Laboratories (Burlington, ON)</td>
<td>23631</td>
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<tr>
<td>LB Broth</td>
<td>Sigma-Aldrich Corp. (Oakville, ON)</td>
<td>L3022</td>
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<td>Glycerol</td>
<td>Sigma-Aldrich Corp. (Oakville, ON)</td>
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<td>Phosphate Buffer Saline Solution</td>
<td>Sigma-Aldrich Corp. (Oakville, ON)</td>
<td>P5493</td>
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<td>Agar Plates</td>
<td>Sigma-Aldrich Corp. (Oakville, ON)</td>
<td>L5542</td>
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<td>Ringers Solution</td>
<td>Sigma-Aldrich Corp. (Oakville, ON)</td>
<td>S5886</td>
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<tr>
<td>Sodium Chloride</td>
<td>Caledon Laboratories (Georgetown, ON)</td>
<td>5920-1</td>
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<tr>
<td>Potassium Chloride</td>
<td>Caledon Laboratories (Georgetown, ON)</td>
<td>2520-1</td>
</tr>
<tr>
<td>Calcium Chloride</td>
<td>Caledon Laboratories (Georgetown, ON)</td>
<td>7260-1</td>
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<tr>
<td>Sodium Bicarbonate</td>
<td>Caledon Laboratories (Georgetown, ON)</td>
<td>7260-1</td>
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</table>
4.3.3 Photocatalytic Material Preparation and Characterization

All materials to be coated were cleaned by rinsing with acetone and DI water. Aluminum foams of 5, 10, 20 and 40 PPI were purchased from ERG materials and Aerospace. A dipping solution was made by mixing 20% wt of Aeroxide P-25® TiO₂ (Evonik Industries) into distilled water and adding 10% HNO₃ dropwise until a pH of 2.4 was achieved. The foams or film were then dipped in the solution for 5 minutes, and sonicated in a water bath for 10 minutes to improve the heterogeneity of the coating. The foams were then dried at 80 °C for 10 min in a Sybron Thermolyne muffle furnace (Fischer Scientific). Oven temperature was increased at a rate of 2.5°C/min to 600°C and held constant for 1 hour. After 1 hour samples were allowed to cool naturally (~12 hours cooling). The mass of the coating was determined by weighing the samples before and after treatment.

4.3.4 Bench-Scale Solar Simulator System Set-up

Irradiation experiments were performed in a Photoemission Tech SS150AA solar simulator. This simulator employs a xenon short arc lamp and an AM1.5 G (Atmospheric Mass 1.5; Global) filter to deliver solar spectrum light. The reactor section of the simulator is shown in Figure 4-2. The system produced a square field of illumination of 156 x 156 mm. Prior to experimentation, the system was adjusted to produce light equivalent to a one sun intensity. Spatial and temporal uniformity of the light (rated at ≤ 2%) were confirmed by external calibration and verification with a photo-diode and a multi-meter. Spatial non-uniformity was determined to be 0.84% across the x-axis and 1.19% across the y-axis, which was also the maximum non-uniformity. Temporal non-uniformity over a 4.5 hour period was determined to be 1.25%. Temperature in the reactor was also monitored during experimentation. The temperature was observed to rise steadily over the first 60 minutes, and then remain constant throughout the remainder of the time. The average ambient room temperature was 22.5°C and the maximum temperature reached inside the reactor was 32.5 °C. During experimentation the sides of the reactor were covered with a dark material to prevent ambient light from hitting the samples from the side. Samples were arranged as shown in Figure 4-3 with the control sample in the centre and each other sample spaced evenly around the centre. This arrangement ensures that each of the samples containing catalyst was an equal distance from the centre of the reactor.
Figure 4-2: Photoemission Tech SS150AA solar simulator

4.3.5 Evaluating Photocatalytic Activity

Seven small crystallizing dishes (70 mm x 50 mm; Fisher Scientific) arranged as shown in Figure 4-3 were placed in the solar simulator illumination area and filled with 75 mL DI water. Each container was then dosed with a single contaminant as described below and briefly stirred to create a homogeneous mixture. The first sample was taken immediately after dosing. Suspended Aeroxide P-25® TiO₂, TiO₂ coated aluminum foams and flat aluminum materials were then added to the dishes. The samples were kept in the dark for a 30 minutes dark reaction, and then the solar simulator lamp shutter was opened. For the 1,4-dioxane and organic dye samples one aliquot from each container was removed at 0, 5, 10, 20, 40, 80, 120 and 160 minutes. *E. coli* were removed at 0, 15, 30, 45, 60 and 75 minutes. Samples were not stirred.

Figure 4-3: Acid orange 24 dosed samples arranged in photoreactor during treatment. (Centre: control; clockwise from the centre right: suspension, 40 PPI foam, 20 PPI foam, 10 PPI foam, 5 PPI foam, fixed-film)
continuously throughout the exposure in order to mimic SODIS reactor conditions; however, each sample was briefly stirred immediately prior to sampling to achieve an accurate uniform distribution of contaminant prior to measurement.

4.3.6 Contaminant Dosing and Detection

4.3.6.1 Organic Dyes
Acid orange 24 (AO24) and methylene blue (MB) dye were purchased from Sigma-Aldrich. These two dyes were selected for their variation in size and composition, providing greater variation in the properties of the compounds that were studied. Structures AO24 and MB are shown in Figure 4-4 and Figure 4-5, respectively.

Figure 4-4: Acid orange 24 (Sigma-Aldrich, 2013); 448.43 g/mol; C_{20}H_{17}N_{4}NaO_{5}S

![Acid orange 24](image)

Figure 4-5: Methylene blue (Sigma-Aldrich, 2013); 139.85 g/mol; C_{16}H_{18}ClN_{3}S

Dye samples were prepared by dissolving 200 mg/L of dye into DI water. 2 mL of this solution per liter of water sample was added to the photoreactor immediately prior to experimentation to achieve a starting concentration of 4 mg/L. Concentrations of AO24 and MB were determined using a diode array UV-vis spectrophotometer at 430 nm and 607 nm, respectively. Suspension samples were spun down in a centrifuge before analysis to pellet and remove the TiO$_2$. 
4.3.6.2 1,4-Dioxane

1,4-dioxane was purchased from Sigma-Aldrich. The compound was chosen because it is a recalcitrant organic that is not known to break down or be removed by conventional methods. It is a common pollutant and is stable and persistent in natural water systems (Luck, 2007).

![1,4-dioxane](image)

**Figure 4-6:** 1,4-dioxane (Sigma-Aldrich, 2013); 88.11 g/mol; C₄H₈O₂

A 100 ppm standard was prepared following the method outlined in Appendix B.4. 1 mL per 100 mL of water sample was added to the photoreactor immediately prior to experimentation to achieve a concentration of 1 ppm. Suspension samples were filtered through a 0.45 μm filter before analysis.

Dioxane in the water sample was extracted using a liquid-liquid extraction with a solution of hexane-dichloromethane (80:20, v/v) followed by concentration through solid phase extraction and elution with acetonitrile. 1.5 mL of the water samples with a fixed concentration of an isotopic labeled internal calibration standard (1,4-dioxane-d₈, Sigma-Aldrich) were added to a 10 mL centrifuge tube (Fischer Scientific) and extracted in 7 mL of extraction solution by vortexing for 1 min and shaking for 30 minutes at 300 rpm. Samples were then centrifuged for 10 minutes at 2200 rpm and transferred to C₁₈ SPE cartridge (18% carbon loading, 500 mg sorbent weight, and 6 mL column size, SPE-PAK, Waters) which had been conditioned with one column volume each of acetonitrile and extraction solution. Samples were processed slowly under gravity and eluted twice with 0.5 mL of acetonitrile. The eluted sample was collected in 2 mL amber vials (Type 1, Class A borosilicate glass) with rubber septa polypropylene screw caps (Target DP®, National Scientific, VWR International) and stored in the dark at 4°C until analyzed. The concentration of 1,4-dioxane was determined through correlation with standards and by relating the MS response of 1,4-dioxane’s quantification ion (m/z 88) to the response of the 1,4-dioxane-d₈’s quantification ion (m/z 96).
4.3.6.3 *Escherichia coli*

Bacterial preparation and enumeration were performed following ATCC guidelines and standard aseptic practices. A lyophilized *E. coli* stock culture (ATCC® 23631) was grown from a seed culture purchased from Cedarlane Laboratories. The lyophilized stock was revived by adding 0.5 mL of LB broth (Sigma-Aldrich) directly to the stock culture and mixing well. This 0.5 mL was then transferred to a sterile aeration test tube containing 5-6 mL of LB broth. This tube was incubated overnight at 37°C while shaking at 300 rpm.

The following day, this starter culture was diluted 1/500 by transferring 0.5 mL of the starter culture to 250 mL sterile LB broth in a 1 L Erlenmeyer flask. The culture was allowed to grow incubating at 37°C while shaking at 300 rpm until it reached a logarithmic growth phase in which the OD$_{600}$ was increasing to a value of 1.6. Glycerol stocks were prepared by adding 0.75 mL of logarithmic phase culture to 0.50 mL 50% glycerol which had been filter sterilized and added to autoclaved cryovials. Each vial was briefly vortexed to ensure even mixing and then immediately placed on ice. Vials were then stored cryogenically frozen at -80°C.

The evening prior to experimentation, a portion of the *E. coli* stock was reanimated by touching a sterile pipette tip to the frozen culture then immersing the tip in 250 mL of LB broth. The inoculated solution was incubated overnight at 37°C until it reached a concentration of $10^9$ CFU/mL as confirmed by measuring the OD$_{600}$.

A portion of the stationary culture at $10^9$ CFU/mL was transferred to a sterile autoclaved 50 mL centrifuge tube and spun down at 3000 rpm for 10 minutes. The growth media was removed and the pellet suspended in 25 mL ¼ strength Ringers solution. This process was repeated twice to ensure all growth media was removed from the solution. 1 mL of this solution was added to 25 mL ¼ Ringers to make a stock solution for inoculation. Immediately prior to experimentation, 1 mL of the stock solution was added to 75 mL ¼ Ringers in each photoreactor configuration, resulting in a starting concentration of ~$10^6$ CFU/mL. At the indicated time intervals, the bacterial levels were enumerated using the following standard spread plate count method:

1 mL sample was taken from the culture and serially diluted with sterile phosphate buffer saline (PBS; Sigma-Aldrich) solution. 100 µL of each dilution was pipetted into the middle of a sterile pre-poured LB agar 10 cm petri plate (Sigma-Aldrich) and manually spread using a spin table.
and sterile spreader. Plates were incubated at 37°C for 24 hrs after which the colonies were counted. All dilutions and plating procedures were conducted inside of an operating biosafety cabinet and following standard sterile techniques. The dilution media, agar and pipette tips were sterilized using a Sterilmatic autoclave operating at 121°C for 20 minutes.

4.4 RESULTS AND DISCUSSION

4.4.1 Photocatalytic Coatings

Photocatalytic coatings with good adhesion were produced using the dip-coating method outlined above. The mass of catalytic coating achieved in each round of treatment was consistent, although the mass of the coating varied between samples. This is caused by the larger surface area available in the finer pore size foams (20 and 40 PPI) allowing the material to support a larger coating mass. Table 4-3 shows the average mass of catalyst applied to each support and the variation between samples. Details regarding the coating for all samples used for experimentation are further described in the Appendix C.3.

Table 4-3: Mass and variation in photocatalytic TiO₂ coatings

<table>
<thead>
<tr>
<th>Coating Mass</th>
<th>5 PPI Foam</th>
<th>10 PPI Foam</th>
<th>20 PPI Foam</th>
<th>40 PPI Foam</th>
<th>Fixed Film</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>0.59 g</td>
<td>0.62 g</td>
<td>1.08 g</td>
<td>1.16 g</td>
<td>1.13 g</td>
</tr>
<tr>
<td>Standard Dev</td>
<td>0.06 g</td>
<td>0.07 g</td>
<td>0.06 g</td>
<td>0.07 g</td>
<td>0.05 g</td>
</tr>
</tbody>
</table>

Scanning Electron Microscope (SEM) images of the foam coating were taken using a JOEL JSM6610-Lv in Secondary Electron Imaging (SEI) mode in order to characterize the morphology and surface topography of the coating. Images show that an effective distribution of the coating over the foam surface was achieved; however, there were different characteristics in the coating of foams with varying pore size. The large pore size samples (5 and 10 PPI) showed a coating with more cracks, which could be a result of the longer struts and greater distance between curves and bends, which can help to support the coating during heat treatment. Small cracks can be seen along the curved edge of the coating in Figure 4-5a and Figure 4-5b.
Figure 4-7: Scanning Electron Microscope (SEM) Secondary Electron Images (SEI) of TiO$_2$ coated aluminum foams

The 20 and 40 PPI foams showed less cracks in the coating, although more clogged pores, pores in which an agglomeration of TiO$_2$ accumulated, were identified. It is hypothesized that these clogs, as depicted in the bottom right hand corner of Figure 4-5d, were formed by surface tension in the coating which allowed a bubble like structure to form and solidify in the pore during heat treatment. This is supported by the partially blocked pore seen in upper right Figure 4-5c, which has a structure resembling a popped bubble. It is likely that the greater portion of clogged pores also contributed to the large jump in average mass coating for the 20 and 40 PPI samples.
4.4.2 Organic Dye Results

Reactive dyes methylene blue (MB) and acid orange 24 (AO24) were the first compounds used to investigate the performance of each of the photoreactor configurations: suspension, foams with 5, 10, 20 and 40 PPI, and fixed films. Coloured dyes are resistant to conventional degradation process and the concentration are easily measured using spectrophotometric methods- this makes them particularly good candidates for an initial investigation. Tables showing the complete degradation results are shown in Appendix C.1 and calibrations for determining contaminant concentration are shown in Appendix B.1.

A suspension of TiO$_2$ was able to completely degrade a 4 mg/L solution of the MB dye. This can be seen in Figure 4-8, which shows a time series change in dye concentration for each reactor configuration. The control sample showed some dye removal over the 160 minute sampling period; this is consistent with degradation that can occur by direct photolysis. All other samples showed intermediate performance between the suspension and control with the notable exception of the 40 PPI foam, which performed the worst, achieving less dye removal than the control sample. No significant removal was observed during the initial 30 minute dark reaction.

![Figure 4-8: Relative loss of methylene blue for suspension, fixed film and foams of 5, 10, 20 and 40 pores per inch (PPI)](image-url)
The trends between the intermediate samples can be more clearly assessed by considering the mass of TiO₂ applied to each sample. Due to variation in foam surface area and coating thickness, the mass of catalyst applied in each configuration varied on average between 0.60 g and 1.16 g of TiO₂. To account for this variation, **Figure 4-9** shows the relative concentration at each sampling time normalized by the mass of TiO₂. When the amount of catalyst is considered, the trends between the intermediate samples become more apparent. The 5 and 10 PPI foams are the top performers, with the 10 PPI able to achieve approximately the same total removal as the suspension per g TiO₂. The fixed film and 20 PPI foam were intermediate performers, and the 40 PPI is the least effective configuration.

**Figure 4-9**: Relative loss of methylene blue per g of TiO₂ for Suspension, Thick Film and Foams of 5, 10, 20 and 40 pores per inch (PPI)

The same sets of experiments were performed with the AO24 dye to determine if the trends between the performances for different configurations were consistent between target degradation compounds of varying properties. **Figure 4-10** shows the relative concentration of AO24 in each sample. The AO24 control sample showed little to no degradation over the 160 minute sampling period and the fixed film sample showed a minimal drop in dye concentration;
however, the foam samples all showed nearly a complete removal by 40 minutes. In addition to this stark removal, results from the initial dark reaction show up to 60% dye removal in 30 minutes with no light exposure. It is hypothesized that the dark reaction removal and the high removal rate shown in these samples may be related to the absorption of the dye to the surface of the foam.

![Figure 4-10](image)

**Figure 4-10**: Relative loss of acid Orange 24 for suspension, fixed film and foams of 5, 10, 20 and 40 pores per inch (PPI)

When standardized for the mass of catalyst applied, as shown in **Figure 4-11**, the foams are shown to outperform the suspension, with the performance of the fixed film trailing behind all other configurations. The results from the MB and AO24 experiments are summarized in **Figure 4-12**, which shows the total removal of dye from each configuration compared directly as a relative value and as a value standardized for the mass of catalyst applied. It is evident that the degradation results vary greatly between the two dyes. It was hypothesized that the variation in results could be contributed to two main factors: the ability of the compound to be removed by direction photolysis and the adsorption of the compound to the surface of the foam structure. In order to test these conjectures, a set of supplementary experiments were set up to quantify the effect of the photoactivity of MB and the absorption of AO24 to the foam supports.
Figure 4-11: Relative loss of acid orange 24 per g of TiO$_2$ for suspension, fixed film and foams of 5, 10, 20 and 40 pores per inch (PPI)

Figure 4-12: Total Dye Removed
In order to determine the effect of the photolytic degradation of MB on the TiO₂ foam experiments, an experiment to quantity the amount of light obscured by the foams was designed. 5 samples, a control sample (water only) and uncoated aluminum foam of each pore size, were dosed with 4 mg/L MB and the degradation of the dye was determined for 160 minutes under simulated solar light radiation. The change in concentration with time is shown in Figure 4-13. The control sample showed the most dye removal, followed by the 10 and 5 PPI foam; however, the drop between dye loss for the control and the foam samples was not a statistically significant variation. Conversely, the 20 and 40 PPI foams showed a larger drop in the total dye removed that was significantly lower than the control sample.

![Figure 4-13: Relative loss of methylene blue for light reaction using uncoated aluminum foams](image)

It was apparent from the AO24 experiment that a significant amount of the dye was being removed from the samples containing the foams during the dark reaction. To test the hypothesis that the dye was adsorbing to the surface of the foams, an experiment was performed using a control sample and aluminum foam of each pore size coated with TiO₂. All samples were dosed with 4 mg/L AO24 and the concentration of dye was monitored throughout a 160 minute dark reaction.
The results from this investigation are shown in Figure 4-14. No loss of dye was observed in the control samples compared to the foam samples which showed an average dye loss of 71.3%. There was no significant difference in the removal of dye through adsorption for foams of different pore sizes. Adsorption as the removal mechanism for these results was also supported qualitatively: when the samples were emptied and the foams were rinsed, a visible amount of dye colour was observed being washed from the foam. This colour was not present when the foams were cleaned after light reaction experiments with TiO$_2$ and AO24.

![Figure 4-14](image)

**Figure 4-14:** Relative loss of acid orange 24 dye in a dark reaction with TiO$_2$ coated aluminum foams

A summary of the results from these complimentary experiments is shown in Figure 4-15. In this figure, the significance between sample results is made clearer. Differences were considered significant if the range of values (shown by the error bars) did not overlap. Using this test, it can be seen that the difference between the control sample and the 20 and 40 PPI foams is significant for the test of light obscured; and the foam samples are significantly different from the control sample in the adsorption test.
1,4-dioxane is a recalcitrant organic and is known to be resistant to traditional methods of decomposition, but has been shown to be effectively treated using advanced oxidation processes. This makes it an excellent candidate for characterizing the performance of advanced oxidation treatment systems. As anticipated, the control sample did not show any degradation of 1,4-dioxane over a 160 minute time period, as shown in Figure 4-16. Although the fixed film sample showed some degradation, it performed the worst of the catalyst containing samples, able to remove just over 20% of the 1,4-dioxane in the water sample in 160 minutes. The foam samples were intermediate performers, able to remove between 40 and 60% of the contaminant. The TiO$_2$ performed by far the best, being the only configuration able to completely degrade the contaminant.
Figure 4-16: Relative loss of 1,4-dioxane

When standardized for the mass of catalyst applied, the trends between the foam samples of varying pore sizes becomes more apparent. Figure 4-17 shows the relative removal of 1,4-dioxane per g of TiO$_2$ applied for each photoreactor configuration. Figure 4-18 shows the total amount of 1,4-dioxane removed from each sample as a percent of the starting concentration. As mentioned previously, the suspension is by far the best performing configuration. The 10 PPI foam, followed by the 5 PPI foam, are the next most effective configurations, both before and after normalizing for amount of catalyst. Degradation efficiency decreases as number of pores per inch increases after 10 PPI, which is attributed to the reduced amount of light entering the foam material. An association between the foam material and 1,4-dioxane was not noted in these results, as there was no removal observed during the 30 minute dark reaction and the foam samples did not display any advantage over the suspension configuration, which could indicate adsorption to the foam surface allowing for a greater proximity between the contaminant and the radical species.
Figure 4-17: Relative loss of 1,4-dioxane per g of TiO₂

Figure 4-18: Total percent of 1,4-dioxane removed from sample
4.4.4 E. coli Results

Photocatalytic materials are known to enhance the traditional SODIS mechanism for inactivation of E. coli, therefore it was anticipated that the light exposed control sample, which contained only DI water spiked with E. coli bacteria, would show some inactivation over the 75 minute time period and that the samples containing photocatalytic TiO₂ would show faster and/or more complete inactivation. Each foam sample consisted of aluminum foam coated with TiO₂ by the method described in section 0. The thin film was a flat piece of aluminum coated in this same manner. The control sample achieved nearly a 2-log inactivation on E. coli over 75 minutes, however, the 40 PPI foam performed worse than the control, showing less than 0.5-log reduction. As indicated by the dye experiments, this appears to be caused by the very fine pore size of the foam, which prevents light from radiating through the material. Log-removal results for each configuration are shown in Figure 4-19. The suspension, film and 5 PPI foam were able to completely inactivate the E. coli present in 75 minutes, performing far better than the 10, 20, 40 PPI foam or control samples.

![Figure 4-19: Log-removal of E. coli](image)

When standardized for the mass of catalyst applied, the trends become more apparent. The relative inactivation of E. coli per g of TiO₂ applied for each of the photoreactor configurations is
shown in **Figure 4-20.** **Figure 4-21** shows the same degradation efficiency relative to mass of catalyst applied for each configuration, but the efficiency has now been normalized to the performance of the suspension reactor in order to better illustrate the comparative performance of each configuration. It is interesting to note that the 5 PPI configurations is by far the most effective, operating with over twice the overall efficiency of the suspension or thin film configuration. Based on the supplementary experiments performed with the organic dyes, it was determined that aside from mass transport and reactor configuration, there were two factors which were important in determining the photoreactor efficiency: the amount of light allowed to pass through the catalytic material and the adsorption of the analyte to the surface of the catalyst. The inactivation results indicate that *E. coli* can become associated with the surface of the foam support which increases its proximity to the catalyst, improving the inactivation performance. However, it should be noted that this was determined to occur for initial tests with the catalyst and that the life-time of this association was not verified. When the pore size of the foam becomes too small, too much light is being obscured and the amount of photocatalytically-produced radicals becomes limited. This assertion is further supported by the initial 30 min dark phase reaction, which showed just over a 0.5 log reduction for the 5 PPI foam. Slightly smaller dark reaction reductions were also seen in the 20 and 40 PPI samples and little to no change for the other samples.

**Figure 4-20:** Relative removal of *E. coli* per g of TiO$_2$
Based on these experiments, a photocatalytic 5 PPI foam would enhance the inactivation of *E. coli* in a batch reactor requiring ~38 minutes to achieve a 3-log reduction compared to traditional SODIS methods, which would take ~6 hours.

### 4.4.5 Comparing Contaminants

For all target contaminants, the distribution of the catalyst and the transmission of light throughout the reactor were important factors in determining the efficiency of each system. **Table 4-4** summarizes the best and worst performing configurations for each target contaminant. For all contaminants, the 40 PPI foam was one of the worst performers. Based on the complimentary dye experiments, it was determined that the 20 and 40 PPI foams obscured a significant amount of light; this prevents photons from reaching the catalyst inside the foam structure and would reduce both the photocatalytic radical degradation and the degradation by direct photolysis, if applicable. Based on the degradation observed in the control sample, it was determined that methylene and *E. coli* showed degradation by both direct photolysis and advanced oxidation. In these cases, the effect of the light blocking was magnified and the 40 and 20 PPI foams were observed to be by far the worst performers. Acid orange 24 and 1,4-dioxane did not show any degradation in the control sample, for both these compounds, the worst
performer was the fixed film, followed by the 40 PPI foam. The performance of the fixed film is attributed to the poor proximity between catalyst and contaminant in this configuration.

**Table 4-4: Summary of degradation performance results**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Methylene Blue</th>
<th>Acid Orange 24</th>
<th>1,4-Dioxane</th>
<th>E. coli</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Top Performers ↑</strong></td>
<td>1. Suspension</td>
<td>1. 10 PPI Foam</td>
<td>1. Suspension</td>
<td>1. 5 PPI Foam</td>
</tr>
<tr>
<td></td>
<td>2. 10 PPI Foam</td>
<td>2. 5 PPI Foam</td>
<td>2. 10 PP Foam</td>
<td>2. Fixed Film</td>
</tr>
<tr>
<td><strong>Worst Performers ↓</strong></td>
<td>1. 40 PPI Foam</td>
<td>1. Fixed Film</td>
<td>1. Fixed Film</td>
<td>1. 40 PPI Foam</td>
</tr>
<tr>
<td></td>
<td>2. 20 PPI Foam</td>
<td>2. 40 PPI Foam</td>
<td>2. 40 PPI Foam</td>
<td>2. 20 PPI Foam</td>
</tr>
<tr>
<td><strong>Action Observed</strong></td>
<td>Photolysis</td>
<td>Adsorption</td>
<td>None</td>
<td>Adsorption Photolysis</td>
</tr>
</tbody>
</table>

Among the top performing configurations, the 10 PPI foam appears the most frequently. This is likely due to the good balance between catalyst distribution and light transmittance achieved by the configuration. A third key factor in the success of the 10 PPI foam samples was identified to be the adsorption of the contaminant to the surface of the foam support. This adsorption was clearly observed in the AO24 samples, and confirmed through complimentary dark reaction experiments. A lesser, but still present, dark reaction reduction was observed in the E. coli samples. The adsorption of the contaminant to the surface of the foam enhanced the performance of the foams, which performed better than the suspension configurations for these contaminants.

1,4-dioxane was the only sample in which no photolysis or adsorption was observed. For this contaminant, the suspension of the foam was closely approached by the 10 PPI foam, identifying a good balance between distribution and light transmission for this configuration. E. coli was the only contaminant to display characteristics of both adsorption and photolysis. The control sample indicated that E. coli can be significantly inactivated by sunlight only and the effect of the light being obscured was strongly detrimental for the 40, 20 and 10 PPI foam samples which showed the least removal. The 5 PPI foam was by far the most effective configuration and its enhanced performance over the suspension is attributed to a combination of the unhindered transmission of light through the large pores as well as the adsorption of the contaminant to the surface of the foam. The improved performance of the fixed film, which was anomalous in
comparison with the other contaminants, is likely related to the transmission of light, as the 10, 20 and 40 PPI foams, as well as the suspension sample would prevent a significant amount of light from entering the system. The effect of reduced proximity between catalyst and contaminant may have also been lessened for *E. coli* since bacteria is known to sink in pure water solutions when there are no organic matter or other suspended particles with which they can become associated.

### 4.5 SUMMARY AND CONCLUSIONS

This study has investigated the comparative performance of a suspension to 5 configurations of immobilized photocatalyst with 4 different contaminants in a photocatalytic TiO$_2$ enhanced batch reactor under simulated solar radiation. The immobilized configurations considered were a fixed film of TiO$_2$ and TiO$_2$ coated aluminum foams with 5, 10, 20 and 40 pores per inch. The degradation of methylene blue, and acid orange 24 was quantified using spectrophotometry, 1,4-dioxane degradation was monitored by GC-MS, and *E. coli* counts were determined using a spread plate method.

For both dyes, the 5 and 10 PPI foams were among the top performers, with performance deteriorating with the 20 and 40 PPI foams. For 1,4-dioxane the suspension and 10 PPI foam were the top performers. The 40 PPI foam was a poor performer with all contaminants; indeed for the *E. coli* samples, the 40 PPI foam performed worse than the control. This appeared to be caused by the very fine pore size of the foam, which prevent light from radiating through the material. The suspension, film and 5 PPI foam were able to completely inactivate 10$^6$ CFU/mL of *E. coli* in 75 minutes. This suggests that the immobilized catalyst offers improved treatment relative to the control (simulated solar light only) up to a certain limiting pore size, beyond which performance deteriorates.

Based on supplementary experiments performed with the organic dyes, it was determined that aside from mass transport and reactor configuration, there were two factors that were important in determining the photoreactor efficiency: the amount of light allowed to pass through the catalytic material and the adsorption of the analyte to the surface of the catalyst. The inactivation results indicate that *E. coli* can become associated with the surface of the foam support which increases its proximity to the catalyst, improving the inactivation performance. However, it should be noted that these experiment were performed with new foam materials, foams were not
re-used and such the re-occurrence of the absorption mechanism was not determined. When the pore size of the foam becomes too small, too much light is being obscured and the amount of photocatalytically-produced radicals is reduced. 1,4-dioxane was the only sample in which no photolysis or absorption was observed. For this contaminant, the suspension of the foam was closely approached by the 10 PPI foam, identifying a good balance between distribution and light transmission for this configuration. It should also be noted that the comparative performance of the 10 PPI foam is likely specific to the path length and volume of water investigated. At longer path lengths, a larger pore size foam may be more effective (and the converse may also be true at shorter path lengths).

These results examined the relationship between target contaminant degradation and reactor configuration. It was found that a catalyst immobilized on a foam support could match the efficiency of a suspension configuration due to effective mass transport and association between the analyte and the foam. Efficiency was related to pore size and an optimum pore size of 10 PPI was observed. These experiments exhibit the potential for photocatalytic foams to improve water quality in small scale batch reactor solar disinfection systems by enhancing the inactivation of microbes and oxidizing organic pollutants.

### 4.6 REFERENCES


Luck, Anni (2007) UV/TiO$_2$ for drinking water treatment: concurrent degradation of 1,4-dioxane and removal of iron and manganese. University of Toronto, Department of Civil Engineering.


5 COMPARING PHOTOCATALYSIS TO CONVENTIONAL SMALL-SCALE SOLAR PURIFICATION SYSTEMS

ABSTRACT

Solar photocatalysis has been heavily researched for its application in low cost and low energy production of clean water; however, it is a fairly new technology and therefore has often been overlooked in past investigations comparing point-of-use treatment options. Characterizing the potential of this method is required to fundamentally compare photocatalysis to other solar disinfection methods. In this study, a comparative model has been developed that compares photocatalytic treatment under optimal conditions to various other solar-powered purification methods including photovoltaic powered UV-C lamps, chlorine generators, heat treatment and SODIS. Results show solar-powered chlorine generation is the conventional system with the greatest capacity to use solar energy to produce clean water, well beyond the capacity of currently available photocatalytic treatment systems. Results stress the fundamental limitations involved in improving the efficiency of solar photocatalytic technology without harnessing the visible light range of wavelengths; however, it indicates that a successful visible light photocatalysis would far surpass the other systems considered in terms of treatment capacity and simplicity.

5.1 INTRODUCTION

Universal access to safe drinking water is recognized as a basic human right and an essential element of protecting the health of a population. A key component of effective health policy, reliable sources of clean drinking water have an extensive effect on the community by reducing disease and health care costs, alleviating poverty and greatly improving the overall quality of life in the region (WHO 2011). Without the proper infrastructure, gaining access to clean drinking water can be a daunting task particularly in rural and impoverished communities where it is difficult to access raw materials, a power supply or skilled labour. Producing a consistent supply of clean water is an energy intensive process and considering that many current methods of producing energy require large amounts of water for successful operation, it is clear that there is
a close and complex relationship between the availability of energy and clean water in a community. This intense nexus presents difficulties for communities in which the infrastructure to access both clean water and energy is lacking. Coupled with the global regional coincidence that areas with the greatest water stress tend to receive the most consistent solar flux, this provides strong support for the application of solar water disinfection methods to improve access to clean water in such regions.

Innovations in solar technologies have produced a wide range of water purification methods that use solar energy as the sole power source. These methods include systems powered directly from the sun as well as methods that require mediation by photovoltaics to convert solar energy into electricity. Photocatalysis has been recognized as a particularly elegant method for harnessing solar energy for water disinfection because it requires little infrastructure or maintenance, can be applied in a variety of regions and is effective on a broad range of contaminants including organic pollutants such as pharmaceuticals, pesticides, heavy metals, and disease causing organisms (Byrne et al. 2012, Murray et al. 2007, Dutta et al. 2005, Lonnen et al. 2005, Shannon et al. 2008). Although solar photocatalysis has been eagerly researched for its application in low cost and low energy production of clean water, it is a fairly new technology and therefore has often been overlooked in past comparative investigations (Burch & Thomas et al. 1998, Ibeto et al. 2010, Mintz et al. 2001). When photocatalysis has been considered, it was generally agreed to be cost prohibitive in its current state (Furqua 2010, Malato et al. 2009, Shannon et al. 2008, Byrne et al. 2012, Blanco et al. 2009). Aside from the attractive qualitative factors, the quantitative potential of this technique is poorly defined. Comparative studies consistently promote further research to improve the efficiency of photocatalytic technologies; however, studies have not been performed that compare the quantitative potential of photocatalytic water treatment to alternative small scale purification options. Accordingly, this investigation will have the two-fold goal of characterizing the purification potential of photocatalysis and comparing this potential to the performance of other small-scale solar powered purification systems including portable chlorine generators, UV-C lamps, SODIS methods and heat treatment methods.

5.2 Objective

The objective of this study is to characterize the potential of solar photocatalytic water treatment and to compare it to other solar purification methods using key quantitative and qualitative
performance parameters. The key quantitative parameter will be an assessment of the amount of water the system can treat given the amount of energy provided by the sun in 6 hours over an area of 1 m².

5.3 SMALL SCALE TREATMENT METHODS

5.3.1 Survey of Conventional Small Scale Purification Systems

The first stage in developing this comparative model was to conduct a survey of existing small-scale solar water purification techniques. For each technique, the purification mechanism was detailed and the flow of solar energy throughout the treatment process was characterized. This information was used to answer the following key question: Given a specific solar flux received over a 1 m² area in a six hour time period, how much water can be treated to a standard 2-log (99%) reduction of Escherichia coli? This standard treatment level was chosen because E. coli is a common contaminant in drinking water globally and a good indicator organism for predicting the presence of other microorganisms. There is also a vast wealth of research that has been conducted on the treatment of E. coli using a variety of treatment methods (Acra et al. 1990, Cho et al. 2004, Lonnen et al. 2005, WHO 2011).

The following section will outline four conventional solar water purification systems: two systems that use solar energy directly, solar disinfection (SODIS) and heat treatment, and two that are powered using photovoltaic cells, photovoltaic powered ultraviolet lamps (PVC-UV) and solar chlorine generation (PCV-Cl₂). The fundamental details of the system are presented, along with the method used to determine the solar treatment capacity of the system. All calculations and coding were performed in MATLAB R2012a. Code and additional computational details are shown in Appendix A.2.

5.3.1.1 Solar Disinfection

Solar disinfection using irradiated polyethylene terephthalate (PET) bottles filled with water, known as SODIS, is a very cheap method to kill pathogens in water currently practiced in many rural regions of the globe. SODIS is a cost effective and easy to implement water disinfection method, however, the quality of water produced is variable and the disinfection mechanism is poorly characterized (EAWAG & SANDEC 2002). Although the exact manner by which SODIS works is still unknown, the current theory attributes the disinfection mechanism to the synergistic
effects of high energy UV-A irradiation and increased temperature from absorption of infrared heat energy (EAWAG & SANDEC 2002). Therefore, to determine the amount of water treated the temperature of the bottle and the amount of UV-A light it is exposed to must be determined.

![Diagram of a PET bottle with dimensions: H = 25 cm, Volume = 2L, D = 10 cm]

**Figure 5-1:** Dimensions of a typical PET bottle used for SODIS water treatment

According to studies performed by Acra et al. and EAWAG, the European authority on sanitation in developing countries, a 2-log inactivation of E. coli can be achieved with 12.72 Wh/m² of total UV-A fluence (Acra et al. 1990). For bottles that achieve a temperature above 50°C, the fluence requirement is reduced by 1/3, meaning that if the temperature of the water reaches above 50°C then the reaction becomes three times as effective (i.e. requiring either 1/3 the time or 1/3 the fluence) (EAWAG & SANDEC 2002). Therefore, to determine the number of bottles that can be treated, both the fluence and the temperature of the SODIS bottle need to be determined.

The temperature change in a material $\Delta T$ is related to the net energy change $\Delta Q$, the mass $m$ and a material specific property known as the heat capacity $C$ by the following relationship (Shroeder 2000):

$$\Delta Q \ (J) = C \left( \frac{J}{kg \cdot ^\circ C} \right) \cdot m \ (kg) \cdot \Delta T \ (^\circ C)$$

(5.1)

For the purpose of determining the temperature in a SODIS bottle, the input energy is the irradiated IR radiation and the energy lost is the conductive heat lost due to the difference between ambient and internal temperature. The rate of heat loss is related to the thermal conductivity $k$, the surface area exposed to heat loss $SA$, time $t$, barrier thickness $d$ and the temperature difference (Shroeder 2000):

$$\frac{dQ}{dt} \ (J) = -k \left( \frac{W}{m \cdot ^\circ C} \right) \cdot SA \ (m^2) \cdot (T-T_{env}) \ (d \ (m))$$

(5.2)
From these formulae, the temperature of the SODIS bottle can be estimated using the following differential equation, where the incoming energy is the average IR range solar flux $\bar{F}_{IR} \cdot \text{W/m}^2$:

$$\frac{dQ}{dt} = C \cdot m \cdot \frac{dT}{dt} = \bar{F}_{IR} \cdot A \cdot \frac{k \cdot SA \cdot (T(t) - T_{env})}{d}$$

Solving this ODE gives a relationship for the temperature change with time:

$$T(t) = \bar{F}_{IR} \cdot A \left(1 - \exp \left[\frac{-kSA}{Cmd} t\right]\right) + T_{env}$$  \hspace{1cm} (5.3)

This equation was used to create an array tracking the temperature change inside the SODIS bottle. In order to determine the volume of water that can be treated, the fluence requirement of 12.72 Wh/m$^2$ (or 1/3 of this fluence at temperature above 50°C) was used in combination with the time array to find the amount of time required to achieve a 2-log reduction of *E. coli* inside the SODIS bottle under standard UV-A flux conditions.

For example, given standard mid-latitude summer UV-A flux conditions of 26 W/m$^2$ and an average ambient temperature and initial water temperature of 20°C, the SODIS bottle will heat up sustainably not be able to reach a temperature above 50°C, so under these conditions, the flux requirement is 12.72 Wh/m$^2$. The treatment time can be found as follows:

$$\frac{12.72 \text{ Wh/m}^2 \cdot 3600 \text{ s/h} \cdot 26 \text{ W/m}^2}{26 \text{ W/m}^2} = 1761.2 \text{ s} = 29 \text{ mins}$$

Accordingly, it takes 29 minutes to treat one SODIS bottle under these flux conditions and in a six hour exposure period, you could treat 12 sets of bottles. Using the standard dimensions of a PET SODIS bottle, as shown in **Figure 5-1**, 40 bottles can be placed over 1 square meters, thereby treating 360 bottles in six hours. It is recommended that bottles are filled no more than 3/4 full improve the amount of oxygen in the water (EAWAG & SANDEC 2002). So if each bottle contains 1.5 L of water, SODIS can treat 540 L of water in six hours of 26 W/m$^2$ of UV-A exposure.
5.3.1.2 Heat Treatment

Boiling water or heating it to high temperature below the boiling point (known as pasteurization) is an effective method for treating contaminated water. Figure 5-2 shows the set up for a typical solar water heater.

![Parabolic Mirror Diagram]

Figure 5-2: Example of a solar water heating set up. Light energy is concentrated over the parabolic mirror and funneled towards to pot to heat the water to microbe inactivating temperatures.

The flux across a certain area is concentrated using a parabolic mirror and redirected towards the water, contained in a pot for heating. These concentrating mirrors typically have an efficiency around 1/3, effectively delivering 1/3 of the incident light energy to the pot as heat (Rabl, 1976). This concentrated heat is the energy input to the water. Assuming the water is heated in a stainless steel pot and is good heat absorber with few defects ($\alpha = 0.75$), the heat will be lost through the walls of the pot (the pot is assumed to have a stainless steel lid with a perfect seal and is never opened during the heating process). Therefore, the same equation from the SODIS calculation can be used to determine the maximum temperature of the pot:

$$T(t) = \alpha \cdot \frac{1}{3} \cdot \bar{F} \cdot A \left(1 - \exp\left[-\frac{kSA}{C_{md}} t\right]\right) + T_{env}$$  \hspace{1cm} (5.4)
Setting \( t \) as the total exposure time allows for the maximum temperature reached by the water under the given sunlight conditions to be determined. This is important since not all flux conditions will have enough energy to bring the water to its boiling point.

Water can be heat treated by boiling, which instantly achieves above a 2-log reduction of \( E. \) coli. However, it is not necessary to boil water in order to kill bacteria—simply bringing the water to a temperature above 60 °C for around an hour will likewise achieve at least a 2-log reduction of \( E. \) coli (EAWAG & SANDEC 2002). Once the maximum temperature for the water is determined, Equation 5.4 can be rearranged to solve for the time required for the pot to reach either 100°C (if possible) or 60°C (if the flux is not great enough to induce the water to boil):

\[
t = - \frac{C \cdot m \cdot d}{k \cdot S \cdot A} \cdot \ln \left[ \frac{T_{\text{env}} - T}{\alpha 1/3 \cdot F_{\text{IR}} \cdot A} + 1 \right]
\] (5.5)

For example, at standard flux conditions, the IR portion of the spectrum is around 400 W/m². If the ambient temperature of the air and the water was 20 °C then using the standard dimensions and heat constant for a medium sized stainless steel pot:

\[
t = - \frac{4200 \text{ J/kg°C} \cdot 6.2 \text{ kg} \cdot 5/1000 \text{ m}}{16 \text{ W/m°C} \cdot 0.1885 \text{ m}^2} \cdot \ln \left[ \frac{20 \text{ °C} - 100 \text{ °C}}{0.75 \cdot 1/3 \cdot 400 \text{ W/m}^2 \cdot 1 \text{ m}^2} + 1 \right] = 69.46 \text{ sec}
\]

Allowing the water to boil just for one minute, in a six hour time period 167 pots of water could be treated. This standard sized stainless steel pot has a volume of 6 L, therefore 1002 L of water can be treated in six hours at standard flux conditions.

### 5.3.1.3 Photovoltaic Cells

The small-scale methods that will be considered in this section require electricity to operate to harness solar energy, they have to be scaled down and powered by photovoltaic cells. Photovoltaic cells produce energy from the sun by employing the intrinsic electric field of a p-n junction to sweep out the photo-generated charge carriers that are created in a narrow band gap semiconductor upon light irradiation to produce an electric current (Neamen 1992). Solar powered UV-lamps and solar generated chlorine have the capability to produce the required disinfection to meet health standards, although the raw material, maintenance and energy inputs vary widely. Concerns regarding the toxic byproducts produced from chlorination have garnered a greater look into UV technologies, particularly for point-of-use and small scale applications.
where a residual for secondary disinfection is not required (Das 2002). Moreover, the toxic mercury content and high energy requirements of traditional gas discharge UV-C lamps has warranted investigation into PV-powered LED lamps which can be more energy efficient, less environmentally hazardous and more suited for coupling with photovoltaic energy sources owing to the dual semiconductor technology (Close et al. 2006). Although UV-LED devices are particularly promising for solar applications, the intensity produced by these lamps is not yet suitable for rural applications.

The efficiency ($\eta_{sc}$) and power output ($P_{sc}$) of a solar cell is determined by dividing the output by the input solar energy (Neamen 1992). Although the efficiency of solar cells is continually improving, the current typical cell has an efficiency of about 5%. However, because solar cells are made from silicon, which is a narrow band gap material, it can use the entire range of the solar spectrum in order to produce energy. Therefore, the power output of a solar cell is:

$$ P_{sc} = \eta_{sc} (%) \cdot F_{\text{surface}} \left( \frac{W}{m^2} \right) \cdot A \left( m^2 \right) $$

(5.6)

To power a device using solar energy, the energy from the sun is most commonly stored in batteries. Energy losses involved in the conversion through the battery are generally around 12% giving a battery with an efficiency ($\eta_B$) of 88% (Neamen 1992). The total amount of energy harnessed is then determined by:

$$ \text{Energy Harnessed (J)} = P_{sc} (W) \cdot \eta_B (%) \cdot t (s) $$

(5.7)

The specifications and energy requirements of several common UV-C lamps are shown in Appendix A.3, Table A-1. These specifications include the power required for complete operation of the device (W) and the treatment flow ability (L/min). Using these values, a value for water treated normalized by energy required for any of these devices can be obtained as follows:

$$ \text{Energy Usage} \left( \frac{L}{J} \right) = \frac{\text{Flow} \left( \frac{L}{\text{min}} \right)}{\text{Power Consumption} (W)} \cdot \frac{\text{min}}{60 \text{ sec}} $$

(5.8)

The amount of water treated using the energy from the solar cell is then:

$$ \text{Water Treated (L)} = \text{Energy Usage} \left( \frac{L}{J} \right) \cdot \text{Energy Harnessed (J)} $$

(5.9)
Using the AquaSun International largest model as an example UV solar water treatment device (AquaSun Intl Inc. 2012), the system can treat water at a rate of 11 L/min and has a total power draw of 60 W:

\[
\frac{11 \text{ L}}{\text{min}} \cdot \frac{1 \text{ min}}{60 \text{ s}} \cdot \frac{1}{60 \text{ W}} = 3.1 \times 10^{-3} \frac{\text{ L}}{\text{ J}}
\]

Therefore, under standard average flux conditions of 780 W/m², collecting sunlight for 6 hours over an area of 1 m², this UV-C system can treat 2300 L of water. This value includes the entire power required by the system (60 W), while the lamp alone requires 22 W of power to operate. It is possible that batch reactor system could be designed to make this system more efficient and reduce energy requirements.

PV powered solar chlorine generators deliver a sodium hypochlorite solution from electricity, water and salt that can be used to disinfect contaminated waters. A 2-log reduction of \textit{E. coli} can be achieved with a CT of 0.05 mgmin/L (pH 6-7; temperature 5°C; Health Canada 2006), assuming the chlorine is used to treat water in a batch configuration, allowing 1 hour of contact time as a safe estimate recommended by AquaClor (2012). This means that 1 L of water can be treated for every 3 mg of chlorine produced. The specifications and energy requirements of several common portable chlorine generators are shown in Appendix A.3, Table A-2.

These specifications include the power consumption of the device (W) and rate of chlorine production (g\textsubscript{Cl}/hr). Using the AquaClor system as an example (AquaChlor Systems 2012), these values can be used to determine the amount of water treated for given solar flux conditions. The AquaClor system can produce 2 g\textsubscript{Cl}/hr and has a total power consumption of 11 W:

\[
2 \frac{\text{ g}_\text{Cl}_2}{\text{hr}} \cdot \frac{1 \text{ hr}}{3600 \text{ s}} \cdot \frac{1}{11 \text{ W}} \cdot \frac{1 \text{ L}}{3 \times 10^{-3} \text{ g}} = 1.68 \times 10^{-2} \frac{\text{ L}}{\text{ J}}
\]

Therefore, under standard flux conditions of 780 W/m², this system could treat 12500 L of water.
5.3.2 Characterizing Photocatalysis Potential

Photocatalysis is an advanced oxidation process that uses solar light to produce electrons and electron holes in semiconductors that can then migrate to the surface of the catalyst and create radical species in the water. The integration of solar photocatalytic advanced oxidation into traditional solar treatment methods is a comparatively robust method for improving both the microbial and chemical quality of SODIS treated water (Byrne et al. 2012, Blanco et al. 2009, Shannon et al. 2008, Lonnen et al. 2005). The oxidation pathway of photocatalytic systems can treat organic pollutants and microbial contaminants, while the reduction pathway has been shown to precipitate heavy metals such as lead and arsenic (Dutta et al. 2005).

Photocatalysis has been a popular topic in recent studies for its application in low cost and low energy water treatment, however, the technology is still in its infancy and more research is needed to make the technology to practical. Figure 5-3 shows a sampling of semiconductor photocatalysts which have been mapped across their energy band gap and their quantum efficiency. TiO$_2$(anatase), the water treatment industry standard for photocatalysis, is shown to have a relatively poor quantum efficiency and wide band gap compared to other semiconductor photocatalyst. The reason that TiO$_2$ has become a standard is because of its chemical stability, availability and low cost. Although numerous other photocatalysts exist, many of those presented here are unstable in aqueous condition, made from expensive rare earth metals or environmentally toxic. The imagined ideal photocatalyst would fall in the upper right-hand quadrant of Figure 5-3, having a narrow band gap and high quantum efficiency, and it would possess the requisite qualities of abundance, stability, low cost and environmental banality. Although such an ideal photocatalyst does not yet exist, this study aims to characterize the potential of such a system, which is currently poorly defined, to fundamentally compare photocatalysis to other solar disinfection methods.
The simple reaction scheme used to describe contaminant degradation in photocatalytic systems is shown below. It is based on comparing the rate of 3 main reactions: electron/hole production, contaminant degradation and recombination:

\[
\begin{align*}
\text{TiO}_2 + h_0 & \rightarrow e^- + h^+ \\
\text{Electron/Hole Generation} \\
\text{h}^+ + \text{OH}^- & \rightarrow \text{OH}^- \\
\text{Radical: Oxidation Pathway} \\
\text{O}_2 + e^- & \rightarrow \text{O}_2^- + \text{H}^+ \\
\text{O}_2^- + \text{H}^+ & \rightarrow \text{OOH}^- \\
\text{Radical: Reduction Pathway} \\
2\text{OH}^- + \text{R} & \rightarrow \text{R}_2 \\
\text{Contaminant Degradation} \\
e^- + \text{h}^+ & \rightarrow \text{energy} \\
\text{Recombination}
\end{align*}
\]

If holes are the limiting species, then according to the above reaction mechanism at any one instant (Malato 2009):

\[
\frac{d[h^+]}{dt} = k_f h_0 - k_r e^-[h^+] - k_o [h^+] R
\]  

(5.10)

It is well known that in this reaction the rate determining step is the production and migration of the electron hole. Once the hole reaches the surface, it is highly oxidizing and it can be assumed that it undergoes 100% transformation into radical species (Malato et al. 2009). The electron uses dissolved oxygen to produce radicals, therefore a simultaneous reductive pathway is occurring which creates an equal number of hydroxyl radical to the pathway investigated here.
To solve for the concentration of electron holes, some information is required. Let’s begin with determining the amount of incoming radiation \( hv \). The energy of one mole of photons of any particular wavelength can be calculated using Avogadro’s number and Plank’s laws (Neamen 1992):

\[
\frac{h \cdot c}{\lambda} = E_{\text{photon}}
\]

Only energy larger than the material band gap can be used to produce electron holes (i.e., \( F_E > \text{band gap} \)) therefore the number of moles of photons used to generate holes can be determined:

\[
\frac{\text{Moles of incident photons}}{\text{second}} = \frac{F_{E > \text{band gap} \cdot \text{Area}}}{J/\text{mole of photons}}
\]

However, the production and migration of the hole to the surface is a complicated process that depends on the catalyst morphology and its interaction with the photons. The reaction would be considered 100% efficient if for every 1 mole of photons incident on the surface, the catalyst was able to produce 1 mole of effective electron holes (and 1 mol of electrons). When using UV light and a band gap of 400 nm, the flux falls off quickly as you move away from the visible region (Malato et al. 2009), so all the photons can be approximated to have an energy level of 400 nm. From this, we can calculate the number of moles of photons per second that are hitting the catalyst. This is the value of the flux:

\[
\Phi = \frac{F_{\text{UV} \cdot A}}{E_{\text{photon}} \cdot N_A}
\]

This flux has a unit of moles of photons per second and can be used along with our other values to calculate the steady-state concentration for the electron holes by setting our previous equation to equilibrium:

\[
\frac{d[h^+]}{dt} = k_f \Phi - k_r [e^-][h^+] - k_o [h^+] R = 0
\]

\[
[h^+]^2 + \frac{k_o}{k_f} [h^+] R - \frac{k_f}{k_r} \Phi = 0
\]

If the catalyst had very poor efficiency and every electron and hole recombined, then the steady state concentration would be zero, as shown in Equation 5.15. However, since we are considering the ideal situation for our catalyst, if the recombination rate was set to zero so that
everyone photon created an electron hole, then the steady-state concentration of holes (or electrons) can be determined as below in Equation 5.16.

\[
\eta = 0% \quad k_r [e^-][h^+] = k_r \Phi \quad \frac{d[h^+]}{dt} = - k_o [h^+] R = 0 \quad \Rightarrow \quad [h^+] = 0 \quad (5.15)
\]

\[
\eta = 100\% \quad k_r [e^-][h^+] = 0 \quad \frac{d[h^+]}{dt} = k_r \Phi - k_o [h^+] R = 0 \quad \Rightarrow \quad [h^+] = \frac{k_r \Phi}{k_o R} \quad (5.16)
\]

If we combine this assessment with the reduction pathway, then we can see that the steady state concentration of hydroxyl radicals in a 100% efficient system would be:

\[
[\text{OH}^-] = [h^+] + [e^-] = 2[h^+] = 2 \cdot \frac{k_r \Phi}{k_o R} \quad (5.17)
\]

Once the concentration of the radicals is determined, then we can use experimental CT values for 2-log *E. coli* inactivation (Cho *et al.* 2004) and the total flux exposure time to determine the water treatment capacity. For a scenario with point-of-use small scale reactors, the radical mechanism would operate as a compliment to the SODIS mechanism of direct UV-A inactivation, therefore this quantity of water treated by SODIS is added. This calculation is supported by empirical studies which have shown that low efficiency photocatalysts accelerate *E. coli* inactivation in SODIS, requiring 60% of the time to achieve the same log-inactivation (Lonnen *et al.* 2005).

\[
\text{Water Treated (L)} = \frac{\text{Radicals (mg) } \cdot \text{ time (mins)}}{\text{CT (mg min L)}} + \text{SODIS} \quad (5.18)
\]

In order to clarify the details of this scheme, the theory presented above will be followed through to calculate example treatment capacities for both an ideal TiO$_2$ catalyst with 100% quantum efficiency as well as a visible light photocatalyst.

Beginning with a TiO$_2$ photocatalysts, the useful wavelengths of solar flux are all those with wavelengths shorter than the material band gap, 400 nm (3.1 eV), i.e. UV-A light, in the solar spectrum wavelength below this do not penetrate the atmosphere. First, we determine the energy value of a photon at this wavelength:

\[
E_{\text{photon}} = \frac{h \cdot c}{\lambda} = \frac{6.62 \cdot 10^{-34} \cdot 2.998 \cdot 10^8}{400 \text{ nm}} = 4.96 \cdot 10^{-19} \text{ J}
\]
Using a standard UV-A flux of 26 W/m², we can use this value to determine the flux of useful photons in moles of photons per second:

\[
\Phi = \frac{\text{Moles of photons}}{\text{second}} = \frac{F_{UV} \cdot A}{E_{\text{photon}}} \cdot N_A = \frac{26 \text{ W/m}^2 \cdot 1 \text{ m}^2}{4.96 \cdot 10^{-19} \text{ J}} \cdot \frac{\text{mols/photons}}{6.02 \cdot 10^{23}} = 8.7 \cdot 10^{-5} \text{ mols/s}
\]

Now this flux value can be used to find the steady state concentration of electron holes. The rate constant of hole formation, \(k_f = 1\) because every useful photon is assumed to produce an electron hole. The most prominent scavenger to moderate the electron hole concentration is the presence of natural organic matter (NOM) in the water matrix. Therefore, the reactant concentration and the oxidation rate and drawn from literature values for the reaction rate between NOM and the hydroxyl radical at standard temperature, \(k_o = 8.08 \cdot 10^8 \text{ MCs}^{-1}\) (McKay et al. 2012). The concentration on natural organic matter is set relatively low to keep the comparison consistent with the other purification systems whose performances were tested under such conditions.

\[
[\text{OH}^•] = [h^•] + [e^-] = 2[h^•] = 2 \cdot \frac{k_f \Phi}{k_o R} = 2 \cdot \frac{1 \cdot 8.7 \cdot 10^{-5}}{8.08 \cdot 10^8 \text{ MCs}^{-1} \cdot 0.00015 \text{ Mc}} = 1.44 \cdot 10^{-9} \text{ mols}
\]

\[
[\text{OH}^•] = 1.1 \cdot 10^{-9} \text{ mols} \cdot 17.01 \text{ g/mol} \cdot 1000 \text{ mg/g} = 2.44 \cdot 10^{-5} \text{ mg}
\]

Once the concentration of the radicals is determined, then we can use experimental CT value (0.8 \cdot 10^{-5} \text{ mg min/L}; Cho et al., 2005) and the SODIS value for 2-log \(E. \text{coli}\) inactivation:

\[
\text{Water Treated (L)} = \frac{2.44 \cdot 10^{-5} \text{ mg} \cdot 360 \text{ min}}{0.8 \cdot 10^{-5} \text{ mg min/L}} + 720 \text{ L} = 2538 \text{ L}
\]

Therefore, for an ideal UV active photocatalyst with a standard UV-A flux of 26 W/m², the system has the capacity to treat 2538 L of water in 6 hours of exposure to 1 m² of sunlight. The situation is similar for a visible light active photocatalyst, except that a much broader range of the solar spectrum can be used to activate the treatment process. For example, given a narrow band gap photocatalyst that can absorb wavelengths in the visible light range and higher, the useful wavelengths of solar flux are all those with wavelengths shorter than the material band gap, around 780 nm (1.6 eV). In this range of the solar spectrum, the peak flux intensity occurs at
approximately 500 nm, so this will be the value used to determine the energy of an average photon:

\[ E_{\text{photon}} = \frac{h \cdot c}{\lambda} = \frac{6.62 \cdot 10^{-34} \cdot 2.998 \cdot 10^8}{500 \text{ nm}} = 3.96 \cdot 10^{-19} \text{ J} \]

Using a standard flux of 780 W/m\(^2\), the total flux available in the visible light wavelengths and greater is 300 W/m\(^2\). We can use this value to determine the flux of useful photons in moles of photons per second:

\[ \Phi = \frac{\text{Moles of photons}}{\text{second}} = \frac{F_{\text{UV}} \cdot A \cdot N_A}{E_{\text{photon}}} = \frac{300 \text{ W/m}^2 \cdot 1 \text{ m}^2 \cdot 3.96 \cdot 10^{-19} \text{ J}}{6.02 \cdot 10^{23}} = 1.26 \cdot 10^{-3} \text{ mols/s} \]

Now this flux value can be used to find the steady state concentration of electron holes. The same rate constant of hole formation, \( k_f = 1 \), the oxidation rate constant \( k_o = 8.08 \cdot 10^{-8} \text{ M}_c \text{s}^{-1} \) and the low NOM concentration as were used for the TiO\(_2\) calculations:

\[ [\text{OH}^\cdot] = [\text{h}^\cdot] + [\text{e}^-] = 2[\text{h}^\cdot] = 2 \cdot \frac{k_f \Phi}{k_o R} = 2 \cdot \frac{1 \cdot 1.26 \cdot 10^{-3} \text{ mols/s}}{8.08 \cdot 10^{-8} \text{ M}_c \text{s}^{-1} \cdot 0.00015 \text{ Mc}} = 2.07 \cdot 10^{-8} \text{ mols} \]

\[ [\text{OH}^\cdot] = 2.07 \cdot 10^{-8} \text{ mols} \cdot 17.01 \text{ g/mol} \cdot 1000 \text{ mg/g} = 3.52 \cdot 10^{-4} \text{ mg} \]

Once the concentration of the radicals is determined, then we can use experimental CT values and the SODIS treated value for 2-log \( E. coli \) inactivation:

\[
\text{Water Treated (L)} = \frac{3.52 \cdot 10^{-4} \text{ mg} \cdot 360 \text{ min}}{0.8 \cdot 10^{-5} \text{ mg/min}_L} + 720 \text{ L} = 16565 \text{ L} \quad (5.20)
\]

Therefore, for a visible light photocatalyst with a standard total flux of 780 W/m\(^2\), the system has the capacity to treat 16 565 L of water. This is just over 6x the amount of water that could be treated when using the wide band gap photocatalyst.
5.4 Solar Flux and Atmospheric Conditions

For the above calculations, we used a total standard flux value of 780 W/m² to show an example comparison of each treatment technique. However, flux values vary widely global. In this section, the distribution of solar flux across the globe is considered with the aim of expanding the model to encompass regional and seasonal changes in solar flux.

The sun emits energy in the spectrum of a 6000 K blackbody. Therefore, its emission pattern is mainly in the low UV and visible spectrum, tailing off into the infrared. 95% of solar emissions lie between 250 and 2500 nm. At the Sun’s current state of evolution (Marshal & Plumb 2008):

\[ \text{Current Energy Emission Rate: } Q = 3.87 \times 10^{26} \text{ W} \]  

(5.21)

The energy that then reaches the Earth is dependent on the distance from the Earth to the Sun:

\[ \text{Solar Constant } S_o = \frac{Q}{4\pi r^2} = \frac{3.87 \times 10^{26} \text{ W}}{4\pi (150 \times 10^9 \text{ m})^2} = 1367 \text{ W/m}^2 \]  

(5.22)

This value represents the solar flux arriving directly normal to the Earth, which becomes equivalent to the thermal equatorial flux at solar noon, or when the sun is directly above in the sky and the declination of the Earth at that point is zero. The above equation makes the assumption that the distance between the Earth and the sun is constant, when it is actually a dynamic value that is a function of the Earth’s elliptical orbit. However, the variation in the orbital distance is quite small and can be considered negligible for the purpose of this investigation. The instantaneous solar flux at the top of the atmosphere at the mean Earth sun distance can then be considered to be a function of the solar constant \( S_o \) and the solar zenith angle \( \theta \) (Liou 2002):

\[ F(t) = S_o \cos \theta \]  

(5.23)

Using spherical trigonometry, the solar zenith at any time can be described by the latitude \( \phi \), the declination \( \delta \), and the hour angle \( h \):

\[ \cos \theta = \sin \phi \sin \delta + \cos \phi \cos \delta \cosh \]  

(5.24)

The hour angle, which is zero at solar noon, represents the time change of the sun’s motion across the sky. The hour angle can be determined from the time considering that \( 360^\circ = 24 \text{ hrs.} \)
Therefore, the instantaneous solar flux at any number of hours away from solar noon, latitude and declination can be determined by:

\[ F(\varnothing, \delta, t) = S_o \left[ \sin\varnothing\sin\delta + \cos\varnothing\cos\delta \cos \left( \frac{\text{hours from solar noon}}{24 \text{ hrs}} \cdot \frac{360^\circ}{24 \text{ hrs}} \right) \right] \]

This formula can then be used to calculate the average solar flux over any length of time centered about solar noon by averaging the final and noon flux values.

Example: For an exposure time of 6 hours (i.e. beginning at hour angle -3 and continuing to +3) in mid-northern hemisphere summer time (declination 23.5° and latitude 25°) the average solar flux is:

\[ \bar{F}(\varnothing, \delta, t) = \frac{1367}{3} \left[ \frac{2 \left( \sin(25)\sin(23.5) + \cos(25)\cos(23.5) \cos \left( \frac{3 \text{ hrs} \cdot \frac{360^\circ}{24 \text{ hrs}}}{24 \text{ hrs}} \right) \right)}{3} + \left( \sin(25)\sin(23.5) + \cos(25)\cos(23.5) \cos(0) \right) \right] = 1145 \, \frac{W}{m^2} \]

This is the average solar flux incident at the top of the atmosphere. However, before the light reaches the surface it passes through the atmosphere which typically absorbs 20-40% of the radiation depending on daily conditions such as cloud cover and air quality. Therefore, the average flux of energy that reaches the surface of the Earth can be calculated from the atmospheric transmittance \( \tau \) (Thekaekara 1967):

\[ \bar{F}_{\text{surface}} = \bar{F}(\varnothing, \delta, t) \times \tau (\%) \]

Continuing the example from above, on a very clear day giving a transmittance of 80%:

Average Surface Flux = \( \bar{F}(\varnothing, \delta, t) \times \tau (\%) = 1145 \, \frac{W}{m^2} \times 0.80 = 916 \, \frac{W}{m^2} \)

The Earth’s atmosphere is almost completely transparent to visible light, very opaque to UV light and has a variable opacity to IR radiation, depending on the composition of gases. These atmospheric gases absorb the solar energy as it passes through the atmosphere. The wavelength of transmission is dependent on the volume of air through which the sunlight passes. One air mass is considered to be the amount of atmosphere in one vertical path normal to the surface. **Table 5-1** is a table of the percent wavelength transmitted for various types of radiation through
one and a half air masses. One and a half air masses is a convenient average value for the vertical atmospheric path throughout the day.

**Table 5-1:** Percent wavelength transmitted through atmosphere by various energy wavelengths. (Adapted from Thekaekara 1967)

<table>
<thead>
<tr>
<th>Bandwidth (nm)</th>
<th>Percentage at 3/2 Air Mass</th>
<th>Energy Transmitted (W/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultra violet (290-400)</td>
<td>2.76</td>
<td>31.6</td>
</tr>
<tr>
<td>Visible (400-700)</td>
<td>35.8</td>
<td>410</td>
</tr>
<tr>
<td>Short Range IR (700-1100)</td>
<td>27.8</td>
<td>318</td>
</tr>
<tr>
<td>Long Range IR (1100-∞)</td>
<td>13.64</td>
<td>156</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>80</strong></td>
<td><strong>916</strong></td>
</tr>
</tbody>
</table>

The values shown in **Table 5-1** can be considered a representation of the standard summer time flux for mid-northern hemisphere locations. Standard values for varying locations and time of year can be found by adjusting the latitude and declination input. Taking this one step further, MATLAB software was used to calculate the variation in solar flux across all latitudes and declination values. **Figure 5-4** shows the change in solar flux from 0 to 60° latitude across each season. The distribution generated from these calculations was then used to evaluate the water treatment capacity of each small-scale purification system across the range of possible solar flux values. This allowed the range of variation in system capacity as well as its resiliency to changes in solar flux to be characterized. Further details regarding MATLAB code and calculations are shown in **Appendix A.2.1.**
5.5 RESULTS AND DISCUSSION

Based on the calculations and extensive literature review performed on the various solar water purification systems, comparative tables were put together for each water purification technique. Treatment capacity was used as the key quantitative parameters. Other parameters considered include cost, efficacy on alternative contaminants, simplicity of use and implementation, and residual taste and odour concerns resulting from the treatment mechanism. More detailed tabular results are shown in Appendix A.4 and calculations are shown in Appendix A.2.

5.5.1 Solar Disinfection

Solar Disinfection (SODIS) is by far the cheapest and simplest purification method considered in this investigation. It involves almost no infrastructure or skilled operations, requires only access to plastic (PET) bottles and open area with clear, consistent sunlight. SODIS, however, is an
inconsistent mechanism and was determined to be able to produce the smallest quantity of clean water given six hours of sunlight. SODIS is also sensitive to changes in atmospheric conditions and temperature, with its performance dropping off substantially when the flux is not strong enough to heat the bottles to the critical temperature of 50°C at which synergistic effects between the UV-A and heat treatment mechanisms are observed. SODIS is effective for contaminants like *E. coli*, many other bacteria, protozoa and viruses; however, it does not sterilize water and has no effect on other contaminants such as organic pollutants and heavy metals. In some cases, SODIS treatment can encourage the growth of other environmental contaminants such as algae (EAWAG & SANDEC 2002). It should also be noted that there is no current method of determining when the SODIS process is complete. Due to changes in solar flux, cloud cover and temperature, the amount of time required to treat one bottle may vary dramatically. The capacities of treated water suggest in Table 5-2 could only be practically achieved if there was some indication of when treatment was complete. Diosiometric dyes have been suggested as a mechanism for tracking solar exposure; however, their use has not been widely adopted (Byrne *et al.* 2008, Bandala *et al.* 2009). Overall, SODIS is an effective technique, but its inconsistency and low efficiency indicate that it should only be employed when no there is no access to other treatment methods.

**Table 5-2**: Summary of SODIS water treatment performance harnessing 1 m² of sunlight for 6 hours

<table>
<thead>
<tr>
<th>Solar Disinfection</th>
<th>High Flux</th>
<th>Medium Flux</th>
<th>Low Flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treatment Capacity</td>
<td>588 L</td>
<td>530 L</td>
<td>294 L</td>
</tr>
<tr>
<td>Costs*</td>
<td>Capital</td>
<td>Maintenance</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>Low</td>
<td></td>
</tr>
<tr>
<td>Efficacy on Alternative Contaminants</td>
<td>Organic Pollutants</td>
<td>Heavy Metals</td>
<td></td>
</tr>
<tr>
<td></td>
<td>No</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Other</td>
<td>Ease of Use</td>
<td>Taste and Odour Issues</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Easy</td>
<td>No</td>
<td></td>
</tr>
</tbody>
</table>

*Capital Costs: High > $100; $100 > Medium > $10; $10 > Low
Maintenance Costs: High > $100/yr; $100/yr > Medium > $10/yr; $10/yr > Low

### 5.5.2 Heat Treatment

Boiling water is a very effective method for inactivating all pathogens to create potable water. Heating water until it boils creates very safe drinking water; however, it is an energy intensive
process, therefore in solar applications it requires a parabolic concentrator to reach temperatures high enough for pathogen inactivation. Because a parabolic mirror is required, the initial cost for setting up a heat treatment system is greater than a SODIS system although the maintenance costs afterwards remain low. In high flux conditions, it can take less than 1 minute to boil water using a solar concentrator, therefore many more treatment batches can be performed, but the total volume of water treated is limited since all the solar energy in the 1 m² area must be concentrated onto the single heating pot. Heat treatment is also very susceptible to changes in solar flux and cloud cover since poor conditions result in temperatures too low for effective treatment. This makes heat treatment the least resilient method to changes in flux. Additionally, heat treatment will remove volatile compounds (compounds that evaporate at high temperatures) but will concentrate other contaminants as boiling reduces the total volume of the treated water. This can be a serious concern for water systems contaminated with heavy metals such as lead and arsenic that pose very serious public health risks. An advantage of boiling water over SODIS is the visual identification that the water is clean, when the water is seen to boil; it is then known that the water is safe to drink. For SODIS, no such identification mechanism exits. Overall, heat treatment is not recommended for implementation in rural areas because of the capital cost and its inability to treat water in variable flux conditions thereby lowering the reliability of the drinking water supply.

Table 5-3: Summary of boiling treatment performance harnessing 1 m² of sunlight for 6 hours

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>High Flux</th>
<th>Medium Flux</th>
<th>Low Flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treatment Capacity</td>
<td>1240 L</td>
<td>1020 L</td>
<td>31 L</td>
</tr>
<tr>
<td>Costs*</td>
<td>Capital</td>
<td>Medium</td>
<td>Maintenance</td>
</tr>
<tr>
<td>Efficacy on Alternative Contaminants</td>
<td>Organic Pollutants</td>
<td>Will remove volatiles but will concentration non-volatiles</td>
<td>Heavy Metals</td>
</tr>
<tr>
<td>Other</td>
<td>Ease of Use</td>
<td>Medium</td>
<td>Taste and Odour Issues</td>
</tr>
</tbody>
</table>

*Capital Costs: High > $100; $100 > Medium > $10; $10 > Low
Maintenance Costs: High > $100/yr; $100/yr > Medium > $10/yr; $10/yr > Low

5.5.3 Photovoltaic Powered UV-Light
There is a wide range of treatment capacities for solar powered UV-light systems, mostly because of the variety in flow capabilities from small to large systems. These systems work well
in a wide range of flux conditions and because they are powered by solar cells and batteries, they
can store energy short term and are fairly resilient to change in flux conditions. UV-light is an
effective mechanism for inactivating water borne pathogens, although it has no effect on other
contaminants such as organic pollutants and heavy metals. UV-light systems are most useful
with water sources that are relatively clear, as heavily turbid and impacted water systems can
greatly lower the efficacy of the treatment system. UV systems have higher capital costs than
SODIS or heat treatment because of the gas discharge lamp and the more complex interface with
the solar cell power generator; however, the only continual cost is the occasional need to change
the lamp, which may be needed less than once every 3 years depending on the hours of daily
operation (US EPA, 1999). UV systems use only high energy light radiation to purify water and
therefore leave behind no residual and have no effect on the taste or smell of the water treated.

**Table 5-4:** Summary of solar UV-lamp water treatment performance harnessing 1 m² of sunlight
for 6 hours

<table>
<thead>
<tr>
<th>Photovoltaic Powered UV Lamp</th>
<th>High Flux</th>
<th>Medium Flux</th>
<th>Low Flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treatment Capacity</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Large System</td>
<td>2610 L</td>
<td>2170 L</td>
<td>1370 L</td>
</tr>
<tr>
<td>Small System</td>
<td>1740 L</td>
<td>1450 L</td>
<td>910 L</td>
</tr>
<tr>
<td>Costs*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Capital</td>
<td>High</td>
<td>Medium</td>
<td></td>
</tr>
<tr>
<td>Maintenance</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Efficacy on Alternative</td>
<td>Organic Pollutants</td>
<td>Heavy Metals</td>
<td>No</td>
</tr>
<tr>
<td>Contaminants</td>
<td>No</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Other</td>
<td>Ease of Use</td>
<td>Taste and Odour Issues</td>
<td>Medium</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Capital Costs: High > $100; $100 > Medium > $10; $10 > Low
Maintenance Costs: High > $100/yr; $100/yr > Medium > $10/yr; $10/yr > Low

### 5.5.4 Solar Chlorine Generation

Chlorine is a strong chemical disinfect, so only small amounts of liquid chlorine are required to
treat large quantities of drinking water. For this reason, the quantity for water that can be treated
using solar generated chlorine far surpasses the other treatment mechanisms discussed so far,
boasting more than 5x the treatment capacity compared to a large scale solar UV-treatment
system. Chlorinating water is a very consistent treatment method that is not greatly impaired by
water turbidity or inconsistent solar flux and is able to leave behind a residual which prevents
recontamination. Despite these benefits, solar chlorine generation has several limiting factors.
Generating liquid chlorine using solar energy requires the continuous input of salt as a raw material. In some rural areas, there is not consistent access to salt and this can be a significant limiting factor in the implementation of a chlorine treatment system. In this manner, solar chlorination differs significantly from other solar treatment methods because it requires a continuous input of something other than solar energy (i.e. salt) causing significant increases in operations and maintenance costs. The need to continually input raw material, as well as the potentially dangerous nature of the chemical disinfectant, increase the operational skill required to use such a system. In addition, chlorine can have a very strong odour which many people find distasteful. The poor taste and odour that can be a result from chlorine disinfection has been problematic for organizations attempting to implement these systems in rural communities as it was found that some people were so repelled by the smell and taste that they refused to drink the treated water (Fuqua 2010, Ibeto et al. 2010). Overall, solar chlorination is by far the most energy efficient technique available for treating drinking water; however, the required access to salt, and taste and odour problems are significant barriers to the application of solar chlorine generating systems in rural areas.

Table 5-5: Summary of solar chlorine water treatment performance harnessing 1 m² of sunlight for 6 hours

<table>
<thead>
<tr>
<th>Solar Chlorine Generation</th>
<th>High Flux</th>
<th>Medium Flux</th>
<th>Low Flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treatment Capacity</td>
<td>14800 L</td>
<td>12300 L</td>
<td>7730 L</td>
</tr>
<tr>
<td>Costs*</td>
<td>Capital</td>
<td>Maintenance</td>
<td></td>
</tr>
<tr>
<td></td>
<td>High</td>
<td>High</td>
<td></td>
</tr>
<tr>
<td>Efficacy on Alternative</td>
<td>Organic</td>
<td>Heavy Metals</td>
<td></td>
</tr>
<tr>
<td>Contaminants</td>
<td>Pollutants</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Other</td>
<td>Ease of Use</td>
<td>Taste and Odour Issues</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hard</td>
<td>Yes</td>
<td></td>
</tr>
</tbody>
</table>

*Capital Costs: High > $100; $100 > Medium > $10; $10 > Low
Maintenance Costs: High > $100/yr; $100/yr > Medium > $10/yr; $10/yr > Low

5.5.5 Photocatalysis

Photocatalysis has been recognized as a particularly elegant method for harnessing solar energy for water purification because it requires little infrastructure or maintenance, can be applied in a variety of regions, and is effective on a broad range of contaminants including organic pollutants, heavy metals, and disease causing organisms. The implementation and operation of a
A photocatalytic system would be similar to that of a SODIS system with very low maintenance, minimal operations, and low continual costs. The capital cost of the system is nearly entirely dependent on the cost of the catalytic material. If standard photocatalytic TiO$_2$ were employed as the catalyst and a method were developed to recycle the TiO$_2$, then the capital cost would fall in the “low” range, under $10. Assuming the catalyst is immobilized within a bottle or small reactor, the reactor simply needs to be filled with water and placed in the sun until treatment is complete. The system would be resilient to changes in flux, but would have issues with turbidity which similarly affect the SODIS and UV treatment methods.

**Table 5-6:** Summary of photocatalytic water treatment performance harnessing 1 m$^2$ of sunlight for 6 hours

<table>
<thead>
<tr>
<th>Photocatalysis</th>
<th>Treatment Capacity</th>
<th>High Flux</th>
<th>Medium Flux</th>
<th>Low Flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>Visible Light</td>
<td>23900 L</td>
<td>19900 L</td>
<td>12500 L</td>
<td></td>
</tr>
<tr>
<td>Ideal TiO$_2$</td>
<td>1920 L</td>
<td>1640 L</td>
<td>990 L</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Costs*</th>
<th>Capital</th>
<th>Maintenance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unknown</td>
<td>Low</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Efficacy on Other Contaminants</th>
<th>Organic Pollutants</th>
<th>Heavy Metals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Other</th>
<th>Ease of Use</th>
<th>Taste and Odour Issues</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Easy</td>
<td>No</td>
</tr>
</tbody>
</table>

*Capital Costs: High > $100; $100 > Medium > $10; $10 > Low
Maintenance Costs: High > $100/yr; $100/yr > Medium > $10/yr; $10/yr > Low

In this study, the potential treatment capacity for an ideal photocatalytic system was investigated to better characterize the potential treatment capacity. Based on fundamental and empirical calculations, it was determined that a photocatalytic system that uses only UV-A and the higher wavelengths of the solar spectrum will be unable to substantially improve solar water purification compared to conventional techniques.

When compared to solar treatment systems that employ photovoltaics such as solar powered UV lamps and solar chlorine generators, the capacity of even an ideal UV photocatalyst is dwarfed by the treatment capacity of a chlorine generator. This difference in system capacity is depicted in the top graph of **Figure 5-5:** which shows the treatment capacities of each of the systems investigated at a high, medium and low solar flux range.
Figure 5-5: Treatment capacity of visible light photocatalyst, ideal TiO$_2$ photocatalyst, chlorine, PCV-UV (photovoltaic ultraviolet, SODIS and heat treatment systems at high (915 W/m$^2$), medium (762 W/m$^2$) and low (477 W/m$^2$) flux conditions
To put this assessment in perspective, a line is drawn across the graph indicating the estimated current practical capacity of photocatalytic systems, which operate at about 10% quantum efficiency (Byrne et al. 2008, Shannon et al. 2010). This means that only 10% of the incoming photons can be converted to electron-hole pairs by the catalyst and is calculated by reducing the incoming photons to the system by 90%. Photocatalytic system with wide-band gaps are only marginally out performing SODIS and heat treatment.

In contrast, the bottom graph in Figure 5-5: shows the potential capacity for a visible light photocatalytic treatment system. In this scenario, the photocatalytic system far out-performs any of the conventional techniques with about twice the capacity of the chlorine generating system. The line drawn on this graph represents the performance of the best visible light catalyst made in research and laboratory settings. These catalysts have been able to achieve about 10% quantum efficiency; however, they are generally unstable or made of rare materials which make them unsuitable for current applications. Results here indicate that the research potential for even a low efficiency visible light photocatalyst is greater than an optimal efficiency wide band gap catalyst.

**5.6 SUMMARY AND CONCLUSIONS**

This comparative model has been designed to compare the potential of an ideal photocatalytic treatment method to various other solar-powered purification methods. When compared to heat treatment, SODIS, and photovoltaic powered UV-C lamps and chlorine generators the model illustrates the fundamental limitations of a photocatalytic system which is unable to harnessing the visible range of the solar spectrum. This comparison offers perspective to current research on photocatalytic water treatment and the potential for this technology to become economically viable in the near future.

Table 5-7 combines the results for each treatment mechanism and summarizes the results from the model and literature review. Model results are shown under treatment capacity, with flux resiliency being qualified by the drop in capacity with lowered flux conditions. The least resilient treatment systems are SODIS and heat treatment, while the photovoltaic powered systems (PVC-UV and PVC-Cl₂) are the most resilient. When a photovoltaic component is required, the cost and maintenance required for the system increase substantially. Chlorine, although the clear top
performer for conventional system capacity, is the only treatment system which has taste and odour problems associated with its final treated water.

**Table 5-7: Summary of Comparative Model Results**

<table>
<thead>
<tr>
<th>Treatment System</th>
<th>Treatment Capacity (L)</th>
<th>Costs*</th>
<th>Efficacy on Alternative Contaminants</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>High Flux</td>
<td>Medium Flux</td>
<td>Low Flux</td>
<td>Capital</td>
</tr>
<tr>
<td>Visible Light Photocatalysis</td>
<td>23900</td>
<td>19900</td>
<td>12500</td>
<td>-</td>
</tr>
<tr>
<td>Ideal TiO₂ Photocatalysis</td>
<td>1920</td>
<td>1640</td>
<td>920</td>
<td>-</td>
</tr>
<tr>
<td>PVC Chlorine Generation</td>
<td>14800</td>
<td>12300</td>
<td>7730</td>
<td>High</td>
</tr>
<tr>
<td>PVC UV Treatment</td>
<td>2170</td>
<td>1810</td>
<td>1140</td>
<td>High</td>
</tr>
<tr>
<td>Solar Disinfection</td>
<td>588</td>
<td>530</td>
<td>294</td>
<td>Low</td>
</tr>
<tr>
<td>Heat Treatment</td>
<td>1240</td>
<td>1020</td>
<td>31</td>
<td>Low</td>
</tr>
</tbody>
</table>

*Capital Costs: High > $100; $100 > Medium > $10; $10 > Low
Maintenance Costs: High > $100/yr; $100/yr > Medium > $10/yr; $10/yr > Low

This comparison makes it clear that more fundamental research is required and places strong emphasis on the need to study visible light activated catalysts. For conventional systems, solar chlorine generation dominates in terms of energy efficiency and capacity, but it has significant drawbacks in terms of taste and odour issues, cost, maintenance and access to salt raw material. Wide band gap catalysts are currently not a competitive method for solar water disinfection, and even at 100% material efficiency, they will still be out performed by photovoltaic systems. However, the model indicates that a successful visible light photocatalysis would far surpass all conventional systems considered in terms of treatment capacity, range of effected contaminants, simplicity of use and resiliency.
5.7 References

Acra A., M. Jurdi, H. Mu'alleem, Y. Karahagopian, Z. Raffoul (1990). Water disinfection by solar radiation, assessment and application, technical study 66e, IDRC. Sunlight with wavelengths of 315-400 nanometers (nm) on the ultraviolet (UV) range of the electromagnetic spectrum is most effective at destroying bacteria.


Swiss Federal Institute of Environmental Science and Technology (EAWAG) and Department of Water and Sanitation in Developing Countries (SANDEC) (2002) Solar Water Disinfection: A Guide for the Application of SODIS.


6 SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

6.1 SUMMARY AND CONCLUSIONS

The integration of photocatalytic advanced oxidation into solar disinfection is a robust method of improving the microbial and chemical quality of treated water. In this thesis, the performance of photocatalytic solar irradiated batch reactors was evaluated through modeling and experimentation. To begin, an analytic model investigated reactor configuration by simplifying photoreactor geometry to reduce parameters effecting treatment. Model results were divided into two scenarios: unrestricted surface area reactors in which the amount of catalyst is the limiting factor, and restricted surface area reactors in which the amount of catalyst is considered effectively limitless. Results predict that the best configuration in terms of efficiency and treated volume is a thin film of catalyst with a single layer of water above it. The ideal performance of the reactor is attributed to the contract fraction and zero light attenuation that can be achieved with the stacking of a single indivisibly thin layer of water and catalyst. As may be evident from this description, a reactor of this configuration is generally impractical for many applications, particularly small scale SODIS systems. When the area of the reactor is restricted, it was found that a suspension performs best in terms of efficiency and treated volume, but its performance can be closely approached by an immobilized catalyst which is evenly distributed throughout the body of the reactor such as when using a foam or aerogel configuration to support the catalyst. The performance of the suspension and foam are most similar in smaller systems, where the performance of the two systems is predicted to be nearly identical. Based on these model results, an immobilized catalyst should theoretically be able to practically match the performance of a suspension reactor.

To complement this model, experiments were performed to compare the performance of titanium dioxide coated foams of varying pore size to suspended and fixed film configurations through degradation of organic dyes (acid orange 24 and methylene blue), Escherichia coli, and 1,4-dioxane. These experiments examined the relationship between target contaminant degradation and reactor configuration. For both dyes, the 5 and 10 PPI foams were among the top performers, with performance deteriorating with the 20 and 40 PPI foams. For 1,4-dioxane the suspension and 10 PPI foam were the top performers. The 40 PPI foam was a poor performer with all contaminants; indeed for the E. coli samples, the 40 PPI foam performed worse than the control.
This appeared to be caused by the very fine pore size of the foam, which prevents light from radiating through the material. This suggests that the immobilized catalyst offers improved treatment relative to the control (simulated solar light only) up to a certain limiting pore size, beyond which performance deteriorates. Overall, it was found that a catalyst immobilized on a foam support could match the efficiency of a suspension configuration due to effective mass transport and association between the analyte and the foam. This exhibits the potential for photocatalytic foams to improve water quality in small scale batch reactor solar disinfection systems by enhancing the inactivation of microbes and oxidizing organic pollutants.

Photocatalysis is one of many systems currently available for treating water using solar energy. Therefore, a second model was developed to characterize and compare the potential treatment capacity of solar photocatalysis to conventional solar purification methods using key quantitative and qualitative performance parameters. The model approached this objective by quantifying the amount of water the system can treat to a standard 2-log reduction of E. coli given the amount of energy provided by the sun in 6 hours over an area of 1 m\(^2\). The potential of an ideal photocatalytic treatment system was compared to heat treatment, SODIS, and photovoltaic powered UV-lamps and chlorine generators. The least resilient treatment systems were found to be SODIS and heat treatment, while the photovoltaic powered systems are the most resilient. When a photovoltaic component is required, the cost and maintenance required for the system increase substantially. Chlorine, although the clear top performer for conventional system capacity, is the only treatment system which has taste and odour problems associated with its final treated water. Wide band gap catalysts were not found to be competitive for solar water disinfection, as even at 100% quantum efficiency, they will still be out performed by photovoltaic systems. However, the model indicates that a successful visible light photocatalysis would far surpass all conventional systems considered in terms of treatment capacity, range of effected contaminants, simplicity of use and resiliency.

### 6.2 Recommendations For Future Work

The results of the work presented in this thesis are encouraging for research in the field of photocatalytic water treatment. It is evident from the experiments and modeling conducted that solar photocatalytic water treatment has the potential to play an important in new innovation in
point-of-use water treatment. Part of the objective of this thesis was to provide context and guidelines for future studies in this field. Accordingly, several recommendations have been derived from this research.

In order for photocatalytic foam materials to be widely implemented as an augmentation to traditional solar disinfection, the properties of these materials need to be further characterized and optimized. Based on results from the comparative model, it is apparent that a focus of future studies in photocatalysis needs to be adapting the materials to harnessing long wavelength visible light radiation. The effect of varying the foam support material on the efficiency of the photocatalytic coating has not been thoroughly investigated and is poorly characterized in literature. A range of combination of support and coating material exist; both metallic and non-metallic base materials have been tested using a variety of coating mechanisms. The effect of varying the coating deposition method and varying the support material remain important research questions for material optimization. The life-time and re-use potential of these materials, along with the reoccurrence of contaminant adsorption, are likewise poorly defined. It was also evident from this research that the performance of a particular material was largely dependent on the contaminant being degraded and that the superior comparative performance of one photocatalytic material over another cannot be considered transferrable between different contaminants and different environmental conditions. As such, it is recommended that tests on new catalyst are performed on multiple contaminants, and if possible, should be performed using the specific contaminant and environmental conditions in the proposed application.
APPENDICES
A. COMPUTATIONAL METHODS
A.1 MATLAB Code and Output for Optimal Geometry Studies

The following sections detail the computation method used for the calculations performed in Chapter 3: Modeling the Performance of Immobilized Photocatalysts for Water Purification. All programs were written and run in MATLAB version R2011a. A series of loops were used to carry the calculations through the performance parameters for the fixed film, suspension and immobilized catalyst scenarios. Where possible, summation functions were performed using exact analytic methods although some numerical approximations were made for the Case 2 as the analytical calculation were beyond the capacity of the program.

Graphs in each section show the direct MATLAB output for the parameters determined.

A.1.1 Case 1: Unrestricted Surface Area

% Code for determining the performance parameters for Case 1: Unrestricted Surface Area Photoreactor
clear
tic

% Reactor Parameters
dw = 1;
A = 1;
T = 0.5;
n = (1:100);

% Calculations for Suspension
% Total Volume
for i=1:length(n)
    Vts(i) = n(i)*dw*A;
end
% Irradiance Fraction
for i=1:length(n)
    syms a
    Ifs(i) = symsum(((T)/n(i))^(a-1))/n(i),a,1,n(i));
end
% Contact Fraction
for i=1:length(n)
    Cfs(i) = 1/n(i);
end
% Calculating effective volume
Ves = Cfs.*Ifs.*Vts;
% Calculating the efficiency (h)
hs = Cfs.*Ifs;

% Calculations for Thin Films
% Total Volume
for i=1:length(n)
    Vtt(i) = n(i)*dw*A;
end
%Irradiance Fraction
    Ift = ones(1,length(n));
%Contact Fraction
for i=1:length(n)
    Cft(i) = 1/n(i);
end
%Calculating effective volume
Vet = Cft.*Ift.*Vtt;
%Calculating the efficiency (h)
h = Cft.*Ift;

%ploting results
figure(1)
plot(n,Ves, 'b-*')
hold on
plot(n,Vet, 'r-*')
xlabel('number of layers')
ylabel('Effective Volume')
title('Unrestricted Area')
grid on
hold off

figure (2)
plot(n,hs, 'b-*')
hold on
plot(n,ht, 'r-*')
xlabel('number of layers')
ylabel('Efficiency')
title('Unrestricted Area')
grid on
hold off

toc
Figure A-1: Effective Volume for Unrestricted Surface Area, MATLAB graphical output, $\tau = 0.5$. Red is thin film and blue is suspension.

Figure A-2: Efficiency for Unrestricted Surface Area, MATLAB graphical output, $\tau = 0.5$. Red is thin film and blue is suspension.
A.1.2 Case 2: Restricted Surface Area

% Code for determining the performance parameters for Case 2: Restricted Surface Area Photoreactor

clear tic

% Reactor Parameters
dw = 1;
A = 1;
T = 0.95;
p = 0.5;
m = 200;
n = (1:m);
a=n;
N = m;

% Calculations for Foam
% Total Volume
for i=1:m
    Vtf(i) = n(i)*dw*A;
end
% Irradiance Fraction
for i=1:m
    for j=1:m
        I(i,j) = (T^(N/n(j)))^(a(i)-1);
    end
end
If = diag(cumsum(I));
for k = 1:m
    Iff(k) = If(n(k),1)/n(k);
end
% Contact Fraction
for i=1:m
    Cff(i) = p^(n(i)/N);
end
% Calculating effective volume
Vef = Cff.*Iff.*Vtf;
% Calculating the efficiency (h)
hf = Cff.*Iff;

% Calculations for Suspension
% Total Volume
for i=1:m
    Vts(i) = n(i)*dw*A;
end
% Irradiance Fraction
for i=1:m
    for j=1:m
        C(i,j) = (T^(N/n(j)))^(a(i)-1);
    end
end
B = diag(cumsum(C));
for k = 1:m
    Ifs(k) = B(n(k),1)/n(k);
end
% Contact Fraction
Cfs = ones(1,m);
% Calculating effective volume
Ves = Cfs.*Ifs.*Vts;
% Calculating the efficiency (h)
hs = Cfs.*Ifs;

% Calculations for Thin Films
% Total Volume
for i=1:m
    Vtt(i) = n(i)*dw*A;
end
% Irradiance Fraction
Ift = ones(1,m);
% Contact Fraction
for i=1:m
    Cft(i) = 1/n(i);
end
% Calculating effective volume
Vet = Cft.*Ift.*Vtt;
% Calculating the efficiency (h)
ht = Cft.*Ift;

ploteing results
figure(1)
plot(n,Ves, 'b--');
hold on
plot(n,Vet, 'r--');
plot(n,Vef, 'g--');
xlabel('number of theoretical layers')
ylabel('Effective Volume')
title('Restricted Area')
grid on
hold off

figure(2)
plot(n,hs, 'b--');
hold on
plot(n,ht, 'r--');
plot(n,hf, 'g--');
xlabel('number of theoretical layers')
ylabel('Effective Volume')
title('Restricted Area')
grid on
hold off

toc
Figure A-3: Effective Volume for Unrestricted Surface Area, MATLAB graphical output, $\tau = 0.95; \rho = 0.5$. Red is thin film, blue is suspension and green is immobilized catalyst.

Figure A-4: Efficiency for Unrestricted Surface Area, MATLAB graphical output, $\tau = 0.95; \rho = 0.5$. Red is thin film, blue is suspension and green is immobilized catalyst.
A.2 MATLAB Code and Output for Comparative Modeling of Solar Disinfection Mechanisms

The following sections detail the computation method used for the calculations performed in Chapter 5: Comparing Photocatalysis to Conventional Small-Scale Solar Purification Systems. All programs were written and run in MATLAB version R2011a. All constants were drawn from literature as described in Chapter 5. To maintain consistency and comparability between calculations, water was assumed to be at an initial temperature of 20 °C and have a low turbidity of 1.8 mg C/L for all treatment systems. These values were chosen to match the condition under which the literature derived constants were determined.

The graphs shown for each section display the change in treatment capacity for each system tracked across changes in latitude and declination (i.e., regional and seasonal changes).

A.2.1 Solar Flux Calculations

```matlab
% Code for determining the surface flux
clear
tic

% Input Parameters
Ep = 6;                      % Exposure Time
L = (0:60);                  % Latitude
D = (-23.5:23.5);            % Declination (-23.5 to 0 to 23.5 to 0)
T = 0.8;                     % Atmospheric Transparency
Te = 20;                     % Ambient Temperature

% Calculated Parameters
S = 1367;                    % Solar Constant (W/m^2)
h = ((Ep/24)*pi);            % Hour Angle
for i=1:length(L)
    for j=1:length(D)
        Fn(i,j) = S*((sind(L(i))*sind(D(j)))+(cosd(0)*cosd(L(i))*cosd(D(j))));       % Noon Solar Flux (W/m^2)
        Fe(i,j) = S*((sind(L(i))*sind(D(j)))+(cos(h)*cosd(L(i))*cosd(D(j))));     % End Solar Flux (W/m^2)
    end
end
Ft = (Fn+2*Fe)/3;                    % Average Flux (W/m^2)

% Distribution by Wavelength
Fs = Ft*T;                     % Surface Flux (W/m^2)
UV = 0.0345*Fs;                % 290-400 nm
```
Stephanie Loeb

Department of Civil Engineering, University of Toronto

Vis = 0.4475*Fs; %400-700 nm
IR = 0.518*Fs; %700+ nm

figure(2)
mesh(D,L,Fs, 'FaceColor', 'yellow','EdgeColor', 'yellow')
alpha(0.5)
hold on
xlabel('Seasonal Variation')
ylabel('Latitude')
title('Surface Flux')
grid on
hidden off
hold off
toc

A.2.2 Photocatalysis Calculations

%Code for determining the performance of an optimized photocatalytic
%reactor
tic

%Input Parameters
A = 1; %Irradiated Surface Area (m^2)
Bg_UV = 400; %Band gap (nm)
Bg_vis = 780;
W_UV = UV; %UV light capture
W_vis = UV+Vis; %Visible light capture
CT = 0.8e-5; %OH rad CT for 2-log inactivation of E.coli
(mgmin/L)
QE = 0.8;
kf = 1; %formation rate constant
ko = 8.08e8; %oxidation rate constant (1/Mcs)
NOM = 1.8; %TOC of tap water (mgc/L)

%UV PHOTOCAT
%Calculated Parameters
E_UV = W_UV.*A; %Energy Rate (J/s)
Pe_UV = ((6.626e-34)*2.998e8)./(Bg_UV.*(1e-9)); %Photon Energy (J/photon)
F_UV = (E_UV./Pe_UV)./(6.02e23); %Flux (mols of photons/s)
R = NOM/(1000*12) %NOM loading (Mc)

%Kinetics Calculations
H_UV = (kf.*F_UV)./(ko*R); %steady state [h] (mol)
OH_UV = 2*H_UV.*(1000*1.701); %steady state [OH] (mg)
C = CT./(Ep*60); %Concentration for 2-log reduction (mg/L)
WT_Photocatalysis_UV = OH_UV./C + WT_SODIS; %Water Treated (L)

%VIS PHOTOCAT
%Calculated Parameters
E_vis = W_vis.*A; %Energy Rate (J/s)
Pe_vis = ((6.626e-34)*2.998e8)./(Bg_vis.*(1e-9)); %Photon Energy (J/photon)
F_vis = (E_vis./Pe_vis)./(6.02e23); %Flux (mols of photons/s

R = NOM/(1000*12) %NOM loading (Mc)

%Kinetics Calculations
H_vis = (kf.*F_vis)./(ko*R); %steady state [h] (mol)
OH_vis = 2*H_vis.*(1000*17.01); %steady state [OH] (mg)
C = CT./(Ep*60); %Concentration for 2-log reduction (mg/L)
WT_Photocatalysis_vis = OH_vis./C + WT_SODIS; %Water Treated (L)

%plotting region flux map curve
figure(1)
[D,L,WT_Photocatalysis] = peaks
pcolor(D,L,WT_Photocatalysis_UV, 'FaceColor', 'cyan','EdgeColor', 'cyan')
alpha(0.5)
hold on
xlabel('Seasonal Variation')
ylabel('Latitude')
title('UV Light Photocatalytic Water Treated')
grid on
hidden off
hold off

%plotting region flux map curve
figure(2)
[D,L,WT_Photocatalysis] = peaks
pcolor(D,L,WT_Photocatalysis_vis, 'FaceColor', 'magenta','EdgeColor', 'magenta')
alpha(0.5)
hold on
xlabel('Seasonal Variation')
ylabel('Latitude')
title('Visible Light Photocatalytic Water Treated')
grid on
hidden off
hold off

maxOH_UV = max(max(OH_UV))
maxOH_vis = max(max(OH_vis))
maxUV = max(max(WT_Photocatalysis_UV))
max_vis = max(max(WT_Photocatalysis_vis))
toc
Figure A-5: Water treated by traditional UV Light Photocatalysis with yearly flux variation

Figure A-6: Water treated by traditional Visible Light Photocatalysis with yearly flux variation
A.2.3 SODIS Calculations

%Code for determining SODIS bottles treated

tic
%Determining Max Temperature Achieved
%SODIS bottle and environmental parameters
A = 1;                    %Irradiated Surface Area (m2)
Te = Te;                    %Average Ambient Temperature
Dm = 0.1;                    %Bottle diameter (m)
H = 0.25;                    %Bottle height (m)
d = 0.5/1000;               %Bottle thickness (m)
k = 0.2;                    %Thermal conductivity of PET
SA = (pi*Dm*H)/2;            %Surface area exposed to heat loss
CA = Dm*H;                   %Cross Sectional Area
C = 1020000;                  %Specific Heat Capacity of Water
V = ((Dm/2)^2)*pi*H;        %Volume of 1 bottle
m = 1000*0.75*V;             %Mass of water
UVA = 0.76*UV

t = Ep*60*60;               %Exposure time (seconds)
T = Te + IR*CA*(1-exp(-(k*SA*t)/(C*m*d))));

%Dose required for 2-log inactivation of E. coli
for i = 1:size(T,1)
    for j = 1:size(T',1)
        if T(i,j) < 50;
            R(i,j) = 12.72*60*60;            %(Wh/m2*3600=J/m2)
        elseif T(i,j) > 50;
            R(i,j) = (12.72*3600)/3;
        end
    end
end

%Water Treatment Calculation
s = (R./UVA);         %Time required to treat one bottle
st = s+60;            %a minute minute interval is added to switch the bottles
nt = floor(t./st);         %number of bottle that can be treated in given
exposure time
na = floor(A/CA);          %number of bottle that can cover given area
WT_SODIS = nt*na*V*1000;

figure(2)
%[D,L,WT_SODIS] = peaks
%pcolor(D,L,WT_SODIS)
mesh(D,L,WT_SODIS, 'FaceColor', 'yellow', 'EdgeColor', 'yellow')
alpha(0.5)
hold on
xlabel('Seasonal Variation')
ylabel('Latitude')
title('SODIS Water Treated')
grid on
hidden off
hold off

WTmax_SODIS = max(max(WT_SODIS))
toc
Figure A-7: Water treated by traditional SODIS with yearly flux variation

### A.2.4 Photovoltaics Powered Systems

%Code for determining water treated by energy powered through PVCs

%input parameters
A = 1;                  %Irradiated Surface Area (m2)
t = Ep*60*60;           %exposure time (s)
n_sc = 0.05;            %solar cell efficiency
n_b = 0.88;             %battery efficiency

%Electrical Energy obtained from solar cell
Q = n_sc*n_b*Fs*A;
E = Q*t;

%UV LAMP TREATMENT
E_UVs = 2.0e-3;        %system energy usage (L/J)
E_UV1 = 3e-3;          %system energy usage (L/J)
WT_UVs = E_UVs*E;      %Water treated by UV-light
WT_UV1 = E_UV1*E;      %Water treated by UV-light

UVs_max = max(max(WT_UVs))
UV1_max = max(max(WT_UV1))

figure(4)
%[D,L,WT_UVs] = peaks
%pcolor(D,L,WT_UVs)
mesh(D,L,WT_UVs, 'FaceColor', 'black','EdgeColor', 'black')
alpha(0.5)
hold on
xlabel('Seasonal Variation')
ylabel('Latitude')
title('Small UV System Water Treated')
grid on
hidden off
hold off

figure(5)
[D,L,WT_UVl] = peaks
pcolor(D,L,WT_UVl)
mesh(D,L,WT_UVl, 'FaceColor', 'green','EdgeColor', 'green')
alpha(0.5)
hold on
xlabel('Seasonal Variation')
ylabel('Latitude')
title('Large UV system Water Treated')
grid on
hidden off
hold off

%CHLORINE TREATMENT
E_Cl2 = 1.7e-2;                %system energy usage (L/J)
WT_Cl2 = E_Cl2*E;                %Water treated by Chlorine
C12_max = max(max(WT_Cl2))

figure(6)
[D,L,WT_Cl2] = peaks
pcolor(D,L,WT_Cl2)
mesh(D,L,WT_Cl2, 'FaceColor', 'blue','EdgeColor', 'blue')
alpha(0.5)
hold on
xlabel('Seasonal Variation')
ylabel('Latitude')
title('Chlorine Water Treated')
grid on
hidden off
hold off

toc
Figure A-8: Water treated by Solar Powered Chlorine Generation with yearly flux variation

Figure A-9: Water treated by a Large UV treatment system with yearly flux variation
A.2.5 Heat Treatment Calculations

tic
%Code for determining water treated through heat treatment
%input parameters
A = 1;                        %Irradiated Surface Area (m2)
t = Ep*60*60;                 %exposure time (s)
Tw = Te;                      %Average Ambient Temperature
Dr = 0.2;                     %Pot diameter (m)
H = 0.2;                      %Pot height (m)
d = 5/1000;                   %Pot thickness (m)
k = 16;                       %Thermal conductivity of stainless steel
a = 0.75;                      %absorption fraction
SA = pi*Dr*H + 2*pi*((Dr/2)^2); %Surface area exposed to heat loss (m^2)
C = 4200;                     %Specific Heat Capacity of Water (J/kgC)
V = pi*H*((Dr/2)^2);          %volume of pot (m^3)
m = 1000*V;                   %Mass of water (kg)

%Heat Energy Obtained
Q = a*(1/3)*IR*A;  
E = Q*t;

%Calculating maximum temperature reached by water
T = Tw + Q*(1-(exp(-((k*SA*t)/(C*m*d)))));

%Calculating time to reach temperature points
pt_1 = (-((C*m*d)/(k*SA)))*(log(((Tw-60)/Q)+1)); %time to bring water to pasteurization temperature
%set all complex results to zero
for i=1:size(pt_1,1)
    for j=1:size(pt_1',1)
        pt_complex(i,j) = isreal(pt_1(i,j));
    end
end
pt = pt_complex.*(pt_1);

bt_1 = \(-\frac{(C*m*d)}{(k*SA)}\)*(log((\frac{(Tw-100)}{Q})+1));    %time required to bring water to boil (s)
%set all complex results to zero
for l=1:size(bt_1,1)
    for k=1:size(bt_1',1)
        bt_complex(l,k) = isreal(bt_1(l,k));
    end
end
bt = bt_complex.*(bt_1);

%Calculating water treated under each condition
for a = 1:size(T,1)
    for b = 1:size(T',1)
        if T(a,b) < 60
            np(a,b) = pt(a,b).*0;   %not hot enough to treat water
        elseif T(a,b) < 100
            np(a,b) = floor((t./(pt(a,b)+3600)));    %pots treated by pasteurization at 60 for 1 hour
        elseif T(a,b) > 100
            np(a,b) = floor((t./(bt(a,b)+60)));         %pots treated by boiling, factor of one minute added to switch pots
        end
    end
end
WT_heat = np*V*1000;

figure(3)
%[D,L,WT_boiling] = peaks
%pcolor(D,L,WT_boiling)
mesh(D,L,WT_heat, 'FaceColor', 'red','EdgeColor', 'red')
alpha(0.5)
hold on
xlabel('Seasonal Variation')
ylabel('Latitude')
title('Heat Treated Water')
grid on
hidden off
hold off

%print useful values
Tmax = max(max(T))
Tmin = min(min(T))
Hmax = max(max(WT_heat))
Hmin = min(min(WT_heat))
toc
Figure A-11: Water treated by solar heat treatment with yearly flux variation
### A.3 COMPARATIVE MODEL DATA SET

**Table A-1:** List of UV-disinfection system considered in comparative analysis and details regarding their energy consumption and water purification

<table>
<thead>
<tr>
<th>Company</th>
<th>System Name</th>
<th>Lamp Power (W)</th>
<th>Lamp Output (mJ/cm²)</th>
<th>Flow (L/min)</th>
<th>System Power (W)</th>
<th>Energy (L/J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AquaSun</td>
<td>Villagers S1</td>
<td>10</td>
<td>16</td>
<td>3.7</td>
<td>21.5</td>
<td>2.9E-3</td>
</tr>
<tr>
<td>International</td>
<td>Villagers S3-4</td>
<td>22</td>
<td>16</td>
<td>11</td>
<td>60</td>
<td>3.1E-3</td>
</tr>
<tr>
<td></td>
<td>Villagers S6-4</td>
<td>22</td>
<td>16</td>
<td>22</td>
<td>180</td>
<td>2.0E-3</td>
</tr>
<tr>
<td>Sterilight</td>
<td>SC1</td>
<td>10</td>
<td>16</td>
<td>7.5</td>
<td>12</td>
<td>1.0E-2</td>
</tr>
<tr>
<td>Copper</td>
<td>SC2.5</td>
<td>14</td>
<td>16</td>
<td>15.9</td>
<td>16</td>
<td>1.7E-2</td>
</tr>
<tr>
<td></td>
<td>SC4</td>
<td>17</td>
<td>16</td>
<td>28.4</td>
<td>19</td>
<td>2.5E-2</td>
</tr>
<tr>
<td>Wyckomar</td>
<td>UV Solar</td>
<td>N/A</td>
<td>46</td>
<td>16</td>
<td>23.4</td>
<td>1.1E-2</td>
</tr>
<tr>
<td>Trojan</td>
<td>A</td>
<td>14</td>
<td>40</td>
<td>11</td>
<td>22</td>
<td>8.3E-3</td>
</tr>
<tr>
<td></td>
<td>B4</td>
<td>25</td>
<td>40</td>
<td>23</td>
<td>36</td>
<td>1.1E-2</td>
</tr>
<tr>
<td></td>
<td>C4</td>
<td>40</td>
<td>40</td>
<td>60</td>
<td>50</td>
<td>2.0E-2</td>
</tr>
<tr>
<td></td>
<td>D4</td>
<td>40</td>
<td>40</td>
<td>60</td>
<td>50</td>
<td>2.0E-2</td>
</tr>
<tr>
<td></td>
<td>E4</td>
<td>70</td>
<td>40</td>
<td>110</td>
<td>83</td>
<td>2.2E-2</td>
</tr>
<tr>
<td></td>
<td>F4</td>
<td>110</td>
<td>40</td>
<td>170</td>
<td>130</td>
<td>2.2E-2</td>
</tr>
<tr>
<td>Solar Sundance</td>
<td>UV Solar</td>
<td>N/A</td>
<td>40</td>
<td>33</td>
<td>12</td>
<td>4.6E-2</td>
</tr>
<tr>
<td>BioUV</td>
<td>BioSUN</td>
<td>33</td>
<td>40</td>
<td>35</td>
<td>40</td>
<td>1.5E-2</td>
</tr>
</tbody>
</table>

N/A = information not available
Table A-2: List of chlorine disinfection system considered in comparative analysis and details regarding their energy consumption and water purification

<table>
<thead>
<tr>
<th>Company</th>
<th>System Name</th>
<th>Chlorine Generation Rate</th>
<th>Salt Consumed (gNa/gCl2)</th>
<th>Power (W)</th>
<th>Energy (L/J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine Waters</td>
<td>Sunchlor 5</td>
<td>7.5 g/hr</td>
<td>33</td>
<td>37.5</td>
<td>1.85E-2</td>
</tr>
<tr>
<td></td>
<td>Sunchlor 50</td>
<td>32 g/hr</td>
<td>46.875</td>
<td>160</td>
<td>1.85E-2</td>
</tr>
<tr>
<td></td>
<td>Sunchlor 25</td>
<td>62 g/hr</td>
<td>36.29</td>
<td>320</td>
<td>1.79E-2</td>
</tr>
<tr>
<td></td>
<td>Sunchlor 100</td>
<td>120 g/hr</td>
<td>37.5</td>
<td>520</td>
<td>2.14E-2</td>
</tr>
<tr>
<td>AquaChlor Solar</td>
<td>OSEC</td>
<td>2 g/hr</td>
<td>23.4375</td>
<td>11</td>
<td>1.68E-2</td>
</tr>
<tr>
<td>Noble Chlor</td>
<td>NCP-500</td>
<td>0.5 g/hr</td>
<td>N/A</td>
<td>15</td>
<td>3.09E-3</td>
</tr>
<tr>
<td></td>
<td>NCP-1000</td>
<td>1.0 g/hr</td>
<td>N/A</td>
<td>30</td>
<td>3.09E-3</td>
</tr>
<tr>
<td></td>
<td>NCP-1500</td>
<td>1.5 g/hr</td>
<td>N/A</td>
<td>45</td>
<td>3.09E-3</td>
</tr>
<tr>
<td></td>
<td>NCP-15M</td>
<td>15 g/hr</td>
<td>N/A</td>
<td>375</td>
<td>3.70E-3</td>
</tr>
<tr>
<td></td>
<td>NCP-25M</td>
<td>25 g/hr</td>
<td>N/A</td>
<td>625</td>
<td>3.70E-3</td>
</tr>
</tbody>
</table>

N/A = information not available

References


## A.4 Comparative Model Results

**Table A-3:** Potential capacity for each solar water treatment system to achieve a 2-log reduction of *E. coli* solar normalized for varying solar flux conditions. Each flux condition represents the average solar energy received over the strongest six hours of the day.

<table>
<thead>
<tr>
<th>Treatment System</th>
<th>Water Treated (L)</th>
<th>Water Treated (L)</th>
<th>Water Treated (L)</th>
<th>Water Treated (L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>High Flux Φ = 915 W/m²</td>
<td>Medium Flux Φ = 762 W/m²</td>
<td>Low Flux Φ = 477 W/m²</td>
<td>Very Low Flux Φ = 25.9 W/m²</td>
</tr>
<tr>
<td>Visible Light Photocatalysis</td>
<td>23900</td>
<td>19900</td>
<td>12500</td>
<td>659</td>
</tr>
<tr>
<td>Ideal TiO₂ Photocatalysis</td>
<td>1920</td>
<td>1640</td>
<td>920</td>
<td>37.7</td>
</tr>
<tr>
<td>Solar Chlorine Generation</td>
<td>14800</td>
<td>12300</td>
<td>7730</td>
<td>418</td>
</tr>
<tr>
<td>UV Lamp - large system</td>
<td>2610</td>
<td>2170</td>
<td>1370</td>
<td>73.8</td>
</tr>
<tr>
<td>UV Lamp – small system</td>
<td>1740</td>
<td>1450</td>
<td>910</td>
<td>49.2</td>
</tr>
<tr>
<td>Solar Disinfection</td>
<td>588</td>
<td>530</td>
<td>294</td>
<td>0</td>
</tr>
<tr>
<td>Heat Treatment</td>
<td>1240</td>
<td>1020</td>
<td>31</td>
<td>0</td>
</tr>
</tbody>
</table>
B. EXPERIMENTAL PROTOCOLS, CALIBRATION AND QA/QC
**B.1 Preparation of Photocatalytic Foams**

TiO$_2$ is a photocatalytic material which can be used to perform advanced oxidation in the presence of UV-A light. A TiO$_2$ dip-coating solution made from @Degussa P-25 TiO$_2$ was used to coat material with a thin photocatalytic layer. This allows the catalyst to be employed in different immobilized configurations.

**Materials**

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Reagents</th>
</tr>
</thead>
<tbody>
<tr>
<td>muffle furnace</td>
<td>@Degussa P-25 TiO$_2$</td>
</tr>
<tr>
<td>sonicator</td>
<td>Distilled Water</td>
</tr>
<tr>
<td>250 mL beaker</td>
<td>10% HNO$_3$</td>
</tr>
<tr>
<td>Stir plate</td>
<td>Acetone</td>
</tr>
<tr>
<td>Stir bar</td>
<td></td>
</tr>
</tbody>
</table>

**Method Outline**

**Sampling and Storage**

Dip-coating solution can be kept in a sealed amber bottle for up to one week. If stirred periodically, solution can be kept for several months. Coated samples can be stored for 6 months at room temperature with no exposure to light.

**Dip-Coating Solution (20 %w TiO$_2$)**

1. Weigh 37.5 g of @Degussa P-25 TiO$_2$ and add it to a 250 mL beaker
2. Add 150 mL of distilled water to the beaker. Mix with a stir bar until solution appears homogeneous
3. Measure the pH of the solution
4. Add 10% HNO$_3$ drop-wise, continuing to measure the pH until a value of 2.4 is achieved

**Dip-Coating Procedure**

1. Before coating, ensure that materials have been cleaned (with acetone and DI water), rinsed and completely dried
2. Place the beaker containing the TiO$_2$ solution into the ultrasonicator bath water, set to room temperature
3. Using tweezers or a small clamp, slowly lower and completely submerge the material into the TiO$_2$ solution for 5 minutes
4. Without removing the material, turn on the sonicator and sonicate the solution and material for 10 minutes
5. Slowly remove the material from TiO$_2$ solution
6. Immediately place the coated material on an aluminum weighing dishes and put into an oven to dry for 10 minutes at 80 °C
7. Ramp up the oven temperature by 2.5 °C per minutes until it reaches 600 °C. Maintain the temperature at 600 °C for 1 hour
8. Allow sample to cool naturally

**B.2 Photocatalytic Degradation Protocol**

Samples were irradiated with simulated solar light from a Photoemission Tech SS150AAA, a Class AAA solar simulator which simulates 1.5AMG (Atmospheric Mass; Global) solar spectrum radiation at a one sun intensity within 2 % accuracy. The system can be used to mimic the degradation of contaminants in water under real world solar flux conditions. When a photocatalyst is exposed to solar light, strongly oxidizing hydroxyl radicals are produced which can quickly degrade organic contaminants and kill microorganisms present in the water. The solar simulator system operates with a single phase 208 V power supply. The light source is a short arc xenon lamp containing highly pressurized gas.

**Materials**

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Reagents</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS150 PET Solar Simulator</td>
<td>Distilled Water</td>
</tr>
<tr>
<td>50x70 mm crystallizing dish</td>
<td>@Degussa P-25 TiO$_2$ power</td>
</tr>
<tr>
<td>Timer</td>
<td>@Degussa P-25 TiO$_2$ coated on flat aluminum</td>
</tr>
<tr>
<td>Pipette</td>
<td>@Degussa P-25 TiO$_2$ coated on aluminum foams (6 cm diameter by 2 cm height)</td>
</tr>
<tr>
<td></td>
<td>Doses of contaminants to be degraded</td>
</tr>
</tbody>
</table>

**Method Outline**

1. With the shutter closed, place the crystallizing dishes under the mapped out illumination area in the solar simulator (up to 9 dishes can fit within the illumination area)
2. Fill each crystallizing dish with 75 mL of distilled water
3. Place either a TiO$_2$ coated foam, a TiO$_2$ coated film or an estimated mass equivalent amount of TiO$_2$ powered into each dish
4. Spike each dish with a single dose of contaminant and briefly stir to create a homogeneous distribution
5. Immediately remove one aliquot from each dish to be processed accordingly for contaminant concentration
6. With the shutter still closed, begin the timer
7. After 30 minutes remove another aliquot from each dish to be processed
8. After 30 minutes dark reaction, open the shutter and expose the dishes to the light beam
9. Remove additional aliquots from each container to be processed after 5, 10, 20, 40, 80, 120 and 160 minutes of exposure to the light

**B.3 Organic Dye Measurements**

Coloured dyes in a sample absorb light in proportion to their concentration. The peak absorption wavelength of the dye is chosen for detection, which for Acid Orange 24 (AO24) is 430 nm and for methylene blue (MB) is 607 nm. First a standard curve was created by measuring the absorbance for a series of samples where the concentration of dye is known. Samples are then measured and the unknown concentration of dye can be inferred from the standard curve. Dyes can quickly degrade when exposed to light. Samples were analyzed immediately and unnecessary exposure to light and open atmosphere was avoided. Samples were allowed to reach room temperature prior to analysis; this prevents condensation from forming on the spec cell and possibly resulting in erroneous readings.

**Materials**

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Reagents</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV-Vis Spectrophotometer</td>
<td>Acid Orange 24</td>
</tr>
<tr>
<td>125 mL amber glass vials</td>
<td>Milli-Q water®</td>
</tr>
<tr>
<td>Pipette</td>
<td>Methylene Blue</td>
</tr>
<tr>
<td>100 mL volumetric flask</td>
<td></td>
</tr>
<tr>
<td>Spectrometer cuvette</td>
<td></td>
</tr>
</tbody>
</table>

**Method Outline**

**Sampling and Storage**

Collect sample into a clean amber vial and analyze on the same day that they are collected.
Standard Sample

Working Solution (200 mg/L Dye)

1. Weight 20 mg of dye and add it to a 100 mL volumetric flask
2. Top volumetric flask to 100 mL with Milli-Q® water. Cap flask with stopper and mix by inverting or stir with stir bar until dissolved
3. Transfer this solution into an amber vial to protect it from exposure to light

Standard Solutions (0-4 mg/L Dye)

1. Following the table below, use a pipette to add the specific amount of working solution into a 100 mL volumetric flask.
2. Top volumetric flask to 100 mL with Milli-Q® water. Cap flask with stopper and mix by inverting or stir with stir bar until dissolved
3. Transfer this solution into an amber vial to protect it from exposure to light

<table>
<thead>
<tr>
<th>Standard Solution (200 mg/L)</th>
<th>Amount of Working Solution into 100 mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 mg/L</td>
<td>0 µL</td>
</tr>
<tr>
<td>1 mg/L</td>
<td>500 µL</td>
</tr>
<tr>
<td>2 mg/L</td>
<td>1000 µL</td>
</tr>
<tr>
<td>3 mg/L</td>
<td>1500 µL</td>
</tr>
<tr>
<td>4 mg/L</td>
<td>2000 µL</td>
</tr>
</tbody>
</table>

Operation of the spectrophotometer

1. Turn on the spectrophotometer (spec) approximately 15 minutes before analyzing samples to allow instrument to stabilize.
2. Turn on computer controller and set wavelength to 430 nm for AO24 or 607 nm for MB
3. Rinse the cuvette with Milli-Q® water, discard, and re-fill. Wipe the sides of the cuvette with a Kimwipe. Load the cuvette, and zero the reading. This will adjust the spectrophotometer to measure zero absorbance with the dye-free water blank.
4. Next, discard the Milli-Q®. Rinse the cuvette with the sample you wish to analyze, discard, and re-fill. Wipe with Kimwipe.
5. Load the cuvette, and run the sample. The absorbance will be displayed on the screen. Wait for a few seconds, and repeat the measurement. Record these values.
6. To load a new sample, discard cuvette contents, rinse with Milli-Q®, rinse with the new sample, and then re-fill. Wipe with Kimwipe, and repeat step 7. Always place the cell into the spec with the same orientation for every measurement.
UV sample analysis procedure

1. Rinse and fill the selected cell with Milli-Q® water to zero the spec.

2. Arrange samples for measurement beginning with standard solutions in order of increasing concentration, followed by the samples.

3. Remove the cell and discard the sample used to zero the spec. Rinse and fill the cell with the first filtered (cleanest) sample. Dry and clean the cell and place the cell into the spec in the same orientation that was used to zero the cell. Read and record the absorbance.
   
   Note: Place the cell into the spec with the same orientation for every measurement to minimize interference in the absorbance reading due to imperfections in the cells.

4. Repeat step 2 at least once with the same sample. The absorbance of the two measurements should be very similar (i.e., within ~ 0.003 nm). If not, discard the sample and repeat the measurement until this criterion is met. Report the average of all readings.

5. Measure remaining samples according to steps 2 and 3. A Milli-Q® water sample should be analyzed every ten samples. An absorbance significantly different than zero may indicate that the spectrophotometer has drifted or that the sample cell needs to be cleaned. If necessary, re-zero the spec.

B.4 1,4-DIOXANE ANALYSIS

Dioxane in the water sample was extracted with hexane-dichloromethane (80:20, v/v) then transferred to a C_{18} SPE cartridge (18% carbon loading, 500 mg sorbent weight, and 6mL column size, (Waters®, Waters Limitée Mississauga, ON) and eluted with acetonitrile. A fixed concentration (100 ppb) of 1,4-dioxane-d$_8$ was added to the water prior to extraction and carried through the entire sample extraction and analytical process to monitor the extraction efficiency of the method for each sample. The extracted sample was collected in 2 mL amber vials (Type 1, Class A borosilicate glass) with rubber septa polypropylene screw caps (Target DP®, National Scientific, VWR International, Mississauga, ON), and stored in the dark at 4°C until analyzed. The concentration of 1,4-dioxane was determined through correlation with standards and by relating the MS response of 1,4-dioxane’s quantification ion (m/z 96) to the response of the 1,4-dioxane-d$_8$’s quantification ion (m/z 88).
Materials

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Reagents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass syringe</td>
<td>1,4-dioxane</td>
</tr>
<tr>
<td>100 mL volumetric flask</td>
<td>1,4-dioxane-d₈</td>
</tr>
<tr>
<td>125 mL amber glass bottle</td>
<td>Hexane</td>
</tr>
<tr>
<td>Pipette</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>2 mL amber vials</td>
<td>Acetonitrile</td>
</tr>
<tr>
<td>10 mL Teflon® centrifuge tubes</td>
<td>Milli-Q water®</td>
</tr>
<tr>
<td>Vortex</td>
<td></td>
</tr>
<tr>
<td>Centrifuge</td>
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</tr>
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<td>SPE C₁₈ cartridge</td>
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</tr>
<tr>
<td>GC-MS</td>
<td></td>
</tr>
</tbody>
</table>

Method Outline

Sampling and Storage

Store samples and working solution at 4°C for up to 30 days

Standard Samples

Working Solution (1130 ppm, 1,4-dioxane-d₈)

1. Use a glass syringe to transfer 100 µL of 1,4-dioxane-d₈ stock into a 100 mL volumetric flask
2. Top volumetric flask to 100mL with Milli-Q® water. Cap flask with stopper and mix thoroughly

Isotopic Dilution Standard (1 ppm = 1000 ppb 1,4-dioxane-d₈)

1. Use a pipette to transfer 88.5 µL of working solution into a 100 mL volumetric flask
2. Top volumetric flask to 100 mL with Milli-Q® water. Cap flask with stopper and mix thoroughly
3. Transfer isotopic dilution standard to a 125 mL amber glass bottle with Teflon® lined speta and screw cap

Working Solution I (962 ppm 1,4-dioxane)

1. Use a glass syringe to transfer 100 µL of 1,4-dioxane stock into a 100 mL volumetric flask
2. Top volumetric flask to 100 mL with Milli-Q® water. Cap flask with stopper and mix thoroughly

Working Solution II (100 ppm 1,4-dioxane)

1. Pipette 10.395 mL of working solution I into a 100 mL volumetric flask
2. Top volumetric flask to 100 mL with Milli-Q® water. Cap flask with stopper and mix thoroughly

**Working Solution III (10 ppm 1,4-dioxane)**

1. Pipette 10 mL of working solution II into a 100 mL volumetric flask
2. Top volumetric flask to 100 mL with Milli-Q® water. Cap flask with stopper and mix thoroughly

**1,4-Dioxane Standard (1 ppm 1,4-dioxane)**

1. Pipette 10 mL of working solution II into a 100 mL volumetric flask
2. Top volumetric flask to 100 mL with Milli-Q® water. Cap flask with stopper and mix thoroughly

**Calibration Standard Solutions (0–4 mg/L Dye)**

1. Following the table below, use a pipette to add the specific amount of working solution into a 100 mL volumetric flask.
2. Top volumetric flask to 100 mL with Milli-Q® water. Cap flask with stopper and mix thoroughly

<table>
<thead>
<tr>
<th>Standard Solution (100 ppm 1,4-dioxane)</th>
<th>Amount of Standard Solution into 100 mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 000 ppb</td>
<td>1 mL</td>
</tr>
<tr>
<td>750 ppb</td>
<td>750 µL</td>
</tr>
<tr>
<td>500 ppb</td>
<td>500 µL</td>
</tr>
<tr>
<td>250 ppb</td>
<td>250 µL</td>
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</table>

<table>
<thead>
<tr>
<th>Standard Solution (10 ppm 1,4-dioxane)</th>
<th>Amount of Standard Solution into 100 mL</th>
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</thead>
<tbody>
<tr>
<td>100 ppb</td>
<td>1 mL</td>
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<tr>
<td>50 ppb</td>
<td>50 µL</td>
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<tr>
<td>10 ppb</td>
<td>100 µL</td>
</tr>
<tr>
<td>0 ppb</td>
<td>0 µL</td>
</tr>
</tbody>
</table>

**Blank (ACN)**

1. Dispense acetonitrile into 2 mL amber vials with rubber septa polypropylene screw caps

**Method Blank (Milli-Q® Water)**

1. Use Milli-Q® water as sample and 1,4-dioxane extraction procedure

**Standard (500 ppb 1,4-dioxane in Water)**

1. Pipette 5 mL of 10 ppm 1,4-dioxane standard into a 100 mL volumetric flask
2. Top volumetric flask to 100 mL with Milli-Q® water. Cap flask with stopper and mix thoroughly
3. Follow 1,4-dioxane extraction procedure

**Extraction Solution (Hexane-Dichloromethane 80:20, v/v)**

1. Pipette 50 mL of dichloromethane stock into a 250 mL volumetric flask
2. Top volumetric flask to 250 mL with hexane stock. Cap flask with stopper and mix thoroughly
3. Transfer extraction solution amber glass bottle with Teflon® lined speta screw cap

**Procedure**

**1,4-Dioxane Extraction**

1. Pipette 1.5 mL of water sample, 667 μL of 1000 ppb isotopic dilution standard and 7 mL of extraction solution into a 10 mL Teflon® centrifuge tube
2. Vortex for 1 minute at setting #6 on a Fisher Genie 2® vortex
3. Shake for 30 minutes at 300 rpm
4. Centrifuge for 10 minutes at 2200 rpm at room temperature
5. Condition a SPE C_{18} cartridge with 1 column volume acetonitrile and 1 column volume of extraction solution (do not let cartridges run dry during conditioning)
6. Apply organic layer from the centrifuge sample onto the SPE C_{18} cartridge
7. Process the sample through the SPE C_{18} cartridge slowly under gravity only
8. Recover 1,4-dioxane by eluting twice with 0.5 mL acetonitrile
9. Dispense combined elution solution into 2 mL amber vial with rubber septa and polypropylene screw caps

**GC-MS Analysis**

1. Allow blanks, standard and samples to equilibrate to room temperature
2. Load samples into GC-MS auto-sampler tray
3. Distribute blanks and standards every 10 samples
4. Analyze on GC-MS

**GC-MS Instrument Operating Conditions**

All analyses were conducted on a PerkinElmer® AutoSystem XL gas chromatograph coupled with a PerkinElmer® TubroMass mass spectrometer (Connecticut, USA).
### B.5 *E. coli* Culture Preparation

A lyophilized *E. coli* stock culture (ATCC® 23631) is grown from a seed culture purchased from Cedarlane Laboratories, revived and cryofrozen at -80 °C as glycerol stocks. The day before degradation experimentation, *E. coli* stocks were reanimated and grown overnight. This culture is then harvested and used to create a stock for inoculating samples with a concentration of ~10^7 CFU/mL. All pipettes, tubes and equipment used were sterilized by autoclaving at 121 °C for 20 minutes.

#### Materials

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Reagents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pipette</td>
<td>70% ethanol</td>
</tr>
<tr>
<td>Sterile Pipette Tips</td>
<td>10X Phosphate Buffer Saline Solution</td>
</tr>
<tr>
<td>2 mL sterile cryovials</td>
<td>Sodium Chloride</td>
</tr>
<tr>
<td>Sterile Filtered Glycerol</td>
<td>Potassium Chloride</td>
</tr>
<tr>
<td>Ethanol Burner</td>
<td>Calcium Chloride</td>
</tr>
<tr>
<td>Biosafety cabinet</td>
<td>Sodium Bicarbonate</td>
</tr>
<tr>
<td>Lighter</td>
<td></td>
</tr>
<tr>
<td>Aeration tube</td>
<td></td>
</tr>
</tbody>
</table>
250 mL Erlenmeyer Flask
Shaker Incubator at 37 °C
Low temperature freezer at -80 °C
UV-Vis Spectrophotometer
50 mL centrifuge tubes
Centrifuge

Method Outline

*All sample prep is performed in an operating biosafety cabinet in the presence of an ethanol burner with standard aseptic practices*

Media Preparation

**LB Broth**
1. Rehydrate LB powder in DI water using quantity indicated on package and shake until powder is dissolved
2. Pour mixture into a clear autoclave safe bottle
3. Autoclave the mixture for 20 minutes at 121 °C to sterilize

¼ Strength Ringer’s Solution
1. Add the following reagents to 1 L of DI water
   a. 6.5 g Sodium Chloride
   b. 0.42 g Potassium Chloride
   c. 0.25 g Calcium Chloride
   d. 0.2 g Sodium Bicarbonate
2. Stir the mixture until all reagents are dissolved
3. Dilute mix to ¼ strength by adding 250 mL of the to an autoclave safe bottle and topping up to a total volume of 1 L
4. Autoclave the mixture for 20 minutes at 121 °C to sterilize

Phosphate Buffer Solution
1. Add 50 mL of 10X Phosphate Buffer Saline Solution to a 500 mL volumetric flask
2. Top up flask to 500 mL with DI water
3. Pour mixture into a clear autoclave safe bottle
4. Autoclave the mixture for 20 minutes at 121 °C to sterilize

Preparing Glycerol Stocks
1. Add 5-6 mL of LB broth to a sterile aeration tube
2. Unseal lyophilized stock and add 0.5 mL of sterile LB broth directly to the stock culture vial and mix the solution well
3. Add 0.5 mL stock culture to the aeration tube containing LB broth
4. Incubate this starter culture overnight at 37 °C while shaking at 300 rpm
5. Add 0.5 mL of the starter culture to 250 mL sterile LB broth in a 1 L Erlenmeyer flask
6. Grow diluted culture incubating at 37 °C while shaking at 300 rpm until logarithmic growth phase is reached as confirmed by measuring the OD$_{600}$ that is doubling each hour
7. Add 0.75 mL of sterile filtered glycerol to sterile cryovials
8. Add 0.5 mL of logarithmic phase culture to glycerol
9. Seal vial, vortex briefly and immediately place on ice
10. Transfer vials to freezer at -80 °C to be cryogenically frozen until experimentation

**Reanimating Glycerol Stocks for Inoculation**

1. Add 250 mL of sterile LB broth to an autoclaved 1 L Erlenmeyer flask
2. Touch the tip of a sterile pipette to a frozen glycerol stock then immediately immerse the tip in the LB broth
3. Incubate the culture overnight at 37 °C while shaking at 200 rpm until it reaches a concentration of $10^9$ CFU/mL as confirmed by measuring the OD$_{600}$
4. Transfer 40 mL of the overnight culture to a sterile centrifuge tube
5. Centrifuge at 3000 rpm for 10 minutes
6. Remove and discard the media without disturbing the pellet
7. Add 20 mL of $\frac{1}{4}$ strength Ringer’s solution to the pellet resuspend by vortexing
8. Repeat steps 5-8 twice to remove any growth media
9. Add 1 mL of stock to 25 mL $\frac{1}{4}$ Ringers solution
10. Inoculate experiments immediately using this stock culture

**B.6 E. coli Enumeration**

The spread plate method involves depositing a small volume of sample onto the surface of a plate of microbiological media containing agar. After the appropriate dilutions were performed, 100 µL of sample was spread onto a pre-poured agar plate. The sample absorbs into the media and bacterial colonies form on the surface. The sample is absorbed and bacterial colonies form
on the surface. After a set incubation period the bacterial colonies were counted and by multiplied by the dilution factor, the amount of bacteria present in the sample was determined.

**Materials**

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Reagents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pipette</td>
<td>70% ethanol</td>
</tr>
<tr>
<td>Sterile Pipette Tips</td>
<td>Phosphate Buffer Saline Solution (PSB)</td>
</tr>
<tr>
<td>Turntable</td>
<td></td>
</tr>
<tr>
<td>Spreader</td>
<td></td>
</tr>
<tr>
<td>Ethanol Burner</td>
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<tr>
<td>Biosafety cabinet</td>
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</tr>
<tr>
<td>Lighter</td>
<td></td>
</tr>
<tr>
<td>Pre-poured agar plates</td>
<td></td>
</tr>
<tr>
<td>polypropylene dilution tubes</td>
<td></td>
</tr>
<tr>
<td>Incubator at 37 °C</td>
<td></td>
</tr>
<tr>
<td>Vortex Mixer</td>
<td></td>
</tr>
</tbody>
</table>

**Method Outline**

*All dilution and plating is performed in an operating biosafety cabinet in the presence of an ethanol burner with standard aseptic practices*

**Sampling and Storage**

Samples were collected directly into sterile polypropylene dilution tubes and plated immediately

**Serial Dilutions**

1. Prepare polypropylene tubes containing the appropriate volume of phosphate buffer solution for dilution (ex. 100 µL of a 10⁻¹ solution in 9.9 mL of PBS gives a 10⁻³ dilution)
2. Perform sample dilution with a sterile pipette tip, vortexing briefly between each transfer to ensure even mixing

**Bacterial Enumeration**

1. Deposit 100 µL of appropriately diluted sample onto the middle of a pre-poured agar 10 cm petri-plate
2. Spread sample using a ethanol flamed and cooled spreader while gently spinning on a turntable
3. Cover and invert the plate
4. Incubate the plates at 37°C an incubator for 24 hours
5. Count all colony forming units (CFU) on the plate
6. Compute the concentration of bacteria in CFU/100mL using the following:

\[
\text{bacteria CFU/100 mL} = \frac{\text{colonies counted} \times \text{dilution factor}}{\text{mL of sample plates}}
\]

**B.7 Calibration Curves**

![MB Calibration](image)

**Figure B-1:** Methylene blue spectrophotometer transmittance calibration curve
Figure B-2: Acid orange 24 spectrophotometer transmittance calibration curve

Figure B-3: 1,4-dioxane GC-MS response calibration curve (1)
Figure B-4: Quality control charts for 1,4-dioxane analysis (1)

Figure B-5: 1,4-dioxane GC-MS response calibration curve (2)
Figure B-6: Quality control charts for 1,4-dioxane analysis (2)

Figure B-7: 1,4-dioxane GC-MS response calibration curve (3)
**Figure B- 8**: Quality control charts for 1,4-dioxane analysis (3)

**Figure B- 9**: E. coli colony forming units and optical density at 600 nm calibration curve
C. EXPERIMENTAL DATA
## C.1 Primary Degradation Experiment Results

**Table C-1:** Results for the degradation of Methylene Blue

| Sample                  | Measured Concentrations of Methylene Blue (mg/L) | Mass of Catalyst Applied | Control  | Suspension | 5 PPI Foam | 10 PPI Foam | 20 PPI Foam | 40 PPI Foam | Thin Films |
|-------------------------|-----------------------------------------------|---------------------------|----------|------------|------------|--------------|--------------|--------------|-------------|-------------|
|                         |                                               |                           | 0 g      | 1 g        | 0.78 g     | 0.62 g       | 1.16 g       | 1.09 g       | 1.21 g      |
| Replicate 1             |                                               |                           | avg      | std        | avg        | std          | avg          | std          | avg         | std         |
| 0 min dark              | 4.27 ± 0.01                                  | 4.28 ± 0.03               | 4.03 ± 0.02 | 4.38 ± 0.08 | 4.32 ± 0.01 | 4.38 ± 0.03 | 4.31 ± 0.06 |
| 30 min dark/0 min light | 4.32 ± 0.01                                  | 4.23 ± 0.01               | 3.82 ± 0.06 | 3.97 ± 0.07 | 3.94 ± 0.01 | 4.59 ± 0.01 | 3.96 ± 0.02 |
| 5 min light             | 4.18 ± 0.01                                  | 4.03 ± 0.08               | 3.64 ± 0.00 | 3.54 ± 0.03 | 3.64 ± 0.01 | 4.25 ± 0.01 | 3.81 ± 0.08 |
| 10 min light            | 4.11 ± 0.08                                  | 3.31 ± 0.03               | 3.42 ± 0.01 | 3.48 ± 0.06 | 3.56 ± 0.01 | 4.04 ± 0.01 | 3.76 ± 0.08 |
| 20 min light            | 3.86 ± 0.03                                  | 2.46 ± 0.01               | 3.13 ± 0.00 | 3.13 ± 0.01 | 3.25 ± 0.00 | 3.69 ± 0.00 | 3.64 ± 0.03 |
| 40 min light            | 3.62 ± 0.06                                  | 1.83 ± 0.04               | 2.77 ± 0.01 | 2.62 ± 0.02 | 3.17 ± 0.07 | 3.34 ± 0.14 | 3.63 ± 0.01 |
| 80 min light            | 3.18 ± 0.03                                  | 1.43 ± 0.05               | 1.61 ± 0.12 | 2.10 ± 0.01 | 2.52 ± 0.03 | 2.31 ± 0.14 | 3.32 ± 0.08 |
| 120 min light           | 3.05 ± 0.03                                  | 1.09 ± 0.04               | 0.93 ± 0.15 | 1.54 ± 0.02 | 2.16 ± 0.02 | 1.95 ± 0.08 | 3.09 ± 0.01 |
| 160 min light           | 2.96 ± 0.01                                  | 0.18 ± 0.06               | 0.62 ± 0.05 | 1.18 ± 0.07 | 1.68 ± 0.01 | 1.47 ± 0.00 | 2.66 ± 0.04 |
| Replicate 2             |                                               |                           | avg      | std        | avg        | std          | avg          | std          | avg         | std         |
| 0 min dark              | 4.15 ± 0.04                                  | 4.25 ± 0.03               | 4.19 ± 0.13 | 4.36 ± 0.10 | 4.51 ± 0.02 | 4.67 ± 0.14 | 4.16 ± 0.01 |
| 30 min dark/0 min light | 4.13 ± 0.04                                  | 4.14 ± 0.06               | 3.99 ± 0.10 | 4.28 ± 0.09 | 4.54 ± 0.01 | 4.12 ± 0.05 | 4.34 ± 0.09 |
| 5 min light             | 4.10 ± 0.08                                  | 3.99 ± 0.02               | 3.74 ± 0.23 | 3.90 ± 0.02 | 3.51 ± 0.16 | 3.78 ± 0.09 | 4.04 ± 0.02 |
| 10 min light            | 4.01 ± 0.01                                  | 3.18 ± 0.09               | 3.32 ± 0.08 | 3.69 ± 0.16 | 2.92 ± 0.10 | 3.74 ± 0.03 | 3.88 ± 0.04 |
| 20 min light            | 3.81 ± 0.12                                  | 2.52 ± 0.06               | 3.39 ± 0.08 | 2.90 ± 0.02 | 2.34 ± 0.01 | 3.57 ± 0.01 | 3.57 ± 0.02 |
| 40 min light            | 3.30 ± 0.21                                  | 1.88 ± 0.05               | 3.19 ± 0.21 | 2.81 ± 0.06 | 2.35 ± 0.07 | 3.47 ± 0.02 | 3.06 ± 0.11 |
| 80 min light            | 3.10 ± 0.25                                  | 1.50 ± 0.04               | 2.53 ± 0.01 | 2.62 ± 0.03 | 2.24 ± 0.02 | 3.36 ± 0.01 | 2.24 ± 0.03 |
| 120 min light           | 2.41 ± 0.59                                  | 1.18 ± 0.15               | 2.16 ± 0.05 | 2.01 ± 0.06 | 2.22 ± 0.08 | 2.93 ± 0.09 | 2.05 ± 0.09 |
| 160 min light           | 1.95 ± 0.01                                  | 0.22 ± 0.03               | 1.66 ± 0.06 | 0.96 ± 0.91 | 2.05 ± 0.11 | 2.67 ± 0.00 | 1.69 ± 0.10 |
Table C-2: Results for the degradation of Acid Orange 24

<table>
<thead>
<tr>
<th>Sample</th>
<th>Measured Concentrations of Acid Orange 24 (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Control</td>
</tr>
<tr>
<td>Mass of Catalyst Applied</td>
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<tr>
<td>Replicate Number 1</td>
<td>avg</td>
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<td>120 min light</td>
<td>6.73</td>
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<td>160 min light</td>
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<td>Mass of Catalyst Applied</td>
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### Table C-3: Results for the degradation of 1,4-Dioxane

<table>
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<tr>
<th>Sample</th>
<th>1,4-Dioxane (ppb)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Control</td>
<td>Suspension</td>
<td>5 PPI Foam</td>
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<td>40 PPI Foam</td>
<td>Thin Films</td>
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<tr>
<td>0 min dark</td>
<td>930.8</td>
<td>989.5</td>
<td>911.3</td>
<td>991.6</td>
<td>924.0</td>
<td>971.3</td>
<td>931.7</td>
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<tr>
<td>30 min dark/0 min light</td>
<td>871.1</td>
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<tr>
<td>5 min light</td>
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<td>568.8</td>
<td>516.8</td>
<td>769.6</td>
<td></td>
<td></td>
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<tr>
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<td>456.7</td>
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<td>453.6</td>
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<td>510.5</td>
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<td>544.8</td>
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<td>601.1</td>
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<td>770.0</td>
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Table C-4: Results for the degradation of *E. coli*

<table>
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<th>Sample</th>
<th>0 g</th>
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<th>0.56 g</th>
<th>0.54 g</th>
<th>1.32 g</th>
<th>1.49 g</th>
<th>1.26 g</th>
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<td>0.14</td>
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<td>0.00</td>
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<td>0.07</td>
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<td>0.00</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
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<td>6.45</td>
<td>0.04</td>
<td>6.38</td>
<td>0.14</td>
<td>6.13</td>
<td>0.18</td>
<td>6.36</td>
</tr>
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<td>0.03</td>
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<td>0.74</td>
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<td>0.00</td>
<td>0.00</td>
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### C.2 SUPPLEMENTARY DEGRADATION EXPERIMENT RESULTS

Table C-5: Results for the degradation of methylene blue without the presence of a TiO$_2$ coating

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<tr>
<th>Sample</th>
<th>Investigating Amount of Light Obscured by Aluminum Foam</th>
<th>Methylene Blue (mg/L)</th>
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<td>Control</td>
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<tr>
<td>Replicate Number 1</td>
<td>avg</td>
<td>std</td>
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<tr>
<td>0 min light</td>
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<td>0.12</td>
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<td>0.01</td>
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<td>0.05</td>
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<td>20 min light</td>
<td>3.70</td>
<td>0.02</td>
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<tr>
<td>40 min light</td>
<td>3.48</td>
<td>0.14</td>
</tr>
<tr>
<td>80 min light</td>
<td>3.13</td>
<td>0.07</td>
</tr>
<tr>
<td>120 min light</td>
<td>2.60</td>
<td>0.22</td>
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<td>160 min light</td>
<td>2.35</td>
<td>0.03</td>
</tr>
<tr>
<td>Replicate Number 2</td>
<td>avg</td>
<td>std</td>
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Table C-6: Results for the degradation of acid orange 24 in a dark reaction with the presence of a TiO$_2$ coating

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<th>Sample</th>
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<th>Acid Orange 24 (mg/L)</th>
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<tr>
<td>Replicate Number 1</td>
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### C.3 Mass of Applied Photocatalysts

**Table C-7:** Mass of Catalyst Applied to Foams

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<tr>
<td>MB-2</td>
<td>1 g</td>
</tr>
<tr>
<td>AO24-1</td>
<td>1 g</td>
</tr>
<tr>
<td>AO24-2</td>
<td>1 g</td>
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<tr>
<td>Average</td>
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