

**INNOVATIVE WATER REUSE PROCESS USING PHOTOCATALYSIS AND
CATALYTIC CERAMIC MEMBRANE FILTRATION**

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A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

Environmental Engineering - Doctor of Philosophy

2018

ABSTRACT

INNOVATIVE WATER REUSE PROCESS USING PHOTOCATALYSIS AND CATALYTIC CERAMIC MEMBRANE FILTRATION

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Water scarcity has become one of the most challenging problems that humanity must address. Cost-effective water and wastewater treatment technologies are imperative to protect public health and the environment. The objectives of this work were to assess catalytic ceramic membrane filtration-ozonation processes for the mitigation of fouling and calculate the energy cost and environmental impacts of the process; to efficiently use sunlight as energy source for photodegradation and the removal of persistent organics in wastewater; finally, to propose an innovative process that combines photodegradation and membrane filtration process for emerging contaminants removal and industrial water reuse. The first part of the study analyzed the effect of ozone dosage on membrane fouling using catalytic ceramic membranes, and used life-cycle-assessment to assess the energy consumption and environmental impacts of the catalytic ceramic membrane system and compared that to hollow fiber membrane filtration. Results showed that membrane fouling was effectively controlled at ozone dosages of 10 $\mu\text{g/s}$ or greater using manganese oxide coated membranes. At least 15 μg ozone/s was necessary to control membrane fouling with uncoated titanium oxide membranes. Catalytic ceramic membrane filtration resulted in less energy consumption of pressurization and backwashing as compared with hollow fiber membrane filtration, and had a slightly lower environmental impact than hollow fiber membrane filtration. In photodegradation study, three photocatalysts were synthesized and characterized. Photodegradation abilities

were compared using with methylene blue as a model contaminant. Moreover, the deactivation mechanism and photo-deactivation of photocatalysts were also studied. The order of photocatalysis degradation efficacies of methylene blue during illumination was $\text{CdS} > \text{NiFe}_2\text{O}_4 \geq \text{ZnFe}_2\text{O}_4$. It was found that the methylene blue removal efficacy is affected by the absorption range of the photocatalysts, initial dye concentrations, amount of photocatalysts added, and photoreactor conditions. The proposed water reuse process combining photocatalytic reaction and ceramic membrane filtration to achieve safe and high efficient water reuse and reduce energy consumption and operating costs was evaluated using caffeine as a target contaminant. Results show that by using photodegradation and membrane filtration, caffeine could be degraded and photocatalysts could be recovered.

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ACKNOWLEDGEMENTS

I always felt blessed with my whole graduate study: I really enjoy what I'm doing, I have my family's fully support, I receive important guidance, and I obtained so much happiness from my friends. I really hope to express my appreciation to all the support from so many people.

First of all, I would like to express my thanks to my advisor, Dr. Susan Masten. Thank you for your excellent guidance, unconditional support, and all the patience. You are always willing to help and give me all kinds of supports. You make me improve skills throughout the process and teach me stay true. I learned so much from you!

I hope to thank my committee members, Dr. Annick Anctil, Dr. Rebecca Lahr, and Dr. Joan Rose for providing their valuable feedback on my research and suggestions. I would express my thanks to Dr. Anctil again, for offering help and guidance in my research, and expending my research interests. I would also like to thank Dr. Simon Davies, for his fully support and advice, and for his important guidance at the beginning of my research period.

I would like to thank our department research administrator Lori Larnier, and secretary Laura Post. To all the faculty and staff in department of Civil and Environmental Engineering at Michigan State University, thank you for support and useful courses. I also want to thank the students in my TA classes and the other TAs in the classes, I learned a lot from you.

I hope to thank my parents, for your love, courage and support. Although there are thousands of miles of distance between us right now, I always feel your love! Love you! Also, thank my husband, for your company, support and encouragement.

Last, I would like to thank the source of funding, the MSU Discretionary Funding Initiative, MSU College of Engineering and Department of Civil and Environmental Engineering.

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CHAPTER ONE

Introduction and Dissertation Overview

1.1 Background

Although the earth is described as the 'blue planet' with 71% covered by the oceans, only about 2.53% of the total water is fresh. Moreover, the potable fresh water in rivers, lakes and ground water that is easily accessible is approximately 0.3% of the total fresh water. Water scarcity affects almost every continent and nearly 1.2 billion people live in areas of physical scarcity. Another 500 million people live in areas that are approaching conditions resulting in water scarcity. 1.6 billion people are facing economic water shortage where countries lack the necessary infrastructure to safely treat and distribute water from rivers and aquifers ^[1]. Some scientists estimated that, by 2025, two-thirds of the world's population could be living under water stressed conditions ^[2]. With the existing climate change scenario, almost half the world's population will be living in areas of high water stress by 2030, including between 75 million and 250 million people in Africa. In addition, water scarcity in some arid and semi-arid places will displace between 24 million and 700 million people ^[2]. Water scarcity has become one of the most challenging problems to humanity mainly because of the population over-growth.

Safe, clean drinking water access is important for public health. In 2010, the UN recognized the human right to water and sanitation: everyone has the right to sufficient, continuous, safe, acceptable, physically accessible and affordable water for personal and domestic use ^[3]. The key issue for the treatment and reuse of wastewater is the effective

removal of toxic contaminants, particularly organic pollutants, of low concentrations. The demands for high quality water keep driving research for more effective, economical and energy efficient processes for the treatment of water sources ^[4]. Feasible water reuse processes that produce safe, clean water are greatly needed.

Water treatment is the process to achieve the water quality that meets specified goals or standards set by the end user or a community through its regulatory agencies. Goals and standards can include the requirements of regulatory agencies, additional requirements set by a local community, and requirements associated with specific industrial processes ^[5]. Municipal water treatment systems have a history of more than 200 years, and during the last 30 to 40 years there are many changes in both opinions regarding and technologies used for water treatment. Conventional drinking water treatment technologies and processes include lime-soda, ion-exchange, coagulation/flocculation, sedimentation. Choosing the effective water treatment processes and designing water treatment plant should be based on the source water characteristics. The source water includes groundwater, lakes and reservoirs, rivers, seawater, and wastewater impaired waters. The relative concentrations of source water, and other water quality parameters affect treatment depend heavily on local conditions of geology, climate, and human activity ^[6].

Wastewater sources can be classified into domestic wastewater, industrial wastewater, infiltration/inflow, and storm water ^[7]. Like with water treatment design, it is important to choose the appropriate treatment processes based on wastewater characteristics. The

main task of wastewater treatment is to remove hazards from wastewater that would affect the environment. While biological wastewater treatment is effective at reducing the biochemical oxygen demand to levels around 20-30 mg/L and is inexpensive compared to chemical treatment, but there are limitations due to the low concentration of organic contaminants in the influent, the amount of energy needed to produce oxygen to oxidize organics, or the amount of land required for lagoon systems.

In the developed world, industries are typically required to pretreat their wastes before discharge to the sanitary sewers. These same industries often obtain their water from municipal treatment systems. As a result, water is pumped from lakes or underground to the water treatment plant where it is processed and then pumped factories. The wastewater is pretreated and then discharged to the sanitary sewer. After treatment, the water is discharged back to the environment. Energy and costs can be saved if local water reuse process can be adopted, thereby reducing the energy requirements for wastewater/water pumping. These energy savings are significant, as drinking water and wastewater plants typically are the largest energy consumers, accounting for 30 to 40 % of the total energy consumption in the US ^[8]. Moreover, drinking water and wastewater systems account for the release of more than 45 million tons of greenhouse gases annually in the US ^[8].

1.2 Water reuse process with photocatalytic reactors and hybrid membrane-ozonation filtration

Conventional biological treatment methods are not very effective for some resistant

organic pollutants such as organic dyes, emerging contaminants and organic acids. Advanced oxidation processes (AOPs) can be described as aqueous phase oxidation methods based on the use of highly reactive species for the destruction of the target pollutant. Hydroxyl radicals are the predominant reactive species that are used for the degradation of organic pollutants [9]. The water reuse process is designed to achieve safe and high efficient water reuse process and save considerable amounts of energy. The objective of this research is to design and investigate an innovative process combining photodegradation with membrane filtration for the removal of emerging contaminants and the reuse of industrial water. The process has the potential to degrade pharmaceuticals and personal care chemicals, and therefore could be used for the reuse of water in these industries. If successful this would achieve the goal of making wastewater into water source, while saving energy and reduce environmental impacts of water reuse.

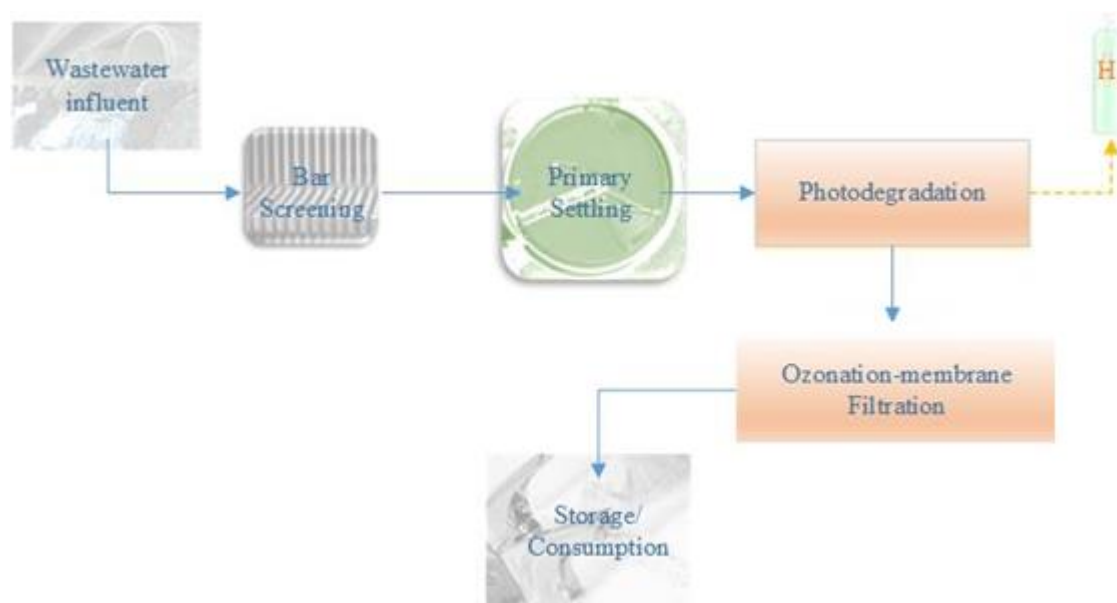


Figure 1.1 Designed water reuse process flow diagram

This designed photodegradation process, which uses sunlight as an energy source to treat wastewater by photocatalysis, could be an effective technique for the removal of organic pollutants and some sulfate inorganics in wastewater. Photocatalysis could significantly decrease energy consumption in wastewater treatment. In addition, the production of hydrogen would be expected by utilizing organics in the wastewater ^[10-13]. Given the expected increase in the cost of fossil fuels and concern about the environmental impact of emissions from the combustion of carbon-based fuels this may become feasible in the future.

The objectives of the research were to efficiently use sunlight as energy source for the photodegradation of persistent organic chemicals; to reduce energy consumption and save costs for the water reuse process compared to water and wastewater treatment processes.

The sub-objectives of the photodegradation are:

1. To evaluate the efficacy of several photocatalysts (CdS , ZnFe_2O_4 , NiFe_2O_4). CdS is the most widely studied photocatalyst for hydrogen production and solar energy storage. ZnFe_2O_4 and NiFe_2O_4 can also act as photocatalysts, and they are comparably more environmentally friendly, and both have a narrow gap band.
2. To determine the mechanism of photodegradation of methylene blue, and find out the factors that affect photodegradation efficiency.
3. To analyze the efficiency of contaminant efficiency and the reasons for photo-deactivation effects during photocatalytic processes.

The sub-objectives of the membrane-ozonation filtration are:

1. To compare membrane performance between manganese oxide catalytic membrane and virgin titania oxide catalytic membrane.
2. To test the difference in cake resistance and permeate flux between cross-flow and dead-end operation mode.
3. To determine the most economical operational mode in membrane system for decreasing fouling and enhancing permeate flux. To determine the ozone dosage for both cross-flow and dead-end of different membrane system under applicable flux/pressure ratio, and calculate the cost for both modes in ozone generation, extra pump operation, and some other cost.
4. To analyze the energy consumption and environmental impacts of the catalytic ceramic membrane system by life-cycle-assessment, which were then compared to that for hollow fiber membrane filtration.

1.3 Ozonation catalytic ceramic membrane filtration

Membrane filtration is an effective technology for water treatment. However, membrane fouling limits the application of microfiltration/ultrafiltration technology. Research has shown that NOM (natural organic matter) is the main component of the membrane surface fouling cake ^[14]. The use of ozone in combination with membrane filtration has been reported to reduce membrane fouling ^[15-18]. Ozone is a powerful oxidant that preferentially oxidizes electron-rich moieties containing carbon-carbon double bonds and aromatic alcohols, with high oxidation potential and high reactivity with NOM ^[14]. Ozonation can also be used as a disinfection process to reduce THMs in drinking water formed during

chlorination ^[19]. Minimizing ozonation dosages also results in the formation of less organic carbon and few halogenated acetic acids (upon chlorination for secondary disinfection).

However, ozonation application to membrane filtration process is limited by the low chemical resistance of most polymeric membrane materials to ozone ^[20]. Because ceramic membranes are chemically stable they can be used in conjunction with ozonation without degradation ^[21]. They also have longer lifetimes than polymeric membranes ^[22, 23]. Moreover, the surface properties of ceramic membranes allow for the use of coating techniques to improve membrane performance. Metal oxides, such as iron oxide, manganese oxide, titania, alumina, and zirconia, act as catalysts for degradation of ozone and the hydroxyl radicals formation ^[16]. These catalytic reactions are assumed to occur when ozone gas is adsorbed on the metal oxide surface ^[14]. Karnik et al. ^[21] used salicylic acid as a probe compound to demonstrate the catalytic reaction during ozone–membrane filtration. Kim et al. ^[24] studied the effect of ozone dosage and hydrodynamic conditions on permeate flux in a hybrid ozonation–ceramic ultrafiltration membrane system by treating natural water, and observed that fouling was mitigated at higher cross-flow velocities at the same ozone dosage and lower transmembrane pressures (TMP).

Studies have been conducted about membrane coating and catalytic membranes. Karnik *et al.* ^[25-26] conducted research about the AFM and SEM characterization of alumina–zirconia–titania (AZT) ceramic membranes coated with iron oxide nanoparticles: they used atomic force microscopy (AFM), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) to characterize the effects of sintering and coating

layer thickness on the microstructure of the ceramic membranes, and found the optimum coating for iron oxide particles on the underlying AZT which meets the stringent EPA regulatory requirements.

Davies *et al.* ^[27] described the use of the layer-by-layer technique to coat ceramic membranes with iron and manganese oxide nanoparticles and figured out the coating layers are thin and relatively uniform and should be enhanced with the performance of the hybrid ozonation-filtration process. With the coated membranes it is possible to significantly reduce fouling, improve the removal of DBP precursors and more effectively kill *Escherichia coli* bacteria.

Corneal *et al.* ^[28] conducted experiments to test the removal efficiency of the coated membranes used to treat water containing natural organic matter (NOM) in a hybrid ozonation–membrane water filtration system and 41% of total organic carbon (TOC) was reduced in the water samples. The manganese oxide surface layer acted as a catalyst for the oxidation of suspended and dissolved organic carbon when the membrane was used in a combined ozonation-membrane filtration system treating natural water. This catalytic activity manifested itself as improved recovery of the permeate flux due to the oxidation of organic contaminants that deposited on the membrane surface. ^[29]

Kim *et al.* ^[30] observed less fouling at higher cross-flow velocities at the same ozone dosage and lower transmembrane pressures (TMP). Ozone transfer efficiency from the gas phase to the bulk liquid phase was found to be higher at higher ozone concentrations,

cross-flow velocities, and TMPs. The accessibility of foulants to ozone at the catalytic membrane surface is believed to be a key factor affecting fouling behavior.

1.4 Photocatalytic degradation of organic contaminants in wastewater treatment application

Over the last few decades, the application of photocatalysis to utilize solar light energy and for the photodegradation of organic compounds present in water and wastewaters is getting more and more popular ^[31]. This is a desired and vital process for both water purification and renewable hydrogen energy production ^[32-35].

Electrons in valence band of photocatalysts are activated and 'jump' to the conduction band by the absorption of a photon with sufficient energy. During this process, electrons and holes are generated in the conduction band (CB) and valence band (VB), respectively ^[36]. The band gap of a photocatalyst is defined as energy gap extending from the top of the filled valence band to the bottom of empty conduction band ^[37]. Considering the overall potential losses, there should be energy provided to excite the electron to overcome bandgap energy of a semiconductor to achieve organic compounds degradation ^[38].

A schematic of semiconductor is shown in fig. 1.2. The process shows on the semiconductor particle and how electrons and holes are generated at valence band and conduction band.

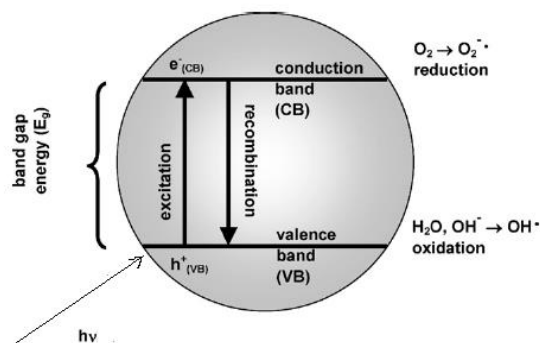


Figure 1.2 Schematic representation of photocatalysts [39]

Generally, semiconductor catalysts have low quantum efficiency because of the high recombination rate of light-induced electron – hole pairs at or near the catalyst surface, which is considered one of the major limitations to obtaining high photocatalytic efficiency [40–42]. Therefore, many efforts have been made to improve the characteristics of semiconductor-based photocatalysts to improve their activity.

“Current doubling” effect [43] arises due to the formation of an intermediate radical that can inject electrons into the CB. “Current doubling” effect can occur with alcohols, such as ethanol and 1-propanol, that carry a hydrogen atom at the carbon atom in α - position to OH group [29]. Other compounds can also generate reducing radicals that react to form the radical anion $\text{CO}_2^{\cdot-}$. Besides oxidation of a scavenger by holes, the scavenging compound may also be oxidized by $\cdot\text{OH}$ radicals formed by the trapping of holes by surface OH groups or adsorbed water molecules [32].

Using sunlight to degrade organic compounds by a semiconductor requires that the conduction band of the photocatalysts be more negative than the potential of the contaminants and the valence band more positive than organics’ potential. Some organic

compounds, such as methanol, are better electron donors than water. They will also produce H^+ , and when they are reduced, hydrogen would be produced. The rate of this hole recombination reaction can be retarded by the deposition of noble metals on the photocatalyst surface, the role of which is to scavenge electrons from the semiconductor, thereby increasing the electron transfer rate to the adsorbed species and decreasing the possibility of their recombination with holes ^[33].

Over 35 organic compounds or waste products that could potentially be photodegraded ^[34], including sugars, alcohols, aldehydes, ketones and organic acids are commonly found in wastes derived from biomass. The degradation of organic pollutants often obeys an overall first order kinetics and its efficiency can be quantitatively characterized with the apparent reaction rate constant of the reaction ^[33]. The rate constant depends on the pollutant concentration and light source intensity, among other things. Moreover, the process is economically advantageous if the photocatalyst can treat the pollutant rapidly and efficiently at high pollutant concentrations. It is thus highly desired to develop Fenton-like photocatalysts that work efficiently at high pollutant concentrations under sunlight illumination.

Many factors can affect the ability of a hole scavenger to donate an electron into the valence band of the semiconductor. In particular, the electron-hole recombination rate in the photocatalyst is very important in determining if the hole can migrate to the surface and react with the scavenger. They can enhance the ability of the photocatalytic process to harvest solar energy, by preventing electron-hole recombination.

The reaction efficiency will increase if the concentration of organic compound increases in water. However, if the concentration is too high, there will be negative effects on reaction. For example, in experiments of oxalic acid as a hole scavenger with zinc ferrite as photocatalysts, excessive oxalic oxide will oxidize photocatalysts and stop the reaction [44-45].

The pH is an important factor in this system, as it can affect the charge of both organic compounds (i.e., the scavengers), and the surface properties of the photocatalyst. The point of zero charge (zpc) describes the condition where the electrical charge density on a surface is zero [46]. When the solution pH is lower than the zpc, the immobilized surface of the photocatalyst becomes positively charged and the attraction force increases the adsorption of molecules onto the activated surface and hence increases the tendency of subsequent photocatalytic reactions [47-49]. Characteristics of organic pollutants in wastewater differ greatly in several parameters, particularly in their speciation behavior, solubility in water, and hydrophobicity. Wastewater pH varies significantly and can play an important role in the photocatalytic degradation of organic contaminants. Electrostatic interaction between a semiconductor surface, solvent molecules, substrate and charged radicals formed during photocatalytic oxidation strongly depends on the solution pH. In addition, protonation and deprotonation of the organic pollutants can take place depending on the solution pH [50].

Zinc ferrite (ZnFe_2O_4) contains earth abundant metals such as ferric, nickel, can be considered as stable and environmental friendly. It is a promising catalyst for both the

production of hydrogen from sunlight and photodegradation ^[51-54]. It has a comparatively low 1.9 eV band gap energy ^[52] and its CB is located at a more negative potential than that for the reduction of water ^[45, 53]. Existing studies have been conducted to utilize spinel photocatalysts or related mixed metal oxides as catalysts for photohydrogen production ^[51-55]. Metal-free semiconductors as photocatalysts in air purification ^[56] and hydrogen generation ^[57] have also been investigated

In order for photodegradation to be effective, the target chemical must be able to donate electrons. This can be assessed by considering the energy level of the highest occupied molecular orbital ^[56]. Another way is to determine the redox potential for the reaction in which an electron donor, RH, loses an electron to form a radical ^[44]. If the redox potential for the couple RH/R[•] is more negative than the energy level of the valence band, then electron transfer is possible. In photocatalytic systems, organic compounds are oxidized and decomposed by the photogenerated holes.

1.5 General purpose of the study

This dissertation investigates two types of advanced oxidation processes: photodegradation and membrane ozonation filtration to provide safe, low cost and high quality of water.

Chapter two describes the investigation of catalytic ozone membrane filtration. The effect of ozone dosage on membrane fouling was studied in both cross-flow and dead-end configurations. The performance of a manganese oxide coated membrane was compared

with that of uncoated titanium oxide membrane.

Chapter three describes the comparison of the operation of hybrid ceramic membrane filtration with conventional polymeric membrane filtration in terms of energy consumption and environmental impact. Treatment specifications for hollow fiber (polymeric) membrane filtration were employed. Life cycle assessment (LCA) was used to assess the environmental impact of the two processes along with the energy consumption.

The investigation of the characteristics of CdS, ZnFe_2O_4 , and NiFe_2O_4 as photocatalysts and their ability to degrade methylene blue is described in chapter 4. The mechanism, kinetics and deactivation effects of methylene blue degradation by photocatalysts was also studied.

Chapter five presents the water reuse process that combine the two processes together for caffeine removal and photocatalysts regeneration. The experimental results of this designed process showed that both CdS and ZnFe_2O_4 could remove caffeine in feed water. Ceramic membrane could effectively filter nanoparticles from water for future water reuse and catalysts recovery.

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CHAPTER TWO

Analysis of energy costs for catalytic ozone membrane filtration

The work in Chapter TWO has been published:

Wang, X., Davies, S. H., Masten, S. J.. Analysis of energy costs for catalytic ozone membrane filtration. *Separation and Purification Technology* 186 (2017): 182-187.

Abstract

Membrane fouling can be reduced through shear stress generated by cross-flow at the membrane surface. Previous work has shown that presence of ozone can reduce membrane fouling. In this work, the effect of ozonation and cross-flow on both membrane fouling on ceramic membranes and the energy cost for the process was studied. The effect of ozone dosage on membrane fouling was studied in both cross-flow and dead-end configurations. The performance of a manganese oxide coated membrane was compared with that of uncoated titanium oxide membrane. Membrane fouling decreased with increasing ozone dosages in the manganese oxide coated catalytic membrane, although increasing the dosage beyond 10–15 $\mu\text{g/s}$ yielded limited improvement. The most energy-efficient mode of operation was found to be dead-end filtration using a manganese oxide coated membrane and a 10 $\mu\text{g/s}$ ozone injection rate.

2.1 Introduction

Ultrafiltration (UF) membrane filtration can effectively remove suspended particles, colloids, bacteria, viruses and significant fraction of natural organic matter (NOM) from feed water ^[1]. There are a number of advantages of UF membrane treatment over conventional water treatment technologies, including reduced sludge production ^[2], smaller footprint ^[3], and the physical exclusion of microorganisms from the product water. However, membrane fouling continues to be one of the main factors that limit the application and increase the operational costs of membrane technologies ^[4]. Fouling results in a decrease in the production rate of purified water and a concomitant increase in the requisite transmembrane pressure ^[5].

In water treatment, NOM is the predominant cause of UF membrane fouling ^[6-9]. The use of ozone in combination with membrane filtration has been reported to reduce membrane fouling ^[10-14]. Ozone, a powerful oxidant, is reactive with NOM ^[15]. Pre-ozonation can also reduce formation of Trihalomethanes (THMs) during subsequent chlorination ^[16].

Ceramic membranes are chemically stable, have longer lifetimes than polymeric membranes, and they can be used in conjunction with ozonation without degradation of the membrane ^[17, 18]. Moreover, the surface properties of ceramic membranes may be altered to improve membrane performance. Metal oxides, such as titania ^[10,11], iron oxide ^[11], and manganese oxide ^[11, 19, 20], can act as catalysts for the degradation of ozone and the formation of hydroxyl radicals. These catalytic reactions are assumed to occur at the metal oxide surface. Kim et al. ^[12] studied the performance of nanoparticle-enhanced

membranes and concluded fouling was dependent upon the physicochemical aspects of nanoparticles, such as particle size, hydrophilicity, and surface charge. Byun ^[11] reported that when used with ozone the performance of the manganese oxide coated membrane was superior to that of Ti and Fe oxide membranes in terms of fouling mitigation and the reduction of TOC in the permeate. In addition, the coating of the membranes with manganese oxide nanoparticles significantly reduced the concentrations of THM and Haloacetic acids (HAA) precursors found in the permeate ^[19]. Szymanska et al ^[13] and Zouboulis et al. ^[21] showed that with hybrid ozonation ceramic membrane microfiltration, mitigation of membrane fouling was well controlled. Wei et al. ^[22, 23] demonstrated that pre-ozonation mitigated fouling on a UF membrane caused by soluble extracellular organic matters released from *Microcystis aeruginosa*. They found that ozone reacted with the cake fouling and gel layers and prevented membrane pore blocking.

The objective of this study was to analyze the energy costs for membrane filtration, in the presence of ozone, using either a manganese oxide coated ceramic membrane or titania oxide coated membrane (virgin membrane). Studies were conducted to determine the optimum ozone dosage and hydrodynamic conditions for this hybrid membrane system. The energy costs for both ozone generation and pumping were evaluated to determine the operating conditions for which the energy costs were minimized.

2.2 Experimental methods

2.2.1 Feed water

The source water was obtained from Lake Lansing (Haslett, Michigan), a borderline eutrophic lake. The water was stored in the dark at 4 °C until use. Water samples were pre-filtered through a 0.5-µm ceramic cartridge micro-filter (Doulton USA, Southfield, MI) to remove larger particles. After filtration, the average TOC concentration in the test water was 10 ± 1 mg C/L. Before commencing each experiment, the temperature of the feed water was adjusted to room temperature ($20 \pm 3^\circ\text{C}$).

2.2.2 Membrane module

The nominal molecular weight cut-off of the virgin membrane (Inside CeRAM, TAMI North America, Saint - Laurent, Quebec, Canada) was 5 KDa. The seven-channel membrane had a total filtering surface area of 131.9 cm^2 , an active length of 25 cm, and an external diameter of 10 mm. The grain size within the support layer and the filtration layer of the virgin membrane varied between 132 nm and 296 nm and between 1.05 and 6.64 nm^[11], supported with titanium oxide filtration layer. The clean water permeability of the coated membrane was $80 \pm 2\text{ L/m}^2\cdot\text{h}$.

The virgin membrane was coated with manganese oxide according to the procedure described by Corneal et al.^[20]. In this study, the performance of a membrane coated twenty times manganese oxide nanoparticles was examined, as higher permeate fluxes were obtained with membrane coated twenty times coated than with those coated thirty or forty times. Byun et al.^[11] found the Mn oxide coating to be crystalline Mn_2O_3 , and that

for the membrane coated 20 times the thickness of coating varied between 14 and 54 nm with 20 times coatings. With the manganese oxide coated membranes, the lower operating pressure was used because the permeability of the manganese oxide coated membrane was higher than that of the uncoated membrane, as sintering at 500 °C leads to coarsening of the grains within the filtration layer ^[19].

2.2.3 Ozone contactor

A schematic for the ozone contactor is shown in Figure 2.1. The water in the contactor was maintained at a constant level using a conductivity water level sensor connected to a programmable logic relay (SG2 PLR, B&B Electronics, IL), which opened or closed a solenoid valve (6013, Bürkert, Germany) to regulate water flow from the sample reservoir to the contactor. Ozone was generated from pure, dry oxygen (99.999%) using a corona discharge ozone generator (Absolute Ozone®, Absolute System Inc., Edmonton, AB, CA). An ozone monitor (Model 450H, Teledyne Technologies Inc., San Diego, CA) was used to measure ozone concentration. The flow rate of ozone gas was controlled at 10 mL/min by a rotameter (Cole-Parmer Inc., Vernon Hills, IL) installed between the ozone monitor and the membrane module. The ozone transfer efficiency in the contactor was determined before each experiment, by measuring the difference in the influent and effluent gaseous ozone concentrations and multiplying that difference by the gas flow rate.

2.2.4 Hybrid ozonation – filtration setup

The schematic of the ozone injection system is shown in Figure 2.1. Nitrogen gas (99%,

Airgas) was used for pressurizing feed tanks. The membrane module housing (TAMI North America, St. Laurent, Québec, Canada) was made of stainless steel. Both dead-end filtration and cross-flow filtration were performed at volumetric flow rate through the membrane of 18 ± 1.5 mL/min. This corresponds to a flux of 81.2 ± 2.8 L/m²·h, which is typical of that used in full-scale water treatment. The flux was maintained using a peristaltic pump (Eldex®, Eldex Laboratories, Inc., Napa, CA). A recirculation pump (Materflex®, Cole Parmer Inc., Vernon Hills, IL) used when operating the system in cross-flow mode to obtain the constant cross-flow velocity of 0.5 ± 0.1 m/s. The transmembrane pressure (TMP) was recorded by a multifunctional sensor (L Series, Alicat Scientific, Tucson, AZ) every 60 s. Temperature and atmosphere pressure were also monitored every 60 s by the multifunctional sensor. The permeate flux was measured using an electronic balance (Adventure Pro Analytical Balance, Ohaus Corp., Pine Brook, NJ) every 60 s. The transmembrane pressure (TMP, bar) and permeate flux (J, L/m²·h) were recorded by Flow Vision SC (Alicat Scientific, Tucson, AZ) data acquisition software.

Experiments were conducted at ozone dosage injection rates of 5, 10, 15, and 20 µg/s. Control experiments were conducted to measure membrane flux without gas injection. The range of ozone dosages was selected based on prior work, which indicated that ozone dosages greater than 20 µg/s resulted in little enhancement in the permeate flux and reduction in membrane fouling [14, 21, 24]. Experiments were halted when the permeability of the membrane decreased to approximately 40% of the initial permeability.

After each experiment, the fouled membranes were cleaned using deionized water and

20 µg/s gaseous ozone for 2-4 h until the initial clean water flux was restored. Before each filtration experiment, the initial flux was measured to ensure that the permeability of the membrane was within (98±2) % of its initial value [11]. After cleaning the initial TMP for the system varied between 1.2 and 1.5 bar.

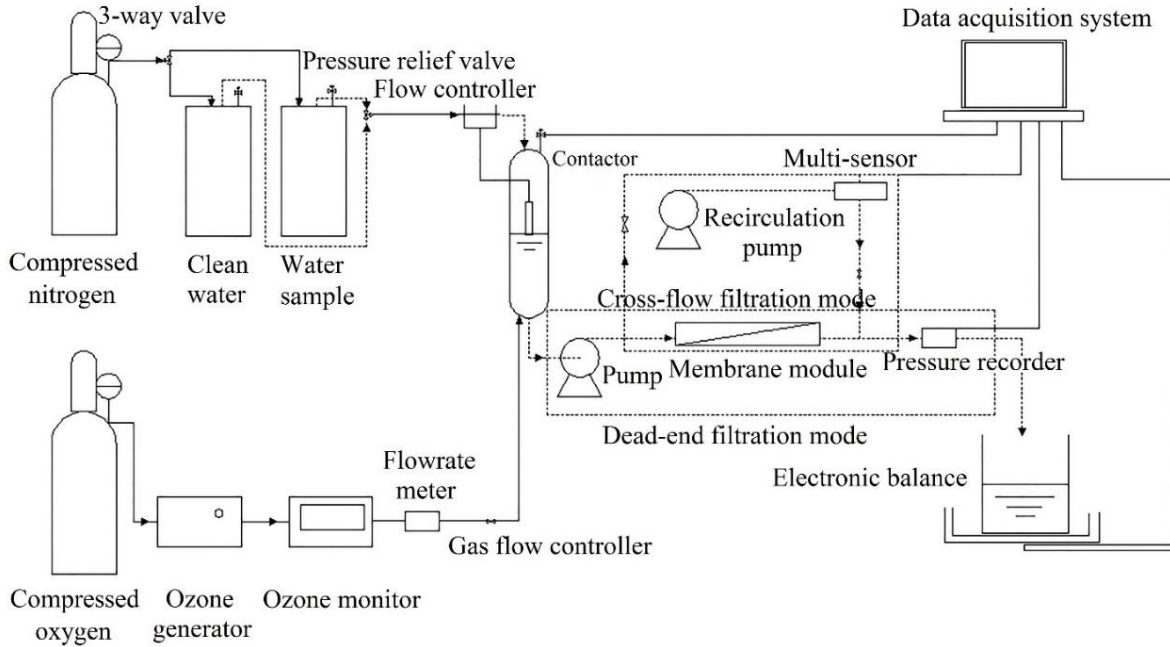


Figure 2.1 Schematic of the ozonation-membrane filtration system

2.2.5 Data Analysis

2.2.5.1 Permeability and resistance fouling

The permeability, L_p , was calculated as shown in Equation 1:

$$L_p = \frac{J}{TMP} \quad (1)$$

where, L_p is given in units of $L/(m^2 \cdot h \cdot bar)$. The greater the permeability, the higher the efficiency of the membrane.

The total resistance across the membrane was calculated from the TMP and flux data

using Darcy's Law:

$$R_t = \frac{TMP}{\mu J} \quad (2)$$

$$R_t = R_m + R_c \quad (3)$$

where, μ is the viscosity of water at $22 \pm 2^\circ\text{C}$ ($0.89 \times 10^{-3} \text{ N}\cdot\text{s}/\text{m}^2$). The total resistance, R_t , is the sum of the intrinsic resistance of the membrane, R_m , and the resistance due to the material deposited on the membrane surface, R_c . R_t was calculated from the final TMP and flux.

2.2.5.2 Calculation of energy consumption

2.2.5.2.1 Energy consumed to pressurize feed water

The power necessary to pressurize the feed water was determined by Equation (4) [25]:

$$P_h = \frac{q \cdot \rho \cdot g \cdot h}{\eta} = \frac{q \cdot TMP}{\eta} \quad (4)$$

where, q (m^3/s) is the average flow rate of the membrane module during the operational period and is calculated by $q = \pi d^2/4 \times v$, v is the velocity of the water in filtration system; ρ (kg/m^3) is the density of feed water at room temperature; g ($9.81 \text{ m}/\text{s}^2$) is gravitational acceleration of the earth; h is the water head (m), TMP (bar) is the transmembrane pressure across membrane module, and is calculated using the equation $TMP = \rho gh$, η is the efficiency of the pressurizing pump which was assumed to be 75%. The power (P_h) is reported in units of kW.

2.2.5.2.2 Energy consumed by recirculation pump

The power required to recirculate water through the system was determined by Equation (5) [25]:

$$P_r = \frac{q \cdot \rho \cdot g \cdot \Sigma h_r}{\eta'} = \frac{q \cdot \Sigma \Delta P}{\eta'} \quad (5)$$

in which P_r is in kW; the total water head ($\Sigma h_r = \Sigma \Delta P / \rho g$) of the recirculation system was determined from pressure drop (ΔP) across the tubing and membrane module, η' is the efficiency of the pressurization pump, which was determined to be 70% based on the pump curve.

The pressure drop in the system was calculated using Darcy-Weisbach equation:

$$\Delta P = \frac{f \rho v^2 L}{2d} \quad (6)$$

$$f R_e = 64 \quad (7)$$

$$R_e = \frac{dv\rho}{\mu} \quad (8)$$

where, v is cross-flow velocity (0.5 ± 0.1 m/s during experiment), f is the Darcy friction factor, d (m) is the hydraulic diameter of the pipe/membrane channels, ρ (kg/m^3) is the density of feed water under room temperature, L (m) is the length of different tubing sections. For the recirculation cycle, ΔP was calculated separately across the different sections of tubing, valves, and membrane channel using an online pressure drop calculator (Pressure Drop Online-Calculator. Software-Factory Norbert Schmitz. <http://www.pressure-drop.com/Online-Calculator/>).

2.2.5.2.3 Energy consumption during ozone generation in backwash and operation cycles

Based on product data sheet ozone generator (Primozone Production AB. <http://www.water-proved.de/en/Downloads/Primozone-Ozone-Generator--System->

[controller.pdf](#)), Ozone Generators parameters (Lenntech BV. <http://www.lenntech.com/otozone.htm>) and published literature ^[26], approximately 10 kWh energy is consumed to produce 1 kg ozone from. The ozone transfer efficiency in the system was determined to be 95% based on the analysis of dissolved ozone concentrations and the ozone concentration in the gas phase before and after the contactor.

The operational period was determined by the filter run time between backwashing. The filters were backwashed when transmembrane pressures reached 2.5 ± 0.1 bar ($>10 \mu\text{g O}_3/\text{s}$) or 3.8 ± 0.2 bar ($<5 \mu\text{g O}_3/\text{s}$). Gaseous ozone was used for membrane backwash cleaning. The operational parameters for the backwashing are shown in Table 2.1. The energy needed for backwashing, including that required for pressurization during backwash process and that for generating ozone. The energy consumed during operation was $W = P \times T$, in which W is in kWh, P (kW) is the power required to pressurize the feed water or recirculate water, and T is the operation time.

Table 2.1 Backwash process operation parameters

Criteria	Parameters
Duration	2-4 hours, take 3 hours as average
Fouled membrane TMP	2.2-2.6 bar for high ozone injection rate ($>10 \mu\text{g/s}$); 3.6-4.0 bar for no ozone injection or $5 \mu\text{g/s}$ ozonation
Cleaned membrane TMP	1.2-1.5 bar
Average membrane TMP during backwash process	Approximately 1.9 bar for high ozone injection rate ($>10 \mu\text{g/s}$); 2.58 bar for no ozone injection or $5 \mu\text{g/s}$ ozonation
Feed water flow rate	~ 18 mL/min
Ozone injection rate	20 g/s

2.3 Result and discussion

2.3.1 Comparison of permeate flux and resistance fouling

Figure 2.2 displays the effect of ozone dosage on permeate flux during catalytic membrane filtration when a manganese oxide coated membrane was employed using dead-end operation mode. As shown in this figure 2.2, irrespective of ozone dosage, the permeability initially declined rapidly during first 30 minutes. In this stage, the fouling cake begins to form at membrane surface. This stage was followed by one in which the permeability decreased at a much slower pace. At an ozone dosing rate of 20 $\mu\text{g/s}$ the permeability was eventually nearly constant. When the permeability reached steady state condition, the rate of formation of the fouling cake due to deposition of natural organic matter on the surface of the membrane is presumed to be similar to the rate of reaction of the accumulated foulants with ozone and OH radicals formed as a result of the catalytic degradation of ozone by manganese oxide ^[19]. Increasing the ozone dosing rate improved the performance of the system as catalytic degradation of the filter cake became increasingly favored over formation of the filter cake.

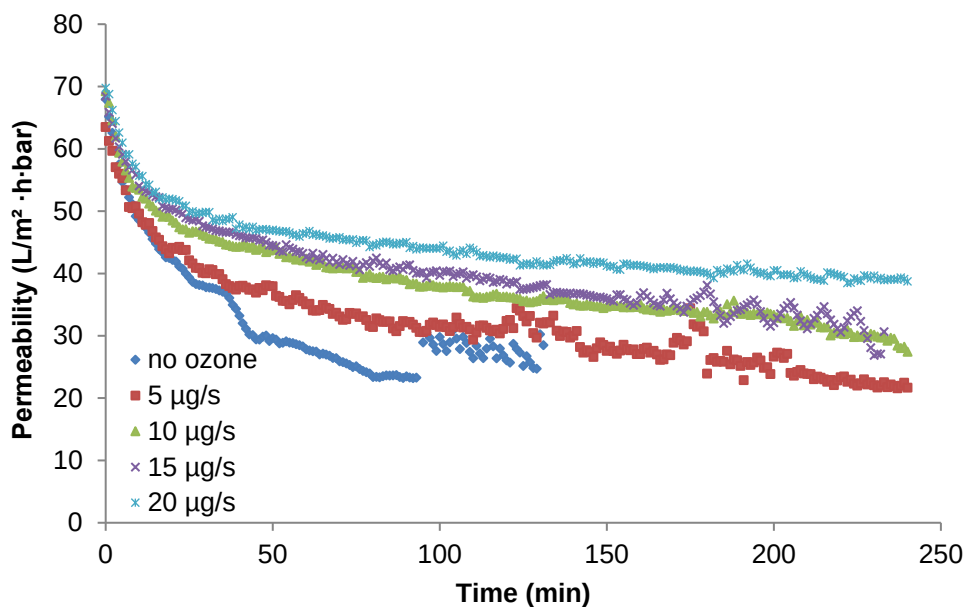


Figure 2.2 Effect of ozone dosage on permeability using manganese oxide coated catalytic membrane filtration – dead-end operation mode (Conditions: permeability in $L/m^2 \cdot h \cdot bar$, Feed TOC=12.1 mg/L, temperature=22±2 °C)

Figure 2.3 shows the effect of ozone dosage on permeate flux during cross – flow operation. While the observed permeability trends for cross-flow and dead-end operational modes are similar, the permeability fluctuated more during cross-flow operation than in dead-end operation. As was the case with dead-end filtration, increasing the ozone dosage resulted in less fouling. In the absence of ozone injection and with ozone injection at dosages of 5-10 $\mu g/s$, the permeability values after 240 min were greater in cross-flow mode than that in dead-end mode. Under these conditions shear created by the recirculation of the retentate appears to disrupt fouling cake formation. However, at higher (15 and 20 $\mu g/s$) ozone dosages the permeabilities observed during operation were similar in cross-flow and dead-end filtration. This suggests that the reaction of ozone and foulants affects the foulants in such a way that the fouling cake less easily dislodged from the membrane surface.

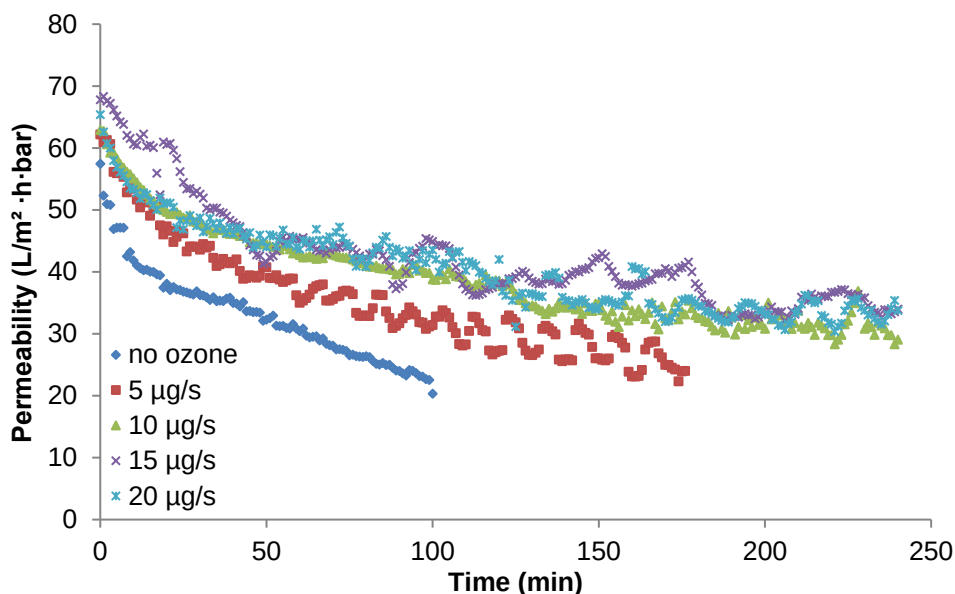


Figure 2.3 Effect of ozone dosage on permeate flux during manganese oxide coated catalytic membrane filtration– crossflow operation mode (Conditions: permeability in L/m²·h·bar, Feed TOC=12.1 mg/L, cross flow velocity = 0.5±0.1 m/s temperature=22±2 °C)

The permeability of the virgin titanium oxide coated catalytic membrane during operation of membrane filtration in both dead–end and cross–flow filtration mode is shown in Figure 2.4. The trends were similar to that observed with the manganese oxide coated membrane, as the extent of fouling decreased with increasing ozone dosage. In the absence of ozone, the extent of fouling was greater on the virgin titania membrane than on the coated membrane. This is likely the result of the electrostatic characteristic of the membrane surface. The point of zero charge of manganese oxide ($\text{pH}_{\text{zpc}} = 2.8\text{--}4.5$ ^[27]) is lower than that of titania oxide ($\text{pH}_{\text{zpc}} = 4.1\text{--}6.2$ ^[10]). At the pH of the treated water is ~8, the hydroxyl groups on the Mn oxide surface would be fully deprotonated. The surface hydroxyl groups on the TiO₂ surface are not completely deprotonated; thus the manganese oxide surface is likely to have higher charge density and the repulsive forces in the Mn oxide membrane system between the negatively charged components of the

NOM and the oxide are probably higher than that observed with the titania oxide membrane. With higher repulsive electrostatic forces, the deposition of organics would be reduced, and with that, the degree of membrane fouling would also be diminished.

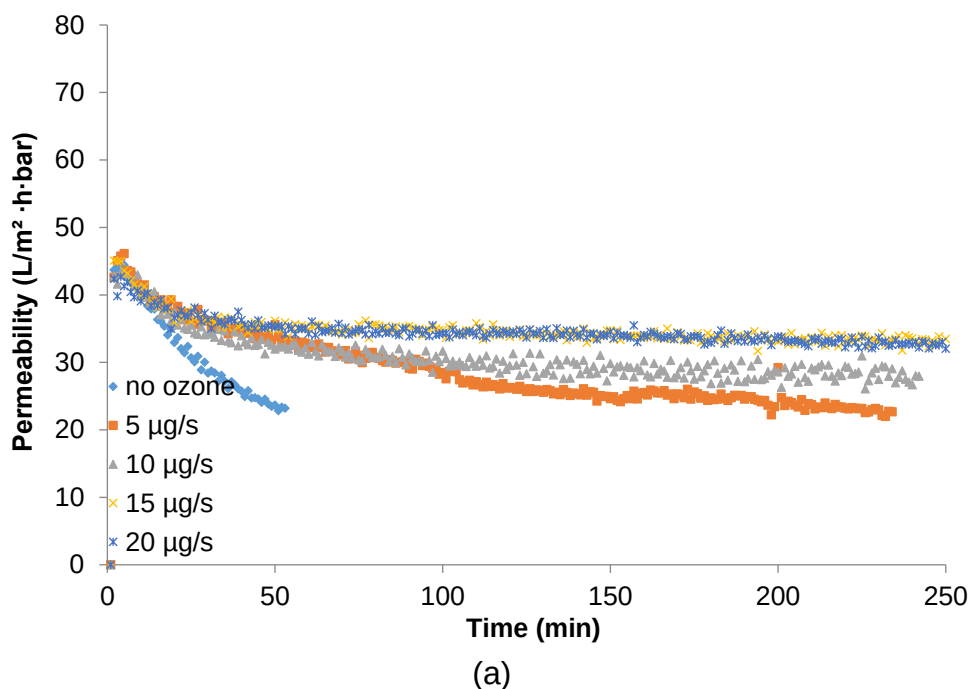
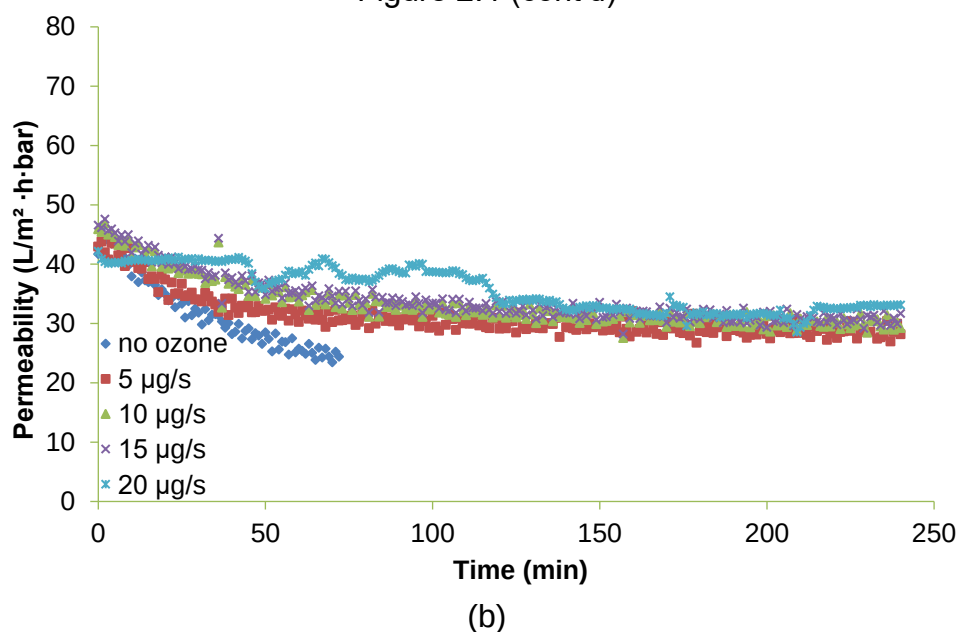


Figure 2.4 Effect of ozone dosage on permeability during titania oxide coated catalytic membrane filtration – (a) dead-end operation mode and (b) crossflow operation mode (Conditions: permeability in L/m²·h·bar, Feed TOC=12.1 mg/L, cross flow velocity = 0.5±0.1 m/s temperature=22±2°C)

Figure 2.4 (cont'd)



The effect of ozone dosage and mode of operation on fouling resistance is shown in figure 2.5. The fouling resistance was determined at 80 min (steady state) for manganese oxide coated catalytic membrane filtration and at 120 min for titania oxide coated catalytic membrane filtration, since as mentioned early, it took longer for steady state conditions to be achieved with the titania oxide coated catalytic membrane filtration. As figure 2.5 shows, the fouling resistance decreased with increasing ozone dosage for both operational modes and membrane types. Recirculation was not as effective as ozonation at reducing fouling resistance. Under identical operational conditions, the resistance of the manganese oxide coated membrane was less than that of the titania oxide coated membrane.

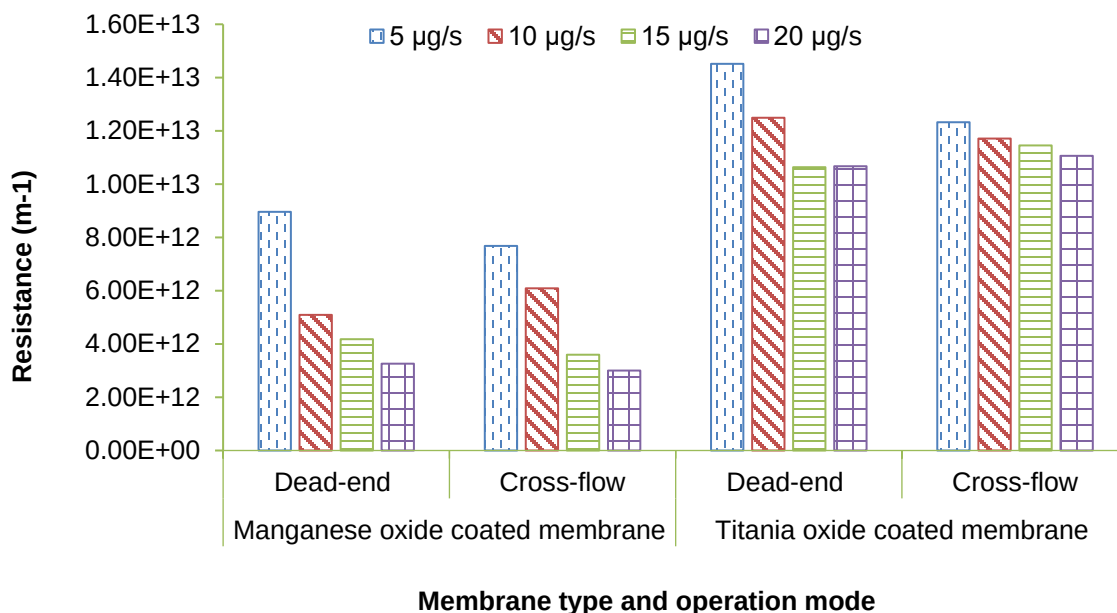


Figure 2.5 Effect of ozone dosage on fouling resistance in manganese oxide coated and titania oxide coated catalytic membrane filtration system

2.3.2 Energy and economic analysis of membrane systems for design applications

As overall resistance of the manganese oxide membrane, and the operational cost would be less with this membrane under same ozone dosage and operation mode compared to the virgin titania membrane. Using experimental results for the coated membrane the energy necessary to filter 1,000 liters of water was calculated (see Section 2.5 and Table 2.2). The energy costs include energy consumption for pumping water across the membrane, ozone generation, and recirculating through the system. It also includes minor losses through the system. As shown in figure 2.6 for the manganese oxide coated membrane the optimal ozone dosing rate is 10 µg/s for dead end operation and for cross-flow mode it is 5-10 µg/s. At these dosing rates the energy consumed is similar for dead-end and crossflow systems. Dead-end operation is simpler and does not require a recirculation pump thus mode of operation is more desirable. Thus, under the conditions

studied for Lake Lansing water, dead-end catalytic membrane filtration using the manganese oxide coated membrane at an ozone dosage of 10 $\mu\text{g/s}$ was determined to be the most efficient operational mode.

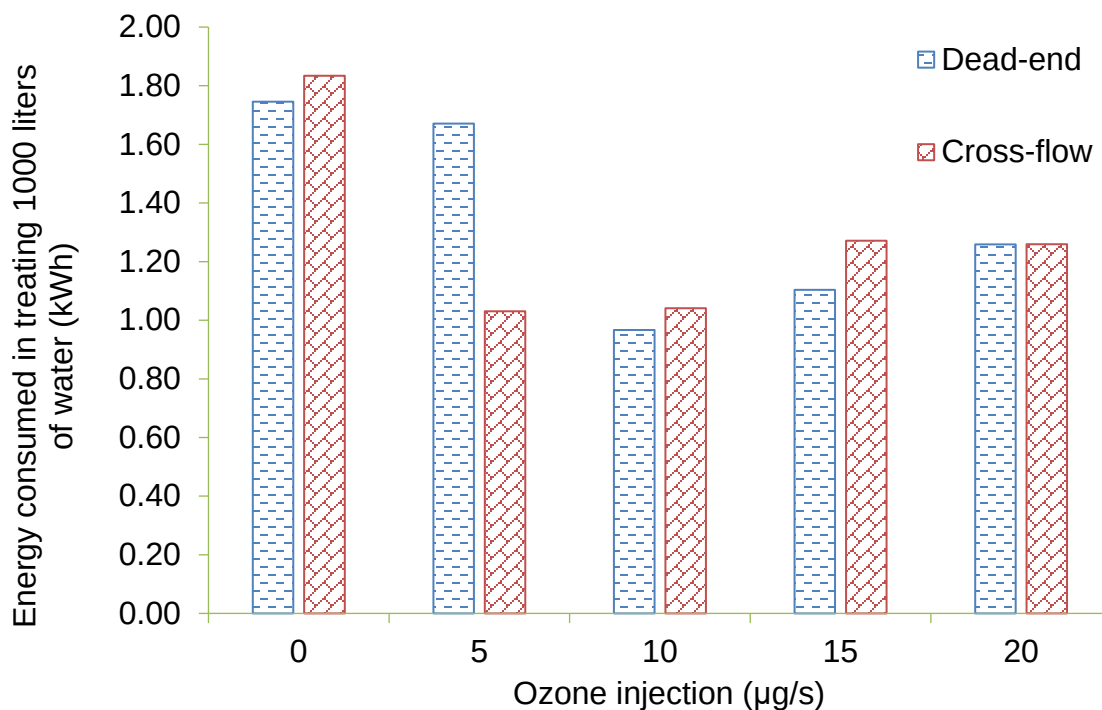


Figure 2.6 Energy consumed during the treatment of in 1,000 liters of water (including backwash cycles)

Calculations for energy consumption for the hybrid-ozonation filtration system are given in section 2.5 data analysis, and results are shown in Table 2.2. The energy needed to filter 1,000 liters of water was estimated assuming there was no deterioration in performance over an extended period of time. Based on these calculations the minimum amount of energy required to filter this volume of Lake Lansing water is 0.97kWh.

Table 2.2 Energy consumption for Mn oxide coated membrane filtration with different ozone dosing rates and operation modes with one membrane module

Operation mode	Ozone dosage ($\mu\text{g/s}$)	Operation period during 1 cycle (min)	Water filtered during 1 cycle (L)	Energy consumed during operation				Approximate energy needed for 1 cycle backwash cycle (kWh)	Time required to treat 1,000 L of water (hours)	Numbers of operation periods	Total energy consumed (kWh)
				Energy consumed in pressurization (kWh)	Energy consumed in ozonation (kWh)	Energy consumed in recirculation (kWh)	Total energy consumed during operation (kWh)				
Dead-end	0	93.0	1.563	1.453×10^{-4}	0	0	1.453×10^{-4}	2.583×10^{-3}	1023.7	640	1.75
	5	98.0	1.839	1.728×10^{-4}	3.158×10^{-4}		4.886×10^{-4}		915.6	544	1.67
	10	255.0	4.638	3.530×10^{-4}	1.629×10^{-3}		1.982×10^{-3}	2.502×10^{-3}	927.2	216	0.97
	15	233.0	4.659	4.054×10^{-4}	2.236×10^{-3}		2.641×10^{-3}		844.2	215	1.10
	20	241.0	4.721	3.592×10^{-4}	3.082×10^{-3}		3.441×10^{-3}		861.3	212	1.26
Cross-flow	0	82.0	1.535	1.594×10^{-4}	0	7.291×10^{-5}	2.323×10^{-4}	2.583×10^{-3}	923.0	652	1.83
	5	175.0	3.541	3.585×10^{-4}	5.526×10^{-4}	1.556×10^{-4}	1.067×10^{-3}		837.8	282	1.03
	10	222.0	4.294	3.679×10^{-4}	1.402×10^{-3}	1.974×10^{-4}	1.967×10^{-3}	2.502×10^{-3}	873.3	233	1.04
	15	250.0	4.238	2.952×10^{-4}	2.368×10^{-3}	2.223×10^{-4}	2.886×10^{-3}		995.0	236	1.27
	20	240.0	4.887	4.066×10^{-4}	3.032×10^{-3}	2.134×10^{-4}	3.652×10^{-3}		828.7	205	1.26

2.4 Conclusion

The energy costs for operation of catalytic membrane filtration were calculated. Membrane fouling was effectively controlled using catalytic membrane filtration. For the manganese oxide coated membrane, membrane fouling was effectively controlled at ozone dosages of 10 $\mu\text{g/s}$ or greater. With the virgin membrane, an ozone dosage of at least 15 $\mu\text{g/s}$ was necessary to control membrane fouling. The overall resistance of the manganese oxide membrane was less with manganese oxide coated membrane under same ozone dosage and operation mode compared to that observed for the virgin titania membrane. Using the flux data obtained, it was determined that for the water studied the most energy-efficient operational mode is 10 $\mu\text{g/s}$ ozone dosage, dead-end operation, with the manganese oxide coated membrane. Future work will include a life-cycle assessment (LCA) to evaluate the environmental impacts of membrane filtration, and compare this technology to other water treatment processes, to determine whether this technology is more energy efficient than conventional processes for treating water.

Acknowledgements

This study was supported by the Department of Civil and Environmental Engineering, Michigan State University, and American Water Works Association, Michigan Section. The authors are grateful for the comments from the reviewers of this manuscript.

APPENDIX

APPENDIX

Supplemental Section:

Samples calculation of energy consumption

Using 5 µg/s ozone injection rate with crossflow operation mode as an example:

Average TMP during 175 min operation period was 2.723 bar, the water head was:

$$h = \frac{TMP}{\rho \cdot g} = \frac{(2.723 \text{ bar}) \left(10^5 \text{ kg} \cdot \frac{\text{m}}{\text{s}^2 \cdot \text{m}^2} / 1 \text{ bar} \right)}{\frac{10^3 \text{ kg}}{\text{m}^3} \times 9.8 \text{ m/s}^2} = 27.78 \text{ m}$$

The power needed at the average TMP was:

$$P_h = \frac{q \cdot TMP}{\eta} = \frac{\left(\frac{18 \text{ ml}}{\text{min}} \right) \cdot \left(\frac{10^{-6} \text{ m}^3}{1 \text{ ml}} \right) \cdot \left(\frac{1 \text{ min}}{60 \text{ s}} \right) \cdot (2.723 \text{ bar}) \left(10^5 \text{ kg} \cdot \frac{\text{m}}{\text{s}^2 \cdot \text{m}^2} / 1 \text{ bar} \right)}{(75\%)} = 0.1229 \text{ watt} = 1.229 \times 10^{-4} \text{ kW}$$

The work/energy provided during the operation period was:

$$P_h T = (1.229 \times 10^{-4} \text{ kW}) \times (175 \text{ min}) (1 \text{ h}/60 \text{ min}) = 3.585 \times 10^{-4} \text{ kWh}$$

The pressure drop (ΔP) during recirculation cycle (except membrane module) was 0.00389 bar, obtained from pressure drop online calculator ^[26]; so the power required during this cycle was:

$$P_{r1} = \frac{q \cdot TMP}{\eta} = \frac{v \cdot A \cdot TMP}{\eta} = \frac{\left(\frac{0.5 \text{ m}}{\text{s}} \right) \times \frac{\pi (10 \times 10^{-3} \text{ m})^2}{4} \cdot 0.00389 \times 10^5 \text{ N} \cdot \text{m}^2}{70\%} = \frac{3.927 \times \frac{10^{-5} \text{ m}^3}{\text{s}} \cdot 0.00389 \times 10^5 \text{ N} \cdot \text{m}^2}{70\%} =$$

$$0.02182 \text{ watt} = 2.182 \times 10^{-4} \text{ kW}$$

The pressure drop (ΔP) in the membrane module was 0.00562 bar (based on membrane length and cut-off area), so the power demand for this part was:

$$P_{r2} = \frac{q \cdot TMP}{\eta} = \frac{v \cdot A \cdot TMP}{\eta} = \frac{\left(\frac{0.5m}{s}\right) \times \frac{\pi(10 \times 10^{-3}m)^2}{4} \cdot 0.00562 \times 10^5 N \cdot m^2}{70\%} = \frac{3.927 \times \frac{10^{-5}m^3}{s} \cdot 0.00562 \times 10^5 N \cdot m^2}{70\%} =$$

$$0.03153 \text{ watt} = 3.153 \times 10^{-4} \text{ kW}$$

The power demand for this pressure drop was:

$$P_r = P_{r1} + P_{r2} = 0.05335 \text{ watt} = 5.335 \times 10^{-4} \text{ kW}$$

Energy demand during operation period for this pressure drop was:

$$P_r T = 5.335 \times 10^{-4} \text{ kW} \times (175/60) = 1.556 \times 10^{-3} \text{ kW}$$

Energy demand for ozone generation was:

$$E_{O_3} = (5 \mu\text{g O}_3/\text{s}) (175 \text{ min}) (60\text{s}/1 \text{ min}) (10 \text{ kwh}/1\text{kg O}_3) (1\text{kg}/10^{-9} \mu\text{g}) / 0.95 = 5.526 \times 10^{-4} \text{ kWh}$$

Energy cost in one operation period was obtained: $Q = P_h T + P_r T + E_{O_3} = 1.067 \times 10^{-4} \text{ kWh}$

During this process, 3.54 L feed water had been treated.

Gaseous ozone was used for membrane backwash cleaning, and the operation parameters are shown in table 2.1. Energy needed for 1 cycle backwash included energy for 20 $\mu\text{g/s}$ ozonation and energy for pressurization during backwash process, there was difference in energy consumption for assorted ozone injection rate as the average TMP varied during backwash cycles:

$$P_{backwash1(>10 \mu\text{g/s})} = \frac{q \cdot TMP}{\eta} = \frac{\left(\frac{18\text{ml}}{\text{min}}\right) \cdot \left(\frac{10^{-6}m^3}{1\text{ml}}\right) \left(\frac{1 \text{ min}}{60 \text{ s}}\right) \left(1.85 \times 10^5 \text{ kg} \frac{m}{s^2 \cdot m^2}\right)}{(75\%)} = 0.076 \text{ watt} = 7.6 \times 10^{-5} \text{ kW}$$

$$P_{backwash2(<5 \text{ ug/s})} = \frac{q \cdot TMP}{\eta} = \frac{\left(\frac{18 \text{ ml}}{\text{min}}\right) \cdot \left(\frac{10^{-6} \text{ m}^3}{1 \text{ ml}}\right) \left(\frac{1 \text{ min}}{60 \text{ s}}\right) (2.58 \times 10^5 \text{ kg} \cdot \frac{\text{m}}{\text{s}^2 \cdot \text{m}^2})}{(75\%)} = 0.1032 \text{ watt} = 1.032 \times 10^{-4}$$

kW

$$E_{backwash} = \frac{(20 \text{ } \mu\text{g O}_3/\text{s}) (3 \text{ hrs}) (3600 \text{ s}/1 \text{ hour}) (10 \text{ kWh}/1 \text{ kg O}_3) (1 \text{ kg}/10^{-9} \text{ } \mu\text{g})}{0.95} = 2.274 \times 10^{-3} \text{ kWh}$$

Energy cost during backwash:

$$Q_{backwash1(>10 \text{ ug/s})} = P_{backwash1(>10 \text{ ug/s})} T_{backwash} + E_{backwash} = 2.583 \times 10^{-3} \text{ kWh}$$

$$, \text{ or } Q_{backwash1(<5 \text{ ug/s})} = P_{backwash1(<5 \text{ ug/s})} T_{backwash} + E_{backwash} = 2.502 \times 10^{-3} \text{ kWh}$$

It would take 282 cycles to treat 1,000 L of water in one membrane module, so the total energy for treating 1000 liters of water using 5 $\mu\text{g/s}$ ozone injection rate with crossflow operation mode would be 1.03 kW.

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CHAPTER THREE

Energy consumption and environmental impact of ozonation catalytic membrane filtration system and comparison with hollow fiber membrane for water treatment

The work in Chapter Three has been accepted:

Wang, X., Anctil, A., Masten, S. J.. Energy consumption and environmental impact analysis of ozonation catalytic membrane filtration system for water treatment. Environmental Engineering Science

Abstract

The productivity of water filtration can be improved with ceramic membranes as compared to polymeric membranes because of their higher stability, longer lifetime, and higher permeability. The use of ozonation in combination with manganese oxide coated ceramic membrane filtration has been shown to reduce membrane fouling. In this study, life-cycle-assessment was conducted to analyze the energy consumption and environmental impacts of the catalytic ceramic membrane system, which were then compared to that for hollow fiber membrane filtration. For both systems, the analysis was accomplished for a treatment plant with a capacity of 9 MGD. Energy consumption and environmental impacts were determined for membrane pressurization, backwashing, chlorine injection for hollow fiber membrane treatment disinfection or ozone injection for ceramic membrane fouling control and disinfection processes, and membrane modules manufacturing. The results showed that ceramic membrane combined with ozonation could save energy costs for pressurization and backwashing, but ozone generation consumed more energy than chlorine disinfection. The total energy consumption for catalytic ceramic membrane filtration with ozonation was 7% greater than for hollow fiber membrane filtration. However, catalytic membrane filtration had a slightly lower normalized environmental impact than polymeric membrane filtration. Innovative technologies to reduce energy consumption for production of ozone, or the use of less energy intensive oxidants for fouling mitigation are expected to make the ceramic membrane filtration processes more energy-efficient and environmental-friendly.

3.1 Introduction

Membrane technology has become more economical, and the use of membrane filtration has increased rapidly ^[1]. There are a number of advantages in membrane process over conventional drinking water treatment technologies, including less sludge production, smaller footprint, and the physical exclusion of microorganisms from the product water ^[2]. However, during membrane filtration process, the deposition of materials, such as rejected colloids, chemicals, microorganism on the membrane surface results in a decrease in the production of purified water or a concomitant increase in the requisite pressure ^[3].

Compared to polymeric membranes, ceramic membranes are chemically stable, have longer lifetimes ^[4, 5], low operation cost, greater recyclability, and higher permeability ^[6]. Moreover, the surfaces of ceramic membranes can be coated with metal oxides, which serve as catalysts and thereby improve membrane performance ^[2]. The chemical stability of ceramic membranes allows its application in conjunction with ozonation ^[5]. Metal oxides, such as iron oxide, manganese oxide, titania, alumina, and zirconia, act as catalysts for degradation of ozone and the formation of hydroxyl radical radicals ^[2]. These catalytic reactions have been shown to occur when ozone molecules are adsorbed on the metal oxide surface ^[7]. However, the capital costs of ceramic membranes are higher than polymeric ultrafiltration/microfiltration membranes, and the materials are brittle ^[6].

The use of ozone in combination with membrane filtration has been reported to reduce membrane fouling ^[7-9]. Byun ^[10] evaluated the performance of the coated and uncoated

membranes, showing that manganese oxide coated membrane was superior to that of the other membranes tested. Song *et al.* ^[11] studied the effect of ozonation on protein-based ceramic membrane fouling and confirmed that the bovine serum albumin membrane fouling mechanism changed from cake-intermediate to cake-standard with ozonation at high ozone dosage. Song *et al.* also found ^[12] that pre-ozonation and *in-situ* ozonation were both effective in controlling membrane fouling, and *in-situ* ozonation with ceramic membrane filtration increased the generation of hydroxyl radical, thus improving the oxidation of the accumulated foulants on the membrane surface and effectively reducing both reversible and irreversible membrane fouling. Yu *et al.* ^[13] evaluated the performance of coagulation followed by ozonation with a low dosage for pretreatment before ultrafiltration. They found that the addition of ozone into the UF membrane tank reduced membrane fouling, increased the suspended solids concentration in the membrane tank, and reduced the concentration of bacteria.

Wang *et al.* ^[14] demonstrated that hybrid manganese oxide coated ceramic membrane with ozonation system, dead-end filtration with ozone injection was more energy-efficient than crossflow operation mode or either mode without ozone injection. Membrane fouling was also shown to decrease with increasing ozone dosages ^[14].

Ozonation has the advantage over chlorination, in that it is a more powerful disinfectant, and its use with membrane filtration has been shown to reduce the formation of trihalomethanes (THMs) formation in drinking water ^[15, 16-19] and achieve a greater level of microorganism inactivation ^[20].

In this study, catalytic ceramic membrane filtration was compared to conventional polymeric membrane for water treatment. In a conventional polymeric membrane filtration plant, water passes through pretreatment, polymeric membrane filtration, disinfection, usually with chlorine as disinfectant, and then stored in tanks and distributed for use. Filtration service runs usually last 30-90 minutes (depend of feed water properties and flow rate), after which the membranes are cleaned by backwashing with water, and in some cases with water and air ^[17]. With hybrid catalytic ceramic membrane filtration involving ozonation, the source water flows through pretreatment, and ozone is injected at the membrane inlet. Ozone serves as disinfectant, and at the same time, reacts with organic matter in feed water so that fouling on membrane surface is controlled.

The objective of this study was to determine whether ceramic membrane combined ozonation has advantages in saving energy and reducing environmental impacts in water treatment application compared with conventional polymeric membrane filtration. Treatment specifications for hollow fiber (polymeric) membrane filtration were employed. Additionally, the identification of the most energy consumptive and least environmentally friendly aspects of the two processes can be used to guide future research efforts. Life cycle assessment (LCA) was used to assess the environmental impact of the two processes along with the energy consumption.

3.2 Experimental

3.2.1 Goal and scope definition

3.2.1.1 Goal

The goals of this study were to determine the cumulative energy demand, as well as environmental impact, of the hybrid manganese oxide coated catalytic ceramic membrane system (CC), and compare these results with that of a hollow fiber membrane (HF) filtration system. Calculations were performed assuming that both systems would be used for drinking water treatment plant over their entire life cycle. The results are used to make recommendations regarding future improvements for ceramic membrane, and to interpret whether there is a benefit of using catalytic ceramic membrane combined with ozonation vs hollow fiber membrane filtration.

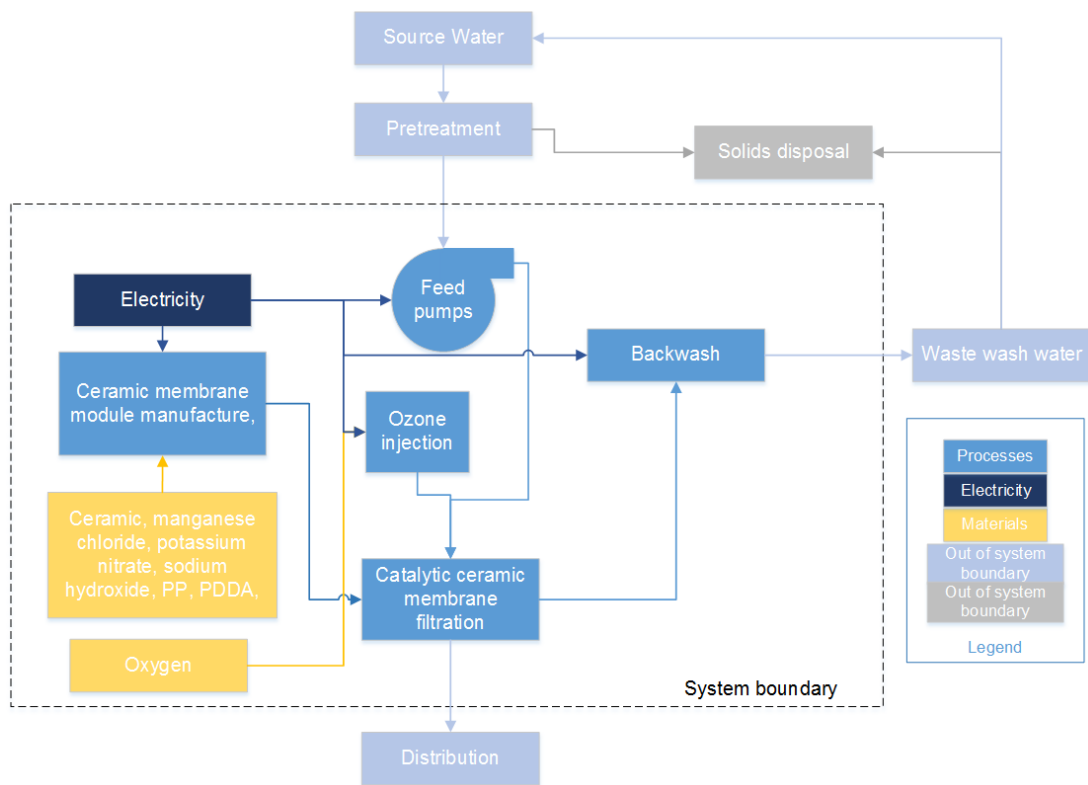
3. 2.1.2 Assumptions

The following assumptions were made for all scenarios:

- The source of the feed water is surface water. The quality of the source water is constant over the course of the system life.
- For the scenarios, treated water meets all regulatory requirements ^[21].
- The lifetimes of the treatment plants are 20 years.
- Hollow fiber membranes are replaced every 4 years, and ceramic membranes are typically reported to have a 20-year lifetime.
- For catalytic membrane, the calculations are based on laboratory data ^[14] and scaled to industrial-scale.
- Both membrane treatment processes would be installed at the same location.

3.2.1.3 System definition and boundaries

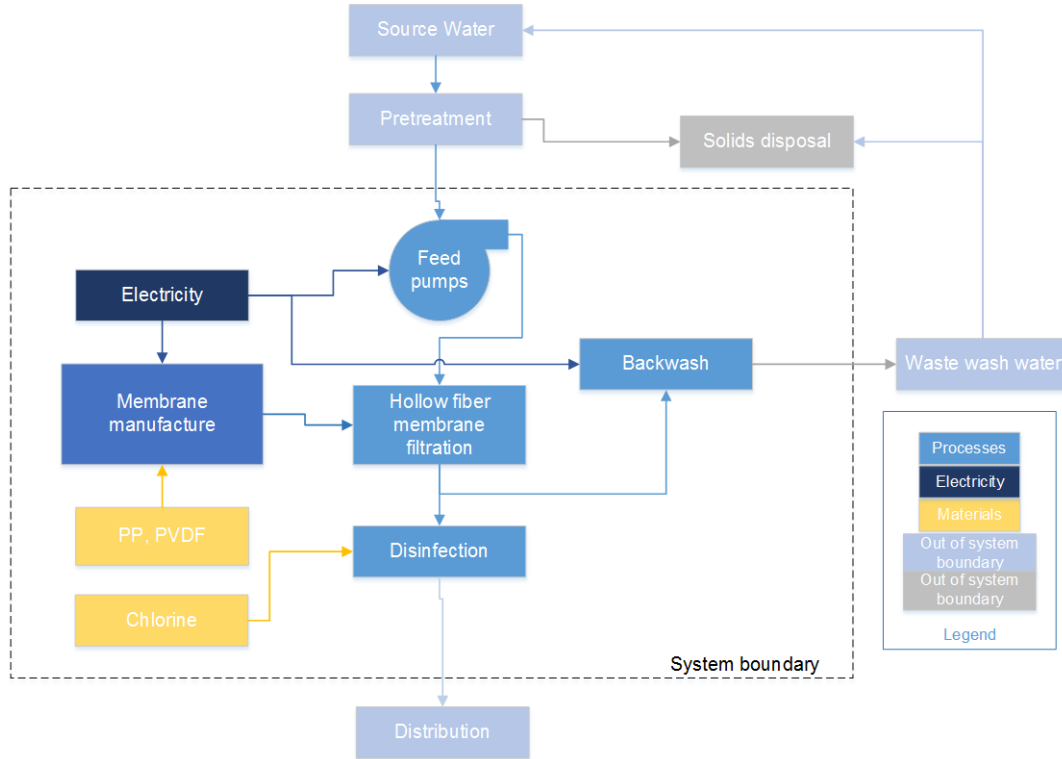
As figure 3.1 shows, the focused stages were the water treatment process involving membrane filtration as well as membrane module. The life cycle assessment was evaluated via four main categories: Feed water pressurization, disinfection/ozone injection, filter backwashing, and membrane manufacturing. Neither pre- nor post-treatment was considered.



(a)

Figure 3.1 System boundaries of the study in (a) catalytic ceramic ozonation membrane filtration processes and (b) hollow fiber membrane processes with chlorine as disinfectants

Figure 3.1 (cont'd)



(b)

Table 3.1 lists the main processes in the membrane filtration life cycle and materials/energy consumption. Maintenance and labor were not considered because of the uncertainty in costs and needs. As it was assumed that both treatment processes were installed at the same location in Michigan, US, transportation of materials was not considered. Feed pumps, feed piping, and ancillary equipment were not considered in the comparison. Neither were pretreatment, storage and distribution processes considered. The membrane filtration systems were assumed to more than 95% of recovery and minimal sludge production. As such, solids disposal was not considered in the system evaluation [22].

Table 3.1 Main processes in the membrane filtration life cycle and materials/energy consumption

Processes	CC	HF
Pressurization	Energy (electricity)	Energy (electricity)
Ozone injection (CC) / Disinfection (HF)	Oxygen, energy (electricity)	Chlorine
Backwash	Treated water, cleaning chemicals (sodium bisulfate, citric acid), energy (electricity)	Treated water, cleaning chemicals (sodium bisulfate, citric acid), energy (electricity)
Membrane Manufacture	Energy (electricity), ceramic, manganese chloride, ozone, potassium nitrate, Poly(diallyldimethylammonium chloride) (PDDA), sodium hydroxide	Energy (electricity), polypropylene, polyvinylidene fluoride

3.2.1.4 Functional Unit

In this study, a daily clean water production rate of 9,000,000 gallons per day (9 MGD) was used as the functional unit. This functional unit (FU) corresponded to a reference flow to which all flows of the system are related. The membrane manufacturing energy and materials consumption were distributed over the life time on a daily basis.

3.2.2 Data Collection

For catalytic ceramic membrane filtration, feed water was assumed to be pressurized throughout the treatment processes, and energy was provided by electricity. Energy consumption for pressurization was calculated from water flux, membrane filtration area, filtration rate, and transmembrane pressure, which were based on laboratory results and scaled up industrial data ^[14, 23]. Ozone injection rate was selected from former lab results ^[24] and scaled up with membrane surface area ratio to a full scale 9 MGD system (4.55×10^{-5} lbs/gal), and ozone was assumed to be generated from pure oxygen using the corona-discharge method. The injection amount was scaled up by membrane area ratio ^[14]. The chemicals used for backwashing were assumed to be the same for both ceramic and hollow fiber membrane; however the backwashing pressures were different and based on the literature ^[14, 22]. With ceramic membrane manufacturing, data obtained in our laboratory were scaled up to industrial scale ceramic membrane filtration ^[23, 25].

For hollow fiber membrane filtration, energy consumption for pressurization was also calculated from water flux and transmembrane pressure, which were based on treatment plant capacity and the literature ^[22]. The chlorine injection rate and dosage were also based on published data ^[22]. Backwash chemicals and amounts were based on an existing hollow fiber water treatment plant ^[26], and backwash pressure was obtained from literature ^[22]. Polypropylene (PP), polyvinylidene fluoride (PVDF), acrylonitrile butadiene styrene (ABS), polyurethane (PU) and energy are consumed during hollow fiber membrane manufacturing ^[27-30] and therefore, included in the analysis.

The life cycle assessment was analyzed by SimaPro (8.4.0.0, Pre Consultants, the Netherlands. 2018). SimaPro could help effectively apply life cycle assessment calculation, and measure the energy cost and environmental impacts across the entire processes. The electricity consumption for pumping, membranes manufacturing, ozone generation, backwash and other were determined using Michigan eGrid electricity (RFCM, 2010) and the USLCI inventory data base. Data for chemicals such as chlorine in disinfection process, oxygen for ozone generation, backwash chemicals, and materials for membrane manufacturing were obtained from Ecoinvent version 3.0.

3.2.3 Impact Assessment

Cumulative Energy Demand (CED) 1.09 was used to calculate the quantitative energy consumption, with the indicator of GJ and weighting factor of 1, by Ecoinvent version 3.0 in SimaPro 7 database. For assessing environmental impacts and ecotoxicity, TRACI 2.1 (US 2008) was used. TRACI is the midpoint oriented life cycle impact analysis (LCIA) methodology developed by the U.S. Environmental Protection Agency specifically for the US using input parameters consistent with US locations ^[31]. Environmental impacts, including ozone depletion, climate change, smog, acidification, eutrophication, carcinogenic, non-carcinogenic, respiratory effects, ecotoxicity, fossil fuel depletion, were normalized and evaluated for both ceramic membrane and hollow fiber membrane filtration processes. Each characterized environmental impact was analyzed by its units, and the normalized impact was calculated by characterized value times a given weight. Both normalized and characterized environmental impacts were compared between catalytic membrane and hollow fiber membrane filtration systems. To simplify and clarify

the study, the materials that represent less than 0.1% of the functional unit are not shown in the results.

3.3 Results and discussion

3.3.1 Catalytic ceramic membrane with ozonation energy and environmental impacts analysis

For the catalytic ceramic membrane filtration system, pressurization consumed the most of the energy, as Figure 3.2 shows. On the other hand, ozone generation resulted in almost one-third of the energy consumed. This is not surprising as ozone generation by corona discharge, the common method of producing ozone, consumes ~ 7 kW·h/kWh electricity per kg of ozone generated [24, 32].

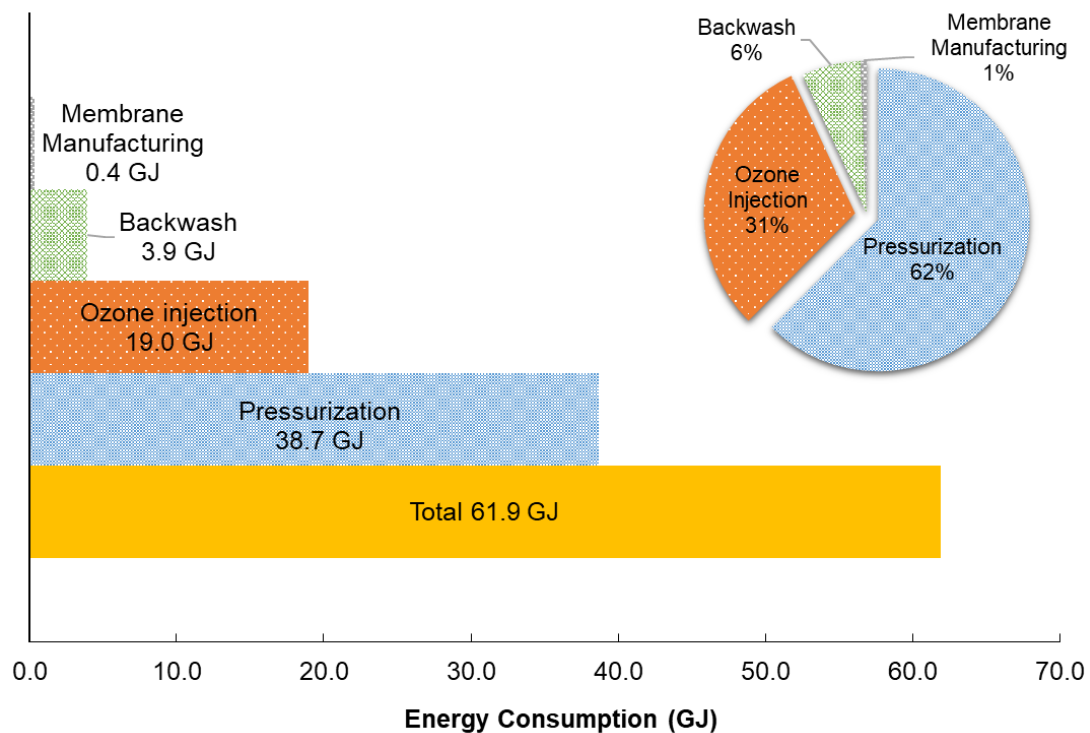


Figure 3.2 Embodied energy consumption of total and different processes in catalytic ceramic membrane

Figure 3.3 illustrates the environmental impacts of catalytic ceramic membrane filtration. The data are normalized to daily water production. Normalization results came from transforming by the selected reference values or information for each impact. Higher normalization results have greater impacts than lower ones [33]. They present that acidification should be paid attention in the desired processes as it was the highest normalized environmental impact. Carcinogenicity and ecotoxicity of pollutants generated, along with that due to smog, and global warming were also significant. Pressurization contributed 49% of all the environmental impacts, and ozone injection resulted in 43% of the impacts. The environmental impacts of the ozone injection process were due to carcinogenicity and ecotoxicity of pollutants generated.

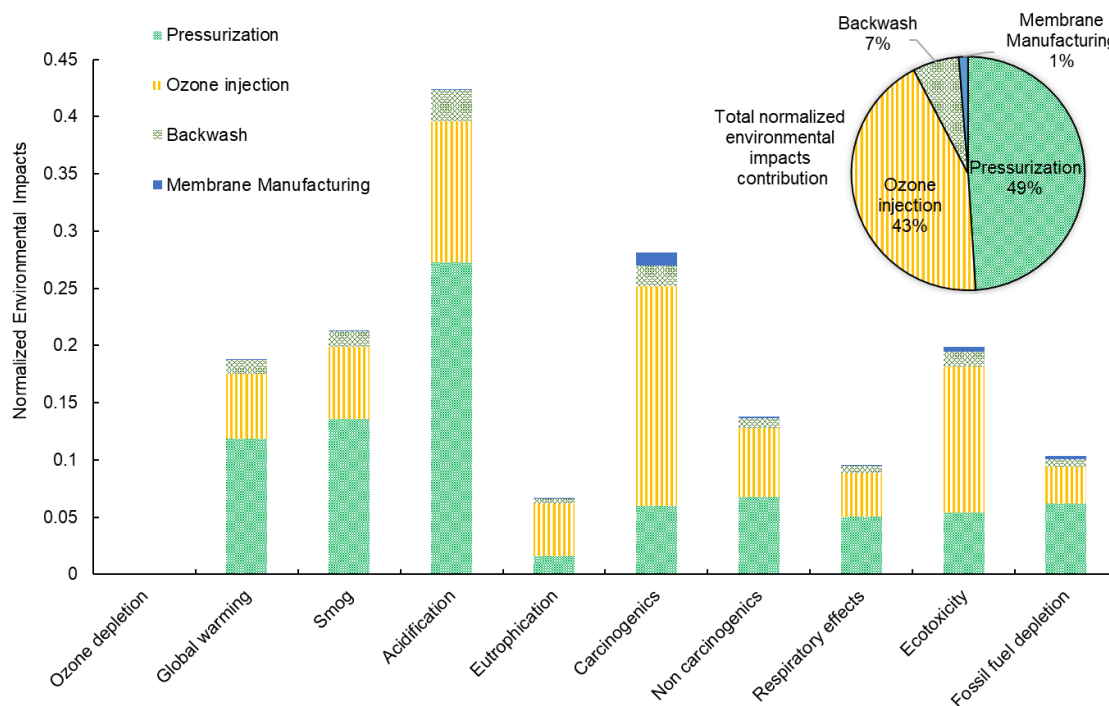


Figure 3.3 Environmental impacts normalization results for catalytic ceramic membrane filtration processes

As discussed in the introduction, ozone can react with natural organic matter in water and that collected at the membrane surface, thus, effectively controlling membrane fouling and reducing the costs of membrane pressurization [16, 34]. Wang et al. demonstrated that with hybrid ozone-membrane filtration, increasing the ozone injection rate resulted in a decrease in the transmembrane pressure, thereby reducing the energy required for pressurization and also extending the operation period and decreasing backwash times [14]. Although higher ozone injection rate has proved to effectively control membrane fouling, the total energy cost increased by 17.5% (10.85 GJ) when the ozone injection rate was doubled. As Figure 3.4 shows, when ozone injection rate was doubled, the energy for pressurization decreased by 19.8% (6.4 GJ), which is consistent with previous work showing that fouling can be controlled using ozone injection [7-9,10]. However, as ozone generation consumes a significant amount of energy, the energy saved during pressurization and backwash was not sufficient to offset the increased energy consumption from ozone production. This underscores the importance of operating the hybrid system at the lowest possible ozone injection rate and optimizing ozone mass transfer so that ozone is not wasted in the system.

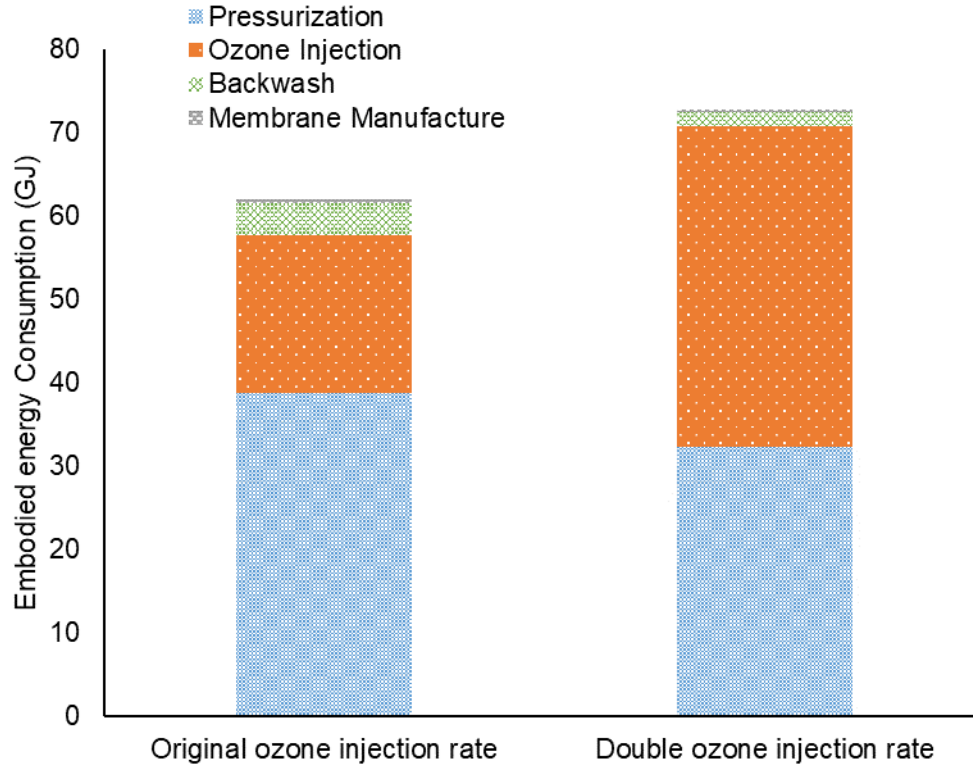


Figure 3.4 Comparison of energy consumption with high ozone injection rate in catalytic ceramic membrane filtration system.

3.3.2 Comparison between catalytic ceramic membrane and hollow fiber membrane in energy consumption and environmental impacts

At the conditions studied, energy consumption for pressurization is 25% lower for catalytic ceramic membrane filtration process as compared to that for hollow fiber membrane filtration. As is apparent in Figure 3.5, the largest fraction of energy consumed during operation is for membrane pressurization. This underscores the importance of operating a system at the lowest possible pressure required to achieve the desired treatment. When comparing the two processes, energy consumption for backwashing and membrane manufacturing is 15% and 30% lower, respectively, for hybrid membrane filter vs hollow

fiber membrane filtration. The energy consumed for manufacturing of membranes is lower with CC than with HF. As a result of the large amount of energy consumed in ozone generation, the total energy consumption for catalytic membrane filtration is 7.6% higher than that for hollow fiber membrane filtration. Improvements in energy- and mass transfer efficiency of ozone generation is critical to the reduction in energy consumption for CC applications. Electricity contributed to 95% of embodied energy usage for both treatment processes.

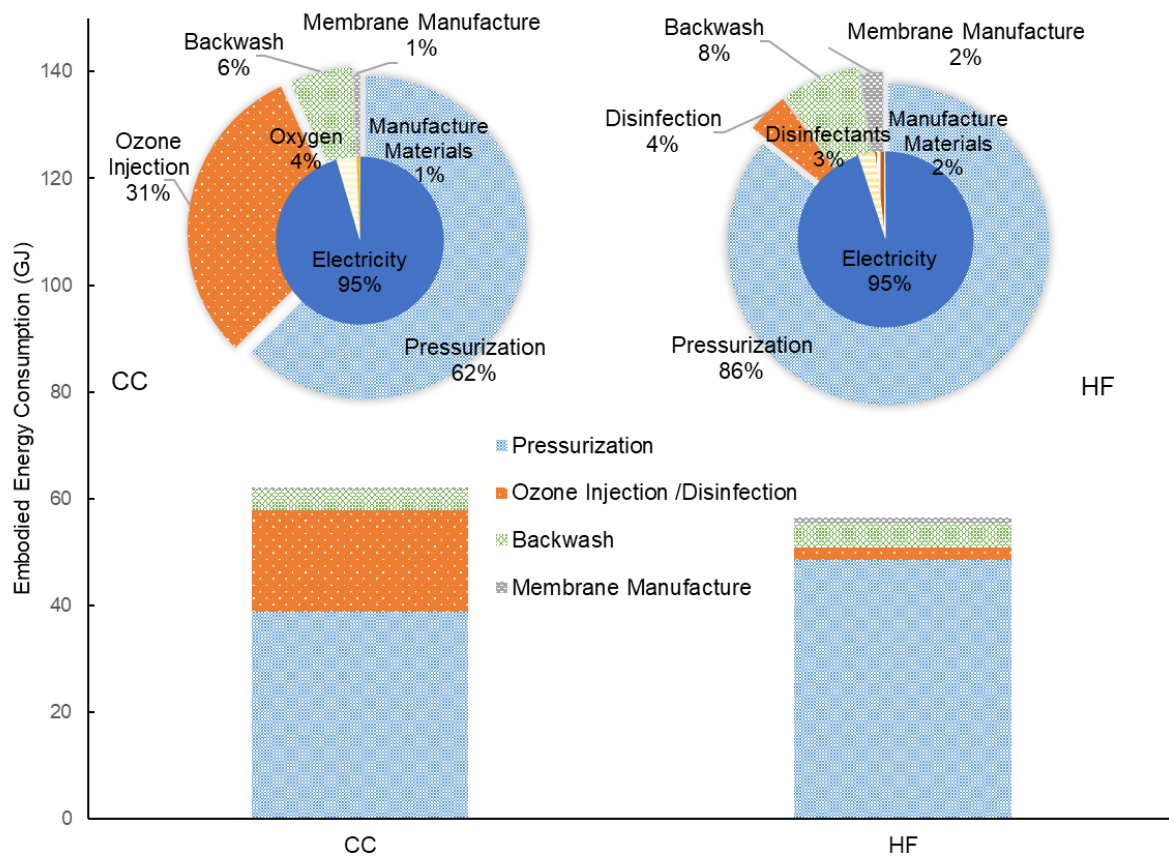


Figure 3.5 Embodied energy consumption in catalytic ceramic membrane (CC) and hollow fiber membrane (HF) filtration in water treatment application

In terms of environmental impacts, CC had a slightly lower total impacts. It had lower

environmental impacts on ozone depletion and carcinogenicity, non-carcinogenics, and ecotoxicity of pollutants, as shown in Figure 3.6 and Table 3.2. Based on published literature [19, 35-36], CC can be used to minimize the formation of carcinogenic by-products such as THMs and bromate. Ozonation ceramic membrane filtration was also shown to effectively inactivate *E. coli*, eliminating the need for disinfection of backwash water, thereby further reducing its environmental impacts compared to polymeric membrane filtration. Although energy consumption for CC was greater than for HF, CC had a lower environmental impact because of more environmental-friendly membrane manufacturing processes, and the lower energy required for pressurization.

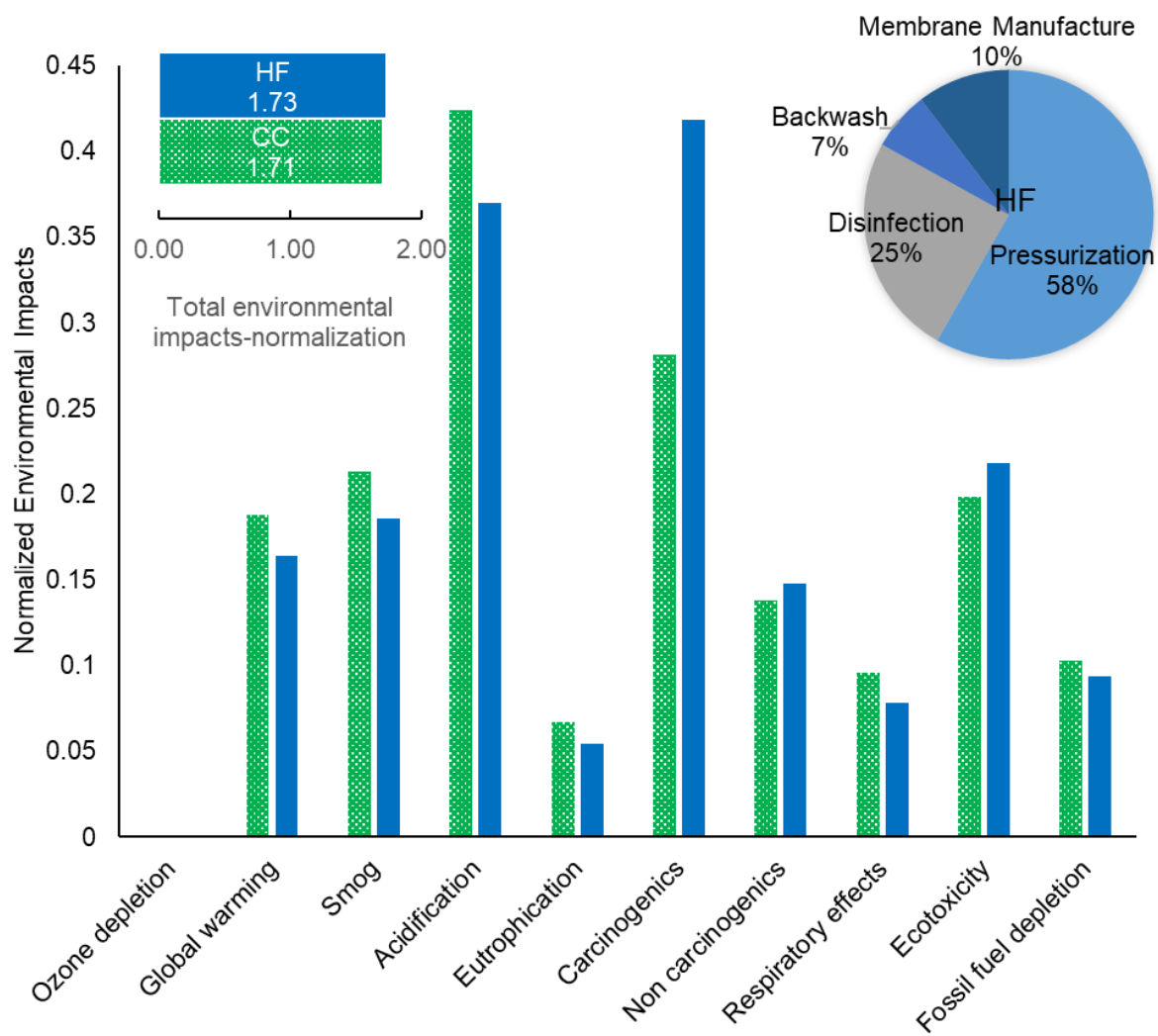


Figure 3.6. Comparison of environmental impacts normalization results for catalytic ceramic membrane (CC) and hollow fiber membrane (HF) filtration processes with HF impacts processes percentage

Table 3.2 Characterized environmental impacts in catalytic membrane (CC) and hollow fiber (HF) membrane filtration processes

Impact category	Unit	CC	HF
Ozone depletion	kg CFC-11 eq	1.40×10^{-5}	9.18×10^{-5}
Global warming	kg CO ₂ eq	4550	3960
Smog	kg O ₃ eq	296	259
Acidification	kg SO ₂ eq	38.5	33.6
Eutrophication	kg N eq	1.44	1.18
Carcinogenics	CTUh	1.48×10^{-5}	2.20×10^{-5}
Non carcinogenics	CTUh	1.45×10^{-4}	1.55×10^{-4}
Respiratory effects	kg PM _{2.5} eq	2.32	1.90
Ecotoxicity	CTUe	2200	2410
Fossil fuel depletion	MJ surplus	1940	1770

3.4 Conclusions

In this study, LCA was conducted to assess the energy consumption and environmental impacts of catalytic ceramic membrane with ozonation filtration at the industrial scale, and the results were compared to that for hollow fiber membrane filtration for water treatment. The results suggest that:

- For catalytic ceramic membrane filtration, pressurization resulted in the majority of energy consumed (62%). Energy consumption for pressurization plus ozone

generation consumed 93% of total energy input.

- Acidification, carcinogenicity and ecotoxicity of pollutants, smog, and climate change in catalytic ceramic membrane filtration processes had higher environmental impacts in normalization. Ozone injection resulted in 43% of environmental impacts while pressurization with 49%.
- Doubling the ozone injection rate resulted in a 17.5% increase in the energy consumption for catalytic ceramic membrane filtration. Although the energy for pressurization and backwash were reduced, ozone generation also consumed significant amount of energy contributed in higher energy consumption.
- Catalytic ceramic membrane filtration resulted in less energy consumption of pressurization and backwashing as compared with hollow fiber membrane filtration.
- Catalytic ceramic membrane filtration had a slightly lower environmental impacts than hollow fiber membrane filtration.
- Energy consumption for ozone generation underscores the need for research to develop more efficient methods to generate ozone and to optimize mass transfer. Alternatively, alternative and less energy consumptive methods to reduce membrane fouling would less both energy consumption and environmental impacts of catalytic ceramic membrane filtration, making it clearly favorable over polymeric membrane filtration.

APPENDIX

APPENDIX

Supporting Information

Energy consumption and environmental impact analysis of ozonation catalytic membrane filtration system and comparison with hollow fiber membrane in water treatment application

Hollow fiber membrane inventory analysis

Process Diagram

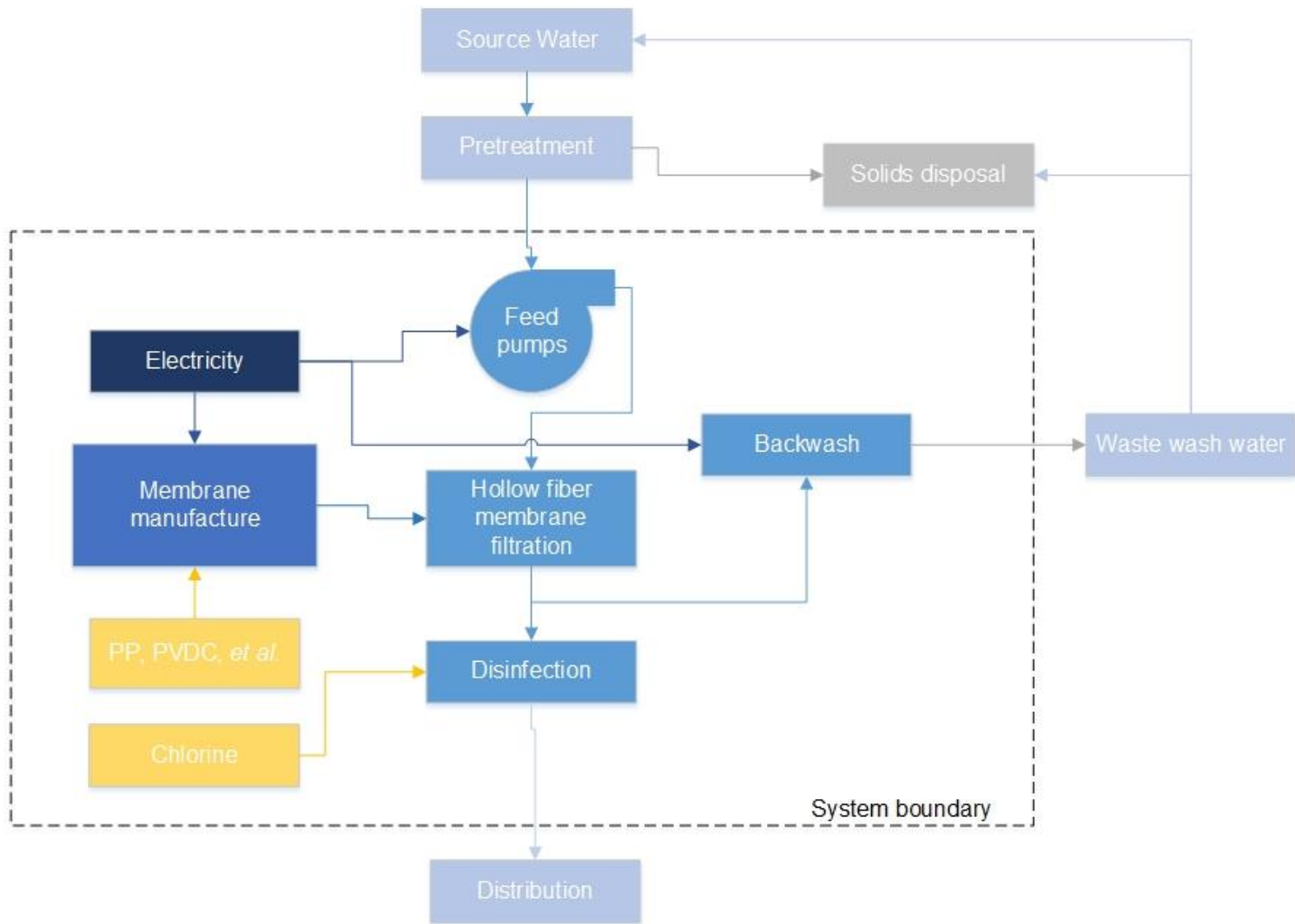


Figure 3.A.1. System boundaries of hollow fiber membrane processes with chlorine as disinfectants

Overall process

Output:

Flow	Amount	Range	Unit	Description
Hollow fiber membrane water treatment clean water production	9,000,000	8,000,000 – 10,000,000	gal	Assumed daily water production for a town with about 100,000 people. Each person uses about 80-100 gallons of water per day ^[1] .

Input: (Daily input)

Flow	Quantity	Range	Unit	Description
Pressurization	9,000,000		gal	Pressurization throughout the processes
Membrane cartridges	1.315		items	Total 1920 membrane cartridges ^[2] in hollow fiber membrane treatment plant. Treatment plant with 20 years lifetime. Cartridge would be replaced every 4 years.
Disinfection	9,000,000		gal	All water are going to be disinfected
Backwash	351,000		gal	3.9% of total water flow consumed during backwashing ^[3] . $9000000 * 3.9\% = 35100$

(A) Pressurization

Output:

Flow	Amount	Unit	Description
Pressurization	1	gal	

Input:

Flow	Amount	Unit	Description
Electricity at eGrid, RFCM.	4.2069×10^{-4}	kwh	Energy cost in pressurization could be calculated from water flow rate and transmembrane pressure ^{(a) (b) (c)} [3-6]

(a) Flux check

Based on 9 MPG daily water production and hollow fiber membrane water flux capacity, 1720 cartridges, each contained 7400 fibers can achieve the daily water production in 24 hours (one day).

Average membrane filtration rate:

$$9 \text{ MPG} = 34068.7 \text{ m}^3/\text{day} = 1419.529 \text{ m}^3/\text{h}$$

Total cartridge number = 1920

Each cartridge filtration rate $q = (1419.529 \text{ m}^3/\text{h}) \div 1920 = 0.7393 \text{ m}^3/\text{h}$

Effective areas = $7400 \times 0.00102 \text{ m}^2 = 7.523 \text{ m}^2$ [4] [5]

Permeate flux = $(0.7393 \text{ m}^3/\text{h}) \div (7.523 \text{ m}^2) = 0.09828 \text{ m/h}$

Within the range of $q = 0.03 - 0.17 \text{ m/h}$ [3], which is acceptable

(b) Transmembrane pressure for 5 kda (same grain size as ceramic membrane)

TMP = 3.0 bar = 300 kPa = $3 \times 10^5 \text{ N/m}^2$ [5, 6]

(c) Energy calculation

Assume pump energy efficacy $\eta = 75\%$ (same for ceramic membrane pressurization)

$Ph = q \cdot \text{TMP} / \eta = 0.7393 \times (3 \times 10^5) / 0.75 = 82.1625 \text{ Watt} = 0.0821625 \text{ kW}$

In which, q - flow in m^3/h , TMP - transmembrane pressure, pa, and Ph - power pumping water, kW.

So the average rate power transfer of each cartridge is 0.0821625 kW.

Filtration time for 1 gal of water: $t = (3.785 \times 10^{-3} \text{ m}^3) / (0.7393 \text{ m}^3/\text{h}) = 5.1202 \times 10^{-3} \text{ h}$

for every gal water, energy consumption is $0.0821625 \text{ kW} \times 5.1265 \times 10^{-3} \text{ h} = 4.2069 \times 10^{-4} \text{ kW} \cdot \text{h}$

(B) Membrane cartridge

Output:

Flow	Amount	Unit	Description
Membrane cartridges	1	item	

Input:

Flow	Amount	Unit	Description
Electricity at eGrid, RFCM	50	Wh	Estimated electricity cost in manufacturing the cartridge. Estimated power of manufacturing machines 500 w with 1 min producing 1 cartridge unit. (similar estimation in ceramic membrane supporting)
Membrane fibers	7400	items	1920 membrane cartridges, 7400 membrane fibers. Cartridges were replaced every 4 years, and membrane fibers were also replaced every 4 years ^[2] .
100% polypropylene media	6.923	kg	Estimation of materials input in one membrane cartridge: each cartridge is 764 mm long with material density of 946 kg/m ³ , ID (based on 7400 fibers and 0.7-0.8 mm fiber diameter) = 70 mm, OD = 130 mm ^[7] .

(C) Membrane fibers

Output:

Flow	Amount	Unit	Description
Membrane fiber	1	item	

Input:

Flow	Amount	Unit	Description
Electricity, at eGrid, RFCM	1	Wh	Estimated electricity cost in manufacturing the cartridge. Estimated power of manufacturing machines 500 w with 5 seconds producing 1 cartridge unit.
PVDF	0.41546	g	For each hollow fiber, OD = 700-800 um, ID = 400-500 um, length of membrane ~760 mm, so the volume of each hollow fiber is $2.334 \times 10^{-7} \text{ m}^3$, and density of PVDF is 1.78 g/cm^3 , so weight is 0.41546 g ^[8] ^[9] .

(D) Disinfection

Output:

Flow	Amount	Unit	Description
Disinfection	1	gal	

Input:

Flow	Amount	Unit	Description
Chlorine	13.154	mg	Average typical application dose for chlorine disinfection is 29 lb free chlorine/ MG water ^[10] ^[11] $29 \text{ lb} \times (1 \text{ mg}/2.2046 \times 10^{-6} \text{ lb}) \div 1000000 \text{ gallons water} = 13.154 \text{ mg chlorine/gal water.}$

(E) Backwash

Output:

Flow	Amount	Unit	Description
Backwash	1	gal	

Input:

Flow	Amount	Unit	Description
Hollow fiber membrane water treatment clean water production	1	gal	Use treated water for membrane backwash.
Sodium bisulfate	2.125	ug	
Citric Acid	2.62	ug	[10]
Sulfuric acid	0.125	ug	
Electricity, at eGrid, RFCM	5.4736×10^{-4}	kWh	For each membrane module, assumed average backwash $TMP_{wash} = 1.3TMP_{operation}$, ^[3] and backwash $Q = 1.4786 \text{ m}^3/\text{h}$ ^[3], pump energy efficiency $\eta = 75\%$ $Ph = q \cdot TMP / \eta = 0.213564 \text{ kW}$, for every gal water, calculated energy consumption is $5.4736 \times 10^{-4} \text{ kW} \cdot \text{h}$

Catalytic membrane with ozonation inventory analysis

Process Diagram

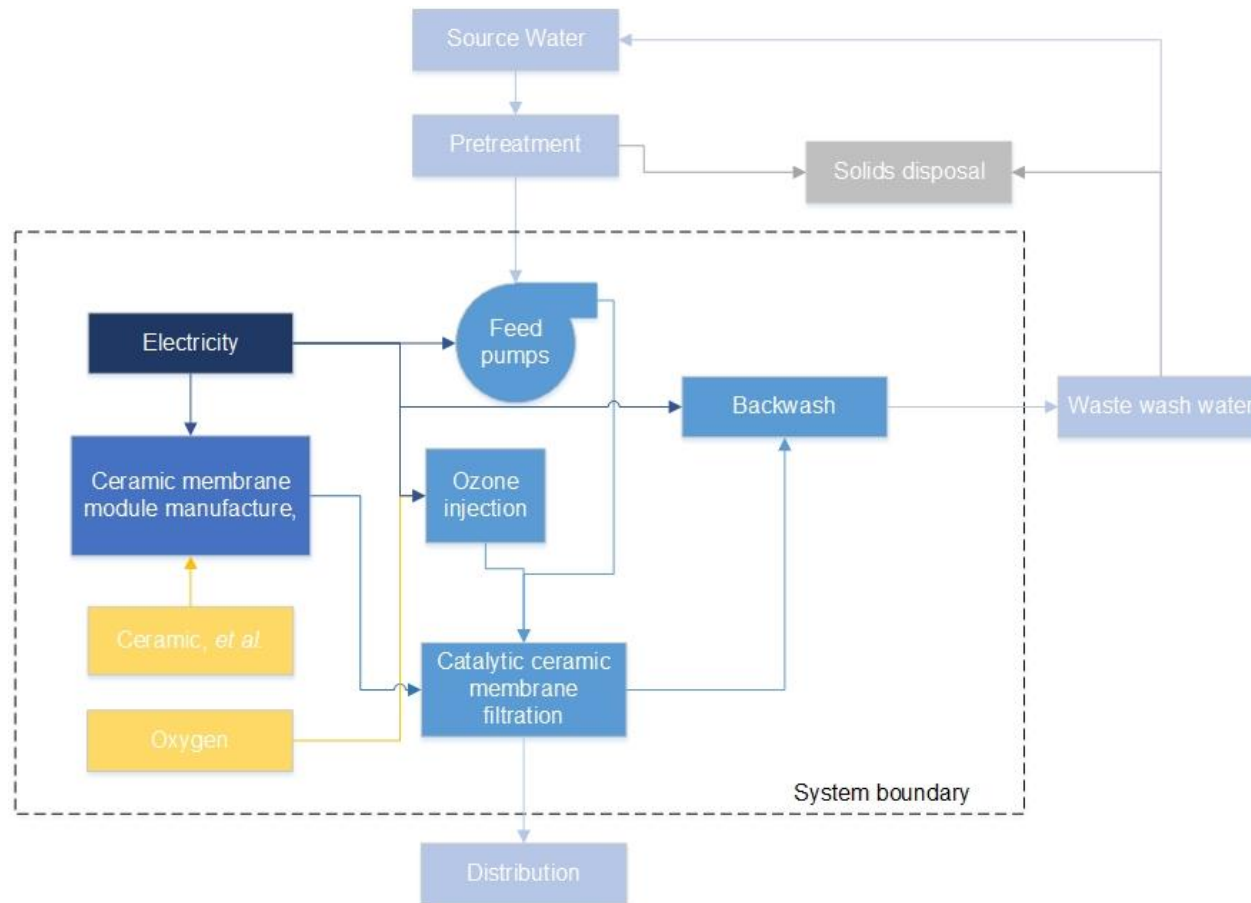


Figure 3.A.2. System boundaries of the study in catalytic ceramic ozonation membrane filtration processes

Overall process

Output:

Flow	Amount	Range	Unit	Description
Catalytic ceramic membrane water treatment clean water production	9,000,000	8,000,000 – 10,000,000	gal	Same assumption as hollow fiber membrane: daily water production for a town with about 100,000 people. Each person uses about 80-100 gallons of water per day ^[1] .

Input:

Process	Amount	Unit	Description
Pressurization	9000000	gal	Assumed daily water production amount
Ozone injection	185.9	kg	With 5 ug/s ozone injection, scaled up with membrane surface area scaled up ratio (131.9 cm ² vs. 5 m ²). ^{[13] [14]}
Backwash	315900	gal	Catalytic ceramic membrane can filtrate water for 100 min between backwashes instead of 90 min in hollow fiber membrane, So 3.9%*(9/10) = 3.51%. 9000000*3.51% =315900. ^{[3] [13]}
Membrane Manufacture	0.311297	item	Membrane water filtration rate = 1.25 m ³ /h, 9 MGD, 365 days, last 10 years for ceramic membrane, Replace every 10 years. Lab results scaled up to industrial scale. ^{[13] [14]}

(A) Pressurization

Output:

Flow	Amount	Unit	Description
Pressurization	1	gal	

Input:

Flow	Amount	Unit	Description
Electricity at eGrid, RFCM	3.50×10^{-4}	kW·h	Water flux = 0.25 m ² /h, filtration area = 5 m ² , filtration rate Q = 1.25 m ³ /h, average TMP during treatment = 2.4621 bar, pump efficacy = 75% (same as hollow fiber membrane), Ph = QTMP/efficiency. When use the same pore size membrane, transmembrane pressure at the same flux will not change much after scaled up. ^[13] ^[14]

(B) Ceramic Membrane array

Output:

Flow	Amount	Unit	Description
Membrane cartridges	1	item	

Input:

Flow	Amount	Unit	Description
Electricity, at eGrid, RFCM	50	Wh	Estimated electricity to manufacture the cartridge. (Similar as hollow fiber membrane)
Catalytic manganese oxide coated ceramic membrane	1	items	1 membrane array contain 1 membrane unit, but membrane need to be changed every 10 years
100% polypropylene media	13.58	kg	Use the same membrane supporting material as hollow fiber membrane. Length: 864 mm. Out Diameter: 203 mm, inner diameter: 143 mm, density: 946 kg/m ³ . [7]

(C) Ceramic membrane unit

Output:

Flow	Amount	Unit	Description
Catalytic ceramic membrane unit	1	item	

Input:

Flow	Amount	Unit	Description
Electricity, at eGrid, RFCM	1540	Wh	For every 20 membranes: 20 W·h (centrifuged) + 29 W·h (sonic) +1000 W·h (500 Celsius 45 min) + 50 W·h ceramic membrane manufacture (1100 W·h every 20 membrane). Scale up ratio (490.87 cm ³ vs. 1.37×10 ⁷ ml): 28 ^[13] ^[14] . Energy cost: 55*28 =1540 W·h. ^[15] ^[13]
Ceramic	5.582	kg	Each ceramic membrane weighs 0.2 kg, times volume ratio
Manganese chloride	9.55	g	Solution to synthesis catalytic membrane, lab value times surface ratio (131.9 cm ² vs. 5 m ²) ^[13] ^[14] .
Ozone	538	g	
KNO3	1.9159	g	
Poly(diallyldimethylammonium chloride) (PDDA)	379	g	
NaOH	151.6	g	

(D) Ozone injection

Output:

Flow	Amount	Unit	Description
Ozone injection	1	kg	

Input:

Flow	Amount	Unit	Description
Oxygen	1	kg	Corona-discharge method. $3\text{O}_2 \leftrightarrow 2\text{O}_3$. ^[16]
Electricity	7	kW·h	Energy consumption is less than 7 kW per kilo ozone produced. ^{[16] [17]}

(E) Backwash

Output:

Flow	Amount	Unit	Description
Backwash	1	gal	

Input:

Flow	Amount	Unit	Description
Ceramic membrane water treatment clean water production	1	gal	Same as hollow fiber membrane filtration.
Sodium bisulfate	2.125	ug	
Citric Acid	2.62	ug	
Sulfuric acid	0.125	ug	
Electricity, at eGrid, RFCM	3.7345×10^{-4}	kWh	Pump energy efficiency $\eta = 75\%$ $Ph = Q_{backwash} \cdot TMP_{wash} / \eta = 246.67$ watt, for every gal water, calculated energy consumption is 3.7345×10^{-4} kW·h [13] [14]

Higher ozonation - catalytic membrane with ozonation inventory analysis

Overall process

Output:

Flow	Amount	Range	Unit	Description
Catalytic ceramic membrane water treatment clean water production	9,000,000	8,000,000 – 10,000,000	gal	Same assumption as hollow fiber membrane: daily water production for a town with about 100,000 people. Each person uses about 80-100 gallons of water per day ^[1] .

Input:

Process	Amount	Unit	Description
Pressurization	9000000	gal	Assumed daily water production amount
Ozone injection	371.87	kg	With 10 ug/s ozone injection, scaled up with membrane surface area scaled up ratio (131.9 cm ² vs. 5 m ²). ^[13] ^[14]
Backwash	315900	gal	Catalytic ceramic membrane can filtrate water for 100 min between backwashes instead of 90 min in hollow fiber membrane, So 3.9%*(9/10) = 3.51%. 9000000*3.51% =315900. ^[3] ^[13]
Membrane Manufacture	0.311297	item	Membrane water filtration rate = 1.25 m ³ /h, 9 MGD, 365 days, last 10 years for ceramic membrane, Replace every 10 years. Lab results scaled up to industrial scale. ^[13] ^[14]

(A) Pressurization

Output:

Flow	Amount	Unit	Description
Pressurization	1	gal	

Input:

Flow	Amount	Unit	Description
Electricity at eGrid, RFCM	2.877×10^{-4}	kW·h	Water flux = 0.25 m ² /h, filtration area = 5 m ² , filtration rate Q = 1.25 m ³ /h, average TMP during treatment = 2.0515 bar, pump efficacy = 75% (same as hollow fiber membrane), Ph = QTMP/efficiency. When use the same pore size membrane, transmembrane pressure at the same flux will not change much after scaled up. ^[13] ^[14]

(B) Ceramic Membrane array

Output:

Flow	Amount	Unit	Description
Membrane cartridges	1	item	

Input:

Flow	Amount	Unit	Description
Electricity, at eGrid, RFCM	50	Wh	Estimated electricity to manufacture the cartridge. (Similar as hollow fiber membrane)
Catalytic manganese oxide coated ceramic membrane	1	items	1 membrane array contain 1 membrane unit, but membrane need to be changed every 10 years
100% polypropylene media	13.58	kg	Use the same membrane supporting material as hollow fiber membrane. Length: 864 mm. Out Diameter: 203 mm, inner diameter: 143 mm, density: 946 kg/m ³ . ^[7]

(C) Ceramic membrane unit

Output:

Flow	Amount	Unit	Description
Catalytic ceramic membrane unit	1	item	

Input:

Flow	Amount	Unit	Description
Electricity, at eGrid, RFCM	1540	Wh	For every 20 membranes: 20 W·h (centrifuged) + 29 W·h (sonic) +1000 W·h (500 Celsius 45 min) + 50 W·h ceramic membrane manufacture (1100 W·h every 20 membrane). Scale up ratio (490.87 cm ³ vs. 1.37×10 ⁷ ml): 28 ^[13] ^[14] . Energy cost: 55*28 =1540 W·h. ^[15] ^[13]
Ceramic	5.582	kg	Each ceramic membrane weighs 0.2 kg, times volume ratio
Manganese chloride	9.55	g	Solution to synthesis catalytic membrane, lab value times surface ratio (131.9 cm ² vs. 5 m ²) ^[13] ^[14] .
Ozone	538	g	
KNO ₃	1.9159	g	
Poly(diallyldimethyl ammonium chloride) (PDDA)	379	g	
NaOH	151.6	g	

(D) Ozone injection

Output:

Flow	Amount	Unit	Description
Ozone injection	1	kg	

Input:

Flow	Amount	Unit	Description
Oxygen	1	kg	Corona-discharge method. $3\text{O}_2 \leftrightarrow 2\text{O}_3$. [16]
Electricity	7	kW·h	Energy consumption is less than 7 kW per kilo ozone produced. [16]

(E) Backwash

Output:

Flow	Amount	Unit	Description
Backwash	1	gal	

Input:

Flow	Amount	Unit	Description
Ceramic membrane water treatment clean water production	1	gal	Pump energy efficiency $\eta = 75\%$ $Ph = Q_{\text{backwash}} \cdot \text{TMP}_{\text{wash}} / \eta$, for every gal water, calculated energy consumption is $3.109 \times 10^{-4} \text{ kW}\cdot\text{h}$ [13] [14]
Sodium bisulfate	2.125	ug	
Citric Acid	2.62	ug	
Sulfuric acid	0.125	ug	
Electricity, at eGrid, RFCM	3.109×10^{-4}	kWh	

Results: Catalytic ceramic membrane with ozonation energy network

Table 3.A.1 Catalytic ceramic membrane energy network

Inflows (4)	Quantity	Unit
Total	61.9	GJ
Pressurization	38.7	GJ
Ozone Injection	19	GJ
Backwash	3.91	GJ
Membrane Manufacturing	0.38	GJ

Table 3.A.2 Process contribution in energy consumption

Process	Unit	Total	Catalytic pressurization	Catalytic membrane array	Ozone injection	Ozone backwash
Remaining processes	MJ	79.30	30.47	32.07	12.59	4.17
Bituminous coal	MJ	49468.08	32758.82	5.14	13535.43	3168.68
Crude oil	MJ	1528.35	1012.11	0.16	418.19	97.90
Natural gas	MJ	7363.65	4876.37	0.77	2014.84	471.68
Oxygen	MJ	2368.43	0	0	2210.92	157.51
Polypropylene	MJ	313.41	0	302.63	0	10.78

Results: Catalytic ceramic membrane with ozonation environmental impacts score

Table 3.A.3 Catalytic ceramic membrane environmental impacts - normalization

Impact category	Total	Impact category	Pressurization	Ozone injection	Backwash	Membrane Manufacturing
Ozone depletion	8.70E-05	Ozone depletion	3.03E-07	7.85E-05	5.71E-06	2.57E-06
Global warming	1.88E-01	Global warming	1.18E-01	5.71E-02	1.20E-02	4.83E-04
Smog	2.13E-01	Smog	1.35E-01	6.33E-02	1.36E-02	3.99E-04
Acidification	4.24E-01	Acidification	2.73E-01	1.24E-01	2.72E-02	5.02E-04
Eutrophication	6.67E-02	Eutrophication	1.63E-02	4.53E-02	4.35E-03	7.72E-04
Carcinogenics	2.81E-01	Carcinogenics	5.98E-02	1.92E-01	1.81E-02	1.10E-02
Non carcinogenics	1.38E-01	Non carcinogenics	6.78E-02	5.98E-02	8.86E-03	1.23E-03
Respiratory effects	9.56E-02	Respiratory effects	5.06E-02	3.81E-02	6.14E-03	8.31E-04
Ecotoxicity	1.99E-01	Ecotoxicity	5.38E-02	1.28E-01	1.29E-02	4.17E-03
Fossil fuel depletion	1.03E-01	Fossil fuel depletion	6.16E-02	3.25E-02	6.55E-03	2.45E-03

Results: Comparison of catalytic membrane with higher ozonation energy inputs

Table 3.A.4 Catalytic ceramic membrane environmental impacts - normalization

Processes	Unit	Original ozone injection rate	Double ozone injection rate
Pressurization	GJ	38.7	32.3
Ozone Injection	GJ	19	38.5
Backwash	GJ	3.91	1.65
Membrane Manufacture	GJ	0.378	0.383

Results: Comparison of catalytic membrane with ozonation and hollow fiber membrane energy inputs

Table 3.A.5 Comparison of catalytic membrane and hollow fiber membrane energy network

Processes	Unit	Ceramic membrane	Hollow Fiber membrane
Pressurization	GJ	38.7	48.4
Ozone Injection /Disinfection	GJ	19	2.34
Backwash	GJ	3.91	4.48
Membrane Manufacture	GJ	0.378	1.24

Results: Comparison of catalytic membrane and hollow fiber membrane environmental impacts

Table 3.A.6 Comparison of catalytic membrane and hollow fiber membrane environmental impacts - characterization

Impact category	Unit	Catalytic Ceramic membrane	Hollow Fiber membrane
Ozone depletion	kg CFC-11 eq	1.40E-05	9.18E-05
Global warming	kg CO2 eq	4550.55	3964.06
Smog	kg O3 eq	296.17	258.65
Acidification	kg SO2 eq	38.50	33.60
Eutrophication	kg N eq	1.44	1.18
Carcinogenics	CTUh	1.48E-05	2.20E-05
Non carcinogenics	CTUh	1.45E-04	1.55E-04
Respiratory effects	kg PM2.5 eq	2.32	1.90
Ecotoxicity	CTUe	2198.94	2413.77
Fossil fuel depletion	MJ surplus	1940.28	1767.86

Table 3.A.7 Comparison of catalytic membrane and hollow fiber membrane environmental impacts - normalization

Impact category	Catalytic Ceramic membrane	Hollow Fiber Membrane
Ozone depletion	8.70E-05	5.69E-04
Global warming	1.88E-01	1.64E-01
Smog	2.13E-01	1.86E-01
Acidification	4.24E-01	3.70E-01
Eutrophication	6.67E-02	5.45E-02
Carcinogenics	2.81E-01	4.18E-01
Non carcinogenics	1.38E-01	1.48E-01
Respiratory effects	9.56E-02	7.83E-02
Ecotoxicity	1.99E-01	2.18E-01
Fossil fuel depletion	1.03E-01	9.39E-02

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CHAPTER FOUR

Effects of methylene blue photocatalytic degradation under visible light

irradiation by ZnFe_2O_4 , NiFe_2O_4 and CdS

Abstract

Conventional biological and physical treatment technologies cannot effectively degrade many recalcitrant contaminants in water. Research has been conducted to develop highly effective photocatalysts for the degradation of such recalcitrant contaminants. This study synthesized and evaluated at the characteristics of three photocatalysts: CdS, ZnFe₂O₄, and NiFe₂O₄ and compared their photodegradation ability using methylene blue as a model contaminant. The results showed that methylene blue could be successfully degraded by all three catalysts under visible light at room temperature, and the order of photocatalytic efficacies was CdS > NiFe₂O₄ ≥ ZnFe₂O₄. CdS had the widest absorption range, compared to NiFe₂O₄ and ZnFe₂O₄. The absorption range of photocatalysts, initial dye concentrations, amount of photocatalysts addition, and photoreactor conditions affected methylene blue removal efficacy.

4.1 Introduction

Up to 20% of the total mass of dyes produced worldwide is released in the textile effluents [1]. Organic dyes such as methylene blue contain aromatic rings, so conventional biological treatment methods are not very effective for dye degradation. Physical treatment technologies such as adsorption, coagulation, and membrane filtration transfer organic compounds from water but cannot degrade the molecules [2]. Additionally, the regeneration of adsorptive capacity and the post-treatment of concentrated wastes are expensive [3]. Ozonation and chlorination are being used for the removal of dyes but limited due to their high operating costs [4]. Therefore, there is a need to develop more cost-effective methods for the degradation of dye effluents.

Conventional wastewater treatment is energy-intensive [5]. Developing ways to effectively treat wastewater yet minimize energy consumption is of increasing interest [6]. The application of photocatalysis that utilize solar light energy for the photodegradation of organic compounds present in water and wastewaters is of particular importance. More than 50 types of organic compounds or waste products that potentially could be photodegraded, include organic dyes, sugars, alcohols, aldehydes, ketones and organic acids [7]. Photocatalytic degradation is an oxidation-reduction reaction. When the catalyst is irradiated and absorbs photons of energy greater than or equal to its bandgap, electrons move from the valence band to the conduction band, resulting in the formation of electron (e^-) and holes (h^+). The electrons (e^-) are generated at conduction band and holes (h^+) are collected at valence band. The electrons can react with electron acceptors on the surface of catalysts. The generated holes can oxidize the molecules on the photocatalysts

surface, or oxidize OH^- and H_2O into $\cdot\text{OH}$ radicals, a strong oxidizing agent that is capable of oxidizing many dyes ^[8].

Numerous studies have investigated the photocatalytic degradation of a variety of dyes. For example, Pirhashemi et al ^[9] prepared $\text{ZnO}/\text{Ag}/\text{Ag}_2\text{WO}_4$ nano-particles by an ultrasonic-assisted method and investigated the photocatalytic degradation of RhB, and the results demonstrated that the oxidative ability of $\cdot\text{O}_2^-$ was greater than that of h^+ and $\cdot\text{OH}$ species for ZnO as photocatalysts. On the other hand, Daneshvar et al ^[10] studied the photocatalytic degradation of azo dye acid red 14 with ZnO and found that that hydroxyl radicals were the main reactive species and that positive holes were involved in the reactions. Moreover, the results of Daneshvar et al ^[10] also indicated that the degradation efficiency of acid red 14 was affected by illumination time, pH, and photocatalyst amount. The rate of photodegradation increased with the addition of hydrogen peroxide, but was inhibited with addition of ethanol. Houas et al ^[11] investigated the photocatalytic degradation of methylene blue (MB) under UV light with titanium oxide in aqueous heterogeneous suspensions. This study showed that the cationic functional group of MB molecule was likely adsorbed to the TiO_2 surface, and MB was mineralized resulting in the formation of numerous inorganic byproducts (i.e., CO_2 , SO_4^{2-} , NH_4^+ and NO_3^-) during the photodegradation process.

Based on current research, the efficiency of photocatalysts in organic pollutants degradation are affected by many factors including, the type of photocatalyst, pH, illumination time, particle size of photocatalyst ^[12], band gap, oxidizing agents, calcination

temperatures, and catalyst loadings ^[10,13]. In this study, the efficacy and kinetics of three photocatalysts (CdS, ZnFe₂O₄ and NiFe₂O₄) to degrade methylene blue were evaluated. Cadmium sulfide is a photocatalyst that has been extensively studied as photocatalyst due to its activity under visible-light and potential to degrade organic contaminants resulting in hydrogen production ^[14, 15]. Spinel semiconductors such as ZnFe₂O₄ and NiFe₂O₄ are a group of minerals. Research have shown that certain spinels have excellent photocatalytic properties ^[16-20]. Spinel usually have more narrow band gap energies than does CdS and contain earth abundant metals. As spinels are not highly toxic, the ferrites are likely to be environmentally benign. The abilities of CdS, ZnFe₂O₄, and NiFe₂O₄ in degrading methylene blue were compared in this study. Band gaps, SEM and absorption spectrum of the photocatalysts were determined. The impact of the concentration of methylene blue on removal efficacies was examined.

4.2 Materials and Methods

4.2.1 Materials preparation

All chemical reagents used in this experiment were from Alfa Aesar (Tewksbury, MA, US), of analytical grade.

4.2.1.1 Synthesis of CdS

CdS was prepared according to the hydrothermal method ^[15]. A Na₂S solution (300 mL, 0.14 M) was slowly added to a cadmium acetate (Cd(OAc)₂) solution (300 mL, 0.14 M) under vigorous stirring. A yellow precipitate formed. The mixture was stirred for 24 h, settled for 1 day, and filtered through a 20 µm size filter. The yellow solid was then

suspended in pure water (120 mL) and transferred to a Teflon-lined stainless-steel autoclave (150 mL) and heated at 200 °C for 72 h (hydrothermal treatment). The yellow solid was filtered, washed with water and ethanol subsequently, filtered again, and kept in a desiccator for 24 h.

4.2.1.2 Synthesis of ZnFe_2O_4

ZnFe_2O_4 was prepared by the sol–gel method ^[19]: 0.016 mol of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 0.008 mol of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 20 mL deionized water. Citric acid (0.036 mol) was then dissolved in the mixture. While magnetically stirred at 60 °C, 12 mL ammonia (25%) was added dropwise into the mixture to adjust the pH of the aqueous mixture to 7.0, and the mixture became a sol during this process. After stirring for about 6 h, the sol became a black gel. The gel was then dried at 120 °C for 12 h, during which its volume expanded about 10-fold. The dried gel was ground and calcined at 700 °C for 4 h until a brown product formed.

4.2.1.3 Synthesis of NiFe_2O_4

Synthesis of NiFe_2O_4 was carried out by the hydrothermal method in a stainless-steel autoclave. $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.001 mol) and 0.002 mol of $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ was dissolved separately in 100 mL of deionized water. Then 0.036 mol of citric acid powder was dissolved in the mixture. The mixed solution was precipitated with addition of 1 M NaOH solution until pH was 9.7, followed by the addition of 0.1 g of isopropyl alcohol under constant and vigorous magnetic stirring for 5 min. The suspension was poured into the stainless-steel autoclavable container for the hydrothermal treatment. The temperature

was controlled at 100°C for 3 h, and cooled to room temperature. Finally, the product was washed several times with absolute ethanol, and then dried in a desiccator for 24 h to obtain Ni-ferrite nanoparticles ^[21].

4.2.2 Photocatalysts characterization

The photocatalysts samples were mounted on aluminum stubs using high vacuum carbon tubes (SPI Supplies, West Chester, PA). Samples were coated with iridium to an approximate thickness of 2.7 nm in a Quorum Technologies/Electron Microscopy Sciences Q150T turbo pumped sputter coater (Quorum Technologies, Laughton, East Sussex, England BN8 6BN) purged with argon gas. The size and morphology of the photocatalyst samples were examined in a LEOL 7500F (field emission emitter) scanning electron microscope (JEOL Ltd., Tokyo, Japan) operated at accelerating voltage of 5 kV. For elemental analysis, energy dispersive X-ray spectroscopy was employed using an Oxford Instruments Aztec system (Oxford Instruments, High Wycomb, Bucks, England), software version 3.1 using a 150 mm² Silicon Drift Detector (JEOL 7500F SEM) and an ultra-thin window. The bandgap of the photocatalysts was investigated by a UV–vis spectrophotometer (Shimadzu, UV-2600, Japan) in the wavelength range from 200 nm to 800 nm.

4.2.3 Evaluation of photocatalysts in degradation ability

Photoreactions were performed in a Pyrex glass reactor containing methylene blue solution. The initial concentration was varied between 2 and 20 µmol/L. A selected amount of photocatalyst (CdS, ZnFe₂O₄, NiFe₂O₄) was added to the solution. The

photoreactor was illuminated using a solar simulator (Abet Technologies' model 11002 SunLite™, Milford, Connecticut, US), ozone-free Xe Arc Lamp of 100 W, with continuous stirring for 4 hours (batch system). Samples (10 mL) were collected at 0 min, 5 min, 10 min, 30 min, 1 h, 1.5h, 2 h, 3 h and 4 h. At the end of experiment, methylene blue concentrations were determined by visible spectroscopy (Shimadzu, UV-2600, Japan) at its absorption peak (665 nm) after centrifugation at 3200 rpm for 10 min. (Clay ADAMS™, COMPACT II CENTRIFUGE).

4.3 Results and Discussion

4.3.1 XRD analysis of ZnFe₂O₄

The structure of the ZnFe₂O₄ composites was investigated by the X-ray diffraction. Figure 4.1 shows the XRD patterns of ZnFe₂O₄. The pure ZnFe₂O₄ is in the spinel phase, and the distinctive peaks at 29.9, 35.2, 42.8, 53.1, 55.6, and 62.16 matched well with the (220), (311), (400), (422), (511) and (440) crystal planes of ZnFe₂O₄.

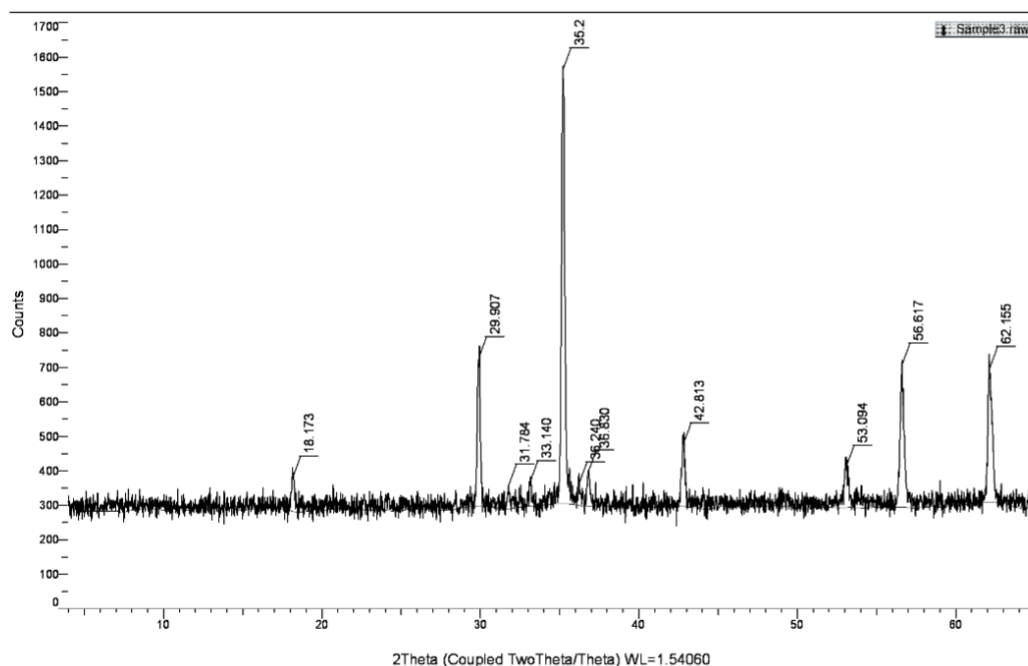
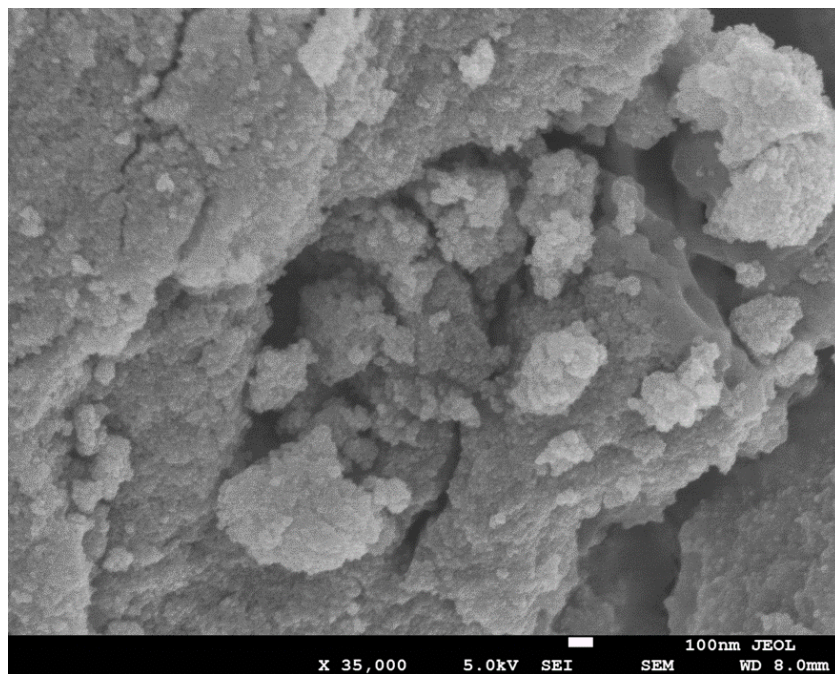


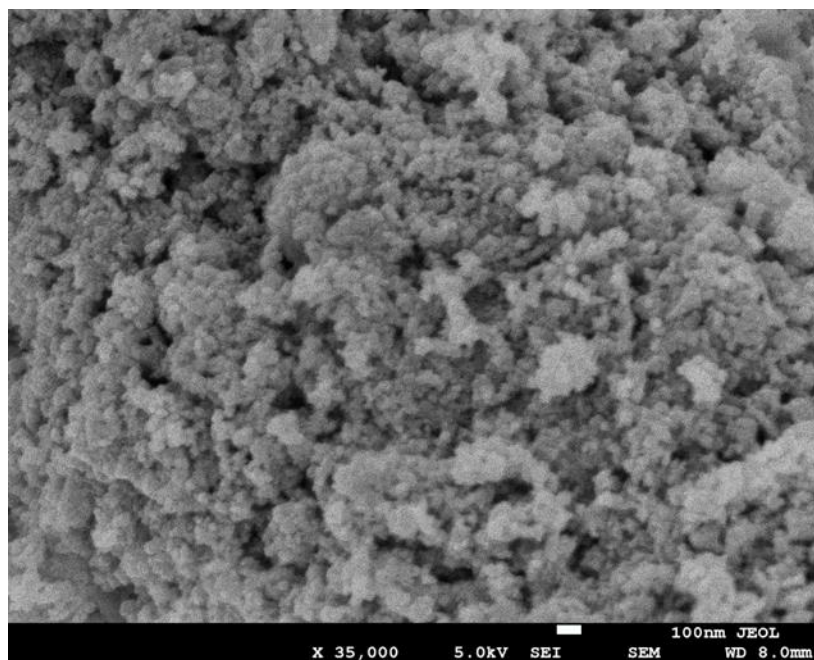
Figure 4.1 XRD patterns of the obtained ZnFe_2O_4

4.3.2 SEM analysis

The SEM images of CdS , ZnFe_2O_4 , and NiFe_2O_4 are shown in figure 4.2. The particle size for CdS ranged from 50-400 nm (figure 4.2(a)). ZnFe_2O_4 was mainly composed of spherical grains with sizes of 50-400 nm (figure 4.2(b)), although the majority of particles were in range of 75-190 nm. NiFe_2O_4 particles ranged in size from 50-700 nm (figure 1(c)). The surface of the NiFe_2O_4 appeared to be more porous, and small particles adhered to large irregular particles, probably due to magnetic characteristics of NiFe_2O_4 . The size of NiFe_2O_4 particles were a wide range; larger particles were likely the result of the different synthesis method.



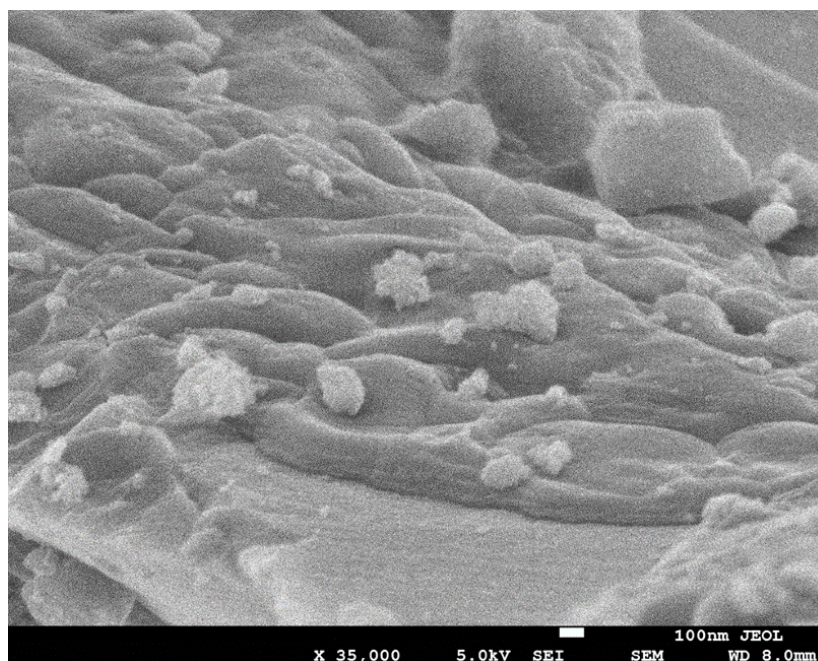
(a) CdS



(b) ZnFe₂O₄

Figure 4.2 SEM images of (a) CdS, (b) ZnFe₂O₄, and (c) NiFe₂O₄

Figure 4.2 (cont'd)

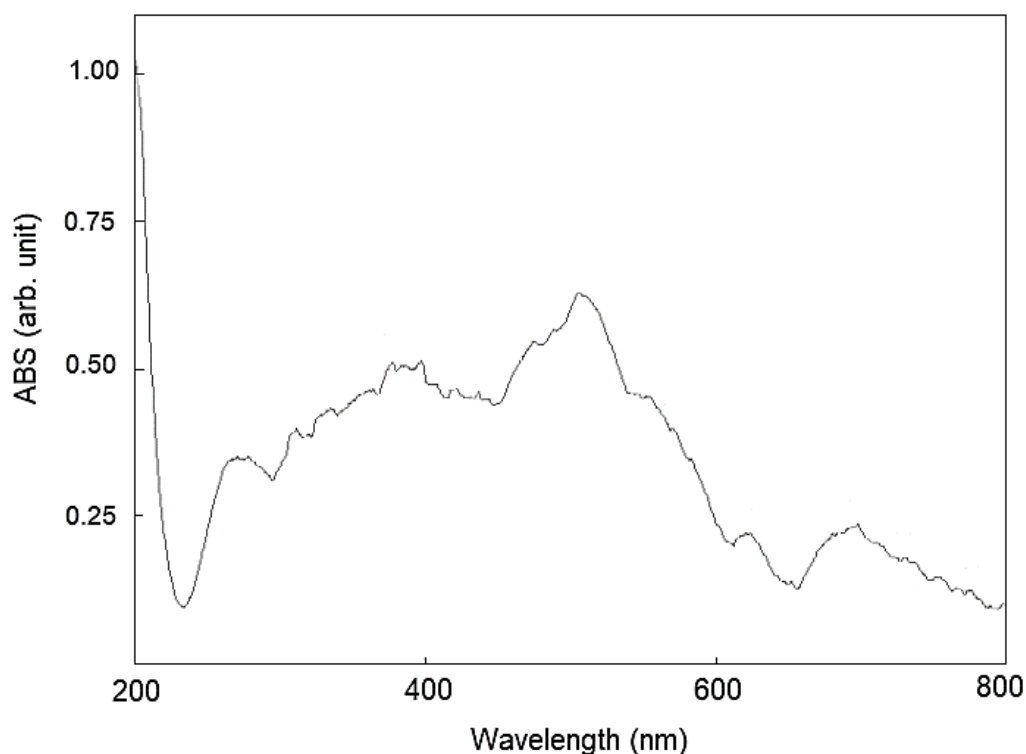


(c) NiFe₂O₄

4.3.3 UV-vis analysis

UV-vis spectroscopy was used to investigate the absorptive properties of the catalysts. The results are shown in figure 4.3. All photocatalysts had visible light absorption. The absorption peaks of synthesized CdS, ZnFe₂O₄, and NiFe₂O₄, were at 506 nm, 385 nm and 280 nm, respectively. The absorption edge of CdS was at ~770 nm, and those of ZnFe₂O₄, and NiFe₂O₄ were at 410 nm and 400 nm, respectively. CdS nanoparticles had the widest absorption range. ZnFe₂O₄ and NiFe₂O₄ had a relatively narrow visible light absorption range and relative steep edge. According to reported literature, CdS had a band gap of 2.28 – 2.4 eV under different thermal annealing temperature ^[22], while ZnFe₂O₄, and NiFe₂O₄ as spinel n-type semiconductor, had a comparatively low band gap energy as approximately 1.9 eV ^[23] and 1.7 eV ^[24], separately.

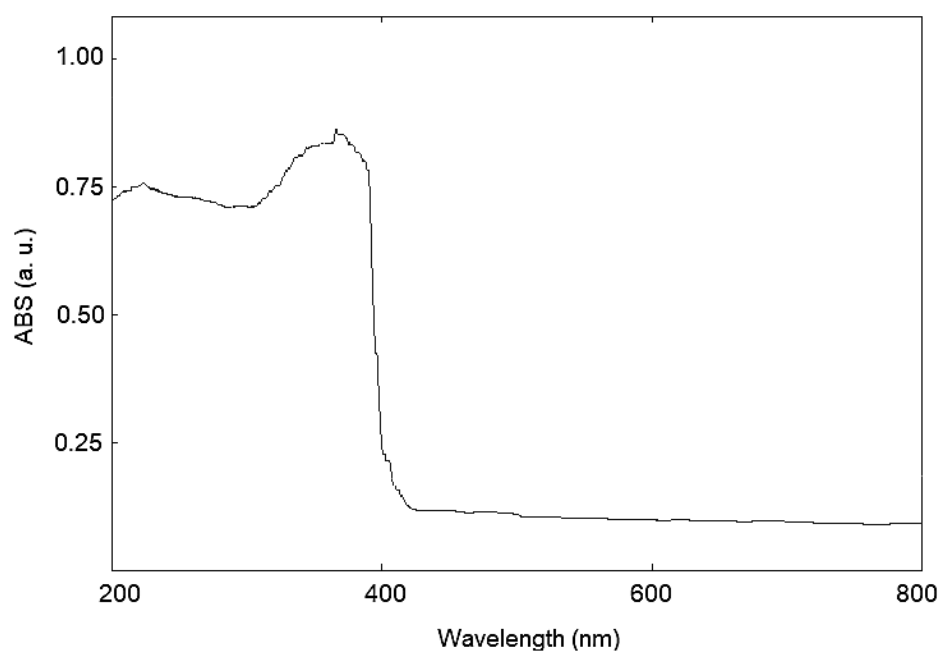
The spectra also showed that the formulated CdS had excellent visible-light absorption, from 210 nm to 800 nm. ZnFe_2O_4 had a relatively narrow visible light absorption range and relative steep edge. ZnFe_2O_4 nanoparticles were characterized as spinels, with tetrahedral and octahedral sites occupied by Zn^{2+} and Fe^{3+} cations [25]. According to Lv *et al* [26], the transition of photoexcited electrons from the 2p level of O into 3d level of Fe can explain the absorption of visible light with ZnFe_2O_4 , with the assumption that the O 2p orbital serves as the valence band and the Fe 3d orbital acts as the conduction band. For NiFe_2O_4 , Ni^{2+} and Fe^{3+} also occupy the tetrahedral and octahedral sites [27].



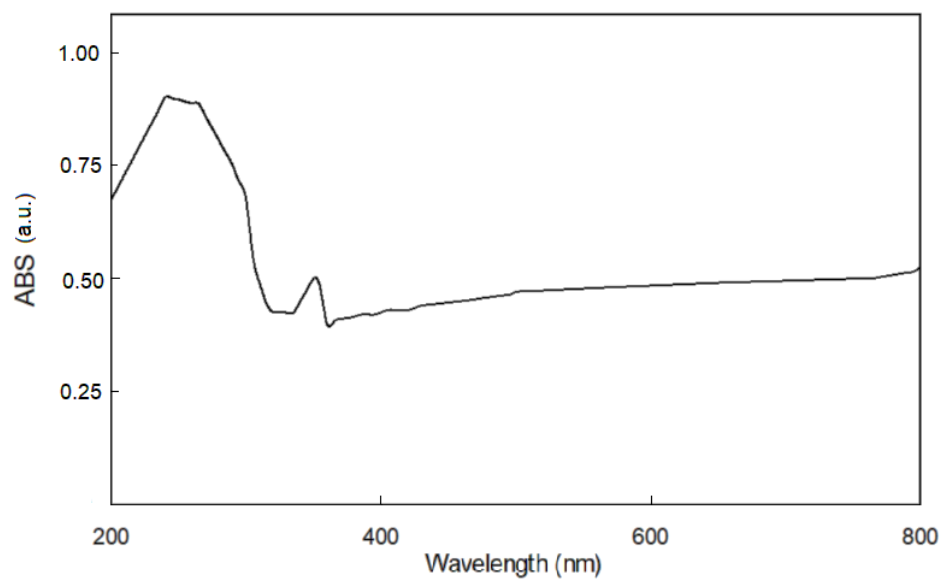
(a) CdS

Figure 4.3 UV-vis absorption spectra of different photocatalysts (a) CdS (b) ZnFe_2O_4 and (c) NiFe_2O_4

Figure 4.3 (cont'd)



(b) ZnFe₂O₄



(c) NiFe₂O₄

4.3.4 Photocatalytic degradation of methylene blue test

4.3.3.1 Methylene blue removal efficiencies by different photocatalysts

The efficacy of all three photocatalysts were evaluated using methylene blue as the target chemical. The absorption peak of methylene blue is at 665 nm. The initial concentration of the methylene blue was controlled at 8 $\mu\text{mol/L}$. The amount of photocatalyst used was 1.0 g/L.

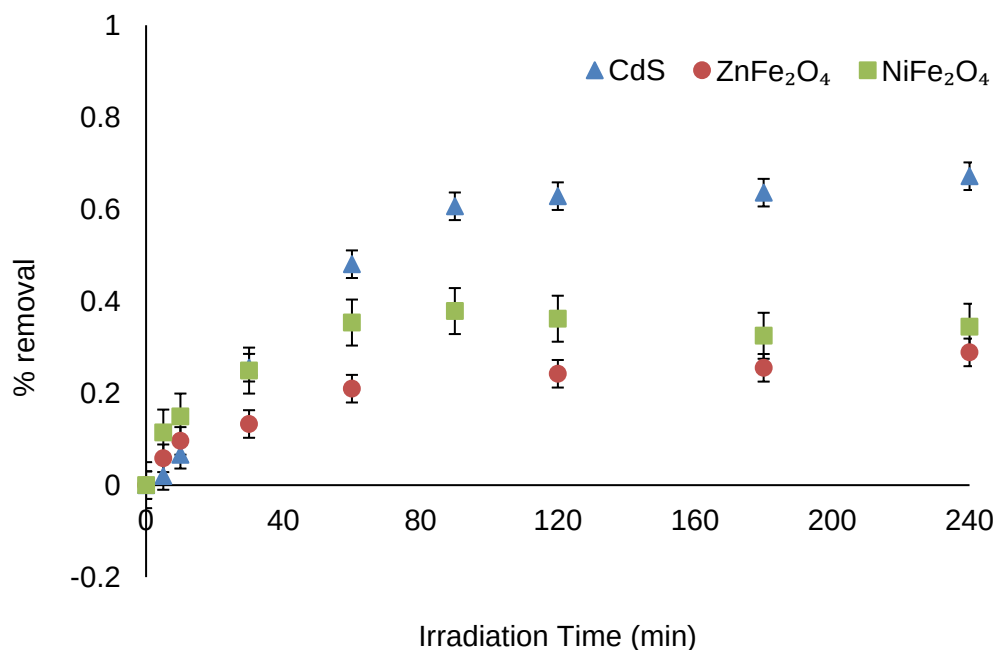


Figure 4.4 Degradation curves of methylene blue over different photocatalysts, initial methylene blue concentration of 8 $\mu\text{mol/L}$, with the amount of photocatalyst used controlled at 1.0 g/L.

The kinetics of disappearance of MB by various photocatalysts are shown in Figure 4.4. During illumination, methylene blue concentrations decreased rapidly initially; the rate decreased after 100 min. According to Xu ^[11], MB degradation is initiated by cleavage of C–S+=C bonds in MB. The decrease in reaction rate is consistent with the hypothesis

that as products are formed, they also absorb light, resulting in a reduction in the rate of photolysis of MB.

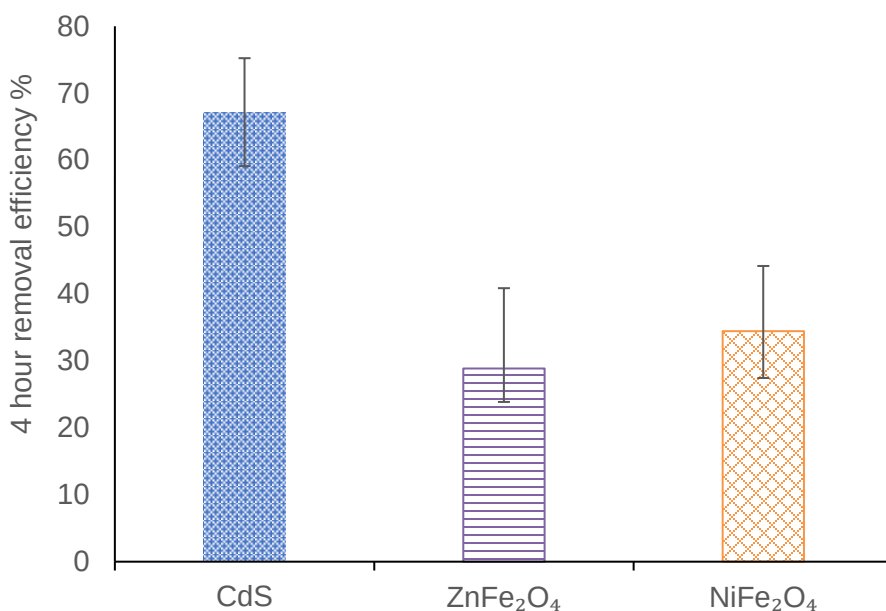


Figure 4.5. Comparison of removal efficiency of different photocatalysts, initial concentration of MB at 8 $\mu\text{mol/L}$, at 25 $^{\circ}\text{C}$

As Figure 4.5 shows, the removal efficacies of methylene blue were: $\text{CdS} > \text{NiFe}_2\text{O}_4 \geq \text{ZnFe}_2\text{O}_4$. The reason for the greater photolysis rate with CdS is likely due to the wide absorption range of CdS. As such, during irradiation, CdS nanoparticles can utilize a wider range of photon energy than the other photocatalysts. Although ZnFe_2O_4 has a slightly wider absorption range than NiFe_2O_4 , the band gap of ZnFe_2O_4 is greater than that of NiFe_2O_4 , thus the electrons in the valence band would be harder to excite during irradiation.

4.3.3.2 Methylene blue removal efficiencies by different initial concentrations

The effect of initial concentration was determined by varying the initial concentration of

methylene blue between 2 and 20 $\mu\text{mol/L}$. The mass of ZnFe_2O_4 photocatalyst remained constant at 1 g/L.

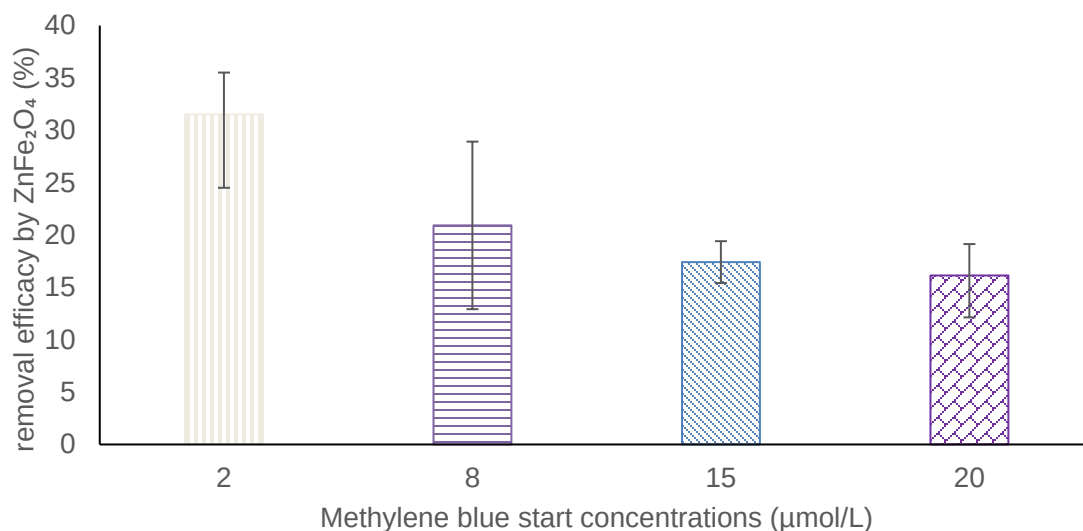


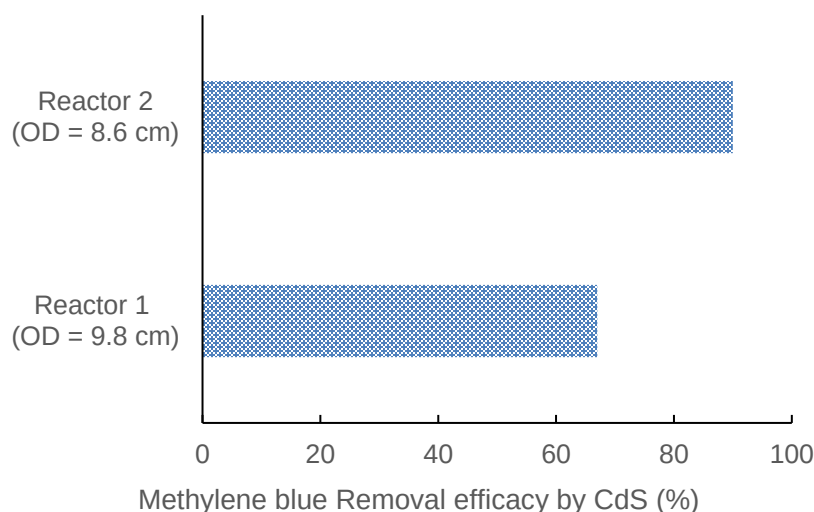
Figure 4.6 Different concentrations of methylene blue removal efficacy with ZnFe_2O_4 under visible light, at 25 °C

As shown in figure 4.6, the efficacy of photodegradation decreased as methylene blue concentration increased. As the methylene blue concentrations were increased, the concentration of photocatalysts available to provide the electron loop necessary for oxidation became rate limiting. The lowest concentration (2 $\mu\text{mol/L}$ MB) had the highest removal efficacy (31.51%), and it was twice that observed when the initial methylene blue concentration was 20 $\mu\text{mol/L}$.

4.3.3.3 Other factors that affected methylene blue removal efficiencies

The effect of reactor volume and illumination area was studied using two Pyrex glass

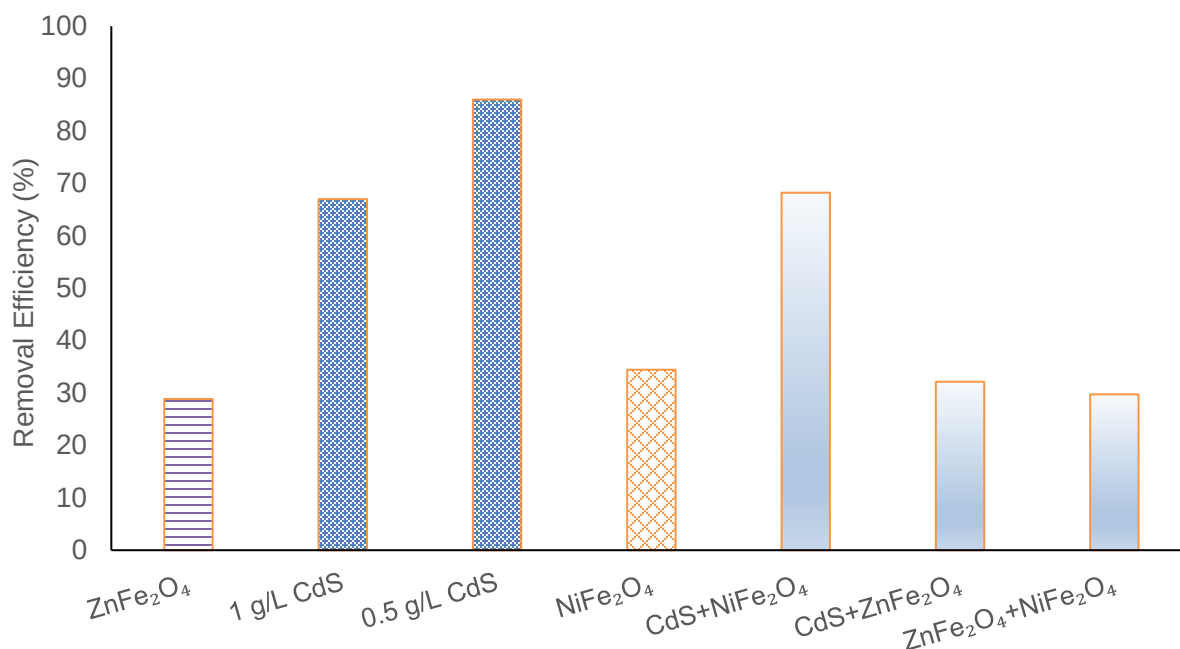
reactors with different diameters (9.8 cm outside diameter (OD) and 8.6 cm OD). The initial methylene blue and CdS concentrations were 8 $\mu\text{mol/L}$ and 1 g/L CdS, respectively. All other conditions were the same. The photoreactors were illuminated with continuous stirring for 4 hours. As figure 4.7 (a) shows, the removal efficiency was significantly greater in the reactor with a smaller diameter. Moreover, different amounts of CdS (1 g/L and 0.5 g/L) and equal mixed of two kinds of nanoparticles (1 g/L of equal mixed of CdS, ZnFe_2O_4 , NiFe_2O_4), separately, were in the same reactor under visible light illumination with continuous stirring for 4 hours (batch system), shown in figure 4.7 (b).



(a)

Figure 4.7 Methylene blue removal efficacy with different (a) reactors and (b) amounts of nanoparticles under visible light, initial MB concentration of 8 $\mu\text{mol/L}$, at 25 $^{\circ}\text{C}$

Figure 4.7 (cont'd)



(b)

As figure 4.7 (a) shows, reactor with a smaller diameter had a higher removal efficiency (~23% more). The reason for this could be that light would be easier to transmit through the reactor and there would be higher light intensity at the back of the reactor. Figure 4.7 (b) showed that for CdS, 0.5 g/L nanoparticles had higher removal efficiency of methylene blue under visible light compared to 1 g/L of same nanoparticles. The photodegradation activities were affected availability of active sites on the catalyst surface and the penetration of light transmitted ^[28]. At 1 g/L CdS suspension, although the availability of active sites increased, there is also an increase in the turbidity and a decrease in photon penetration as a result of increased scattering effect, so the photodegradation activity decreased ^[29]. The initial objective of mixing two kinds of nanoparticles together and ran the tests was check if it would increase the methylene blue removal efficiency, as all nanoparticles had different absorption range, and the photo excitation of one kind of

nanoparticles might produce current and trigger the nanoparticles near them. However, as figure 4.7(b) shows, the trend with mixed nanoparticles was not clear in this study.

4.3.5 Methylene blue degradation kinetics by CdS

The photodegradation activities of CdS photoreaction with methylene blue is shown in figure 4.8. After 4 hours, the removal efficiency of methylene blue was 91%.

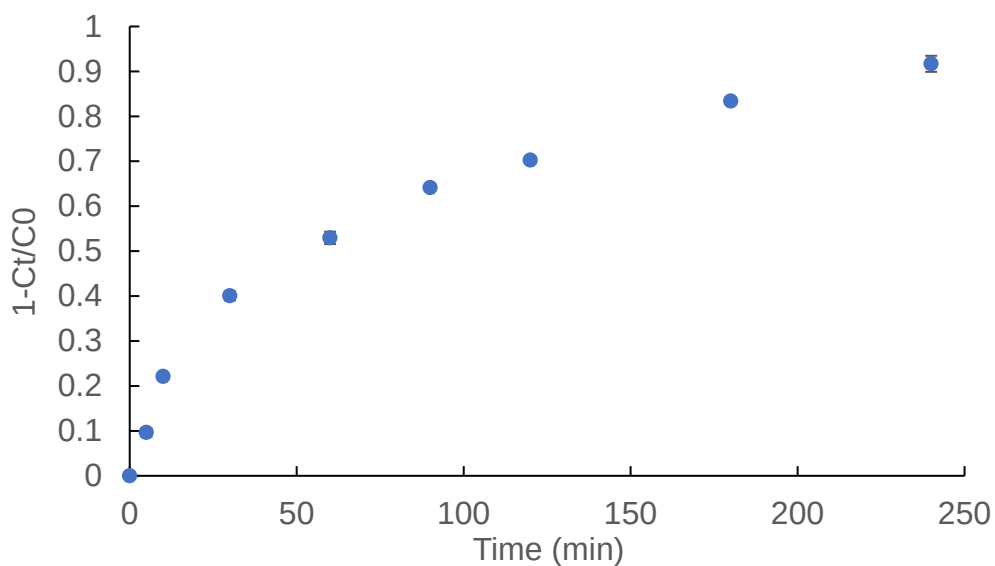
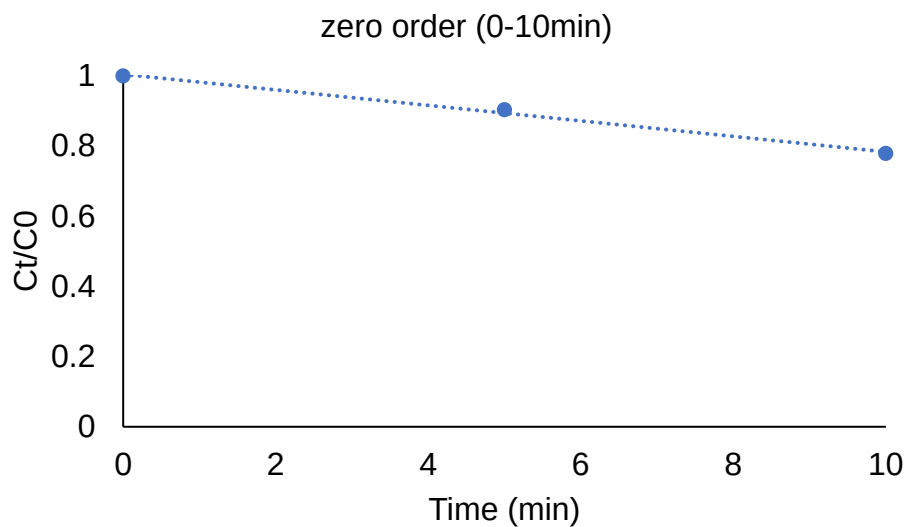
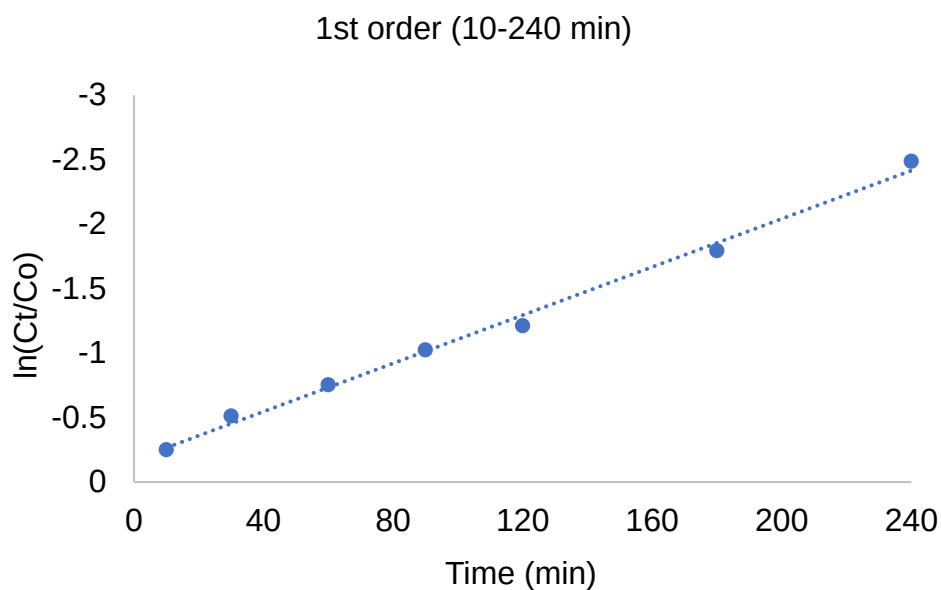


Figure 4.8 Degradation curve of methylene blue with CdS



(a) Zero-order plots for first 10 min methylene blue degradation



(b) Pseudo-first-order plots for 10 min – 4 h methylene blue degradation

Figure 4.9 Kinetics plots for methylene blue degradation by CdS: (a) Zero-order plots for first 10 min methylene blue degradation; (b) Pseudo-first-order plots for 10 min – 4 h methylene blue degradation

The kinetics of degradation of MB by CdS presented a two-stage reaction ^[30]. During first stage (0-10 min), as figure 4.9 (a) shows, there is a rapid degradation in zero-order kinetics with a reaction rate of 0.2 min^{-1} . The reaction rate should not relate to the concentration of methylene blue, but the available 'holes' on the surface of the catalysts. It was also interesting to notice it fit the Langmuirian type absorption with an equilibrium adsorption with a linear rate reaction ^[31]. After 10 min, a first order reaction and a lower reaction rate were observed (figure 4.9(b)), with reaction rate of 0.0093 min^{-1} . The reaction related to methylene blue concentration. During this stage, surface of the catalysts had absorbed methylene blue molecules, and hydroxyl radicals were produced during the photo-excitation process, resulting in oxidation of methylene blue.

4.3.6 Methylene blue degradation mechanism by CdS

As mentioned, there are two possible ways for methylene blue degradation: MB molecules attached to the surface of CdS and got oxidized, or MB reacted with hydroxyl radicals that produced by Fenton process in the solution. To investigate the oxidation process, same amount of tert-butyl alcohol was added as hydroxyl radicals scavengers.

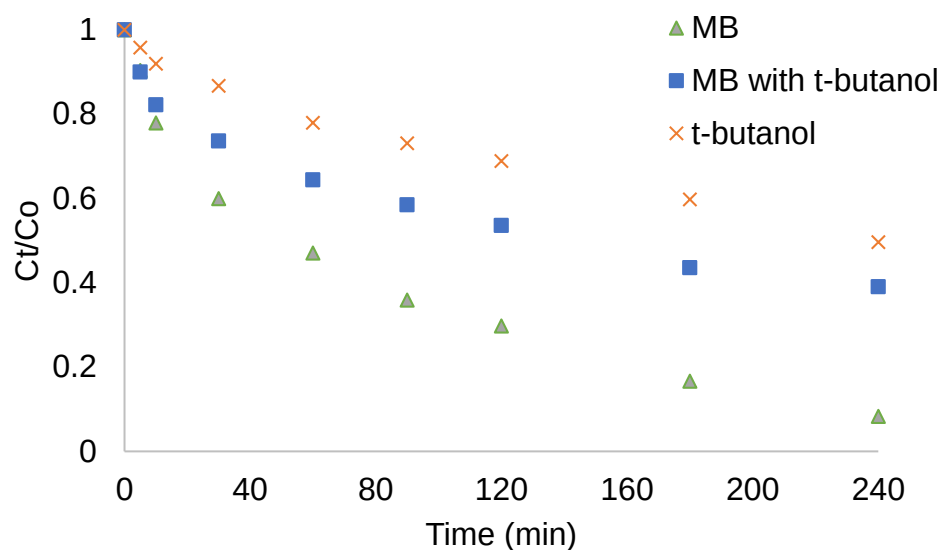


Figure 4.10 Effect of radical scavengers on the degradation of MB with CdS

From figure 4.10, 0-10 min, methylene blue degradation rate did not get affected much with addition of tert-butyl alcohol, which proved the hypothesis that during first stage, MB molecules were mainly oxidized by the h^+ on the surface of CdS nanoparticles. However, after 30 min, the degradation of MB slowed down and inhibited by the presence of t-butanol. At the end of 4 h experiment, MB removal efficiency dropped from 91.7% to 61.0%, indicating that about 30 % of methylene blue degradation by CdS was oxidized by hydroxyl radicals in the solution.

4.3.7 Photo-deactivation of CdS

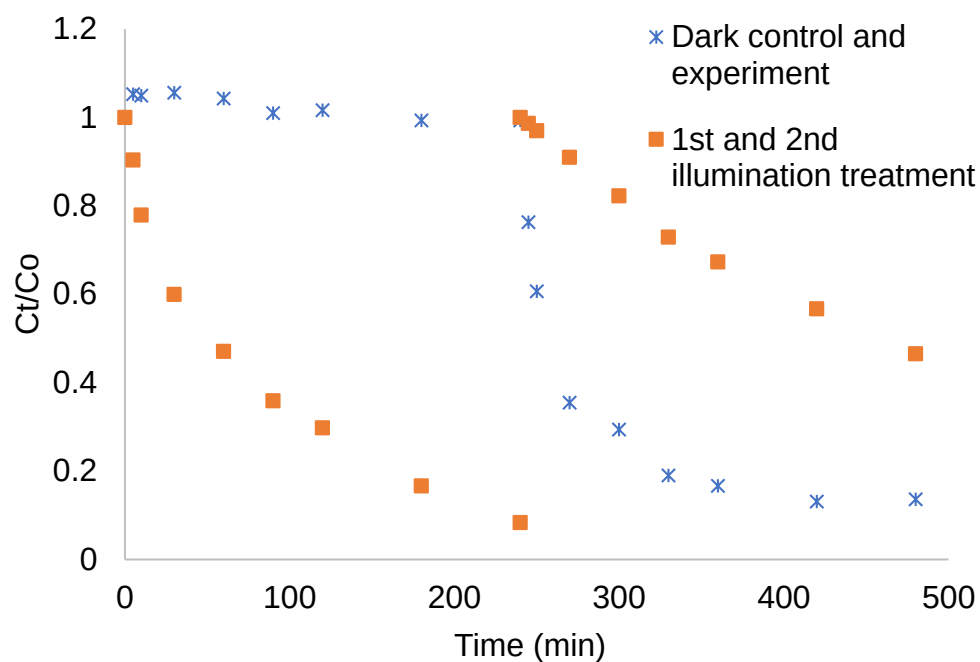


Figure 4.11 Methylene blue degradation over time by continued treatment using CdS

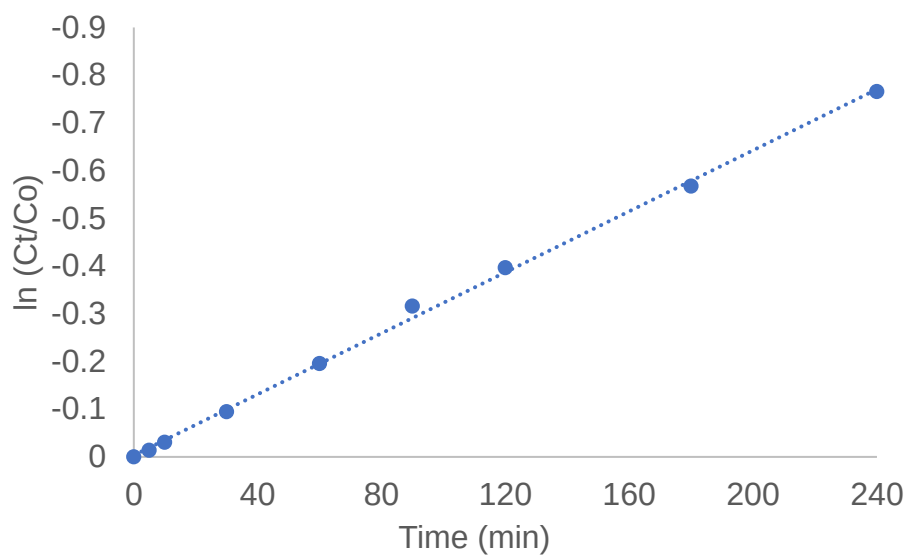
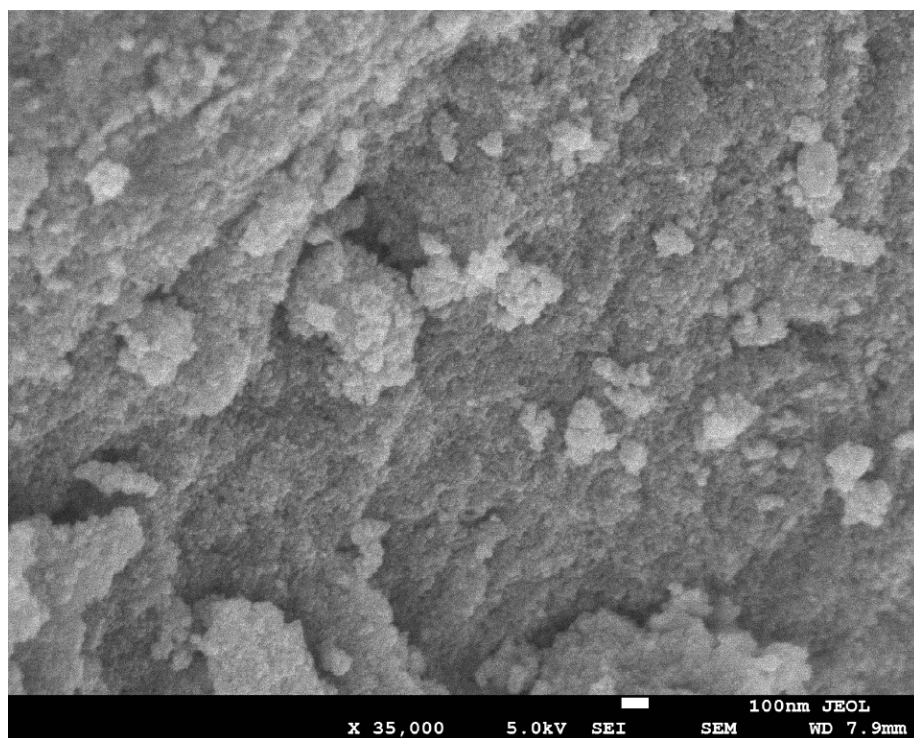


Figure 4.12 First-order plots of 2nd illumination treatment with CdS

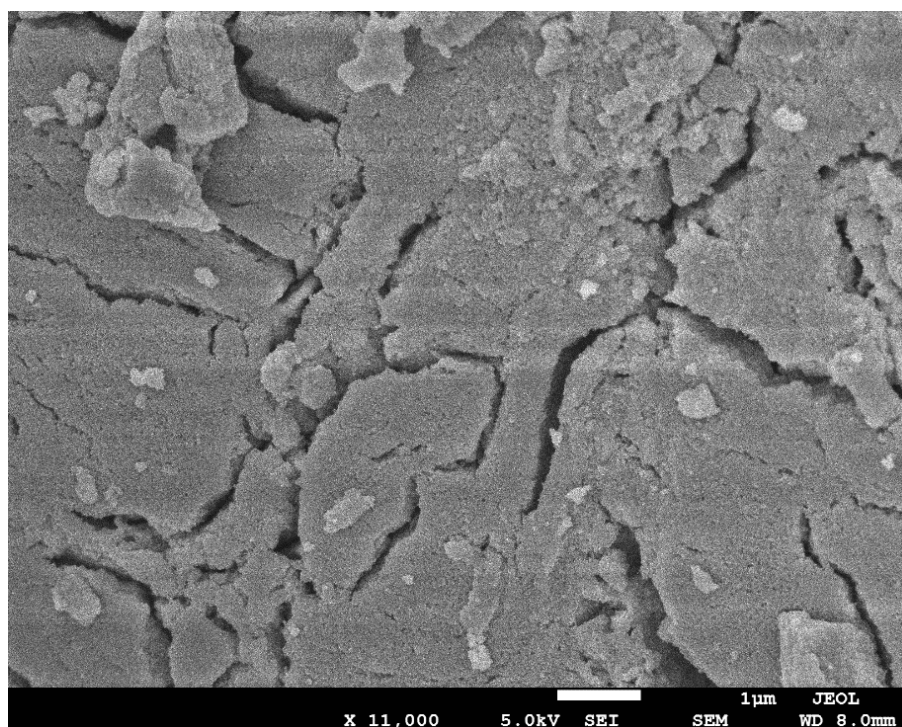
Photocatalysis deactivation happens when there is prevention of electron excitation, methylene blue molecules cannot reach the surface of CdS, or formation of hydroxyl radical is interrupted. Researchers studied methylene blue degradation using anatase TiO₂ by HRTEM ^[32] and found that the TiO₂ surface induced by chemical adsorption of methylene blue molecules is a crucial intermediate step during photocatalysis degradation. Figure 4.11 shows degradation of methylene blue during first and second treatment. It is obviously that during second illumination treatment, there was a main drop in degradation efficiency. Moreover, the deactivation of CdS only happened with first time illumination. Dark stirring for 4 hours did not affect the methylene blue photodegradation removal efficiency. Figure 4.12 shows that there was only 1 stage during 2nd illumination treatment. It was first order kinetics with reaction rate of 0.0032 min⁻¹. The drops in reaction rate and efficiency could be due to the chemical adsorption of the degraded products blocked the spots of the catalysts surface, so that MB molecules could not reach the spots.

4.3.8 SEM and EDS of used CdS

The SEM images of CdS before and after 4 hours illumination treatment are shown in figure 4.13. As there is vacuumed dry after treatment, the photocatalysts became flat sheeted and formed cracks on the surface, and the particle sizes got larger (diameters range 0.45-0.98 μm). That might be the reason for reduced removal efficiency. For both before and after, the particles were intended to accumulate together and form larger particles.

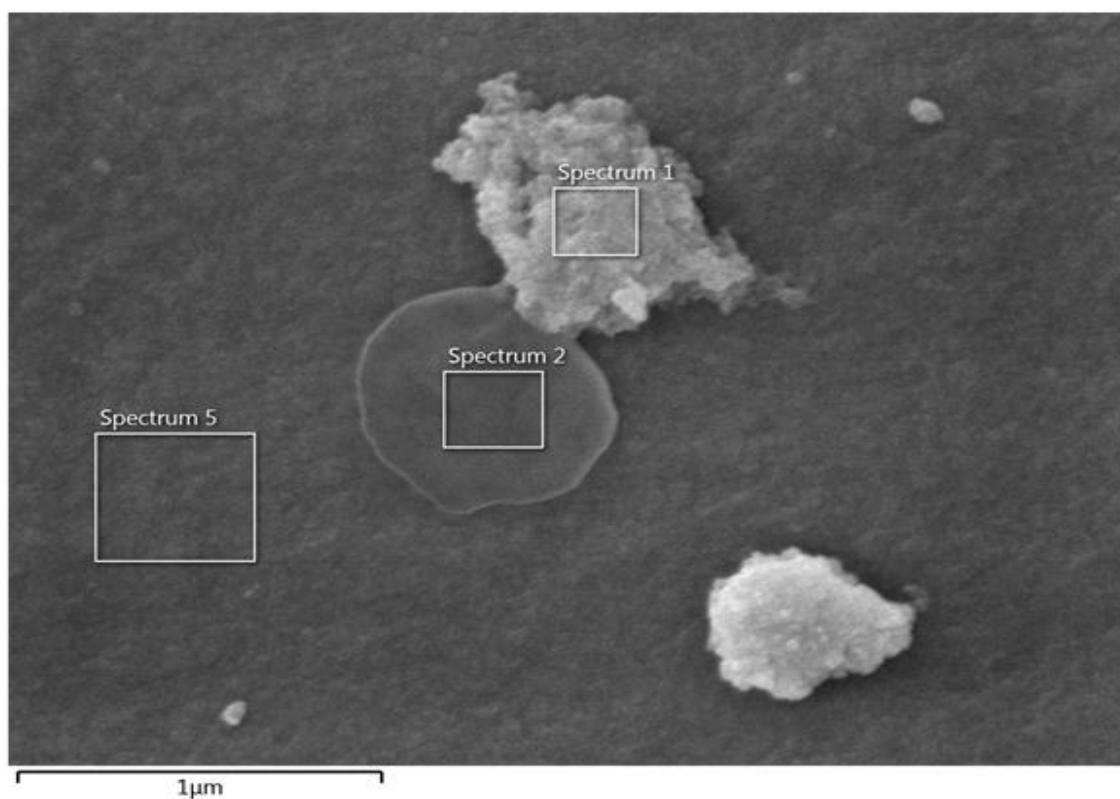


(a) CdS before photo-treatment

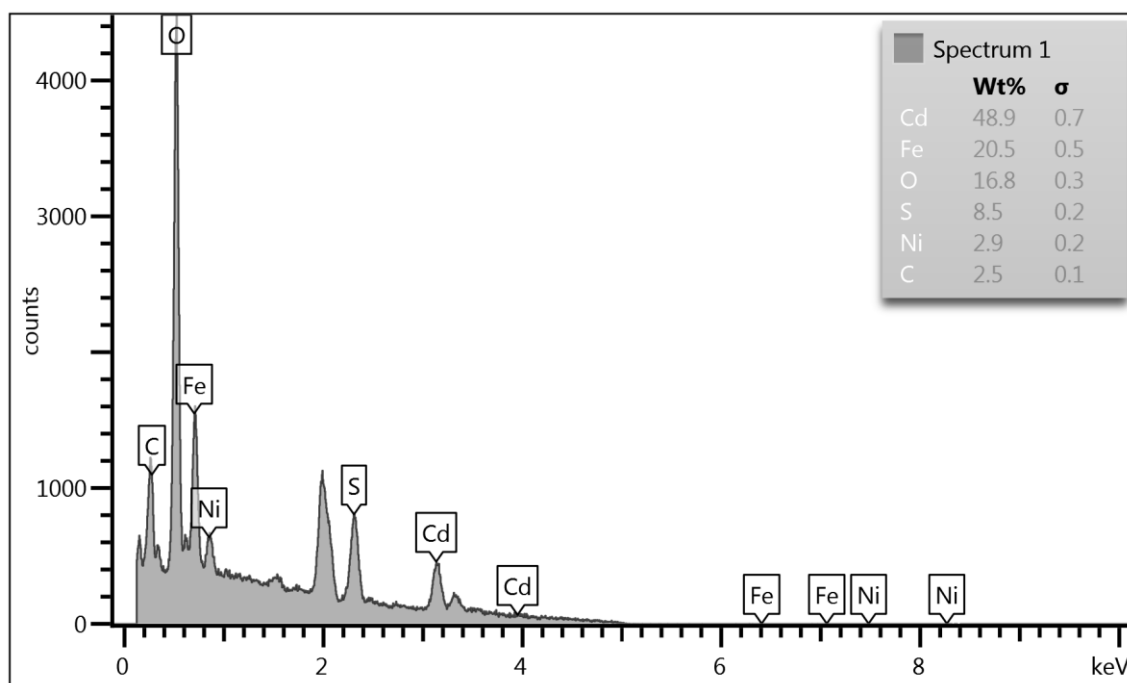


(b) CdS after photo-treatment

Figure 4.13 SEM images of CdS before and after photo-treatment



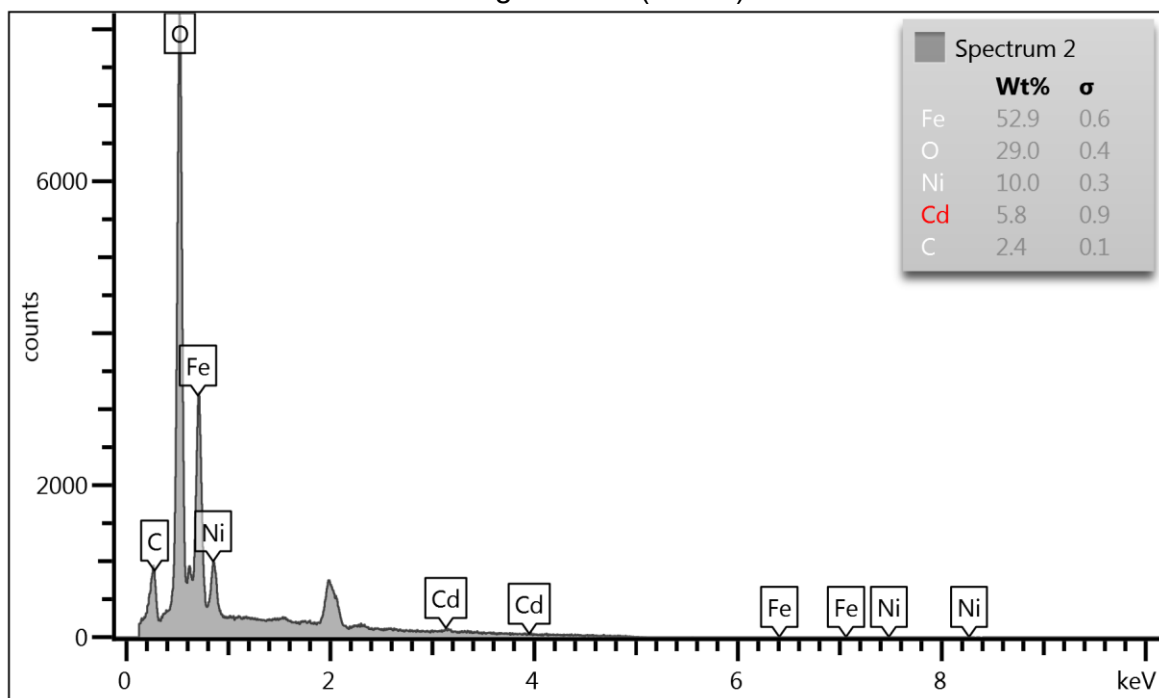
(a) EDS images of used CdS and NiFe₂O₄



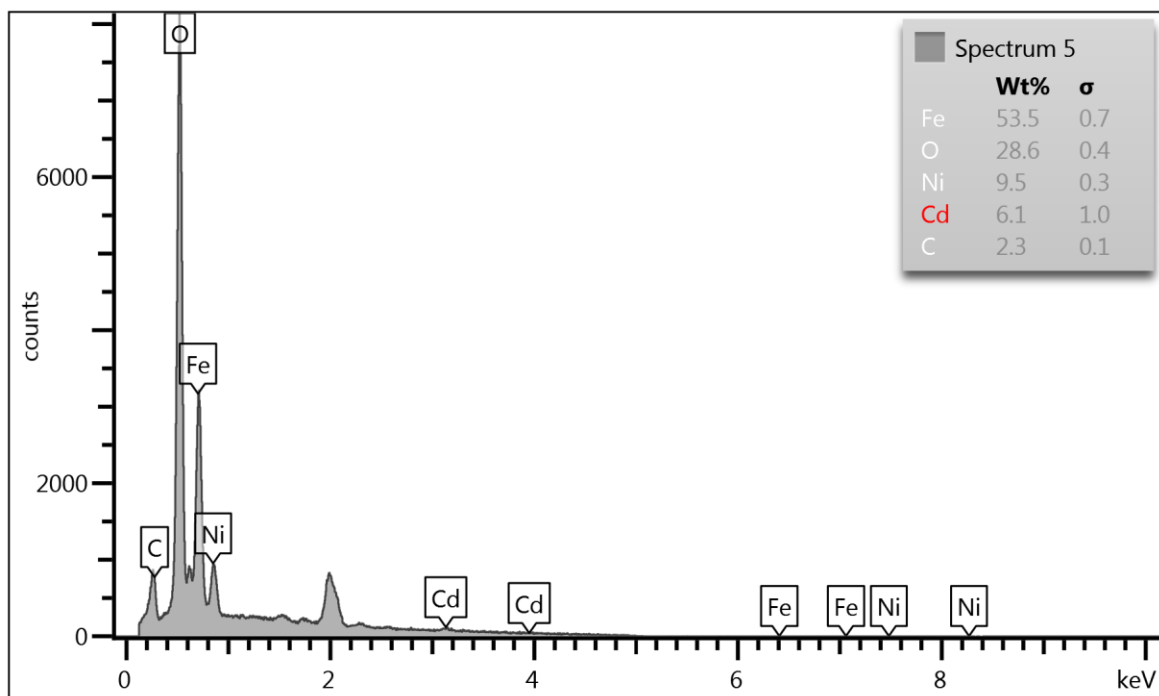
(b) Element analysis of spectrum 1

Figure 4.14 EDS analysis of used CdS and NiFe₂O₄

Figure 4.14 (cont'd)



(c) Element analysis of spectrum 2



(d) Element analysis of spectrum 5

Figure 4.14 showed the EDS images of used CdS and NiFe₂O₄ catalysts. The image showed that there were molecules attached to the surface of photocatalysts, based on element analysis, it should be methylene blue degradation products as there was carbon element detected in spectrum. This also proved that one mechanism way of photodegradation was that molecules attached to surface of catalysts.

4.4 Conclusions

In this study, CdS, ZnFe₂O₄, and NiFe₂O₄ materials were synthesized. Methylene blue could be successfully decolorized and degraded by all three photocatalysts under visible light at room temperature. The absorption, nanoparticle surface and degradation characteristics of the nanoparticles were studied. All the synthesis nanoparticles had visible light absorption, while CdS had a great absorption range within invisible light spectra. The order of photocatalysis degradation efficacies of methylene blue during illumination was CdS > NiFe₂O₄ ≥ ZnFe₂O₄, the reason could be that the absorption spectra results showed that CdS had the widest absorption range, compared to NiFe₂O₄ and ZnFe₂O₄. It was indicated that the methylene blue removal efficacy could be affected by absorption range of photocatalysts, initial dye concentrations, amount of photocatalysts addition, and photoreactor conditions. The kinetics of degradation of MB by CdS presented a two-stage reaction. Removal efficiency of methylene blue decreased as methylene blue concentration went up, so when designing photodegradation application, it would not only to consider which photocatalyst to be chosen, but also be an important thing to figure out the feed water contaminants concentrations, shapes and sizes of photoreactor, and amounts of nanoparticles added.

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CHAPTER FIVE

Innovative Water Reuse Process with Photocatalytic Reactors and Catalytic Ceramic Membrane Filtration

Abstract

Technically feasible and economical processes that produce safe, clean water is highly in demand. This chapter describes an innovative water reuse process that combines photocatalysis and ceramic membrane filtration. This proposed process replaces biological treatment with sunlight-based photocatalysis to treat emerging contaminants in wastewater. This would reduce energy consumption and sludge production, and has the potential to generate hydrogen. A catalytic membrane filtration system was used in the water treatment process to remove turbidity, large molecules, and recover the catalysts. Experiments were conducted to determine the removal efficiency of caffeine using CdS and ZnFe_2O_4 as photocatalysts in a batch system followed by manganese oxide coated ceramic membrane filtration. Results showed that there was 20.7% caffeine removal by ZnFe_2O_4 – membrane system, and 23.3% for CdS – membrane system. Turbidity of the water reached 0.16 NTU after membrane filtration for both photolytic systems. For future improvements, photodegradation could be combined with an advanced oxidation process such as pre-ozonation or addition of hydrogen peroxide to improve the removal of caffeine and other emerging contaminants.

5.1 Introduction

Emerging contaminants, including pharmaceuticals, personal care products and endocrine disruptors, are persistent and recalcitrant ^[1]. These contaminants are largely extensdsively and many are toxic. Conventional wastewater treatment is ineffective at removing many of the emerging contaminants, resulting in the release of many of these compounds to the environment. Moreover, the risk of human exposure to most emerging contaminants is difficult to ascertain their ecotoxicological data are not available ^[2]. Therefore, appropriate and effective water reuse technology for emerging contaminants is in high demand. After treatment, the reused water must meet water standards and demands.

Caffeine is widely used, commonly found in tea, coffee, drugs, etc. ^[3] It is observed in effluents from sewage treatment plants at concentrations about 2 µg/L ^[4]. Caffeine residues have been even detected at remote locations far from human settlements ^[5]. Therefore, effective treatment processes for caffeine are necessary.

Conventional biological treatment methods are ineffective for recalcitrant organic pollutants, such as organic dyes, emerging contaminants, and organic acids. Among the many existing wastewater treatment technologies and processes, oxidative degradation of organic contaminants is a very important tool in the engineer's toolbox. Advanced oxidation processes (AOPs) have been used effectively for the degradation of many organic pollutants (e.g., see [6]). Advanced oxidation processes can be described as aqueous phase oxidation methods based on the intermediacy of highly reactive species

in the mechanisms leading to the destruction of the target pollutant. One of the mainly used reactive species is hydroxyl radicals, used for the degradation of organic pollutants and yielding CO₂ and inorganic ions with high degradation efficiencies and sludge-free operation [6]. Photodegradation can also be used for contaminants oxidation in wastewater reuse process. Moreover, the need for energy efficient and sustainable processes have encouraged extensive research on solar energy utilization [7, 8]. Semiconductor catalysts irradiated with light of an appropriate wavelength can be used to generate highly reactive transitory oxidative species (i.e., •OH, •O₂, and •HO₂) for the mineralization of organic impurities and pollutants [7, 8]. There are a range of strategies have been studied for the photocatalytic degradation of organic dyes using semiconductor photocatalysts [9–11]. This Fenton-like processes have been applied to and demonstrated with the degradation of a wide range of model pollutants, including RhB, methylene blue (MB), methyl orange (MO), nitrobenzene, 4-chlorophenol, acid orange II, and nalidixic acid [12–15]. Organic compounds commonly found in fermented biomass, such as organic acids are expected to significantly improve photocatalytic hydrogen production as compared to that in the absence of scavengers.

Cadmium sulfide (CdS) has been extensively studied as a photocatalyst for hydrogen production [17–19] and photodegradation [20–22]. It has a direct band gap of about 2.4 eV [16] and most of the absorption spectra is in the visible region. CdS has been used for the photocatalytic degradation of methylene blue [16, 23] with a relatively high removal efficacy (see chapter four).

Studies showed that certain spinel semiconductors have excellent photocatalytic properties. They have band gap energies less than 2.2 eV and have good absorption in the visible light range ^[24-26]. ZnFe_2O_4 is one of several photoactive spinel semiconductors. It is advantageous over CdS as it contains earth abundant, non-toxic metals. Experimental work (see chapter four) demonstrated that it degrades methylene blue, is stable, is environmentally friendly.

Over the last decade, as membrane technology has improved and become more economical, the use of membrane filtration has increased rapidly ^[27]. The objective of membrane filtration is to remove microorganisms and other particles from water. There are a number of advantages over conventional water treatment technologies in membrane process, including less sludge production, smaller footprint ^[28], and the physical exclusion of microorganisms from the product water. However, membrane fouling continues to be one of the main factors limiting the application and increasing operational costs of membrane technology ^[29]. If membrane fouling can be well controlled, membrane filtration can be applied more generally. Additionally, if the cost of membrane technology can be reduced, it is possible to choose it as one of the water reuse selections.

Moreover, conventional wastewater treatment plant consumed significant amounts of energy. This process could use sunlight as energy resource to oxidize organics and possibly produce hydrogen. Also, the photocatalysts could be recovered from surface of ceramic membrane for future reuse. In this study, the process was simulated in a laboratory scale to figure out if this process is effective for caffeine removal.

5.2 Materials and Methods

5.2.1 Photocatalysts preparation and characterization

Synthesis procedures of CdS and ZnFe₂O₄ were the same that described in chapter 4, following hydrothermal method for CdS ^[30] and sol-gel method for ZnFe₂O₄ ^[31]. Both CdS and ZnFe₂O₄ were investigated their UV-visible absorption abilities and scanning electron microscope images to determine their surface properties and particle size.

5.2.2 Ceramic membrane filtration process set up

The membrane system has been described in chapter 2. The virgin membrane used in this study was coated 20 times with manganese oxide. The grain size within the support layer and the filtration layer of the virgin membrane varied between 132 nm and 296 nm and between 1.05 and 6.64 nm. The membrane module had a total filtering surface area of 131.9 cm², an active length of 25 cm, and an external diameter of 10 mm. The grain size within the support layer and the filtration layer of the virgin membrane varied between 132 nm and 296 nm and between 1.05 and 6.64 nm ^[32].

5.2.3 Test of the designed water reuse process

The water reuse treatment process included two processes, a batch system for photodegradation by either cadmium sulfide (CdS) or zinc ferrite (ZnFe₂O₄) for organic chemical oxidation and ceramic membrane process. Photodegradation process was designed as an alternative to conventional secondary treatment to degrade caffeine. The ceramic membrane system achieved filtration and the recovery of the photocatalyst for reuse.

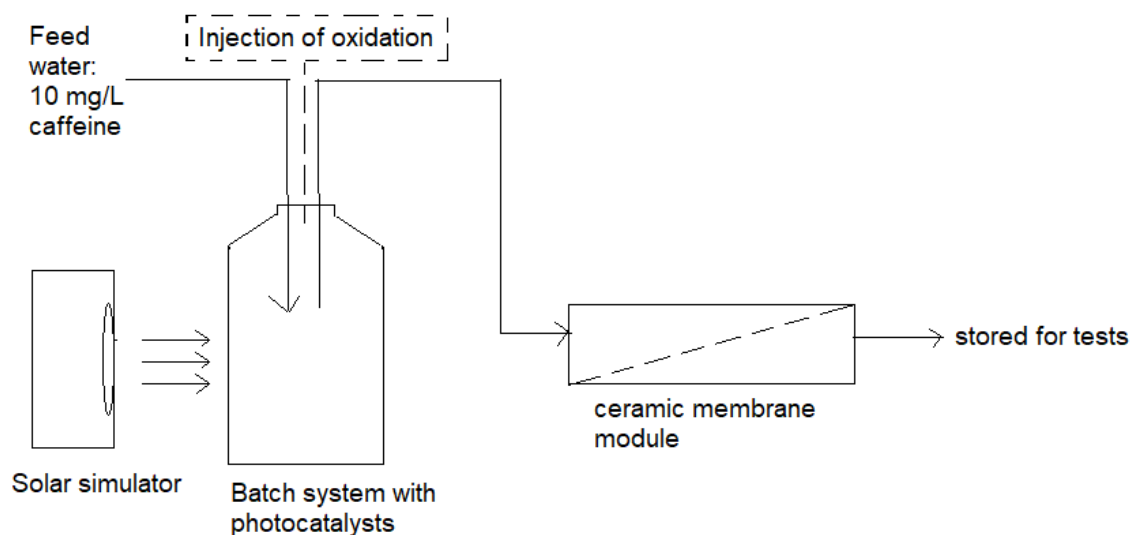
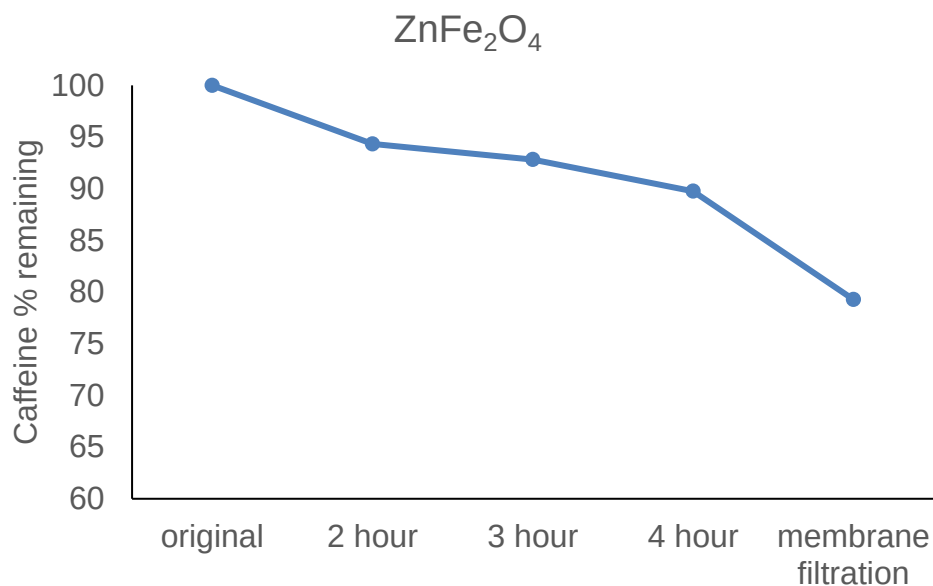


Figure 5.1 Schematic of the proposed water reuse process

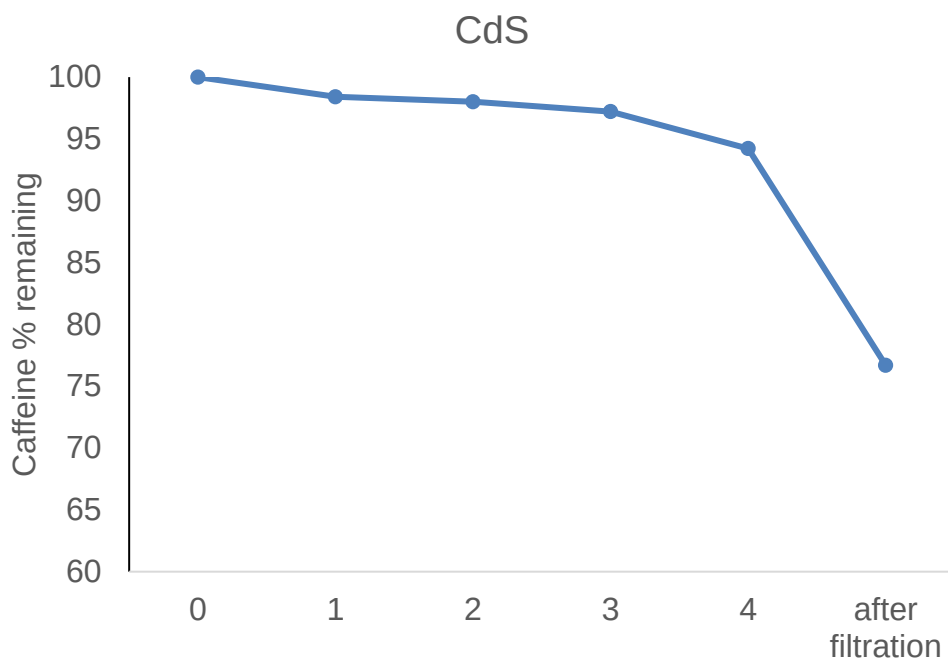
A Pyrex® glass photoreactor containing caffeine about 10 mg/L was used as the photoreactor. A selected amount (0.25 g) of photocatalysts (ZnFe_2O_4 or CdS) were added in the container. The photoreactor was exposed to visible light by using 250 W Xe-lamp with continuous stirring for 4 hours. Water samples were collected at the beginning and end of illumination. After illumination, the water was pumped through a ceramic filter and collected outgoing water samples. At the end of experiment, the water samples were tested by UV-vis to determine the caffeine concentrations.

5.3. Results

The removal efficiency of ZnFe_2O_4 and Cds of the entire designed process is shown in figure 5.1.



(a) Caffeine treatment process using ZnFe_2O_4 as photocatalysts



(b) Caffeine treatment process using ZnFe_2O_4 as photocatalysts

Figure 5.2 Caffeine removal efficiency by designed treatment process with no oxidation during membrane filtration

The results indicated that for ZnFe_2O_4 , about 10% of caffeine was removed at the end of photodegradation, and total process removed 20.73% caffeine. For CdS, 5% of caffeine was removed during photodegradation, and 23.3% at the end of process. For both systems, the turbidity reached about 0.16 NTU after membrane filtration. As a comparison, US EPA regulations require that the turbidity of drinking water be less than or equal to 0.3 NTUs in at least 95 percent of the samples in any month ^[33]. The photodegradation of caffeine was not very effective. The results show that filtration removes more of the caffeine than does photocatalysis, however, the reported removal efficiencies might have been affected by the presence of nanoparticles in the solution, as caffeine concentration was detected by UV-vis spectra. Ozonation has been shown to effectively degrade caffeine in water after 200 s with pH of 10 (90% removal) ^[34]. Pre-ozonation with light illumination is expected to achieve removal efficiency greater than this. Future research on this combination is recommended.

5.4 Conclusions

This study focused on designing an innovative water reuse process using both photodegradation for caffeine oxidation and ceramic membrane filtration. In this designed water reuse process, wastewater from industries containing emerging contaminants could be treated onsite. During photodegradation, caffeine in wastewater was oxidized. Pre-oxidation was recommended to improve caffeine remove efficiency. The effluent from photoreactor was filtered through a 5 kDa ceramic membrane. The experiment results of this designed process showed that both CdS and ZnFe_2O_4 could remove caffeine in feed water. Ceramic membrane could effectively filter nanoparticles from water sample for

future water reuse and catalyst recovery. However, both removal process were not very effective, with only about 20 % removal efficacy for caffeine. For future application, improvements in the photocatalysts are important to improve the organics removal efficiency and achieve a safe and highly efficient water reuse process and save considerable amounts of energy and money.

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CHAPTER SIX

Conclusions and Future Perspective

This research focused on photocatalysis and catalytic ceramic membrane filtration in water and wastewater treatment application. The objectives were to use photodegradation to efficiently oxidize the organics in the wastewater using sunlight as energy source, and to reduce membrane fouling and analyze the energy cost savings in manganese oxide coated catalytic ceramic membrane filtration combined with ozone injection to replace regular membrane filtration.

In ceramic membrane filtration ozonation system, membrane fouling was effectively controlled at ozone dosages of 10 $\mu\text{g/s}$ or greater for the manganese oxide coated membrane. With the virgin membrane, an ozone dosage of at least 15 $\mu\text{g/s}$ was necessary to control membrane fouling. The overall resistance of the manganese oxide membrane was less with manganese oxide coated membrane under same ozone dosage and operation mode compared to that observed for the virgin titania membrane. Using the flux data obtained, it was determined that for the water studied the most energy-efficient operational mode is 10 $\mu\text{g/s}$ ozone dosage, dead-end operation, with the manganese oxide coated membrane.

Based on life-cycle-assessment, pressurization resulted in the majority of energy consumed (62%) in catalytic ceramic membrane filtration with ozonation. Energy consumption for pressurization plus ozone generation consumed 93% of total energy input. Acidification, carcinogenicity and ecotoxicity of pollutants, smog, and climate

change in catalytic ceramic membrane filtration processes had higher environmental impacts in normalization. Ozone injection resulted in 43% of environmental impacts while pressurization with 49%. Catalytic ceramic membrane filtration resulted in less energy consumption of pressurization and backwashing as compared with hollow fiber membrane filtration. Catalytic ceramic membrane filtration had a slightly lower environmental impacts than hollow fiber membrane filtration.

Energy consumption for ozone generation underscores the need for research to develop more efficient methods to generate ozone and to optimize mass transfer. Alternatively, alternative and less energy consumptive methods to reduce membrane fouling would less both energy consumption and environmental impacts of catalytic ceramic membrane filtration, making it clearly favorable over polymeric membrane filtration.

The order of photocatalysis degradation efficacies of methylene blue during illumination was $\text{CdS} > \text{NiFe}_2\text{O}_4 \geq \text{ZnFe}_2\text{O}_4$. CdS had a great absorption range within invisible light spectra, and it was one of the important factor that it had a good photodegradation abilities for methylene blue. It was indicated that the methylene blue removal efficacy could be affected by absorption range of photocatalysts, initial dye concentrations, amount of photocatalysts addition, and photoreactor conditions. Removal efficiency of methylene blue decreased as methylene blue concentration went up, so when designing photodegradation application, it would not only to consider which photocatalyst to be chosen, but also be an important thing to figure out the feed water contaminants concentrations, shapes and sizes of photoreactor, and amounts of nanoparticles added.

When it came to the whole water reuse process, both CdS and ZnFe_2O_4 could remove caffeine in feed water. And ceramic membrane could effectively filtrate nanoparticles from water sample for future water reuse and catalysts recovery. However, both removal process is not very effective, at about 20 % removal efficacy. For future application, improvements and revisions for photocatalysts would be important to improve the organics removal efficiency. It is supposed to reach a higher caffeine removal efficiency to inject ozone or hydrogen peroxide during photodegradation. Research have been conducted on hydrogen production by photocatalysts, future studies could focus on how to use sunlight degradation contaminants while at the same time produce hydrogen as energy source. Due to equipment limitations, collection of hydrogen was not set up. But it is to achieve safe and high efficient water reuse process and save considerable amounts of energy and money.