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Sustainable methods for the removal of bacteria and NOM from drinking water

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Submitted for the degree of Doctor of Philosophy

The University of Edinburgh



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and Environment

Declaration

This is a declaration that this thesis, containing only the work of myself, was completed solely by Dan Gowland, under the supervision of Dr Efthalia Chatzisyneon. Full reference is given when other sources are used. This work has not been submitted for any other degree or professional qualification.

Dan Gowland

31/01/2024

Abstract

Climate change alters natural organic matter (NOM) and pathogen concentrations in surface waters, causing increasing strain on water treatment infrastructure. More effective NOM and pathogen removal from drinking water supplies is required to develop a robust and versatile water treatment process for the future. Photocatalysis has been regularly reported to have high efficacy for the removal of NOM, as well as pathogens, from water at laboratory scale. This Thesis aims to assess the practical limitations of photocatalytic water treatment with the goal of making it suitable for implementation at industrial scale.

Primarily this work uses recent advancements in UV-LED technologies and catalyst design and setup to explore how they have made photocatalytic disinfection and NOM treatment more viable for use in industrial water treatment, to alleviate the growing pressures presented on current infrastructure. Shorter wavelength LEDs, such as UVA-LEDs, with significantly higher energy efficiencies and highly tuned wavelength emissions compared to traditional alternatives, have only recently become commercially available, and are therefore sparsely investigated. In addition, this Thesis utilises seldom-used real surface water samples to bridge the gap between lab research and industry application, and modified catalysts, previously untested in their ability to remove NOM from water.

Results from this Thesis show how LED-driven photocatalysis, although not currently viable for use in industry, could prove invaluable as a sustainable water treatment technology as LED technologies continue to develop, provided that the recommendations for operating conditions outlined in this Thesis are considered. Investigations found that inclusion as a tertiary polishing step, given its capacity to remove NOM and pathogens before disinfection, could be effective at reducing threats to public health and drinking water infrastructure.

Lay Summary

Natural organic matter (NOM), a complex mixture of naturally occurring chemicals found in most surface waters, has recently emerged as a threat to current drinking water treatment equipment. NOM has been shown to reduce the efficacy of drinking water treatment methods, increase the required maintenance of drinking water infrastructure, and undergo reactions with chemicals commonly used in the disinfection process to produce carcinogenic and health-damaging compounds. The growing concentrations of NOM in drinking water supplies, as well as rapid changes in its characteristics and treatability, caused by a changing climate, mean new methods must be developed in order to create a diverse range of drinking water treatment techniques that are robust enough to maintain public health.

Photocatalysis harnesses the energy of light to create an assortment of powerful molecules that can be used to break down NOM and harmful microbes found in drinking water supplies. This work investigates the use of photocatalysis to further understand how advancements in LED technologies can be implemented in industry to ensure adaptive and versatile future water treatment infrastructure. This was done by; testing the conditions that affect how efficient photocatalysis can be at removing NOM; testing the conditions that affect how efficient photocatalysis can be at removing harmful microbes; and using computer software to test how the conditions used in photocatalysis affect its sustainability.

Acknowledgements

This thesis would not have been possible without the encouragement and support of several people. First, I would like to give a massive thank you to my supervisor Dr Efthalia Chatzisyneon. My PhD started with a pandemic and national lockdown and the experience would not have been as manageable without such a kind and understanding individual guiding me through the past 4 years. Thank you to my secondary supervisor, Professor Neil Robertson, your depth of knowledge is truly inspiring and I'm so incredibly grateful for the encouragement and support from you both.

I would also like to thank past and present PhD students from the Chatzisyneon and Robertson groups for their support throughout my research journey. It has been an absolute pleasure working with you all, I will remember the memories of the laughs we shared and the help we gave one another. A thank you as well to the members of the Institute for Infrastructure and Environment for creating such a positive work setting over the years.

Thank you to Scottish Water for the financial support of this project. A special thanks to Graeme Moore for the input over the years and the support during the collection of results for this thesis.

I have made several friends for life during my time in Edinburgh who have made a world of difference to my experience living here. A big thank you to Mr Anatoly, Deborah and David, Edinburgh never seemed more like home when I was spending time with you. I would also like to thank my love, Emily, for your support over the duration of writing this thesis. Thank you for being there for me through the highs and lows and helping me believe I could do this. I could not have done it without you and I'm so incredibly privileged to have met you all by circumstance.

Thank you to all who helped and encouraged me during my time in Edinburgh, your help didn't go unnoticed. Thank you to my family, mum, dad, Will, Ellie and Kitty, for the advice, support, and kindness, it made this PhD so much easier to complete. Thank you to my grandparents for their roles in my upbringing and how that led to me being who I am today, I think of you every day.

COVID-19 Statement

The data contained in this Thesis was collected from 01/02/2020 till 31/01/2024. During that time the COVID-19 pandemic significantly affected my research and ability to collect data and therefore influenced the scope, direction, and presentation of the work contained in this thesis. The initial research plan included extensive material synthesis, practical experimentation, and data collection, all of which were scheduled to take place in 2020. However, due to the imposed lockdown measures, my research was severely disrupted. Specifically, from March 2020 to September 2020, there was strictly no access to laboratory facilities, resulting in a complete halt to all experimental work. Following this period, lab access was gradually restored but remained limited, with restricted hours and reduced capacity, for an additional six months (October 2020 to March 2021). This constrained access further delayed the planned experimental work and data collection. In response to these unprecedented challenges, the focus of my research temporarily shifted. During the period of restricted laboratory access, I pivoted to writing a literature review, which was originally intended to complement the experimental findings and was published in early 2021. While this shift in focus allowed for the progression of my research during the pandemic, the interruption to practical work and the consequent delay in data collection had a direct impact on the timing and scope of the experimental component of this thesis.

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List of Abbreviations

AOP	Advanced Oxidation Process
BL	Blacklight
ClO ₂	Chlorine Dioxide
CPI	Controlled period of illumination
DBP	Disinfection by-product
DBPFP	Disinfection by-product formation potential
DI	Deionised water
DOC	Dissolved organic carbon
DWTP	Drinking water treatment plant
HA	Humic Acids
HAA	Haloacetic acid
HPLC	High-Performance Liquid Chromatography
IHSS	International Humic Substances Society
IPCC	Intergovernmental Panel on Climate Change
LCA	Lifecycle impact assessment
LED	Light-Emitting Diode
NOM	Natural organic matter
ROS	Reactive Oxygen Species
SUVA	Specific UV absorbance
THM	Trihalomethanes
TOC	Total Organic Carbon
UP	Ultrapure
UV	Ultraviolet
WWTP	Wastewater Treatment Plant

1 Introduction

Significant changes to the concentrations and characteristics of natural organic matter (NOM) are presenting a strain on current drinking water treatment infrastructure.¹⁻⁵ These changes can be attributed to a variety of causes with changes to climate and environment being the main underlying factor. Some of the identified contributing components include higher levels of NOM solubility due to a natural bounce back from human-caused rain acidification,⁶ increased precipitation frequency causing higher levels of NOM to be flushed into the water system,⁵ and higher temperatures increasing NOM creation and solubility in the environment.⁷ These higher NOM concentrations can cause aesthetic problems, such as colour and taste in drinking water and higher maintenance and treatment costs. Most importantly, recent studies show that certain classes of NOM can react with chemical disinfectants used in the water treatment process, leading to the formation of carcinogenic disinfection by-products (DBPs) and trihalomethanes (THMs).

Similarly, irregular weather conditions caused by climate change have been observed to cause increases in concentrations of water-borne pathogens in surface waters due in part to increased risk of sewage contamination and more ideal conditions for growth.⁸⁻¹⁰ These observed trends in water treatment supply sources show that an improved effort to remove naturally occurring organics and pathogens from drinking water supplies is required to continue the development of highly efficient and versatile water treatment technologies.

Photocatalysis has received increasing interest for water purification due to investigations showing it has some of the highest removal rates of NOM¹¹⁻¹³ and pathogens^{14, 15} from drinking water supplies compared to other individual technologies. This, coupled with no

constant requirements for chemical additives and the management of their waste products, a carbon-intensive and costly activity, makes UV-LED photocatalysis a large area of interest for innovations in drinking water treatment technology. Consequently, this work focuses on the removal of NOM and microorganisms from drinking water sources to determine optimised conditions for sustainable methods and treatments that alleviate the growing pressures presented on current infrastructure.

This Thesis aims to gain a further understanding of the optimal conditions required for the sustainable removal of NOM and pathogens present in raw water during the drinking water treatment process. This is in order to more accurately evaluate where sustainable changes could be made to current and future water treatment works, to combat the challenges presented by NOM and pathogens (discussed in Chapter 2). Various approaches were adopted to increase the overall efficiency, efficacy, and sustainability of the process by tuning the photocatalytic procedure to its optimised conditions while minimising environmental impact. To achieve this the following objectives were set:

- Assess the effect of key operating parameters of a UVA-LED photocatalytic system with an immobilised catalyst for removing NOM from water. (Chapter 4).
- Assess the efficiency of UVA LED-based photocatalytic treatment system for water disinfection and bridge some of the gaps between lab-based research and real-world application. (Chapter 5).
- Evaluate comprehensively the specific environmental impacts associated with suspended and immobilised catalyst types when applied at a pilot scale. Find out which areas various photocatalytic water treatment methods contribute most to environmental issues and assess whether they can be mitigated. (Chapter 6).

With UVA-LEDs being a relatively new and emerging technology, very little has been investigated to show how it can be integrated into photocatalytic water treatment technologies, especially when using real water. Chapters 4 and 5 investigate these novelties as well as comparing the systems to newly available commercial photocatalytic systems. Additionally, the sustainability of LED-driven water treatment is investigated in Chapter 6 with a novel, quantified and systematic lifecycle analysis (LCA) of the full environmental impacts that different configurations of photocatalytic systems would present.

2 Literature Review

2.1 Natural organic matter

Natural organic matter (NOM) constitutes a complex mixture of organic compounds, primarily composed of humic and fulvic substances including anionic macromolecules with diverse molecular weights, featuring aromatic and aliphatic components.¹³ NOM plays a pivotal role in aquatic settings and is ubiquitous in all freshwaters, with a notable presence in surface waters. Due to the intricate interplay between the hydrologic cycle, biosphere, and geosphere, drinking water sources generally contain NOM.¹⁶

2.1.1 Characteristics of NOM

NOM is a complex mixture of, typically, negatively charged compounds possessing a diverse combination of various functional groups, including esteric, phenolic, quinine, carboxylic, hydroxyl, amino, and nitroso groups.¹⁷ Humic substances make up the biggest component of NOM in surface waters and consist of substituted aromatic rings linked by aliphatic chains and contain both hydrophobic and hydrophilic components.¹⁸ The largest proportion of most NOM fractions is generally made up of hydrophobic acids, making up around 50% of the total organic carbon (TOC) in water.¹⁷ These broad groups are usually defined by physical and chemical fractionation of NOM samples at specific pH and separated into operationally defined categories although, depending on the nature of the research being conducted, compounds have also been assigned to a particular fraction according to their chain length and functional groups. Humic acids are generally made up of larger (10,000 to 100,000 Da) molecules that preferentially dissolve in higher pHs, this mostly depends on the origins of the

natural materials they derive from.¹⁹ Fulvic acids (fulvates, molecules bound to minerals, and free-form fulvic acids) on the other hand are usually smaller than humic acids (1000 to 10,000 Da) and are soluble at most pH levels.²⁰

The nature of NOM formation, as well as surface waters often having multiple sources of NOM, leads to a wide variety of organic fractions that differ from any given water source by amount, character, and properties, mostly due to the biogeochemical cycles of their surrounding environments.²¹ These differences can be attributed to the source of organic matter, the water chemistry, temperature, pH, and biological processes occurring in and around the water.²² These factors, as well as differences in weather patterns such as rainfall and snowmelt runoff, can lead to significant variations in NOM character depending on a water's source, location and season.^{4, 23} This presents its own unique challenges to water treatment plants, especially as climate change-driven floods and droughts are expected to increase in frequency and severity.

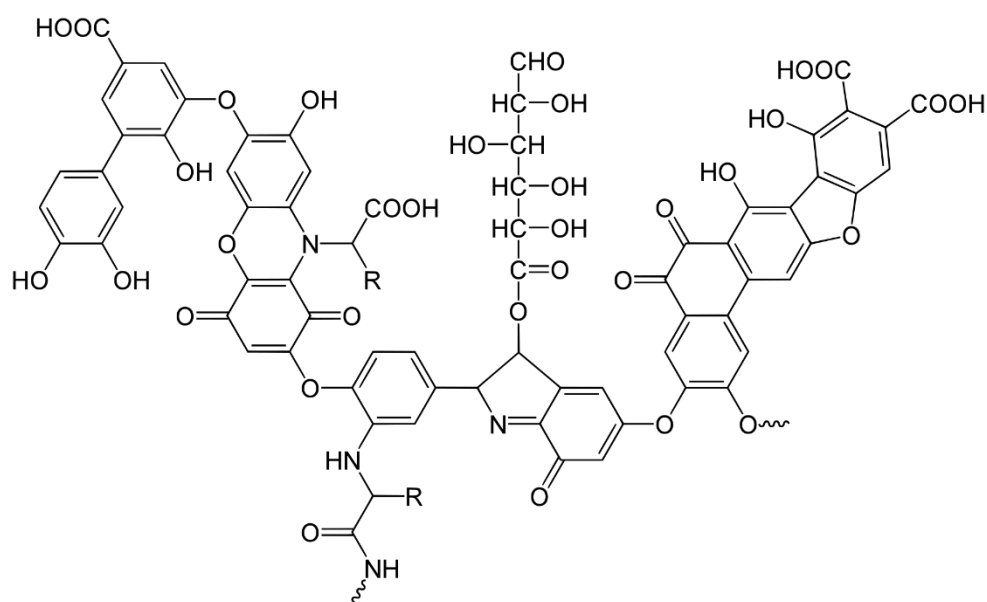


Figure 2.1 - Example of theoretical Humic substance skeleton²⁴

2.1.2 Importance of NOM

The presence of NOM in water sources significantly contributes to the decisions made in the planning and day-to-day of water treatment works as it hugely influences many problems in drinking water treatment such as disinfectant by-product (DBP) formation and undesirable colour, taste, and odour.²⁵ Some of the problems caused by and contributed to by NOM during water treatment include the fouling of membranes and corrosion in water treatment plants and their distribution systems.²⁵ NOM has also been shown to impact the biological stability of water by acting as a source of nutrition for bacteria and can even function as a substrate for bacterial growth. The resulting biofilm growth has then been observed to lead to further membrane fouling and premature saturation of filtration equipment.²⁶

Furthermore, the presence of NOM in surface waters has been observed to interfere with water treatment processes targeting toxic compounds or heavy metals.^{27,28} NOM possesses

a considerable ability to inhibit targeted wastewater treatments for residual pharmaceuticals, significantly decreasing the efficiency of such processes.²⁹

DBPs have become an increasingly studied area of interest in recent years with several hundred compounds of DBPs being identified. Two major groups of DBPs that have been found are trihalomethanes (THMs) and haloacetic acids (HAAs).³⁰ These are thought to be produced when drinking water is disinfected with chemical agents such as chlorine, ozone, chlorine dioxide, and chloramine with each creating varying concentrations and varieties of DBP.³¹ Amongst these DBPs, chlorinated and brominated DBPs have been studied considerably for their effects on human health. Some of these adverse health effects linked with the consumption of tap water with high THM concentrations include bladder cancer,³² children born small for gestational age,³³ and miscarriages.^{34, 35}

NOM levels found in most natural waters range from 0.1 to 20 mg/L, however, an increase in its concentration in environmental water matrices has been observed recently, presenting a strain on current water treatment infrastructure and local ecosystems.^{1, 19, 36} This increase in NOM concentration has been attributed to several changes in climate conditions, one of which is the intensity of precipitation affecting NOM discharged from forested areas. This leads to increased runoff intensities and therefore, increased discharge from soils rich in organic matter.³⁷ Other factors include diminished retention time in lake waters, due to climate change-induced precipitation, which may cause decreased degradation of NOM through microbial and photochemical processes and reduce in-lake NOM coagulation and sedimentation.^{38, 39}

In addition to an observed increase in global NOM levels, apparent changes in the colour and UV absorption of NOM relative to total organic carbon (TOC) content also imply a change in

NOM characteristics and therefore treatability.⁴⁰ These changes in NOM quantity and character mean water treatment processes must adapt their operations in order to avoid any drops in drinking water quality. These dramatic changes in NOM concentrations create challenges for water treatment works when considering process optimisation and control.

2.1.3 Measuring NOM

The problems presented by the wide disparities in NOM concentration and character apparent in natural raw waters necessitate the capability of standardising NOM concentrations and profiles during treatment at lab scale. This is typically done in literature by employing synthetic NOM solutions to improve the reproducibility of results. Common procedures involve dissolving humic and/or fulvic acids in ultrapure water and using them to mimic NOM. The reduction of DBP from drinking water is the subject of many NOM-related projects, therefore simple, refined humic and fulvic acid samples that are commercially available are typically used by researchers, at least in preliminary testing. More complex NOM samples extracted from water (e.g. International Humic Substances Society (IHSS) samples from the Suwannee River and Mississippi River) have also been known to be used to simulate surface waters as they can give results that more accurately reflect the conditions of certain waters in a controlled manner, although they are more expensive than simpler synthetic NOM varieties.⁴¹

Different methods are applied to quantify NOM in water: UV absorbance, total organic carbon analysis (TOC), chemical oxygen demand (COD), fluorescence spectroscopy, high-performance liquid chromatography (HPLC) and mass spectrometric methods. UV-Vis spectroscopy, in the range of 254–280 nm, is commonly used to measure the presence of

unsaturated double bonds and π - π electron interactions typically found in aromatic compounds such as humic acid whereas absorbance at 220nm is associated with both the carboxylic and aromatic chromophores.⁴² Measuring the absorbance at 254nm is fast, simple, and does not require complicated equipment or chemical reagents making it a popular analytical method in NOM-related research.

Colour can also be determined using spectroscopy between 450 and 465 nm wavelengths. The two types of colour measurement, true colour, and apparent colour are used in industry to estimate organics concentration whilst including or omitting suspended solids. True colour is the colour after turbidity has been removed (filtered through a 0.45 μ m pore size) so that all the absorbance measured is due to dissolved material. Apparent colour is measuring the colour of a water sample as is, including both true colour and turbidity. Despite the many advantages to UV₂₅₄ spectroscopy it is still often required to be used in conjunction with other analytical methods such as total organic carbon analysis (TOC) or dissolved organic carbon analysis (DOC) due to its inability to detect the non-aromatic, typically less complex, by-products of NOM degradation. This can be seen in experiments where UV₂₅₄ spectroscopy of solutions containing only synthetic NOM shows near or total removal of NOM from water, but further analysis with gas chromatography-mass spectrometry (GC-MS) reveals significant organic compounds remaining in solution.⁴³⁻⁴⁵ UV₂₅₄ analysis is also non-specific to humic and fulvic substances meaning measurements may be higher than expected due to other non-NOM organic compounds that may be present in the test solution.

TOC analysis, considered the main indicator of NOM in drinking water, determines the organic carbon present in solution by using infrared (IR) spectroscopy to measure the carbon dioxide

produced by heat-catalysed chemical oxidation with a persulfate solution.⁴⁶ Although, compared to UV₂₅₄ spectroscopy, TOC analysis requires a slightly longer runtime and a more complex preparation, it is still a relatively quick and simple method for quantifying NOM in water with many different available conditions to allow for the tailoring of specific test environments. The chemicals generally required in TOC also have low toxicity and are cheaply available compared to other methods available. A drawback to TOC analysis is that the equipment needed is more specialised than most other methods and fairly expensive to buy. Although TOC analysis also does not account for additional non-NOM carbon in solution, it does show the level of mineralisation of contaminants in water quicker than other methods.

Specific UV absorbance (SUVA) is the UV₂₅₄ absorbance of a given sample divided by its TOC concentration. This ratio can be used to describe the hydrophobic character of NOM in water.⁴⁷ A high SUVA indicates the sample has mainly hydrophobic and aromatic character, whereas lower SUVA values suggest that mainly hydrophilic compounds are present.⁴⁸ SUVA is often measured in industry because it is understood that NOM that is easily removable by coagulation typically has a high SUVA value.

Pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) combines the increased compound volatility from pyrolysis with the effective separation of volatile fragment compounds using gas chromatography and the accurate detection of mass spectrometry. This allows for improved confidence in sample identification, a significantly increased range of volatile samples eligible for analysis and improved sensitivity for compounds that are otherwise hard to analyse. This technique gives benefits over the downfalls of the more common techniques used for NOM quantification, such as TOC analysis and SUVA, in which all carbon-containing molecules are measured indiscriminately as specific fractions of NOM.

Although Py-GC-MS can give a highly reliable semi-quantitative analysis of NOM functional groups in wastewater, the high costs of reagents and equipment, longer testing times and the complexity involved in interpreting the results generated by GC-MS are significant drawbacks.^{49, 50}

2.1.4 NOM Removal Techniques

The most common and industrially practical process available for NOM removal is coagulation and flocculation. Coagulation involves the addition of chemical coagulants, such as iron or aluminium salts e.g. aluminium sulphate, ferric sulphate, ferric chloride etc, to the raw water, in order to destabilise and aggregate molecules in water, making them easier to remove. These chemicals are highly charged which neutralises the effective charges of NOM in the water, causing NOM particles to clump together, or coagulate.⁵¹ These aggregated particles become visible as 'flocs' and can be easily removed by filtration from the water through water treatment processes, normally with the use of membranes.

Coagulation is very commonly used in large-scale water treatment to remove turbidity and colour problems. However, optimised conditions for turbidity or colour removal are not necessarily the same conditions as those optimised for NOM removal.⁵² Enhanced coagulation is a process that has optimised the coagulant dose and pH conditions specifically for organic matter and turbidity reduction rather than turbidity removal alone. Enhanced coagulation, by its nature, uses higher quantities of coagulant than those used for baseline coagulation, as well as strict control of pH, order of chemical addition and mixing speeds. This results in a greater removal of TOC rather than just suspended solids.⁵³

The efficacy of NOM removal during coagulation can be influenced by multiple factors including the type of coagulant, coagulant dosage, temperature, NOM character and the presence and concentrations of various ions in solutions such as bicarbonate, chloride and sulphate.⁵⁴ A commonly used coagulant in industrial drinking water production is aluminium sulphate (alum) despite some investigations suggesting that ferric-based coagulants may remove NOM, more effectively than aluminium-based ones. This choice by water treatment facilities is likely due to the corrosive properties of ferric chloride and its volatile pricing.⁵⁵ Coagulation removes a majority of NOM present in water but has been shown to be less effective against the hydrophilic, lower molecular weight fractions of NOM. This is likely because the hydrophobic fraction has a higher specific colloidal charge making it more susceptible to the neutralisation process in coagulation.⁵⁶

Membranes are semi-permeable films that are commonly used to separate particles from water either directly or with the aid of coagulation. This is commonly achieved with the implementation of a pressure differential across the membrane as a driving force, often divided into a dead-end or cross-flow configuration. Dead-end filtration is when the direction of the fluid flow is normal to the membrane surface and raw water permeates through the membrane, any particles larger than the membrane pore size are retained. Whereas in cross-flow configuration, the feed flow is tangential to the surface of the membrane and retentate is removed from the same side further downstream, as shown in Figure 2.2.

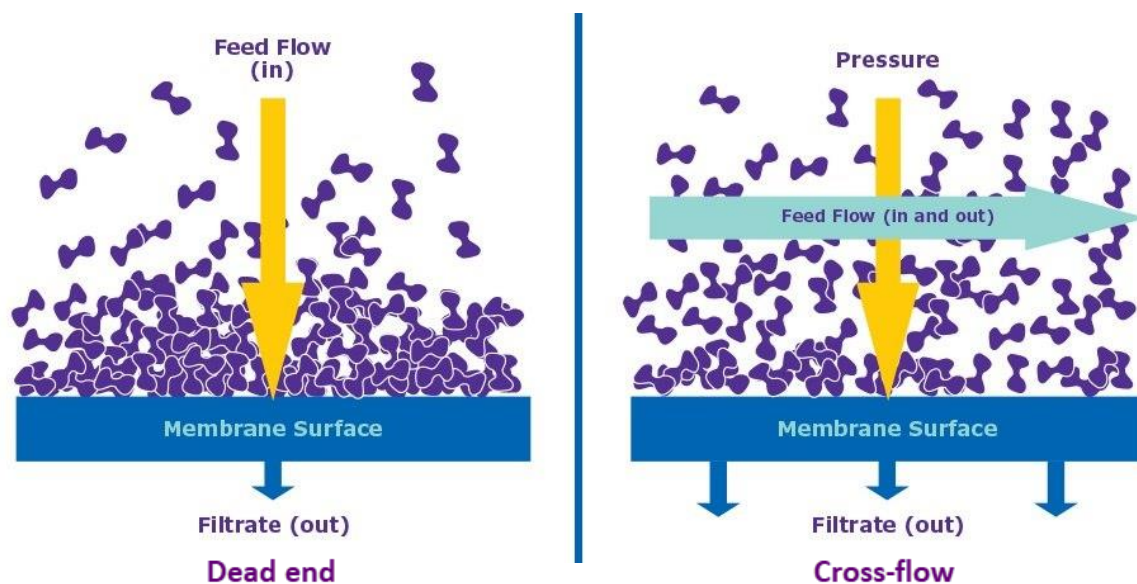


Figure 2.2 – Diagram showing the flow direction and pressure in a dead-end and cross-flow filtration⁵⁷

The membranes reject uncharged macromolecules mainly by size exclusion meaning the rejection is determined by the membrane pore size and distribution compared to the size and shape of the NOM molecules. NOM sizes generally range from 300 Da to over 100 kDa.⁵⁸ This distribution varies between different water sources, but it has been observed that the majority of compounds in NOM are smaller than 1 kDa.⁵⁹ These smaller NOM fractions are made up of degradation products of humic substances.

However, other factors also determine solute rejection such as solute–solute and solute–membrane interactions or the hydrodynamic conditions applied. Repulsive electrostatic forces between the membrane and the solutes have been shown to contribute to higher-than-expected membrane rejection suggesting that both the properties of the membrane and NOM are important factors in NOM membrane filtration.⁶⁰

Furthermore, pore size selection should be based on several factors depending on the given specifications of the water treatment system in use. Microfiltration membranes (pore size = 0.1–5 μm or >100kDa) employ pore sizes that are significantly larger than the size of most NOM fractions and are subsequently only able to remove <10% of NOM from typical raw waters and are more suited to removal of turbidity with over 97% achievable.⁶¹ Ultrafiltration membranes (pore size = 10–100 nm or 1–100 kDa) are sometimes used in more specific industrial cases and are capable of removing larger humic substances and biopolymers.⁶² While NOM removal tends to increase as membrane pore size decreases, smaller pore-sized membranes require much higher operational transmembrane pressures and therefore tend to require higher maintenance costs when compared to larger pore sizes.⁶²

Research into advanced oxidation processes (AOPs) has been steadily increasing over the past few decades due to its potential for removing NOM. The motivation for this interest is largely due to AOPs' ability to degrade or completely mineralise a broad range of organic species under near-ambient conditions with minimal waste products or complex chemical inputs.⁶³ ⁶⁴ AOPs are typically made up of various combinations of oxidants, radiation, and catalysts, including: $\text{O}_3/\text{H}_2\text{O}_2$,⁶⁵ $\text{UV}/\text{H}_2\text{O}_2$,⁶⁶ UV/O_3 ,⁶⁷ UV/TiO_2 ,⁴⁴ $\text{Fe}^{2+}/\text{H}_2\text{O}_2$,⁶⁸ and $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ combined with light.⁶⁹ The central feature of these processes is the generation of highly reactive radical species, particularly hydroxyl radicals ($\bullet\text{OH}$), which work as a powerful oxidant.⁷⁰ Due to the nature of NOM and its broadly varying chemistry, the specific mechanisms for NOM removal through AOPs are case specific but generally work through the generated radicals interacting with the carbon structures, progressing into a chain reaction that can end in total mineralisation of the target and the production of CO_2 .⁷¹ However, it is often observed in AOP research where the concentration of NOM in solution decreases and yet the total organic carbon present is reduced by a lower amount.⁷²⁻⁷⁴ Studies investigating this typically suggest

that the NOM macro-molecules, which consist mostly of large, aromatic molecules are rapidly broken down into smaller by-products that are less susceptible to radicals and therefore are not mineralized completely.^{72, 75} Fractionation studies on AOPs have revealed preferential degradation of hydrophobic compounds with a corresponding increase in the hydrophilic charged NOM fractions.^{76, 77} However, there is still debate surrounding whether these resistive intermediates are more likely to form the harmful THMs, produced by chlorination, as compared to NOM that has not been treated with AOP.^{44, 66, 78-80}

Although a significant amount of research has been done on AOPs for NOM removal, no AOP technology is currently employed at industrial scale water treatment specifically for the removal of NOM. This is possibly due to the high associated costs linked to the electricity usage,⁸¹ lack of proven industry experience when compared to the long used current removal methods, significant pre-treatment requirements due to the highly detrimental effects caused by turbidity and contaminants, as well as the longer operational times and large spaces required for adequate treatment.⁶⁴

2.2 Microorganisms in water treatment

Although the presence of NOM, and its associated DPBs, in water can be cause for many chronic health effects, microorganisms in water present a more acute risk to health. Waterborne illnesses account for a significant amount of recent disease outbreaks around the world which can be attributed to microorganisms, such as bacteria and viruses, found in contaminated drinking water.⁸² Examples of such illnesses include cholera (caused by *Vibrio cholera*), dysentery (caused by *Escherichia coli*), hepatitis A (caused by *Hepatovirus A*) and typhoid (caused by *Salmonella typhi*). Additionally, microorganisms have been known to

cause problems with drinking water infrastructure such as biofilm formation leading to corrosion and the blocking of intake valves.²⁶ For these reasons, disinfection of drinking water from source to tap is a massively important step in water treatment plants.

Not all microbes present a clinical threat to humans, meaning drinking water disinfection methods are typically measured in their ability to remove common pathogens found in water. Different disinfection methods are more effective on specific microbes when compared to others based on their mechanism of operation and the different structures and various adaptations of certain pathogens to survive. When considering pathogenic microbes, such as Bacteria (prokaryote), Viruses (non-living), Unicellular fungi (eukaryote), and Unicellular protists (eukaryote), certain differences must be considered to make water safe for drinking.

2.2.1 Bacteria

Bacteria are one of the most studied groups of microbes in drinking water disinfection studies, in part due to the straightforward nature of culturing and studying them compared to other pathogenic groups. Bacteria are often targeted for disinfection studies due to the observed adaptability and their ability to replicate rapidly in favourable circumstances, meaning seemingly safe water can quickly become harmful to consume if left in the right conditions. Bacteria can be described as being in one of two sub-groups: Gram-negative or Gram-positive. This distinction is made based on the structure of their cell walls, and their reaction to Gram staining.⁸³ Gram-positive bacteria have cell walls made of a thick layer of peptidoglycan, a large polymer made up of sugars and amino acids. Whereas gram-negative bacteria have cell walls that contain only a thin layer of peptidoglycan, as well as an outer membrane that is absent in gram-positive bacteria.⁸³ This difference presents itself when Gram staining, a

technique that uses violet dye that is retained by the thick peptidoglycan layer in the cell walls of gram-positive bacteria.⁸⁴ This staining causes gram-positive bacteria to show up as violet but leaks out of the thin peptidoglycan layer in gram-negative bacteria producing a pink hue. These variations in cell wall structure result in different susceptibilities to disinfection techniques with some Gram-negative bacteria being more resistant to certain antibiotics, such as penicillin, detergents that could normally break down peptidoglycan, and antimicrobial enzymes.⁸⁵⁻⁸⁷ At the same time, some Gram-positive bacteria have been observed to be more resistant to chlorination and UV than Gram-negative bacteria.⁸⁸

Escherichia coli (*E. coli*), a common bacterial species found in many polluted water systems, is used as a marker of faecal contamination due to its presence in the intestines of humans and other animals. Hence more research has been focused on disinfecting *E. coli* using a photocatalytic process. Some bacterium, *E. coli* included, are known to repair UV-damaged DNA by mechanisms such as photoreactivation and excision repair/dark repair,^{89,90} which weakens the disinfection robustness for long-term operation. Photoreactivation is the process by which microorganisms use light (330–480 nm) to activate the photolyase enzyme to split cis–syn cyclobutane pyrimidine dimers (CPD), lesions in the genomic DNA, to recover the damaged DNA.⁹¹ Meanwhile, dark repair is a process which requires the coordination of over a dozen proteins to excise and repair the damaged DNA segment. In TiO₂ photocatalytic disinfection, damage to DNA and proteins in the target microorganisms means the repair mechanism is insufficient to protect the cells.

2.2.2 Viruses

Viruses are less studied in photocatalytic disinfection research but present a significant risk to water treatment plants as they are inherently harder to detect and propagate than

bacteria, meaning much more specialised equipment is required to monitor viral levels in water and study disinfection efficacy. The inability of viruses to reproduce without a host means more complicated methods of genome propagation are required, such as tissue cultures, to reach the minimum detection levels. This increases the cost, complexity, expertise, and time required to work with viruses rather than bacteria.

One way of classifying viruses is the separation of enveloped from non-enveloped viruses. This can be decided by the presence (enveloped viruses) or absence (non-enveloped viruses) of a lipid bilayer membrane on the outer part of the virus.⁹² That is to say when a virus is made up only of the viral genome (can be RNA or DNA) and the virus-coded protein capsid that surrounds the genome, it is a non-enveloped virus. If the virus contains an extra lipid bilayer membrane surrounding the protein capsid, it's called an enveloped virus.⁹² Viruses are inactivated differently due to the morphological and genomic varieties (enveloped or non-enveloped; DNA or RNA viruses) of the different viral species. Typically, enveloped viruses are easier to kill with disinfectants because their phospholipid layer is sensitive to denaturation by temperature and pH. Breaking down this bilayer means a lot of the fusion proteins contained within this envelope that make it infectious are destroyed and the virus is left vulnerable to the effect of the disinfectant.⁹³ Additionally, viruses containing double-stranded DNA can allow the genome to be more easily repaired by its host after infecting a cell, therefore allowing it to remain active and cause disease, unlike some other RNA-based viruses.⁹³

2.2.3 Fungi

Although waterborne fungi are less studied for their pathogenic effects, their presence in waters can result in biofilms that cause complications in water treatment and distribution infrastructure. These biofilms reduce the efficiency of water treatment processes as well as provide other microbes with a support to thrive. It has also been noted that many fungi have adaptations that make them particularly unphased by common industrial disinfection methods such as physically strong outer membranes containing chitin & glucans or UV-absorbing compounds such as melanin which gives a resistance to UV disinfection.⁹⁴

2.2.4 Protists

Protists include a wide variety of organisms that can cause concern in a variety of means. Protists present in drinking water have been known to cause severe gastrointestinal illnesses like the intestinal cryptosporidiosis caused by *Cryptosporidium parvum*, a coccidian parasite that infects the epithelial cells of the intestinal tract, and giardiasis caused by *Giardia intestinalis*.⁹⁵ Cysts of *Giardia* and oocysts of *Cryptosporidium* are both stages in the respective lifecycles of the protozoa that cause these infections. These cysts and oocysts have adaptations in their cell walls that lead to them being highly resistant to chlorination disinfection and UV treatments.⁹⁶ Protists have also been shown to harbour various kinds of other pathogens inside them, creating a so-called trojan horse effect and allowing otherwise neutralised pathogens to bypass certain disinfection treatments.⁹⁷ The interactions between protist hosts and inhabiting microorganisms are generally species-specific but some microbes, such as some *Legionella* species, can infect multiple kinds of protists. This host behaviour can greatly increase the longevity of the infecting microbes by protecting them from extreme

temperatures and desiccation. The host protists also protect the internal microbes from a variety of disinfection treatments including chlorine, monochloramine, hydrogen peroxide and UV treatment.⁹⁸

2.2.5 Disinfection Methods

Generally, disinfection techniques used in water treatment can be split into either chemical, radiation, or heat-based methods. Heat-based methods are normally reserved for emergencies as boiling water is very energy intensive. Drinking water is typically disinfected industrially by chlorination but can also be disinfected by a variety of physical or chemical methods such as filtration, adsorption, UV radiation or ozonation.

Chlorination usually involves adding controlled amounts of chlorine in gas or liquid form after organics removal. In this process, the added chlorine or chlorine by-product reacts with water to form hypochlorous acid (HOCl) and hypochlorite ions (OCl⁻) as shown in **eq 2.2**.



The equilibrium of **eq 2.2** depends primarily on the pH and temperature of the water. The concentration of hypochlorous acid and the hypochlorite ion (OCl⁻) are approximately equal at pH 7.5 and 25°C. These reactive species are strong oxidisers and are believed to function through the breaking up of a pathogen's outer layers.⁹⁹

The main advantage of chlorination is that it persists in water as residual chlorine after dosing which helps ensure that the water remains microbially safe as it passes through long distribution networks.¹⁰⁰ Chlorination is a highly cost-effective treatment that is capable of disinfecting a wide variety of pathogens in water. However, a few downsides to chlorination

include the requirement for specialist safety measures to ensure no chlorine leaks occur as well as a detrimental effect on the taste and odour of the final drinking water. Additionally, the chlorination process has also been shown to produce more than 40 different DBPs, with trihalomethanes (THMs) and haloacetic acids (HAAs) being the most abundant.¹⁰¹ Many of these DBPs are associated with adverse health risks. Due to the possible formation of DBPs during the chlorination step, a measurable benefit to public health could be made by reducing the creation of DBPs and THMs by not only limiting the levels of organics in water at the disinfection stage but also by decreasing the required dose of chlorine. This could be done via an additional pre-disinfection step that lowers microorganism concentrations without the use of halogenated chemicals.

Monochloramine (NH_2Cl) is formed by dosing chlorine and ammonia under similar operating conditions to chlorination. This chloroamination process is less effective at disinfection than chlorination and so is generally used as a secondary disinfectant during distribution, rather than for primary disinfection as it produces fewer taste and odour issues when compared to chlorination. Although chloroamination produces fewer of the regulated DBPs, the byproducts that are formed and their health effects, if any, are less understood.¹⁰²

Chlorine dioxide (ClO_2) is a more powerful oxidising agent and therefore more potent disinfectant than chlorine and chloramine. Its low stability means that on-site production is required and can be done through several different reaction pathways, all of which require high levels of safety considerations due to the explosive nature of ClO_2 . This means that the operating costs of ClO_2 disinfection are higher than chlorination, but its disinfection efficacy is less pH-dependent than chlorine and still provides a residual effect. Additionally, the use of chlorine dioxide can help treat problem areas of industrial water treatment such as the

removal of taste, odour, iron, and manganese from drinking water. Chlorine dioxide use has also been shown to produce chlorites and chlorates, DBPs that are linked to the development of methemoglobinemia and haemolytic anaemia in humans.¹⁰³ However, THMs and HAAs are formed in lower concentrations in water when using ClO_2 versus chlorine.

Ozone is an unstable gas consisting of three oxygen atoms (O_3) that readily degrade back to oxygen (O_2), producing free radical oxygen ($\text{O}\bullet$) in the process. The free oxygen radical is highly reactive and will typically only exist for a few milliseconds at a time. Ozone is typically generated onsite by passing dry oxygen or air through a system of high-voltage electrodes, meaning high energy inputs are needed to run ozonation setups. It is one of the most effective disinfectants, requiring lower concentrations and contact time than other chemical disinfectants to achieve similar disinfection rates.¹⁰⁴ Additionally, ozone is strong enough to reduce iron, manganese, and sulphur concentrations by oxidising them into insoluble metal oxides and elemental sulphur.¹⁰⁵ Moreover, ozonation is one of the only chemical disinfectants that can inactivate *Cryptosporidium* and *Giardia*.¹⁰⁵

Although ozonation is increasing rapidly in popularity, its lack of residual effect, high operational costs and additional pre/post treatment requirements present problems when implemented as a drinking water disinfection technology. Depending on the properties of the water being ozonated, the system may require pretreatment for hardness reduction or the addition of polyphosphate to prevent the formation of carbonate scale. Post-treatment to remove metal oxides and the byproducts formed when reacting with bromide and organic matter (ketones, aldehydes, and bromates) may be required as well.¹⁰⁵

Commercial UV disinfection of water is typically performed by passing the treatment water through pipes containing UV lamps with a wavelength of 254 nm. Most systems tend to use

low-pressure mercury lamps that run at a relatively low partial pressure of mercury, low external temperatures (50-100 °C), and lower power inputs. These lamps produce a near monochromatic UV light with a wavelength of 254 nm, which is often described as within the optimum range that nucleic acids absorb UV energy (240-280 nm). This UV absorption results in the direct photolysis of the nucleic acid bonds, resulting in the inactivation of the microorganism. The efficacy of this process is strongly linked with exposure time, lamp intensity, and general water quality such as turbidity and true colour. 7 mJ/cm² and over is required to start inactivating coliform bacteria with some pathogens requiring up to 150 mJ/cm² for inactivation.¹⁰⁶ A major downside to UV treatment is that it has no residual in treated water, meaning further disinfection treatments are required if the water is to be safely fed through distribution infrastructure. Additionally, depending on the quality of the water entering the UV system, constant maintenance may be required as NOM and biofilms present in the water can foul the surfaces of the lamps causing a reduction in the effective applied UV intensity. If not maintained this could lead to ineffective disinfection of harmful pathogens. This typically means that UV disinfection has to be one of the last stages in water treatment, so as to ensure the highest water quality and clarity entering the system. Moreover, the lamps used in UV disinfection consume large amounts of energy over their entire lifetime, from manufacture to continuous operation/maintenance to the eventual disposal/ recycling of the heavy metals they utilise. This of course may be negated in the near future by the advancement and implementation of UVC LEDs with higher efficiencies than their current rate.

Although photocatalysis hasn't been employed significantly at an industrial level for drinking water disinfection, there is a significant amount of research surrounding it at the lab scale. This research tends to focus on visible light as the irradiation source, for applications in solar

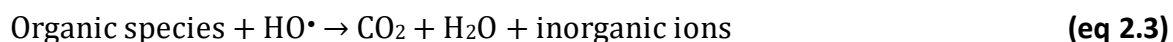
disinfection as a sustainable, low-cost treatment method. However, UVA-based research has markedly less interest, possibly owing to the impressive efficacy of UVC lamps for similar levels of electricity consumption to UVA low pressure lamps. With the improvements in LED technologies making UVA-LEDs much more commercially viable, UVA photocatalytic disinfection becomes much more of an attractive prospect.

It has been proposed that the mechanism for photocatalytic disinfection consists of oxidative damage to the cell wall, followed by the underlying cell membrane, eventually leading to increased permeability and eventually the free efflux of intracellular contents, as well as disruption to genetic material, causing cell death.¹⁰⁷⁻¹⁰⁹ The mechanism of bacterial inactivation is thought to be due to a combination of damage to DNA and proteins of the microorganisms present, caused by the formation of reactive oxygen species (ROS), such as singlet oxygen, superoxide, hydrogen peroxide and hydroxyl radicals. UVA light (315 - 400 nm) can induce protein oxidation and aggregation within exposed bacteria, leading to disruptions of metabolic function and accelerated cell ageing.¹¹⁰ It has been shown that the enzyme components of the respiratory chain are affected, resulting in the inhibition of Adenosine triphosphate (ATP) generation.¹¹¹

2.3 Advanced Oxidation Processes

Advanced oxidation processes (AOPs) are a growing area of interest for highly effective water treatment technologies due to their ability to remove low biodegradability and high chemical stability pollutants. AOP mechanisms rely on the in-situ formation of highly reactive oxidant species, mainly hydroxyl radicals ($\text{OH}^\bullet$). The $\text{OH}^\bullet$ radicals are highly effective, powerful, ubiquitous in nature, and non-selective with electrophilic behaviour and redox potential of

2.8 V, which accelerate the oxidation and degradation of a wide range of contaminants in wastewater by abstracting a hydrogen atom from aliphatic carbon or adding a hydrogen atom to the double bonds and aromatic rings.¹¹²



The organic compounds containing carbon-carbon double bonds in their structure are more reactive toward $\text{HO}^\bullet$. However, the lifetime of $\text{HO}^\bullet$ is extremely short ($t < 10^{-3}$ s), and once the $\text{HO}^\bullet$ has formed, it can give rise to several elementary reactions. Other radicals and active oxygen species generated in AOPs are superoxide radicals ($\text{O}_2^{\bullet-}$), hydroperoxyl radicals ($\text{HO}_2^{\bullet-}$), and organic peroxy radicals ($\text{ROO}^{\bullet-}$). These radicals are formed from a less reactive primary oxidant such as hydrogen peroxide (H_2O_2) or ozone (O_3).¹¹³ The generation of these reactive agents can be achieved with the use of several processes, including sonolysis, ozone-based processes (ozonation), ultraviolet (UV) irradiation, Fenton oxidation, photo-Fenton oxidation, ultrasound, photocatalysis, and various combinations of these technologies.⁷⁰

2.3.1 The photocatalytic process

Within the area of AOPs, photocatalysis is an up-and-coming area of research due to its, until recently, untapped wide potential for possible environmental engineering applications. Photocatalysis is commonly categorised into either heterogeneous or homogeneous depending on whether the catalyst is in a different phase from the reactants (heterogeneous) or the same phase (homogeneous). The most common heterogeneous photocatalysts are transition metal oxides and semiconductors, TiO_2 being the most researched due to its high photocatalytic activity, excellent physical and chemical stability, low cost, and nontoxicity to humans and the environment. Other common heterogeneous photocatalysts include zinc

oxide (ZnO),¹¹⁴ which also shows great photocatalytic activity, and graphitic carbon nitride (g-C₃N₄),¹¹⁵ which is being increasingly used because of its preferable bandgap for visible light reactions.

Heterogeneous photocatalysis gives practical advantages as it allows easy separation of the reaction media from the catalyst as well as high levels of chemical stability and reusability with many new compounds being developed each day. Alternatively, homogeneous photocatalysis may require more complicated steps for catalyst removal but has shown very high photocatalytic activity. The most commonly used homogeneous systems are based on the photo-Fenton process (Fe²⁺/H₂O₂) where the hydroxy radicals produced are the reactive species.

Ongoing research on photocatalytic NOM removal is based on the use of semiconductors as sensitizers for light-induced redox processes. The electronic band structure of TiO₂, presented in Figure 2.3, consists of an electron-filled valence band (VB) and a vacant conduction band (CB). When TiO₂ is illuminated with photons of energy equal to or greater than its band gap energy ($E_g = 3.2$ eV; band gap wavelength < 380 nm), an electron from the VB is excited to the CB, leaving a positive hole behind in the VB.¹¹⁶ In the absence of a suitable scavenger (e.g. oxygen), the electron-hole (e⁻ - h⁺) pair recombines dissipating the stored energy within a few nanoseconds. Recombination is prevented in the presence of scavengers that trap the hole or the electron triggering reduction-oxidation (redox) reactions.¹¹⁷

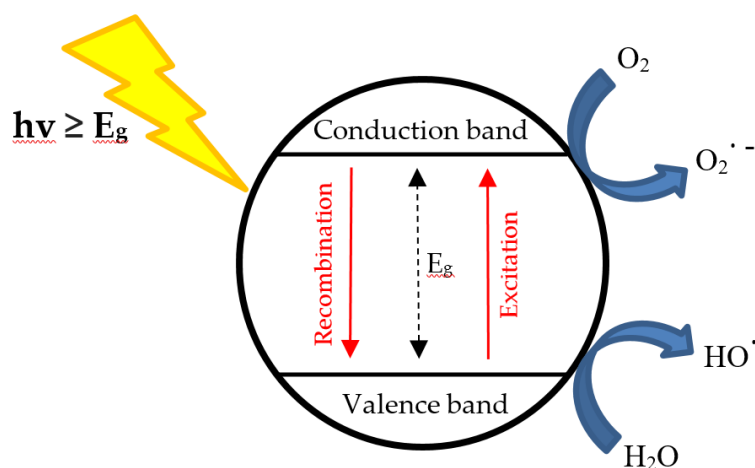
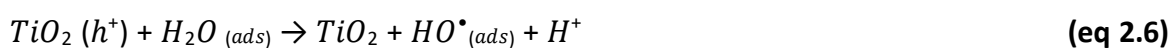
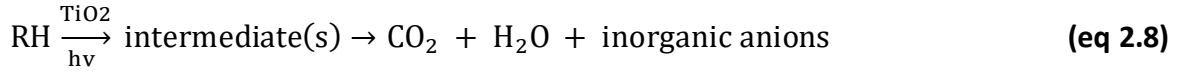


Figure 2.3 - Principal mechanism of photocatalysis¹¹⁸

The generated photoexcited electrons are capable of reducing dissolved oxygen to form superoxide radical ions, $O_2^{\bullet -}$, while the positive holes react with H_2O and OH^- adsorbed on the surface of TiO_2 to produce surface adsorbed hydroxyl radicals, $HO_{(ads)}^{\bullet}$:



Hydroxyl radicals are a highly reactive species and generally attack organic compounds via three different pathways; electrophilic addition (**eq 2.9**); hydrogen atom abstraction (**eq 2.10**); and (iii) electron transfer (**eq 2.11**). This then leads to the target compounds' degradation and possible mineralisation into carbon dioxide, water, and inorganic ions.¹¹⁷



With this in mind, photocatalytic degradation (**eq 2.8**) can be broken down into six independent steps: (i) diffusion of the target molecule in the liquid phase to TiO_2 surface, (ii) adsorption of the target molecule onto the photoactivated TiO_2 surface, (iii) photonic activation of TiO_2 , (iv) photocatalytic reaction on TiO_2 surface, (v) desorption of reaction products from TiO_2 surface, and (vi) products diffuse from interface region into liquid phase.¹¹⁷

It has been widely shown that photocatalytic degradation of organic target molecules fits well to a pseudo first order kinetic model.¹¹⁹⁻¹²² The Langmuir-Hinshelwood model is commonly applied to quantify the reaction kinetics. This ultimately gives the equation that will frequently be used throughout this Thesis to determine the pseudo first order rate constant for each material tested:

$$r = -\frac{dC}{dt} = \frac{K_r KC}{1+KC} \quad (\text{eq 2.12})$$

where r is the rate of target degradation ($\text{min}^{-1} \text{mg/L}$), C is the target concentration at any time (mg/L), k_r is the apparent reaction rate constant and K is the equilibrium constant for adsorption of the target onto the catalyst. When the target concentration and its adsorption onto catalyst are relatively low, **eq 2.12** can be reduced to:

$$-\frac{dC}{dt} = kKC = k_{app}C \leftrightarrow \ln \frac{C_0}{C} = k_{app}t \quad (\text{eq 2.13})$$

where k_{app} (min^{-1}) is a pseudo-first-order kinetic constant and C_0 is the initial target concentration (mg/L).

2.3.2 Parameters affecting the photocatalytic removal of NOM

Current work surrounding photocatalysis has seen a recent shift from low-pressure mercury lamps to the use of solar and high-efficiency light-emitting diodes (LEDs) in search of improving the energy efficiency of the process. LEDs have shown several benefits over UV lamps, including the exclusion of toxic heavy metals (mercury) utilised in low-pressure lamps, higher efficiency, highly specific and tuneable emission spectrums, and longer lifespans.¹²³ As a result, the investigation of conventional UV lamps in photocatalytic systems has mostly been phased out in areas focussing on scale-up due to their high operational and maintenance costs, possible health risks, and low sustainability. Additionally, various life cycle analyses (LCA) have shown the increased environmental impacts of UV photocatalysis when compared to other AOPs due to the increased CO_2 emissions and fossil depletion associated with running UV lamps, as well as the environmental hazards related to their content in toxic chemicals.¹²⁴

LEDs are semiconductor p-n junction diodes that emit light when activated due to the recombination of electrons and holes. LEDs have shown great promise in recent years due to their high energy efficiency, extended lifetime, and increased durability which makes them interesting candidates for application in industrial settings. Moreover, the small footprint of LEDs, directional light output, and tuneable near-monochromatic emission spectra allow for flexible design and development of compact, miniaturised, or portable water photochemical systems. Furthermore, LEDs can be programmed for high-frequency, periodic illumination, which has been found to have a beneficial effect on photocatalytic kinetics.¹²⁵

Natural sunlight is a free and renewable energy source that can be used instead of UV lamps as an irradiation source. Solar heterogeneous photocatalysis makes use of the near-UV band of the solar spectrum to excite the photocatalysts.¹²⁶ Solar photocatalysis has attracted a lot of interest as an affordable, sustainable, and simple treatment option in areas with high solar energy potential such as rural locations within the tropics.¹²⁷ However, this dependence on solar availability and limitations in performance due to low UV character in sunlight (<5%) limits its current possible areas of application. Other issues to be taken into consideration are the requirement of large area and high capital costs, difficulty integrating into existing water treatment setups, and reduced efficacy compared to UV-based systems.

An observed gap between lab-based experiments and the real-world application of photocatalytic NOM removal is the use of commercially available humic acid sources as NOM substitutes. This is because the chemical composition of water largely affects the photocatalytic efficiency. Inorganic ions (e.g. Cl^- , SO_4^{2-} , NO_3^- , NO_2^- , PO_4^{3-} , and HCO_3^-) present in raw waters but not in synthetic test waters have been found to significantly reduce reaction kinetics.¹²⁸ It has been posited in investigations that anions in solution can affect the formation and stability of the active sites on the catalyst surface. Additionally, it is thought that some ions (Cl^- , CO_3^{2-} , HCO_3^- , NO_3^- , and SO_4^{2-}) may compete with reactive species on the catalyst surface for adsorption as well as undergoing separate redox reactions with $\text{HO}^\bullet$ and h^+ on the catalyst surface, scavenging some of the reactive oxygen species and producing less reactive species resulting in a diminished degradation efficiency.¹²⁹ For instance, hydroxyl radicals in the presence of chlorides can be converted into chlorine radicals, reducing degradation efficiency due to their lower oxidation potential, as shown in **eq 2.14 – 2.16**.



Other examples of common inorganic ions acting as hydroxyl radical scavengers, and subsequently reducing the reaction rate, are shown below.



pH is also a significant influence on photocatalytic performance as it can affect TiO_2 charge and cluster formation size.¹³⁰ However, it has been noted that variations at pH levels normally observed in surface levels (between pH 4 and 10) do not present noticeable variations in the efficiency of photocatalytic oxidation. Varying away from the zero-point charge (pH_{zpc}) of a catalyst, (4.5 – 7 for TiO_2) results in the catalyst becoming negatively or positively charged, as shown below:¹³¹



In suspended catalyst systems, aggregation studies have shown that TiO_2 nanoparticles are very stable at low or neutral pH with particle clusters around 300 nm being formed at pH well outside this range, which can increase up to 2 - 4 μm at pH close to pH_{zpc} . When pH reaches pH_{zpc} , large TiO_2 aggregates form with zero-electrostatic surface potential to keep apart the catalyst particles.¹³² Therefore, attention should be paid to these conditions given that

photon absorption may be reduced, and more vigorous mixing may be needed to prevent TiO₂ sedimentation. Certain groups of organic compounds, such as carboxylic acids, strongly adsorb onto TiO₂ surfaces at low pH values whilst others, such as alcohols and saturated long-chain aliphatic compounds, do not.

Table 2.1 shows several publications focusing on the treatment of NOM in water by means of heterogeneous TiO₂ photocatalysis. Some of the earliest work on the photocatalytic degradation of NOM was done by Bekbölet et al.^{133,134} where suspensions of P25-TiO₂ were used to explore the limitations and general trends observed when changing the reaction conditions in standard photocatalytic procedures. Although these early papers reported on the most favourable conditions for photocatalytic NOM removal, much more work has been done since on optimizing the resultant degradation of NOM by altering basic operational parameters.

Table 2.1 - Publications on the heterogeneous photocatalytic treatment of NOM.

Water matrix	Catalyst type	Reaction time	Irradiation source	Other operating parameters	Removal efficiency	Other important findings	Reference
Humic acid solution	P25 – TiO ₂	120 min	UVA – 125 W	Ambient pH [HA] = 50 mg/L [TiO ₂] = 1 g/L	88% TOC 99% Vis ₄₀₀	THMFP* = 14.5 µg/L	Bekbölet et al. (1996) ¹³⁴
Humic acid solution	P25 – TiO ₂ , UV100 - TiO ₂	60 min	UVA – 125 W λ = 300-420 nm	Ambient pH [HA] = 10 mg/L [TiO ₂] = 0.25 g/L	P25: 70% TOC UV100: 50% TOC	NOM removal rate constant: P25 = 1.9x10 ⁻² min ⁻¹ UV100 = 1.2x10 ⁻² min ⁻¹	Bekbölet et al. (2002) ¹³³
Reservoir water: M-Myponga site W-Woronora site	P25 – TiO ₂	150 min	UVA – 20 W λ = 365 nm	pH ~ 7 TOC _M = 10.6 mg/L TOC _W = 3.5 mg/L [TiO ₂] = 0.1 g/L	M: 80% TOC 100% UV ₂₅₄ W: 80% TOC 100% UV ₂₅₄	THMFP*: M = <20 µg/L W = <20 µg/L	Liu et al. (2010) ⁷⁶
Sand-filtered treatment plant water	N-Pd-TiO ₂	120 min	Solar simulator 500 W	pH ~ 6.73 TOC = 2.38 mg/L [N-Pd-TiO ₂] = 5 g/L	HPO** = 71% HPI** = 35% TPI** = 15% UV ₂₅₄		Nkambule et al. (2012) ¹³⁵
Reverse osmosis isolate and	AgSiO ₂ -TiO ₂	30 min	Solar simulator λ = 400-1100 nm	pH ~ 8.2 TOC _I = 3.7 mg/L [TiO ₂] = 0.1 g/L	20% TOC 42% UV ₂₅₄	219 ± 40 µg THMFP* per g TiO ₂	Gora et al. (2018) ¹³⁶

alginic acid solution							
Humic acid solution	Al:Fe-TiO ₂ (1%)	15 min	UVC – 37 W $\lambda = 254$ nm	pH ~ 7 [HA] = 10 mg/L [TiO ₂] = 0.1 g/L O ₃	63.2% TOC 79.4% UV ₂₅₄	Increasing HCO ₃ ⁻ concentration decreases the NOM reduction rate	Yuan et al. (2013) ¹³⁷
Humic acid solution	ZnBO on g-C ₃ N ₄	300 min	12x Vis, UVA & UVC lamps – 8 W	pH ~ 4 [HA] = 5 mg/L [ZnBO] = 1.5 g/L	77.9% DOC 97.9% UV ₂₅₄	DOC removal rate constant: $3.4 \times 10^{-3} \text{ min}^{-1}$	Truong et al. (2019) ¹³⁸
Reservoir water: MV-Midvaal P-Plettenberg bay	MWCNT/N, Pd-TiO ₂ ***	120 min	Solar simulator 300 W	[MWCNT/N, Pd-TiO ₂ ***] = 1 g/L	MV: 69.4% P: 97.7% UV ₂₅₄		Ndlangamandla et al. (2018) ¹³⁹
Humic acid solution	TiO ₂ nanotubes	120 min	UVC – 11 W $\lambda = 254$ nm	[HA] = 50 mg/L [TiO ₂] = 0.5 g/L	98.27% DOC 100% UV ₄₃₆	Humic acid removal rate: $0.0607 \text{ mol m}^{-3} \text{ s}^{-1}$	Zhang et al. (2009) ¹⁴⁰
Humic acid solution	Cu ₂ O nanocrystal	120 min	$\lambda \geq 400$ nm	[HA] = 40 mg/L [Cu ₂ O] = 0.5 g/L	99.5% UV ₂₅₄		Jing et al. (2014) ¹⁴¹
Humic acid solution	Ce-ZnO	60 min	Solar simulator $\lambda = 300 - 800$ nm	[HA] = 4.8 mg/L [Ce-ZnO] = 0.25 g/L		Humic acid removal rate constant: $5.79 \times 10^{-2} \text{ min}^{-1}$	Birben et al. (2017) ¹⁴²
Landscape surface water	Bi ₂ O ₃ -TiO ₂	10 min	Vis – 300 W $\lambda = 400-780$ nm	pH ~ 8.13 TOC _i = 2.2 mg/L [Bi ₂ O ₃ -TiO ₂] = 2 g/L	20.2% TOC 24.4% UV ₂₅₄		Wang et al. (2019) ¹⁴³
Pre-treated (coagulation-flocculation) water	P25 - TiO ₂ , TiO ₂ /β-SiC	220 min	Solar simulator – 1500 W	pH ~ 6.7 P25: TOC _i = 7.8 mg/L [TiO ₂] = 0.5 g/L	P25: 80% TOC β-SiC: 80% TOC		Ayekoe et al. (2017) ¹⁴⁴

				β -SiC: TOC _i = 5.5 mg/L [TiO ₂] = 0.5 g/L			
Treatment plant inlet water in immersed ultrafiltration module	P25 - TiO ₂	120 min irradiation 43hour total treatment	UVC – 15 W λ = 254 nm	pH ~ 7 DOC = 5.48 mg/L [TiO ₂] = 0.1 g/L	60% DOC 90% UV ₂₅₄	THMFP* = 25 µg/L	Rajca et al. (2016) ¹⁴⁵
Humic acid solution	LiCl- TiO ₂ doped PVDF*** membrane	30 min	UVA – 100 W λ = 365 nm	pH ~ 7.5 [HA] = 2 mg/L	80-84% UV ₂₅₄		Song et al. (2014) ¹⁴⁶
Extracted river NOM	P25 - TiO ₂	120 min	UVC – 8 W λ = 254 nm	pH ~ 8.2 TOC _i = 10 mg/L [TiO ₂] = 1 g/L	80% TOC 100% UV ₂₅₄	NOM degradation rate constant: 0.0163 min ⁻¹	Huang et al. (2008) ¹⁴⁷
River water	Nano- TiO ₂ on diatomite	360 min	3x UVC lamps – 16 W λ = 254 nm	pH ~ 8.0-8.5 TOC _i = 9.84–13.18 mg/L [TiO ₂] = 0.5 g/L	28.5% TOC 40% UV ₂₅₄		Sun et al. (2014) ¹⁴⁸
Humic acid solution	TiO ₂ nanoparticles/ granular activated carbon (GAC)	180 min	UVA – 500 W λ = 365 nm	pH ~ 4.2 TOC _i = 5.04 mg/L [TiO ₂ /GAC] = 2 g/L	99.5% UV ₂₅₄	Significantly lower degradation (70% UV ₂₅₄) at pH = 11	Xue et al. (2011) ¹⁴⁹
Humic acid solution	Cu-doped ZnO nanoparticles	120 min	Natural sunlight	pH ~ 7 [HA] = 20 mg/L [Cu-ZnO] = 1.5 g/L	99.7% UV ₂₅₄		Maleki et al. (2015) ¹⁵⁰

***THMFP – Trihalomethane formation potential**

****HPO – Hydrophobic, HPI – Hydrophilic, TPI – Transphilic**

*****Multi-walled carbon nanotubes/nitrogen, palladium co-doped titanium dioxide**

******Polyvinylidene difluoride**

The concentration of the catalyst is an important parameter for photocatalytic oxidation processes. In general, photocatalytic oxidation is enhanced when catalyst concentration is increased up to a value at which the removal rate reaches a plateau. Bekbölet et al.¹³⁴ observed that an optimal catalyst concentration for NOM removal is 1 g/L and this is high enough to provide a large surface area to adsorb NOM but not so high that the slurry significantly reduces the availability of light throughout the reaction mixture. This upper limit has been noted to depend on the geometry and the working conditions of the photoreactor.¹⁵¹ This same study evaluated the trihalomethane formation potential (THMFP) of various humic acid concentrations with respect to time, which also opened up the possibility for more research on the area by showing up to 94% reductions in THMFP (below the United States Environmental Protection Agency limits) after 120 min of photocatalytic treatment. A similar experiment by Maleki et al.¹⁵⁰ investigated the effects of catalyst concentration on humic acid degradation using Cu-doped ZnO nanoparticles. The same characteristic rise and plateau in degradation rate was observed when increasing the catalyst concentration from 1.5 g/L to 2 g/L, which was attributed to partial catalyst agglomeration and a consequent decrease in the active catalyst surface at higher dosages of catalysts.

Another early paper by Bekbölet et al.¹³³ investigated the differences in performance between; the standard P25 – TiO₂, a 20:80 mix of rutile: anatase titania, and another commercially available HOMBIKAT UV 100 – TiO₂, made entirely of anatase phase. Here it was shown that P25 – TiO₂ showed better photocatalytic activity when it came to humic acid degradation. This correlated with the adsorption experiments also performed, which revealed that the P25 adsorbed 3 times as much humic acid at a set loading than the UV100 despite having a much lower BET surface area. Due to its proven high-performance rate P25 – TiO₂ is often the comparative standard used in NOM photocatalytic degradation studies of various

semiconductor loadings. Huang et al. 2008¹⁴⁷ studied the photocatalysis' effect on NOM by analysing its compositions in water before and after irradiation. There was observed preferential removal of high molecular weight, hydrophobic NOM molecules, which are the major NOM fraction responsible for membrane fouling.^{76,135} Further research by Valencia et al.¹⁵² using size-exclusion chromatography with respect to operating pH levels during photocatalytic degradation showed that changes in pH values affected the adsorption of NOM onto TiO₂. It was established that the pH determines the mechanism, but not the sequence of the photocatalytic degradation and therefore, regardless of pH, the degradation of the NOM preferentially removed the larger molecular size fraction in comparison to the middle and small fractions. Other comprehensive work on operating parameters includes that done by Espinoza et al.¹⁵³ on the effect of metal ions (Cu²⁺, Fe³⁺, Zn²⁺, Mn²⁺) in solution on the photocatalytic degradation of NOM. Photocatalytic degradation experiments with and without the addition of various combinations of CuSO₄ or CuCl₂·2H₂O, FeCl₃, ZnCl₂, and MnCl₂ solutions revealed an apparent reduction in photoactivity and prevention of certain degradation products when in the presence of added Cu²⁺ ions (10µM). The addition of Mn²⁺ was observed to change the magnitude of the effect of added Cu²⁺ a larger inhibiting effect from added Cu²⁺ was observed in the absence of added Mn²⁺ during the degradation of large molecular weight NOM. It was suggested by Espinoza et al. that these observations could be explained by a stabilization of the NOM against degradation by HO• by complexation with Cu²⁺, which would increase the longevity of NOM in aquatic systems. Adding Fe³⁺ and Zn²⁺ to the experiments showed no significant effects.

Many investigations on photocatalytic reactions are performed under UV light due to the band gap energy of pure TiO₂ (3 or 3.2 eV in rutile or anatase phase), which means that there is very limited photocatalytic activity in the visible range. On top of this, unmodified TiO₂ can

be characterised by a high recombination rate for the photo-produced electron and hole pairs, and a significant difficulty in strongly binding to some support materials.¹⁵⁴ Therefore, a significant amount of research surrounding the photocatalytic degradation of NOM is focussed on improving the photo-efficiency of TiO₂ and its degradation efficiency of organic compounds. Various approaches to do so consist of chemical and structural modification of TiO₂, in order to enable light absorption in the visible region. These studies include several chemical modification schemes that report promising options to improve photocatalytic activity. Chemical modifications to TiO₂ involve the addition of various other species, typically involving: metals (such as Fe, Pd or Ag)^{135, 137, 155, 156}/metal oxides (such as Bi₂O₃)¹⁵⁷⁻¹⁶⁰ which can either facilitate electron-hole separation and promote interfacial electron transfer or decrease the TiO₂ band gap. This promotes electron transfer from the valence band to the conduction band, facilitating the formation of oxidative species such as hydroxyl radicals.¹⁶¹

Other chemical modifications include the addition of non-metals (such as C, N, S or F) which have also been shown to form new impurity levels close to the valence or conduction band of TiO₂, thereby lowering the optical gap and shifting the absorption edge to the visible light region.¹⁶² The work done by Nkambule et al. (2012)¹³⁵ focuses on N-doped TiO₂, a growing area of photocatalysis which has been shown to increase visible light photocatalytic activity when coupled with co-dopant metals by reducing the band gap of TiO₂ and shift the absorption into the visible light region.^{139, 163} The Pd-modified N-doped TiO₂ catalyst synthesised by Nkambule et al. in 2012¹³⁵ showed a particularly successful shift in titania's visible light absorption with an over 70% removal in hydrophobic NOM fractions using a solar simulator. A drawback to these N-doped TiO₂ species would be that the doping of N into the lattice of TiO₂ usually results in the formation of oxygen vacancies in the bulk material.¹⁶⁴ These defects can act as recombination centres for carriers and therefore, compared to pure

TiO₂, a loss of UV-activity is usually found for N-doped TiO₂, which is due to the rapid recombination rate of generated electrons and holes introduced by the impurity level. The addition of non-metals to metal-doped TiO₂ can also be utilised to improve the stability of the photocatalyst, for example, forming a thin layer of SiO₂ around a catalyst's surface to prevent oxidation of metal nanoparticles like Gora et al.¹³⁶ in their 2018 investigation on modified TiO₂ for solar photocatalysis. This work saw a Ag-TiO₂ nanoparticle co-catalyst reduce NOM levels by 42% UV₂₅₄ in only 30 min of treatment time. This study also found significant changes to the disinfectant by-product formation potential (DBPFP) of NOM wherein the different modifications to TiO₂ followed the same trend in DBPFP level changes but by differing amounts.

Similar approaches (chemical/ structural modifications) to improve the overall photoactivity and efficiency under visible light have also been applied to other heterogeneous catalysts such as Ce-doped ZnO nanoparticles,¹⁴² Cu₂O nanocrystals,¹⁴¹ Zinc Bismuth oxide on graphitic carbon nitride,¹³⁸ and a hybridized photocatalysis–microfiltration system with iron oxide-coated membranes.¹⁶⁵

Alongside the chemical changes, various nano-structured TiO₂ materials have been tested with enhanced visible light photoactivity such as nanoparticles,¹⁶⁶ nanotubes,¹⁴³ nanowires,¹⁶⁷ and nanofilms.¹⁶⁸ Studies have shown that, in general, slurry systems perform better than those based on immobilised catalysts.¹⁶⁹ This stems from the uniform catalyst distribution, the lack of mass-transfer limitations, and the high ratio of illuminated catalyst surface to the effective reactor volume provided by the slurry photoreactors. However, this approach suffers several drawbacks, such as the need for a catalyst-recovery step at the end of treatment, aggregation of TiO₂ particles, and the difficulty in operating in a continuous flow

mode. Many researchers apply membrane filtration for the separation of nanosized TiO_2 from treated water however serious membrane fouling usually occurs as the TiO_2 forms a cake layer and blocks membrane pores.

Work done by Zhang et al.¹⁴⁰ showed that creating titania nanotubes can not only improve upon P25 – TiO_2 's ability to photocatalytically degrade NOM, most likely due to increased surface area, but also significantly reduces the amount of membrane fouling caused by catalyst separation. Another approach to reducing the need for catalyst separation when photocatalytically degrading NOM is producing hybrid materials by combining TiO_2 with carbon materials such as multi-walled carbon nanotubes¹³⁹ and activated carbons.¹⁴⁹ A particularly successful example of this is the work done by Xue et al.¹⁴⁹ where a TiO_2 nanoparticle/granular activated carbon composite (GAC) was prepared by a sol-dipping–gel process. This investigation displayed a synergetic relationship between adsorption upon GAC and degradation involving TiO_2 where a humic acid removal of 99.5% UV_{254} was achieved as well as improved filterability. Hybrid membranes combining TiO_2 with various polymeric compounds such as polyvinylalcohol, pyrrolidone¹⁷⁰ and poly (amide–imide)¹⁷¹ also show a solution to catalyst separation. These hybrid membranes exhibit great potential for water treatment since they combine filtration and photodegradation in a single unit. Blending photocatalytic nanoparticles into a polymeric thin film can cause the entrapped photocatalyst to show reduced catalytic activity due to the agglomeration and shielding effects in the polymer matrix.¹⁷²

The most widely used processes for the removal of NOM from water sources are separation and purification technologies including (micro, ultra and nano) membrane filtration, reverse or forward osmosis, and coagulation. One approach to improving the overall efficiency of

water treatment facilities is combining one or more of these technologies with heterogeneous photocatalysis. This includes the combining of photocatalysts with membrane filtration^{145-147, 165, 170, 173, 174} and adsorption,¹⁷⁵ as well as coagulation systems.¹⁴³ An example of such systems would be Wang et al.¹⁴³ whose work showed that pre-treatment by photocatalysis with Bi₂O₃-TiO₂(4%) could improve the removal of organic matter compared to polyaluminium chloride (PACl) coagulation treatment alone. This study saw removal rates of 20.2% and 24.4% UV₂₅₄ after just 10 min of photocatalytic treatment which increased to 37.93% TOC and 58.75% UV₂₅₄. Photocatalytic oxidation prior to coagulation has been observed to decrease coagulation efficiency by 15%, most likely because the oxidation changes the characteristics of NOM and degrades NOM molecules towards smaller molecular mass fractions.¹⁷⁶ However, when oxidation was performed after coagulation, about 32% DOC and 33% UV₂₅₄ enhancements to the removal of NOM occurred.

Recent interest in homogeneous photocatalytic NOM removal has increased due to reports of lower chemical doses, and therefore lower residual levels of chemicals post-treatment when compared to conventional NOM removal methods such as coagulation.¹¹ Although heterogeneous photocatalysis, such as a standard TiO₂/UV NOM removal mentioned previously, has the added benefit of easy separation after treatment is completed, homogeneous photocatalysis reactions have the advantage of providing a greater degree of interaction between the catalyst and the specified target due to the increased accessibility of the catalytic sites whilst in solution. The homogeneous photocatalytic degradative removal of organic compounds from water is mainly based on the generation of high amounts of hydroxyl radicals from either ozone or hydrogen peroxide. These generated hydroxyl radicals can degrade the organic matter commonly through hydrogen abstraction from aliphatic carbon atoms and electrophilic addition to double bonds or aromatic rings.¹⁷⁷ This is ideal for the

degradation of the large hydrophobic NOM fractions which are major precursors for DBP formation.¹⁷⁸ A comparative study by Goslan et al.¹⁷⁹ showed that the addition of Ferrous sulphate increased UV/H₂O₂'s ability to remove NOM from reservoir water by forming a photo-Fenton reaction.



In the photo-Fenton process (**eq 2.23** and **eq 2.24**), the Fenton reaction rates are strongly increased by irradiation with UV–vis light. The positive effect of irradiation on the degradation rate is due to the photo-chemical regeneration of ferrous iron (Fe²⁺) by photo-reduction of ferric complexes, which leads to additional ·OH generation.¹⁸⁰⁻¹⁸² The ferrous iron generated in solution reacts with H₂O₂ yielding a second ·OH radical and ferric ion (**eq 2.24**), and the cycle continues. A major advantage of the photo-Fenton reagent is that the reaction's light absorption maximum wavelength is roughly 600 nm which gives a much larger absorption overlap with natural sunlight compared to many other common photocatalysts.

An interesting comparison to homogeneous photocatalysis is the work done with homogeneous hybrid photolysis for NOM treatment by enhancing the oxidative capabilities of common oxidising species (e.g. ozone and peroxides) with light. The advantages of these hybrid processes, as well as other AOPs including O₃/UV, H₂O₂/UV and H₂O₂/O₃, were explored by Lamsal et al. in 2011.⁷⁵ This study specifically investigated the treatment process impact on the change of molecular weight distribution (MWD) and disinfection by-product

formation potential (DBPFP) with the UV/ozone hybrid showing a significantly improved removal of NOM and reduced DBPFP when compared to UV or ozone treatment alone.

Many factors decide on the optimum H_2O_2 dosage in UV degradation reactions. For UV/ H_2O_2 NOM removal, the characteristics and concentration of the organic compounds can directly influence the overall mineralisation ability. The amount of hydroxyl radicals produced upon UV irradiation depends on the H_2O_2 concentration whilst H_2O_2 can also react with these radicals and inhibit hydroxyl radical evolution. Additionally, H_2O_2 absorbs UV energy therefore reducing the availability of UV photons for oxidising pollutants at higher H_2O_2 concentrations. Wang et al.¹⁸³ found, for the oxidation of humic acid, that the hydroxyl radical scavenging effect (the production and then combination of $\text{HO}_2\cdot$ into H_2O_2 and O_2) became significant when the H_2O_2 concentration was higher than 0.1% making this the optimum dosage. This study also noted that the presence of bicarbonate/carbonate species has a negative effect on NOM degradation due to competition for hydroxyl radicals, especially at high concentrations of H_2O_2 .

Ozone can degrade NOM directly through ozonolysis which has been found to be fairly selective and relatively slow^{184, 185} so most NOM degradation research is focused on increasing the generation of hydroxyl radicals from the decomposition of ozone in water. This includes the combination of ozone with UV irradiation to degrade NOM through quick, non-selective ozonation. Study results from Ratpukdi et al.¹⁸⁶ on the optimal operating conditions for UV/ozone hybrid photolysis procedures revealed that the mineralization rate of DOC provided by the processes tested ranked in the following order: vacuum ultraviolet (VUV)/ozone > VUV > UV/ozone > ozone > UV. The study also showed that the highest DOC mineralisation rate and biodegradability increase was at a neutral pH 7 rather than in a basic

environment (pH 9 and pH 11) with extremely basic conditions (pH 11) showing no synergistic hybrid effect from combining UV and ozone at all.

Research comparing O₃ NOM degradation with and without the addition of UVC shows a clear enhancement effect from UV light. Work by Chin & Bérubé⁷⁹ concluded that the combined UV/O₃ treatment is more effective at reducing organic constituents, as well as the DBP-FP, in raw water than either the ozone or UV treatment alone. Lamsal et al.⁷⁵ investigated this hybrid effect further by showing how several AOP treatment processes impacted the change of molecular weight distribution (MWD) and disinfection by-product formation potential (DBPFP). The UV/ozone hybrid in this side-by-side study showed a significantly improved removal of NOM and reduced DBPFP when compared to UV or ozone treatment alone. It was also noted that this UV/ozone process induced a near-complete alteration of the molecular weight of NOM from >900 Da to <300 Da.

2.3.3 Photocatalytic Disinfection

The mechanism for photocatalytic disinfection is generally accepted as being the ROS and hydroxy radicals breaking down cell walls and membranes.¹⁰⁷ This damage to the phospholipid bilayer of the bacterial cell membrane can lead to ion leakage, nuclear material damage and lipid peroxidation. Major cell wall disruption can also cause internal cellular organelles and components to be released leading to cell death. ROS can also directly interact with the nuclear DNA and enzyme proteins which hinder mutation, inhibition of transcription and enzyme inhibition.¹⁸⁷ For viral disinfection, it is thought that the capsid protein is affected by ROS.¹⁸⁸

In these solar-based research projects, a common aim is to modify common semiconductors to broaden or red shift the band gap to the visible light wavelengths more abundant in sunlight. The intrinsic benefits of UVA LED-driven photocatalysis as a method of water disinfection present themselves best in a system set up for the deactivation of pathogens in water located in less sunny areas. This approach combines the cost-effectiveness and safety benefits of UVA LEDs, over conventional mercury low-pressure UV lamps used in UVC disinfection, with the enhanced efficacy of UV-based photocatalytic systems in both NOM removal and disinfection when compared to solar-based systems.

Since disinfection works through the formation of ROS, many of the strategies for improving photocatalytic NOM removal also apply to solar photocatalysis. Heterojunctions are commonly employed to help broaden and shift a photocatalyst's wavelength range to overlap better with solar emissions. The type II heterostructures, Z-scheme,¹⁸⁹ and S-scheme¹⁹⁰ heterostructures have been shown to be effective strategies to enhance the performance of composite catalysts. Z-scheme and S-scheme photocatalysts are two different ways of using heterostructures to generate efficient electron-hole pairs at altered wavelengths. Typically, the S-scheme photocatalyst is composed of two n-type semiconductors, while the Z-scheme is composed of n-type and p-type semiconductors. Z-scheme photocatalysts utilise a redox mediator to connect two different semiconductors in series to generate e^- and h^+ pairs by sequential excitation of the two materials. This starts with the photon absorption of one semiconductor which generates an e^- and h^+ pair. This charge separation is then transferred to the redox mediator and subsequently to the second semiconductor, which has a lower energy bandgap than the first semiconductor. This proceeds to go on to excite the second semiconductor and generates the e^- and h^+ pairs that are used for photocatalysis.¹⁹¹

S-scheme photocatalysts, on the other hand, generate e^- and h^+ pairs by simultaneous excitation of two different semiconductors that are materials connected in parallel. The two semiconductors have different energy bandgaps and produce e^- and h^+ pairs simultaneously under irradiation. The e^- and h^+ pairs then migrate to the respective surfaces of the semiconductors, where they participate in photocatalytic reactions.¹⁹² This way, visible light can be utilized more efficiently, especially in the Z-scheme heterojunction as the separation efficiency is significantly improved by the charge distribution through its energy levels. MoS_2/ZnO ,¹⁹³ and $\text{MoS}_2/\text{BiVO}_4$ ¹⁹⁴ are examples of photocatalysts utilising Z-scheme heterojunctions to enhance their solar photocatalytic disinfection. The S-scheme heterostructures can maintain the maximum redox capacity in the CB and VB of the catalyst, establishing an effective charge-transfer mode during photocatalysis. Effective examples of photocatalytic disinfection by novel S-scheme hybrids include $\text{MoS}_2/\text{Bi}_4\text{O}_5\text{Br}_2$ ¹⁹⁵ and $\alpha\text{-Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4$.¹⁹⁰

Disinfection efficiency under UV irradiation tends to perform better under shorter wavelengths as the effects of direct photolytic are strongly pronounced. Nyangaresi et al.¹⁹⁶ investigated the effect of UV disinfection of *E.coli* in the absence and presence of TiO_2 under 265, 275, 310, and 365 nm UV-LEDs. Their results showed that the highest disinfection efficiency of *E. coli* under both direct-photolysis and TiO_2 photocatalysis was the 265 nm UV-LED. It was also shown that the disinfection rate decreased to increase LED wavelength irradiance.

Although the pH of the solution during photocatalysis has a definite effect on the adsorption of bacteria on TiO_2 and therefore the activity towards the destruction of bacteria by TiO_2 , varying results have been reported in the literature. This is likely due to the varying optimum

pH levels of differing microorganisms as some studies have observed bacteria being more sensitive towards photocatalysis at a starting pH of 4.0 or 9.0 than at an initial pH of 7.0.¹²⁹

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The addition of some inorganic ions like HCO_3^- , HPO_4^{2-} , Cl^- , NO_3^- and SO_4^{2-} to the suspension affects the sensitivity of bacteria to sunlight in the presence and the absence of TiO_2 . The addition of HCO_3^- and HPO_4^{2-} resulted in a meaningful decrease in photocatalytic bactericidal effect while literature reports a weak influence of Cl^- , SO_4^{2-} and NO_3^- . The effect of counter ions (Na^+ and K^+) is not negligible and can modify the photocatalytic process as the anions. Bacteria inactivation was affected even at low concentrations (0.2 mmol/l) of SO_4^{2-} and HCO_3^- .¹²⁹

2.4 Design of the photocatalytic reactors

Photocatalytic reactors are often categorised based on a key design feature such as the nature of the light source (artificial light or solar-powered), its geometry (annular or planar) or the state of the photocatalyst (suspended or immobilised). Despite a wealth of reactor designs being theorised and tested, few have been developed for full-scale industrial application, perhaps due to cost, inefficient catalysts and/or difficulty integrating into other water treatment systems. In addition to this, multiple engineering factors come into play, such as fluid pumping energy, pressure drop, temperature and possibly solar availability.¹⁹⁸

The most common reactor setup seen in the literature is slurry reactors that simply suspend catalyst particles in the water matrix. This results in a simple to setup and reproduce reactor with a catalyst yielding a high specific surface area. However, a lot of practical-based literature focuses on methods of catalyst immobilisation, this allows the facile employment of high

throughput continuous modes and eliminates the need for a further catalyst separation step. The disadvantage of this approach is the resultant low area-to-volume ratio, which can lead to slower reaction rates.¹⁹⁹ This disadvantage could possibly be mitigated by a proper reactor design if catalyst illumination and solution circulation is prioritised.

Catalyst concentration is also an important design parameter as it affects the radiation distribution and, therefore, the photocatalytic activity. Slurry reactors have a peak optimal concentration as reaction rates increase with catalyst availability until the dispersed catalyst itself starts scattering light away from other catalyst particles, reducing photon penetration.²⁰⁰ Similarly, certain immobilised systems have optimal catalyst concentrations depending on the lighting configuration. A fixed-film reactor, where the light is shone from the support side, reaches optimal concentration when increasing the film thickness beyond a certain value reduces the light penetration and therefore the reaction rate. Alternatively, a reactor design where the light is shone from the solution side will reach optimum thickness and then the reaction rate will no longer increase or decrease.²⁰⁰

The light availability is another important factor with solar-based reactor units typically employing large, exposed surface areas to maximise solar incident light intensity. Similarly, solar concentrator systems (e.g. parabolic reflectors, Fresnel lenses, and optical fibres) can also increase solar light intensity.²⁰¹ Further considerations for solar reactor designs involve the mitigation of unfavourable weather conditions such as low light levels or fouling of the reaction vessel due to open-air conditions. The designs of several common reactor types are shown below in Figure 2.4.

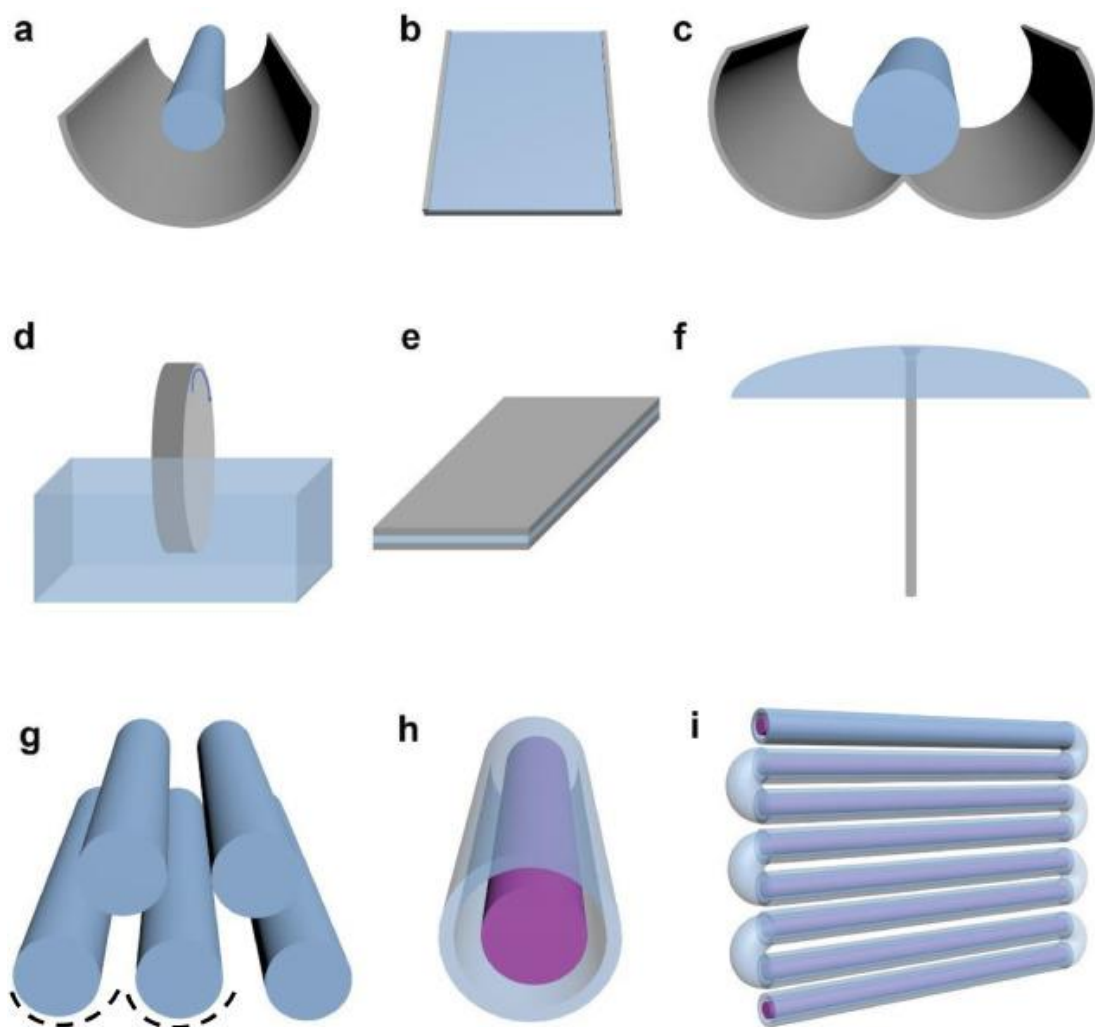


Figure 2.4 - Geometry of several typical PWT pilot-scale reactors: (a) Parabolic Trough Reactor, (b) Free Falling Thin Film Slurry Reactor, (c) Compound Parabolic Collector, (d) Rotating Disk or Drum, (e) Double Skin Sheet Reactor, (f) Water Bell Fountain (g) Offset Multi Tubular Photoreactor, dash line is to show the reactors are placed in a parabolic way, (h) Annular Thin Film Slurry Reactor mounted vertically, and (i) Serpentine Assembly of Annular Thin Film Slurry Reactors. Figure by Wang et al.²⁰²

An ultrafiltration unit is typically required to separate the catalysts from the treated water in slurry reactors. The catalysts can be reused in the treatment process again after the

membrane unit is backwashed although studies on TiO_2 nanoparticle separation have shown retention rates generally above 95%, implying that up to a few grams per day could be released when processing industrial volumes of water. TiO_2 release was found to predominantly occur in the first minutes after the membrane cartridge was cleaned, which is related to cake layer formation. This suggests additional separation steps such as sedimentation may be required to avoid the possible health and environmental implications associated with the presence of TiO_2 nanoparticles in water.

2.5 LED-based Photocatalysis

Mercury UV lamps have long been the main irradiation source for research on organic material degradation by photocatalysis and have been utilised in some urban wastewater treatment plants for disinfection. These lamps have fixed emission patterns determined by the inherent properties of mercury, which are either monochromatic (low pressure) or polychromatic (medium pressure) depending on the gas pressure. Although most photocatalytic research employs mercury lamps, their industrial-scale application is limited as they are typically built from fragile materials, require high voltages and energy inputs, have short lifetimes, and pose a risk of mercury release.

Although electroluminescence was first discovered in the early 20th century, shorter wavelength LEDs weren't commercially introduced until the 1960s when red LEDs became available. The discovery and development of GaN p-type (semiconductor with an excess of electron holes) layers being deposited on top of an n-type layer (semiconductor with an excess of electrons) meant blue and later white LEDs were able to be mass-produced with high efficiency. In this process, electrons are injected from the n-type layer into the p-type

material, and upon recombining with the holes, photons of a specific wavelength are emitted. Further developments in GaN-based LEDs led to commercially viable UV-LEDs being produced in the mid-2000s when LED-based photocatalysis started to take an interest. LED technology has opened up new opportunities for water treatment through its high efficiency, long lifespan, and flexibility in wavelength selection.²⁰³ Compared to traditional lamps, UV LEDs are smaller, have no warm-up time, and their wavelengths can be precisely controlled for optimal target treatment. Visible light LEDs have shown remarkably high efficiencies of around 70% and are being practically applied in many areas although have limited utility in photocatalytic research due to the higher band gap energies of most commonly used photocatalysts.²⁰⁴ The interest in creating visible light photocatalysts has been described in previous sections of this chapter but is mainly focussed on harnessing visible light from solar sources to further decrease the energy demand of photocatalytic water purification. Despite this, some research on micropollutant degradation has been conducted using visible light LEDs to varying levels of success.

Shorter wavelength LEDs have significantly lower efficiencies when compared to visible light-LEDs with UVA LEDs having around a 40% efficiency. This is still significantly higher than traditional mercury lamps (~15% efficiency) but a drastic reduction in energy efficiency is seen in UVC LEDs (~1.5% efficiency), limiting their current implementation in industrial systems.^{204,}

²⁰⁵ This lower energy efficiency in UV LEDs has been noted to cause greater heat generation, which can lead to an overheating phenomenon if not taken into consideration during the design of the photoreactor. Despite this, LED-driven photocatalysis has shown great efficacy in the water treatment of a variety of targets including micropollutants, dyes,²⁰⁶ heavy metal removal,²⁰⁷ NOM,²⁰⁸ and the inactivation of different pathogens including bacteria,¹⁹⁶ and viruses,²⁰⁹ including recent investigations with coronavirus inactivation.¹⁴

The lack of LED warm-up time has led to a budding area of interest in photocatalysis whereby the light sources are rapidly turned on and off at intervals of milliseconds. This takes advantage of the incredibly high speed of photon absorption ($\sim 10^{-15}$ seconds) by the catalyst which initiates the photocatalytic process. Subsequent reaction steps up until pollutant oxidation do not depend on light exposure and take place at a significantly slower rate (10^{-9} – 10^{-4} seconds). This means the energy efficiency of a photocatalytic reaction can be increased by employing a controlled period of illumination (CPI) by connecting the LEDs to a control board containing a pulse width modulation program of the electrical current.^{208, 210} CPI involves LEDs alternating between light and dark periods whereby the aim is to create a cycle where there is little to no time between the consumption of the last residual radical and the light turning back on again. This method has been theorised to prevent the continuous introduction of photons that would result in the build-up of charges (e^- / h^+) and photogenerated intermediates ($\cdot OH / O_2^{\cdot -}$). This charge buildup can lead to undesirable reactions and therefore lower the efficiency of the photocatalytic process.

2.6 Process integration and scale-up

The most common and economically feasible processes to remove NOM are coagulation and flocculation followed by sedimentation/flotation and filtration. The effectiveness of this process has been shown to remove high content of humic acid with different coagulants such as traditional aluminium salts alone or combined with other products such as chitosan, polyferric cationic polymer dual coagulants, or synthesized coagulants (polytitanium coagulant).^{51, 54, 56} Coagulation-flocculation removes most of the NOM, especially its hydrophobic fraction, which is generally more aromatic and larger in molecular size than the hydrophilic fraction.^{47, 56} Moreover, it generally allows DBP mitigation through the physical

removal of the organic precursor material. However, coagulation-flocculation cannot be used alone for the inactivation of concerned pathogens and at optimal performance can leave a residual 30% to 40% of NOM in treatment waters therefore increasing DPF potential.⁵⁴ As the existing water treatment process is projected to become insufficient, further treatment is thus necessary to remove humic substances to safe levels. Photocatalytic processes can be implemented as a final polishing step for the degradation of stubborn organic compounds to further reduce the DBPFP before disinfection is undergone. This method of process integration has been tested with separate coagulation/ flocculation steps¹⁴³ as well as a combined single step.¹⁴⁴ Separating the steps found an increased efficacy in the photocatalytic stage, likely due to the increased penetration of light through the clarified water.^{144, 211} Whereas combining the steps saw improved DBPFP reduction as well as a bridging effect of coagulants, promoted by the easy agglomeration of photocatalysts, thus forming a floc complex with photocatalyst as the floc core, meaning that the floc complex after coagulation can achieve rapid sedimentation.¹⁴⁴ Few studies have reported the efficiency of photochemical oxidation processes as a post-treatment step after coagulation at lab and pilot-scale and the implementation of these technologies at full-scale is still pending. This can be attributed to the relatively high treatment costs (e.g. electricity for the artificial light sources, etc.) of photochemical oxidation technologies as well as the relatively high treatment times leading to decreased throughput.

The wide application of photochemical oxidation technologies sets a requirement for the reduction of their treatment cost. To accomplish this, strategies should be adopted aiming at the minimisation of energy demand, the use of reagents, and the need for effluent pre/post-treatment. Energy efficiency can be achieved using UV-LEDs and efficient reactor designs where applicable. Additives which improve process efficiency either in terms of kinetics or

operational pH range, as well as operation at optimised conditions can significantly reduce the energy and resources required for separate water treatment stages.^{129,183,212} Meanwhile, taking steps to improve the process of catalyst immobilisation, separation or matrix recycling can significantly improve the sustainability of photocatalytic treatments.^{124,213-215} In this view, the major challenges arising to date regarding process implementation at full scale can be summarised into:

- The development of catalysts with improved photocatalytic efficiency via enhanced charge transport and trapping.
- The identification of cost-effective solid-liquid separation processes for slurry photoreactors; alternatively, the development of immobilised catalysts with high durability of the coating, improved light penetration, and increased lifetime.
- The design and fabrication of engineering proper photoreactors providing increased and uniform light distribution to provide competitive throughput times.

2.7 State-of-the-art NOM removal by TiO₂-based LED photocatalysis

Most research conducted into NOM photocatalysis has utilised mercury lamps as a light source, that is until recent years when UV-LEDs have improved significantly in price, availability, and efficiency. This has seen a definite shift in the volume of research utilising LEDs for photocatalytic NOM degradation with research investigating UVC photocatalysis being the major outlier due to the efficiency and price problems previously discussed in Chapter 2. Most of the literature surrounding UV-LED photocatalysis has picked up from the previous studies using mercury lamps although there is a notable lack of research directly comparing light sources for the photocatalytic degradation of NOM. Instead, most of the

cutting-edge LED-based research is split into a few different avenues including; hybridised photocatalytic filtration systems,^{173, 209, 211, 216 125, 217} novel photocatalysts,²¹⁸⁻²²⁰ and the mitigation of photocatalyst fouling.^{146, 160, 171}

Table 2.2 - State-of-the-art TiO₂-based photocatalytic NOM removal methodologies.

Water matrix	Catalyst type	Reaction time	Irradiation source	Other operating parameters	Removal efficiency	Reference
Suwannee River NOM solution (SRNOM), Sand filter effluent of a Beijing water (SFEB) treatment plant	Ceramic membranes functionalised with titanium dioxide graphene oxide (TiO ₂ -rGO)	3 h	275, 300, and 365 nm UV-LEDs	TOC _{SRNOM} = 5.5 mg/L, TOC _{SFEB} = 2.3 mg/L, pH = 7.5	25%	Li et al. ²¹⁷
Suwannee River NOM solution (SRNOM)	Silver-doped TiO ₂ (Ag-P25)	1 h	405 and 365 nm UV-LEDs	Ag-P25 = 0.1 g/L pH = 8–8.5	UV254 = 77% DOC = 30%	Fattahi et al. ¹²⁵
Humic acid solution	P25 TiO ₂	3.4 min	365 nm LED array	P25 = 0.1 g/L	UV254 = 56.9%	Liu et al. ²²¹

					DOC = 58.1%	
Humic acid solution	P25 TiO ₂	1 h, multiple cycles	365 nm LED	TiO ₂ = 1 g/L	-	Yang et al ²²²

Currently, although studies using a variety of water matrices have been investigated, there remains a lack of definitive knowledge on how the removal of NOM using LED photocatalysis is directly affected by the complexity of a water matrix and how this complexity impacts the operational parameters of NOM degradation. Chapter 4 explores the use of different water matrices and process conditions and the implications for photooxidative degradation of natural organic compounds in an industrial water treatment setting.

2.8 State-of-the-art water disinfection by LED photocatalysis

Most of the research surrounding photocatalytic disinfection is focused on the development of visible light photocatalysts for use in solar-based water treatment scenarios. Subsequently, a very small proportion of literature is focused on UV-LED based disinfection using photocatalysis. This is most likely explained by the reasoning that, given the choice of artificially irradiated disinfection systems, UVC germicidal lamps are a more practical standalone setup given the lack of catalyst required and a much higher rate of disinfection. While the majority of photocatalytic disinfection research is focused on improving solar-based systems, there has been an increase in interest in recent years for LED-driven photocatalysis. This is due to its efficacy against stubborn pathogens of high concern and the lack of chemical

disinfectants required. These disinfectants, such as chlorine or chloramine, require significant health and safety measures and are therefore less suited for smaller-scale point-of-use applications in drinking and wastewater applications.

Table 2.3 - State-of-the-art photocatalytic disinfection methodologies.

Target pathogen	Catalyst type	Reaction time	Irradiation source	Other operating parameters	Disinfection efficiency	Reference
Human adenovirus type 2 (HAdV-2, ATCC number VR-846)	metal-free heterojunction consisting of carbon, nitrogen, and oxygen (CNO)	8.4 h hydraulic retention time	White Vis-LED	CNO = 320.30 mg/L	5-log	Zhang et al. ²⁰⁹
Multi-drug-resistant coliform bacteria Klebsiella pneumonia	Hybrid CdS nanorods ultra sonification reactor	20 min	Blue LED (220 W)	6-log CFU/mL starting concentration CdS = 250 mg/L	Total	Mukherjee et al. ²²³
<i>E. coli</i> strain CGMCC 1.3373	TiO ₂ anatase	40 min	265, 275, 310 and 365 nm	TiO ₂ = 1 g/L	365 nm = 4-log	Nyangaresi et al. ¹⁹⁶

Studies investigating the use of photocatalytic disinfection in a few water matrices have been investigated, however, a significant gap remains in the lack of definitive knowledge on how photocatalytic disinfection is directly affected by the complexity of a water matrix and how this complexity impacts the operational parameters of NOM degradation. Chapter 5 explores what influences the use of different water matrices and process conditions in UV-LED photooxidative deactivation of microorganisms and the possibilities for application as an industrial water treatment polishing step.

2.9 State-of-the-art environmental sustainability and life cycle assessment in photocatalytic water treatment

Of the various methodologies used to assess the environmental sustainability of a product or process, the most commonly utilized are multi-criteria analysis (MCA), environmental performance indicators (EPIs), and life cycle assessment (LCA). Of these methodologies, there is a significant amount of research dedicated to the environmental impact of photocatalytic water treatment,^{124,224,225} perhaps because of the economic and performance issues holding it back from widespread implementation in industry. LCAs help highlight contributing factors to the problems factoring in the entire process, a recent example of this being an investigation by Foteinis et al.²¹⁴ that assessed the removal of 1 mg 17 α -ethynylestradiol (EE2), a commonly occurring micropollutant and endocrine disrupting chemical, per litre of wastewater using several common AOPs. The findings of this paper suggested that the environmental sustainability of AOP water treatment was directly proportional to treatment efficiency but inversely proportional to treatment time. This was attributed to the large energy input per unit time as electricity consumption was the main environmental contributor in all the light-driven processes that were included.

The big-picture approach of LCAs can also help determine optimum conditions for a reaction by balancing the efficacy with its environmental impact, such as this study by Costamagna et al²²⁶. This work suggested a photocatalyst concentration that optimised the environmental impact over the efficiency of the reaction. It was calculated that despite the highest degradation efficiency occurring with 1700 mg/L of cerium-doped zinc oxide from nitrate precursor, a photocatalyst concentration of 800 mg/L may be preferable to reduce the overall environmental impact. This was a compromise between the reaction rate and the input of electrical energy and the synthesis of the material. This is a result that may not be immediately clear without the utilisation of an LCA.

Other recent examples of using an LCA to quantify conditions that are important for the scale-up of photocatalytic methods would be assessing whether or not a modified catalyst's improved efficacy is worth the environmental footprint of the additional steps taken to modify said catalyst; defining the turning point of recycling or reuse that a process becomes environmentally more viable.

Although there are a multitude of investigations into photocatalysis for water treatment, the majority of these papers focus on the removal of specific micropollutants rather than general NOM. Furthermore, the use of immobilised over suspended photocatalysts is almost taken for granted due to the practicalities in reactor design and operation. This comparison with catalyst states for photocatalytic NOM removal is a missing gap that could prove to be an important study to consider when designing a water treatment works. Chapter 6 explores this comparison as well as what scenarios would influence the sustainability of the catalyst state by quantifying the whole life cycles of these reactor types.

3 Instrumentation and Experimental Techniques

This chapter describes the general analytical techniques and materials used to collect the data presented in this thesis. The first section details how the catalysts used in all experiments throughout this thesis were produced, including the modifications made to the catalyst compared in Chapters 4 and 5. The second section then goes on to describe the various water matrices used in all experiments of this thesis including their collection sites. Thirdly, the materials used in the bacterial tests shown in Chapter 5 are detailed. Fourthly, the methodology used for all the experiments in this thesis are detailed including the analytical techniques and kinetic models used to describe results. Finally, this chapter describes the Lifecycle analysis software used to generate the results in Chapter 6.

3.1 Preparation of Catalyst Coatings

Commercially bought TiO_2 , Aeroxide P25 (P25) from Evonik Industries, was used to prepare the catalysts used in this thesis. The full details of the catalysts used and prepared in this thesis are detailed in Table 3.1 below.

Table 3.1 - Photocatalysts and their assigned names. The preparations of BTO²²⁷ and C-TiO₂-TiCl₄²²⁸ were characterised by Odling et al.

Catalyst	Description	Catalyst properties	Bandgap
TiO ₂ slide	P25 TiO ₂ immobilised on glass via calcination	Particle sizes of 20–30 nm	3.18 eV
Aeroxide P25 (P25)	P25 catalyst supplied by Evonik industries	Particle sizes of 21 nm; S _{BET} = 50 ± 15 m ² g ⁻¹ ; anatase: rutile 80:20	3.18 eV
BTO	Bismuth titanate / TiO ₂ composite material prepared via SILAR method. Supported on a glass slide.	BTO forms mostly from the [101] plane of anatase TiO ₂ ; particle sizes of ~50–100 nm.	2.98 eV
C-TiO ₂ -TiCl ₄	Carbon-coated TiO ₂ glass slide with a TiCl ₄ treatment.	Particle sizes of (5 – 10 nm) from TiCl ₄ hydrolysis.	-
TiO ₂ slurry	P25 TiO ₂ suspended in the water matrix, without a support medium	Particle sizes of ~25 nm; S _{BET} = 54–55 m ² g ⁻¹ ; anatase: rutile 80:20	3.18 eV

3.1.1 General slide coating

During the initial stages of research, several techniques were explored for the preparation of catalyst-coated slides. Sanding and ozone/UV treatment of glass slides were tested to best prepare glass surfaces for catalyst immobilisation until chemical etching was found to be the

most consistent and stable preparation method. Several formulas for a doctor blading technique were also tested but none were found to produce a coated slide stable, consistent or thick enough to continue testing. For this purpose, an immersion coating technique was used to prepare all films on glass-supported media to ensure consistency. This coating method suspends P25 TiO_2 particles in a sol system and is well-known in the literature. The technique used for all initial catalyst coatings is outlined as follows:

Etching: Etching enhances adhesion to the glass surface and therefore ensures a good surface area and amenable surface structure between the surface and the catalyst coating. Initially, all glass slides are placed in an appropriate plastic container with a solution of potassium bifluoride (10 mg/mL). The glass is then left like this for four days with occasional agitation. Other alternatives to this step were initially tested due to the risk involved with handling potassium bifluoride and its by-product hydrofluoric acid.

Cleaning: After four days, the solution is neutralised with calcium carbonate and the glass is rinsed with de-ionised water and sonicated for 15 min. This rinsing step is then repeated twice and then once more using ethanol instead of water. The etched glass is then dried at 100 °C for 30 min on a hotplate.

Conditioning: Once the glass is cooled to room temperature, a final chemical pre-treatment step is performed. The glass is placed in a beaker filled with a solution of TiCl_4 (40 mM), covered, and then heated to 70 °C for 30 min. This is done to activate the glass surface further to allow for improved bonding of the TiO_2 to the surface and help prevent charge recombination at the glass-catalyst interface. The glass is then rinsed several times in water and ethanol as done in the cleaning step and once again dried on a hotplate. Once dried, the treated glass is heated to 500 °C for 30 min in a muffle furnace. These steps were typically

done in bulk to avoid excessive risk due to the potassium bifluoride, as well as the long processing times.

Coating: A suspension of the selected catalyst powder (P25) is prepared by mixing titanium butoxide, $\text{Ti}(\text{OBu})_4$, (1 mL) with n-butanol (20 mL) and HCl (0.23 mL, 37%) under vigorous stirring. Afterwards, the P25 catalyst (0.667 g) is added whilst maintaining vigorous stirring to produce the desired catalyst suspension. This suspension is then left to stir overnight and sonicated prior to coating to prevent any aggregation. The fully etched glass support is then immersed in the suspension and agitated for 5 min, before being removed and drying at 150 °C to remove solvent. The films are then sintered at 500 °C for one hour in a muffle furnace to enhance adhesion between the particles and the support. The sintered catalyst slide is then allowed to cool slowly to avoid thermal shock. The best results were achieved when the glass slide was coated and sintered three times to build up a thick enough film.

3.1.2 Modified catalyst slide preparation

C- TiO_2 - TiCl_4 synthesis was conducted according to the method described by Odling et al.²²⁸ and is summarised briefly here:

P25-coated slides were dipped into catechol (5 mg/mL) for 30 min, this saw the usually white TiO_2 surface turn a pale yellow. The slides were then rinsed thoroughly with de-ionised water before being placed in a solution of titanium tetrachloride (40 mM) and heated at 65 °C for 30 min. Afterwards, the slides were washed thoroughly once again with de-ionised water and allowed to air dry before heating under N_2 (10 min at 200 °C, 30 min at 300 °C). This was achieved by placing the slides on a hotplate with a large, upside-down, glass funnel covering the whole slide. This funnel was then connected to a nitrogen line and kept under positive pressure throughout the treatment. This oxygen-less heat treatment saw the yellow slides

darken to a brown colour, indicating the thermal decomposition of the catechol-TiO₂ surface complex.

BTO-TiO₂ synthesis was conducted according to the SILAR method described by Odling et al.²²⁷ and is summarised briefly here:

P25-coated slides were dipped for 300 sec into a beaker containing an aqueous solution of Bi(NO₃)₃ (5 mM). The slide was then washed with de-ionised water for 300 sec, then dipped into a beaker containing an aqueous solution of KBr (5 mM) for 300 sec, before finally washing with water for a further 300 seconds. This entire process of dipping the slides into Bi(NO₃)₃, washing, KBr, washing, was repeated a further 8 times to give 9 total SILAR cycles. The coated glass slide was then annealed at 600 °C in a muffle furnace for 1 hour and allowed to cool to room temperature slowly.

3.1.3 Catalyst characterisation

TiO₂ slide, C-TiO₂-TiCl₄, and BTO characterisation was conducted by Odling et al.²²⁸ and is summarised briefly here:

The TiO₂ slide and C-TiO₂-TiCl₄ samples were found to be semi-transparent, and therefore UV/Vis transmission experiments were performed to ascertain the film's absorption characteristics as shown in Figure 3.1 below. It was noted that C-TiO₂-TiCl₄ displayed superior visible-light absorption in comparison to TiO₂ slide. The following Figures also include data relating to other catalysts such as TiO₂-TiCl₄, C-TiO₂, BTO x3, BTO x5, and BTO x7. These catalysts are not relevant to this Thesis.

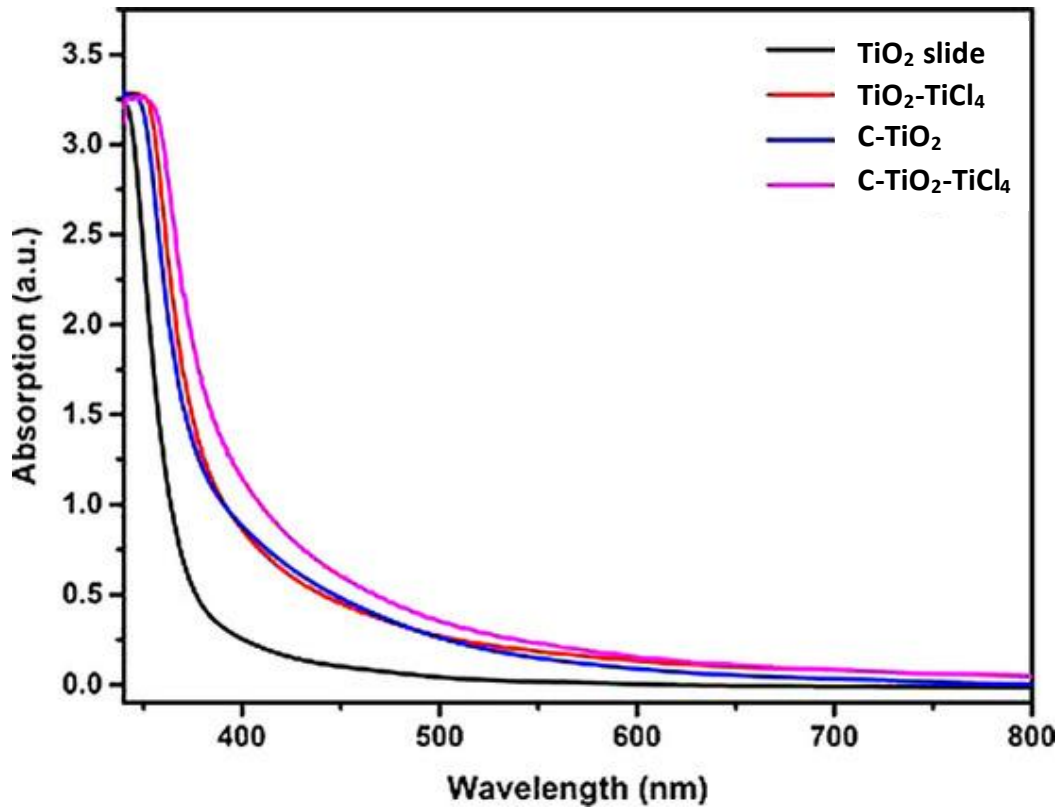


Figure 3.1 - UV/Vis absorption characteristics of TiO₂ and C-TiO₂-TiCl₄ photocatalyst films.²²⁸

The crystal structure of a material can be helpful for explaining the performance of a photocatalyst. A common method for determining this is X-ray diffraction (XRD) which utilises X-ray beams with wavelengths similar to the spacing between crystal planes. The incident beams can then interact with diffracted and reflected beams, leading to interference patterns that can be interpreted to learn about the crystal spacing. Bragg's Law is used to obtain this information, which can be expressed through **eq 3.1** as:

$$n\lambda = 2d_{hkl} \sin\theta \quad (\text{eq 3.1})$$

Where n is the diffraction order ($n=1$ is first order, $n=2$ is second order, $n=3$ is third order), and h , k and l are Miller indices which define the crystal plane. θ is the angle of incidence of the X-ray beam.

X-ray diffraction traces of TiO_2 slide, $\text{C-TiO}_2\text{-TiCl}_4$, and BTO are given in Figures 3.2 and 3.3 below.

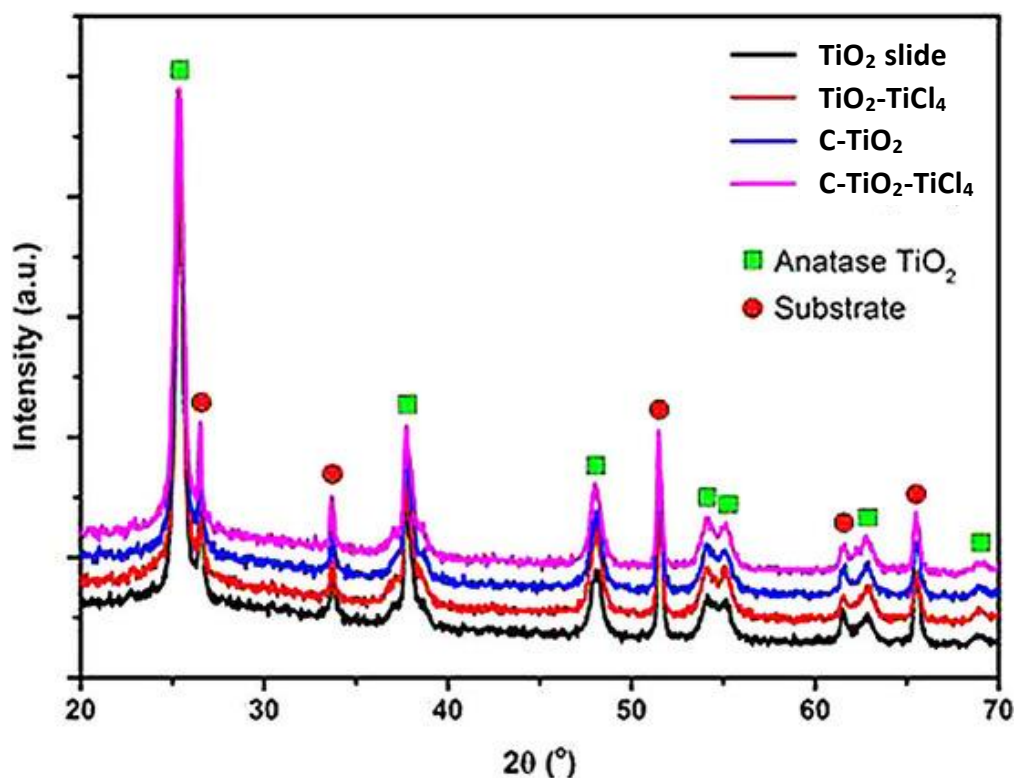
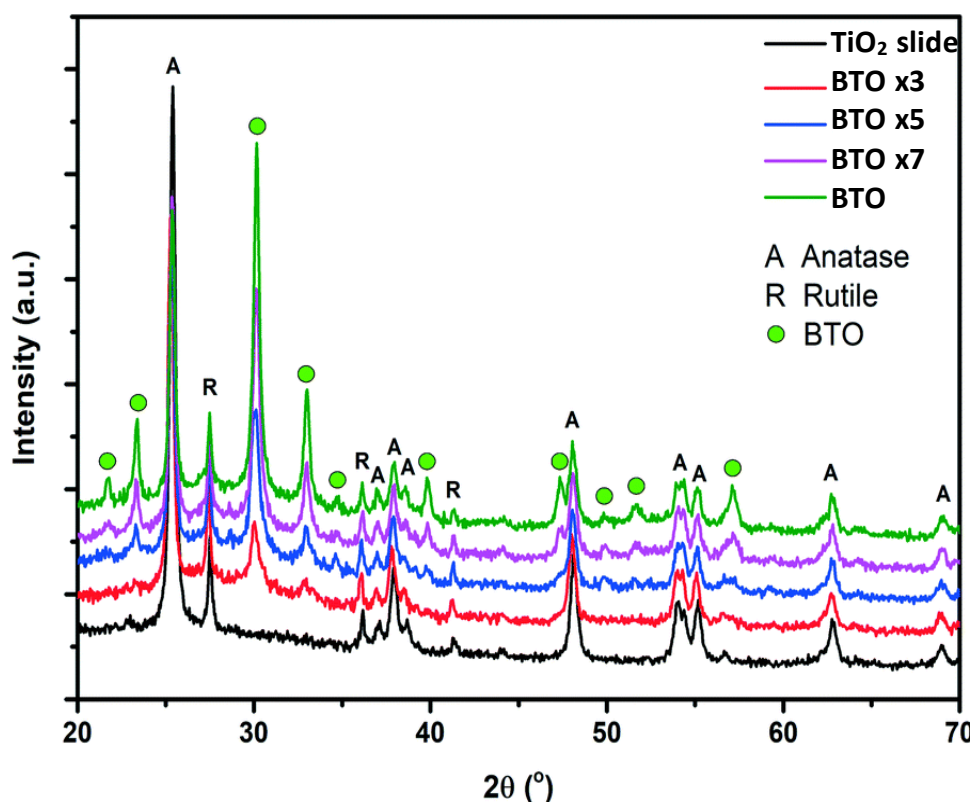


Figure 3.2 - XRD traces of TiO_2 slide and $\text{C-TiO}_2\text{-TiCl}_4$ photocatalyst films.²²⁸

Several peaks relating to the reported 2θ values for anatase TiO_2 , and the fluorine-doped tin oxide (FTO) glass substrate are identified. Upon modification of the film, no new peaks were found, suggesting either amorphous materials and/or their presence in too low a concentration to be detectable by XRD analysis. The crystallinity of the underlying TiO_2 film is found to be largely unaffected by the modifications made, keeping high crystallinity after modification.



X-ray diffraction (XRD) traces of TiO_2 and BTO samples are given in Figure 3.3. The BTO used in this Thesis was synthesised using 9 cycles of SILAR coating and is labelled as BTO, other iterations using various numbers of cycles of SILAR are also shown in Figure 3.3 but are not relevant to this Thesis. Upon SILAR modification and annealing, a variety of new peaks appeared when compared to the pristine TiO_2 slide, which can be assigned to the orthorhombic Aurivillius structure of BTO. These peaks were found to increase in intensity as the number of SILAR cycles increased, corresponding to the formation of larger amounts of BTO. Two major peaks were observed at 2θ values of 30.2 and 33.0 corresponding to the [171] and [200] planes of BTO respectively. Other bismuth titanate phases such as $\text{Bi}_2\text{Ti}_2\text{O}_7$ and $\text{Bi}_{12}\text{TiO}_{20}$ have been previously reported, however peaks for these phases were not observed, indicating a single pure phase of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. The intensity of the major TiO_2 peaks were found

to decrease with increasing numbers of SILAR cycles, with some decreasing more than others, indicating the conversion of some TiO₂ into BTO.

UV-vis diffuse reflectance spectroscopy (DRS) can be used for estimating the band gap (E_g) of semiconductor materials, an important parameter that can explain many of the semiconductor's properties. DRS uses the principle that a sample irradiated with light will absorb light corresponding to the transition of electrons from the valence band to the conduction band. Light reflected off of an irregular surface will result in a diffuse reflectance and cause scattering of the light in many directions. The technique measures the reflectance of incident light so as the scan proceeds and the sample absorbs photons, there will be a consequent drop in reflectance. From this, the band gap can be calculated using a Tauc plot, which utilises the Kubelka-Munk function, $F(R_\infty)$:

$$F(R_\infty) = \frac{(1-R_\infty)^2}{2R_\infty} = \frac{K}{S} \quad (\text{eq 3.2})$$

Where R_∞ is the reflectivity of the sample as a percentage, K is the absorption coefficient and S is the scattering coefficient at a particular wavelength of incident light. From this, the Tauc plot can be produced from the following equation:

$$(F(R_\infty)h\nu)^{1/n} = A(h\nu - E_g) \quad (\text{eq 3.3})$$

Where h is Planck's constant (6.626×10^{-34} Js), ν is the frequency of incident light (s^{-1}), A is the absorption constant, and n describes the type of band gap the semiconductor possesses. By plotting $(F(R)h\nu)^{1/n}$ as a function of $h\nu$ (which gives the photon energy in electron volts), the band gap can be extrapolated from the gradient of the linear region of the plot.

The light absorbing properties of BTO was analysed using UV-visible DRS with the data being converted into a Tauc plot, as shown in Figure 3.4 below.

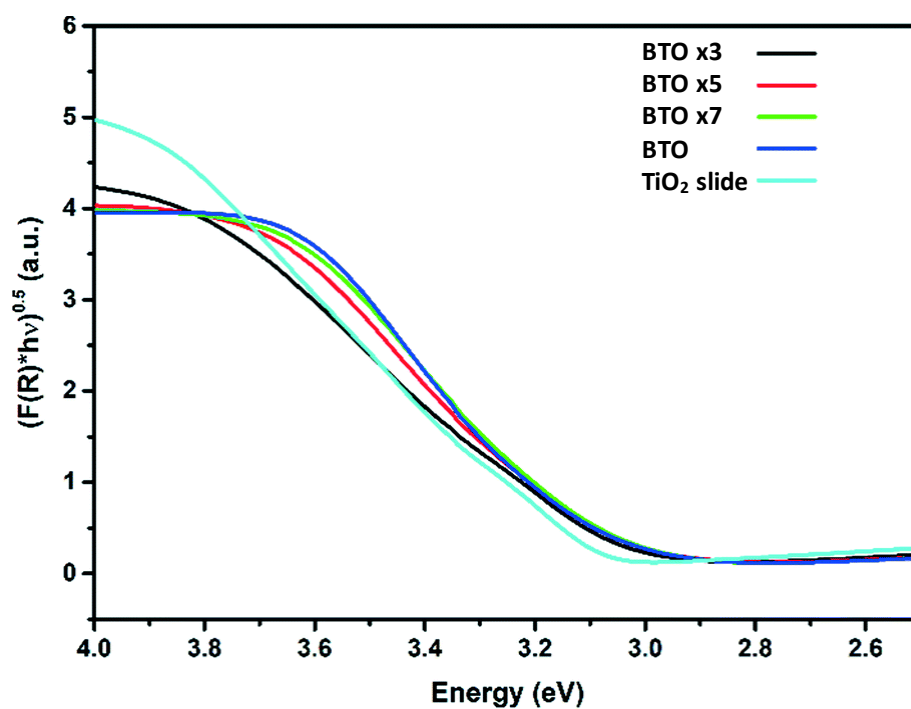


Figure 3.4 - Tauc plots of TiO₂ and BTO derived from diffuse reflectance measurements.²²⁷

The BTO exhibited a band gap of 2.98 eV when compared to the 3.18 eV band gap of the TiO₂ slide.

3.2 Water matrices

The following water matrices shown below were used to investigate photocatalytic processes during this thesis.

Table 3.2 – Water matrices and their assigned names.

Water matrix	Description	Physicochemical properties
Ultrapure water (UPW)	Deionised and ultrafiltered water with a resistivity of 18.2 MΩ·cm	pH=7.1; $abs_{254}=0.0$; TOC= 0.10 mg/L; turbidity=0 NTU
Pateshill water (SW1)	Filtered water from Pateshill water treatment works reservoir (site 1)	pH=8.2; ORP=-93 mV; $abs_{254}=0.5416$; TOC= 12.71 mg/L; turbidity=3.2 NTU
Blackford water (SW2)	Filtered water from Blackford Glen, a small running stream (site 2)	pH=8.1; $abs_{254}=0.1316$; TOC=6.437 mg/L; turbidity=2.8 NTU
Carron valley water (SW3)	Filtered water from Carron Valley Water Treatment Works reservoir (site 3)	pH=7; $abs_{254}=0.215$; TOC=6.04 mg/L; turbidity=2.1 NTU

Commercially available humic acid (CAS - 1415-93-6) from Alfa Aesar was used to produce a humic acid stock solution by dissolving a prescribed amount of HA in 0.1M NaOH and further diluting it in ultrapure water. As NOM has such diverse character depending on multiple factors, it is not possible to define an accurate value for the molar extinction coefficient (ϵ) when comparing different water sources or even the same water source collected at different times. This is why commercial humic acid is often used to make synthetic raw water with reliable results.

Site 1 - Pateshill

Pateshill raw water was collected from the influent flow of the Pateshill water treatment works, shown in Figure 3.5, during April 2021 where it was subsequently processed in the Edinburgh University lab space by filtering through 0.45 μ m PVDF filters to remove any suspended solids. This water was then kept refrigerated in between experiments in a sealed borosilicate glass container. The general physicochemical properties of this undiluted university-treated water are shown above in Table 3.2.



Figure 3.5– An aerial map of Pateshill water treatment works and its main water source Cobbinshaw Reservoir.

Site 2 – Blackford

Blackford raw water was collected from Braid Burn, a stream running next to the University of Edinburgh's Kings building campus (shown in Figure 3.6), during August 2021 where it was subsequently processed in the Edinburgh University lab space by filtering through 0.45 μm PVDF filters to remove any suspended solids. This water was then kept refrigerated in between experiments in a sealed borosilicate glass container. The general physicochemical properties of this undiluted university-treated water are shown above in Table 3.2.



Figure 3.6 – An aerial map of Blackford and the site's water source Braid Burn

Site 3 – Carron Valley

Carron Valley raw water was collected from the influent flow of the Carron Valley water treatment works, shown in Figure 3.7, during October 2021 where it was subsequently processed in the Edinburgh University lab space by filtering through 0.45 μm PVDF filters to remove any suspended solids. The surface water was then acidified using HCl to $\text{pH} \sim 2$, degassed with N_2 gas then neutralised with NaOH back to $\text{pH} 7$. This was to remove any carbonates or bicarbonates that were present in the raw water that could interfere with photocatalytic degradation. Water was then kept refrigerated in between experiments in a sealed borosilicate glass container. The general physicochemical properties of this undiluted university-treated water are shown above in Table 3.2.

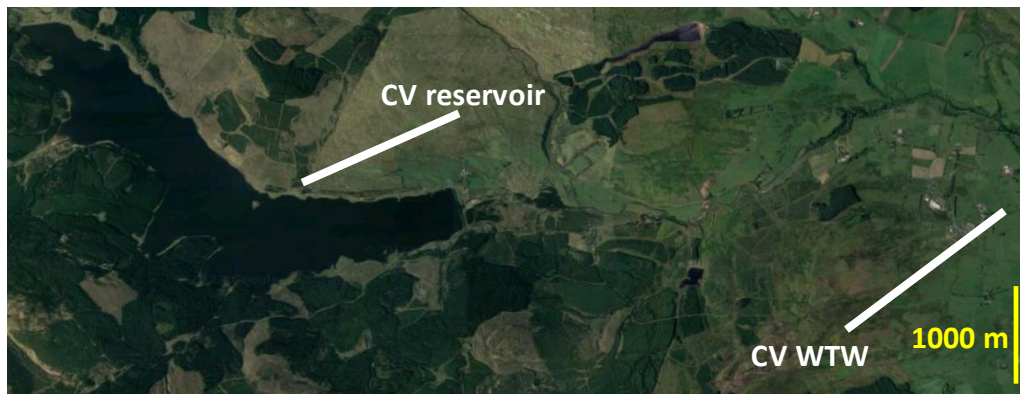


Figure 3.7 – An aerial map of Carron Valley water treatment works and its main water source Carron Valley reservoir.

3.3 Materials for Microbiological Tests

E. coli was selected as a test specimen for the microbiological tests done for this thesis due to its common use as a faecal contamination marker. *Escherichia coli* (Migula) Castellani and Chalmers (EMG 2:K (lambda)), K-12 wild type was used for these tests due to its safety and well-understood characteristics. This *E. coli* sample was received in a freeze-dried state and was revived and stored in Luria-Bertani (LB) broth (from Sigma) (25 g/L).

Samples were propagated using Brilliance *E. Coli* Coliform Selective Medium (from OXOID) (28 g/L). This medium uses two enzyme substrates to differentiate between *E. coli* and other coliforms. One chromogenic substrate is cleaved by glucuronidase, which is specific to *Escherichia coli*. The other chromogenic substrate is cleaved by galactosidase, an enzyme produced by most coliforms. This means that *E. coli* colonies were marked as purple, as they can cleave both the chromogenic substrates and coliforms presented as pink colonies, as they are only able to cleave the galactosidase chromogen. This meant that contamination was more easily identified and therefore ruled out.

3.4 Photocatalytic Testing

3.4.1 Photocatalytic Tests

Following the synthesis of a selected catalyst, an investigation of their performance under various conditions was undertaken to assess their suitability for industrial applications. Depending on the stage of materials testing, the scale, and thus experimental set-up, of the photocatalytic testing was adjusted. For initial screening on the smallest scale, a 3X1 cm glass slide was placed in a cuvette (4 cm³) as the reaction vessel, see Figure 3.8A, such that it can be transferred directly to a UV-Vis spectrometer for analysis. For larger-scale setups (Figure 3.8B), the LED assembly was placed directly above the reactor and a quartz protective plate was placed between them as shown in Figure 3.8. Immobilised catalysts were coated on a 7.5x2.5 cm glass slide and then placed in a glass dish (400 cm³) with agitation so that water moved but the slides remained still, and any suspensions used didn't settle out of solution.

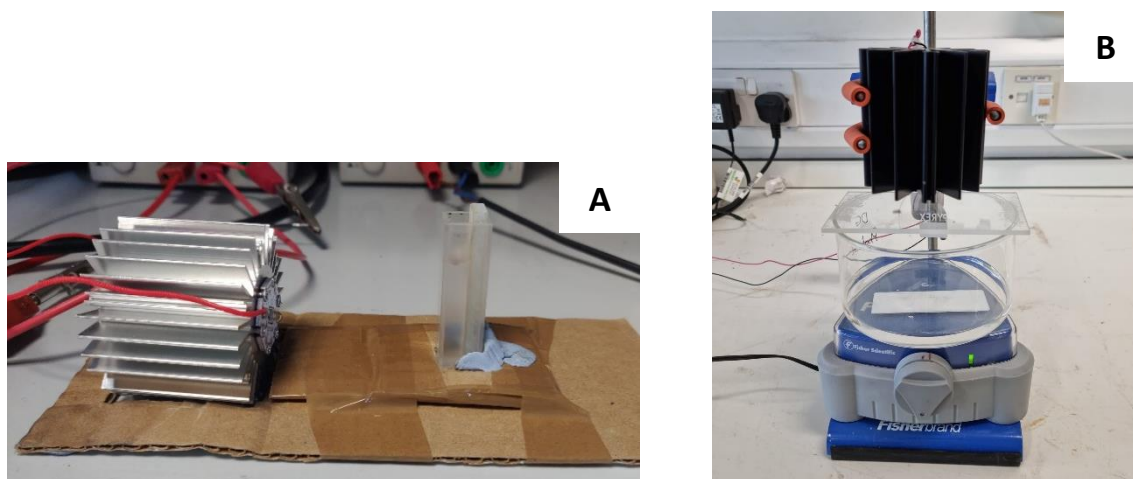


Figure 3.8 – LED reactor setups for (A) small-scale testing, and (B) larger-scale testing.

Experiments were performed in batch-operated photoreactors at a larger lab scale using an indium gallium nitride (InGaN) UVA emitter (UVA-LED; $\lambda = 365 \text{ nm}$; LZ4-00U600, LED Engin) providing continuous irradiation. The UVA emitter was mounted onto a heat sink (588-SV-LED-176E, Ohmite S Series) to prevent radiant flux decrease due to temperature rise. The LED assembly was placed directly above the reactor and a quartz protective plate was placed between them (Figure 3.8B) to prevent particulates from falling into the reaction mixture. The reactor was then placed on a MaxQ™ HP Tabletop Orbital Shaker at 40 rpm.

Both set-ups were covered with an aluminium shield to prevent light diffusion out of the reactors and minimise penetration of ambient light. LEDs were driven by an electrical power of 11 W and were connected in series to a DC power supply. The irradiance was measured with a Labsphere spectral irradiance receiver head (E1000), and it was found to be 1005 W/m^2 .

At the beginning of each experiment, the tested reaction solution was covered in the reactor for 30 min to reach equilibration of adsorption-desorption of organics onto the catalyst surface. The LED was then switched on, initiating the photocatalytic redox reactions as described. During regular UV/Vis measurements, the LED was switched off thus halting the reaction and a small aliquot was taken and placed in a clean cuvette for measurement, after which the sample was placed back in the reactor and the reaction was allowed to proceed. Samples were taken and measured for UV-Vis spectroscopy at 254 nm to follow the decrease in organics concentration during treatment but also measurements included TOC and assessing inactivation of microorganisms.

As a comparison to commercial large-scale photocatalytic reactor systems, a Puralytics Shield 1500 was tested for its capabilities, as shown in Figure 3.9. The Puralytics process uses UVA

LEDs to excite a nanotechnology mesh which drives light-activated treatment processes including AOP. The manufacturer states that the reactor is rated for water production between 0.5 – 3.9 L/min with a pressure drop of 13.8 - 48 kPa within these rates whilst consuming 570 W. The reactor holds and treats 500 cm³ at any given time. A UVC germicidal lamp is employed right before the effluent exit to ensure high disinfection rates.



Figure 3.9 – Puralytics Shield 1500 reactor

3.4.2 UV-Vis Absorption Spectroscopy

UV-Vis spectroscopy was the primary method used to measure the concentration of NOM during photocatalytic degradation reactions. These measurements were taken using a

Shimadzu UV-Pro 1800 instrument using UV-Pro software set between 253 nm and 255 nm to use the aromatic character of NOM as a marker for its concentration as described in section 2.1.3. The concentration of NOM can be calculated with UV-Vis spectroscopy by using the Beer-Lambert Law:

$$A = \varepsilon cl \quad \text{(eq 3.4)}$$

Where A is the absorbance of light (dimensionless), ε is the molar extinction coefficient ($\text{L mol}^{-1} \text{cm}^{-1}$), c is the concentration of the solution (mol L^{-1}), and l is the path length of light through the sample (cm). Change in absorbance is also a common metric used to show photocatalytic degradation, given as C_t/C_0 where C_t is the absorbance at a given time point and C_0 is the initial absorbance. This ratio can be used to measure concentration change since absorbance is directly proportional to the concentration as the reaction proceeds. This is shown with dilution calibration tests where absorbance is plotted for the same sample over the expected concentration range to demonstrate a linear relationship between absorbance and concentration, as shown in Figure 3.10.

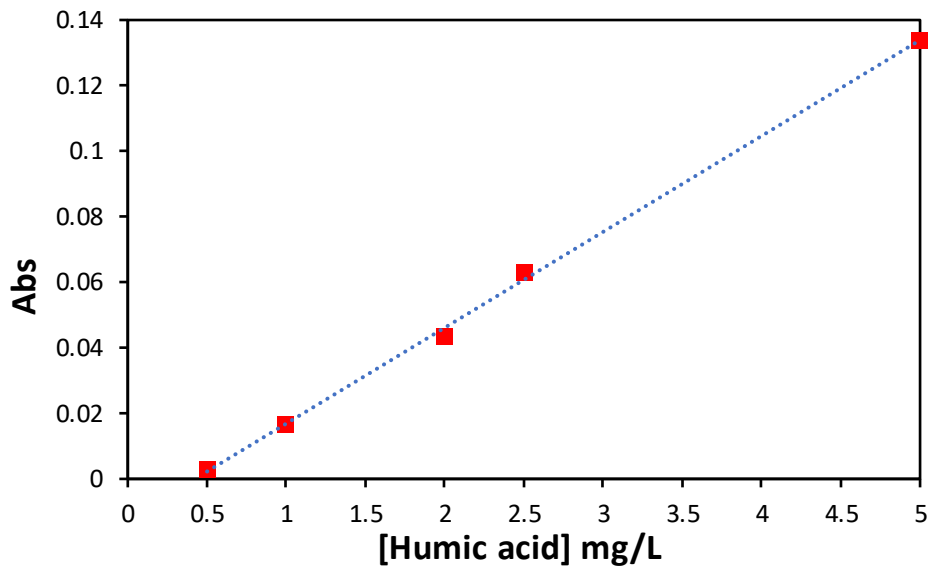


Figure 3.10 – Absorbance at 254 nm vs the concentration of commercial humic acid solution

Degradation efficiency can also be shown by comparing the final concentration of NOM to that of the initial concentration. This is simply presented as a percentage loss of the NOM and is given by:

$$\text{Degradation efficiency} = \left(1 - \frac{c_t}{c_0}\right) \times 100 \quad (\text{eq 3.5})$$

3.4.3 Total organic carbon (TOC)

TOC was measured with a Shimadzu TOC-VCPH analyser with the non-purgeable organic carbon (NPOC) mode. This mode acidifies samples with HCl and then sparges with N₂ before analysis to remove inorganic carbon such as carbonates and bicarbonates. The sample is then heated to 680 °C with a platinum catalyst with oxygen to undergo complete combustion. The resultant CO₂ can be quantified by an infrared gas analyser (NDIR) which is used to calculate the concentration of organic carbon in the sample.

3.4.4 Degradation Kinetic Model

A common methodology used to quantify the reaction kinetics for heterogeneous catalysis reactions is derived from the Langmuir-Hinshelwood model. Using **eq 3.6** the pseudo first-order rate constant of each reaction can be determined.

$$-\ln \frac{C_t}{C_0} = kt \quad (\text{eq 3.6})$$

Rearranging this equation means that plotting $-\ln(C_t/C_0)$ against time gives a plot where the slope can be used to estimate k , the reaction rate.

3.4.5 Microbiological Testing

The commercially acquired *E. coli* were received in a freeze-dried state and required rehydration and propagation before use. When doing this, as well as with all subsequent microbiology experiments, all equipment used was autoclaved first at 121 °C and 1 bar of pressure for 15 min. A nutrient broth (Sigma-Aldrich, 13 g/L) was made up of sterile deionised water. The freeze-dried *E. coli* sample was then added to 1.5 mL of room temperature broth which was then transferred to three sterile test tubes (0.5 mL in each). Each test tube was then made up to 5 mL, covered, and then incubated overnight at 37 °C. The *E. coli* solution was then transferred to small Eppendorf tubes for long-term storage in the freezer (-18 °C) in a 1:1 ratio with sterile 90% glycerol giving a medium that could then be used to spike water for disinfection reactions.

Before starting experiments, Petri dishes with nutrient agar were prepared. Following the instructions for the medium, molten media was then poured into the Petri dishes and left to cool to form the solid gel. The *E. coli* was then propagated by adding 50 µL of the stored broth

solution onto a Petri dish and incubating overnight at 37 °C. The propagated E. coli was then removed from the dish and added to 50 mL of water. This was then mixed and allowed to acclimatise to the diluted solution for 5 min after which further dilutions were made to achieve the desired starting concentration. The water sample was then used in place of the water in Figure 3.8B.

Measurements were then taken at 30-min intervals (including after a preliminary period of 30 min in the dark) by taking 200 µL of the spiked sample and spreading it on a Petri dish using an inoculation loop. Serial dilutions were also made for the sample taken at each time point to ensure the number of colonies on the Petri dish was quantifiable. Serial dilutions were made by taking 0.5 mL of the sample and adding to an aliquot of 4.5 mL sterile 0.8% NaCl solution. All dishes were then incubated overnight before counting the resulting colonies. Dishes with more than 150 colonies were not included in the data set as the error was too high. Once all of the colonies were counted, the data was converted into units of CFU / mL. For this **eq 3.7** was used:

$$Colony\ forming\ units / mL = \frac{colonies \times \frac{1\ mL}{sample\ volume}}{dilution\ factor} \quad (eq\ 3.7)$$

3.5 Life cycle assessment (LCA)

SimaPro (software package SimaPro 9.2.0.1) was chosen as the LCA software due to its broad inventory, wide use in industry/academia, and its ability to access a wide variety of sustainability impacts.

3.5.1 Impact Assessment Methods

To assess the environmental sustainability of suspended and immobilized photocatalytic NOM treatments, two of the impact assessment methods were used, IPCC 2021 and ReCiPe 2016. The IPCC method refers to climate change only, comparing processes based on CO₂ emissions equivalent to measure the impact on global warming. The ReCiPe framework is made up of a set of midpoint categories resulting in a sustainability assessment that transforms the Lifecycle impact (LCI) results into a limited number of indicator scores that are expressed per environmental impact category and as an aggregated single score.

This LCA method assesses the effects a process has on climate change by calculating a process' emissions contributing to climate change. This method uses factors set out by the Intergovernmental Panel on Climate Change (IPCC) for which it's named. This methodology evaluates the CO₂ equivalent (CO₂eq) emissions of a process with respect to a specified time parameter (20 years, 100 years, or 500 years) as different greenhouse gases vary in their lifetime. For example, methane has a relatively short lifetime, staying in the environment for about 12 years, meaning it is more prominent in the short-time perspective. Whereas longer-lasting substances, such as nitrous oxide, can stay in the environment for well over 100 years, and are therefore more prominent in long-term climate evaluations.

ReCiPe 2016 is a globally recognised impact assessment method comprising three sets of impact categories with associated sets of characterization factors for use at the normalization stage. At the midpoint level, 18 impact categories are addressed which are then collected into 9 damage pathways. At the endpoint level, the midpoint impact categories are multiplied by damage factors and aggregated into three endpoint categories.

The three endpoint categories utilised in ReCiPe 2016 are Human Health, Ecosystems and Resource Availability and are defined as:

1. Human Health - Number of years of life lost and the number of years lived disabled, combined as Disability Adjusted Life Years (DALYs). Measured in years.
2. Ecosystems - Loss of species over a certain area, during a certain time. Measured in years.
3. Resource scarcity - Surplus costs of future resource production over an infinitive timeframe (assuming constant annual production), considering a 3% discount rate. Measured in USD 2021.

3.5.2 Ecoinvent Library

The Ecoinvent 3 - allocation, cut off by classification library was used for the materials in this LCA. This method assumes that the primary production of materials is always given to the first user of the material. Once a material is recycled, that primary producer does not receive any credit for delivering the recyclable materials. Therefore, in the recycling process, recyclable materials are available burden-free and secondary recycled materials only carry impacts from recycling processes.

This investigation focused on the market for activities such as these as this more accurately depicts some of the realities of modern-day industry. A market activity includes inputs from production in several or a single country, as well as inputs from transport processes. The market processes include the product, transportation to the next user and any transport or trade losses.

3.5.3 Functional Unit

Based on the experimental data presented in Chapter 4 comparing the degradation of humic acid using immobilized and suspended TiO_2 , the treatment of 1 L of water with an initial NOM concentration of 7.8 mg/L and a final concentration of 1 mg/L was taken as a functional unit.

3.5.4 SimaPro Inventory

The weights of all the relevant lab equipment were noted and then related to the weights of the functional unit. A mass fraction was calculated whereby the reactor setups for the experimental 20 mL solution was scaled to treat 1 L and then scaled by their time used and their functional lifetime, as shown in **eq 3.5**. This gave a mass fraction for each component that treating 1L of water would essentially consume. For some of the components such as the LED, a simple multiple was taken whereby if one was required to treat 20 mL, then 50 would be required to treat 1 L. Reusability experiments were undertaken for both catalyst types and the mass fractions were calculated based on how much water a single catalyst slide could treat before no longer meeting the treatment requirements. It was assumed that the LED cover and starboard would have the same life span as the light-emitting diode itself.

$$\text{Mass fraction} = \text{mass for 1L (Kg)} \times \frac{\text{treatment time (h)}}{\text{functional lifetime (h)}} \quad (\text{eq 3.8})$$

4 LED-driven photocatalytic removal of NOM in water

4.1 Introduction

Over the past decades, the prospect of utilising photocatalysis for water treatment has slowly become closer, but never quite achieved on a large scale. A commonly mentioned disadvantage of photocatalysis in its early days was the energy-intensive black light lamps that presented a health hazard if broken near the treatment water. Now that modern UV LEDs are significantly cheaper and more efficient to run,^{229,230} photocatalysis still has not made its way into industrial water treatment plants. The aim of this study is to investigate the effects of key operating parameters on NOM degradation when using a UVA-LED photocatalytic system and to assess the overall feasibility of photocatalysis as an industrial water treatment process, giving further insights into where it fits into the drinking water treatment process. Additionally, some of the difficulties that have prevented industrial photocatalytic NOM removal from becoming a reality thus far, despite a wealth of research and many materials being developed, are discussed.

In this chapter, an initial screening of several modified TiO₂ photocatalysts took place to explore NOM removal. One modified photocatalyst investigated in this chapter was a carbon-coated TiO₂ film with a TiCl₄ treatment.²²⁸ This catalyst also showed great potential when previously investigated.²²⁸ To be more specific, the doping of chlorine into the structure resulted in a substantial increase in photocatalytic activity for the degradation of organic pollutants, disinfection of *E. coli* as well exhibiting good activity for the photoreduction of Cr^{VI} to Cr^{III}.

Also investigated are the effects of NOM present in natural surface waters. The variable complexity, concentration, solubility, and pH of NOM present in water influents add complications for use in an industrial water treatment plant. These variations, caused by seasonal changes, weather or climate change, aren't often investigated in literature which makes the implementation of LED photocatalysis difficult due to the rate and efficacy of photocatalytic processes being heavily influenced by these factors. Therefore, the added complexities of treating real surface waters compared to synthetic equivalents are investigated in this chapter.

This chapter also studies catalyst stability and reusability. Photocatalysis attracts great interest in water treatment due to the lack of consumable chemicals or equipment required. However, catalyst deactivation caused by fouling incurred during NOM treatment is a significant problem that hasn't been extensively studied. This fouling has the potential to significantly reduce the efficiency of photocatalytic water treatment meaning more regular time and energy-costly catalyst replacements or rejuvenation processes are required.

Finally, industrial water treatment often balances treatment efficacy and speed. The addition of photocatalysis into a treatment process requires efficiency high enough to warrant the additional time added to the overall process. Identification of the capabilities of one of the only commercially available pilot-scale photocatalytic reactors and the conditions necessary for efficient LED-driven NOM treatment are investigated in this chapter.

Results of this work will create important scientific knowledge on the kinetic rates of NOM degradation in real water, under an LED irradiation source and how these can be affected by altering basic operating parameters. The existence of an environmentally friendly, low-cost irradiation source with constant availability is a large technical barrier that impedes the large-

scale application of TiO_2 -mediated photocatalytic water treatment. Therefore, findings of this work can be used as a tool for researchers and water industry to further scale-up the process by choosing a setup that will enable an effective and sustainable treatment of water. Moreover, to the author's knowledge, the effects of operating parameters on the degradation of NOM in real water under UVA-LED irradiation in the presence of TiO_2 P25 suspensions or immobilised, as well as the use of BTO and C- TiO_2 - TiCl_4 for NOM degradation have not been reported in the literature yet.

4.2 Experimental

4.2.1 Materials

The materials used in this Chapter are described in further detail in Chapter 3. P25 TiO_2 was used as a suspension as well as immobilised and modified as described in Section 3.1 of Chapter 3 along with detailed descriptions of the synthesis routes. The water matrices utilised in this Chapter, described further in Section 3.2 of Chapter 3, were a mix of humic acid solutions and real waters.

4.2.2 Synthesis of Photocatalysts

Immobilised TiO_2 films on glass slides as well as their modified variants were produced according to the procedures outlined in Section 3.1 of Chapter 3.

4.2.3 Photocatalytic testing

Tests were conducted according to the procedures outlined in Section 3.4 of Chapter 3, using humic acid solutions & filtered real water as models.

4.3 Results and Discussion

4.3.1 Screening of modified TiO₂ catalysts

For the initial screening tests to ascertain which materials performed well relative to commercial standard P25 TiO₂, samples were tested as thin films on glass slides using humic acid as a raw water model. The procedure used for these tests is summarised in Section 3.4 of Chapter 3. Plots were produced of the NOM $[C/C_0]$ against time, where C is the concentration of humic acid at a given time point measured by its absorbance at 254nm, and C_0 is the initial concentration. The results are shown below in Figure 4.1. and it was found that C-TiO₂-TiCl₄ was the most promising in terms of resulting activity and experimental practicality as it required no catalyst separation process, allowing facile measurements during and after treatment.

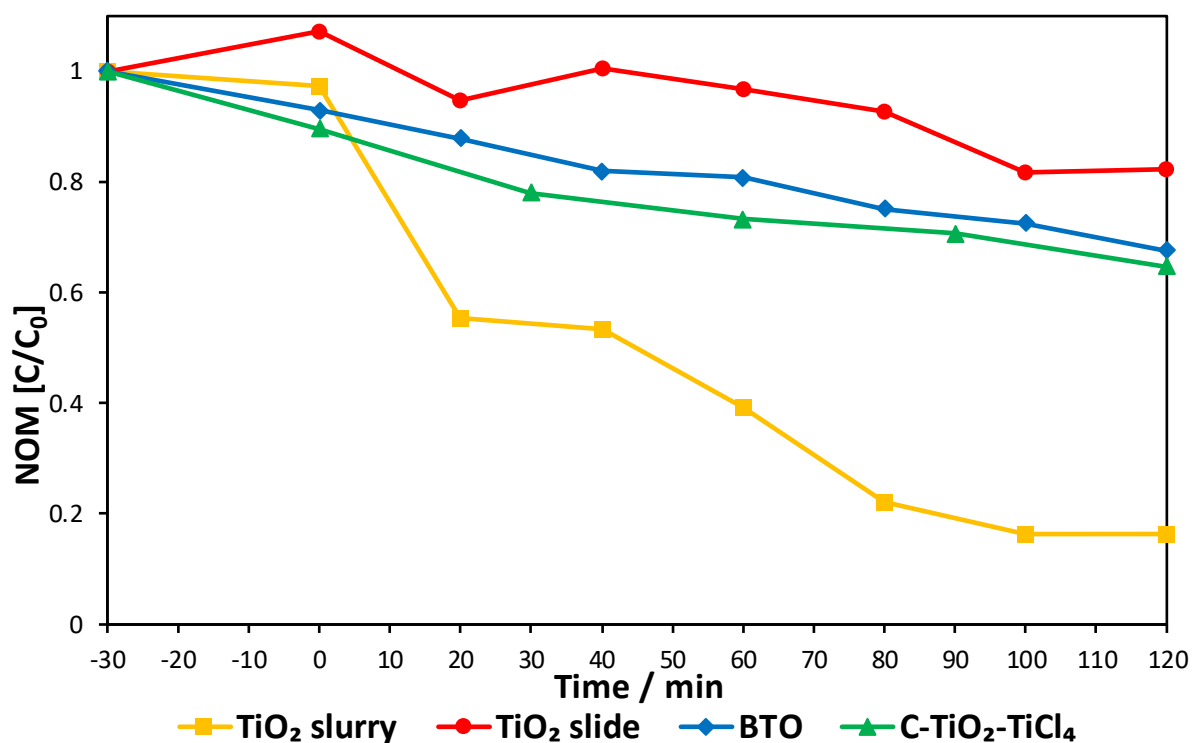


Figure 4.1 - Rate of NOM removal for various catalysts. Experimental conditions: Ultrapure water; pH ambient; 370 nm UV-LED; water volume = 3 mL; initial concentration of humic acid = 2 mg/L.

Figure 4.1 shows that, for the unmodified TiO₂ slide, NOM was reduced by 18% over 120 min followed by a significant increase in performance from the BTO and C-TiO₂-TiCl₄ which produced a 34% and 36% reduction in NOM respectively. The highest reduction was seen with the TiO₂ slurry, showing an 84% reduction in NOM after 120 min of UV-LED irradiation.

These initial tests showed an increased performance in NOM degradation for both the modified catalysts when compared to the unmodified TiO₂ slide. This enhanced degradation from the BTO and the C-TiO₂-TiCl₄ could be explained by a few possible factors. For the BTO, Odling et al.²³¹ notes BTO to have a markedly improved charge separation due to offset valence and conduction bands when composited with TiO₂. This would significantly improve

the rate of recombination due to the formation of the heterojunction with $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. This has been observed in other bismuth titanate modified TiO_2 studies where the addition of a separate semiconductor means the interface between the two materials allows charges to be separated in space, hindering recombination and increasing the efficiency of the photocatalytic process.^{161, 232, 233} Although most literature surrounding bismuth titanate / TiO_2 composite materials focuses on the catalyst's enhanced visible light performance, the use of TiO_2 – semiconductor heterojunctions to increase the catalyst performance is a common tactic meaning this result fits with literature findings.^{234, 235} The C- TiO_2 - TiCl_4 modified catalyst's enhanced performance is most likely due to factors stemming from the 2 main steps in its modification, the first being the carbon coating. As Zhang et al.²³⁶ have reported, electronic contact between a semiconductor and graphite-like carbon can result in an efficient separation of electron-hole pairs which minimise recombination, subsequently leading to higher photocatalytic activity under UV irradiation. Similarly, Odling et al.²²⁸ have proposed that the high conductivity of the carbon layer can improve photocatalytic activity by reducing charge recombination in inorganic semiconductors due to the high migration efficiency of photoinduced electrons at the graphite-like carbon/semiconductor interface. The second likely reason for this catalyst's increased performance compared to P25 TiO_2 is the TiCl_4 treatment which was believed to give a "healing" effect on the imperfections of the surface of the TiO_2 as well as doping Cl ions into the lattice as a dopant, also as suggested by Odling et al.²²⁸ This effect is perhaps minor when compared to the carbon coating as the Cl doping is more focused on the red shifting of the band gap into the visible light region it is possible that some charge recombination effects are seen by this Cl doping.²³⁷

As a preliminary test for the possible general reactor setups that could be used, a suspension of P25 TiO_2 was assessed for comparison and showed a significantly higher efficacy in humic

acid degradation when compared to the other catalysts. This increased efficiency is often observed and attributed to a much higher level of surface area in photocatalyst suspensions when compared to their immobilised counterparts.^{169, 238} This creates a reactor setup with a high ratio of illuminated catalyst surface to reactor volume and small maximal diffusional distances.^{239, 240} However, at larger scales the catalyst particles must be filtered rigorously before discharging the treated water as to reuse all possible photocatalyst as well as the many, still under investigation, impacts on human and environmental health.²⁴¹ This means that although the immobilised catalysts used here presented a significantly lower performance in NOM degradation, the advantages offered at higher scales, such as no separation step and the possibility of a continuous flow setup, keep immobilised catalyst reactors in contention. It is due to the reduced practicality of dealing with photocatalyst suspensions vs immobilised catalysts that this chapter focuses mainly on immobilised catalysts, but this comparison is discussed in further detail in Chapter 6.

4.3.3 Effect of initial NOM concentration on photocatalytic efficiency

The concentration of the target pollutant can significantly affect the performance of photocatalytic oxidation.^{242, 243} Experiments were performed to assess how the initial concentration of NOM, using either humic acid as a simulant or raw water, can affect the operation of UV-LED photocatalysis. Experiments with humic acid solutions in initial concentrations ranging from 2 mg/L to 15 mg/L were carried out and the results are shown in Figure 4.2. This range of concentrations was chosen due to this being around the average range of NOM concentrations found in surface waters globally with concentrations higher than 15 mg/L rarely being seen at inlets at Scottish Water treatment plants.^{36, 244, 245} Subsequently, experiments with raw water (RW1) were carried out where the initial reservoir

water (1:0) was compared against itself when diluted with ultrapure water at various dilution factors (1:2, 1:4) to apply the humic acid synthetic wastewater scenario to a real-world situation (shown in Figure 4.3). Experiments were carried out in triplicates to assess the repeatability of the process.

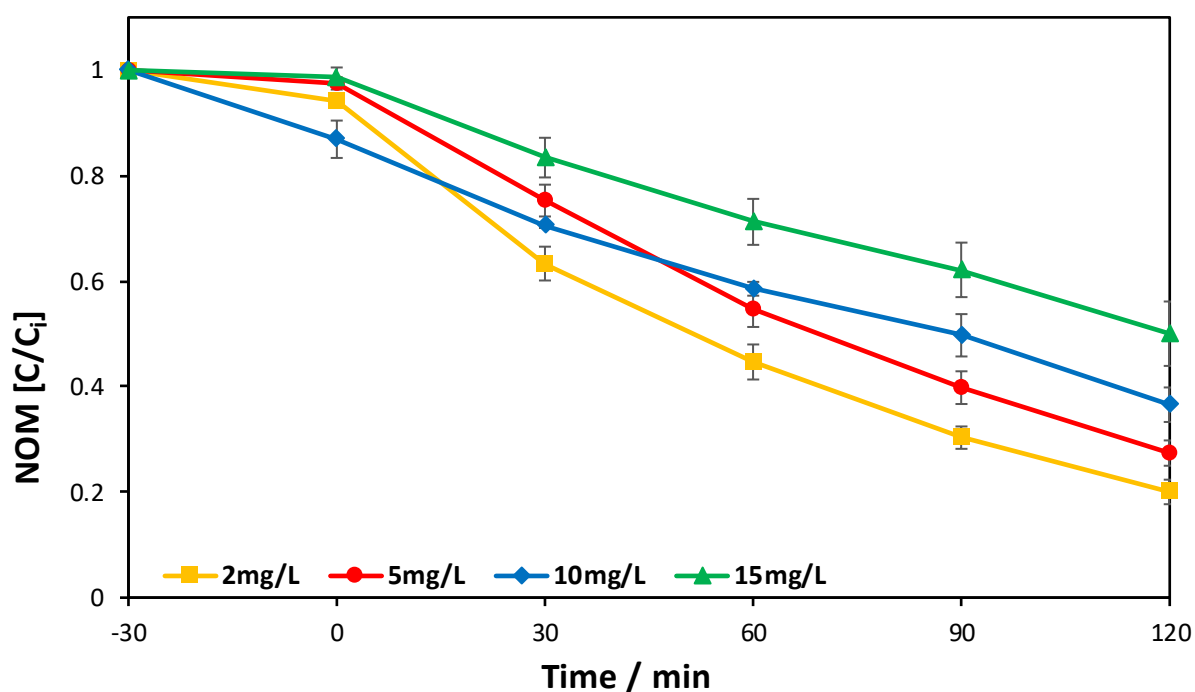


Figure 4.2 - Rate of NOM removal for various initial concentrations of humic acid. Experimental conditions: Ultrapure water; pH ambient; 370nm UV-LED; catalyst = TiO₂ slide; water volume = 20 mL.

The results (shown in Figure 4.2) show that the increased concentration of humic acid imposes a significant detrimental effect on the rate of removal of humic acid. The 2 mg/L humic acid solution underwent rapid degradation with an 80% removal of humic acid and 65% removal of TOC after 120 min treatment. The treatment of 5 mg/L humic acid resulted in a significant decrease in humic acid degradation; Humic acid degradation decreased to 73% and TOC

removal to 60%. This drop in degradation rate continued with the 10 mg/L humic acid which had 63% humic acid degradation and 49% TOC removal. The 15 mg/L concentration had the lowest rate of degradation with 31% humic acid degradation and 23% TOC removal. The pseudo-first-order kinetic rate constants for these data were calculated and are shown in Table 4.1 below.

Table 4.1 - Pseudo-first order reaction rate constants for photocatalytic NOM removal in various dilutions of humic acid.

Humic acid concentration (mg/L)	1 st order rate constant (min ⁻¹)	R ²
2 (TOC = 1.812 mg/L)	0.0128	0.9993
5 (TOC = 4.610 mg/L)	0.0106	0.996
10 (TOC = 8.997 mg/L)	0.0069	0.9879
15 (TOC = 13.628mg/L)	0.0055	0.9949

This overall trend of higher initial concentrations having lower photocatalytic degradation rates has also been observed in literature²⁴⁶ and is usually explained by generated radical concentrations being constant in all solutions, so solutions with lower concentrations of humic acid will have a higher degradation rate than a solution with a high concentration due to the relative abundance of hydroxyl radicals in the low concentration humic acid solution. More specifically, the same trend has also been seen in experiments using TiO₂ suspensions with UVC lamps by Huang et al.¹⁴⁷ who attributed the observation to a larger contribution from TiO₂ adsorption to the overall NOM removal at lower initial NOM concentrations as well

as the difference in intermediate products at different initial concentrations. However, this experiment by Huang et al.¹⁴⁷ did not compensate for differences in adsorption onto the catalyst surface with a period of dark catalyst contact as was performed in the experiment shown in Figure 4.2. Thus, while adsorption differences were likely to contribute to the results published by Huang et al.¹⁴⁷, this Thesis was able to examine the effects of initial NOM concentration, without the confounding effect of adsorption, revealing that generated radical concentrations and differences in intermediate products at different initial concentrations alone may have notable effects.

Decreasing NOM concentrations showing higher photocatalytic degradation rates has impacts on the usability of industrial-sized photoreactors for water treatment as seasonal variations and sudden changes in weather patterns can lead to large differences in the initial raw water quality.^{247, 248} These differences in organics levels for an industrial-sized photoreactor may lead to significant differences in the resulting treated water and/or required contact time. This could suggest that photocatalysis is best used as a finishing technique used later in the water treatment process, reducing the chemical load on current systems but ensuring a steady range of organics concentrations are supplied.

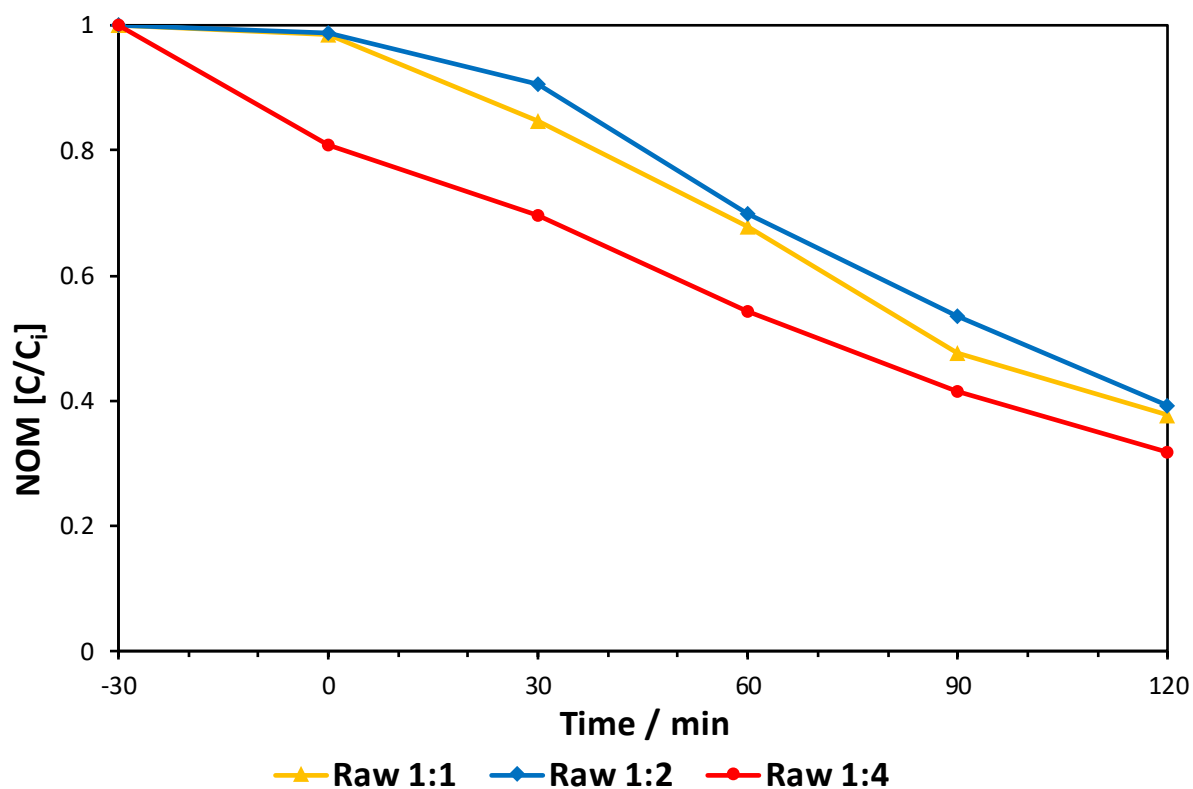


Figure 4.3 - Rate of NOM removal for various dilutions of Pateshill raw water (SW1).

Experimental conditions: Pateshill raw water; pH ambient; 370nm UV-LED; catalyst = TiO₂ slide; water volume = 20 mL.

The results, shown in Figure 4.3, show that for the undiluted raw sample 1:1, humic acid concentrations were reduced by 62% over 120 min followed by the raw 1:2 diluted sample which produced a 61% reduction in humic acid. The highest reduction was seen with the raw 1:4 sample, showing a 69% reduction in humic acid after 120 min of UV-LED irradiation. The pseudo-first-order kinetic rate constants for these data were calculated and are shown in Table 4.2 below.

Table 4.2 - Pseudo-first order reaction rate constants for photocatalytic NOM removal in various dilutions of Pateshill raw water.

Raw water dilution	1 st order rate constant (min ⁻¹)	R ²
1:1 (TOC = 12.71 mg/L)	0.0083	0.9827
1:2 (TOC = 6.889 mg/L)	0.0079	0.971
1:4 (TOC = 3.267 mg/L)	0.0079	0.9901

Figure 4.3 shows a similar rate of degradation for all three samples which was not seen in the humic acid concentration study shown in Figure 4.2 where a clear increase in degradation rate is seen at each decreasing denomination of concentration. This could be explained due to the wide array of ions present in the raw water that are not in the humic acid solution. It has been widely observed like in the work done by Subramanian et al.²⁴⁹ that many ions commonly found in surface waters have some kind of inhibitory effect on the rate of photocatalysis.²⁴⁹⁻²⁵¹ The effect of chloride is mainly due to adsorption whereas in the cases of carbonate and bicarbonate, it is due to both adsorption and their ability to act as scavengers of hydroxyl radicals.²⁵² Therefore, in waters concentrated with substances which are weakly adsorbed, the presence of chloride is more pronounced whereas with water high in strongly adsorbing species, the effect of carbonate and bicarbonate is predominant.²⁵³ This is to say, raw surface waters can vary greatly in their composition and therefore their reaction to photocatalysis depending on the time of year, location, or current weather patterns. This again suggests that photocatalysis is best suited to be placed towards the end of the water treatment process as unreliable reaction rates would matter less if the initial concentration

was lower as the total removed NOM would vary less, and the system could be perhaps more optimised for specific molecules that the current wastewater system currently has difficulty containing.

4.3.4 Effect of stirring on photocatalytic NOM degradation

Experiments were performed in an attempt to improve the performance of the TiO_2 slide catalyst and gain further insight into the impact stirring the water matrix would have for a photoreactor treating real surface water. Experiments were performed using Carron Valley surface water that had been filtered through a $0.45\ \mu\text{m}$ PVDF filter, acidified using HCl to pH ~ 2 , degassed with N_2 gas then neutralised with NaOH back to pH 7. This was to remove any carbonates or bicarbonates that were present in the raw water that could interfere with photocatalytic degradation. This was done to try to closely mimic raw water that had been through the organics removal process in a water treatment plant with the photocatalytic treatment being a polishing process. Reactions were then set up as shown in Section 3.4 of Chapter 3 with a test being performed with the addition of an orbital mixer, placed so that the distance between the light source and the catalyst slide was maintained, unobstructed and identical to previous tests. 40 rpm was chosen as this was the highest speed that did not cause any displacement of the catalyst slide. The subsequent results are shown in Figure 4.4.

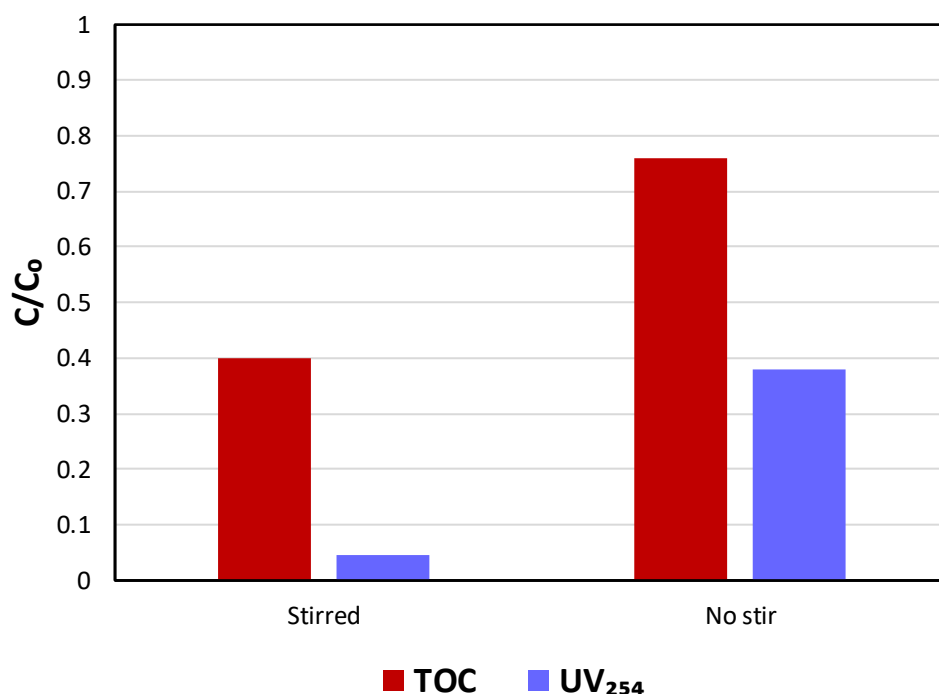


Figure 4.4 – Final NOM and TOC concentration of reactions performed with and without stirring. Experimental conditions: Water = SW3; pH = 7; 370 nm UV-LED; water volume = 20 mL; catalysts; TiO₂ slide; orbital mixer stirring (40 rpm); irradiation time = 100 min.

The results (shown in Figure 4.4) show a significant increase in the rate of removal of NOM when a reaction vessel is stirred. The unstirred reaction degraded 62% of NOM present in the SW3 with a 24% reduction in TOC after 100 min of treatment. The inclusion of stirring in the reaction saw an increase in NOM removal with 95% UV₂₅₄ NOM degradation and 60% mineralisation of TOC after 100 min treatment.

Although stirring is commonly used in suspended catalyst reactors to maintain homogeneity, the comparison of unstirred vs stirred is rarely directly reported with immobilised catalysts. Work by Bouarioua et al.²⁵⁴ showed a significant increase in photocatalytic activity when stirring speed was increased which then declined when speeds were reached that caused vortices to form. This was explained by the higher stirring speed of solution being essential to

ensure sufficient possible interaction between the target molecules and the catalyst particles and thus promote the chance for them to meet. It has been reported in studies using immobilised TiO₂ that organic target molecule removal increases with stirring speed in batch reactors or flow rate in recirculated batch reactors.²⁵⁴⁻²⁵⁶ This is linked to an increase in catalyst and target as higher stirring speeds increased the interaction rates between the target molecules until this was no longer the limiting factor. The apparent increase in photocatalytic NOM removal caused by stirring the reaction mixture was utilised in further experiments to optimise conditions for a more accurate imitation of a larger-scale, photocatalytic batch reactor.

4.3.5 Suspended vs immobilised photocatalysis

Immobilising a catalyst into a substrate greatly improves the practicality of a reactor setup as no further processing is required to remove the test water from the catalyst after testing. This is discussed further in Chapter 6. Experiments were performed to assess the differences in photocatalytic NOM removal performance when using an immobilised or suspended catalyst (200 mg/L). Experiments were performed using SW3, pre-treated Carron Valley surface water that was processed to closely mimic raw water that had been through the organics removal process in a water treatment plant. This data was later used in Chapter 6 as the basis for a life cycle assessment of catalyst state in a possible industrial water treatment photocatalytic reactor. Reactions were then set up as shown in Section 3.4 of Chapter 3 with the exception of additional stirring on an orbital mixer (40 rpm) previously shown in Section 4.3.4 to improve degradation performance. The subsequent results are shown in Figure 4.5.

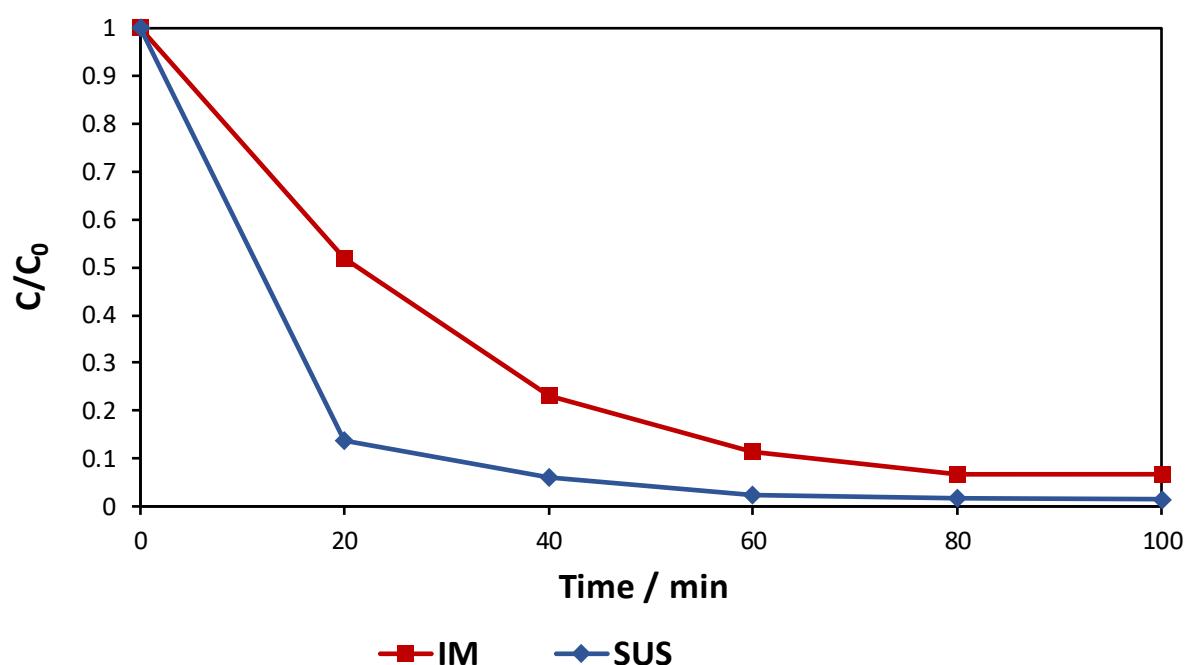


Figure 4.5 – Rate of NOM removal for various states of photocatalyst. Experimental conditions: water = SW3; pH = 7; 370 nm UV-LED; water volume = 20 mL; orbital mixer stirring (40 rpm). Catalysts; TiO₂ slide, Slurry.

The results (shown in Figure 4.5) show that immobilising the TiO₂ catalyst results in a significant reduction in the rate of removal of NOM. The suspended catalyst underwent rapid degradation with a 99% removal of NOM and 64% removal of TOC after 100 min treatment although the rate of removal levelled off after 60 min of treatment. The immobilisation of the TiO₂ catalyst resulted in a significant reduction in the rate of removal; NOM removal decreased to 95% and TOC removal to 60%. The pseudo-first-order kinetic rate constants for these data were calculated and are shown in Table 4.3 below, the rate of the suspended catalyst was calculated from the first 60 min of reaction before the degradation tapers off.

Table 4.3 – Pseudo-first order reaction rate constants for photocatalytic NOM removal using different catalyst states in SW3.

Catalyst	1 st order rate constant (min ⁻¹)	R ²
Suspension	0.0599	0.952
TiO ₂ slide	0.0346	0.996

This fits with various literature observations^{169, 257, 258} such as those described by Manassero et al.¹⁶⁹ who singled out differences in photonic efficiency between suspended and immobilised catalyst setups. When measuring the photonic efficiency as the ratio between the observed reaction rate and the rate of incident radiation, Manassero et al.¹⁶⁹ calculated that the value for suspended catalysts was more than twice the value of the immobilised setup, suggesting that the photons absorbed in the suspended catalyst setup are more efficiently employed to degrade the target molecule. The suggested reasoning for this is the lower interfacial area available for photocatalytic reactions in the immobilised catalyst setup. Similar studies have also suggested similar reasonings such as a high average convective diffusion distance from fluid to the catalyst surface.^{259, 260} In contrast, Ballari et al.¹⁷² propose that suspended catalyst reactors at the optimal catalyst concentration tend to have a determinately small average interparticle distance so that the rate of target molecule degradation isn't dictated by catalyst-target distance and is more likely determined by light availability due to high rates of scattering.¹⁷² Additionally, Krýsa et al.²⁶¹ have reported cases where the thermal treatment used in the process of immobilisation plays a role as high levels of heating can easily transform anatase TiO₂ to its rutile phase, the most stable phase of TiO₂.^{261, 262} It has been widely reported²⁶³ that anatase phase TiO₂ has better photocatalytic

activity due to its larger bandgap and higher surface energy.²⁶³ Anatase TiO_2 can be transformed into rutile at temperatures well within those used during the immobilisation process (450 - 850 °C), depending on the fabrication method and precursors.²⁶⁴ This observation has impacts on the usability of industrial-sized photoreactors for water treatment as the efficiency and simplicity afforded by a suspended catalyst reactor system may well be cancelled out by the cost and energy requirements of the additional separation steps it necessitates. These considerations for an industrial-sized photoreactor would benefit from a further systematic, overarching investigation of the resource and environmental implications these two reactor setups would have. This is explored in Chapter 6 using a life cycle assessment methodology comparing immobilised and suspended catalyst systems for photocatalytic treatment of drinking water.

4.3.6 Catalyst reusability

Catalyst reuse greatly impacts the economics of a process when used in industry as producing new catalysts or rejuvenating unusable catalysts is energy-intensive and time-consuming. The reusability of slurry-based reactions was tested to compare the viability of suspended catalysts and immobilised catalysts in an industrial setting. This is discussed further in Chapter 6. Experiments were performed using Carron Valley surface water that had been filtered through a 0.45 μm PVDF filter, acidified using HCl to $\text{pH} \sim 2$, degassed with N_2 gas then neutralised with NaOH back to $\text{pH} 7$. 20 mL of this pre-treated Carron Valley surface water (pt-SW3) was mixed with P25 TiO_2 (200 mg/L) and used for photocatalytic treatment in the reactor setup described in Section 3.5 of Chapter 3, after which, the catalyst was removed, by centrifuge (6000 rpm) for 30 min and then reused in a fresh sample of pt-SW3. For comparison, an immobilised catalyst was used in the reactor setup described in Section 3.5

of Chapter 3. The immobilised catalyst was used to treat 20 mL of pt-SW3, after which the catalyst was removed, rinsed with UP water, dried, and reused in a fresh sample of pt-SW3. The subsequent results are shown in Figure 4.6.

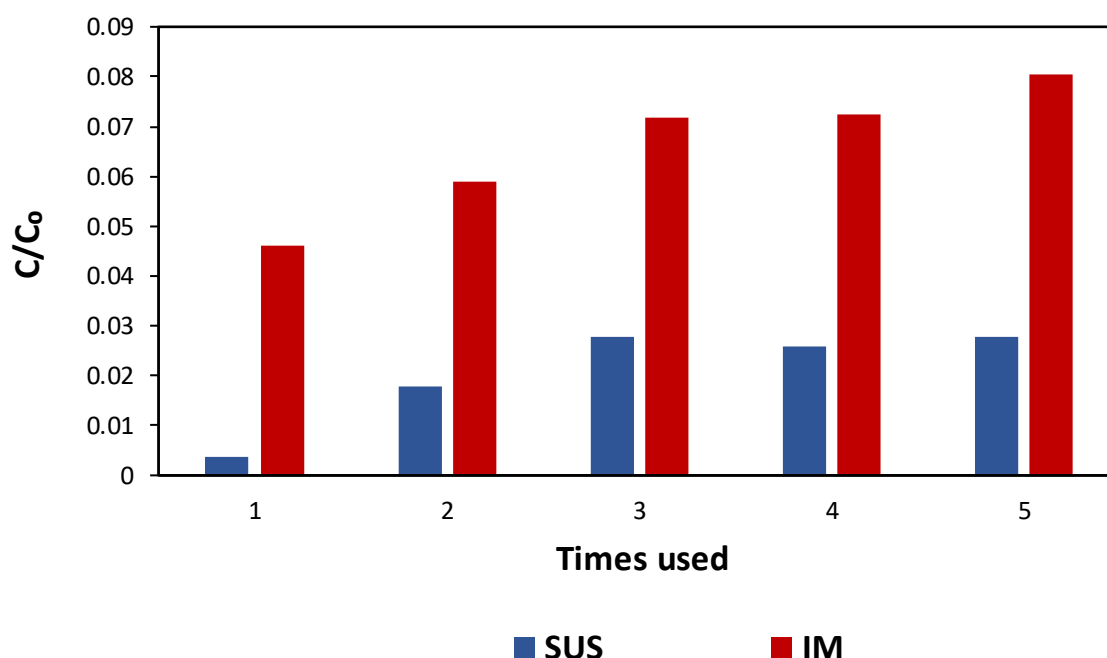


Figure 4.6 – Final NOM concentration after repeated use. Experimental conditions: Water = pt-SW3; pH = 7; 370 nm UV-LED; water volume = 20 mL; orbital mixer stirring (40 rpm); catalysts; Slurry (200 mg/L), TiO₂ slide; irradiation time per use cycle = 100 min.

The results (shown in Figure 4.6) show that reusing both immobilised (TiO₂ slide) and suspended (slurry) catalysts causes a reduction in their degradation ability. The slurry catalyst underwent rapid degradation with a 99.6% removal of NOM after the initial 100 min treatment, this removal then decreased to 98.2% with a second 100 min treatment and then stabilised at around 97.2% NOM removal in the subsequent repeats. Similarly, NOM removal using the TiO₂ slide decreased from an initial 95.3% after the first use to 94.1% after a second

treatment with degradation decreasing fairly regularly with each subsequent use ending at 91.9% degradation after the 5th use.

A relatively small amount of research into the deactivation of TiO₂ in water has been undertaken. Yang et al.²²² investigated NOMs' impact on suspended TiO₂ reusability using humic acid solutions and 2,4,6-trichlorophenol (TCP) as target molecules for photocatalysis. This study observed that, although target pollutant molecules such as TCP alone showed very little deactivation of the catalyst degradation ability, the presence of 5 mg/L humic acid induced the gradual deactivation of TiO₂ after 10 cycles, and the deactivation was more severe with higher humic acid concentrations. This was attributed mainly to the adsorption of humic acid degradation byproducts during photocatalysis. It has been shown that NOM forms a significant amount of oxygen-containing groups during photocatalytic oxidation, many of which have a high affinity for TiO₂.²⁶⁵ It was found that these byproducts block the active sites on TiO₂'s surface and were attributed with being the major contributor to the deactivation of the TiO₂.²⁶⁵ This would explain the observed reduction in photocatalytic ability shown in Figure 4.6 with the effect perhaps being more pronounced due to the added complexity of the NOM from the surface water as opposed to a standard humic acid solution. Additionally, Figure 4.6 shows that the deactivation effect is slightly more pronounced in the TiO₂ slide. The observations made by Yang et al.²²² may suggest that this is due to the immobilised TiO₂ slide having a smaller surface area and therefore it is more affected by a reduction in surface area due to NOM byproducts binding to the catalyst surface.

This observation has impacts on the viability of industrial-sized photoreactors for water treatment as the efficiency and maintenance of a photocatalytic reactor system would be negatively impacted if constant fouling were to reduce the system's degradation ability. These

data can be factored into a further systematic, overarching investigation of the resource and environmental implications that an industrial photocatalytic water treatment system would have. This is explored in Chapter 6 using a life cycle assessment methodology comparing immobilised and suspended catalyst systems for photocatalytic treatment of drinking water.

4.3.4 Pilot-scale LED photocatalysis

Some further tests were conducted using a commercial, pilot-scale LED-photocatalytic reactor setup. This was done to draw together the data acquired from the previous bench-scale organics removal experiments and conclude some implications for industry-scale LED reactor setup and operation. A detailed setup of the Puralytics Shield system is specified in detail in Section 3.4.1.2 of Chapter 3. In short, the Puralytics Shield 1500 uses a photocatalyst mesh surrounded by an array of UVA LEDs in a continuous flow setup (0.6 L/min), a UVC lamp is also placed immediately before the exit of the system to ensure that all biological contaminants are killed during treatment.

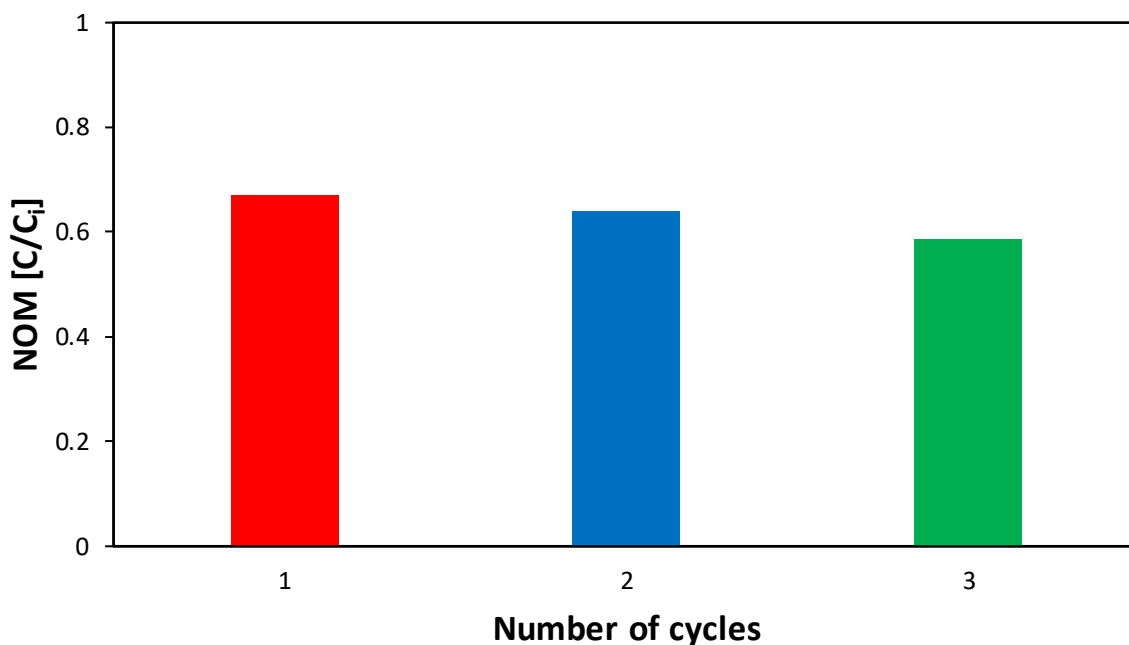


Figure 4.7 - NOM removal in Pateshill raw water for various cycles through the Puralytics shield photoreactor. Experimental conditions: Pateshill raw water; pH ambient; UV-LED; catalyst = NanoMesh Cartridge; single cycle treated water volume = 24 L; flow rate = 0.6 L/min.

Initial tests showed that a single cycle through the Puralytics shield reduced NOM concentrations in a 2 mg/L humic acid solution by 39%. This was then further tested with several subsequent cycles testing Pateshill raw water as shown in Figure 4.7. These tests showed an initial 33% reduction in NOM after the first cycle through the Puralytics reactor which then followed a 4% reduction after a second cycle through the reactor. A third cycle through the reactor then saw an 8% reduction in NOM summing to a 41% total reduction in NOM after 3 cycles. This level of degradation was seen after 10-17 min of 20 mL batch treatments with slurry or TiO₂ slides, although slurry reactions would require a further catalyst separation stage.

This diminishing return on cycling the raw water through the Puralytics suggests that the flow rate was fairly well optimised for this system, and it was the constitution of the organics in the water itself that was preventing the subsequent reductions from being as effective.²⁶⁶ This could be explained by the hydrophobic fractions in the raw water having a higher rate of degradation as they are generally composed of aromatic and other high molecular weight organic compounds.²⁶⁶ These groups of compounds are reported to be more reactive to oxidative treatment^{44,76,80} and therefore could be responsible for the dramatic reduction in UV₂₅₄ absorbance after the first cycle, leaving less reactive hydrophilic compounds in the subsequent runs.

It is sometimes the case where industrial processes balance treatment efficacy and speed but with <45% removal rates from NOM compared to >95% removal rates possible with simple bench scale reactors it is clear that there are significant gaps between research and application of photocatalysis.

4.4 Conclusions

Based on the results presented in this chapter, and the supporting literature, several implications can be proposed for the design, setup, and operation of larger-scale LED-driven photocatalytic reactor setups when focussing on NOM removal. A large amount of the materials development side of photocatalytic research is focused on improving the visible light capabilities of TiO₂-based photocatalysts but, as the results in Figure 4.1 corroborate, the utility of modified catalysts for UV-LED-based photocatalysis is something worth exploring at a larger scale. Additionally, much of the research is focused on immobilised catalysts owing to the many practical advantages that come along with these catalyst types. Given the considerably improved performance of the slurry TiO₂ displayed in Figure 4.1 compared to

the immobilised catalysts, further research considering the advantages of immobilised vs suspension-type setups for large-scale LED photocatalytic reactors has been undertaken and presented in Chapter 6. Figures 4.2 and 4.3 suggest a relationship between NOM concentration and photocatalytic degradation which is blurred when the complexity of the NOM is increased. This could indicate that photocatalysis in an industrial setting, such as drinking water treatment, would be best suited as more of a tertiary treatment rather than the main mechanism for removing organics from raw waters. Raw water sources tend to vary greatly in both the make-up and concentration of their organics depending on the time of year, weather patterns and human activities which could lead to a photocatalytic system outputting wildly different quality treated water or putting strain on the rest of the treatment system by requiring wildly different treatment times to finish water to the required quality. As a system further down the line in the treatment process, large-scale photocatalytic reactors could supply water with lower variations in organics concentrations as well as organics that are more predictable due to the treatments before them. This would also allow for photocatalytic systems to excel in treating NOM types that other water treatment methods fall short such as taste/odour compounds and DBP precursors.^{44, 267} Given the results of this Thesis, it is clear that further research is required before photocatalysis can be implemented into industry with problems being presented at lab and pilot scale. Given the lengthy treatment times of the lab scale setup, it would be worthwhile investigating further how effective UVA-LED photocatalytic treatment could be at removing specific NOM components that can be problem areas for water treatment plants such as geosmin and methylisoborneol. The current literature surrounding many of these difficult to remove compounds is quite promising²⁶⁷⁻²⁶⁹ so finding ways to make photocatalysis quicker at removing these target molecules would make photocatalysis ideal for tertiary treatment in

facilities struggling with water quality caused by such compounds. Nonetheless, the results of this Thesis clearly show that photocatalysis can be a very effective treatment for removing NOM from water with removal levels far higher than alternative treatments. When comparing TOC removal with other methods that don't require constant chemical shipments photocatalysis is markedly higher with 60% TOC removal compared to other methods that don't require constant chemical shipments such as 30-50% removal for similar real water experiments with O₃/UV. Similarly, this Thesis showed that photocatalysis can perform as well, if not better at removing NOM from surface waters when compared to other AOP processes that require constant chemical doses, such as H₂O₂/UV (20-30% TOC removal),^{75, 270} Fenton (20-40% TOC removal) and photo-Fenton (55-65% TOC removal),^{182, 271, 272} which significantly contribute to their environmental sustainability.^{214, 273, 274}

The main conclusions from this chapter are summarised below.

- C-TiO₂-TiCl₄ modified catalyst immobilised on appropriate substrates show potential for large-scale UV-LED based NOM removal.
- Adequately high reactor stirring is required to maintain optimal NOM degradation rate. Reactors using an immobilised catalyst especially should have high but non-turbulent fluid motion.
- Treatment would yield best results when ensuring reactor influent is as low in NOM concentrations as is possible. This could be achieved by placing the reactor as far down the treatment line as possible.
- Batch reactors faired significantly better in overall NOM removal when compared to the commercial continuous feed reactor at the expense of treatment time. This should be considered when evaluating the overall treatment requirements.

- The varied organic composition of real raw water greatly affects the treatability of that water compared to humic acid solution simulants.
- Catalyst state greatly influences NOM degradation with the slurry catalyst showing a high rate of degradation and mineralisation compared to the TiO₂ slide.
- NOM quickly reduces the efficiency of a catalyst over its lifetime with the complexity of the NOM character possibly contributing to this.
- Current pilot scale photoreactors have high throughputs but this is at the expense of overall NOM removal ability with degradation efficiencies over 40% hard to achieve with real water samples.

5 Lab scale, LED-driven photocatalytic removal of bacteria in real water

5.1 Introduction

As well as increasing a photocatalyst's ability to remove NOM, an additional area of interest is a photocatalyst's ability to remove bacteria from contaminated water. This chapter explores the ability of LED photocatalysis to inactivate bacteria since UV treatment is frequently used as a disinfection technology in water treatment. The main aim of this Chapter was to assess how efficacious a UVA LED-based photocatalytic treatment system would be at water disinfection and to bridge some of the gaps between lab-based research and real-world application. This was done by first testing how the changes to the water matrix, and therefore different geographies and seasons, would affect the photocatalytic disinfection treatment speed and efficacy on *E.coli* when using a TiO_2 based setup. Direct comparisons of UVA-LED photocatalytic disinfection in real surface water are not commonly reported in literature despite showing important insights on how an industrial scale reactor would operate in the real world. Additionally, the effects of water volume were briefly explored, giving insights into the capacity and operating conditions a photocatalytic disinfection system could run. Different irradiation sources were also tested, considering the limited application of UVC disinfection in industrial water treatment. These investigations were then tested again using a modified TiO_2 catalyst ($\text{C-TiO}_2\text{-TiCl}_4$) to see how performance was affected. UV-LED photocatalytic degradation of organics is often equated to overall photocatalytic performance, but this is not always true or tested in literature. This Thesis compared the performance of a modified photocatalyst for its disinfection ability, as well as NOM

degradation, showing how the target of photocatalytic water treatment must be considered when making a photocatalyst choice. Finally, a pilot scale commercial photocatalytic system was tested to see how current technologies compare to the bench scale treatments.

Results of this work will create important scientific knowledge on the kinetic rates of photocatalytic disinfection in real water, under a UVA-LED irradiation source and how these can be affected by altering basic operating parameters. The extensive use of chemical disinfectants in industrial water treatment is responsible for the creation of possibly harmful DBPs in drinking water. Therefore, findings of this work can be used as a tool for researchers and the water industry to further scale-up photocatalysis by choosing a setup that will enable an effective and sustainable treatment of water that would reduce the dose of required chemical disinfectant, therefore reducing risk to public health.

5.2 Experimental

5.2.1 Materials

The water matrices utilised in this Chapter are presented in Chapter 3 along with a brief description.

The photocatalysts studied in this Chapter are presented in Chapter 3 along with a detailed description of the synthesis routes in Section 3.1.

The microbiological reagents used in this Chapter are described in detail in Chapter 3 Section 3.3. Briefly described here, *Escherichia coli* (Migula) Castellani and Chalmers (EMG 2:K (lambda)), K-12 wild type was used for these tests. Samples were activated and stored in

Luria-Bertani (LB) broth (25 g/L) and propagated using Brilliance E. Coli Coliform Selective Medium (from OXOID) (28 g/L).

5.2.2 Microbial Photocatalytic Testing

The procedure outlined in Section 3.4.5 of Chapter 3 was used for these experiments, beginning with the contaminated water sample being exposed to the catalyst in the dark for 30 min before irradiating with the different light sources for 2 h. Measurements were taken every 20 min and bacteria were quantified as described using the standard dilution technique.

5.3 Results and Discussion

5.3.1 Effect of water matrix on TiO₂-based photocatalytic disinfection

After testing the optimised operating conditions in Chapter 4, further studies into the efficacy of removing contaminants from water were conducted, this time focusing on microbial content. Here, non-pathogenic *Escherichia coli* was used as a model microbial contaminant, as the presence of *E. coli* is an indicator of faecal contamination, and as such is an important species to study for water treatment. Explored within this section is the effect of the water media on the rate of disinfection, as shown in Figure 5.1. Here, glass slides were immersed in 25 mL aliquots of ultrapure water, humic acid (10 mg/L), 0.8% NaCl solution or filtered raw water from Blackford Glen (SW2). These aliquots were spiked with *E. coli* with testing performed under 370 nm, according to the procedure outlined in Section 3.4.5 of Chapter 3. Fluctuations were seen throughout the experiments, as is expected when working with bacteria, but overall trends could be extrapolated using the averaged CFU/mL calculated from the viable serial dilutions of each time point, typically 3.

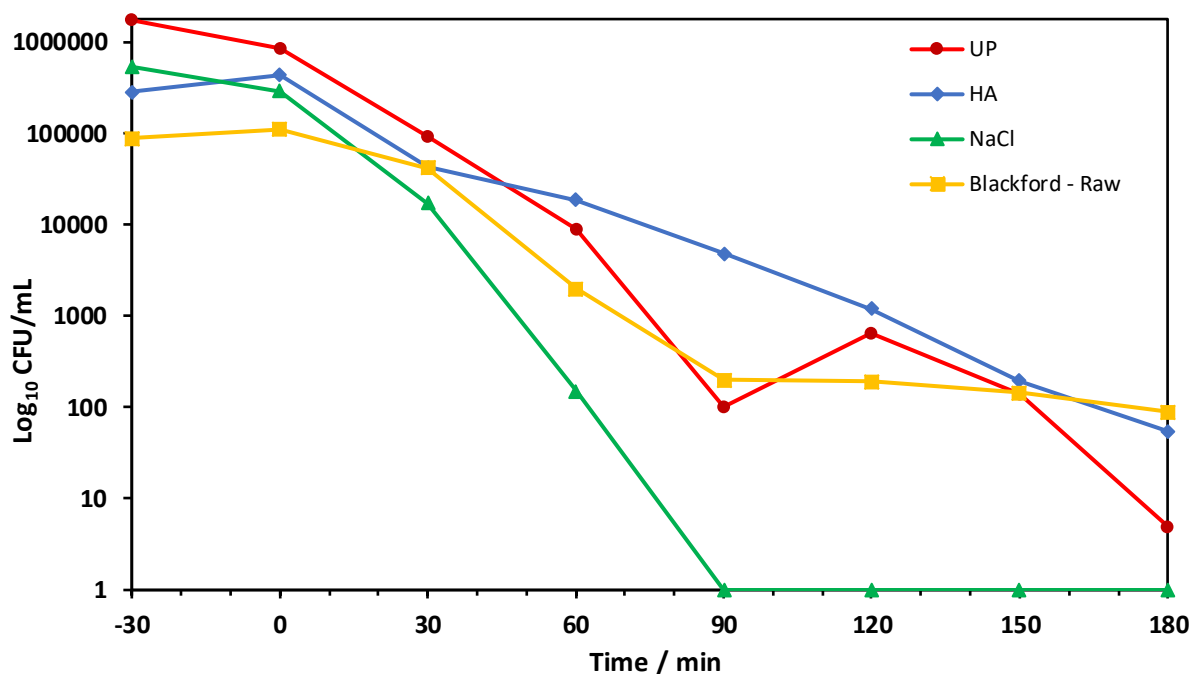


Figure 5.1 - Average concentration of *E.coli* (CFU/mL) in various water matrices: ultrapure water (UP), 10 mg/L humic acid solution (HA), 0.8% NaCl (NaCl), Raw water from Blackford Glen (Blackford – raw). Experimental conditions: catalyst = TiO₂ Slide; water volume = 25 mL; pH ambient; 370 nm UV-LED.

The results shown in Figure 5.1 show clear differences in the rate at which different water matrices can be disinfected by photocatalysis. The Blackford raw and HA solutions show similar rates of disinfection at 0.02067 min^{-1} and 0.0209 min^{-1} respectively. A significant increase in disinfection rate is then seen with the ultrapure water sample with 0.02630 min^{-1} . This fits with observations seen in literature where humic acid and other complex organic molecules are seen to compete with the microorganisms for hydroxyl radicals meaning fewer radicals are available to deactivate said microorganisms. This inhibitory effect of NOM on the photocatalytic disinfection of water has been observed by Fouad et al.²⁷⁵ when investigating visible light driven photocatalytic disinfection in real surface waters, where NOM inhibited

disinfection as concentrations grew higher. Fouad et al.²⁷⁵ attributed this inhibition of disinfection to three concurrent mechanisms; the partial obstruction of incident light due to the absorbance of UV radiation by NOM molecules, the deactivation of the catalyst sites due to the accumulation of NOM on the catalyst surface, and the scavenging of ROS by NOM molecules.

An increased disinfection rate is observed with the NaCl solution with a reaction rate of 0.0616 min^{-1} . The literature surrounding the effects of inorganic salts on TiO_2 -based photocatalytic disinfection is mixed with some researchers observing similar enhanced effects from higher concentrations of NaCl.^{129, 276} Gourmelon et al.²⁷⁷ observed an increased disinfection rate at much higher NaCl concentrations in seawater and attributed this effect to changes in the cell permeability caused by the increase of Cl^- concentration.²⁷⁷ However, disinfection investigations by Marugán et al.²⁷⁸ with similar NaCl concentrations as were used in the experiments shown in Figure 5.1, suggested that photocatalysis can produce reactive chloride radicals ($\text{Cl}\bullet$) which react with excess Cl^- to various radical species that are reactive with both organic substances and bacteria.²⁷⁸⁻²⁸⁰ Another possible end product for these radicals (shown in **eq 5.1 – eq 5.3**) is molecular chlorine, which is also a disinfectant, therefore also accelerating the deactivation rate.¹²⁹



These observations regarding the differences in treatment rate and efficacy of different water matrices are significant as most research around UVA-LED photocatalytic disinfection

focusses on the catalyst type and implementation. As these results show, significant differences in the treated water can arise from changes to the water composition which is important to consider when looking to implement a UV-LED photocatalytic disinfection system in different geographical locations or a location that sees significant changes in water composition due to weather patterns or seasonal changes. As of yet, very little research has been conducted using UVA-LED photocatalytic disinfection systems in real water.

Experiments were performed to calculate the pseudo-first-order reaction rate constants for TiO_2 in various *E. coli* spiked water matrices using the derived rate equation **eq 3.3** as described in Section 3.4.4 of Chapter 3. The results are shown below in Figures 5.2-5.4.

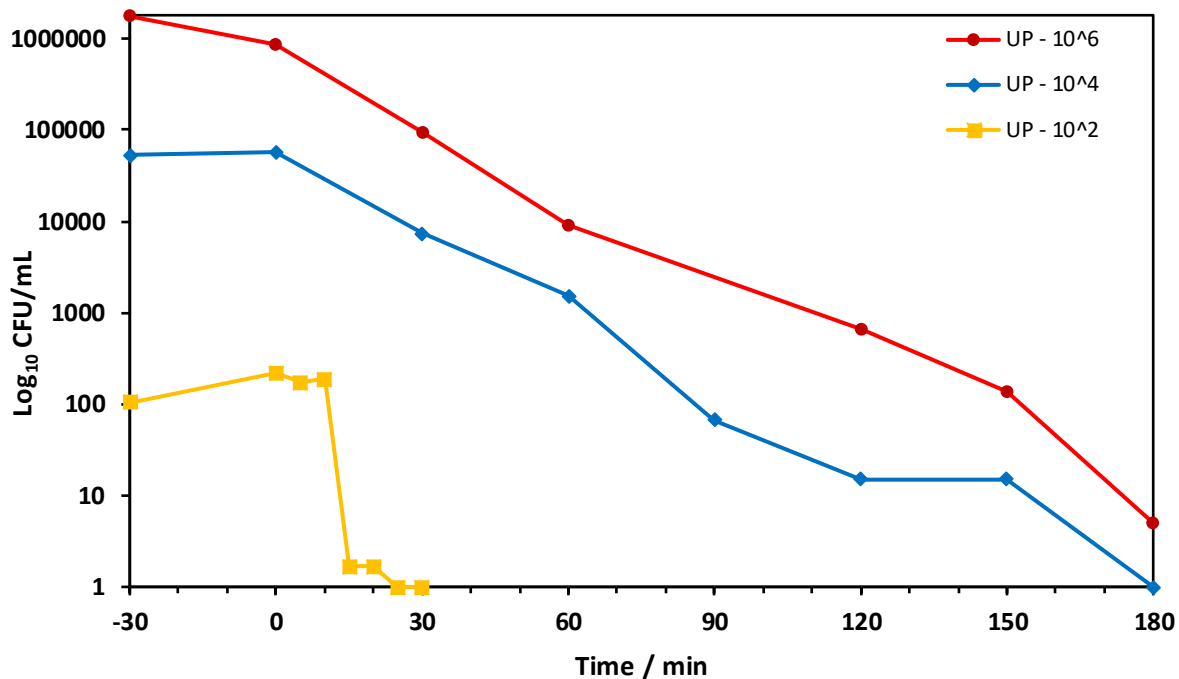


Figure 5.2 - Inactivation of *E. coli* (CFU/mL) at various starting concentrations at 10^6 , 10^4 & 10^2 CFU/mL. Experimental conditions: ultrapure water; catalyst = TiO_2 slide; water volume = 25 mL; pH ambient; 370 nm UV-LED.

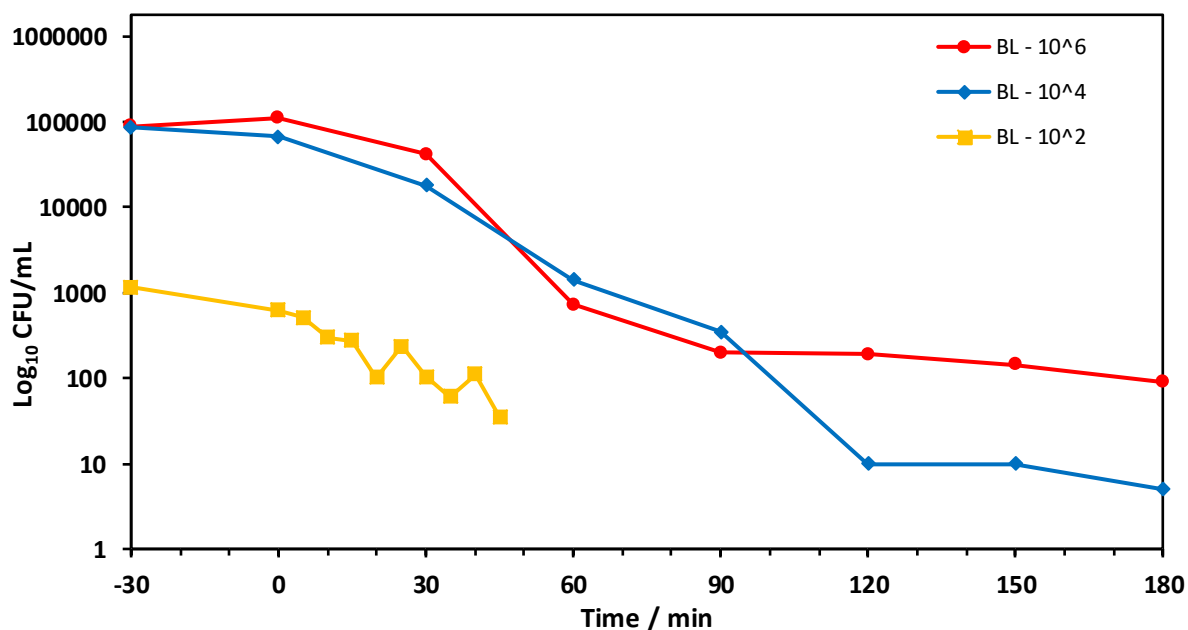


Figure 5.3 - Inactivation of *E. coli* (CFU/mL) at various starting concentrations. Samples spiked with *E. coli* include: Surface water from Blackford Glen (BL) starting at 10^6 , 10^4 & 10^2 CFU/mL.

Experimental conditions: filtered Blackford glen water; catalyst = TiO_2 slide; water volume = 25 mL; pH ambient; 370 nm UV-LED; average concentration deduced from valid serial dilutions.

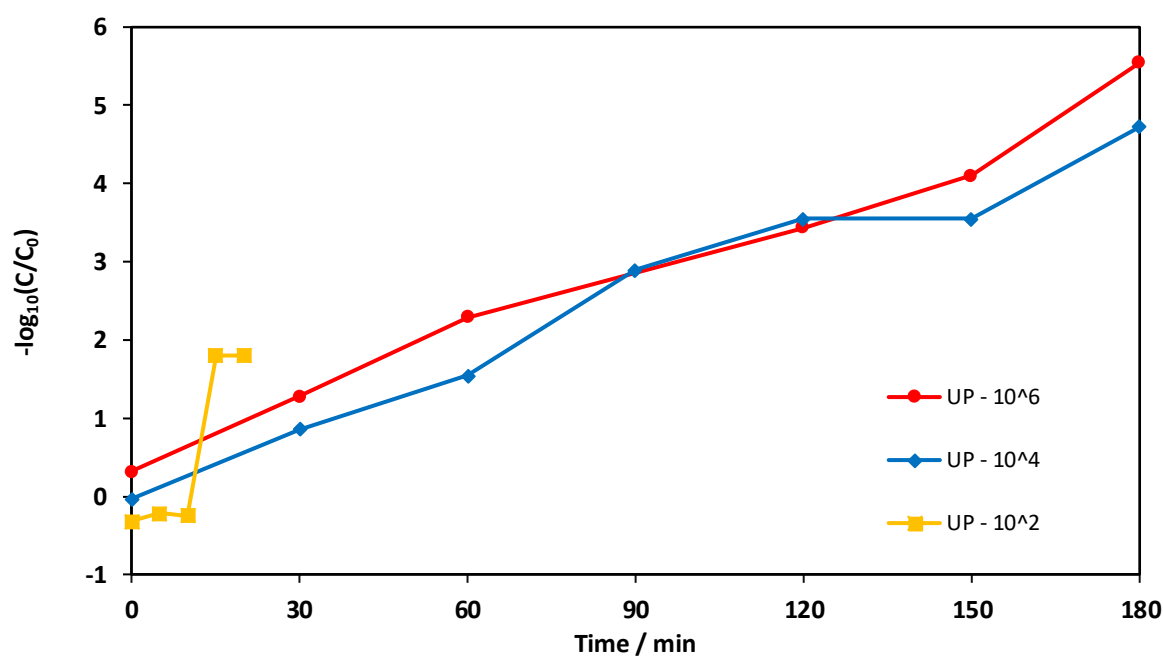


Figure 5.4 - The same data from Figure 5.2 showing the $-\log$ of bacteria concentration relative to starting concentration over time. This data was used to estimate the 1st order rate constants using linear fits beginning at time = 0 min and does not include the 30 min in the dark, such that the rate of just the active photocatalysis was found.

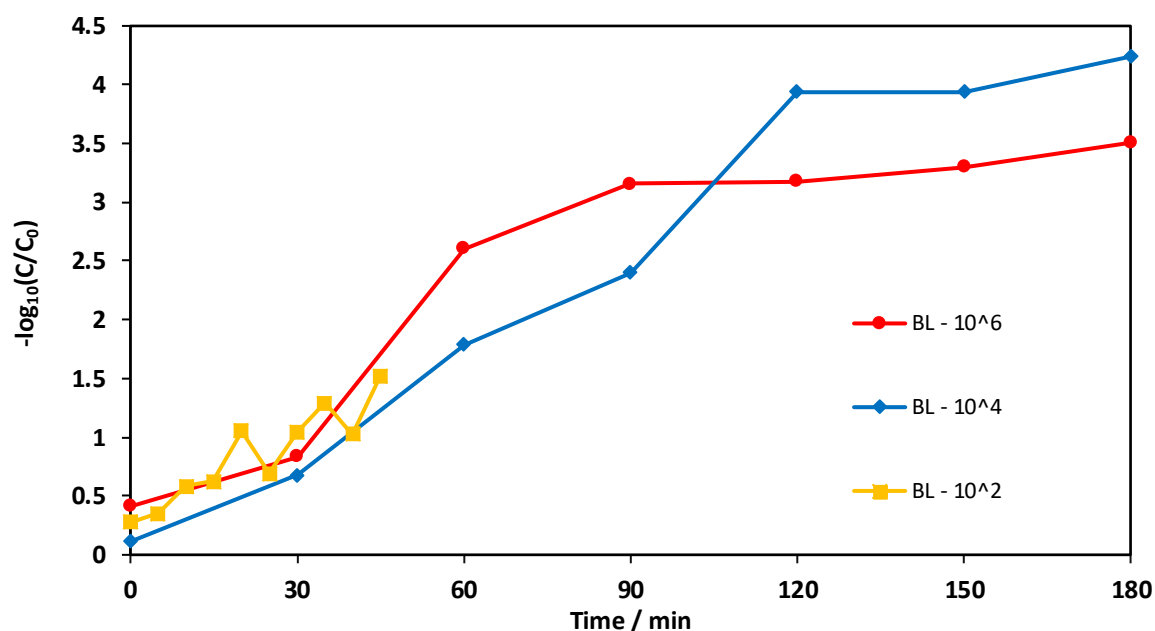


Figure 5.5 - The same data from Figure 5.3 showing the $-\log$ of bacteria concentration relative to starting concentration over time. This data was used to estimate the first-order rate constants using linear fits beginning at time = 0 min and does not include the 30 min in the dark, such that the rate of just the active photocatalysis was found.

Table 5.1 - The same data from Figure 5.3 showing the $-\log$ of bacteria concentration relative to starting concentration over time.

Water Matrix	Rate of disinfection (min^{-1})
Ultrapure water	0.02630
Blackford glen water	0.02067

As can be seen in Table 5.1, there is a decrease in the rate of disinfection when the water matrix is changed from ultrapure water to surface water from Blackford Glen. This could be

explained by the presence of ions in the raw water that are not in the humic acid solution. It is documented that most ions commonly found in surface waters have some kind of inhibitory effect on the rate of photocatalysis.²⁴⁹⁻²⁵¹ Ions in surface waters, as well as more complex NOM, can reduce photocatalytic disinfection by either competition for adsorption onto the catalyst surface or their ability to act as scavengers of hydroxyl radicals.²⁵² This is to say, raw surface waters can vary greatly in their composition and therefore their reaction to photocatalysis depending on the time of year, location, or current weather patterns. This further supports the idea that photocatalytic disinfection is best suited to be placed towards the end of the water treatment process, before a chemical disinfection process, as resilient and persistent organics could be targeted, lowering DBP formation, and disinfection rates would be less affected by other factors in the water. A setup like this would also reduce the required dose of chemical disinfection, further reducing DBP formation as well as improving taste and odour in the final delivered water.

5.3.2 Effect of water volume on TiO₂-based photocatalytic disinfection

The reactant volume can significantly affect the performance of photocatalytic disinfection. To assess the feasibility and operation parameters of an industrial-scale photocatalytic reactor, experiments were performed to evaluate how the volume of the water can affect the operation of UV-LED photocatalysis. Experiments with volumes 25 mL & 35 mL were carried out and the results are shown in Figure 5.6.

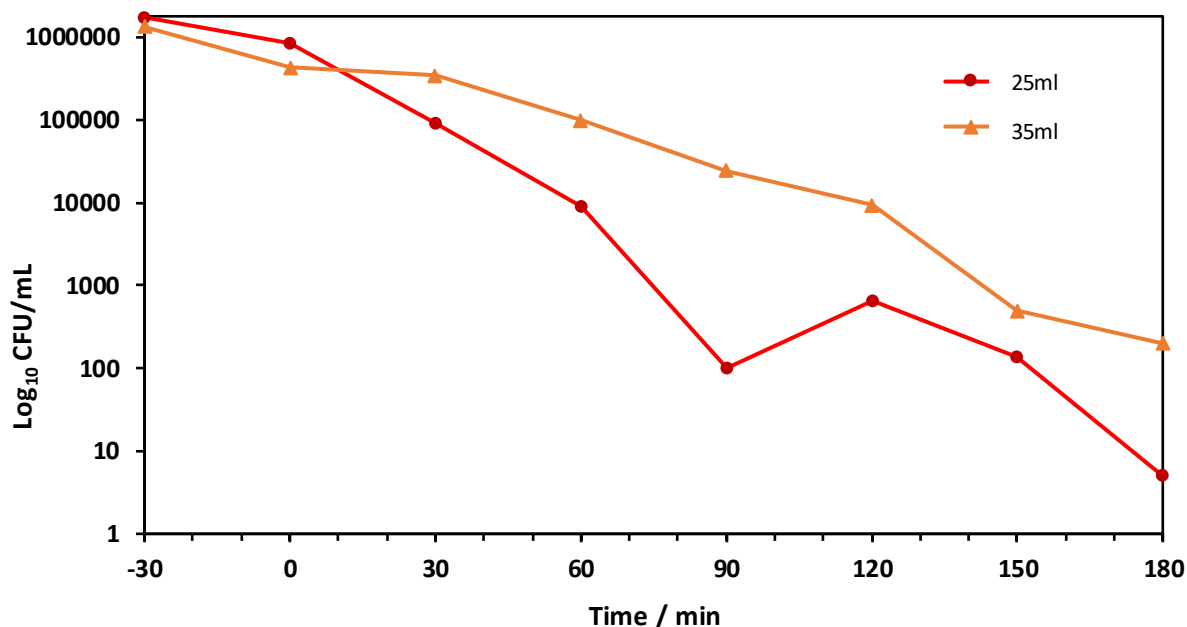


Figure 5.6 - Inactivation of *E. coli* (CFU/mL) in various water volumes. Samples spiked with *E. coli* include: 25 mL of ultrapure water (25 mL), and 35 mL of ultrapure water (35 mL). Experimental conditions: Ultrapure water; catalyst = TiO_2 slide; pH ambient; 370 nm UV-LED; average concentration deduced from valid serial dilutions.

The results shown in Figure 5.6 show the varying rates at which different volumes of water can be disinfected by photocatalysis. The rate of 25 mL water (0.02630 min^{-1}) is decreased when the volume of the water is increased to 35 mL (0.0182 min^{-1}). Similarly to the volume experiments in section 4.3.2, comparable results have been observed in the literature when testing immobilised catalyst concentrations as there is both an increase in the relative adsorption and the relative radical formation.¹⁰⁸ Disinfection studies by Sichel et al.²⁸¹ proposed that solutions with a lower relative concentration of *E. coli* to catalyst surface area will have a higher disinfection rate than a solution with a larger volume due to the relative abundance of hydroxyl radicals in the lower volume solution.²⁸¹ These results show that this

observed trend is still seen in UVA-LED photocatalytic disinfection setups which hasn't been shown in the literature before with most research focussing on visible light and solar irradiation sources. This trend has impacted the usability of industrial-sized photoreactors for water treatment as it greatly limits the throughput capacity of any reactor being designed.

5.3.3 Effect of light source on TiO_2 -based photocatalytic disinfection

UVC lamps are commonly used to deactivate bacteria through direct photolysis. To compare the relative capabilities of photocatalytic reactors to other budding AOP techniques starting to be commercially used in the present day, this section focuses on the photocatalytic disinfection ability of UVA-LEDs compared to UVC germicidal lamps.

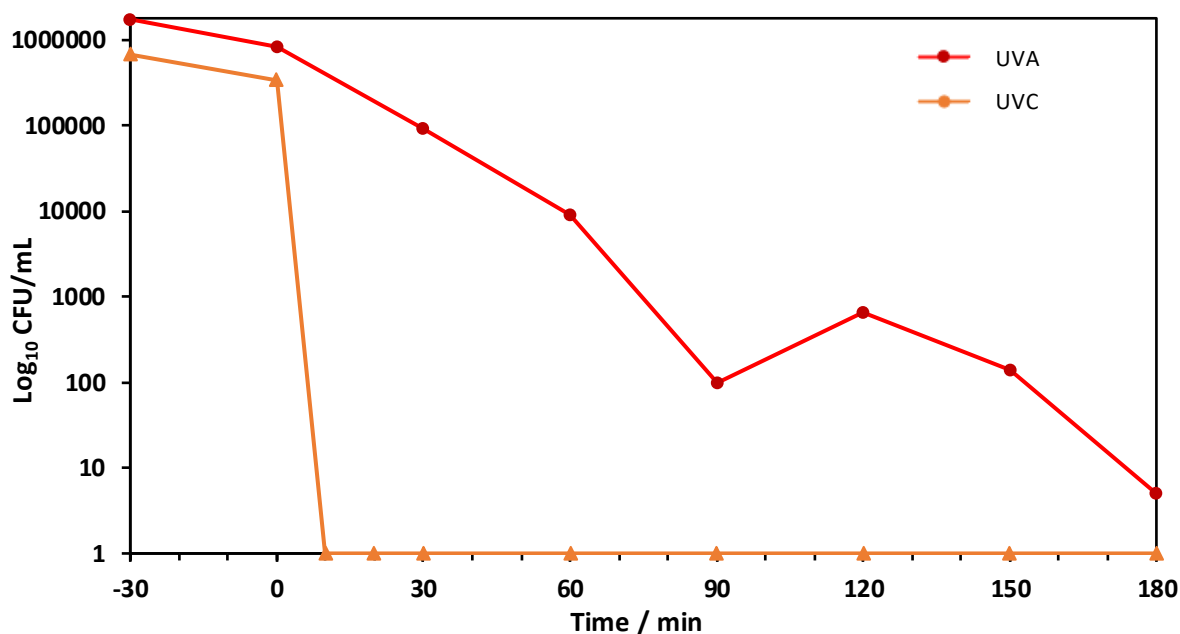


Figure 5.7 - Inactivation of *E. coli* (CFU/mL) in various irradiation sources: UVA LED (UVA), UVC 11W lamp (UVC). Experimental conditions: ultrapure water; catalyst = TiO₂ slide; water volume = 25 mL; pH ambient.

Figure 5.7 compares the rates of photocatalysis using different light sources. The rate observed with the UVC lamp was $>0.5538 \text{ min}^{-1}$ as the disinfection was near instant. This is most likely due to direct photolysis occurring during irradiation which deactivates the *E. coli* at a faster rate than photocatalysis alone. This improved disinfection rate for UVC compared to UVA has been observed in literature using suspended catalysts,^{196, 282} with these results showing an increased rate improvement when moving from UVA to UVC, likely due to the increased irradiance of the lamp compared to the LED and improved light penetration due to the catalyst being immobilised rather than suspended. Although UVA-LED photocatalytic disinfection has been shown to be significantly slower than commonly used UVC germicidal lamp photolysis disinfection, UVA-LED photocatalysis presents an interesting bonus feature

when used at an industrial scale especially considering that it has been reported by Nyangaresi et al.¹⁹⁶ that reactivation of *E. coli* is minimal after partial photocatalytic disinfection. When considering this low level of reactivation and the achievable >5log levels of disinfection, UVA-LED based photoreactors could be used before the chemical disinfection step in a water treatment works to significantly reduce the dosage of chemical disinfectant (chlorine or chloroamine) required to disinfect the drinking water to safe levels for consumption. This would reduce the levels of DBPs produced during disinfection as well as the added consumer benefit of a reduced “chlorine taste” in the final delivered drinking water.

5.3.4 Effect of water matrix on modified-TiO₂-based photocatalytic disinfection

Further bactericidal tests were carried out on a modified C-TiO₂-TiCl₄ catalyst which was screened for its photocatalytic degradation ability in Chapter 4. These tests were conducted to explore whether the enhanced photocatalytic effects observed in Chapter 4 as well as in the literature were present in a variety of water matrices for removing biological pollutants.

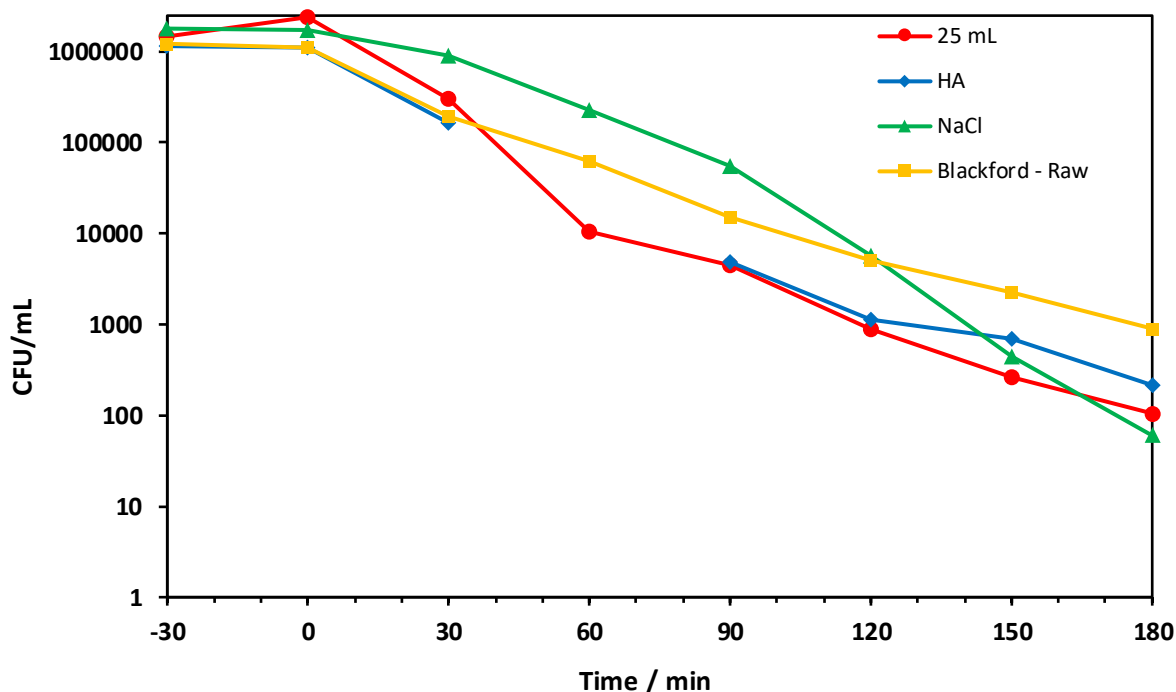


Figure 5.8 - Inactivation of *E. coli* (CFU/mL) in various water matrices: ultrapure water (UP), 10mg/L Humic acid solution (HA), 0.8% NaCl solution (NaCl), Raw water from Blackford glen (Blackford – raw). Experimental conditions: catalyst = C-TiO₂-TiCl₄; water volume = 25 mL; pH ambient; 370 nm UV-LED; average concentration deduced from valid serial dilutions.

The results shown in Figure 5.8 show small differences in the rate at which different water matrices can be disinfected by photocatalysis. The Blackford raw and humic acid solutions show the lowest disinfection rates at 0.0169 min⁻¹ and 0.0208 min⁻¹ respectively. A slight increase in disinfection rate is then seen with the ultrapure water sample with 0.0241 min⁻¹ and the NaCl sample with 0.0257 min⁻¹.

Unlike the results presented in Figure 5.1, no significant increase in disinfection rate was observed with the NaCl solution, this suggests that the possible side reactions that could have been occurring when using the TiO₂ slide in NaCl solution were not present when using C-

TiO₂-TiCl₄. Mechanistic studies on the C-TiO₂-TiCl₄ material by Odling et al.²²⁸ showed that hydroxyl radicals were not the major contributor to the degradation of organic species when using this modified catalyst, with the main oxidising species appearing to be photogenerated holes and, to a lesser extent, the superoxide ion.²²⁸ Although there is little research surrounding the direct production of reactive chlorine radicals from TiO₂ photogenerated holes or superoxide ions, these results suggest that the enhanced photocatalytic disinfection seen in NaCl solutions is greatly diminished when modifying catalysts that produce little to no hydroxyl radicals. This change in reactive oxidative species may also explain the diminished difference in disinfection between the HA and UP samples as NOM has regularly been reported to be largely a hydroxyl radical scavenger in mechanistic studies.^{119, 283, 284} When the generation of hydroxyl radicals is significantly lower, this would make HA and NOM to be significantly less of a hindrance on disinfection.

Although similar trends are observed with the relative rates of disinfection using immobilised C-TiO₂-TiCl₄ when compared to immobilised TiO₂, no significant increase in the rate of photocatalytic disinfection was observed. This contradicts published literature surrounding this specific photocatalyst where a significant improvement in *E. coli* disinfection was observed when compared to standard TiO₂.²²⁸ A likely contributor to this discrepancy is the difference in light sources used, a 370 nm UV-LED compared to an 11W low-pressure blacklight fluorescent lamp. Although it is stated that the fluorescent lamp predominantly emitted 365 nm light, fluorescent lamps tend to emit a much broader spectrum that consists of a higher fraction of photons with $\lambda > 380$ nm.²²⁹ Photons with this $\lambda > 380$ nm wavelengths are outside of the ideal range for standard TiO₂ but very much still in the ideal range for the modified C-TiO₂-TiCl₄ catalyst to produce the cell membrane-damaging hydroxy radicals. This would mean that the bactericidal tests in the literature were under conditions where the C-

TiO₂-TiCl₄ catalyst was able to utilise a higher percentage of the incident light compared to the standard TiO₂ whereas in this experiment, where the UV-LED provided a narrower band emission centred at about 370 nm, both catalysts were utilising similar proportions of the incident light. This could raise possible considerations when designing an industrial-sized photocatalytic reactor with a modified catalyst. Further experiments may show that it is cheaper and more energy efficient to supplement the UV-LED arrays with a certain percentage of longer wavelength LEDs, to fully utilise the benefits of LEDs over fluorescent lamps.

5.3.5 Effect of water volume on modified-TiO₂-based photocatalytic disinfection

The modified C-TiO₂-TiCl₄ catalyst was also tested for its capacity to disinfect spiked waters under the varying operating conditions of the reactor capacity. This was undergone in part to test the optimal conditions for photocatalytic disinfection as well as if the enhanced photocatalytic abilities of the modified catalyst translated into an increased throughput for the reactor setup.

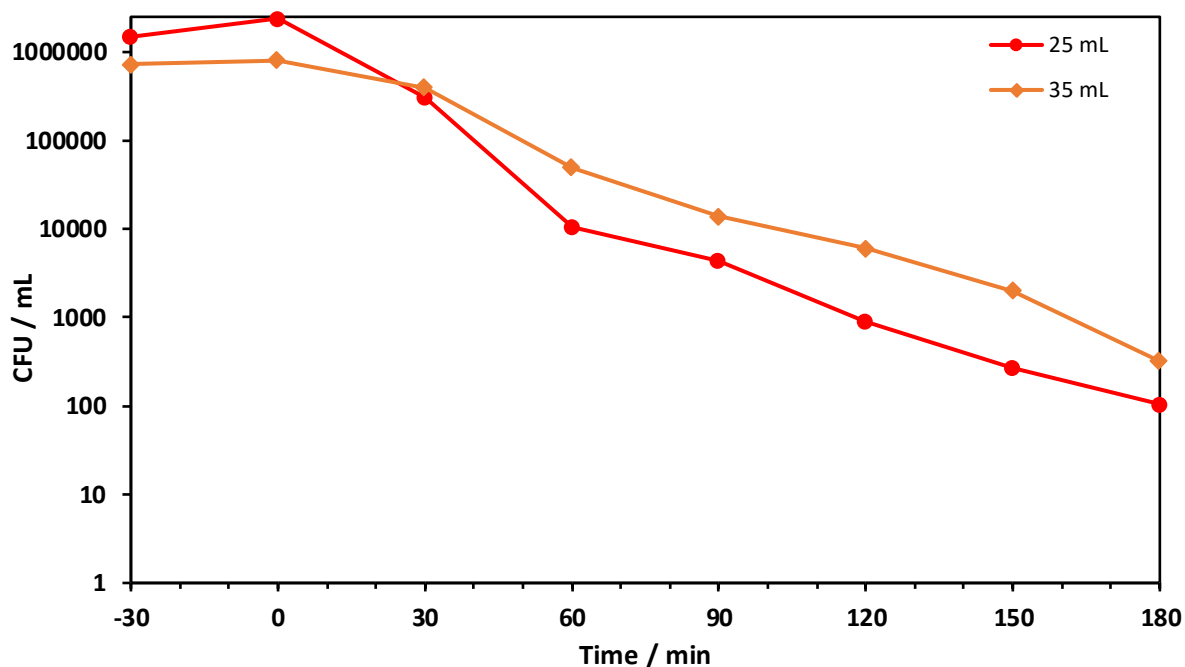


Figure 5.9 - Inactivation of *E. coli* (CFU/mL) in various water volumes: 25 mL and 35 mL of ultrapure water. Experimental conditions: catalyst = C-TiO₂-TiCl₄; pH ambient; 370 nm UV-LED; average concentration deduced from valid serial dilutions.

The results shown in Figure 5.9 show the varying rates at which different volumes of water can be disinfected by photocatalysis. The rate of 25 mL water (0.0241 min^{-1}) is decreased when the volume of the water is increased to 35 mL (0.0187 min^{-1}). These results, comparably to those shown in section 5.3.4, show similar trends observed with the relative rates of disinfection using C-TiO₂-TiCl₄ when compared to TiO₂ slide, although no significant increase in the rate of photocatalytic disinfection was observed. These results can be explained similarly to the results presented in Figure 5.8 of section 5.3.4 and Figure 5.6 of section 5.3.2 with a constant rate of oxidising radicals being formed but larger volumes dilute those radicals to the point where the disinfection rate is significantly reduced.

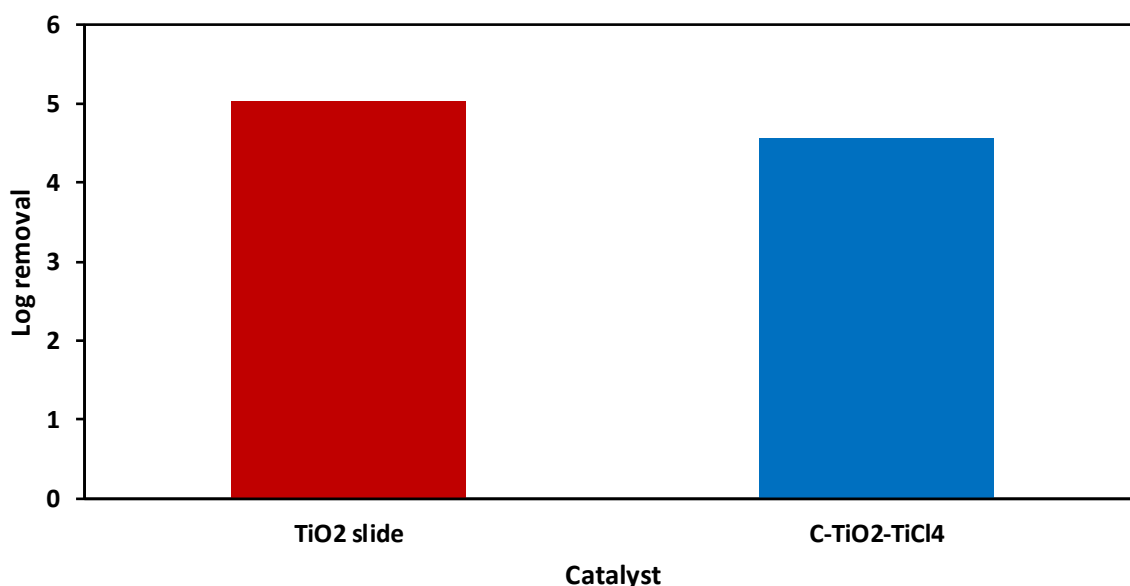


Figure 5.10 – log inactivation of E. coli (CFU/mL) after 180 min of irradiation using various catalysts. Experimental conditions: ultrapure water (UP); water volume = 25 mL; pH ambient; 370 nm UV-LED; average concentration deduced from valid serial dilutions.

Figure 5.10 shows the bacterial inactivation ability of TiO₂ slide and C-TiO₂-TiCl₄ after 180 min of UVA-LED irradiation. Both catalysts displayed statistically similar bacterial inactivation with the TiO₂ slide having a slightly higher removal (5 log or 99.999% inactivation) than the C-TiO₂-TiCl₄ (4.5 log or 99.9968% inactivation). Slightly diminished efficiencies with TiO₂ coated on high-density polyethylene (HDPE) were reported by Pascagaza-Rubio et al.²⁸⁵ after 3 h of treatment, achieving a 3.5-log reduction of E. coli. This study used preliminary tests of photocatalytic degradation of methylene blue as an indicator for which catalysts to use for the subsequent disinfection experiments, which included an Ag-TiO₂ modified catalyst. The preliminary results conducted by Pascagaza-Rubio et al.²⁸⁵ showed P25 TiO₂ to significantly outperform the modified catalyst at methylene blue degradation and was therefore used in

the investigations on disinfection but the results shown in Figure 5.10 and 4.1 show that a catalyst's relative performance in organics degradation does not necessarily directly translate into relative disinfection performance due to the possible differences in ROS being produced and how they interact with different targets.

These observations are significant in that, although much research in photocatalysis is focussed on catalyst modification, very little work has been done looking at modified catalysts for the removal of both NOM and *E.coli*. These results show that even though a catalyst may show significant improvements for NOM removal, these improvements do not necessarily translate into improvements for disinfection. Which would be important when choosing which target to prioritise when setting up an industrial UVA-LED photocatalytic water treatment system.

5.3.6 *E. coli* disinfection in pilot scale photocatalytic reactor

As a comparison, the various water matrices previously tested in this chapter were scaled up and run through a commercial, pilot-scale LED-photocatalytic reactor setup. This was done to draw together the data acquired from the previous bench-scale disinfection experiments and conclude some implications for industry-scale LED reactor setup and operation. A detailed setup of the Puralytics shield system is specified in detail in Section 3.4.1.2 of Chapter 3. In short, the Puralytics Shield 1500 uses a photocatalyst mesh surrounded by an array of UVA LEDs in a continuous flow setup (0.6L/min), a UVC lamp is also placed immediately before the exit of the system.

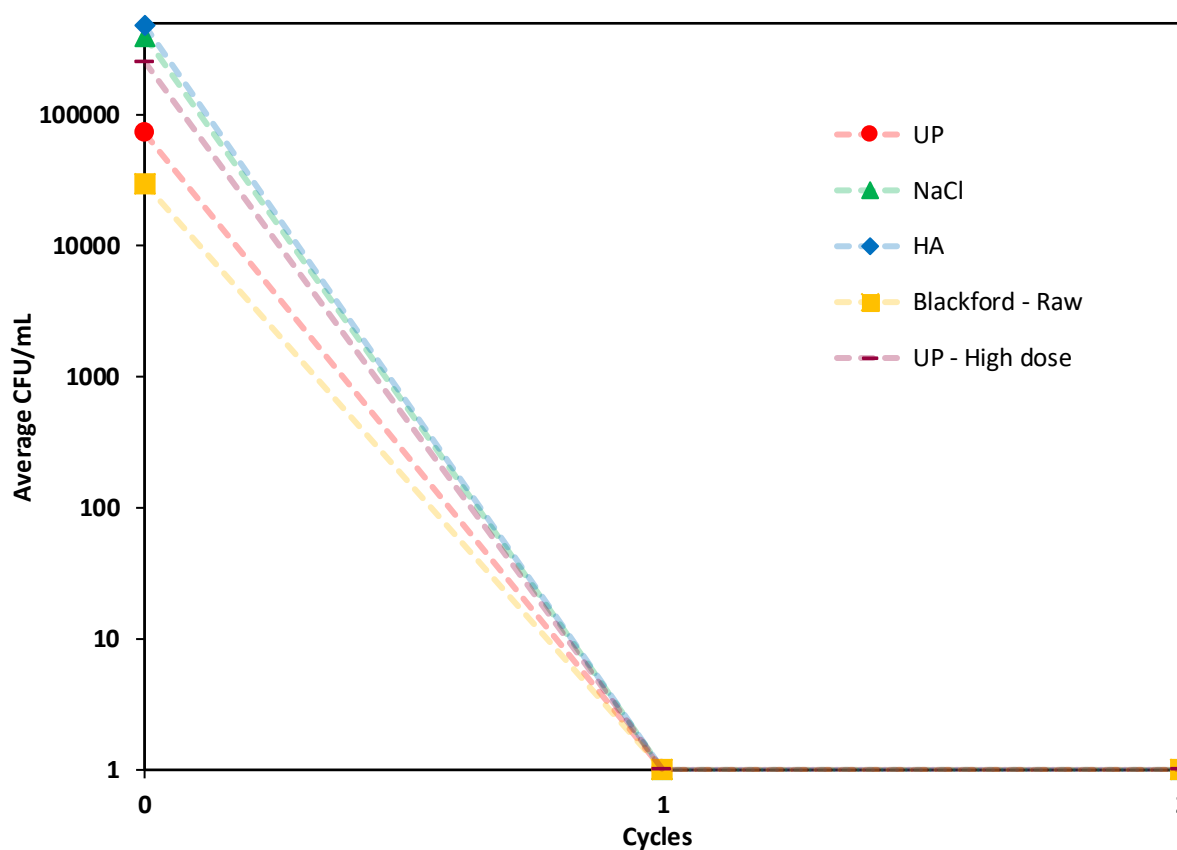


Figure 5.11 - Inactivation of *E. coli* (CFU/mL) after various cycles through pilot scale photocatalytic reactor in various water matrices: ultrapure water (UP), 10 mg/L Humic acid solution (HA), 0.8% NaCl solution (NaCl), Raw water from Blackford glen (Blackford – raw), ultrapure water with a double dose of spiked *E. coli* (UP – High dose). Experimental conditions: 0.6 L/min flow rate, treated volume = 1 L on continuous flow, average concentration deduced from valid serial dilutions.

The results shown in Figure 5.11 showed that total disinfection was achieved after a single run through the photocatalytic reactor. This is most likely due to the UVC lamp situated before the exit of the reactor causing direct photolysis of the *E. coli*'s cell membranes after having undergone photocatalytic treatment. This can be evidenced by comparing the UVC lamp's UV dose to the UV dose measured for the LED reactor setup. It should be noted that the Puralytics

reactor is sold as a water disinfection unit so it should provide the minimum UV disinfection dose according to ISO standard 20468-4. No exact measurement could be made for the Puralytics reactor but given the assumption that it is higher than the DWI standard for minimum disinfection ($\sim 40 \text{ mW.s/cm}^2$).

When comparing these results to those shown in section 4.3.4 in Figure 4.5, the capabilities of this pilot scale reactor differ greatly when removing organics when deactivating *E. coli*. This suggests that the Puralytics system was optimised more towards disinfection than NOM removal when designing the reactor as is evidenced by the results shown on the manufacturer's website.²⁸⁶ These manufacturer-published results show disinfections of various target microbes ranging from 3-log to 6-log disinfection rates whereas the organic target molecule results show a much greater variation with many showing below 40% removal. This is understandable within the context of the pilot scale reactor being marketed heavily towards implementation in areas with non-functioning drinking water treatment infrastructure such as natural disaster sites or remote areas with electricity access but no safe drinking water source, for these cases total organics removal is not necessarily a priority. With these results in mind, the implications for an industrial-scale photocatalytic reactor would sway towards whether the desired target is a high level of disinfection or reduction of organics for improved taste and odour as well as reducing the DBP formation. For implementation in an industrial drinking water treatment plant, disinfection is most likely already a well-developed system and the issues with NOM levels, previously discussed in Chapter 1, are more pressing. Therefore, optimising a photocatalytic reactor in this context would prioritise NOM removal and the energy efficiency decrease from the addition of a dedicated UVC light source for disinfection may be more detrimental than beneficial, especially when considering the need for ensuring disinfection throughout the water network to the end user.

5.4 Conclusions

This chapter explored the removal of bacteria from water using UV-LED-based photocatalysis as a means of relieving pressures on current disinfection infrastructure and ultimately reducing DBPFP. A variety of factors, such as the water matrix, operating volume, light source, and catalyst type, were investigated for their effect on the performance of an LED-based photocatalytic disinfection reactor setup were tested. This provided further insight for evaluating the viability of implementing such a system in industry and any possible improvements that could be implemented. The main conclusions from this investigation are listed below:

- Water matrix complexity plays a key role in photocatalytic disinfection rate. It was observed that the more complex the water matrix the lower the removal of bacteria will be. This shows that UVA-LED photocatalytic disinfection systems must be tested more in real world scenarios using real waters rather than the commonly tested ultrapure water.
- Increasing water volume can affect disinfection rates significantly by effectively reducing the catalyst loading in a system and therefore lowering the rate of disinfection.
- The modified C-TiO₂-TiCl₄ catalyst did not significantly improve disinfection rates, contrary to previous reported literature, despite showing a higher efficiency in NOM removal.
- Photocatalytic treatment could be integrated with UVC germicidal units to reap the advantages of both systems with efficient disinfection and NOM removal

- UV photocatalytic disinfection could be an important tool for easing the resources required by water treatment works (WTW) but not necessarily the main focus of industrial photocatalytic reactor design.

6 Environmental sustainability of immobilised and slurry photocatalytic systems for NOM removal in water

6.1 Introduction

Photocatalytic water treatment has been an increasing area of interest given recent advancements in UV LEDs leading to reduced operational costs and environmental impacts.^{124, 229, 287} A significant bottleneck that photocatalyst researchers must deal with is what state the catalyst is in. Suspending the photocatalyst particles amongst the sample water is perhaps the easiest method, which also leads to efficient use of catalyst surface area and therefore impressive reaction rates, but this also adds a hindering recovery step, often ultrafiltration or centrifuge.²⁵⁷ To get around this, many researchers immobilise catalysts onto a substrate to optimise reusability and limit any leaching of the catalyst into the water supply, the disadvantage tending to be a reduction in reaction efficiency, requiring more catalyst/lighting per unit to treat the water.²³⁹ Herein lies a delicate balance between the practicality (immobilisation) and efficacy (dispersion) of a photocatalytic reactor system designed for drinking water treatment. Many studies have compared the removal efficiencies of slurry vs immobilised systems, such as Manassero et al.¹⁶⁹, where slurry configurations are usually found to be the most efficient setup for target removal with the issue of catalyst removal being brought up as a practical downside. Despite the wealth of interest in this area, a categoric study of the environmental sustainability of these two systems has yet to be undertaken.

The aim of this Chapter is to examine the sustainability of immobilised versus suspended catalyst photocatalytic water treatment systems over their whole life cycles. Additionally,

some of the doubts surrounding industrial photocatalytic NOM, such as energy usage and material usage, are evaluated. Experiments were carried out to investigate the reusability of immobilised and suspended TiO_2 catalysts in real water matrices. Moreover, the sustainability and associated environmental impacts of the treatment processes were analysed by life cycle assessment (LCA) methodology. Alternative scenarios, such as how much of an environmental impact photocatalysis would have in a setting with 100% renewable electricity and how sustainable catalyst support material reuse can be, were also studied.

The results of this work contribute an important insight into the sustainability and environmental impacts of industrial NOM removal in real waters using LED irradiation and how this can be affected by catalyst design. Catalyst immobilisation is often taken for granted as a default in lab scale photocatalytic research but the use of LCA to quantify the environmental sustainability of the immobilisation process and immobilised catalyst use in industry compared to suspended catalysts is yet to be published in literature. Therefore, findings of this work can be used as a tool for researchers and water industry to further scale-up the process by choosing a setup that will enable an effective and sustainable treatment of water.

6.2 Experimental

6.2.1 Materials

The photocatalysts studied in this chapter are presented in Section 3.1 of Chapter 3 along with descriptions of their synthesis routes. In this Chapter, [im] is used as shorthand to describe a TiO_2 slide, P25 TiO_2 immobilised on glass via calcination. Additionally, [sus] is used to describe TiO_2 slurry, P25 TiO_2 suspended in the water matrix, without a support medium.

The raw natural water was collected from the Carron Valley reservoir at the influent of the Carron Valley Water Treatment Works (Falkirk, Scotland) and filtered with 0.45 μm $\times$ 55 mm Polyvinylidene Fluoride (PVDF) Membrane Filters to remove particulate matter. This water is detailed further in Section 3.2 of Chapter 3.

6.2.3 Photocatalytic experiments

Tests were conducted using glass slides and suspensions according to the procedures outlined in Chapter 3 Section 3.4 using SW3.

6.3 LCA methodology

The software package SimaPro 9.2.0.1 was used in this work. SimaPro LCA software package gives full control of databases, unit processes, supply networks, results, and every individual source of impact, offering extensive freedom and adaptation (PRé Sustainability, 2020). ISO (International Organization for Standardization) 14040 and ISO 14044 were followed to perform the LCA (ISO, 2006a, 2006b).

6.3.1 Goal and Scope

The main objective of this study was to determine the most environmentally sustainable photocatalytic process for water remediation at large-scale centralised treatment plants by comparing immobilised UV-LED/TiO₂ [im] ([im]) with suspended UV-LED/TiO₂ [sus] ([sus]) catalysis. The application of solar disinfection and decontamination processes as described for low and middle-income countries²⁸⁸ is outside the scope of this study. The removal of NOM was used as a case study, the environmental hotspots were investigated, and a sensitivity analysis was carried out to identify areas of sustainability improvement.

6.3.2 Functional unit

Treatment of 1 L of polluted water was taken as the functional unit since the focus of this study is on water treatment applications. Both UV-LED/TiO₂ [im] and UV-LED/TiO₂ [sus] photocatalytic treatment processes were compared in the time taken to obtain a final NOM concentration of 1 mg/L. Removal to 1 mg/L was chosen due to targets in NOM levels for industrial water treatment plants as it is a general international consensus that a concentration of dissolved organic carbon (DOC) <2mg/L is preferable in finished drinking water.²⁸⁹

6.3.3 System boundary

The system boundary for each process was determined and shown in Figure 6.1. The main system flows of this work were: (i) the energy inputs (electricity provided from the local grid), (ii) the laboratory units, (iii) the materials that were used (TiO₂ etc.), and (iv) their outputs to nature.

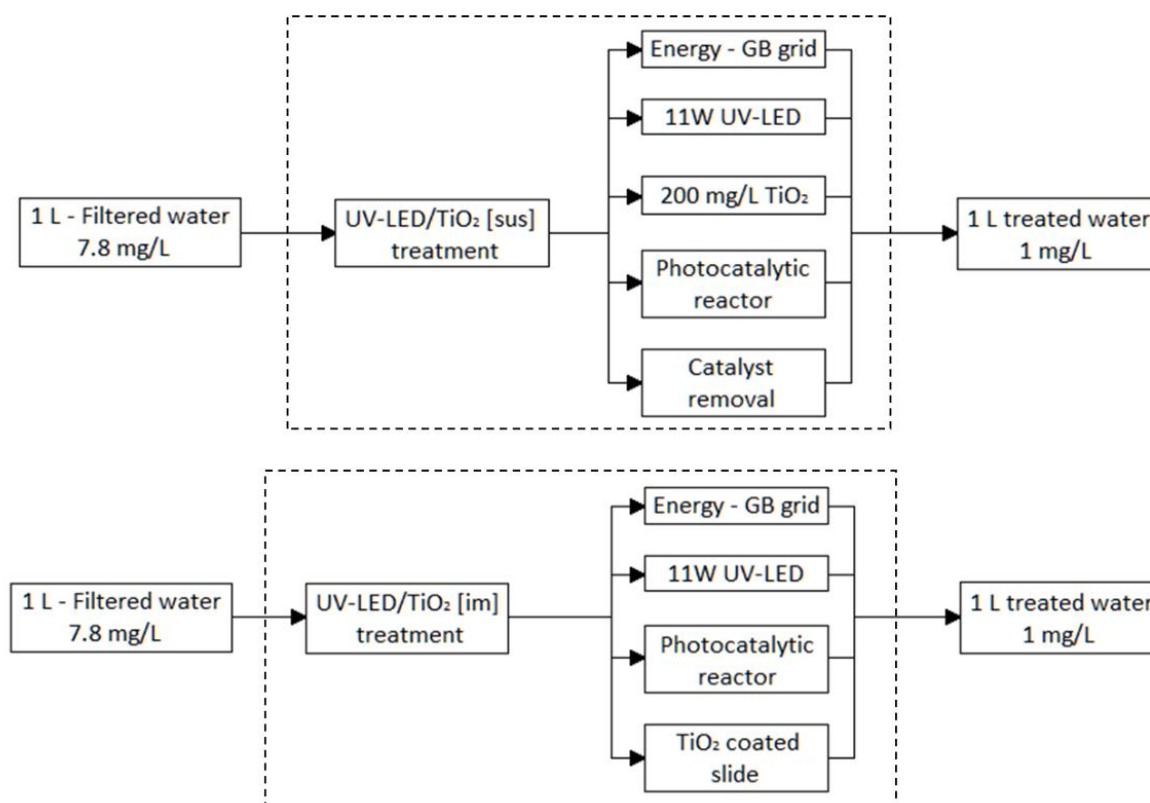


Figure 6.1 - System boundary of this study.

6.3.4 Life cycle inventory

Figure 6.2 shows the experimental set-ups that were used while Table 6.1 contains the raw material and process inputs to SimaPro for both UV-LED/TiO₂ [im] and UV-LED/TiO₂ [sus] process. As shown in Figure 6.2, the reactor set-up comprised of the LED, heat sink, quartz plate, glass dish and orbital stirrer. It was assumed that the LED cover and starboard would have the same life span as the LED itself. Additionally, the heatsink and quartz plate would have identical life spans as well as the magnetic components. SimaPro has a collection of databases which contain extensive information defining many different materials that are often used in manufacturing. Using the Ecoinvent 3 database, an LED array is already defined and can be used for the LCI. Additional components in the experimental equipment are not

specifically included requiring new records to be constructed using the materials documented within the database. For example, Ecoinvent 3 does not include a record of a heatsink, required for the UV-LED, but instead, as it is made of aluminium a new product record can be made using the SimaPro material-aluminium production mix, at the plant. The Ecoinvent 3 cutoff library was used assuming production materials.

To avoid any issues raised by the possible health and environmental impacts of nanoparticles being released into the drinking water supply,^{290, 291} an ultrafiltration module was factored into the [sus] setup as this has been shown to effectively remove measurable nanoparticles from water.²⁹²⁻²⁹⁴

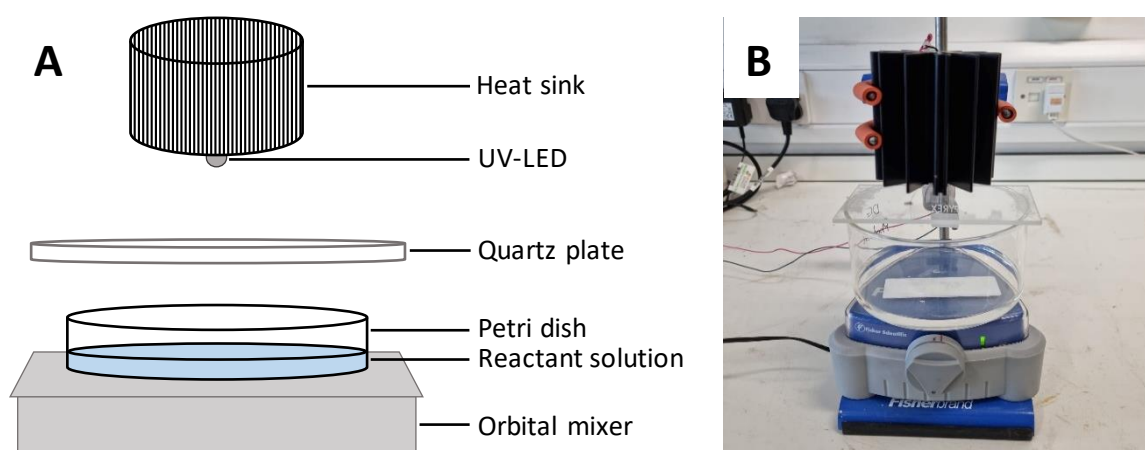


Figure 6.2 – Photocatalytic reactor setup (A) Schematic of the reactor (B) Photograph of the reactor.

Experimental data obtained showed that the reaction rates of [im] and [sus] systems decreased with increasing initial NOM concentrations. From observation of reaction rates, it was established that both systems followed first-order kinetics. Moreover, it was observed that concentrations of 0.8 mg/L and 0.5 mg/L of NOM were removed under [im] and [sus], respectively, after 100 min of treatment with 7.8 mg/L initial NOM concentration. Therefore,

treating water with [im] would require a longer period to achieve 1 mg/L removal of the contaminants. To determine the target treatment time for 1 mg/L NOM using [im] and [sus], the k values were calculated and a treatment time of 75min and 37min. This data is shown and discussed in detail in Section 4.3 of Chapter 4.

Table 6.1 - Raw material and process inputs for UV-LED/TiO₂ [im] and UV-LED/TiO₂ [sus].

Process	Materials/ Assemblies	Items	SimaPro Material	Quantity
Slurry & Immobilised	Light Source	Light emitting diode	Light emitting diode [GLO] production Cut-off, S	0.200 kg
		Heatsink	Aluminium alloy, AlMg3 [RER] production Cut-off, S	3.69 kg
		Starboard	Copper-rich materials [GLO] market for copper-rich materials Cut-off, S Aluminium alloy, AlMg3 [RER] production Cut-off, S	0.400 kg
	Reactor vessel	Glass Beaker	Glass tube, borosilicate [GLO] market for Cut-off, S	0.550 kg
		Quartz Plate	Silicon, metallurgical grade [RoW] production Cut-off, S	0.285 kg
	Lab Equipment	Orbital mixer	Permanent magnet, for electric motor [GLO] production Cut-off, S	0.407 kg
	Catalyst	TiO ₂ catalyst	Titanium dioxide [RER] market for Cut-off, S	200 mg
Slurry	Catalyst separation	Filter	Ultrafiltration module [GLO] ultrafiltration module production, hollow fibre Cut-off, S	1 P
			Water pump operation, electric [RoW] water pump operation, electric Cut-off, S	3.6 kJ
		Pump		
	Electricity	Electrical Connection	Electricity, low voltage market for electricity, low voltage [GB] Cut-off, S	214 KJ
Immobilised	Catalyst	Glass slide	Flat glass, uncoated [RoW] market for flat glass, uncoated Cut-off, S	0.25 kg
		Titanium dioxide	Titanium dioxide [RER] market for Cut-off, S	3.03 g
		Titanium butoxide	Titanium butoxide	4.54 cm ³
		n-Butanol	1-butanol [GLO] market for Cut-off, S	0.077 kg
		Hydrochloric acid	Hydrochloric acid, Mannheim process (30% HCl), at plant/RER Mass	1.05 g
	Electricity	Electrical Connection	Electricity, low voltage [GB] market for electricity, low voltage Cut-off, S	432 KJ

6.3.5 Life Cycle Impact Assessment

Two life cycle impact assessment (LCIA) methods were used, namely ReCiPe 2016 and IPCC 2021. ReCiPe 2016 is globally recognised comprising different sets of impact categories with associated sets of characterization factors for use at the normalization and weighting stage. At the midpoint level, 18 impact categories are addressed which are then collected into 9 damage pathways. At the endpoint level, the midpoint impact categories are multiplied by damage factors and aggregated into three damage categories, i.e., Human Health, Ecosystems and Resources. The IPCC 2021 impact assessment method uses two different time perspectives (20 and 100 years) to compare processes based on CO₂ equivalent (CO₂eq) emissions, i.e., greenhouse gas (GHG) emissions which are used to measure Global Warming Potential (GWP), a standard indicator of environmental relevance. The different timeframes are advantageous as different substances vary in their lifetime. For example, methane has a relatively short lifetime, staying in the environment for about 12 years meaning it is more prominent in the short time perspective, whereas CO₂ remains in the environment for longer than methane with estimations of 30-95 years. Highlighting the importance of the timescales per unit of mass, the impact of methane on climate change over 20 years is 84 times greater than CO₂, but over a 100-year period is less at only 28 times greater (Climate and Clean Air Coalition, 2022). Here 100-year time horizon was selected (IPCC 2013 GWP 100a). ReCiPe also includes a midpoint category relevant to GHG, i.e., Global warming, however it differs from the IPCC 2021 GWP 100a because climate-carbon feedback for non-CO₂ GHGs is included. Since IPCC 2021 is a widely recognised LCIA method by the public as well as by decision-makers and policymakers, was therefore adopted here to express the carbon footprint.

6.4 Results and Discussion

6.4.1 Suspended vs immobilised photocatalysis

Experiments comparing the capabilities of immobilised P25 TiO₂ slides and P25 TiO₂ slurries for the photocatalytic removal of NOM were investigated and discussed in Section 4.3.5 of Chapter 4. These results are displayed again below in Figure 6.3.

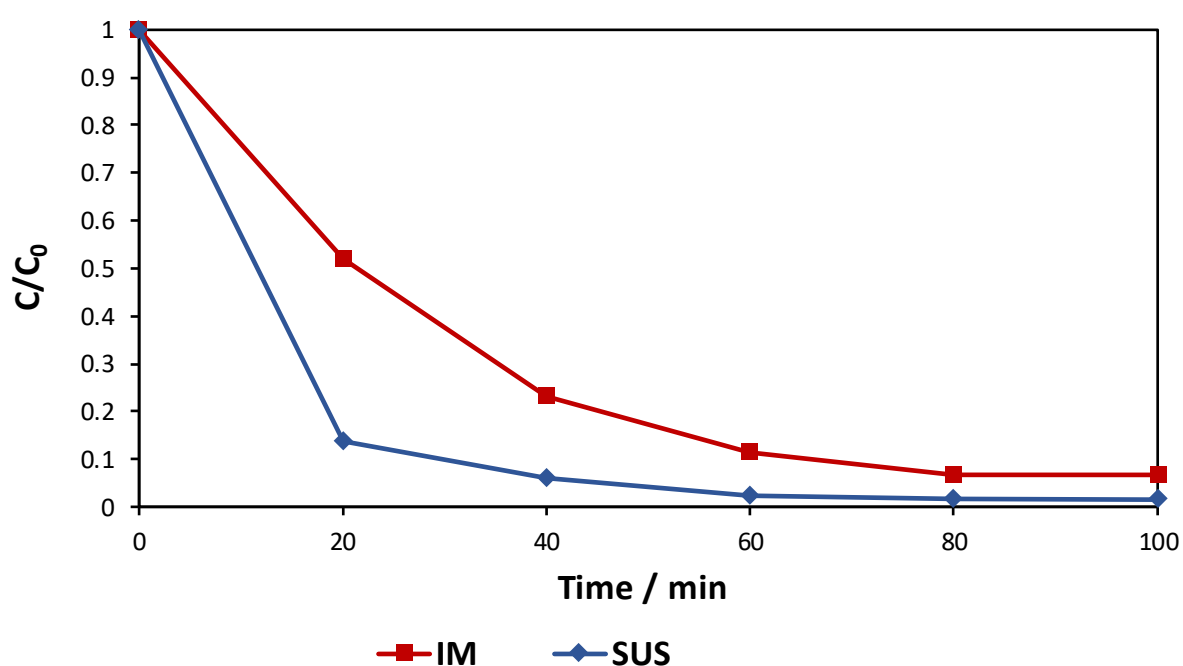


Figure 6.3 - Rate of NOM removal for various states of photocatalyst. Experimental conditions: water = SW3; pH = 7; 370 nm UV-LED; water volume = 20 mL; orbital mixer stirring (40 rpm). Catalysts; [sus] = P25 catalyst slurry (200 mg/L); [im] = TiO₂ slide.

These experiments showed that optimum slurry reactions reached a peak 99% reduction in NOM concentration when compared to a peak 95% reduction from immobilised catalysts with the slurry setup achieving this peak significantly quicker than the immobilised catalyst.

6.4.2 Catalyst reusability

The reusability of slurry-based reactions was tested to compare the viability of the two methods in an industrial process. The results of these experiments were presented and discussed in Section 4.3.5 of Chapter 4. Said experiments used filtered stock water in a photocatalytic reactor setup, after 100 min the catalyst was removed, by centrifuging at 6000rpm for 30 min in the case of the slurry experiments, and then reused in a fresh sample of stock water. The results, displayed again below in Figure 6.4, suggest that not only does a slurry setup have a better rate of removal but also a similar rate of reusability, with the added benefit of being able to easily replace any catalyst that is lost during catalyst separation.

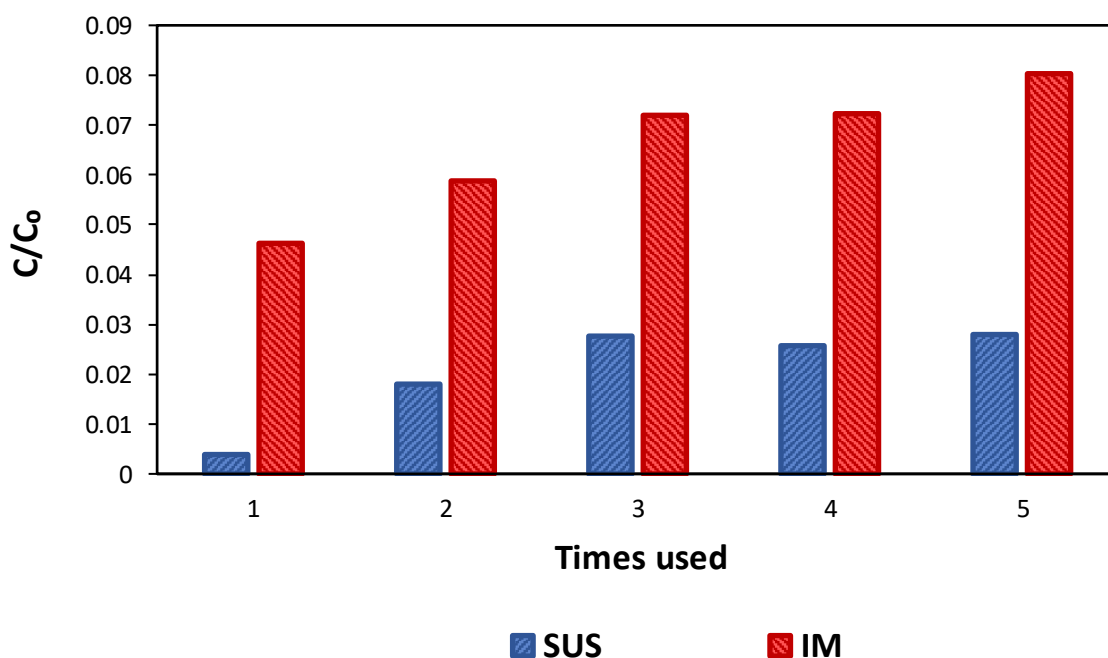


Figure 6.4 - NOM removal during photocatalysis and the consecutive use of [sus] and [im] catalysts.

6.4.3 LCA results

Utilising the IPCC 2021 LCIA method, the GWP for the [sus] and [im] processes were 0.0218 and 0.162 kg CO₂eq, respectively, which represents an 87% decrease in carbon emissions from [im] and [sus]. This is linked back to the time taken to treat the raw water and by extension to the electricity used, i.e., the higher the treatment time the higher the electricity consumption. To be more specific, electricity consumption includes the energy required to light up the UV-LED as well as to continuously stir the reactant mixture. In this case, the [im] process takes 2.03 times longer to treat 1 L of raw water than the [sus] treatment. Therefore, this difference in treatment time had an intuitive impact on the sustainability of the [im] as additional electricity was required to achieve 1 mg/L. As has been observed with Chatzisyneon et al.,²¹³ an AOP's GWP is roughly proportional to energy consumption,^{213, 214} with roughly the same proportionality seen in the results for [sus] and [im]. Therefore, to lower the GWP, methods to reduce energy consumption and/or renewable energy should be introduced. Additionally, the pivotal steps that differentiate the two processes, immobilising titania on a substrate and separating a slurry catalyst after treatment, differ significantly in energy usage. This can be attributed to the lengthy calcination process that requires multiple rounds of high-temperature furnace use as compared to the slurry removal using pumps that, based on reactor design could be gravity-assisted. The immobilisation and catalyst separation processes accounted for 0.120 and 0.00270 kg CO₂eq, respectively, which represents a 97.8% decrease in carbon emissions from UV-LED/TiO₂ [im] and UV-LED/TiO₂ [sus].

Figure 6.5 shows the individual percentage contributions from the separate stages considered in the system boundary to the overall environmental footprint for both [sus] and [im] treatments. These percentages provide an early indication that the contributions to the

environmental sustainability of UV/TiO₂ photocatalysis vary greatly depending on the catalyst setup being used. To be more specific, the biggest variation in contributors to the environmental footprints was the catalyst with 82.5% for the [im] whereas the [sus] setup's environmental footprint comprised only 0.6% from the catalyst production, this [sus] result is in keeping with literature studies like the work done by Foteinis et al.²¹⁴ which recorded a 0.236% contribution from TiO₂, showing how energy and material intensive the immobilisation process can be, although to the best of the authors knowledge a comprehensive LCA of TiO₂ immobilisation techniques hasn't been published. This discrepancy in catalyst contributions is due to the wide variety of materials required in the immobilisation process, including an intensive calcination step for the catalyst whereas the [sus] only required a small amount of P25 titania for the catalyst step. The contributions of the photocatalytic reactor didn't vary as significantly for the two processes with the [sus] input at 16.9% and 1.2% for the [im]. This was expected due to the relative similarity of the reactor setups with the addition of the separation equipment required for the [sus] setup.

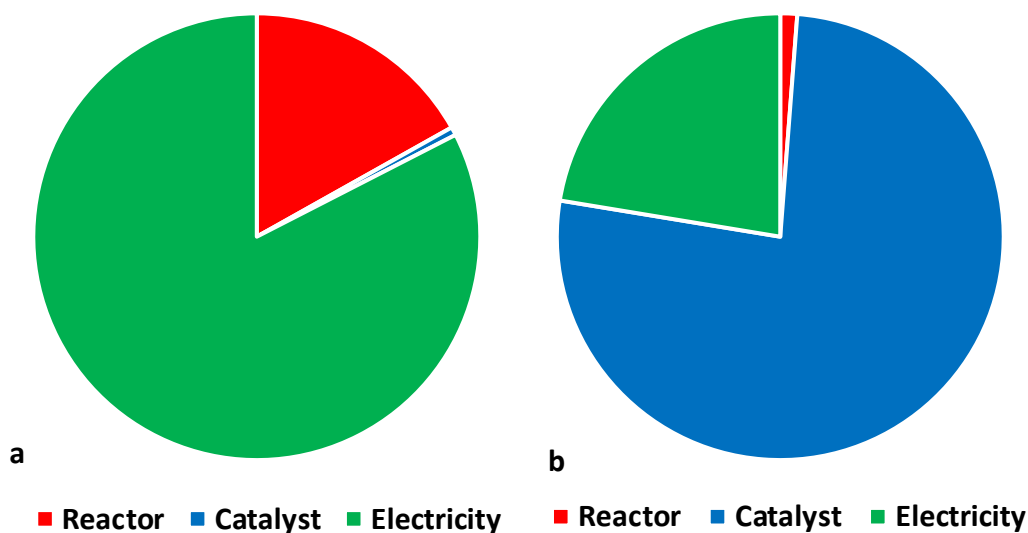


Figure 6.5 - Percentage contributions of the individual components of the (a) [sus] and (b) [im] photocatalytic processes to the environmental impacts.

ReCiPe is a robust multi-issue impact assessment method and therefore it can provide a more holistic overview of the environmental sustainability of the two photocatalytic processes. First, the ReCiPe characterization model (midpoint-oriented indicators) is used to calculate the contribution of each parameter to each of the 18 midpoint impact categories. Figure 6.6 shows the midpoint results (characterisation) when comparing the [sus] and [im] processes to treat SW3. At the midpoint level, the main findings show that the [sus] is more beneficial than the [im], with [sus] having at least 55% less impact than that of [im] in all but 1 category, namely marine eutrophication. The contributions to this category had 33% less impact on [sus] compared to that of [im]. The marine eutrophication category relies on the assumption that marine ecosystems tend to be limited by nitrogen, using a simplified nitrogen air fate and transport assumption that 70% of nitrogen inputs into surface freshwater ecosystems make their way to coastal waters.

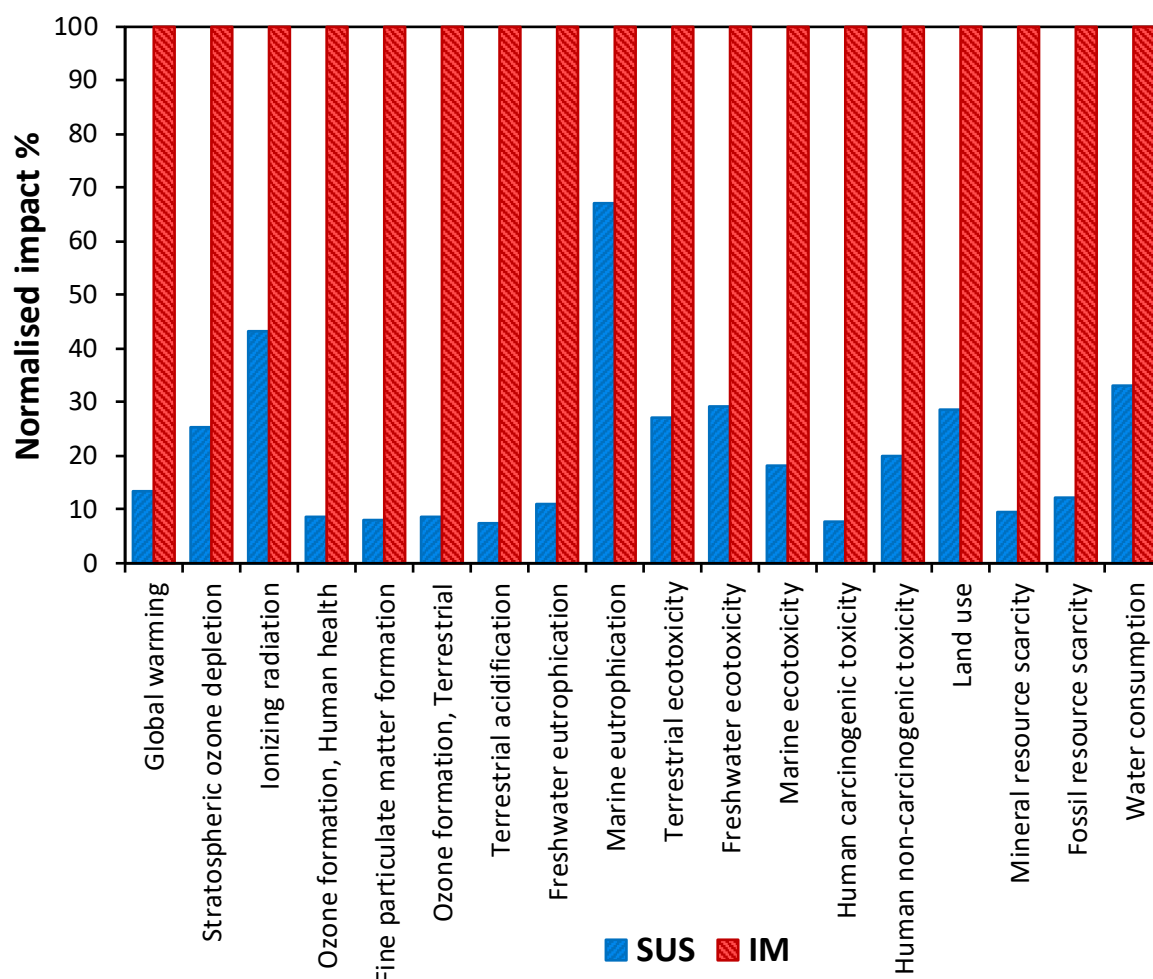


Figure 6.6 - Characterisation output from ReCiPe 2016 impact assessment comparing [sus] and [im] cases.

When the results were normalised, it was identified that the midpoint impact categories that are affected the most are, from higher to lower score, Human carcinogenic toxicity>> Freshwater eutrophication> Ionizing radiation> Fossil resource scarcity> Terrestrial ecotoxicity, while the remaining impact categories exhibited extremely low normalised scores. An LCA study by Ioannou-Ttofa et al.²¹⁵ investigating solar-Fenton treatment for secondary-treated urban effluents also found that many of these (eco)toxicities impact categories were affected, tracing back to fossil fuel (oil) consumption for electricity

generation, thus suggesting that solar energy would eliminate this environmental hotspot as energy consumption for irradiation would be eradicated.²¹⁵ The categories affected most in the investigation by Ioannou-Ttofa et al.²¹⁵ were natural land transformation > marine ecotoxicity > freshwater ecotoxicity > human toxicity > terrestrial acidification > fossil depletion. The reason human carcinogenic toxicity is a more significant factor in the results shown in Figure 6.6 is that the electricity mix used by Ioannou-Ttofa was 92.5% oil based whereas the GB mix used in this study contains a wide variety of sources including coal which contributes significantly higher to human carcinogen toxicity when compared to oil.^{295, 296} Additionally, the setup used by Ioannou-Ttofa et al.²¹⁵ was mostly solar powered so the electricity being used was less of a total contributor to the overall process using only 32.4 KJ per Litre compared to 432 and 214 KJ per Litre for [im] and [sus] treatments respectively.

Following on from the midpoint level, the data was also aggregated using ReCiPe's three endpoint damage categories, namely 'human health', 'ecosystems' and 'resources' (Figure 6.7). Similarly, with the midpoint results, endpoint results indicated that the biggest concerns with photocatalytic oxidation techniques are by far the impacts that they have on human health; [sus] process generated 5.04 mPt for human health compared to only 0.337 mPt for ecosystems and 0.0165 mPt for resources. The same trend was identified with [im] yielding 32.1, 2.11 and 0.139 mPt for human health, ecosystems, and resources, respectively. The damaging effect on human health can be associated with the energy consumed, made worse by not using renewable electricity.

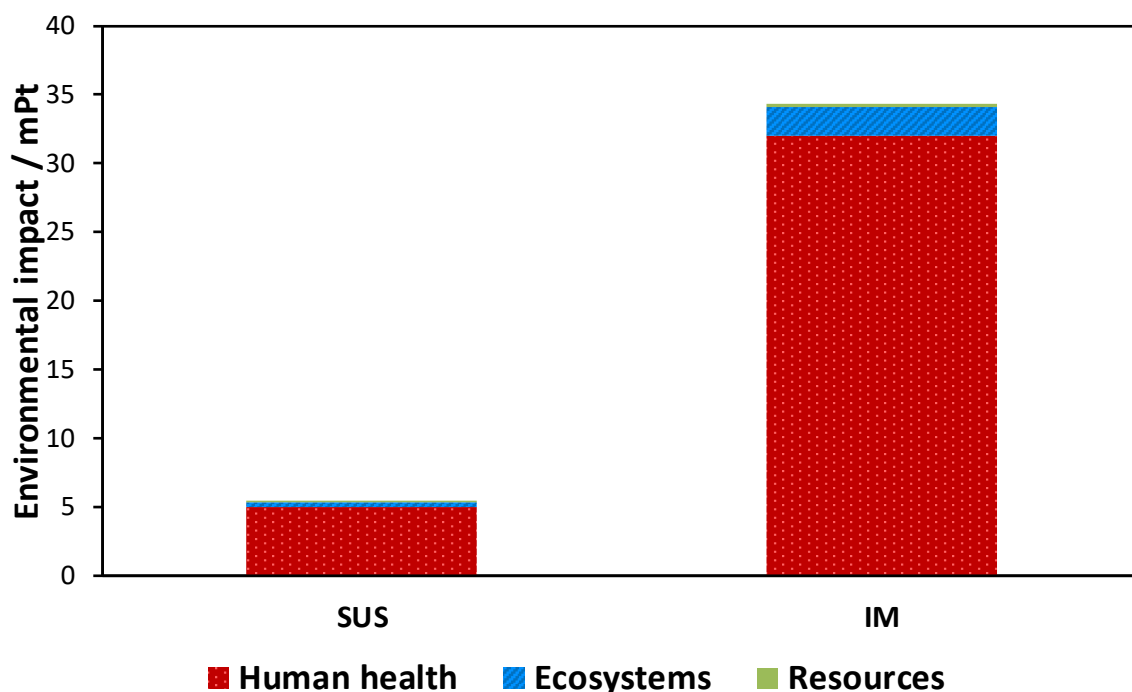


Figure 6.7 – Single Score output from ReCiPe 2016 impact assessment comparing [sus] and [im] cases.

These results are similar to those seen in literature like those published by McKee et al.¹²⁴ where human health effects contributed to 89% of the single score for the photocatalytic degradation of bisphenol-A (BPA) under UVA-LED. This is slightly lower than the 99% and 93% human health contributions for [sus] and [im] respectively, likely owing to the different perspectives used with McKee et al. using the hierarchist perspective for ReCiPe 2016 rather than the egalitarian perspective for ReCiPe 2016. The egalitarian perspective is more precautionary and takes longer timeframes into account which normally leads to higher contributions to long term health from air-based things like emission particulates and radiation.²⁹⁷⁻²⁹⁹

LCA results in alternative scenario 1: Renewable electricity mix

Given the differences shown in Figure 6.5, an alternate scenario to the main comparison was tested using a 100% renewable electricity mixture rather than the current GB electricity mix. This was to gauge if significant improvements in the carbon emissions and health impacts of photocatalytic water treatment could be achieved in the future by moving away from fossil fuel use for electricity generation. This scenario was also tested to see if one treatment's impacts would be affected more than the other due to the source of the electricity production. Many studies have found that the biggest flaw in UV treatment processes is the use of electricity and that further studies should investigate the impact of using renewable electricity. Therefore, the first alternative scenario investigated was the use of an electricity mix based on the renewable electricity output of Scotland. Scotland has built up a reputation as being one of the world's leading nations at sourcing its electricity from renewables; in 2020 97% of its gross electricity consumption came from renewable sources, including about 71% from wind energy and 18.1% from hydro. Comparing this to 43.1% of the UK's electricity coming from renewables in 2020, it is perfectly reasonable to assume that [im] and [sus] water treatment would benefit from a lower carbon-intensive energy source. Table 6.2 shows the respective electricity mix that was used in this scenario and was decided using Scotland's electricity production in 2020. The percentages take the electricity mix from renewables used in 2020 as if they were supplying 100% of the electricity supply as this is the rough proportions that Scotland plans to use for its target net zero electricity consumption. The biggest contributor was onshore wind followed by hydro and offshore wind, with smaller contributions from other sources.

Table 6.2 – The electricity mix used for alternative scenario 1 – 100% renewable electricity sources

Energy source	Scottish electricity generation in 2020 (GWh)	Percentage for renewable electricity mix (%)
Onshore wind	19,594	61.2
Offshore wind	3492	10.9
Hydro	6278	19.6
Bioenergy and Waste	2298	7.18
Solar PV	329	1.02
Wave and Tidal	11	0.0344

Utilising the IPCC 2021 LCIA method, the GWP for the [sus] and [im] processes were 0.00989 and 0.138 kg CO₂eq, respectively, which represents a 93% decrease in carbon emissions from [im] and [sus]. Although both methods saw a decrease in their global warming impact from the original scenario, [im] saw a significantly lower reduction (15%) compared to [sus] (55%) when compared to the original energy mix. This can be explained by the differences in the percentage contributions of the individual components as shown in Figure 6.5. In the original case the [sus] process' percentage electricity contribution (82.5%) is 3.6 times higher than that of the [im] process (22.4%) and is therefore reduced by roughly 3.6 times more when the electricity's contribution is lowered by using renewables (64.4% and 9.9% for [sus] and [im] respectively). These results are in keeping with those in literature, such as the work by Ioannou-Ttofa et al.²¹⁵ which investigated the effects of changing the electricity inputs to renewable sources for solar Fenton oxidation of organic contaminants at pilot scale. This study saw an 83% reduction in GWP when switching to purely solar energy with the chemical

and reactor percentage contributions rising as a result of the electricity contributions lowering.

Figure 6.8 shows the individual percentage contributions from the separate stages considered in the system boundary to the overall environmental footprint for both [sus] and [im] treatments. These percentages show further insight into why the [sus] treatment was affected more by the change in energy supply. The trend shown in contributors to the environmental footprints was that the electricity contribution decreased, and other contributions increased. The catalyst contribution for the [im] increased from 82.5% in the original scenario to 88.7% whereas the [sus] setup's environmental footprint rose from 0.6% to 1.5%. The contributions of the photocatalytic reactor increased dramatically for the [sus], rising from 16.9% to 34.1%. This was expected due to the relative similarity of the reactor setups with the addition of the separation equipment required for the [sus] setup.

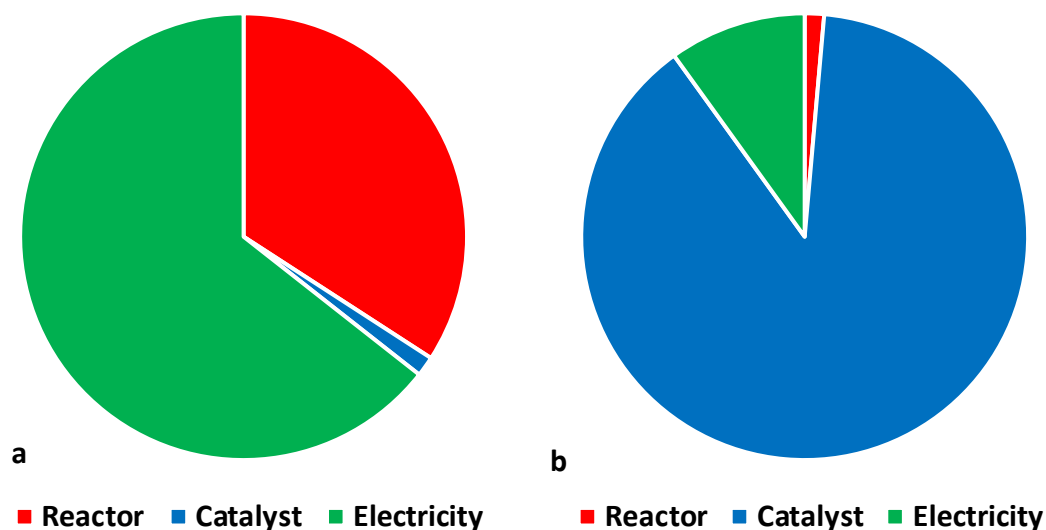


Figure 6.8 - Percentage contributions of the individual components of the (a) [sus] and (b) [im] photocatalytic processes to the environmental impacts.

Using the ReCiPe characterization model (midpoint-oriented indicators) the contribution of each parameter to each of the 18 midpoint impact categories was calculated. Figure 6.9 shows the midpoint results (characterisation) when comparing the [sus] and [im] processes using renewable energy sources. At the midpoint level, the main findings show little change from the original scenario with almost every category increasing the relative difference between [sus] and [im] except notably marine eutrophication. This is likely because the chemicals used for the immobilisation process and the reactor materials are the main contributors to the marine eutrophication categories for [im] and [sus] so the energy supply has less of an effect. In contrast, the investigation by Ioannou-Ttofa et al.²¹⁵ saw a notable relative increase in marine and freshwater ecotoxicity which was explained by the indirect emissions associated with the manufacturing procedure of the PV panels (heavy metals, SO_x, NO_x, particulate matter, and greenhouse gas emissions) and the use of chemicals and their water-borne emissions during the oxidation process. The relative contributions to this

category increased with the [sus] process growing from 67% to 72% when compared to [im].

This is most likely because the reactor setup is a large contributor to this category so changing electricity contributions has little effect.

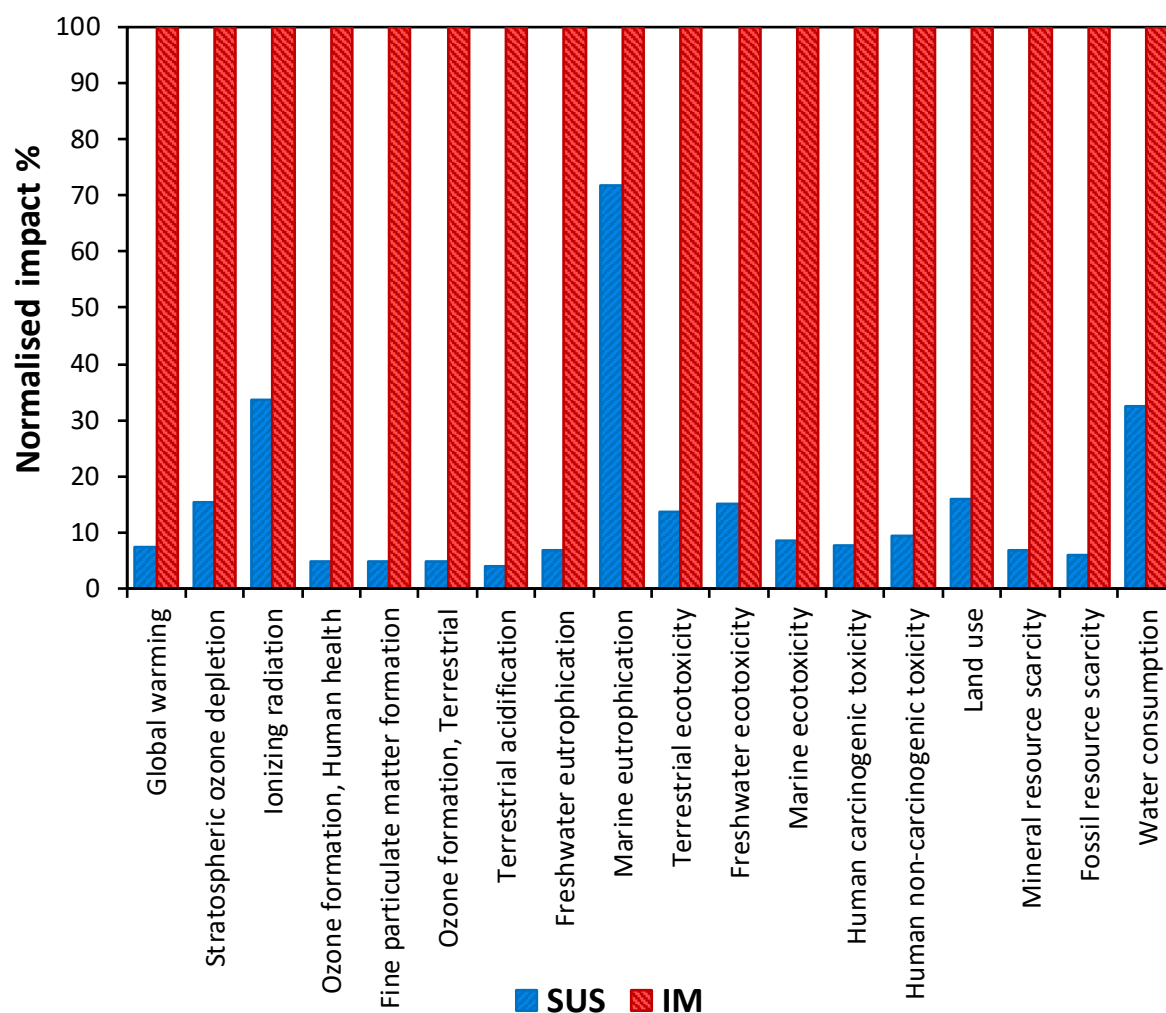


Figure 6.9 - Characterisation output from ReCiPe 2016 impact assessment comparing [sus] and [im] cases.

Following on from the midpoint level, the data was again aggregated using ReCiPe's three endpoint damage categories, namely 'human health', 'ecosystems' and 'resources' (Figure 6.10). Similarly, with the original scenario results, the endpoint results indicated that the biggest concerns with photocatalytic oxidation techniques are by far the impacts that they have on human health; [sus] process generated 2.24 mPt for human health (55% reduction from the original scenario), 0.136 mPt for ecosystems (60% reduction from original scenario), and 0.00658 mPt for resources (60% reduction from original scenario), giving a 56% reduction in total single score impact compared to the original scenario. A similar result was seen by McKee et al. when comparing a renewable energy mix to the standard British energy generation mix, this resulted in a 41% reduction in total single score.

[im] also saw reductions, yielding 26.4, 1.7 and 0.119 mPt for human health, ecosystems, and resources (18%, 19% and 14% reductions) respectively. These data show that the relative reductions in harm to the 3 categories were not proportionately affected when changing the electricity mixture. The impact on resources was reduced much less in the [im] process when compared to [sus], this could again be due to the increased demand for materials for the immobilisation process, making it the most influential factor in deciding the process' environmental impact whereas the [sus] process is mostly dictated by energy demand and source.

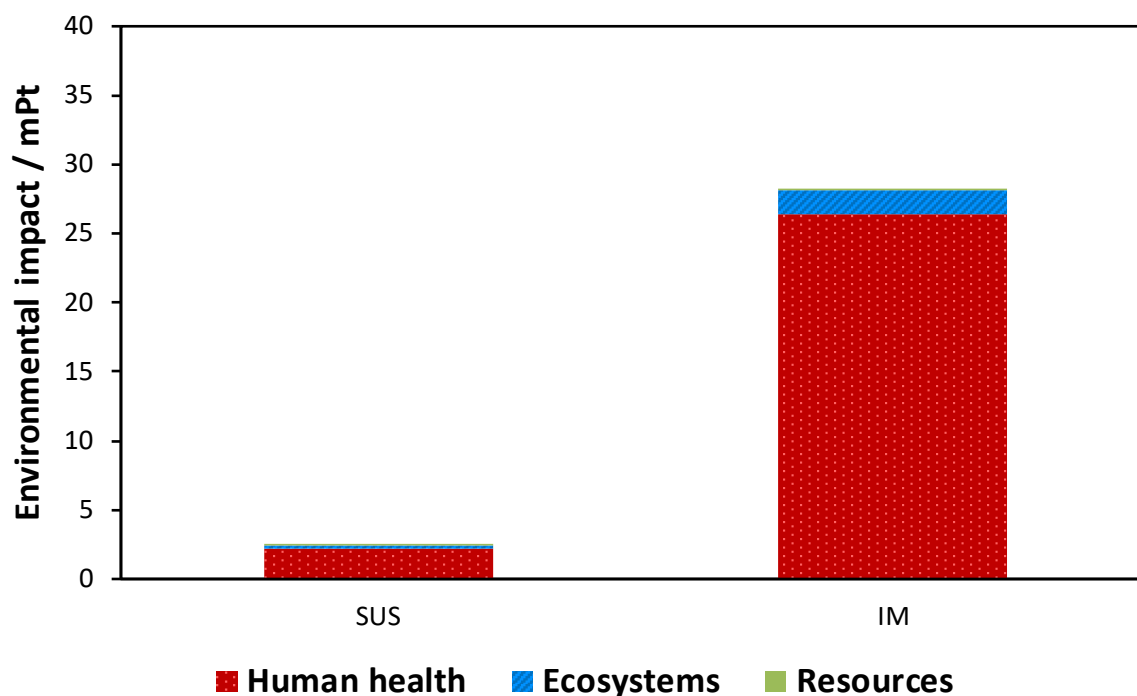


Figure 6.10 – Single Score output from ReCiPe 2016 impact assessment comparing [sus] and [im] cases.

LCIA results in alternative scenario 2: Immobilised catalyst glass reuse

Upon further analysis of the differences shown in Figure 6.5, an alternate scenario to the main comparison was tested where the glass that the catalyst was immobilised on is reused rather than recycled after the catalyst is no longer capable of achieving the desired treatment level. This was to gauge if significant improvements in sustainability could be achieved by creating a robust enough catalyst reuse system. This scenario also tested at what level of reuse and breakage could one achieve to still negate the sustainability impact of creating the catalyst. Whilst analysing the data from the original scenario, it became apparent that the use of fresh glass each time the catalyst was worn out, created a significant proportion of the [im] process's impact on sustainability with glass providing up to 30% of the IPCC result. Therefore,

the second alternative scenario investigated was the level of glass reuse required to reduce the level of impact the [im] process contributed through catalyst production. This area was investigated due to the apparent lack of current literature on photocatalyst immobilisation and support reuse. This required altering the mass fraction of the glass utilised per system unit and therefore altering the impacts created from producing, processing and ultimately disposing of the glass for the catalyst used as well as giving an insight into the required lifetime of the reused glass before significant changes in sustainability are no longer seen. The various levels of reuse are stated below in Table 6.3 with a brief description.

Table 6.3 – The levels of glass reuse investigated in scenario 2: Immobilised catalyst glass reuse.

Name	Times glass is reused before recycling
[im1]	1
[im2]	2
[im5]	5
[im10]	10
[im100]	100
[im1000]	1000

Utilising the IPCC 2021 LCIA method, the GWP for the various processes are displayed below in Figure 6.11. These results show a significant reduction in environmental impact when compared to no reuse in glass with [im1] and [im2] showing 0.136 kg CO₂eq and 0.130 kg CO₂eq, respectively, which represents a 16% decrease in carbon emissions from [im] after a single reuse. This significance in impact reduction quickly decreased as reuse increased with [im10] and [im100] producing 0.115 kg CO₂eq and 0.11 kg CO₂eq, respectively and then

[im1000] producing 0.109 kg CO₂eq in carbon emissions, a 4.3% reduction from [im10] to [im100]. It is assumed that at this level reuse produces diminishing returns with a 0.9% reduction in carbon emissions when increasing reuse from [im100] to [im1000]. It is at this point that the contribution of the glass is no longer a significant contributor to the carbon emissions produced by treating the system unit. This can be seen in Figure 6.11 which shows the GWP100 fossil contributions from each reuse case considered in this scenario. This Figure shows that the percentage contribution of the catalyst for the [im] series of processes started at 76.36% when no glass was reused in catalyst production which then dropped to 71.94% for [im1] and finally 64.89% for [im1000]. This Figure suggests that gaining at least 10 extra uses from the glass before it is broken or no longer usable would largely negate the media's environmental impact.

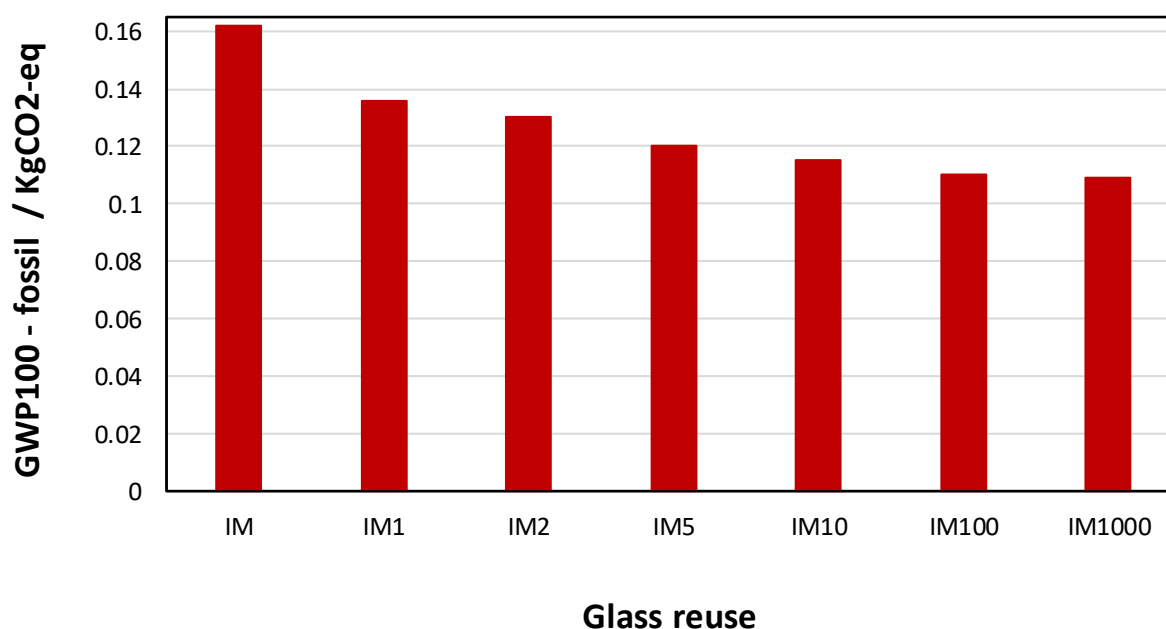


Figure 6.11 – Environmental impact contributions of the individual components of [im] photocatalytic processes with various levels of glass reuse.

The data was again aggregated using ReCiPe's endpoint analysis and a single score value was produced (Figure 6.12). Similarly with the IPCC results, the endpoint results indicated that the diminishing returns on sustainability were yielded after reusing the glass over 5 times with the [im1] process generating 30.5 mPt (11% reduction from original scenario), 28.7 mPt for [im2] (16% reduction from original scenario), and 28.2 mPt for [im5] (17.7% reduction from original scenario). The [im10] and [im100] then showed a significantly lower reduction in single score value with 27.4 mPt and 26.7 mPt respectively (20% & 22% reduction from the original scenario with only a 22% reduction seen for the presumed top-end reduction at [im1000]). This suggests that the carbon contribution of the use of glass is a larger contributor to the environmental impact of the treatment process than the biogenic or land transformation impact.

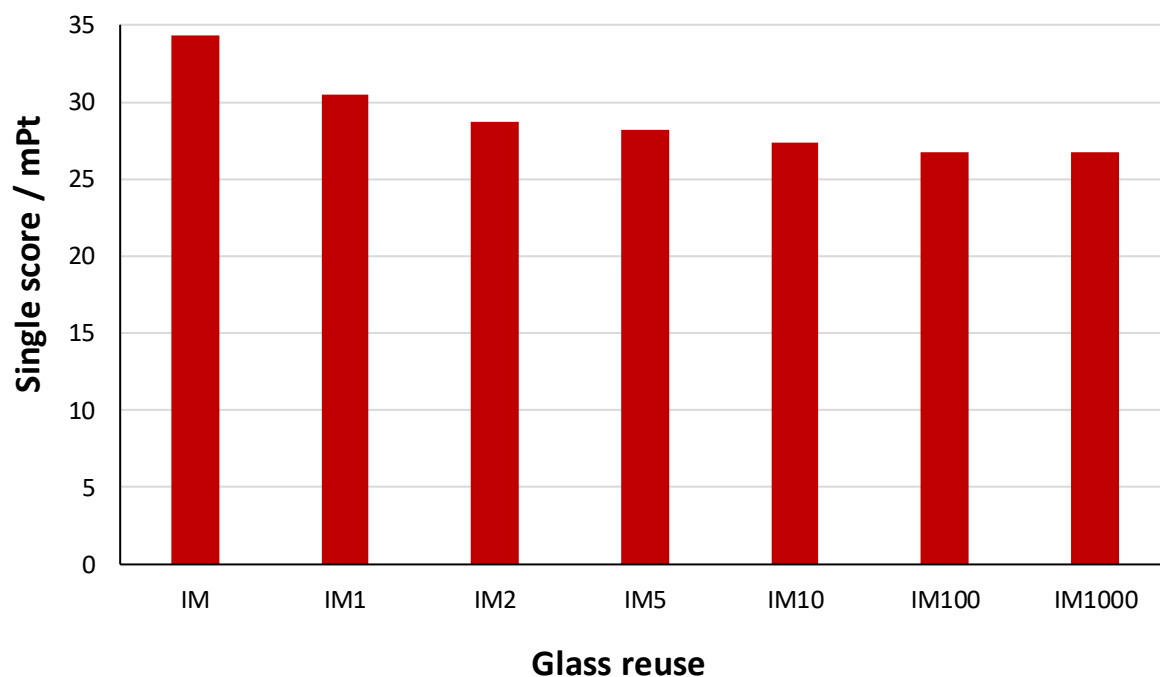


Figure 6.12 – Single Score output from ReCiPe 2016 impact assessment comparing [im] photocatalytic processes with various levels of glass reuse.

This work gives vital insight into scaling up photocatalysis for industry as very little LCA work has been conducted focusing on the reuse of catalyst supports or even immobilised photocatalysts in general. One area of this work that could be expanded is the methods and extent to which supports are reused and recycled as current work on general catalyst support, such as work done by Kressirer et al.³⁰⁰, suggests that the environmental impact of support reuse can depend heavily on the procedures for the coating and the removal of the coating from the plates.

6.5 Conclusions

The environmental sustainability of [im] and [sus] photocatalysis to remove NOM from water was investigated. The life cycle assessment (LCA) methodology was employed to estimate the environmental footprint of the [sus] and [im] processes. The functional unit adopted was the treatment of 1 L of water and the attainment of 1 mg/L NOM. The effect on key impact categories of human health, resources and ecosystems was investigated along with the effect of each treatment on climate change.

The main conclusions from this investigation are listed below:

- [sus] had the lower environmental footprint, by 87%, compared to that of [im] and human health was the endpoint damage category that suffered the most due to the chemical components of the immobilisation process and the fossil fuel sourced electricity used to power the reaction processes.
- It was observed that the main environmental hotspots in the treatment were the energy consumption for the [sus] setup and the catalyst in the case of [im] setup.
- Investigation of a more sustainable source of electricity showed that the sustainability of both methods benefitted from a renewable energy mix with [sus] benefitting more due to energy being its main environmental contributor.
- Recycling of the [im] substrate material was studied with just 10 reuses of the substrate showing to mitigate the environmental impact of using glass for the treatment of 1 L of water.

7 Conclusions and Future Work

This Thesis has investigated photocatalytic methods for the treatment of NOM and microorganisms in drinking water. Chapter 4 focussed on the operational parameters of UV-LED photocatalytic NOM removal and how the properties of real water matrices affect organics degradation. It was determined that modifying the TiO_2 catalyst had the potential to enhance NOM removal in humic acid solutions. This is promising as it can increase efficiency and throughput in real-world applications, although the process of modifying the catalyst would have to undergo further study to ensure easy manufacturing, scaleup, and handling. Subsequent tests investigated the trends observed when changing the conditions of a reactor design. It was observed that increasing the reactor's volume and increasing the concentration of humic acid had a detrimental effect on organics removal. The complications of using real surface waters were then demonstrated by using various dilutions of Pateshill reservoir water which did not show a significant trend in the rate of organics removal. This was attributed to the differences in inhibition and enhancement observed when inorganic ions are present in a photocatalytic reaction mixture at different concentrations. However, the exceptional results from the slurry catalyst prompted the question of how sustainable the added practicality of not requiring a separation step was when using immobilised catalysts when compared to a suspended catalyst reactor. This was explored in Chapter 6 where it was shown that a scaled-up photocatalytic reactor would have significantly more environmental impact when treating 1 L of water if an immobilised catalyst setup was used. This assessment used conclusions from results in Chapter 4 that showed significant TiO_2 catalyst fouling from NOM present in real waters and how that affected the reusability of both immobilised and suspended catalysts. This was important as there was no available literature on the observed deactivation of

immobilised or suspended catalysts when being reused for NOM removal in real waters. Further scenarios were tested observing the differences made to the environmental impact of photocatalytic NOM removal. It was shown that although renewable energy sources improved the sustainability of both catalyst types, suspended catalysts benefitted much more from this. Techniques in immobilised catalyst recycling were also considered with a critical point for the reuse of glass supports for immobilised catalysts being shown to be around 100 reuses. Future work may expand on this by exploring the environmental impact of catalyst rejuvenation, perhaps by heat treatment. This has been shown to increase catalyst lifetime by removing fouling on the catalyst's surface, but the use of high temperatures and the deployment of additional catalysts to replace these catalysts during their rejuvenation process may significantly impact this improved sustainability.

Similarly, Chapter 5 focussed on the operational parameters of UV-LED photocatalytic disinfection and how the properties of real water matrices affect the disinfection rate. It was determined that modifying the TiO_2 catalyst had little effect on the disinfection rate. Although disappointing, the benefits of modifying catalysts for UV-LED NOM removal are worth exploring further for industrial application as no decrease in disinfection was observed either. Subsequent tests investigated the trends observed when changing the conditions of a reactor design. It was observed that increasing the reactor's volume and the complexity of the water matrix had a detrimental effect on photocatalytic disinfection. This is important as much of the research surrounding photocatalytic disinfection utilises *E. coli* in ultrapure water and therefore the application in real-world scenarios is not fully investigated. Future work could focus on investigating UV-LED photocatalytic disinfection of common and disinfection-resistant pathogens such as *Cryptosporidium parvum* or *Hepatovirus A* in real surface waters. The effects of the characteristics of surface waters on the disinfection of these pathogens are

still not fully understood. The light source in the reactor design was also evaluated with the use of a UVC germicidal lamp, this showed incredible disinfection rates and was further explored with the implementation of a UVA/UVC hybrid system in a commercial photoreactor. The Puralytics shield showed quick, efficient disinfection with high throughput, most likely due to the UVC lamp. Although the Puralytics outperformed the batch reactor in disinfection ability, significant improvements are required for implementation in NOM removal as several cycles only yielded 41% NOM degradation.

To this end, the effects of climate change are expected to increase the environmental impact of drinking water treatment plants. Therefore, the application of photocatalytic treatment as a polishing step holds considerable promise. The low requirements for health and safety regulations, potential use of renewable energy sources and increasing efficiency of UV-LEDs indicate possible future applications in drinking water treatment. With a wealth of research into reactor designs, catalyst innovation, and automated coagulation dose control. The future of sustainable drinking water is a bright one.

8 Publications and conference participation

Work published during the completion of this Thesis is listed below:

1. Gowland, D.C.A.; Robertson, N.; Chatzisyneon, E. Photocatalytic Oxidation of Natural Organic Matter in Water. *Water* **2021**, *13*, 288. <https://doi.org/10.3390/w13030288>
2. Gowland, Dan C. A., Neil Robertson, and Efthalia Chatzisyneon. "Life Cycle Assessment of Immobilised and Slurry Photocatalytic Systems for Removal of Natural Organic Matter in Water." *Environments* 11, no. 6 (2024): 114. <https://www.mdpi.com/2076-3298/11/6/114>.

Proceedings of international scientific conferences attended:

Gowland, D.C.A.; Chatzisyneon, E.

LED-Driven Photocatalytic Oxidation Technology for Water Purification

International conference on catalysis and chemical engineering

March 20-21, 2023

Rome, Italy

9 Bibliography

1. F. Worrall, R. Harriman, C. Evans, C. Watts, J. Adamson, C. Neal, E. Tipping, T. Burt, I. Grieve, D. Monteith, P. Naden, T. Nisbet, B. Reynolds and P. Stevens, *Biogeochemistry*, 2004, **70**, 369-402.
2. J. Zhang, J. Hudson, R. Neal, J. Sereda, T. Clair, M. Turner, D. Jeffries, P. Dillon, L. Molot, K. Somers and R. Hesslein, *Limnology and Oceanography*, 2010, **55**, 30-42.
3. Q. Dong, P. Li, Q. Huang, A. A. Abdelhafez and L. Chen, *Journal of Environmental Sciences*, 2014, **26**, 1843-1850.
4. E. L. Sharp, S. A. Parsons and B. Jefferson, *Science of The Total Environment*, 2006, **363**, 183-194.
5. L. E. Anderson, I. DeMont, D. D. Dunnington, P. Bjorndahl, D. J. Redden, M. J. Brophy and G. A. Gagnon, *Science of The Total Environment*, 2023, **858**, 159699.
6. B. L. Skjelkvåle, J. L. Stoddard, D. S. Jeffries, K. Tørseth, T. Høgåsen, J. Bowman, J. Mannio, D. T. Monteith, R. Mosello, M. Rogora, D. Rzychon, J. Vesely, J. Wieting, A. Wilander and A. Worsztynowicz, *Environmental Pollution*, 2005, **137**, 165-176.
7. R. Swinamer, L. E. Anderson, D. Redden, P. Bjorndahl, J. Campbell, W. H. Krkošek and G. A. Gagnon, *Environmental Science & Technology*, 2024, **58**, 11958-11969.
8. I. Young, B. A. Smith and A. Fazil, *Journal of water and health*, 2014, **13**, 1-17.
9. A. Sterk, J. Schijven, T. de Nijs and A. M. de Roda Husman, *Environmental Science & Technology*, 2013, **47**, 12648-12660.
10. J. A. Patz, S. J. Vavrus, C. K. Uejio and S. L. McLellan, *American Journal of Preventive Medicine*, 2008, **35**, 451-458.
11. C. A. Murray and S. A. Parsons, *Water Supply*, 2004, **4**, 113-119.
12. C. A. Murray and S. A. Parsons, *Water Science and Technology*, 2004, **49**, 267-272.
13. M. Sillanpää, *Natural organic matter in water: Characterization and treatment methods*, Butterworth-Heinemann, 2014.
14. A. Kumar, V. Hasija, A. Sudhaik, P. Raizada, V.-H. Nguyen, Q. V. Le, P. Singh, D. C. Nguyen, S. Thakur and C. M. Hussain, *Environmental Research*, 2022, **209**, 112814.
15. G. Zhang, W. Li, S. Chen, W. Zhou and J. Chen, *Chemosphere*, 2020, **254**, 126831.
16. A. Bhatnagar and M. Sillanpää, *Chemosphere*, 2017, **166**, 497-510.
17. E. M. Thurman, *Organic geochemistry of natural waters*, Springer Science & Business Media, 2012.
18. J. Świetlik, A. Dąbrowska, U. Raczyk-Stanisławiak and J. Nawrocki, *Water Research*, 2004, **38**, 547-558.
19. T. G. Reyes and J. M. Crisosto, *Journal of Chemistry*, 2016, **2016**, 1537370.
20. C. W. K. Chow, R. Fabris and M. Drikas, *Journal of Water Supply: Research and Technology - AQUA*, 2004, **53**, 85-92.
21. R. Fabris, C. W. K. Chow, M. Drikas and B. Eikebrokk, *Water Research*, 2008, **42**, 4188-4196.
22. J. A. Leenheer and J.-P. Croué, *Environmental Science & Technology*, 2003, **37**, 18A-26A.
23. D. M. Owen, G. L. Amy, Z. K. Chowdhury, R. Paode, G. McCoy and K. Viscosil, *Journal AWWA*, 1995, **87**, 46-63.
24. A.-M. Petrescu, A. Lukinich-Gruia, V. Paunescu and G. Ilia, *Chemistry & Biodiversity*, 2019, **16**.
25. S. Tak and B. P. Vellanki, *Journal of water and health*, 2018, **16**, 681-703.
26. K. M. Usher, A. H. Kaksonen, I. Cole and D. Marney, *International Biodeterioration & Biodegradation*, 2014, **93**, 84-106.
27. L. Wang, S. Wei and Z. Jiang, *Scientific Reports*, 2020, **10**, 19663.
28. D. P. Sounthararajah, P. Loganathan, J. Kandasamy and S. Vigneswaran, *Int J Environ Res Public Health*, 2015, **12**, 10475-10489.
29. H. Męczykowska, P. Stepnowski and M. Caban, *Microchemical Journal*, 2019, **144**, 500-505.

30. S. Dubey, D. Gusain, Y. C. Sharma and F. Bux, in *Disinfection By-products in Drinking Water*, ed. M. N. V. Prasad, Butterworth-Heinemann, 2020, DOI: <https://doi.org/10.1016/B978-0-08-102977-0.00016-0>, pp. 371-391.
31. J.-C. Lou, C.-E. Huang, J.-Y. Han and Y.-J. Huang, *Environmental Monitoring and Assessment*, 2010, **162**, 365-375.
32. N. Costet, C. M. Villanueva, J. J. K. Jaakkola, M. Kogevinas, K. P. Cantor, W. D. King, C. F. Lynch, M. J. Nieuwenhuijsen and S. Cordier, *Occupational and Environmental Medicine*, 2011, **68**, 379-385.
33. J. Grellier, J. Bennett, E. Patelarou, R. B. Smith, M. B. Toledano, L. Rushton, D. J. Briggs and M. J. Nieuwenhuijsen, *Epidemiology*, 2010, **21**, 300-313.
34. K. Waller, S. H. Swan, G. DeLorenze and B. Hopkins, *Epidemiology*, 1998, **9**, 134-140.
35. J. M. Wright, A. Evans, J. A. Kaufman, Z. Rivera-Núñez and M. G. Narotsky, *Environmental Health Perspectives*, 2017, **125**, 269-277.
36. C. Volk, L. Wood, B. Johnson, J. Robinson, H. W. Zhu and L. Kaplan, *Journal of Environmental Monitoring*, 2002, **4**, 43-47.
37. B. Eikebrokk, R. D. Vogt and H. Liltved, *Water Supply*, 2004, **4**, 47-54.
38. J. Kaal, C. Plaza, K. Nierop, M. Pérez-Rodríguez and H. Biester, *Geoderma*, 2020, **378**, 114635.
39. A. Korth, C. Fiebiger, K. Bornmann and W. Schmidt, *Water Science and Technology: Water Supply*, 2004, **4**.
40. K. Grunewald and a. co-author, *Increase in colour and amount of organic matter in surface waters*, 2003.
41. Y. Ye, H. Bruning, W. Liu, H. Rijnaarts and D. Yntema, *Journal of Photochemistry and Photobiology A: Chemistry*, 2019, **371**, 216-222.
42. G. V. Korshin, M. M. Benjamin and C.-W. Li, *Water Science and Technology*, 1999, **40**, 9-16.
43. O. Kaarela, M. Koppanen, T. Kesti, R. Kettunen, M. Palmroth and J. Rintala, *Journal of Water Process Engineering*, 2021, **41**, 102001.
44. S. Liu, M. Lim, R. Fabris, C. Chow, M. Drikas and R. Amal, *Environmental Science & Technology*, 2008, **42**, 6218-6223.
45. S. Liu, M. Lim, R. Fabris, C. Chow, K. Chiang, M. Drikas and R. Amal, *Chemosphere*, 2008, **72**, 263-271.
46. B. Wallace, M. Purcell and J. Furlong, *Journal of environmental monitoring : JEM*, 2002, **4**, 35-42.
47. A. D. Archer and P. C. Singer, *Journal AWWA*, 2006, **98**, 110-123.
48. J. Swietlik and E. Sikorska, *J. Environ. Stud.*, 2006, **15**.
49. A. Bruchet, C. Rousseau and J. Mallevialle, *Journal AWWA*, 1990, **82**, 66-74.
50. H.-R. Schulten, *Journal of Analytical and Applied Pyrolysis*, 1993, **25**, 97-122.
51. J. G. Jacangelo, J. DeMarco, D. M. Owen and S. J. Randtke, *Journal AWWA*, 1995, **87**, 64-77.
52. J. Yu, D. Wang, M. Yan, C. Ye, M. Yang and X. Ge, *Environmental Monitoring and Assessment*, 2007, **131**, 377-386.
53. G. C. Budd, A. F. Hess, H. Shorney-Darby, J. J. Neemann, C. M. Spencer, J. D. Bellamy and P. H. Hargette, *Journal AWWA*, 2004, **96**, 102-113.
54. J.-Q. Jiang, *Current Opinion in Chemical Engineering*, 2015, **8**, 36-44.
55. M. Sillanpää, M. C. Ncibi, A. Matilainen and M. Vepsäläinen, *Chemosphere*, 2018, **190**, 54-71.
56. G. Korshin, C. W. K. Chow, R. Fabris and M. Drikas, *Water Research*, 2009, **43**, 1541-1548.
57. Merck, Tangential Flow Filtration in Downstream Bioprocessing, https://www.sigmaaldrich.com/GB/en/technical-documents/technical-article/pharmaceutical-and-biopharmaceutical-manufacturing/downstream-processing/tangential-flow-filtration-downstream-bioprocessing?utm_campaign=everyonesocial&utm_medium=social-media&utm_source=linkedin&es_id=1fcfa7e453).
58. B. Ericsson and G. Trägårdh, *Desalination*, 1997, **108**, 117-128.

59. L. Fan, J. L. Harris, F. A. Roddick and N. A. Booker, *Water Research*, 2001, **35**, 4455-4463.
 60. M. Sillanpää, S. Metsämuuronen and M. Mänttari, 2015.
 61. M. D. Kennedy, H. K. Chun, V. A. Quintanilla Yangali, B. G. J. Heijman and J. C. Schippers, *Desalination*, 2005, **178**, 73-83.
 62. E. Aoustin, A. I. Schäfer, A. G. Fane and T. D. Waite, *Separation and Purification Technology*, 2001, **22-23**, 63-78.
 63. M. Sievers, in *Treatise on Water Science*, ed. P. Wilderer, Elsevier, Oxford, 2011, DOI: <https://doi.org/10.1016/B978-0-444-53199-5.00093-2>, pp. 377-408.
 64. C. Comninellis, A. Kapalka, S. Malato, S. A. Parsons, I. Poullos and D. Mantzavinos, *Journal of Chemical Technology & Biotechnology*, 2008, **83**, 769-776.
 65. W. H. Glaze, J.-W. Kang and D. H. Chapin, *Ozone: Science & Engineering*, 1987, **9**, 335-352.
 66. H.-C. Lin and G.-S. Wang, *Desalination*, 2011, **270**, 221-226.
 67. H.-w. Wang, X.-y. Li, Z.-p. Hao, Y.-j. Sun, Y.-n. Wang, W.-h. Li and Y. F. Tsang, *Journal of Environmental Management*, 2017, **191**, 244-251.
 68. J. J. Molnar, J. R. Agbaba, B. D. Dalmacija, S. D. Rončević, S. P. Maletić and M. M. Kragulj, *Journal of Advanced Oxidation Technologies*, 2011, **14**, 54-62.
 69. C. A. Murray and S. A. Parsons, *Chemosphere*, 2004, **54**, 1017-1023.
 70. C. Dong, W. Fang, Q. Yi and J. Zhang, *Chemosphere*, 2022, **308**, 136205.
 71. G. Kleiser and F. H. Frimmel, *Science of The Total Environment*, 2000, **256**, 1-9.
 72. Sanly, M. Lim, K. Chiang, R. Amal, R. Fabris, C. Chow and M. Drikas, *Separation Science and Technology*, 2007, **42**, 1391-1404.
 73. C. S. Uyguner, S. A. Suphandag, A. Kerc and M. Bekbolet, *Desalination*, 2007, **210**, 183-193.
 74. Y. Nie, C. Hu, L. Zhou, J. Qu, Q. Wei and D. Wang, *Journal of Hazardous Materials*, 2010, **173**, 474-479.
 75. R. Lamsal, M. E. Walsh and G. A. Gagnon, *Water Research*, 2011, **45**, 3263-3269.
 76. S. Liu, M. Lim, R. Fabris, C. Chow, M. Drikas and R. Amal, *Organic Geochemistry*, 2010, **41**, 124-129.
 77. W. Buchanan, F. Roddick and N. Porter, *Chemosphere*, 2006, **63**, 1130-1141.
 78. N. Ates, M. Kitis and U. Yetis, *Water Research*, 2007, **41**, 4139-4148.
 79. A. Chin and P. R. Bérubé, *Water Research*, 2005, **39**, 2136-2144.
 80. F. C. Kent, K. R. Montreuil, R. M. Brookman, R. Sanderson, J. R. Dahn and G. A. Gagnon, *Water Research*, 2011, **45**, 6173-6180.
 81. D. B. Miklos, C. Remy, M. Jekel, K. G. Linden, J. E. Drewes and U. Hübner, *Water Research*, 2018, **139**, 118-131.
 82. WHO, Drinking-water, <https://www.who.int/news-room/fact-sheets/detail/drinking-water>, (accessed 13 September 2023).
 83. T. J. Silhavy, D. Kahne and S. Walker, *Cold Spring Harbor perspectives in biology*, 2010, **2**, a000414.
 84. N. Tripathi and A. Sapra, in *StatPearls*, StatPearls Publishing
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85. T. G. Slama, *Critical Care*, 2008, **12**, S4.
 86. A. Pellegrini, U. Thomas, R. von Fellenberg and P. Wild, *Journal of Applied Bacteriology*, 1992, **72**, 180-187.
 87. K. Nixdorff, J. Gmeiner and H. H. Martin, *Biochimica et Biophysica Acta (BBA) - Biomembranes*, 1978, **510**, 87-98.
 88. X. Chen, Z. Chen, H. H. Ngo, Y. Mao, K. Cao, Q. Shi, Y. Lu and H.-Y. Hu, *Environmental Pollution*, 2023, **333**, 122007.
 89. C. Jungfer, T. Schwartz and U. Obst, *Water Res*, 2007, **41**, 188-196.
 90. P. C. Hanawalt, P. K. Cooper, A. K. Ganesan and C. A. Smith, *Annual review of biochemistry*, 1979, **48**, 783-836.

91. G. C. Walker, *Microbiological Reviews*, 1984, **48**, 60-93.
92. H. R. Gelderblom, in *Medical Microbiology*, ed. S. Baron, University of Texas Medical Branch at Galveston

Copyright © 1996, The University of Texas Medical Branch at Galveston., Galveston (TX), 1996.

93. Q. Lin, J. Y. C. Lim, K. Xue, P. Y. M. Yew, C. Owh, P. L. Chee and X. J. Loh, *VIEW*, 2020, **1**, e16.
94. M. Novak Babič, N. Gunde-Cimerman, M. Vargha, Z. Tischner, D. Magyar, C. Veríssimo, R. Sabino, C. Viegas, W. Meyer and J. Brandão, *Int J Environ Res Public Health*, 2017, **14**, 636.
95. E. Gerace, V. D. M. Lo Presti and C. Biondo, *European journal of microbiology & immunology*, 2019, **9**, 119-123.
96. J. Samuelson, G. G. Bushkin, A. Chatterjee and P. W. Robbins, *Eukaryotic cell*, 2013, **12**, 1578-1587.
97. F. L. Henriquez, R. Mooney, T. Bandel, E. Giammarini, M. Zeroual, P. L. Fiori, V. Margarita, P. Rappelli and D. Dessì, *Frontiers in microbiology*, 2020, **11**, 616213.
98. L.-J. Li, C. Lin, X.-R. Huang, X.-L. An, W.-J. Li, J.-Q. Su and Y.-G. Zhu, *Environment International*, 2023, **171**, 107723.
99. C. Venkobachar, L. Iyengar and A. V. S. Prabhakara Rao, *Water Research*, 1977, **11**, 727-729.
100. R. V. Goyal and H. M. Patel, *Applied Water Science*, 2015, **5**, 311-319.
101. C. Tian, R. Liu, H. Liu and J. Qu, *Water Research*, 2013, **47**, 5901-5910.
102. A. C. Diehl, G. E. Speitel Jr, J. M. Symons, S. W. Krasner, C. J. Hwang and S. E. Barrett, *Journal-American Water Works Association*, 2000, **92**, 76-90.
103. C. Korn, R. C. Andrews and M. D. Escobar, *Water Research*, 2002, **36**, 330-342.
104. N. F. Gray, in *Microbiology of Waterborne Diseases (Second Edition)*, eds. S. L. Percival, M. V. Yates, D. W. Williams, R. M. Chalmers and N. F. Gray, Academic Press, London, 2014, DOI: <https://doi.org/10.1016/B978-0-12-415846-7.00033-0>, pp. 599-615.
105. S. Tripathi and T. Hussain, in *Development in Wastewater Treatment Research and Processes*, eds. M. Shah, S. Rodriguez-Couto and J. Biswas, Elsevier, 2022, DOI: <https://doi.org/10.1016/B978-0-323-85583-9.00015-6>, pp. 139-172.
106. J. P. Malley, *Inactivation of pathogens with innovative UV technologies*, American Water Works Association, 2004.
107. H. A. Foster, I. B. Ditta, S. Varghese and A. Steele, *Applied microbiology and biotechnology*, 2011, **90**, 1847-1868.
108. Y. Shimizu, M. Ateia, M. Wang, D. Awfa and C. Yoshimura, *Chemosphere*, 2019, **235**, 1041-1049.
109. M. Martín-Sómer, C. Pablos, C. Adán, R. van Grieken and J. Marugán, *Science of The Total Environment*, 2023, **885**, 163963.
110. F. Bosshard, K. Riedel, T. Schneider, C. Geiser, M. Bucheli and T. Egli, *Environmental Microbiology*, 2010, **12**, 2931-2945.
111. A. Saravanan, P. S. Kumar, S. Jeevanantham, S. Karishma and A. R. Kiruthika, *Environmental Technology & Innovation*, 2021, **24**, 101909.
112. X. Wang and L. Zhang, *RSC advances*, 2018, **8**, 40632-40638.
113. Y. Nosaka and A. Y. Nosaka, *Chemical Reviews*, 2017, **117**, 11302-11336.
114. K. M. Lee, C. W. Lai, K. S. Ngai and J. C. Juan, *Water Research*, 2016, **88**, 428-448.
115. J. Wen, J. Xie, X. Chen and X. Li, *Applied Surface Science*, 2017, **391**, 72-123.
116. B. Ohtani, 2013, DOI: 10.1016/B978-0-444-53872-7.00006-6, pp. 121-144.
117. L. Wang and J. Yu, in *Interface Science and Technology*, eds. J. Yu, L. Zhang, L. Wang and B. Zhu, Elsevier, 2023, vol. 35, pp. 1-52.
118. D. C. A. Gowland, N. Robertson and E. Chatzisyseon, *Water*, 2021, **13**, 288.
119. M. Drosos, M. Ren and F. H. Frimmel, *Applied Catalysis B: Environmental*, 2015, **165**, 328-334.
120. M. Ren, M. Drosos and F. H. Frimmel, *Chemical Engineering Journal*, 2018, **334**, 968-975.
121. C. S. Uyguner and M. Bekbolet, *International Journal of Photoenergy*, 2004, **6**, 236350.

122. N. B. Parilti, C. S. U. Demirel and M. Bekbolet, *Journal of Photochemistry and Photobiology A: Chemistry*, 2011, **225**, 26-35.
123. W.-K. Jo and R. J. Tayade, *Industrial & Engineering Chemistry Research*, 2014, **53**, 2073-2084.
124. S. M. McKee and E. Chatzisyseon, *Environmental Impact Assessment Review*, 2022, **97**, 106886.
125. A. Fattahi, M. J. Arlos, L. M. Bragg, R. Liang, N. Zhou and M. R. Servos, *Journal of Environmental Chemical Engineering*, 2021, **9**, 104844.
126. D. Ljubas, *Energy*, 2005, **30**, 1699-1710.
127. A. Pandey, R. R. Kumar, B. Kalidasan, I. A. Laghari, M. Samykano, R. Kothari, A. M. Abusorrah, K. Sharma and V. Tyagi, *Journal of Environmental Management*, 2021, **297**, 113300.
128. J. Wang and S. Wang, *Chemical Engineering Journal*, 2021, **411**, 128392.
129. A.-G. Rincón and C. Pulgarin, *Applied Catalysis B: Environmental*, 2004, **51**, 283-302.
130. M. N. Chong, B. Jin, C. W. Chow and C. Saint, *Water Res*, 2010, **44**, 2997-3027.
131. D. Friedmann, C. Mendive and D. Bahnemann, *Applied Catalysis B: Environmental*, 2010, **99**, 398-406.
132. C.-E. Hsiung, H.-L. Lien, A. E. Galliano, C.-S. Yeh and Y.-h. Shih, *Chemosphere*, 2016, **151**, 145-151.
133. M. Bekbolet, A. S. Suphandag and C. S. Uyguner, *Journal of Photochemistry and Photobiology A: Chemistry*, 2002, **148**, 121-128.
134. M. Bekbölet and G. Özköşemen, *Water Science and Technology*, 1996, **33**, 189-194.
135. T. I. Nkambule, A. T. Kuvarega, R. W. M. Krause, J. Haarhoff and B. B. Mamba, *Environmental Science and Pollution Research*, 2012, **19**, 4120-4132.
136. S. Gora, A. Sokolowski, M. Hatat-Fraile, R. Liang, Y. N. Zhou and S. Andrews, *Environmental Science: Water Research & Technology*, 2018, **4**, 1361-1376.
137. R. Yuan, B. Zhou, D. Hua and C. Shi, *Journal of Hazardous Materials*, 2013, **262**, 527-538.
138. H. B. Truong, B. T. Huy, Q. V. Ly, Y.-I. Lee and J. Hur, *Chemosphere*, 2019, **224**, 597-606.
139. N. G. Ndlangamandla, A. T. Kuvarega, T. A. M. Msagati, B. B. Mamba and T. T. I. Nkambule, *Physics and Chemistry of the Earth, Parts A/B/C*, 2018, **106**, 97-106.
140. X. Zhang, J. H. Pan, W. Fu, A. J. Du and D. D. Sun, *Water Supply*, 2009, **9**, 45-49.
141. H.-Y. Jing, T. Wen, C.-M. Fan, G.-Q. Gao, S.-L. Zhong and A.-W. Xu, *Journal of Materials Chemistry A*, 2014, **2**, 14563-14570.
142. N. C. Birben, M. C. Paganini, P. Calza and M. Bekbolet, *Photochemical & Photobiological Sciences*, 2017, **16**, 24-30.
143. N. Wang, X. Li, Y. Yang, Y. Shang, X. Zhuang, H. Li and Z. Zhou, *Chemical Engineering Journal*, 2019, **374**.
144. C. Y. P. Ayekoe, D. Robert and D. G. Lanciné, *Catalysis Today*, 2017, **281**, 2-13.
145. M. Rajca, *Chemical Engineering Journal*, 2016, **305**, 169-175.
146. H. Song, J. Shao, J. Wang and X. Zhong, *Desalination*, 2014, **344**, 412-421.
147. X. Huang, M. Leal and Q. Li, *Water Research*, 2008, **42**, 1142-1150.
148. W. Sun, H. Chu, B. Dong, D. Cao and S. Zheng, *CLEAN – Soil, Air, Water*, 2014, **42**, 1190-1198.
149. G. Xue, H. Liu, Q. Chen, C. Hills, M. Tyrer and F. Innocent, *Journal of Hazardous Materials*, 2011, **186**, 765-772.
150. A. Maleki, M. Safari, B. Shahmoradi, Y. Zandsalimi, H. Daraei and F. Gharibi, *Environmental Science and Pollution Research*, 2015, **22**, 16875-16880.
151. J.-M. Herrmann, *Catalysis Today*, 1999, **53**, 115-129.
152. S. Valencia, J. Marín, J. Velásquez, G. Restrepo and F. H. Frimmel, *Water Research*, 2012, **46**, 1198-1206.
153. L. A. Tercero Espinoza, E. ter Haseborg, M. Weber, E. Karle, R. Peschke and F. H. Frimmel, *Water Research*, 2011, **45**, 1039-1048.
154. A. Di Paola, E. García-López, G. Marci and L. Palmisano, *Journal of Hazardous Materials*, 2012, **211-212**, 3-29.

155. N. C. Birben, C. S. Uyguner-Demirel, S. S. Kavurmaci, Y. Y. Gürkan, N. Turkten, Z. Cinar and M. Bekbolet, *Catalysis Today*, 2017, **281**, 78-84.
156. P. K. Sharma, M. A. L. R. M. Cortes, J. W. J. Hamilton, Y. Han, J. A. Byrne and M. Nolan, *Catalysis Today*, 2019, **321-322**, 9-17.
157. S. Sood, S. K. Mehta, A. S. K. Sinha and S. K. Kansal, *Chemical Engineering Journal*, 2016, **290**, 45-52.
158. Y. Liu, F. Xin, F. Wang, S. Luo and X. Yin, *Journal of Alloys and Compounds*, 2010, **498**, 179-184.
159. N. Geng, W. Chen, H. Xu, T. Lin, M. Ding, Y. Wang, H. Tao and K. Hu, *Materials Science in Semiconductor Processing*, 2019, **102**, 104593.
160. S. Khan, J. Kim, A. Sotto and B. Van der Bruggen, *Journal of Industrial and Engineering Chemistry*, 2015, **21**, 779-786.
161. S. G. Kumar and L. G. Devi, *The Journal of Physical Chemistry A*, 2011, **115**, 13211-13241.
162. M. V. Dozzi and E. Selli, *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, 2013, **14**, 13-28.
163. J. Zhang, Y. Wu, M. Xing, S. A. K. Leghari and S. Sajjad, *Energy & Environmental Science*, 2010, **3**, 715-726.
164. S. Sakthivel, M. Janczarek and H. Kisch, *The Journal of Physical Chemistry B*, 2004, **108**, 19384-19387.
165. P. Yao, K.-H. Choo and M.-H. Kim, *Water Research*, 2009, **43**, 4238-4248.
166. S. L. Gora and S. A. Andrews, *Chemosphere*, 2017, **174**, 363-370.
167. X. Zhang, J. H. Pan, A. J. Du, W. Fu, D. D. Sun and J. O. Leckie, *Water Research*, 2009, **43**, 1179-1186.
168. L. Rizzo, C. S. Uyguner, H. Selcuk, M. Bekbolet and M. Anderson, *Water Science and Technology*, 2007, **55**, 113-118.
169. A. Manassero, M. L. Satuf and O. M. Alfano, *Chemical Engineering Journal*, 2017, **326**, 29-36.
170. H. K. M. Ng, A. H. Sabran, C. P. Leo, A. L. Ahmad and A. Z. Abdullah, *Journal of Membrane Science and Research*, 2016, **2**, 95-101.
171. S. Rajesh, S. Senthilkumar, A. Jayalakshmi, M. T. Nirmala, A. F. Ismail and D. Mohan, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2013, **418**, 92-104.
172. M. d. I. M. Ballari, R. Brandi, O. Alfano and A. Cassano, *Chemical Engineering Journal*, 2008, **136**, 242-255.
173. C. P. Athanasekou, S. Morales-Torres, V. Likodimos, G. E. Romanos, L. M. Pastrana-Martinez, P. Falaras, D. D. Dionysiou, J. L. Faria, J. L. Figueiredo and A. M. T. Silva, *Applied Catalysis B: Environmental*, 2014, **158-159**, 361-372.
174. L. M. Pastrana-Martínez, S. Morales-Torres, J. L. Figueiredo, J. L. Faria and A. M. T. Silva, *Water Research*, 2015, **77**, 179-190.
175. S. S. Kaplan Bekaroglu, N. O. Yigit, B. I. Harman and M. Kitis, *Journal of Chemistry*, 2016, **2016**, 3108034.
176. C. S. Uyguner and M. Bekbolet, *Catalysis Today*, 2005, **101**, 267-274.
177. O. Legrini, E. Oliveros and A. M. Braun, *Chemical Reviews*, 1993, **93**, 671-698.
178. L.-C. Hua, S.-J. Chao, K. Huang and C. Huang, *Science of The Total Environment*, 2020, **727**, 138638.
179. E. H. Goslan, F. Gurses, J. Banks and S. A. Parsons, *Chemosphere*, 2006, **65**, 1113-1119.
180. R. G. Zepp, B. C. Faust and J. Hoigne, *Environmental Science & Technology*, 1992, **26**, 313-319.
181. P. Wardman and L. P. Candeias, *Radiation Research*, 1996, **145**, 523-531.
182. L. Clarizia, D. Russo, I. Di Somma, R. Marotta and R. Andreozzi, *Applied Catalysis B: Environmental*, 2017, **209**, 358-371.
183. G.-S. Wang, S.-T. Hsieh and C.-S. Hong, *Water Research*, 2000, **34**, 3882-3887.
184. S. A. Carr and R. B. Baird, *Water Research*, 2000, **34**, 4036-4048.
185. B. Otieno, S. Apollo, J. Kabuba, B. Naidoo and A. Ochieng, *Ozone: Science & Engineering*, 2019, **41**, 551-561.

186. T. Ratpukdi, S. Siripattanakul and E. Khan, *Water Research*, 2010, **44**, 3531-3543.
187. C. A. Juan, J. M. Pérez de la Lastra, F. J. Plou and E. Pérez-Lebeña, *International journal of molecular sciences*, 2021, **22**.
188. A. Habibi-Yangjeh, S. Asadzadeh-Khaneghah, S. Feizpoor and A. Rouhi, *Journal of colloid and interface science*, 2020, **580**, 503-514.
189. X. Chen, Y. Jin, P. Huang, Z. Zheng, L.-P. Li, C.-Y. Lin, X. Chen, R. Ding, J. Liu and R. Chen, *Applied Catalysis B: Environmental*, 2024, **340**, 123235.
190. H. Yang, D. He, C. Liu, T. Zhang, J. Qu, D. Jin, K. Zhang, Y. Lv, Z. Zhang and Y.-n. Zhang, *Chemosphere*, 2022, **287**, 132072.
191. Y. Yuan, R.-t. Guo, L.-f. Hong, X.-y. Ji, Z.-d. Lin, Z.-s. Li and W.-g. Pan, *Materials Today Energy*, 2021, **21**, 100829.
192. F. Li, G. Zhu, J. Jiang, L. Yang, F. Deng, Arramel and X. Li, *Journal of Materials Science & Technology*, 2024, **177**, 142-180.
193. L. Chen, M.-L. Tsai, Y. Chuang, C.-W. Chen and C.-D. Dong, *Carbon*, 2022, **196**, 877-889.
194. P. Ju, L. Hao, Y. Zhang, J. Sun, K. Dou, Z. Lu, D. Liao, X. Zhai and C. Sun, *Separation and Purification Technology*, 2022, **299**, 121706.
195. H. Shi, J. Wan, X. Dong, J. Xi, L. Zhang, W. Wang, X. Zhang, Y. Shi and Z. Tang, *Applied Surface Science*, 2023, **607**, 155056.
196. P. O. Nyangaresi, Y. Qin, G. Chen, B. Zhang, Y. Lu and L. Shen, *Catalysis Today*, 2019, **335**, 200-207.
197. J. H. Castillo-Ledezma, J. L. Sánchez Salas, A. López-Malo and E. R. Bandala, *European Food Research and Technology*, 2011, **233**, 825-834.
198. M. E. Leblebici, G. D. Stefanidis and T. Van Gerven, *Chemical Engineering and Processing: Process Intensification*, 2015, **97**, 106-111.
199. a. i. b. American Chemical Society, *Environmental science & technology.*, 1991, **25**, 1522-1529.
200. E. A. Emam, *Water Environment Research*, 2016, **88**, 687-693.
201. J. Colina-Márquez, F. Machuca-Martínez and G. Li Puma, *Environmental Science & Technology*, 2009, **43**, 8953-8960.
202. D. Wang, M. A. Mueses, J. A. C. Márquez, F. Machuca-Martínez, I. Grčić, R. Peralta Muniz Moreira and G. Li Puma, *Water Research*, 2021, **202**, 117421.
203. M. Kneissl, T.-Y. Seong, J. Han and H. Amano, *Nature Photonics*, 2019, **13**, 233-244.
204. J. L. Davis, K. Rountree, R. Pope, C. Clayton, A. Dart, M. McCombs and A. Wallace, *Initial benchmarks of UV LEDs and comparisons with white LEDs*, RTI International, Research Triangle Park, NC (United States), 2021.
205. M. Martín-Sómer, C. Pablos, R. van Grieken and J. Marugán, *Applied Catalysis B: Environmental*, 2017, **215**, 1-7.
206. L. Z. Fogaça, J. C. M. Vicentini, C. F. de Freitas, M. de Souza, M. L. Baesso, W. Caetano, V. R. Batistela and M. H. N. O. Scaliante, *Materials Chemistry and Physics*, 2021, **272**, 125020.
207. W. Xie, E. Pakdel, Y. Liang, D. Liu, L. Sun and X. Wang, *Journal of Photochemistry and Photobiology A: Chemistry*, 2020, **389**, 112292.
208. A. Fattahi, M. J. Arlos, L. M. Bragg, R. Liang, N. Zhou and M. R. Servos, *Journal of Environmental Chemical Engineering*, 2021, **9**, 104844.
209. C. Zhang, Y. Li and J. Li, *Chemical Engineering Journal*, 2020, **392**, 123687.
210. R. Liang, L. C. M. Li Chun Fong, M. J. Arlos, J. Van Leeuwen, E. Shahnam, P. Peng, M. R. Servos and Y. N. Zhou, *Journal of Environmental Chemical Engineering*, 2017, **5**, 4365-4373.
211. N. Wang, X. Li, Y. Yang, Z. Zhou, Y. Shang and X. Zhuang, *Journal of Cleaner Production*, 2020, **265**, 121790.
212. G. S. Wang, C. H. Liao, H. W. Chen and H. C. Yang, *Environmental Technology*, 2006, **27**, 277-287.
213. E. Chatzisyseon, S. Foteinis, D. Mantzavinos and T. Tsoutsos, *Journal of Cleaner Production*, 2013, **54**, 229-234.

214. S. Foteinis, A. G. L. Borthwick, Z. Frontistis, D. Mantzavinos and E. Chatzisyneon, *Journal of Cleaner Production*, 2018, **182**, 8-15.
215. L. Ioannou-Ttofa, S. Foteinis, E. Chatzisyneon, I. Michael-Kordatou and D. Fatta-Kassinou, *Journal of Chemical Technology & Biotechnology*, 2017, **92**, 1315-1327.
216. L. Song, B. Zhu, V. Jegatheesan, S. R. Gray, M. C. Duke and S. Muthukumaran, in *Water Scarcity and Ways to Reduce the Impact: Management Strategies and Technologies for Zero Liquid Discharge and Future Smart Cities*, eds. M. Pannirselvam, L. Shu, G. Griffin, L. Philip, A. Natarajan and S. Hussain, Springer International Publishing, Cham, 2019, DOI: 10.1007/978-3-319-75199-3_6, pp. 95-113.
217. C. Li, W. Sun, Z. Lu, X. Ao, S. Li, Z. Wang, F. Qi and O. Ismailova, *Water Research*, 2022, **226**, 119298.
218. S.-Y. Yu, Z.-H. Xie, X. Wu, Y.-Z. Zheng, Y. Shi, Z.-K. Xiong, P. Zhou, Y. Liu, C.-S. He, Z.-C. Pan, K.-J. Wang and B. Lai, *Chinese Chemical Letters*, 2024, **35**, 108714.
219. N. Turkten and M. Bekbolet, *Journal of Photochemistry and Photobiology A: Chemistry*, 2020, **401**, 112748.
220. H. B. Truong, B. T. Huy, Y.-I. Lee, H. T. Nguyen, J. Cho and J. Hur, *Chemical Engineering Journal*, 2023, **453**, 139777.
221. B. Liu, B. Zhang, G. Dong, F. Wu and B. Chen, *Journal of Cleaner Production*, 2023, **429**, 139395.
222. X. Yang, H. Sun, G. Li, T. An and W. Choi, *Applied Catalysis B: Environmental*, 2021, **294**, 120252.
223. A. Mukherjee, S. Das and Y.-H. Ahn, *Journal of Environmental Chemical Engineering*, 2022, **10**, 108460.
224. J. F. J. R. Pesqueira, M. F. R. Pereira and A. M. T. Silva, *Science of The Total Environment*, 2021, **761**, 143258.
225. M. Elhami, N. Bahramifar, H. R. Bijanzadeh and H. Abyar, *Journal of Water Process Engineering*, 2023, **56**, 104425.
226. M. Costamagna, L. Ciacci, M. C. Paganini, P. Calza and F. Passarini, *Journal of Cleaner Production*, 2020, **252**, 119762.
227. G. Odling, E. Chatzisyneon and N. Robertson, *Catalysis Science & Technology*, 2018, **8**, 829-839.
228. G. Odling, A. Ivaturi, E. Chatzisyneon and N. Robertson, *ChemCatChem*, 2018, **10**, 234-243.
229. K. Davididou, C. McRitchie, M. Antonopoulou, I. Konstantinou and E. Chatzisyneon, *Journal of Chemical Technology & Biotechnology*, 2018, **93**, 269-276.
230. K. Davididou, R. Nelson, J. M. Monteagudo, A. Durán, A. J. Expósito and E. Chatzisyneon, *Journal of Cleaner Production*, 2018, **203**, 13-21.
231. G. Odling, Z. Y. Pong, G. Gilfillan, C. R. Pulham and N. Robertson, *Environmental Science: Water Research & Technology*, 2018, **4**, 2170-2178.
232. Z. Yin, X. Zhang, X. Yuan, W. Wei, Y. Xiao and S. Cao, *Journal of Cleaner Production*, 2022, **375**, 134112.
233. X.-x. Zhang, Y.-g. Xiao, S.-s. Cao, Z.-l. Yin and Z.-Q. Liu, *Journal of Cleaner Production*, 2022, **352**, 131560.
234. C. Wang, C. Shao, X. Zhang and Y. Liu, *Inorganic Chemistry*, 2009, **48**, 7261-7268.
235. H. Wang, L. Zhang, Z. Chen, J. Hu, S. Li, Z. Wang, J. Liu and X. Wang, *Chemical Society Reviews*, 2014, **43**, 5234-5244.
236. L.-W. Zhang, H.-B. Fu and Y.-F. Zhu, *Advanced Functional Materials*, 2008, **18**, 2180-2189.
237. X.-K. Wang, C. Wang, W.-Q. Jiang, W.-L. Guo and J.-G. Wang, *Chemical Engineering Journal*, 2012, **189-190**, 288-294.
238. R. Thiruvengatachari, S. Vigneswaran and I. S. Moon, *Korean Journal of Chemical Engineering*, 2008, **25**, 64-72.
239. D. Chen, F. Li and A. K. Ray, *Catalysis Today*, 2001, **66**, 475-485.
240. D. Chen, F. Li and A. K. Ray, *AIChE Journal*, 2000, **46**, 1034-1045.

241. F. Fiordaliso, P. Bigini, M. Salmona and L. Diomedea, *Environmental Science: Nano*, 2022, **9**, 1199-1211.
242. N. Quici, M. L. Vera, H. Choi, G. L. Puma, D. D. Dionysiou, M. I. Litter and H. Destailats, *Applied Catalysis B: Environmental*, 2010, **95**, 312-319.
243. C. Lai, M.-M. Wang, G.-M. Zeng, Y.-G. Liu, D.-L. Huang, C. Zhang, R.-Z. Wang, P. Xu, M. Cheng, C. Huang, H.-P. Wu and L. Qin, *Applied Surface Science*, 2016, **390**, 368-376.
244. K. Toming, J. Kotta, E. Uuemaa, S. Sobek, T. Kutser and L. J. Tranvik, *Scientific Reports*, 2020, **10**, 8471.
245. C. D. Evans, D. T. Monteith and D. M. Cooper, *Environmental Pollution*, 2005, **137**, 55-71.
246. V. Oskoei, M. H. Dehghani, S. Nazmara, B. Heibati, M. Asif, I. Tyagi, S. Agarwal and V. K. Gupta, *Journal of Molecular Liquids*, 2016, **213**, 374-380.
247. M. R. Teixeira and L. M. Nunes, *Desalination and Water Treatment*, 2011, **36**, 344-353.
248. V. V. Tsirkunov, A. M. Nikanorov, M. M. Laznik and Z. Dongwei, *Water Research*, 1992, **26**, 1203-1216.
249. V. Subramanian, V. G. Pangarkar and A. A. C. M. Beenackers, *Clean Products and Processes*, 2000, **2**, 149-156.
250. D. S. Bhatkhande, V. G. Pangarkar and A. A. C. M. Beenackers, *Journal of Chemical Technology & Biotechnology*, 2002, **77**, 102-116.
251. M. Rajca, *Environment Protection Engineering*, 2015, **41**, 29-39.
252. A. Haarstrick, O. M. Kut and E. Heinzle, *Environmental Science & Technology*, 1996, **30**, 817-824.
253. W. W.-P. Lai, Y.-C. Chuang and A. Y.-C. Lin, *Environmental Science and Pollution Research*, 2017, **24**, 14595-14604.
254. A. Bouarioua and M. Zerdaoui, *Journal of Environmental Chemical Engineering*, 2017, **5**, 1565-1574.
255. C. M. Ling, A. R. Mohamed and S. Bhatia, *Chemosphere*, 2004, **57**, 547-554.
256. M. Shargh and M. A. Behnajady, *Water Science and Technology*, 2016, **73**, 2804-2814.
257. M. F. J. Dijkstra, A. Michorius, H. Buwalda, H. J. Panneman, J. G. M. Winkelman and A. A. C. M. Beenackers, *Catalysis Today*, 2001, **66**, 487-494.
258. R. Scotti, M. D'Arienzo, F. Morazzoni and I. R. Bellobono, *Applied Catalysis B: Environmental*, 2009, **88**, 323-330.
259. D. F. Ollis, E. Pelizzetti and N. Serpone, *Environmental Science & Technology*, 1991, **25**, 1522-1529.
260. C. S. Turchi and D. F. Ollis, *The Journal of Physical Chemistry*, 1988, **92**, 6852-6853.
261. J. Krýsa, M. Keppert, J. r. Jirkovský, V. Štengl and J. Šubrt, *Materials Chemistry and Physics*, 2004, **86**, 333-339.
262. D. A. H. Hanaor and C. C. Sorrell, *Journal of Materials Science*, 2011, **46**, 855-874.
263. T. Luttrell, S. Halpegamage, J. Tao, A. Kramer, E. Sutter and M. Batzill, *Scientific Reports*, 2014, **4**, 4043.
264. I. S. Grover, S. Singh and B. Pal, *RSC Advances*, 2014, **4**, 24704-24709.
265. D. D. Sun and P. F. Lee, *Separation and Purification Technology*, 2012, **91**, 30-37.
266. M. G. Antoniou, C. Zhao, K. E. O'Shea, G. Zhang, D. D. Dionysiou, C. Zhao, C. Han, M. N. Nadagouda, H. Choi, T. Fotiou, T. M. Triantis and A. Hiskia, in *Photocatalysis: Applications*, eds. D. D. Dionysiou, G. Li Puma, J. Ye, J. Schneider, D. Bahnemann, J. Schneider, D. Bahnemann, J. Ye, G. Li Puma and D. D. Dionysiou, The Royal Society of Chemistry, 2016, DOI: 10.1039/9781782627104-00001, p. 0.
267. T. Fotiou, T. M. Triantis, T. Kaloudis and A. Hiskia, *Chemical Engineering Journal*, 2015, **261**, 17-26.
268. S. L. Pettit, L. Rodriguez-Gonzalez, J. T. Michaels, N. A. Alcantar, S. J. Ergas and J. N. Kuhn, *Catalysis Letters*, 2014, **144**, 1460-1465.

269. R. Yuan, S. Wang, D. Liu, X. Shao and B. Zhou, *Chemical Engineering Journal*, 2018, **353**, 319-328.
270. R. Toor and M. Mohseni, *Chemosphere*, 2007, **66**, 2087-2095.
271. A. Moncayo-Lasso, A.-G. Rincon, C. Pulgarin and N. Benitez, *Journal of Photochemistry and Photobiology A: Chemistry*, 2012, **229**, 46-52.
272. A. V. Vorontsov, *Journal of Hazardous Materials*, 2019, **372**, 103-112.
273. S. Zhang, H. Zheng and P. G. Tratnyek, *Nature Water*, 2023, **1**, 666-681.
274. S. Arzate, S. Pfister, C. Oberschelp and J. A. Sánchez-Pérez, *Science of The Total Environment*, 2019, **694**, 133572.
275. M. Fouad, M. Gar Alalm, H. K. El-Etriby, D. C. Boffito, S. Ookawara, T. Ohno and M. Fujii, *Journal of Hazardous Materials*, 2021, **402**, 123514.
276. H. Schwegmann, J. Ruppert and F. H. Frimmel, *Water Research*, 2013, **47**, 1503-1511.
277. M. Gourmelon, J. Cillard and M. Pommepuy, *Journal of Applied Bacteriology*, 1994, **77**, 105-112.
278. J. Marugán, R. van Grieken, C. Sordo and C. Cruz, *Applied Catalysis B: Environmental*, 2008, **82**, 27-36.
279. G. G. Jayson, B. J. Parsons and A. J. Swallow, *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases*, 1973, **69**, 1597-1607.
280. K. Selvam, M. Muruganandham, I. Muthuvel and M. Swaminathan, *Chemical Engineering Journal*, 2007, **128**, 51-57.
281. C. Sichel, J. Blanco, S. Malato and P. Fernández-Ibáñez, *Journal of Photochemistry and Photobiology A: Chemistry*, 2007, **189**, 239-246.
282. A. K. Benabbou, Z. Derriche, C. Felix, P. Lejeune and C. Guillard, *Applied Catalysis B: Environmental*, 2007, **76**, 257-263.
283. J. Brame, M. Long, Q. Li and P. Alvarez, *Water Research*, 2015, **84**, 362-371.
284. Y.-J. Lee, Y. Jae Jeong, I. Sun Cho, C.-G. Lee, S.-J. Park and P. J. J. Alvarez, *Chemical Engineering Journal*, 2023, **476**, 146785.
285. H. D. Pascagaza-Rubio, S. Godbout, J. H. Palacios, D. Cinq-Mars, C. Côté, A. N. Rousseau and S. Fournel, *Water*, 2022, **14**, 3808.
286. Puralytics®, Puralytics shield manufacturer results <https://puralytics.com/shield-product>, (accessed N/A, 2023).
287. K. P. Sundar and S. Kanmani, *Chemical Engineering Research and Design*, 2020, **154**, 135-150.
288. V. Porley, E. Chatzisyneon, B. C. Meikap, S. Ghosal and N. Robertson, *Environmental Science: Water Research & Technology*, 2020, **6**, 809-816.
289. A. Ferretto, R. Brooker, R. Matthews and P. Smith, *Journal of Environmental Management*, 2021, **300**, 113688.
290. F. Grande and P. Tucci, *Mini-Reviews in Medicinal Chemistry*, 2016, **16**, 762-769.
291. Z. Luo, Z. Li, Z. Xie, I. M. Sokolova, L. Song, W. J. G. M. Peijnenburg, M. Hu and Y. Wang, *Small*, 2020, **16**, 2002019.
292. K. Sopajaree, S. A. Qasim, S. Basak and K. Rajeshwar, *Journal of Applied Electrochemistry*, 1999, **29**, 1111-1118.
293. M. Purnima, K. Pakshirajan and G. Pugazhenth, *Journal of Water Process Engineering*, 2022, **49**, 103123.
294. W. Xi and S. U. Geissen, *Water Res*, 2001, **35**, 1256-1262.
295. K. Treyer, C. Bauer and A. Simons, *Energy Policy*, 2014, **74**, S31-S44.
296. N. Haque, in *Future Energy (Third Edition)*, ed. T. M. Letcher, Elsevier, 2020, DOI: <https://doi.org/10.1016/B978-0-08-102886-5.00029-3>, pp. 633-647.
297. A. M. De Schryver, R. van Zelm, S. Humbert, S. Pfister, T. E. McKone and M. A. J. Huijbregts, *Journal of Industrial Ecology*, 2011, **15**, 796-815.
298. H. MAJ, S. ZIN, E. PMF, S. G, V. F, V. MDM, H. A, Z. M and v. Z. R, *Journal*, 2016.

299. Y. Shi, X. Yuan, Y. Tang, Y. Li, Q. Wang, Q. Ma, J. Zuo and H. Liu, *Sustainable Production and Consumption*, 2022, **29**, 36-45.
300. S. Kressirer, L. N. Protasova, M. H. J. M. de Croon, V. Hessel and D. Kralisch, *Green Chemistry*, 2012, **14**, 3034-3046.