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THE USE OF OZONATION AND CATALYTIC OZONATION COMBINED WITH ULTRAFILTRATION FOR THE CONTROL OF NATURAL ORGANIC MATTER (NOM) AND DISINFECTION BY-PRODUCTS (DBPS) IN DRINKING WATER

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By

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ABSTRACT

THE USE OF OZONATION AND CATALYTIC OZONATION COMBINED WITH ULTRAFILTRATION FOR THE CONTROL OF NATURAL ORGANIC MATTER (NOM) AND DISINFECTION BY-PRODUCTS (DBPS) IN DRINKING WATER

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Commercially available titania membranes, with a molecular weight cut-off of 15, 5, 1 kD were used in a ozonation/membrane system that was fed with water from Lake Lansing. The effects of ozonation on permeate flux recovery and membrane fouling was investigated. In addition the effects of ozonation/membrane filtration hybrid process on the removal of the natural organic matter (NOM) and the formation of disinfection by-products (DBPs) were monitored. The commercial membrane (CéRAM Inside, Tami North America, St. Laurent, Québec, Canada) was coated with iron oxide nanoparticles (4-6 nm in diameter) using a layer-by-layer technique and sintered in air for 30 minutes. The number of coatings was varied from 20 layers to 60 layers and sintering temperatures of 500 and 900 °C were used. Surface characterization was carried out using electron microscopy techniques and atomic force microscopy, to study the changes in structure and surface morphology of the membranes. The removal and survival of bacteria in the process was also evaluated using fluorescence microscopy and microbial assays. Finally the surface catalytic reaction was investigated to propose the mechanism responsible for the improved performance of the hybrid process in terms of degradation of NOM and the control of disinfection by-products.

The permeate flux through a titania coated ceramic membrane was significantly affected by ozonation and the pH of the feed water in the system; a minimum threshold ozone concentration (2.5 g/m^3) could achieve complete recovery of permeate flux after fouling. Ozonation/filtration resulted in the formation of partially oxidized compounds from NOM that were less reactive with chlorine, decreasing the concentration of simulated distribution system total trihalomethanes (SDS TTHMs) and simulated distribution system halo acetic acids (SDS HAAs) by up to 80% and 65%, respectively. With catalyst coated membranes, the concentration of dissolved organic carbon was reduced by >85% and the concentrations of SDS TTHMs and SDS HAAs decreased by up to 90% and 85%, respectively. With the coated membrane, the concentrations of aldehydes, ketones, and ketoacids in the permeate were reduced by >50% as compared to that obtained with the uncoated membranes, thus reducing the risk of potential regrowth of bacteria in the distribution system. Furthermore, with the hybrid process, greater than 7 log removal of bacteria was achieved. Surface characterization showed that optimum water quality was achieved at 40 layers, which corresponds to a surface coating morphology consisting of a uniform, coarse-grained structure with open, nano-sized interconnected pores. A mechanism is proposed showing strong surface catalytic effect, where ozone first adsorbs on the membrane surface then decomposes resulting in the formation of hydroxyl radicals that degrade NOM and other organic compounds and thus improved the performance of the ozone-membrane filtration hybrid process. Thus we can meet the regulatory requirements for DBPs using a 5 kD membrane, 40 layers, sintered at 900 °C and a gaseous ozone concentration of 2.5 g/m^3.

To my parents, for their love, motivation, support and sacrifice.

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ABBREVIATIONS

2, 3-DHBA	2, 3-Dihydroxy benzoic acid
2, 5-DHBA	2, 5-Dihydroxy benzoic acid
AOC	Assimilable organic carbon
AOPs	Advanced oxidation processes
BDOC	Biodegradable organic carbon
DBPs	Disinfection by-products
DOC	Dissolved organic carbon
HAAs	Haloacetic acids
HS	Humic substances
MF	Microfiltration
MWCO	Molecular weight cutoff
NF	Nanofiltration
NHS	Non-humic substances
NOM	Natural organic matter
RO	Reverse Osmosis
SA	Salicylic acid
SDS HAAs	Simulated distribution system HAAs
SDS THMs	Simulated distribution system THMs
THMs	Trihalomethanes
TOC	Total organic carbon

UF	Ultrafiltration
UV-254	Ultraviolet absorbance measured at 254 nm

CHAPTER ONE

INTRODUCTION

1.1 SIGNIFICANCE

There is an increasing interest in the application of ozone and membrane filtration by water utilities in order to meet the requirements of the Surface Water Treatment Rule (SWTR), the Disinfectant and Disinfection By-Product Rule (D/DBPR), and the Long Term 1 Enhanced Surface Water Treatment Rule (LT1ESWTR) (USA EPA). Collectively, the SWTR, D/DBPR, and LT1ESWTR place stringent treatment requirements on systems using surface water as a source. Membrane processes are considered one of the best available technologies (BAT) for meeting the Stage 2 D/DBP requirements (Arora et al., 1997). Indeed the development of better membranes and the characterization of membrane surfaces along with an increased understanding of membrane fouling make membrane filtration a effective tool in meeting regulatory requirements (Lin et al., 2001; Carroll et al. 2000; Clark et al., 1998). In addition, for systems using conventional and direct filtration, the Filter Backwash Recycling Rule (FBRR) complements the surface water treatment rules by reducing the potential for microbial pathogens, particularly, *Cryptosporidium* oocysts, to pass through the filters into the finished water. These rules reduce the risks of the presence of microbial pathogens in the finished water, thereby providing additional protection to consumers.

Ozone is an effective alternative disinfectant and a more powerful oxidant than chlorine, which is widely used as a disinfectant in the United States. Ozone is capable of decreasing the numbers of microorganisms (Lee and Deininger, 2000) and the concentration of DBP precursors (Yavich, 1998; Cipparone et al., 1997). It also reacts with organic substances and increases their biodegradability (Leiknes et al, 2005; Takeuchi et al. 1997). The use of ozonation in water treatment processes decreases the formation of THMs and halo acetic acids (HAAs) (Zhang et al, 2001; Richardson et al., 1999). The reactions that occur during ozonation produce by-products that are of particular concern due to their mutagenicity and carcinogenicity (Bull and McCabe, 1984). These by-products are easily biodegradable and can serve as substrates for microbial regrowth in the distribution system. These by-products can be easily be removed by biofiltration (Yavich and Masten, 2003; Griffini et al, 1999). In addition, catalytic ozonation would reduce the concentration of ozonation by-products, thereby generating more biologically stable water.

In addition catalytic ozonation is a promising technology for water treatment as it can result in the effective degradation of NOM and other organic compounds that serve as DBPs precursors (Legube and Karpel Vel Leitner, 1999). Based on extensive research involving various ozonation methods for drinking water treatment, catalytic ozonation has been determined to be the best alternative for the oxidation of ozone by-products to carbon dioxide, and the reduction in the chlorine demand (Volk et al., 1997; Alleman et al., 1993). Ceramic membranes are ozone resistant and when combined with ozonation, generate very high and stable permeate fluxes without membrane damage (Schlichter et al., 2004; Kim et al., 2001; Kim et al., 1999). Also, it has been found when metal or metal oxide catalysts are used as the support for ceramic membranes the degradation of NOM by ozone results (Ernst et al., 2004). Ozone in the presence of different metal oxide catalysts, including manganese oxide, titania, alumina, and zirconia, degrades refractory compounds, including saturated carboxylic acids, phenols, aromatic hydrocarbons, dyes, humic substances and herbicides (Beltran et al., 2003a, 2003b; Ni and Chen, 2001; Radhakrishnan and Oyama, 2001; Gracia et al., 1996, 2000a, 2000b; Legube and Karpel Vel Leitner, 1999). Thus, catalyst coated ceramic membranes will enhance degradation of NOM and improve the quality of the treated water. Also, these membranes are expected to result in further deceases in the concentration of DBPs than achievable with ozone. This process further facilitates the inactivation and complete removal of pathogens and microorganisms. Thus, the proposed ozone-membrane filtration process combines the advantages of ozonation and membrane filtration to produce water meeting required regulatory standards. In addition, the optimum ozone doses evaluated will reduce membrane fouling and maintain stable permeate fluxes without membrane damage.

1.2 OBJECTIVES

The objective of this research is to determine the feasibility of using a combined ozonation and membrane filtration system to control disinfection by-products (DBPs) precursors in drinking water treatment process. Commercially available ceramic membranes and ceramic membranes coated with a nano-crystalline catalyst like iron oxide colloidal particles, that decompose ozone will be used in the study.

In particular this study will try to attain the following four objectives:

1. To determine the effect of ozonation on the permeate flux of the nano-crystalline ceramic membranes.
2. To investigate the effects of combined ozonation and membrane filtration on disinfection by-product formation in drinking water treatment systems.

3. To develop ceramic membranes coated with catalytic metal oxide nanoparticles and to study the effect of catalytic ozonation and membrane filtration on the formation of disinfection by-products.
4. To study the removal and survival of bacteria with treatment using the catalyzed ozonation–membrane filtration hybrid process.

1.3 HYPOTHESES

The following hypotheses of this proposed ozonation-membrane filtration will be tested:

1. The combined ozonation-membrane filtration can maintain stable permeate flux and extend the operation period.
2. The reaction of ·OH radicals generated at the surface with natural organic matter (NOM) sorbed on the ceramic membrane surface will reduce membrane fouling and will result in better water quality.
3. The molecular ozone and ·OH radical reactions in the bulk water and on the ceramic membrane surface will cause a reduction in the UV-254 absorbance, dissolved organic carbon and result in the conversion of the humic substances to non-humic substances.
4. The ozonation will further reduce the chlorine demand and result in a decrease in the disinfection by-product formation.
5. Conventional sol-gel and sintering methods can produce coated membranes with the desired molecular weight cut-off (MWCO), permeability and favorable catalytic properties.
6. The use of a metal oxide, such as iron oxide, for coating of ceramic membranes will enhance ozone decomposition as a result of changes in the surface morphology,

which enhance the formation of the ·OH radicals and other reactive species at the membrane surface, thereby further improving the water quality and degrading NOM and reducing the formation of DBPs.

7. The metal oxide further facilitates the sorption or catalytic oxidation of ozonation by-products such as aldehydes, ketones, ketoacids on the catalytic coated surfaces, thus the concentration of these compounds in the treated water is very low. This results in water that is biologically stable water with low concentrations of biodegradable organic carbon.
8. The catalytic ozonation-nanofiltration will produce biologically stable water, which will further result in the reduced regrowth potential of bacteria; also the iron-oxide coating traps the bacteria by sorption or filtration. As such, the combined effect of these processes will produce water free of bacteria.

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CHAPTER TWO

LITERATURE REVIEW

Present and future regulations concerning drinking water quality necessitates the use of new techniques over conventional water treatment processes, including prechlorination, coagulation/ flocculation, sedimentation, rapid sand filtration, disinfection and biological treatment, to meet the increasing stringent regulations of Surface Water Treatment Rule (SWTR), Interim Enhanced Surface Water Treatment Rule (IESWTR) and Disinfectants/Disinfectant By Product Rule (D/DBPR) which have together introduced tighter limits on turbidity and particle removal requirements, with additional microorganism removal and limits on disinfectants and disinfections by-product formed in the process.

2.1 MEMBRANE FILTRATION

Membrane filtration is considered to be one of the best available technologies to meet these regulations (Arora et al., 1997). Membrane filtration i) serves as an absolute barrier to suspended particulate matter and pathogens; ii) provides treatment and disinfection without supplemental chemical addition beyond ozone; iii) provides consistent filtered water quality irrespective of the feed water; iv) results in the formation of minimal amounts of chemical sludge and, therefore, minimizes residual disposal costs; v) is simple, reliable, and can be easily automated; and vi) offers a compact modular construction (Cleveland 1999; Nakatsuka et al., 1996; Rachwal 1995). Pressure driven membrane processes, including microfiltration (MF), ultrafiltration (UF), nanofiltration

(NF) and reverse osmosis (RO), are among the most promising new techniques for the treatment of water and waster water treatment processes. (Bruggen et al., 2003; Cleveland, 1999). UF and MF can be used in combination with traditional treatment or as a partial replacement of traditional methods including prechlorination, coagulation/flocculation, sedimentation, rapid sand filtration, disinfection and biological treatment to meet the increasing stringent regulations. MF can be used for the removal of colloidal particles, microorganisms and other particulate material, so it can serve as a pretreatment to UF or in combination with traditional treatment methods (Mavrov et al., 1998). UF allows for the efficient removal of suspended particles and colloids, turbidity, algae, bacteria, parasites and viruses for clarification and disinfection purposes, but must be preceded by effective particulate removal using coagulation/sedimentation or MF. The current trend in water treatment is to use UF rather than MF as a single treatment option or to use UF in combination with other treatment processes because UF is more efficient at removing viruses, and also are less prone to fouling by fine particles than MF (Guigui, C. et al., 2002). Researchers found that the combination of membrane filtration with other treatment options, such as coagulation, adsorption, oxidation, and biological treatment, enhances the efficacy of the treatment system, produces higher quality water, and improves system performance as compared to the operation of membrane filtration alone (Freeman et al., 2002; Lai et al., 2002; Westrell et al., 2002; Ødegaard et al., 1986).

Several researchers demonstrated the efficacy of membrane filtration for effective removal of natural organic matter (NOM) and disinfection by-product (DBPs) precursors (Jacangelo 1995; Laîné et al., 1993). Thompson (2001) demonstrated the use of UF membranes as an effective barrier to microorganisms and organic matter in highly turbid surface water sources with minimal pre-treatment and pre-filtration requirements. Siddiqui et al. (2000) found that NF was very effective at removing DBPs from low turbidity surface water when compared to MF and UF. Similar results were reported by Mijatović and collegues (2004) who showed that NF should be used, rather than UF, for the removal of NOM from lake water or to improve the quality of conventionally treated water because most of the organic molecules had relatively low molecular weight and cannot be separated by UF alone. Karakulski et al. (2001) reported that over 80% of total trihalomethanes (TTHMs) were retained on the RO membranes. Some of the researchers found that the efficiency of organic matter removal was around 99% of the total organic carbon (TOC) on the ceramic membrane and 90% of the TOC on the polymeric membrane used in these studies (Klomfas and Konieczny, 2004; Konieczny et al., 2002; Adham et al., 1993, 1991). The UF hybrid process achieved the removal of DBP precursors and dissolved organic materials, humic materials, fulvic acids and hence reduced the formation of DBPs (Ngo et al., 2000; Jacangelo et al., 1995). UF is the preferred option for NOM and DBP removal due to its fairly low pressure and high permeate flux in comparison to NF and RO (Bruggen et al., 2003).

Until the recent decade, it was not feasible to use membrane technology for the production of drinking water because of economic constraints and problems related to fouling (Cho et al., 2002; Lee et al., 2001). One of the major challenges associated with the operation of membrane filtration plants is the decrease in the permeate flux due to membrane fouling (Siedel and Elimelech, 2002; US EPA, 2001; Crozes et al., 1997). The deposition of NOM on the filter surface is a primary cause of membrane fouling (Fan et al., 2001; Lee et al., 2001; Nilson and DiGiano, 1996; Ravindran et al., 1993). Fouling not only reduces the efficiency of the membrane, but the characteristics of the foulants also control the rejection of other substances by the membrane (Schafer et al., 2000). In drinking water natural organic matter is a major reason for membrane fouling (Fan et al., 2001; Lee et al., 2001; Carroll et al., 2000; Nilson and Digiano et al., 1997). Fouling can be controlled either by preventing the particles from reaching the membrane and resulting in cake formation or by flushing them out using pretreatment options (Milisic, 1986). Another option for the removal of organic compounds is the addition of powdered activated carbon (PAC) which reduces irreversible fouling regardless of membrane hydrophobicity (Laîné et al., 1993).

Several researchers have showed that the permeability rates of ceramic membranes are superior to the permeability rates of polymeric membranes and are more effective for the treatment of textile waste water, alkaline and acidic solutions (Weber et al., 2003). Lee and Cho (2004) compared ceramic membranes with polymeric membranes for the removal of NOM and found that a tight-ultrafiltration ceramic membrane showed the same potential as a similar nanofiltration polymeric membrane in terms of reducing the formation of haloacetic acid formation, and was comparable for the removal of NOM to polymeric membranes with similar molecular weight cut-off (MWCO). The higher chemical, mechanical and thermal stability of the ceramic membranes over polymeric membranes is increasing their popularity for filtration applications (Benfer et al. 2004).

2.2 OZONATION

Ozone (O_3) is a strong and powerful oxidant that preferentially oxidizes electron-rich moieties containing carbon-carbon double bonds and aromatic alcohols (Bablon et al., 1991). It oxidizes the naturally occurring organic matter (NOM) that is believed to be largely responsible for the fouling of membranes (Yavich et al., 2004). The reaction with ozone can be either direct reaction with molecular ozone or indirect one with the hydroxyl radicals formed by the decomposition of ozone in water at elevated pH (Bablon *et al.*, 1991). The decomposition reactions are catalyzed by hydroxide ions and NOM, where OH radicals reacts to dissolved organic compound and accelerate decomposition of ozone (Bablon et al., 1991; Staehelin and Hoigné, 1985). The reaction between OH^- ions and ozone lead to the formation of super-oxide anion radical $O_2^{\bullet -}$ and hydroperoxyl radical $HO_2^{\bullet}$. Reaction between ozone and super oxide anion radical results in the formation of the ozonide anion radical ($O_3^{\bullet -}$), which decomposes immediately, giving rise to the $^{\bullet}$OH radical (Acero *et al.*, 1999).

The overall reaction being,

$$3O_3 + OH^- + H^+ \rightarrow 2^{\bullet}OH + 4O_2$$

The bicarbonate and carbonate play an important role as scavengers of $^{\bullet}$OH radicals in the natural systems. The products of reaction between $^{\bullet}$OH radical and carbonate or bicarbonate ions are passive carbonate or bicarbonate radicals which do not interact further with ozone or organic compounds (Acero *et al.*, 1999).

The $^{\bullet}$OH radical reactions can bring about mineralization of the natural organic water, reducing the concentration of TOC and hence that of the DBPs precursors. It is a well known fact that the addition of a strong oxidant such as ozone or hydrogen peroxide (H_2O_2) to water containing humic substances can bring about decolorization of that water and the degradation of organic matter. The concentration of UV absorbing organic compounds decreased following ozonation. The dissolved organic carbon content was also reduced following ozonation (Schlichter et al., 2004; Hashino et al., 2000; Koechling et al., 1996; Shukairy et al., 1994; Amy et al., 1988; Ødegaard et al., 1986). Also replacing chlorination with ozonation can significantly reduce the concentration of some of the DBP precursors and the overall DBP-formation potential (Guay, 2005; Schlichter et al., 2004; Chang et al., 2002; Hu et al., 1999). The permeate flux was also seen to increase with increase in ozone concentration (Schlichter et al., 2004; Park, 2002). Ma (1999) showed that the pre-ozonation of the water reduced the formation of the DBPs as a result of the conversion of the hydrophobic groups contained in the humic acid to hydrophilic ones.

The ozonation of water containing organic compounds and humic substances results in formation of ozonation by-products including formaldehyde, aldehydes, ketones, ketoacids and carboxylic acids (Gracia et al., 1996; Glaze et al., 1989). These biodegradable compounds can cause problem of microbial regrowth in the distribution network. Some of the aldehydes like formaldehyde, acetaldehyde are of particular concern after being identified as carcinogenic and mutagenic in nature (Richardson, 1998).

2.3 CATALYTIC OZONATION

Another way to accelerate ozonation reaction is use of catalysts. Several metal oxides and ions have been studied and significant decomposition of targeted compound is reported. The dissolved ozone is adsorbed on the catalyst surface, where it decomposes to form $^{\bullet}OH$ radicals. The refractory character of some of the organic pollutants, such as dyes, phenols, chlorinated hydrocarbons, pesticides and herbicides, humic substances and the limited oxidation of the by-products formed, necessitates a more thorough oxidation by the generation of hydroxyl radicals, using advanced oxidation processes.

The use of catalytic ozone resulted in significant decrease in the concentrations of TOC and COD (Acero et al., 1999; Legube *et al.*, 1999; Paillard *et al.*, 1991). Several studies showed that catalytic ozonation results in the complete degradation of such compounds as salicylic acid, which are only very slowly oxidized by molecular ozone (Legube *et al.*, 1999; Paillard *et al.*, 1991). In the presence of different metal oxide catalysts, such as iron oxide, manganese oxide, titania, alumina and zirconia, ozone degrades organic compounds, including saturated carboxylic acids, phenols, aromatic hydrocarbons, dyes, humic substances and herbicides (Trapido et al., 2005; Ernst at al., 2004, Beltran et al., 2003a, 2003b; Ni and Chen 2001; Radhakrishnan and Oyama 2001; Gracia et al., 2000a, 2000b, 1996). Masten and Davies (1997) reported that the presence of reactive soil surfaces catalyzed the decomposition of ozone and contaminants sorbed on the soil. Paillard et al. (1991) reported that TiO_2-catalyzed ozonation was more efficient than ozone alone for the degradation of humic acid. Pines and Reckhow (2003) showed that ozonation using metal oxides, such as titanium dioxide, cobalt oxide, nickel oxide, copper oxide and mixed metal oxide of these compounds, was very effective for the destruction of recalcitrant micropollutants in water as a result of hydroxyl radical reactions. Beltran et al. (2005) demonstrated that the use of catalytic ozonation with homogeneous Fe (III) and heterogeneous (Fe_2O_3/Al_2O_3) led to total mineralization of oxalic acid. Similarly Park et al. (2004) showed removal of para-chlorobenzoic acid using iron type catalyst in combination with ozonation. Huang et al. (2005) showed that the combined use of ozone and ZnO catalyst generated hydroxyl radicals during the oxidation process, leading to effective degradation of trichlorophenol in water.

2.4 OZONATION-MEMBRANE FILTRATION

Several researchers have attempted to combine ozone with polymeric membranes with little success. As ozone is a powerful oxidant, polymeric membranes are prone to destruction by the ozone (Hashino et al., 2000; Shanbag et al., 1998; Castro and Zander 1995; Shen et al., 1995). Ceramic membranes are ozone resistant and have been shown to maintain stable permeate fluxes without membrane damage (Schlichter et al., 2004; Kim et al., 2001, 1999; Allemane, 1993). When attempts were made to combine ceramic membranes with ozone filtration, researchers found this hybrid process to be more efficient in eliminating DBPs and other organic contaminants in raw water, without membrane damage (Schlichter, 2004; Shioyama et al., 2001). Sawada et al. (2001) observed that ozonation of the water prior to filtration, resulted in the decomposition of organic matter by the residual ozone in the membrane filtrate, making the organic matter easily detachable, resulting in a suppression of fouling (Sawada et al., 2001).

The oxidation/membrane filtration leads to an elimination of mineral compounds, color, turbidity and suspended solids, bad tastes and odors, in addition to the degradation of natural organic matter, the degradation of toxic micropollutants, the elimination of trihalomethane precursors, an increase in the biostability of water and the deactivation of microorganisms (Camel *et al.*, 1998). The ozonation of water containing humic substances results in the formation of hydroxyl, carbonyl, and carboxyl groups, and aliphatic and alicyclic ketones (Glaze et al., 1989). Ozonation / membrane filtration can effectively remove these biodegradable compounds generating biostable water and also controlling NOM induced fouling (Leiknes et al., 2005).

2.5 REFERENCES

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CHAPTER THREE

Karnik, Bhavana.S., Davies, Simon.H., Chen, Kuang.C., Jaglowski, Dan.R., Baumann, Melissa.J. and Masten, Susan.J., (2005). Effects of ozonation and pH on the permeate flux of nanocrystalline ceramic membranes. Water Research, 39(4): 728-734.

CHAPTER THREE

EFFECTS OF OZONATION ON THE PERMEATE FLUX OF NANOCRYSTALLINE CERAMIC MEMBRANES.

3.1 ABSTRACT

Titania membranes, with a molecular weight cut-off of 15 kD were used in a ozonation/membrane system that was fed with water from Lake Lansing, which had been pre-filtered through a 0.45 μm glass fiber filter. The application of ozone gas prior to filtration resulted in significant decreases in membrane fouling. The effects of ozonation could not be explained by physical scouring of the filter cake. Decreases in the pH resulted in a concomitant increase in the dissolved ozone concentration in the feed water and in an improvement in permeate flux recovery. Increasing the ozone concentration beyond a threshold value had no beneficial effect on permeate flux recovery. Ozone decomposition, resulting in the formation of ·OH or other radicals at the membrane surface, is thought to result in the decomposition of organic foulants at the membrane surface and reduce the extent of membrane fouling.

Keywords: ceramic membranes; membrane filtration; ozonation; permeate flux; fouling.

3.2 INTRODUCTION

Membrane filtration is an effective method to remove particles, microorganisms and organic matter from drinking waters. Compared to conventional treatment methods, membrane processes i) can provide higher quality water, ii) minimize disinfectant demand, iii) are more compact, iv) provide easier operational control and less maintenance, and v) generate less sludge (Cleveland, 1999; Nakatsuka et al., 1996).

One of the major challenges associated with the operation of membrane filtration plants is an increase in the operational cost as a result of the decrease in the permeate flux due to membrane fouling (Siedel and Elimelech, 2002; US EPA, 2001; Crozes et al., 1997). It is important to enhance membrane performance, so that these systems can become more affordable and reliable.

As ozone has been employed for the intermittent cleaning of membranes in chemical processing (Kim et al., 1999), it could also be used for membrane cleaning in drinking water treatment applications. Ozone is a powerful oxidant that preferentially oxidizes electron-rich moieties containing carbon-carbon double bonds and aromatic alcohols (Bablon et al., 1991). It oxidizes the naturally occurring organic matter (NOM) that is believed to be largely responsible for the fouling of membranes (Yavich et al., 2004). However, few researchers have investigated the combination of ozonation and membrane processes. This is most likely because polymeric membranes, commonly used in the water industry, are prone to destruction by ozone (Hashino et al., 2000; Shanbhag et al., 1998; Castro et al., 1995; Shen et al., 1990). Ceramic membranes, which are ozone-resistant, in combination with ozonation achieved a high permeate flux without membrane damage (Schlichter et al., 2004; Chen, 2003; Kim and Somiya, 2001; Bablon et al., 1991). In addition, intermittent ozonation is effective in preventing membrane fouling caused by particle accumulation on the membrane surface (Kim and Somiya, 2001; Verberk et al., 2001; Klijn et al., 2000; Laborie et al., 1998; Laborie et al., 1997; Cui and Wright, 1994; Bablon et al., 1991; Moulin et al., 1991). Most commercial ceramic membranes are fabricated from metal oxides, such as titania, alumina and zirconia. These metal oxides are known to promote ozone decomposition and the formation of ·OH or other radicals (Gracia et al., 2000a; Gracia et al., 2000b; Legube and Vel Leitner, 1999; Gracia et al., 1996). Therefore, the reaction of ozone on the membrane surface is likely to facilitate the removal of organic foulants.

In this work we have considered the effects of ozone gas concentration and pH on the permeate flux using continuous and pulsed ozonation with membrane filtration. The effect of scouring on the permeate flux was also studied.

3.3 MATERIALS AND METHODS

3.3.1 Membrane Filtration System

The ozone-membrane filtration system used in these experiments is illustrated in Figure 3.1. Tubular ceramic membranes (Clover-leaf (three channels) design, CéRAM Inside, Tami North America, St. Laurent, Québec, Canada) with a molecular weight cut-off 15 kD were used. Teflon tubing, stainless steel joints and stainless steel valves were used throughout the system. Other components included: 3.5-liter and 1.5-liter water-jacked glass reservoirs made of Pyrex glass, and a simple Y inline mixer (Ozone Service, Burton, B.C., Canada). The external diameter of each titania membrane was 10 mm and the active length was 25 cm. The filter had a total filtering area of 41.2 cm^2. The membranes can be operated in the pH range, from 0-14.

Pure oxygen gas from a gas cylinder was dried using a molecular sieve trap, and then fed to the ozone generator (Model OZ2PCS, Ozotech Inc., Yreka, Calif.). The gaseous ozone concentration was controlled by varying the voltage applied to the ozone generator. The excess ozone gas was vented by passing the gas through a 2% potassium iodide (KI) solution to destroy any residual ozone gas. A constant temperature was maintained during the experiment using the external refrigerating and heating bath circulator (NESLAB RTE-10, Thermo Electron Corp). The transmembrane pressure for the system was fixed at a value of approximately 0.17 bar to prevent degasification in the 3.5 L reservoir tank.

3.3.2 Water Source

Experiments were carried out using samples taken from Lake Lansing (Haslett, MI). Lake Lansing is a borderline eutrophic lake. The typical characteristics of the Lake Lansing waters are shown in Table 3.1. The samples were collected at the boat ramp at the Lake Lansing Park-South, Haslett, Michigan in five-gallon carboys and stored at 4°C. The maximum storage period was seven days. Water samples were pre-filtered through a 0.45-µm mixed cellulose ester (Millipore-HA) filters before testing.

Table 3.1
Typical Characteristics of Lake Lansing Water (Haslett, MI) [a]

Parameters	**Lake Lansing**
TOC (mg/L)	8.6 to 11.6
pH	7.7 to 8.6
Alkalinity (mg/L as $CaCO_3$)	145 to 157
UV-254 (abs.)	0.160 to 0.180
SDS THM[b] (µg/L)	240
SDS HAA[b] (µg/L)	75
BDOC (mg/L)	1.0 to 4.1
Nitrate (mg/L)	0.44
Total Phosphate (mg/L)	0.06
Hardness (mg/L as $CaCO_3$)	190 to 198

[a] *All data reported is obtained Lake Lansing Watershed Advisory Committee Report(1998) except for SDS THM and SDS HAA, which were measured as part of this study*

[b] *SDS THM and SDS HAA were measured using Standard Method 5710 and USEPA Method 552.2 respectively.*

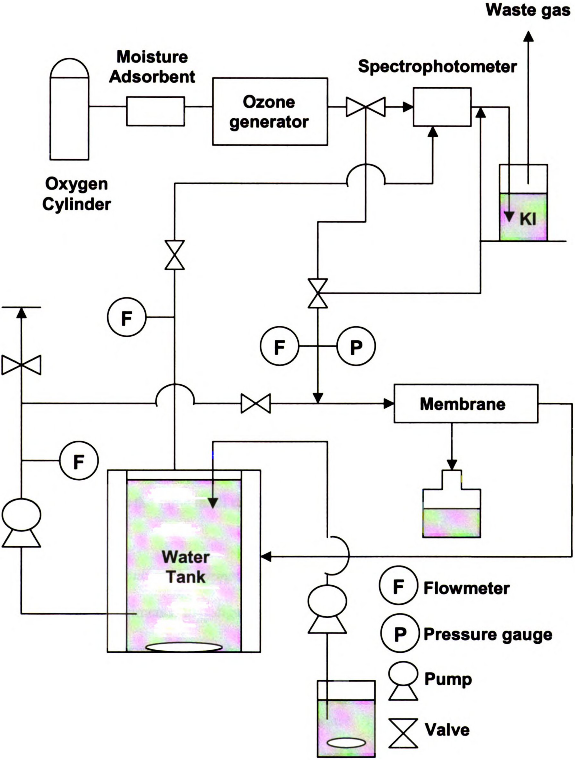

Figure 3.1 Schematic Representation of the Ozone-Membrane Filtration System

3.3.3 Gas-phase Ozone Analysis

The concentration of ozone in gas phase was measured at a wavelength of 254 nm with a Milton Roy Genesis-5 spectrophotometer (Milton Roy, Inc., Rochester, NY) using a 2-mm quartz flow-through cell. An extinction coefficient of 3000 $M^{-1}cm^{-1}$ at 254 nm (Hoigné, 1988) was used to calculate the ozone concentration.

3.3.4 Membrane cleaning and preparation

Prior to each experiment the membrane was thoroughly cleaned by soaking the membrane in a sodium hydroxide solution (15 g/L) at 85°C for 30 minutes; following this, the membrane was rinsed with distilled deionized (DDI) water. Then the membrane was soaked in a nitric acid solution (0.1M) at 50°C for another 30 minutes followed by thorough rinsing with DDI water. Finally the membrane was steam sterilized at 121°C for 30 minutes. The effectiveness of the cleaning procedure was verified by measuring the permeate flux through the membranes using DDI water to ensure that the initial membrane flux was the same in all experiments.

3.3.5 Experiments

3.3.5.1 Effect of ozone on the permeate flux

For the experiments investigating permeate flux recovery, a centrifugal pump (Model 4RH12, Dayton Electric Mfg. Co., Niles, Illinois) was used to circulate water from the 3.5-liter water reservoir through the membrane module. A magnetic stirrer at the bottom of the reservoir was used to mix the water. The permeate flux was monitored by measuring the volume of the permeate in a graduated cylinder over specified time intervals. A peristaltic pump (Masterflex Model 7520-35, Cole-Parmer Co., Chicago, Illinois) was used to pump the water from the 1.5-liter water tank into the 3.5-liter water reservoir to maintain the constant volume of water in the larger reservoir. The operating conditions used are listed in Table 3.2. The system was operated without ozone injection until the permeate flux decreased to 60% of the initial flux. At this time, ozone gas was injected through the Y inline mixer into the feed water stream of the membrane module.

Table 3.2
Operating Conditions for the Ozone–Membrane Filtration System

Water source	**Lake Lansing (Haslett, MI)**
Water flow rate	2.75 LPM
Water temperature	20°C
Ozone gas flow rate	100 mL/min
TMP	0.17 bar

The experiment was repeated for different ozone gas concentrations (1, 1.5, 2.5, 5 and 12.5 g/m^3). Also, the experiment was repeated with pulsed ozonation, wherein the ozone gas was introduced for period of one minute every five minutes.

3.3.5.2 Effect of scouring on the permeate flux

The recovery in the permeate flux after ozonation could result from the reaction of ozone with the NOM in the filter cake/gel layer or it could be due to the dislodging of the cake/gel as a result of the turbulence caused by the ozone/oxygen bubbles. To determine the effect of turbulence induced by gas bubbles, the distance between inline Y-mixer and the membrane module was increased from 10 cm to 50 cm and the decline in permeate flux was studied. The operating conditions were maintained as in Table 2. Experiments were conducted using gaseous ozone concentrations of 12.5, 5.0, 2.5, and 1.5 g/m^3. An experiment was also conducted using pure oxygen.

3.3.5.3 Effect of the feed water pH on the permeate flux

The decomposition of ozone in solution to form ·OH radicals is highly pH dependent (Masten and Davies, 1994). In order to study the effect of pH on permeate flux recovery, the natural pH of the Lake Lansing water was reduced using concentrated hydrochloric acid and the permeate flux recovery was investigated using a gaseous ozone concentration of 1.5 g/m^3, the minimum ozone concentration shown to achieve permeate flux recovery in previous experiments. The other operating conditions are listed in Table 2. The permeate flux was measured at pH values of 4.0, 6.0, 7.0 and at the natural pH of the feed water. The system was operated with continuous ozonation.

3.4 RESULTS AND DISCUSSION

3.4.1 Effect of ozone on the permeate flux

The trends in the permeate flux during 12 hours of filtration are shown in Figure 3.2. As a result of membrane fouling, the permeate flux decreased to about 60 % of its initial value within 12 hours of operation. After this time, ozonation was begun and continued for 2 hours. When ozone was applied to the system, the permeate flux recovered to approximately 95% of the initial permeate flux within a period of 30 to 40 minutes. Figure 3.3 shows the effect of ozone dosage on fouling. The permeate flux recovered to 100% following ozonation at an ozone concentration of 12.5 g/m^3 and 5 g/m^3. The reduction in the ozone concentration from 12.5 to 5.0 g/m^3 had no significant difference in the final permeate flux ($p>0.05$). However, when the ozone gas concentration was further reduced to 2.5 g/m^3 there was a significant decrease in permeate flux to about 90% of the initial value ($p< 0.05$). No permeate flux recovery was observed at an ozone concentration of 1.0 g/m^3. When the permeate flux recovery experiment was repeated for an ozone concentration of 1.5 g/m^3, differences in the permeate flux recovery were statistically insignificant from that obtained at an ozone concentration of 2.5 g/m^3 (*p*> *0.05)*. Thus, a minimum threshold ozone concentration is required to obtain a permeate recovery; the greater the ozone concentration, the greater the permeate flux. However, beyond a certain ozone gas concentration, further increases in ozone concentration do not affect the permeate flux (as the flux is essentially equivalent to the permeate flux achieved with pure water).

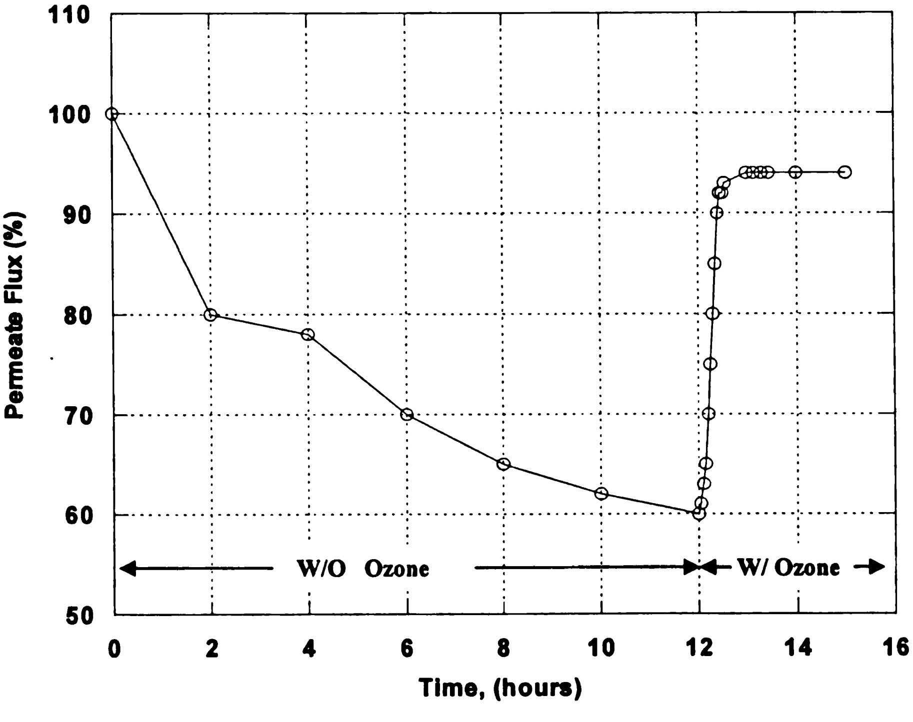

Figure 3.2 Permeate Flux Recovery Pattern with Ozonation.
(Operating Conditions: Table 3. 2, Initial Specific flux 153L/m^{2}h-bar, pH 8.2, Gaseous ozone concentration 12.5 g/m^3).

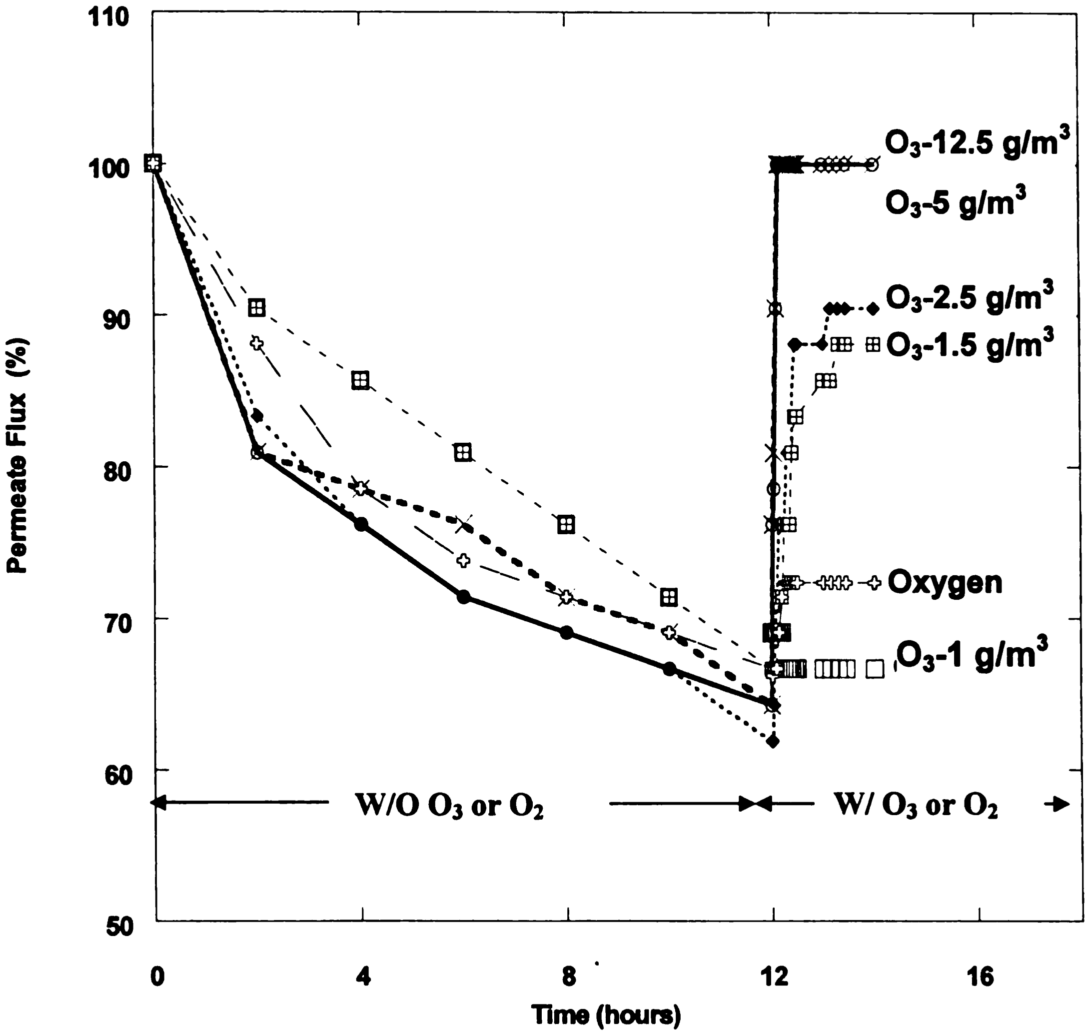

Figure 3.3 Effect of Ozone or Oxygen on Permeate Flux Recovery
(Experimental setup: Fig. 3.1. Operating Conditions: Table 3.2).
Initial Specific flux 153L/m²h-bar, pH 8.2.)

When the experiment was performed by introducing pure oxygen at operating conditions in Table 3.2, after 12 hours of operation, the permeate flux was only 72% of the initial value (see Figure 3.3); also the extent of permeate flux did not improve significantly under continuous oxygenation, resulting in a final recovery of only 76%. The results shown in Figure 3.4, which compare continuous oxygenation and continuous ozonation, suggest that the permeate recovery is largely due to the reaction of NOM with ozone and/or ·OH (or other) radicals, presumably due to a reduction in the thickness and/or resistance of the filter cake formed during filtration. An experiment was conducted to compare the results under continuous and pulsed ozonation. As shown in Figure 3.5, when ozone gas was injected into the system for two hours in pulses lasting one minute at an interval of five minutes and when ozone was injected continuously for 2 hours, the results were similar. This shows that continuous rather than intermittent ozonation could possibly be used in full-scale operations. This could result in considerable savings in capital and operating costs.

3.4.2 Effect of scouring on the permeate flux of the nanofiltration ceramic membrane

Increasing the distance between the Y inline mixer and the membrane module did not result in any measurable change in the steady state permeate flux. As shown in Figure 3.5, there is no significant difference in the permeate flux when the in-line mixer was placed 50 cm from the membrane module (no scouring) and when it was placed 10 cm from the membrane module (scouring). Increasing the distance between the mixer and the inlet would have reduced the

turbulence effects at the membrane interface. As the permeate flux was not affected by this change, it appears that the flux recovery is largely due to the reactions of ozone and/or ·OH radicals with the NOM, rather than the dislodging of the filter cake due to the increased turbulence created by gas bubbles in the feed water.

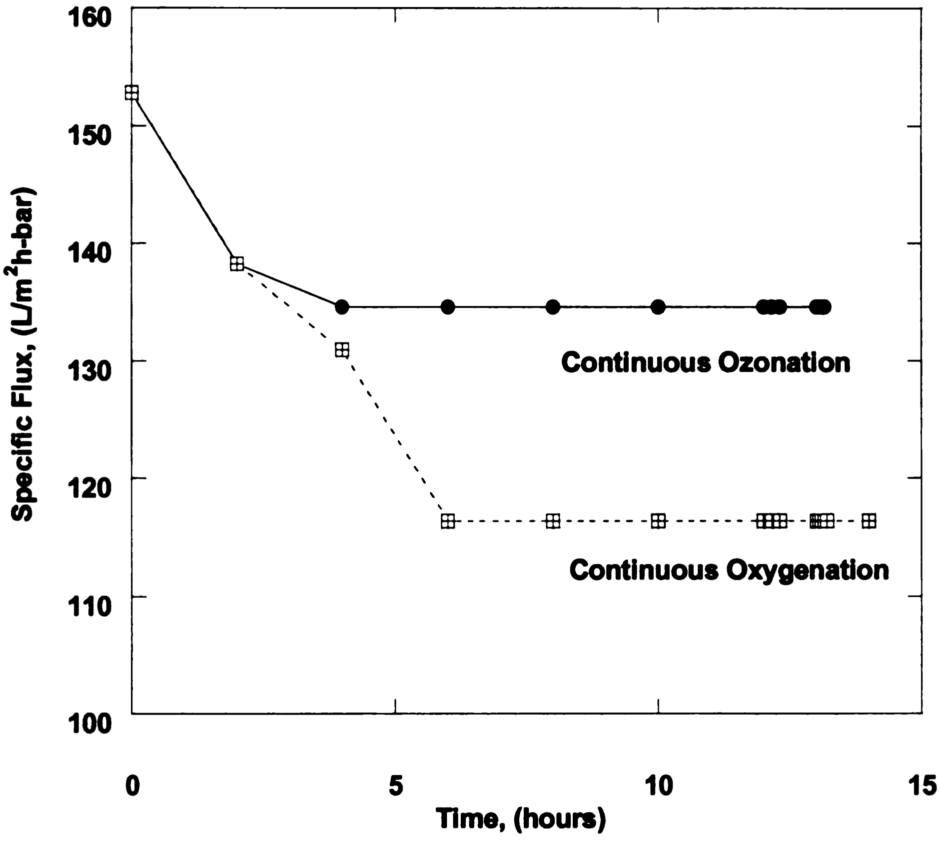

Figure 3.4 Effect of Continuous Ozone or Oxygen on Permeate Flux Recovery
(Experimental setup: Fig. 3.1. Operating Conditions: Table 3. 2.
Continuous Ozonation (Ozone gas concentration 1.5 g/m^3) and Continuous Oxygenation, Initial Specific flux 153L/m^{2}h-bar, pH 8.2.)

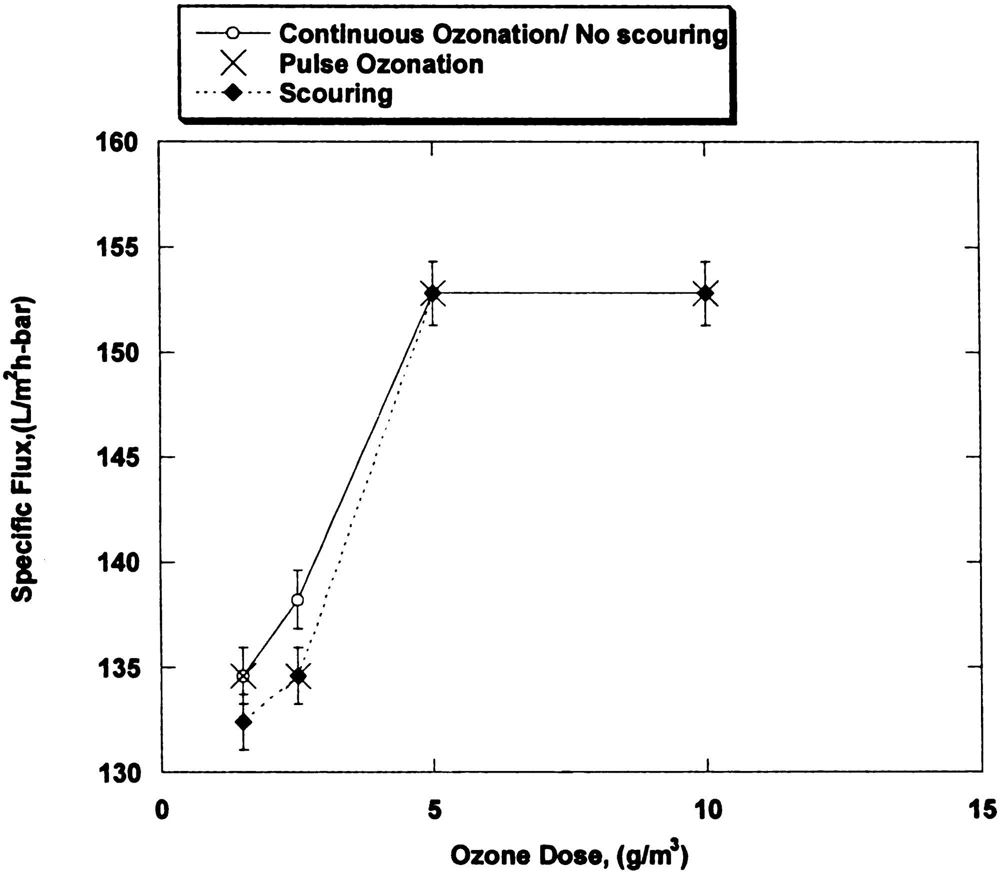

Figure 3.5 Effect of Ozone on Permeate Flux Recovery under different conditions

(Experimental setup: Fig. 3.1. Operating Conditions: Table 3.2. Continuous ozonation/No Scouring: ozone concentrations of 12, 5, 2.5, 1.5 g/m^3 used after12 hours operation, Pulsed Ozonation: Pulse of ozone lasting 1 minute at frequency of very 5 minutes, ozone concentration 12, 5, 2.5, 1.5 g/m^3 after12 hours operation and Scouring-increase distance between Y-line mixer and

3.4.3 Effect of the feed water pH on the permeate flux

The effects of pH of the feed water on permeate flux recovery are shown in Figure 6. Unlike experiments discussed earlier, in these experiments, the filter was not fouled before ozonation was commenced. At the natural pH of the water (pH 7.9) no dissolved ozone was detected in the feed water, although ozone was supplied at a concentration of 1.5 g/m^3. Over the first eight hours of operation, the permeate flux decreased to approximately 79% of the initial flow (Figure 3.6). After 8 hours of operation, the permeate flux began to recover and reached a steady state value that was 84% of the initial flux. Similar results occurred at pH 7.0; again the flux decreased in first eight hours of operation to approximately 80% of the initial flux. As observed when the pH was 7.9, the specific flux began to recover after 8 hours of ozonation. In this case, it was observed that the dissolved ozone concentration also began to increase after 8 hours.

When the pH of the feed water was further decreased to 4.0 and 6.0, the permeate flux decreased initially, although the recovery occurred earlier (6 hours for pH 6.0 and 4 hours for pH 4.0). The steady state specific flux also increased with decreasing pH. The extent of recovery was statistically significant when the natural pH (7.9) was reduced to a pH of 4.0 ($p<0.05$).

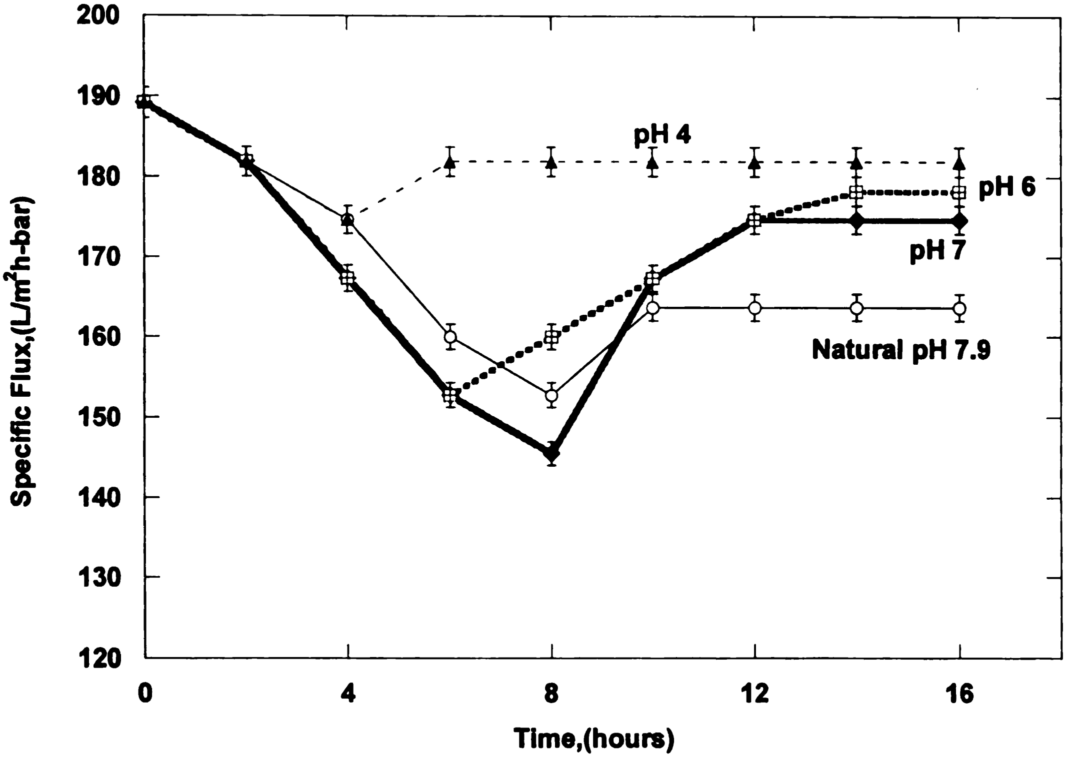

Figure 3.6 Effect of pH on Permeate Flux Recovery
(Experimental setup: Fig.3.1 Operating Conditions: Table.3.2, Continuous Ozonation, Ozone gas concentration: 1.5 g/m^3, pH: natural pH, 7.0, 6.0 and 4.0)

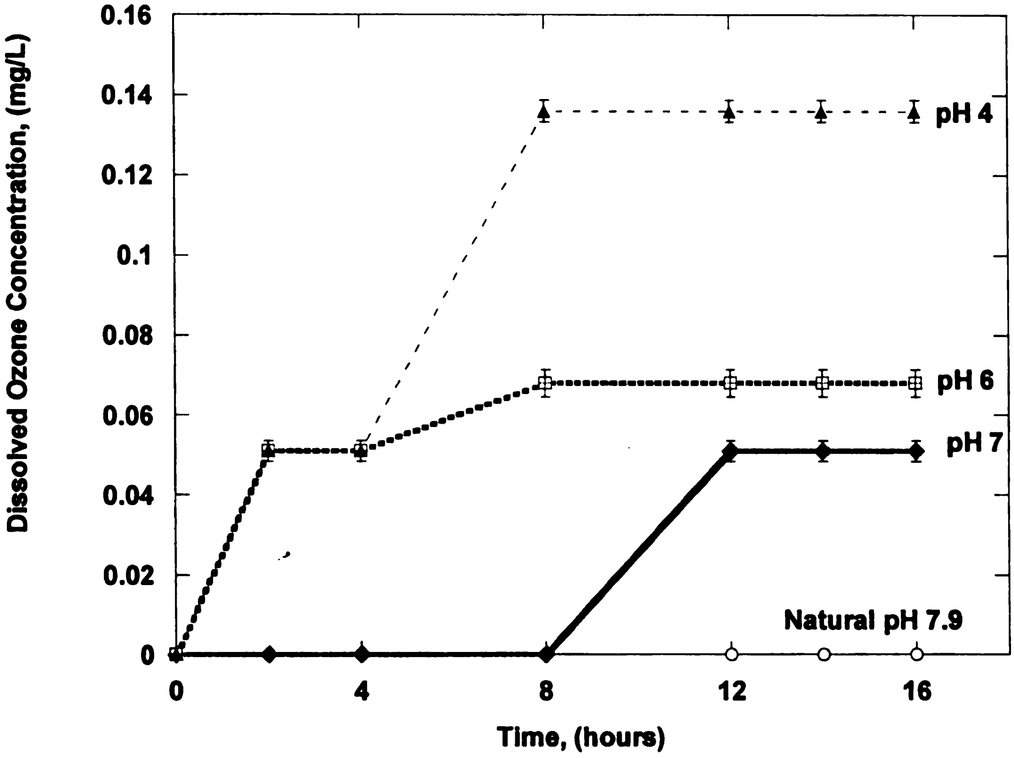

Figure 3.7 Dissolved Ozone Concentration in Feed water
(Experimental setup: Fig.3.1 Operating Conditions: Table3.2, Continuous Ozonation, Ozone gas concentration: 1.5 g/m^{3}, pH: natural pH, 7.0, 6.0 and 4.0)

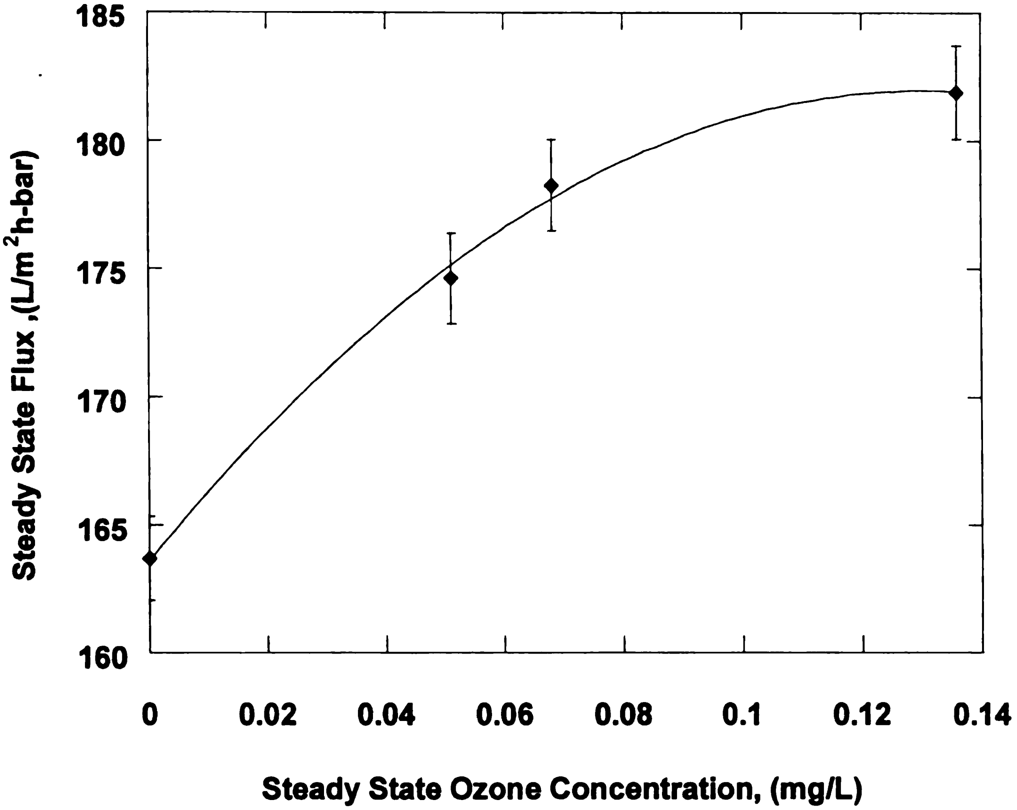

Figure 3.8 Relationship between Steady State Flux and Steady State Ozone Concentration

As shown in Figure 3.7, the dissolved ozone concentration profiles are related to the specific flux profiles. Changes in the steady state ozone concentrations and increases in the specific flux occur at similar time. Higher dissolved ozone concentrations resulted in higher steady state fluxes, and at pH 4.0, when the dissolved ozone concentration was 0.14 mg/L, the steady state specific flux was nearly 95% of the initial flux. The relationship between specific flux and dissolved ozone concentration is seen in Figure 3.8. A minimum ozone concentration of 0.05 mg/L in the recirculation feed water is required to obtain steady permeate fluxes that are >95% of the initial value. Thus, it appears that membrane fouling can be effectively reduced and stable fluxes can be maintained throughout the operation if the concentration of dissolved ozone is greater than 0.05 mg/L in the recirculation water.

We hypothesize that the increase in dissolved ozone concentration results in an increase in the concentration of the ·OH or other radical species at the membrane surface. These very reactive species decompose the organic foulants present at the surface and bring about the degradation of the cake/ gel layer, thereby reducing the membrane fouling and increasing the permeate flux.

3.5 CONCLUSIONS

The permeate flux through a titania coated ceramic membrane was significantly affected by ozonation and the pH of the feed water in the system. Increase in the ozone gas concentration resulted in a concomitant increase in the permeate flux. Also, beyond a particular ozone gas concentration (5 g/m^3), further increases in gaseous ozone concentration had no effect on the level of permeate flux recovery, thus a minimum threshold concentration could achieve complete recovery. The permeate flux recovery in these experiments was found to be due to the reaction of ozone with potential foulants and not the increased turbulence created at the membrane surface by gas bubbles. The pH of the feed water affected the permeate flux. As expected, the dissolved ozone concentration increased with decreasing pH. The improved permeate flux recovery at lower pH may be due to the higher concentration of dissolved ozone that is present under these conditions, resulting in a greater extent to which the ozone reacts with the NOM species that are responsible for fouling.

3.6 ACKNOWLEDGEMENTS

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CHAPTER FOUR

Karnik, Bhavana S.; Davies, Simon H.; Baumann, Melissa J.; Masten, Susan J. (2005). The effects of combined ozonation and filtration on disinfection by-product formation. Water Research, 39(13): 2839-2850.

CHAPTER FOUR

THE EFFECTS OF COMBINED OZONATION AND FILTRATION ON DISINFECTION BY-PRODUCT FORMATION

4.1 ABSTRACT

The effects of combined ozonation and membrane filtration on the removal of the natural organic matter (NOM) and the formation of disinfection by-products (DBPs) were investigated. Ozonation/filtration resulted a reduction of up to 50% in the dissolved organic carbon (DOC) concentration. Furthermore, humic substances were converted to non-humic substances, with changes in the humic and non-humic substance concentrations of up to -50% and +20%, respectively. Ozonation/filtration resulted in the formation of partially oxidized compounds from NOM that were less reactive with chlorine, decreasing the concentration of simulated distribution system total trihalomethanes (SDS TTHMs) and simulated distribution system halo acetic acids (SDS HAAs) by up to 80% and 65%, respectively. Reducing the MWCO of the membranes resulted in reductions in the concentrations of SDS TTHMs and SDS HAAs. Using a membrane with a 5kD MWCO, the minimum gaseous ozone concentration required to bring about effective NOM degradation and meet regulatory requirements for chlorinated DBPs was 2.5 g/m^3.

Keywords: ceramic membranes, nanofiltration, ultrafiltration, ozonation, disinfection by-products (DBPs), water quality, natural organic matter (NOM).

4.2 INTRODUCTION

Natural organic matter (NOM) is composed of a heterogeneous mixture of organic compounds that can be of human origin or the result of natural processes. NOM can be broadly divided into two fractions: humic substances, which are composed of fulvic and humic acids, and non-humic substances, which include carbohydrates, lipids, and amino acids.

In water treatment systems, the presence of NOM is a cause of concern because of its reaction with disinfectants. Chlorination of drinking water results in the formation of disinfection by-products (DBPs), such as trihalomethanes (THMs), some of which are known carcinogens (Morris et al., 1992; Mughal, 1992; Kool et al., 1985). While humic substances have been recognized as the primary precursors of chlorination byproducts (Ichihashi et al., 1999; Manahan, 1993; Reckhow et al., 1990; Collins et al., 1986), non-humic substances also result in the formation of many regulated or potentially regulated DBPs. The non-humic fraction of the NOM is generally more biodegradable and, as such, supports bacterial regrowth in water distribution systems (Yavich, 1998; Mogren et al., 1990).

The use of ozonation in water treatment processes results in a decrease in the formation of THMs and halo acetic acids (HAAs) upon subsequent chlorination (Zhang et al., 2001; Richardson et al., 1999). Increases in ozone dosages result in a concomitant decrease in the concentrations of THMs and HAAs formed from subsequent chlorination (Lee, 2001; Cipparone, 1997; Amy et al., 1988). Ozonation results in the formation of more polar compounds and an increase in the biodegradability of the chemicals found in the water as compared to that generated with chlorination (Koechling et al., 1996; Owen et al., 1995; Amy et al., 1992). The reactions that occur during ozonation produce by-products, including aldehydes (formaldehyde, glyoxal, and methylglyoxal), ketones, gyloxylic acid, and pyruvic acid (Paode et al., 1997; Weinberg and Glaze, 1996). Some of these by-products are of particular concern due to their mutagenicity and carcinogenicity (Bull and McCabe, 1984). Also, as they are easily biodegradable, they can serve as substrates for microbial regrowth in the distribution system. The ozonation by-products can be easily removed by biofiltration (Yavich and Masten, 2003; Griffini et al., 1999).

Membrane filtration is an effective method to remove particles, microorganisms and organic matter from drinking waters. Compared with conventional treatment methods, membrane processes i) can provide higher quality water, ii) minimize disinfectant demand, iii) are more compact, iv) provide easier operational control and less maintenance, and v) generate less sludge (US EPA, 2001; Cleveland, 1999; Nakatsuka et al., 1996).

One of the major challenges associated with the operation of membrane filtration plants is the decrease in the permeate flux due to membrane fouling (Siedel and Elimelech, 2002; US EPA, 2001; Crozes et al., 1997). The deposition of NOM on the filter surface is a primary cause of membrane fouling (Lee et al., 2001; Nilson and DiGiano, 1996; Ravindran et al., 1993). Fouling not only reduces the efficiency of the membrane, but the characteristics of the foulants also control the rejection of other substances by the membrane (Schafer et al., 2000). The application of ozonation prior to membrane filtration reduces membrane fouling and enhances permeate flux (Karnik et al., 2005; Schlichter et al., 2004, 2003; Hashino et al., 2000; Hyung et al., 2000; Kim et al., 1999). The use of ozonation in combination with membrane processes has not been extensively investigated; however, the limited research in this area has shown that ceramic membranes in combination with ozonation achieved a high permeate flux without membrane damage (Schlichter et al., 2004; Chen, 2003; Kim et al., 1999; Kim and Somiya, 2001; Moulin et al., 1991; Bablon et al., 1991).

In this study, we have investigated the quality of water after combined ozonation-membrane filtration. The permeate collected was used to determine the effect of treatment on the UV absorbance measured at 254 nm (UV-254), DOC, humic substances (HS), and non-humic substances (non-HS). The concentrations of SDS TTHMs, SDS HAAs, aldehydes, ketones, and ketoacids were also evaluated. The effect of gaseous ozone concentration on the water quality of the permeate was investigated.

4.3 MATERIALS AND METHODS

4.3.1. Ozonation/ Membrane Filtration

A schematic representation of the ozonation/membrane system is shown in Figure 4.1. Tubular ceramic membranes (Clover-leaf design (containing three channels), CéRAM Inside, Tami North America, St. Laurent, Québec, Canada) with molecular weight cut-offs of 15, 5, and 1 kD were used. The external diameter of each titania membrane was 10 mm and the active membrane length was 25 cm. The membrane had a total filtering area of 41.2 cm^2. A stainless steel filter holder, Teflon® tubing and stainless steel or Teflon® joints and valves were used throughout the system. Other components included: 3.5-liter and 1.5-liter water-jacked glass reservoirs made of Pyrex glass, and a simple Y inline mixer (Ozone Service, Burton, B.C., Canada). Ozone gas was added into the water stream through the simple Y inline mixer just before entering the membrane module.

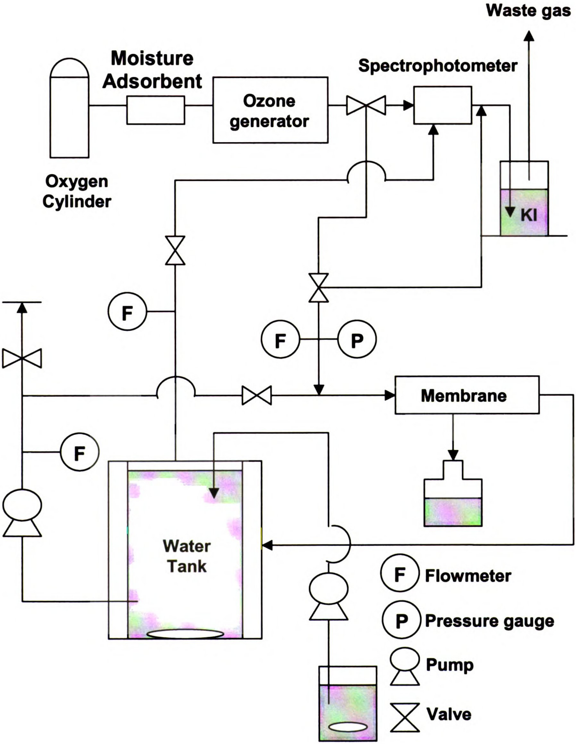

Figure 4.1 Schematic Representation of the Ozone-Membrane Filtration System

To generate ozone, pure oxygen gas (99.999%) from a pressurized cylinder was dried using a molecular sieve trap, and then fed to the ozone generator (Model OZ2PCS, Ozotech Inc., Yreka, Calif.). Varying the voltage applied to the ozone generator controlled the gaseous ozone concentration. The excess gas was vented after passing the gas through a 2% potassium iodide (KI) solution to destroy any residual ozone gas. The water level in the 3.5-liter reservoir was maintained at a constant level during the experiments using a peristaltic pump (Masterflex Model 7520-35, Cole-Parmer Co., Chicago, Illinois) to transfer water from the 1.5-liter reservoir into the 3.5-liter reservoir. A constant water temperature of 20°C was maintained using a recirculating water bath. The operating conditions used are given in Table 4.1. The gaseous ozone concentration was 2.5 g/m^3, unless otherwise stated.

Table 4.1
Operating Conditions for the Ozone –Membrane Filtration System

Water recirculation rate	2.75 LPM
Water temperature	20°C
Ozone gas flow rate	100 mL/min
TMP	0.2 bar

The experiments were performed with membrane cross flow velocity of 0.6 m/s; the flow was turbulent with Reynolds number in the range of approximately 6000. Previous studies in our laboratory considered such important factors, as gas flow rate, water flow rate, and the characteristics of the source water, which influence the ozone transfer efficiency (Chen, 2003). The ozonation/membrane system used in this study can achieve high ozone mass transfer, and thus, requires a lower ozone dose, gas flow rate, and water flow rate than comparable systems (Chen, 2003). The volumetric mass transfer coefficient for ozone in the experimental setup was determined to be 0.138 min^{-1} (Chen, 2003).

Ceramic membranes with molecular weight cut-offs of 15, 5, and 1 kD were used. The specific flux for 15, 5 and 1 kD membranes were 60, 20 and 8 L/m^2-bar, respectively. The permeate flux recovery trends are discussed in detail in our earlier work (Karnik et al., 2005). The conductivity remained practically unchanged for the duration of the experiment (< 0.01 μS/cm).

Permeate samples were collected in bottles covered with Parafilm® and stored in an ice-bath for the duration of the experiment. The first 400 mL of permeate collected was labeled as P1 and latter 1000 ml as P2. P1 and P2 samples were collected to study the effect of ozone contact time on the water quality.

Samples of the pre-filtered raw water (FRW), P1, P2 and from the 3.5-liter water tank reservoir (WT) were analyzed for UV-254 absorbance, dissolved organic carbon (DOC), humic substances and non-humic substances, chlorine residual, SDS total trihalomethanes (SDS TTHMs), SDS halo acetic acids (SDS HAAs), aldehydes, ketones and ketoacids. The effect of gaseous ozone concentration on water quality was investigated using a membrane with a MWCO of 15 kD. The gaseous ozone concentration was varied between 1.5 and 10 g/m^3.

To study the effect of pH on the process, the pH of Lake Lansing water (initial pH 8.2) sample was adjusted to 7.0 by the addition of hydrochloric acid (concentrated, ACS reagent grade). We chose a pH of 7 because earlier studies revealed no difference in the permeate flux recovery at pH 6 and pH 7 (Karnik et al., 2005). The membranes used in these experiments had MWCOs of 5 and 15 kD.

4.3.2 Water Source

Experiments were carried out on samples taken from Lake Lansing (Haslett, MI). The typical characteristics of the water from Lake Lansing, a borderline eutrophic lake, are given in Table 4.2. The samples were collected at the boat ramp at the Lake Lansing Park-South, Haslett, MI in five-gallon polyethylene carboys and stored at 4°C. The maximum storage period was seven days. Water samples were pre-filtered through a 0.45-µm mixed cellulose ester (Millipore-HA) filter before testing.

Table 4.2
Typical Characteristics of Lake Lansing Water (Haslett, MI) [a]

Parameters	**Lake Lansing**
TOC (mg/L)	8.6 to 11.6
pH	7.7 to 8.6
Alkalinity (mg/L as $CaCO_3$)	145 to 157
UV-254 (abs.)	0.160 to 0.180
SDS THMs[b] (µg/L)	240
SDS HAAs[b] (µg/L)	75
BDOC (mg/L)	1.0 to 4.1
Nitrate (mg/L)	0.44
Total Phosphate (mg/L)	0.06
Hardness (mg/L as $CaCO_3$)	190 to 198

[a] *All data reported is obtained from the Lake Lansing Watershed Advisory Committee Report(1998) except for SDS THMs and SDS HAAs, which were measured as part of this study*

[b] *SDS THM and SDS HAA were measured using Standard Method 5710 and USEPA Method 552.2 respectively.*

4.3.3 Membrane cleaning and preparation

Prior to each experiment, the membrane was thoroughly cleaned using a procedure based on that developed by Xing et al. (2003). Membranes were soaked in a sodium hydroxide solution (15 g/L) at 85°C for 30 minutes; following this, the membrane was rinsed with distilled deionized (DDI) water. The membrane was then soaked in a nitric acid solution (0.1M) at 50°C for another 30 minutes followed by thorough rinsing with DDI water. Finally, the membrane was steam sterilized at 121°C for 30 minutes. The effectiveness of the cleaning procedure was verified by measuring the permeate flux through the membranes using DDI water to ensure that the initial membrane flux was the same in all experiments.

4.3.4 Analytical Methods

Gas-phase Ozone Analysis

The absorbance of ozone in the gas phase was measured at 254 nm with a Milton Roy Genesis-5 spectrophotometer (Milton Roy, Inc., Rochester, NY) using a 2-mm path length quartz flow-through cell. An extinction coefficient of 3000 $M^{-1}cm^{-1}$ (Hoigné, 1988) was used to calculate the ozone concentration.

UV-254 absorbance

The UV absorbance of the water samples was measured at a wavelength of 254 nm with a Milton Roy Genesis-5 spectrophotometer (Milton Roy, Inc., Rochester, NY) using a 1 cm quartz cell.

Dissolved Organic Carbon (DOC)

DOC was analyzed using an OI Analytical Model 1010 analyzer. The TOC analyzer uses the UV/persulfate method (Standard Method, 1998). To ensure the reliability of the method, standards having TOC concentrations of 2.5, 5, 7, 10 mg/l (OI Analytical) were run and samples were analyzed in triplicate. A blank was also run with every set of samples.

Humic substances and Non-humic substances

The humic substances in the samples were isolated from the water samples by adsorption on XAD-8 resin according to Method 5510C (Standard Methods, 1998). A 100 mL sample was acidified with concentrated phosphoric acid and eluted through a 10 mm diameter (ID) x 15 cm long column at a flow rate of 2 mL/min. The effluent from the column was collected and then analyzed for TOC, which represented the non-humic fraction of the dissolved organic matter in the water sample. The resin-packed column was then back eluted with 100 mL of 0.1 N sodium hydroxide at a flow rate of 2 mL/min. The eluent was collected and acidified with concentrated phosphoric acid to a pH less than 4, purged with high-purity helium for 3 minutes to remove inorganic carbon, and analyzed for TOC. The organic content of the eluent represented the concentration of humic substances.

Chlorine residual

Chlorine residual was measured using the iodometric method, Method 4500B (Standard Methods, 1998).

SDS total trihalomethanes (SDS TTHMs) and SDS halo acetic acids (SDS HAAs).

Water samples were dosed with a chlorine concentration that ensured a residual chlorine concentration in the range of 0.5 to 2 mg/L after 48 hours incubation at room temperature according to the procedures in Standard Method 2350 (Standard Methods 1998). The trihalomethane (THM) compounds, chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$), and bromoform ($CHBr_3$), were extracted from the water samples using hexane and analyzed by gas chromatography (Method 5710, Standard Methods 1998). A Perkin Elmer Autosystem gas chromatograph (Perkin Elmer Instruments, Shelton, CT) equipped with an electron capture detector (ECD), an auto sampler, and a 30 m × 0.25 mm I.D., 1 µm DB-5ms column (J&W Scientific, Folsom, CA) was used for the analysis. The oven temperature was ramped from 50 °C to 150 °C at a rate of 10°C/min. The flow rate of the carrier gas (N_2) was 12.0 mL/min. The injector temperature and detector temperature were 275 and 350 °C, respectively.

SDS HAAs were produced by chlorination as described above. The concentrations of monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), bromochloroacetic acid (BCAA), trichloroacetic acid (TCAA), and dibromoacetic acid (DBAA) were determined using US EPA Method 552.2. A Perkin Elmer Autosystem gas chromatograph (Perkin Elmer Instruments, Shelton, CT) equipped with an ECD, an autosampler, and a 30 m × 0.32 mm I.D., 3 µm DB-1 column (J&W Scientific, Folsom, CA) was used for the analysis. The oven temperature was programmed to hold for 15 minutes at 32°C, then increased to 75 °C at a rate of 5°C/min and held 5 minutes, then increased to 100 °C at a rate of 5°C/min. The carrier gas flow (nitrogen) was 1.0 mL/min with the injector temperature and detector temperatures at 200 °C and 260 °C, respectively.

Aldehydes, Ketones and Ketoacids

USEPA Method 556 (Munch et al., 1998) was used to monitor for formaldehyde, propionaldehyde, glyoxal, methyl glyoxal, acetone, and 2-butanone, ketomalonic acid, pyruvicacid and gyloxylic acid. A Perkin Elmer Autosystem gas chromatograph (Perkin Elmer Instruments, Shelton, CT) equipped with an ECD, an autosampler, and a 30 m × 0.25 mm I.D., 0.5 µm DB-5ms column (J&W Scientific, Folsom, CA) was used in the analysis. The oven temperature was programmed to hold for 1 minute at 50 °C, then increased to 220 °C at a rate of 4°C/min followed by an increase to 250 °C at a rate of 20 °C/min with a 5 minute hold time. The carrier gas flow was 1.0 mL/min and the injector temperature and detector temperatures were 180 °C and 300 °C, respectively.

4.4 RESULTS AND DISCUSSION

All data is reported as a percent decrease as compared to the concentrations present in the raw feed water. The results found for the feed water are given in Table 4.3.

4.4.1 Effect of ozonation, ultrafiltration, and ozonation-ultrafiltration on water quality.

A study was conducted to compare the improvements in water quality results achieved using ultrafiltration, ozonation, and ozonation-ultrafiltration. The apparatus illustrated in Figure 4.1 was used for all three experiments. In the case of the ozonation experiment, the membrane filter element was removed and the permeate collection ports were sealed. In the ozonation experiment, samples were collected from the 3.5 L reservoir after the same time as used for sampling in the ozonation-UF experiment. As shown in Table 4.4, ultrafiltration was the least effective of the three processes for the removal of DOC, HS, NHS, SDS TTHMs, and SDS HAAs. The quality of the treated water was further improved when ozonation and ultrafiltration were combined. Not only was the removal of UV-254, DOC, HS, NHS, SDS TTHMs, and SDS HAAs enhanced over either of the processes used alone, but also the combined process resulted in the production of lower concentrations of aldehydes, ketones, and ketoacids than ozonation alone. This suggests a synergy between ozonation and membrane filtration in providing high quality water.

Table 4.3

Initial concentrations of filtered raw water from Lake Lansing.

Parameters	Filtered raw water (Initial Concentration)							
	Effect of MWCO[a]			Effect of ozone dose[b]			Effect of pH[b]	
Experiment[C]	15 kD	5 kD	1kD	10	2.5	1.5	15 kD	5 kD
	natural pH 7.9 to 8.2			natural pH 7.9 to 8.2			pH adjusted to 7.0	
UV-254 (Abs)	0.174 ± 0.001	0.174 ± 0.001	0.174 ± 0.001	0.174 ± 0.003	0.174 ± 0.003	0.174 ± 0.003	0.171 ± 0.005	0.171 ± 0.056
DOC (mg/L)	10.6 ± 1.9	10.6 ± 1.9	10.6 ± 1.9	10.9 ± 0.2	10.9 ± 0.2	10.9 ± 0.2	11.9 ± 0.49	11.9 ± 0.49
HS (mg/L)	4.75 ± 0.45	4.75 ± 0.46	4.75 ± 0.47	5.0 ± 0.84	5.0 ± 0.84	5.0 ± 0.84	6.1 ± 0.5	6.1 ± 0.49
NHS (mg/L)	4.36 ± 0.19	4.36 ± 0.19	4.36 ± 0.19	2.99± 0.20	2.99 ± 0.20	2.99 ± 0.20	3.94 ± 0.77	3.94 ± 0.79
SDS TTHMs (µg/L)	195.3 ± 12.5	195.3 ± 12.5	195.3 ± 12.5	242.3 ± 20.0	242.3 ± 20.0	242.3 ± 20.0	230 ± 9.1	230 ± 9.1
SDS HAAs (µg/L)	81.1 ± 4.23	81.1 ± 4.2	81.2 ± 4.2	82.3 ± 4.2	82.3 ± 4.25	82.3 ± 4.25	87.7 ± 1.6	87.7 ± 1.6
Aldehydes-Ketones (µg/L)	24.8 ± 2.8	24.8 ± 2.8	24.8 ± 2.8	24.0 ± 2.7	24 ± 2.7	24 ± 2.7	6.2 ± 1.1	6.2 ± 1.1
Ketoacids (µg/L)	1.7 ± 2.5	1.7 ± 2.5	1.7 ± 2.5	0.67 ± 0.48	0.67 ± 0.48	0.67 ± 0.48	1.83 ± 0.86	1.83 ± 0.86

The values are reported in actual concentration values ± standard deviation.

[a] n=9, triplicate experiments with each analysis run in triplicate

[b] n = 6, duplicate experiments with each analysis run in triplicate.

[c] These entries provide a cross reference to the relevant experiments described in this study.

Table 4.4

Comparison of performance parameters for Ozonation alone, UF alone, and combined Ozonation/UF

Parameters	FRW	Permeate 1 (% Reduction)			Permeate 2 (% Reduction)		
Experiment‡	**Initial values**	**UF**	**Ozonation**	**Ozonation+UF**	**UF**	**Ozonation**	**Ozonation+UF**
UV-254 (Abs)	0.174 ± 0.001	48.1 ± 2.8	65.2 ± 3.2	78.8 ± 1.4	48.2 ± 1.2	70.1 ± 2.9	83.9 ± 4.6
DOC (mg/L)	10.6 ± 1.9	12.3 ± 2.9	21.2 ± 0.6	26.6 ± 0.2	17.3 ± 1.0	42.1 ± 1.2	37.1 ± 7.9
HS (mg/L)	4.75 ± 0.45	5.4 ± 2.1	37.3 ± 6.1	48.0 ± 0.2	13.2 ± 3.0	50.2 ± 3.8	59.8 ± 12.0
NHS (mg/L) (% Increase)	-4.4 ± 0.19	-2.1 ± 0.6	-14.2 ± 0.6	-17.0 ± 0.1	-4.2 ± 2.0	-16.2± 2.0	-23.4 ± 7.7
SDS TTHMs (µg/L)	195.3 ± 12.5	4.2 ± 1.1	15.0± 1.3	16.5 ± 1.4	10.1 ± 2.1	35.4± 1.2	44.7 ± 3. 3
SDS HAAs (µg/L)	81.2 ± 4.2	3.4 ± 0.4	10.2 ± 0.5	24.7 ± 3.7	13.2 ± 0.4	19.2 ± 2.6	34.7 ± 1.9
*Aldehydes-Ketones (µg/L)	24.8 ± 2.8	20.3 ± 0.3	201.3 ± 8.3	173.8 ± 4.0	19.2 ± 3.0	501.2 ± 10.2	386.1 ± 0.3
*Ketoacids (µg/L)	1.8± 2.5	1.5 ± 0.3	224.3 ± 15.4	156.2 ± 3.8	1.0 ± 0.1	890.0± 14.2	746.5 ± 0.1

‡Experimental Setup Figure 4.1, Experimental conditions Table 4.1.
The membrane had a MWCO of 15 kD.
** The concentrations of aldehydes, ketones and ketoacids increase in P1 and P2. Also the P1 and P2 values are the actual concentrations of these compounds.*

The effects of ozonation time on the removal efficiencies can be observed by comparing the results for permeate 1 and 2. The longer ozone contact time did not result in a large increase in the removal efficiency for UV-254 (65.2 vs. 70.1%), suggesting that most of the UV-254 absorbing material were degraded in the time necessary to collect the first 400 mL of sample (i.e., within 4-5 hours). On the contrary, the removal efficiencies of DOC, SDS TTHMs, and SDS HAAs for permeate 2 were roughly twice that for permeate 1, indicating that the reaction of ozone with TTHM and HAA precursors is slower than that for ozone with the UV-absorbing material.

4.4.2 Effect of membrane MWCO on the water quality

As shown in Figures 4.2 and 4.3, there is a little difference in the DOC levels in the P1 samples for all three membranes. However, for the P2 samples, there is a statistically significant ($p<0.05$) decrease in the DOC levels when the molecular weight cutoff of the membrane was decreased from 5 kD to 1 kD. One explanation for this result is that after extended ozonation a significant fraction of the DOC is in the molecular size range from 1-5 kD. Ozonation of NOM is known to result in a decrease in the molecular weight of the organic matter (Mellema 1998), which would then result in these compounds passing through the coarser membranes, but not through the 1 kD membrane. An alternate explanation is that the 1 kD membrane is a more effective catalyst for the degradation of NOM than are the coarser membranes, presumably because the smaller pores have a greater surface area. If this is the case, then with the 1 kD membrane prolonged ozonation could result in the mineralization of a greater portion of the NOM to CO_2 and water.

As shown in Figures 4.2 and 4.3, for the 5 and 15 kD membranes, the molecular weight cut off of the membranes did not have a statistically significant effect on the UV-254 of the P1 and P2 samples ($p>0.05$). Also, as the results for the P1 and P2 samples were not very different, increasing the ozone contact did not lead to a great increase in the removal of UV absorbing substances. Even after extensive ozonation, approximately 15% of the UV-254 absorbance of P2 samples remains in the samples, suggesting that while most of the UV absorbing substances react with ozone, there is a recalcitrant fraction that does not react with ozone.

The data presented in Table 4.4, shows that the removal of UV-254 was much greater with ozonation than with ultrafiltration. This suggests that the removal of the UV-254 absorbing compounds is predominately due to the reaction of ozone with these substances and not due to filtration. These results are consistent with previous research on the ozonation of Lake Lansing water. Yavich and Masten (2003) found that ozone reacts rapidly with aromatic fraction of the NOM, resulting in a significant decrease in UV-254 even at low ozone dosages. These workers also found that after this initial decrease increasing the ozone contact time did not lead to a further large decrease in the UV-254.

Only with the 1 kD membrane, did extended ozonation result in an increase in the removal of UV-254. The lower removal of UV-254 absorbance in P1 samples with the 1 kD membrane (as compared to that with the 5 and 15 kD membranes) cannot be explained by differences in the seasonal nature of the NOM, since replicate experiments (for the 1 kD membrane) were conducted in May and November, yielding consistent results.

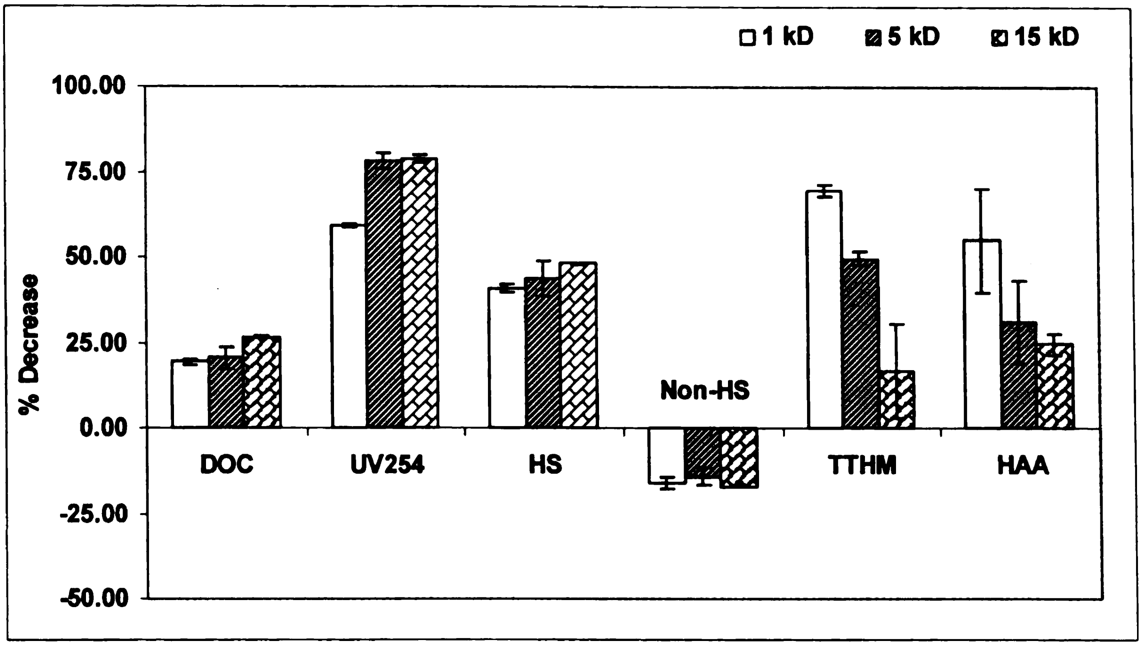

Figure 4.2 Effect of molecular weight cut-off on Permeate 1 (first 400 mL of the sample)

*Experimental setup: Fig.4.1 Operating Conditions: Table 4.1.Ozone Dose: 2.5 g/m^3, Membrane Size: 15, 5 and 1 kD.*All values are average of triplicates within experiments and duplicate experiments. The values have a maximum std. deviation of 5 %*

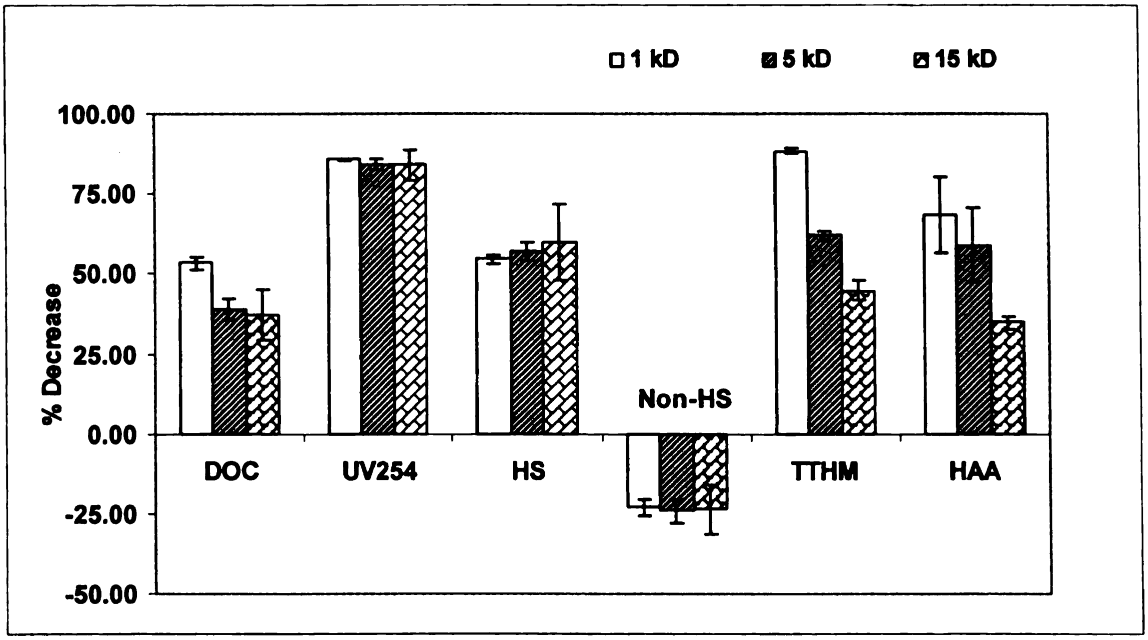

Figure 4.3 Effect of molecular weight cut-off on Permeate 2 (Latter 1000 mL of the sample)

*Experimental setup: Fig.4.1 Operating Conditions: Table 4.1.Ozone Dose: 2.5 g/m^3, Membrane Size: 15, 5 and 1 kD.*All values are average of triplicates within experiments and duplicate experiments. The values have a maximum std. deviation of 5 %*

It is possible that with the 1 kD membrane there are catalytic reactions that produce UV absorbing compounds that pass through the membrane. It should also be noted that as the molecular weight cut off of the membranes is reduced, the permeate flux decreased, thus, the ozone contact time increased, as the time required to collect equal volumes of sample increases. While we plan to continue to investigate this phenomenon, one should note that this result does not negate our conclusions regarding the overall effectiveness of the hybrid process in reducing the concentrations of disinfection byproducts.

With all three membranes, ozonation/membrane filtration resulted in a reduction of approximately 45% in the humic substance (HS) concentration in the P1 samples and an approximately 55% reduction in the P2 samples (see Figures 4.2 and 4.3). This reduction is, in part, due to the reaction of NOM with either ozone or $^{\cdot}OH$ radicals, since an increase in the non-humic substance (non-HS) concentration after ozonation/filtration was observed. The increase in non-HS concentration could only be caused by the conversion of HS to non-HS. Filtration would not have resulted in such a conversion. This conclusion is substantiated by data shown in Table 4.4, which show that the percent removal of HS using ultrafiltration is 5.4 and 13.2% for P1 and P2, respectively, while for the P1 and P2 samples, 37.3 and 50.2%, respectively, of the HS were removed by ozonation.

The concentrations of non-HS measured in P1 samples increased by approximately 10%, while that in P2 samples increased by approximately 20% (see Figures 4.2 and 4.3), indicating that the reaction of HS to form non-HS continued throughout the course of the experiment. The increased reduction in the concentration of humic substance in the P2 samples compared to that in P1 samples provides further evidence of the importance of oxidation reactions. If the humic substances were removed purely by filtration, the level of removals would not likely change with ozonation time. These results are consistent with those of Mellema (1998), who found that ozonation resulted in a significant reduction in the concentration of humic substances with an apparent molecular weight of 3 to 7 kD (Mellema, 1998). For the UF experiment, the increase in HS removal from 5.4% to 13 % in the P1 and P2 samples, respectively, suggests that there may be some formation of a fouling layer that results in improved removal of HS. If this is the case, then the presence of a fouling layer did not have a detrimental effect on permeate flux.

Ozonation/filtration resulted in a significant reduction ($p<0.05$) in the SDS TTHMs and SDS HAA formed after chlorination (see Figures 4.2 and 4.3), as compared to that removed by filtration alone (see Table 4.4). This reduction was seen in both the P1 and P2 samples. The reduction in SDS TTHMs found in the chlorinated P2 samples increased from 44 to 88% when the membrane pore size was decreased from 15 kD to 1 kD. The reduction in SDS TTHMs was significantly greater in the P2 than in the P1 samples ($p<0.05$). This decrease in the concentration of TTHM precursors with extended ozonation, along with the data comparing removal efficiencies for the hybrid system with ozonation alone and membrane filtration alone (see Table 4.4), is further confirmation of the importance of oxidation reactions in the removal of DBP precursors. This is consistent with the work of Lee (2001) and Chen (2003) who showed that ozonation resulted in a significant decrease in SDS TTHM formation after chlorination. Similar trends were observed for SDS HAAs, although the levels of reductions were less than that achieved for SDS TTHMs (38% compared to 68%), indicating that the precursors of TTHMs and HAAs react at different rates with ozone and/or OH radicals, resulting in different removal efficiencies. In both cases it appears that after ozonation a significant fraction of the TTHM and HAA precursors that remain are in molecular weight range from 1 to 15 kD.

As shown in Figure 4.4 and Table 4.4, the concentrations of aldehydes, ketones and ketoacids increased after both ozonation and ozonation/membrane filtration and with ozone contact time (compare P1 and P2 results). The concentrations of these species found in the permeate after ultrafiltration was less than 10% of that after ozonation or ozonation/filtration, indicating the importance of ozonation in forming these chemicals. The influence of ozone contact time on the concentrations of these chemicals is consistent with the work of Lee (2001) who found that the concentration of ketoacids in treated Lake Lansing water ranged from a 42 to 370 μg/L for retention times of 4 to 25 min at an ozone dose of 1 mg/mg C, and that the concentrations increased with increasing retention time. Similar concentration ranges were reported by Chen (2003) who found that the concentration of ketoacids in treated Lake Lansing water ranged from 40 to 1200 μg/L for an ozone dose of 2.5 mg ozone/mg C. As shown in Figure 4.4, the concentration of aldehydes, ketones and ketoacids decreased ten-fold when the membrane MWCO was decreased from 5 to 1 kD. This is quite surprising, since the molecular weights of these compounds measured are much smaller than 1 kD and would be expected to pass through the 1 kD membrane. Again these results suggest that oxidation reactions play a significant role in determining the effectiveness of the ozone/membrane system and that the catalytic oxidation of compounds appears to be more effective on the 1 kD membrane than that on the 5 or 15 kD membrane.

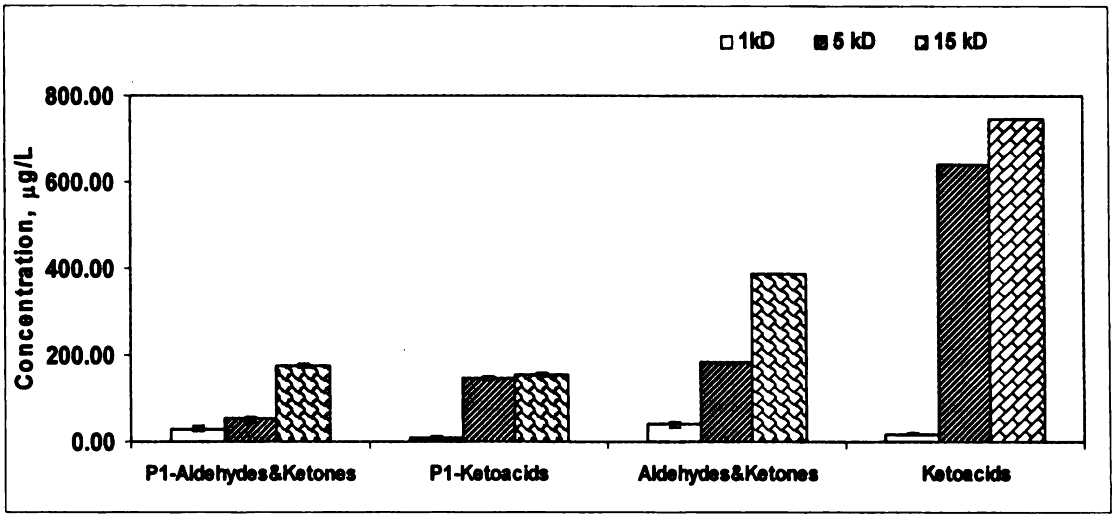

Figure 4.4 Effect of molecular weight cut-off on Ozonation By-products
*Experimental setup: Fig.4.1 Operating Conditions: Table 4.1.Ozone Dose: 2.5 g/m³, Membrane Size: 15, 5 and 1 kD.*All values are average of triplicates within experiments and duplicate experiments. The values have a maximum std. deviation of 5 %*

4.4.3 The effect of gaseous ozone concentration on water quality.

Ss shown in Figures 4.5 and 4.6, with 15 kD MWCO membrane, variations in the gaseous ozone concentration (over the range from 1.5 to 10 g/m^3) had little effect on the extent DOC removal. An explanation for this behavior is that, at the dosages used in this experiment, only a small fraction of the DOC is mineralized (converted to CO_2 and water) and that ozone simply converts larger molecules into smaller ones, which then pass through the membrane. Chen (2003) and Mellema (1998) also found, that at ozone dosages in the range 1 to 4 mg/mg C, little of the organic carbon was mineralized. This was confirmed by the apparent molecular weight distribution of the organic carbon, which increased in lower molecular weight compounds (<1000 Daltons) at ozone doses of 2.0 and 7.0 mg/mg C (Mellema, 1998).

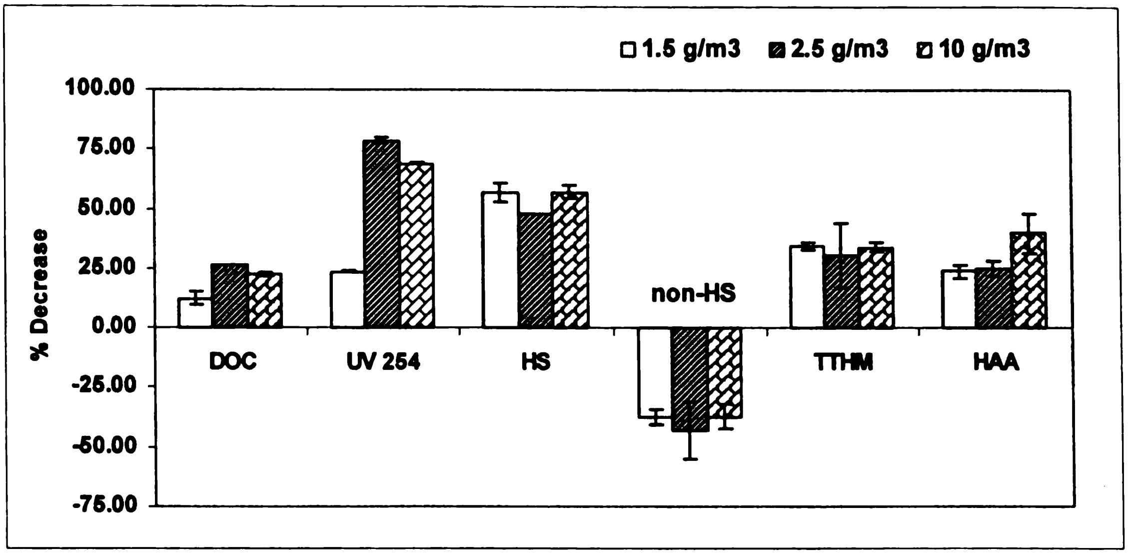

Figure 4.5 Effect of gaseous ozone concentration on Permeate 1 (First 400 mL of the sample)

*Experimental setup: Fig.4.1 Operating Conditions: Table 4.1.Ozone concentration: 1.5, 2.5 and 10 g/m^3 Membrane Size: 15 kD.*All values are average of triplicates within experiments and duplicate experiments. The values have a maximum std. deviation of 5 %*

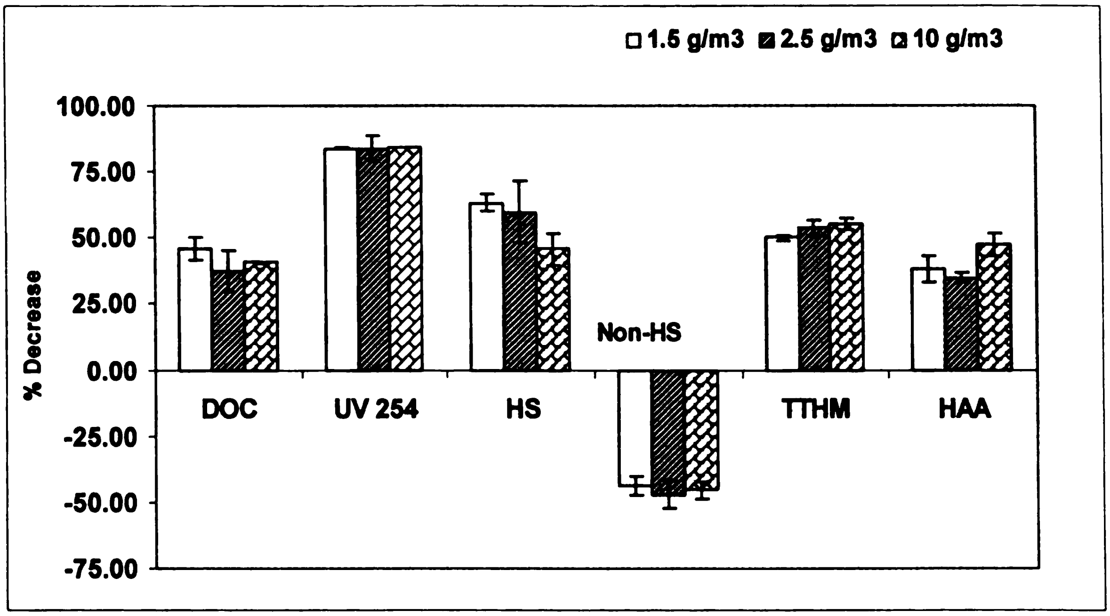

Figure 4.6 Effect of gaseous ozone concentration on Permeate 2 (Latter 1000 mL of the sample)

*Experimental setup: Fig.4.1 Operating Conditions: Table 4.1. Ozone Dose: 1.5, 2.5 and 10 g/m^3 Membrane Size: 15 kD.*All values are average of triplicates within experiments and duplicate experiments. The values have a maximum std. deviation of 5 %*

Increasing the gaseous ozone concentration from 1.5 to 2.5 g/m^3 resulted in an increase in the percent reduction of both UV-254 in the P1 samples, suggesting that, at the lower ozone gas concentration, the ozone dosage was not sufficient to remove the reactive UV-254 absorbing compounds.

As shown in Figure 4.6, the levels of SDS TTHMs in P2 were reduced by about 50% by ozonation/membrane filtration. The levels of SDS HAAs decreased by approximately 35 to 45% compared to that in the filtered raw water. No statistically significant decreases were observed in the concentration of SDS TTHMs when the ozone concentration was increased from 1.5 to 10 g/m^3 ($p<0.05$). There was a smaller reduction in the overall levels of the SDS HAAs compared to the SDS TTHMs in the P1 and P2 samples (Figures 4.5 and 4.6).

The results given here support the previously mentioned hypothesis that the precursors of TTHMs and HAAs have different reaction rates with ozone. Chen (2003) also found that TTHMs and HAAs precursors had different reaction rates with ozone. He observed the concentrations of SDS TTHMs decreased by approximately 40 to 45% whereas, the concentrations of SDS HAAs decreased by around 30%. Ko et al. (2000) also reported that the TTHMs and HAAs produced following ozonation and chlorination had different formation rates. The concentrations of aldehydes and ketones increased with increasing gaseous ozone concentrations. Also, the concentrations of these compounds in the P2 samples were greater than those in P1 samples, due to increased contact time with ozone. The concentration of ketoacids is almost twice that of the aldehydes and ketones (see Figure 4.7). While the highest ketoacid concentrations were observed when the ozone gas concentration was 10 g/m^3, there was no significant difference ($p>0.05$) in the ketoacids concentrations found at the two lower ozone gas concentrations (i.e., 1.5 and 2.5 g/m^3).

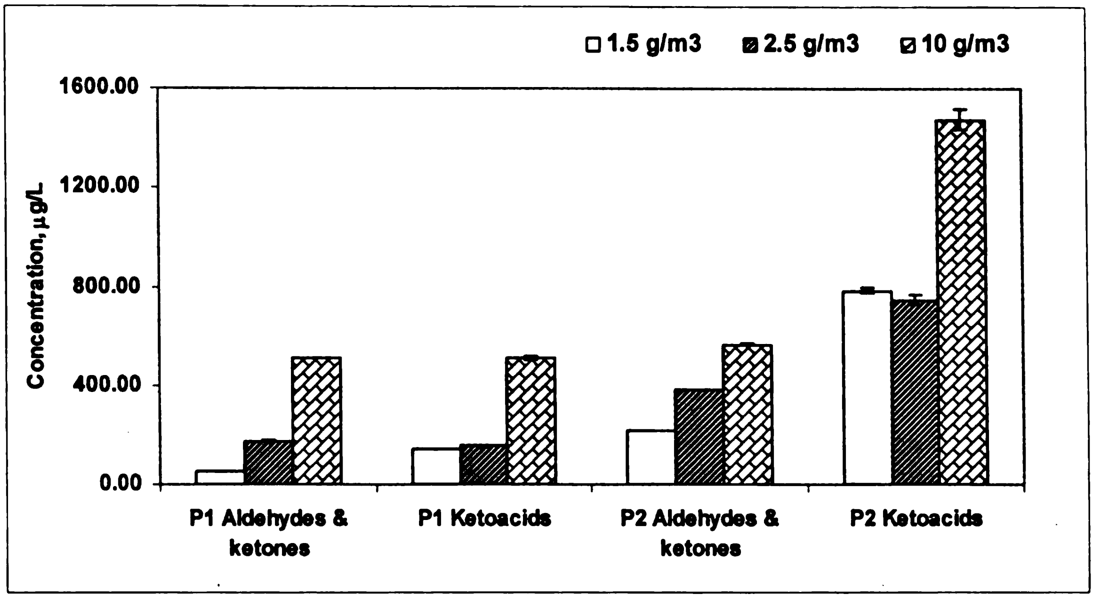

Figure 4.7 Effect of gaseous ozone concentration on Ozonation By-products
*Experimental setup: Fig.4.1 Operating Conditions: Table4.1.Ozone concentration: 1.5, 2.5 and 10 g/m^3, Membrane Size: 15 kD.*All values are average of triplicates within experiments and duplicate experiments. The values have a maximum std. deviation of 5 %*

4.4.4 Effect of pH on the water quality

Membranes with molecular weight cut-offs of 5 and 15 kD were used to evaluate the performance of the system at pH 7.0 and pH 8.2 with an ozone dose of 2.5 g/m^3 (Figure 4.8a to Figure 4.10b). The pH was measured during the course of the experiment and it did not change appreciably. The results show that decreasing the pH from 8.2 to pH 7.0 resulted in significant changes in the permeate characteristics. As shown in Figure 4.8b, ozonation/filtration through the 15 kD membrane resulted in a reduction in the DOC concentration of around 35% at pH 8.2 and approximately 45% at pH 7.0 (in P2). With the membrane having a 5 kD molecular weight cut off, the DOC removal for P2 was approximately 46% at pH 8.2 and > 95% at pH 7.0 (Figure 4.8b).

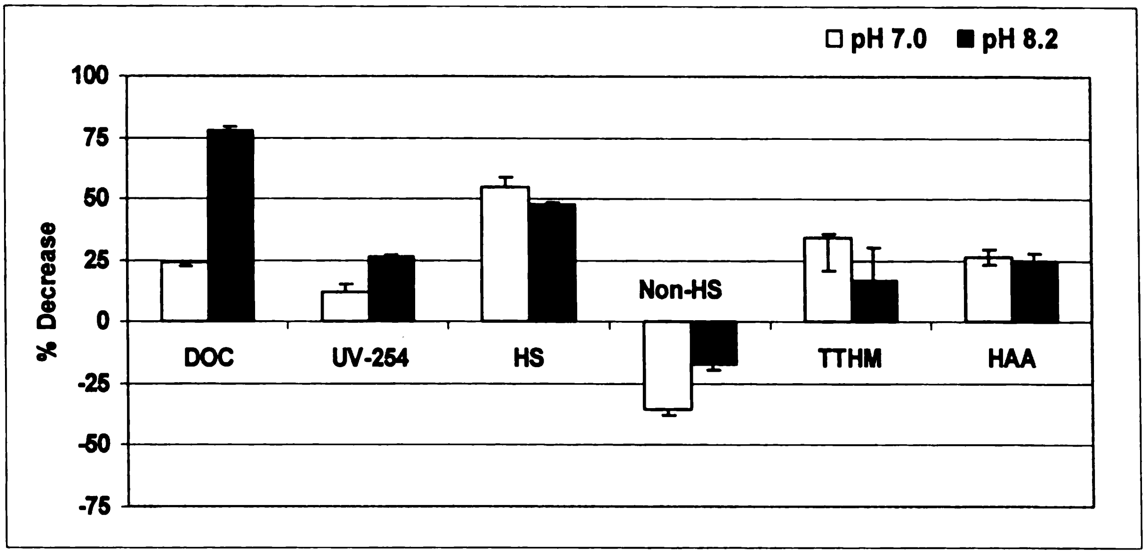

Figure 4.8a Effect of pH on Permeate 1 of 15 kD molecular weight cut off membrane

*Experimental setup: Fig.4.1 Operating Conditions: Table 4.1.Ozone Dose: 2.5 g/m^3, Membrane Size: 15 kD, pH 7 and 8.2.*All values are average of triplicates within experiments and duplicate experiments. The values have a maximum std. deviation of 5 %*

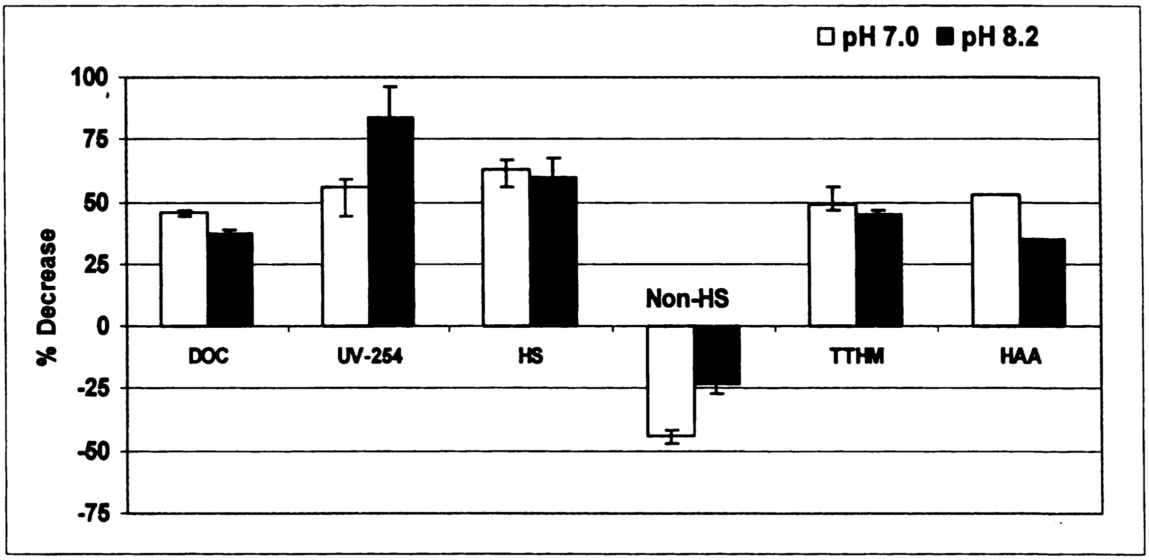

Figure 4.8b Effect of pH on Permeate 2 of 15 kD molecular weight cut off membrane

*Experimental setup: Fig.4.1 Operating Conditions: Table 4.1.Ozone Dose: 2.5 g/m^3, Membrane Size: 15 kD, pH 7 and 8.2.*All values are average of triplicates within experiments and duplicate experiments. The values have a maximum std. deviation of 5 %*

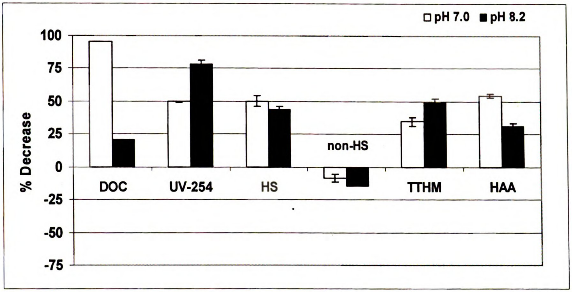

Figure 4.9a Effect of pH on Permeate 1 of 5 kD molecular weight cut off membrane

*Experimental setup: Fig.4.1 Operating Conditions: Table 4.1.Ozone Dose: 2.5 g/m³, Membrane Size: 5 kD, pH 7 and 8.2.*All values are average of triplicates within experiments and duplicate experiments. The values have a maximum std. deviation of 5 %*

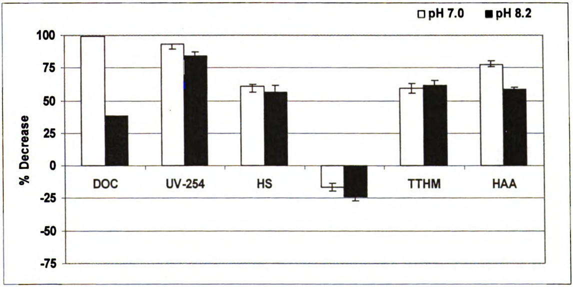

Figure 4.9bEffect of pH on Permeate 1 of 5 kD molecular weight cut off membrane

*Experimental setup: Fig.4.1 Operating Conditions: Table 4.1.Ozone Dose: 2.5 g/m³, Membrane Size: 5 kD, pH 7 and 8.2.*All values are average of triplicates within experiments and duplicate experiments. The values have a maximum std. deviation of 5 %*

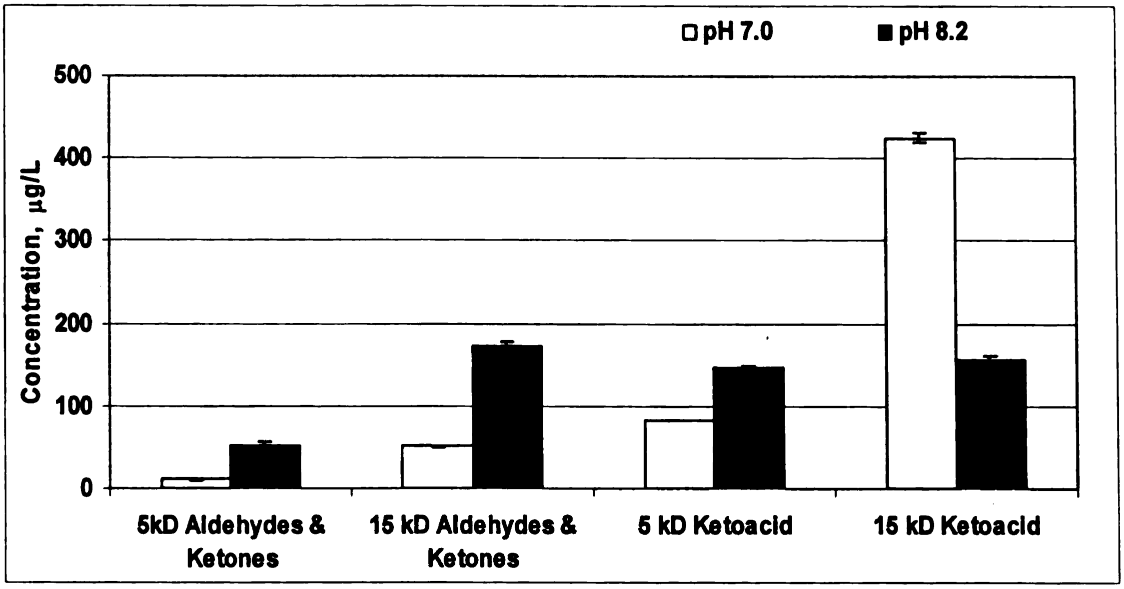

Figure 4.10a Effect of pH on Ozonation By-products in Permeate 1 of 15 kD & 5 kD molecular weight cut off membrane

*Experimental setup: Fig.4.1 Operating Conditions: Table 4.1.Ozone Dose: 2.5 g/m^3, Membrane Size: 5 and 15 kD, pH 7 and 8.2.*All values are average of triplicates within experiments and duplicate experiments. The values have a maximum std. deviation of 5 %*

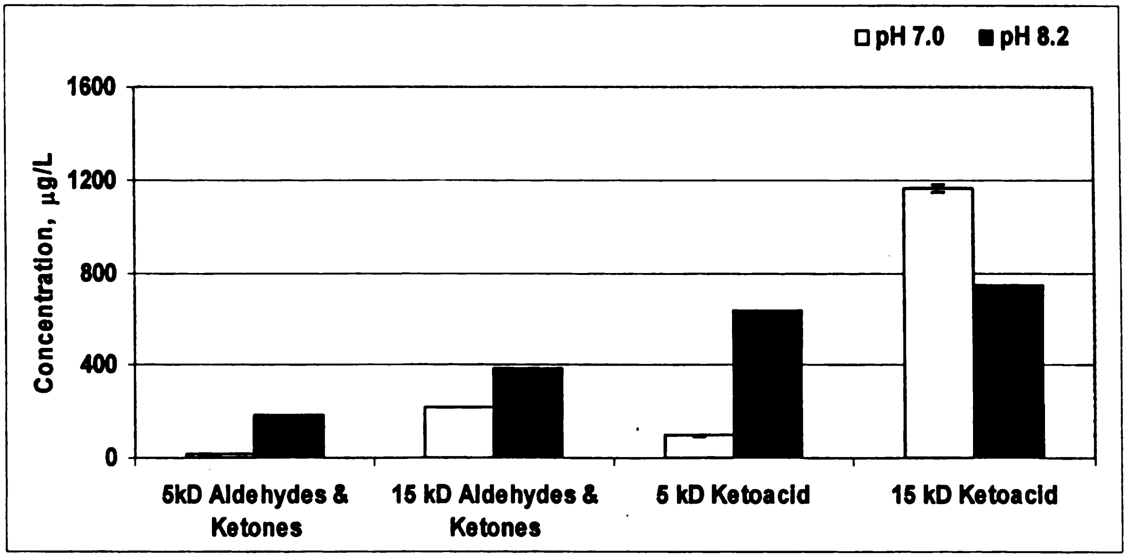

Figure 4.10b Effect of pH on Ozonation By-products in Permeate 2 of 15 kD & 5 kD molecular weight cut off membrane

*Experimental setup: Fig.4.1 Operating Conditions: Table 4.1.Ozone Dose: 2.5 g/m^3, Membrane Size: 5 and 15 kD, pH 7 and 8.2.*All values are average of triplicates within experiments and duplicate experiments. The values have a maximum std. deviation of 5 %*

Similar results were observed with the 5 kD membrane and for the P1 samples (Figures 4.8a and 4.9a). Thus, DOC removal is favored at the lower pH, where ozone is more stable, and the dissolved ozone concentrations are higher (Karnik et al., 2005).

For the 5 kD MWCO membrane, the UV-254 absorbance of the permeate was similar at both pH 7.0 and 8.2. For the 15 kD membrane, the reduction in the UV–254 absorbance was greater at the higher pH, suggesting that an OH radical mechanism may play a role in degrading UV absorbing substances under these conditions. Also, greater reductions in UV-254 were seen for the 5kD membrane than for the 15 kD membrane. However, the direct comparison of the results for the two membrane sizes is difficult, since, due to the lower permeate flux for the 5 kD membrane, the contact time with ozone is longer than it is for the 15 kD membrane.

Neither varying the molecular weight cut-offs of the membrane nor the pH resulted in a statistically significant change in the reduction of HS. The greater extent of conversion of HS to non-HS substances could be attributed to the increased residual ozone concentration at circumneutral pH (Karnik et al., 2005).

Decreasing the pH resulted in a statistically significant ($p< 0.05$) decrease in the concentrations of SDS TTHMs and SDS HAAs found after chlorination in the permeate samples of both the 5 kD and the 15 kD membranes (see Figures 4.8a to 4.9b). The higher of residual ozone concentration (Karnik et al., 2005) found at pH 7 is the likely cause for the lower concentrations of SDS TTHMs and SDS HAAs found at this pH.

For the aldehydes and ketones (shown in Figures 4.10a and 4.10b), there is a reduction of at least 50% in the concentrations of these compounds at pH 7.0, compared to pH 8.2. With a 5 kD MWCO membrane, there is greater reduction in the concentrations of these compounds as compared to that obtained with the 15kD MWCO membrane at pH 8.2 (see Figures 4.10a & 4.10b). If the formation of these compounds is predominately due to a radical mechanism, then the lower concentrations of these compounds found at pH 7.0 may be explained by the slower formation of these compounds at the lower pH, where the radical concentration would be expected to be lower as ozone degradation is slower. Alternatively, it may also be explained by the catalytic degradation of these compounds at the membrane surface. Further studies are required to confirm the reaction mechanism. For the 15 kD MWCO membrane, a higher concentration of ketoacids is found at pH 7.0 than at pH 8.2. For the 5 kD MWCO membrane, the opposite is true. At this time we have no clear explanation for this behavior.

4.5 CONCLUSIONS

Use of the combined ozonation/filtration treatment system resulted in significant improvements in water quality compared to the filtered raw water and to that using either ozonation or membrane filtration alone. The levels of DOC, UV absorbing compounds, SDS TTHMs and SDS HAAs were reduced by ozonation/membrane filtration, as compared to either ozonation or filtration alone. The concentration of aldehydes, ketones and ketoacids after ozonation/filtration were significantly less than the concentrations of these compounds found after ozonation (at the same ozone dosage).

4.6 ACKNOWLEDGEMENTS

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CHAPTER FIVE

Karnik, Bhavana.S.; Davies, Simon.H.; Baumann, Melissa. J.; Masten, Susan. J. (2005). Fabrication of catalytic membranes for the treatment of drinking water using combined ozonation and ultrafiltration. Environmental Science Technology 39(19): 7656-7661.

CHAPTER FIVE

FABRICATION OF CATALYTIC MEMBRANES FOR THE TREATMENT OF DRINKING WATER USING COMBINED OZONATION NANOFILTRATION.

5.1 ABSTRACT

The removal of disinfection by-products and their precursors was investigated using a combined ozonation-ultrafiltration system. A commercial membrane was coated 20 or 40 times with iron oxide nanoparticles (4-6 nm in diameter). With this membrane, the concentration of dissolved organic carbon was reduced by >85% and the concentrations of simulated distribution system total trihalomethanes and simulated distribution system halo acetic acids decreased by up to 90% and 85%, respectively. When the coated membrane was used, the concentrations of aldehydes, ketones, and ketoacids in the permeate were reduced by >50% as compared to that obtained with the uncoated membranes. Hydroxyl or other radicals produced at the iron oxide coated membrane surface as a result of ozone decomposition are believed to have enhanced the degradation of the natural organic matter, thereby reducing the concentration of disinfection by-products. While increasing the number of times the membrane was coated from 20 to 40 did not significantly reduce the concentrations of most of the parameters measured, it did result in a significant decrease in the concentrations of ozonation by-products. Increasing the sintering temperature from 500 °C to 900 °C also resulted in an improvement in the removal of the ozonation by-products.

Keywords: Catalytic ozonation; ceramic membranes; iron oxide; Disinfection By-products (DBPs), ozonation, nanofiltration, ultrafiltration

5.2 INTRODUCTION

The increased demand for water has lead many water utilities to use water sources that elevated levels of natural organic matter (Bursill, 2001; Skjelkvåle et al., 2000), making them undesirable as water sources. This increasing demand, combined with stricter government regulations, necessitates improved drinking water treatment. The presence of natural organic matter (NOM) in the source water is a cause of concern to health professionals and environmental engineers because the reaction of NOM with disinfectants, such as chlorine, results in the formation of disinfection by-products (DBPs), such as trihalomethanes (THMs) and haloacetic acids (HAAs). Because of their toxicity (Mughal, 1993; Morris et al., 1992; Kool et al., 1985) the trihalomethanes and haloacetic acids are regulated by the U.S. Environmental Protection Agency (US EPA).

In the United States there is an increasing interest in the application of both ozone and membrane filtration for DBP and DBP precursor removal in order to meet the requirements of the Surface Water Treatment Rule (SWTR), the Disinfectant and Disinfectant By-products Rule (D/DBPR), and the Long Term 1 Enhanced Surface Water Treatment Rule (LT1ESWTR). Several researchers have attempted to combine ozone with polymeric membranes with limited success, in part because the organic membranes, which are commonly used in water and wastewater treatment applications, are prone to destruction by ozone (Hashino et al., 2000; Shanbag et al., 1998; Castro and Zander, 1995; Shen et al., 1990). Hashino et al., (2000) studied the use of ozonation combined with an ozone resistant polyvinylidenefluoride (PVDF) microfiltration membrane. They found that ozone prevented foulants from adhering to the membrane surface, thus decreasing membrane fouling. However, high dissolved ozone concentrations (> 1 mg/L) were necessary to obtain high permeate fluxes and prevent membrane fouling.

Ceramic membranes are ozone resistant and when these membranes are used in combination with ozone, stable permeate fluxes can be achieved without membrane damage (Karnik et al., 2005a; Schlichter, 2004; Kim et al., 2001; et al., 1999; Allemane et al., 1993). Kim and colleagues (2001) used ceramic membranes to investigate the effect of ozone bubbling on flux recovery. The results showed that intermittent ozonation effectively maintained high permeate fluxes and prevented membrane fouling caused by particle accumulation on the membrane surface. Our earlier work demonstrated that stable fluxes can be obtained with ozonation-ceramic membrane filtration. Ultrafiltration alone did not achieve the levels of treatment obtained with combined ozonation/ membrane filtration. Ozonation-filtration resulted in a reduction of 50% in the dissolved organic carbon (DOC) concentration. It also resulted in the formation of partially oxidized compounds from NOM that were less reactive with chlorine, decreasing the concentration of simulated distribution system total trihalomethanes (SDS TTHMs) and simulated distribution system halo acetic acids (SDS HAAs) by up to 80% and 65%, respectively (Karnik 2005a;2005b).

Catalytic ozonation has been used to degrade NOM and other organic compounds in drinking water and wastewater (Legube and Karpel Vel Leitner, 1999). In the presence of different metal oxide catalysts, such as iron oxide, manganese oxide, titania, alumina and zirconia, ozone degrades organic compounds, including saturated carboxylic acids, phenols, aromatic hydrocarbons, dyes, humic substances and herbicides (Beltran et al., 2003a; 2003b; Ni and Chen, 2001; Radhakrishnan and Oyama 2001; Gracia et al., 2000a; 2000b; 1996; Legube and Karpel Vel Leitner, 1999). Based on extensive research involving various ozonation methods for drinking water treatment, catalytic ozonation has been determined to be the best alternative for the oxidation of ozone by-products to carbon dioxide, and the reduction in the chlorine demand (Volk et al., 1997; Allemane at al., 1993). Masten and Davies (1997) reported that the presence of reactive soil surfaces catalyzed the decomposition of ozone and contaminants sorbed on the soil. Paillard et al. (1991) documented that TiO_2-catalyzed ozonation was more efficient than ozone alone for the degradation of humic acid. Mn(II) is effective for the catalytic degradation of carboxylic acids that do not react appreciably with molecular ozone. It is believed that Mn(II) complexes with these carboxylic acids to form an intermediate by-product that is more easily degraded by ozone (Andreozzi et al., 2000; 1998a; 1998b; 1992). Ma et al., (2000; 1999) confirmed that the degradation of compounds by ozone in the presence of manganese follows a radical mechanism. Pure alumina, which is often used as a support material for metal or metal oxide catalysts, was also found to be an effective catalyst for the degradation of NOM by ozone (Ernst et al; 2004). Pecchi and Reyes (2003) prepared iron oxide coatings supported on TiO_2 and Al_2O_3 using the sol gel method. These coatings catalyzed the degradation of phenol by ozone.

This work focuses on the fabrication of ceramic membranes with catalytic properties using a layer-by-layer method to deposit iron oxide particles on a titania coated membrane. We have tested the application of these membranes in a combined ozonation-nanofiltration process to remove disinfection by-products and their precursors.

5.3 MATERIALS AND METHODS

5.3.1 Membrane Preparation and Characterization

Tubular AZT (a mixture of alumina, zirconia, and titania) ceramic membranes (Clover-leaf design (containing three channels), CéRAM Inside, TAMI North America, St. Laurent, Québec, Canada) with nominal molecular weight cut-offs of 15 kilodaltons (kD) and 5 kD were used as a support for the catalytic coatings. The external diameter of each membrane was 10 mm and the active membrane length was 8 cm. The total filtering area of the membrane was approximately 11 cm^2 and the membranes can be operated in the pH range from 0-14. The initial permeability of the membranes was tested using DDI water (Karnik et al., 2005a).

The colloidal particles used for coating the membranes were prepared by Sorum's method (Mulvaney et al., 1998 The procedure used was as follows: double deionized water (DDI) water (450 mL) was heated until it boiled vigorously; then 50 mL of freshly prepared 20 mM $FeCl_3$ solution was added at a rate of approximately two drops per second. The sol rapidly turned golden brown and finally deep red. After all the ferric chloride solution was added, the suspension was allowed to boil for an additional 5 minutes; it was then cooled to room temperature and dialyzed, using cellulose dialysis tubing with an average flat width of 33 mm, for 48 hours against a dilute nitric acid solution having a pH of 3.5.

Transmission electron microscopy (TEM) characterization was performed using a JEOL 100CX at an accelerating potential of 100 kV and magnifications ranging from 5,000X to 370,000X. The TEM protocol for the particle characterization involved diluting the suspension with DDI water in the ratio of 1:4. Double-sided sticky tape was attached to a glass slide (76.2 mm × 25.4 mm × 1 mm), leaving a small section (approximately 2-3 mm) of the tape hanging off the long side of the slide. Masking tape was then used to cover the portion of the double-sided tape, which rested on the glass slide, leaving the excess double-sided sticky tape uncovered. Grids (0.25% Formvar and carbon) were placed on the overhanging double-sided sticky tapes with light tweezer pressure to ensure that the grids would stick. The suspension was then placed in a dropwise manner onto the grids and the excess suspension was removed by lightly wiping across the grid with filter paper. The grids were then air-dried in a dust free environment until TEM analysis. Photomicrographs were collected using a Megaview III digital camera. The photomicrographs, which are provided in the Figure 5.1, showed that the average particle diameter was 4 to 6 nm.

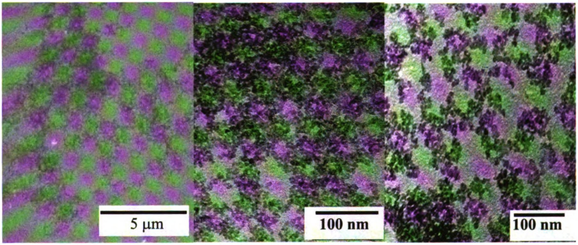

Figure 5.1 TEM characterization of the iron oxide particles (average size 4-6nm)
TEM: JEOL 100CX, Accelerating voltage: 100 kV, Imaging system: Analysis, Digital imaging: Mega view III

The layer-by-layer technique used to coat the membranes is based on a protocol described by McKenzie et al., (2002) for coating doped tin oxide electrodes. for coating doped tin oxide electrodes. The membrane was immersed in the colloidal suspension for one minute and then rinsed with DDI water. Then, the membrane was immersed in an aqueous phytic acid (40 mM) for one minute and rinsed with the DDI water. This sequence was repeated the desired number of times (20 or 40). After coating, the membrane was either sintered at 500 °C for 60 minutes or sintered at 900 °C for 30 minutes. These two temperatures were chosen to produce membranes on which the iron oxide particles were attached but not fused to each other (500 °C) or completely sintered to each other and to the membrane surface (900°C).

5.3.2 Ozonation/ Membrane Filtration

A schematic representation of the ozonation/membrane system is shown in Figure 5.2. A stainless steel filter holder, Teflon® tubing and stainless steel or Teflon® joints and valves were used throughout the system. Other components included: 3.5-liter and 1.5-liter water-jacked glass reservoirs made of Pyrex® glass, and a simple Y inline mixer (Ozone Service, Burton, B.C., Canada). The membranes described above were used for membrane filtration. A Teflon® valve was placed in the retentate line of the membrane system to create transmembrane pressures of 0.2 to 0.5 bars. Ozone gas was added into the water stream through a simple Y inline mixer, just before the aqueous stream entered the membrane module.

To generate ozone, pure oxygen gas (99.999%) from a pressurized cylinder was dried using a molecular sieve trap, and then fed to the ozone generator (Model OZ2PCS, Ozotech Inc., Yreka, Calif.). The voltage applied to the ozone generator was varied to control the gaseous ozone concentration. The excess gas was vented to the atmosphere after it was passed through a 2% potassium iodide (KI) solution to destroy any residual ozone. The water in the 3.5-liter reservoir was maintained at a constant level during the experiments using a peristaltic pump (Masterflex Model 7520-35, Cole-Parmer Co., Chicago, Illinois) to transfer the water from a 1.5-liter reservoir into the 3.5-liter reservoir. A constant water temperature of 20 °C was maintained using a recirculating water bath. The experiments were performed with a membrane cross flow velocity of 0.6 m/s; the flow was turbulent with a Reynolds number of approximately 6000.

The operating conditions are shown in Table 5.1. The operating conditions were determined based on the previous experiments with uncoated membranes (Karnik et al., 2005a; 2005b; Chen, 2003). The conductivity remained practically unchanged for the duration of the experiment. The change in conductivity was < 0.01 μS/cm.

Permeate samples were collected in bottles covered with Parafilm® and stored in an ice-bath throughout the duration of the experiment. The first 400 mL of permeate collected was labeled as P1 and the latter 1000 ml as P2.

Table 5.1
Typical Characteristics of Lake Lansing Water (Haslett, MI) [a]

Parameters	**Lake Lansing**
TOC (mg/L)	8.6 to 11.6
pH	7.7 to 8.6
Alkalinity (mg/L as $CaCO_3$)	145 to 157
UV-254 (abs.)	0.160 to 0.180
SDS THM[b] (μg/L)	240
SDS HAA[b] (μg/L)	75
BDOC (mg/L)	1.0 to 4.1
Nitrate (mg/L)	0.44
Total Phosphate (mg/L)	0.06
Hardness (mg/L as $CaCO_3$)	190 to 198

[a] All data reported is obtained from the Lake Lansing Watershed Advisory Committee Report(1998) except for SDS THM and SDS HAA, which were measured as part of this study

[b] SDS THM and SDS HAA were measured using Standard Method 5710 and USEPA Method 552.2 respectively.

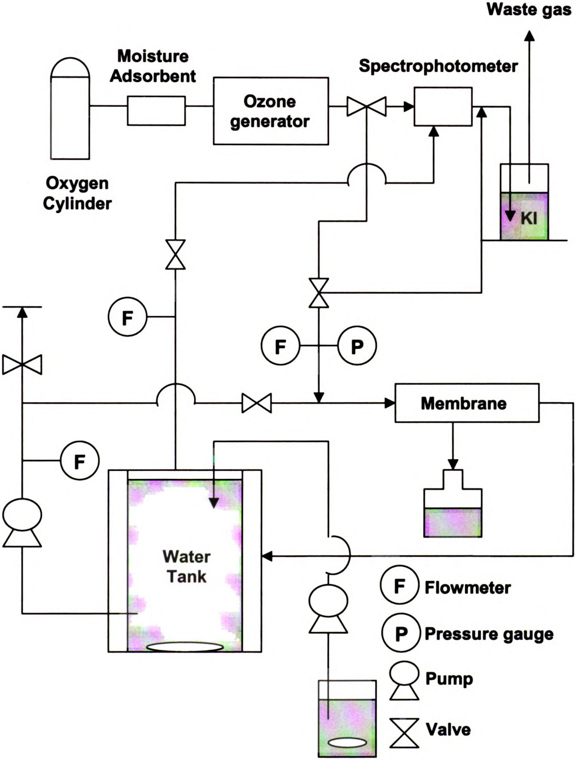

Figure 5.2 Schematic Representation of the Ozone-Membrane Filtration System

5.3.3 Water Source

Experiments were carried out using samples taken from Lake Lansing (Haslett, MI), which is a borderline eutrophic lake. The typical characteristics of the water from Lake Lansing, are given in Table 5.1. The samples were collected at the boat ramp at the Lake Lansing Park-South, Haslett, MI in five-gallon polyethylene carboys and stored at 4°C. The maximum storage period was seven days. Water samples were pre-filtered through a 0.45-µm mixed cellulose ester filter (Millipore-HA) before testing.

5.2.4 Analytical Methods

The absorbance of ozone in the gas phase was measured at 254 nm with a Milton Roy Genesis-5 spectrophotometer (Milton Roy, Inc., Rochester, NY) using a 2-mm path length quartz flow-through cell. An extinction coefficient of 3000 $M^{-1}cm^{-1}$ (Hoigné, 1988) was used to calculate the ozone concentration.

The UV absorbance of the water samples was measured at a wavelength of 254 nm with a Milton Roy Genesis-5 spectrophotometer (Milton Roy, Inc., Rochester, NY) using a 1 cm quartz cell.

DOC was analyzed using an OI Analytical Model 1010 analyzer. The TOC analyzer uses the UV/persulfate method (Standard Method, 1998). To ensure the reliability of the method, standards having TOC concentrations of 2.5, 5, 7, 10 mg/l (OI Analytical) were run and samples were analyzed in triplicate. A blank was also run with every set of samples.

The concentrations of humic substances in the samples were measured by adsorption on an XAD-8 resin according to Method 5510C (Standard Methods, 1998). A 100 mL sample was acidified with concentrated phosphoric acid to a pH of 2, the acidified sample was then eluted through a 10 mm diameter (ID) x 15 cm long column at a flow rate of 2 mL/min. The effluent from the column was collected and then analyzed for TOC, which represents the non-humic fraction of the dissolved organic matter in the water sample. The resin-packed column was then back eluted with 100 mL of 0.1 N sodium hydroxide at a flow rate of 2 mL/min. The eluent was collected and acidified with concentrated phosphoric acid to a pH less than 4, purged with high-purity helium for 3 minutes to remove the inorganic carbon, and analyzed for TOC. The organic content of the eluent represents the concentration of humic substances.

Water samples were dosed with a chlorine concentration that ensured a residual chlorine concentration in the range of 0.5 to 2 mg/L after 48 hours incubation at room temperature, according to the procedures in Method 2350 (Standard Methods 1998). The THM compounds, chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$), and bromoform ($CHBr_3$), were extracted from the water samples using hexane and analyzed by gas chromatography (Method 5710, Standard Methods 1998). A Perkin Elmer Autosystem gas chromatograph (Perkin Elmer Instruments, Shelton, CT) equipped with an electron capture detector (ECD), an auto sampler, and a 30 m × 0.25 mm I.D., 1 μm DB-5ms column (J&W Scientific, Folsom, CA) was used for the analysis. The oven temperature was ramped from 50°C to 150 °C at a rate of 10 °C/min. The flow rate of the carrier gas (N_2) was 12.0 mL/min. The injector temperature and detector temperature were 275 and 350 °C, respectively.

SDS HAAs were produced by chlorination as described above. The concentrations of monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), bromochloroacetic acid (BCAA), trichloroacetic acid

(TCAA), and dibromoacetic acid (DBAA) were determined using US EPA Method 552.2. A Perkin Elmer Autosystem gas chromatograph (Perkin Elmer Instruments, Shelton, CT) equipped with an ECD, an autosampler, and a 30 m × 0.32 mm I.D., 3 μm DB-1 column (J&W Scientific, Folsom, CA) was used for the analysis. The oven temperature was programmed to hold for 15 minutes at 32°C, then increased to 75 °C at a rate of 5 °C/min and held 5 minutes, then increased to 100 °C at a rate of 5 °C/min. The carrier flow (nitrogen) was 1.0 mL/min with the injector temperature and detector temperatures at 200 °C and 260 °C, respectively.

USEPA Method 556 (Munch et al., 1998) was used to monitor formaldehyde, propionaldehyde, glyoxal, methyl glyoxal, acetone, and 2-butanone, ketomalonic acid, pyruvic acid and glyoxylic acid. A Perkin Elmer Autosystem gas chromatograph (Perkin Elmer Instruments, Shelton, CT) equipped with an ECD, an autosampler, and a 30 m × 0.25 mm I.D., 0.5 μm DB-5ms column (J&W Scientific, Folsom, CA) was used in the analysis. The oven temperature was programmed to hold at 1 minute at 50 °C, then increased to 220 °C at a rate of 4°C/min followed by an increase to 250 °C at a rate of 20 °C/min with a 5 minute hold time. The carrier flow was 1.0 mL/min and the injector temperature and detector temperatures were 180 °C and 300 °C, respectively.

5.3.5 Ozone-membrane filtration experiments

The ozone-filtration system used in these experiments is shown in Figure 5.2. The operating conditions used are shown in Table 5.2.

Permeate samples were collected in bottles covered with parafilm and stored in an ice-bath throughout the duration of the experiment. The first 400 mL of permeate collected was labeled as P1 and latter 1000 ml as P2.

Table 5.2
Operating Conditions for the Ozone–Membrane Filtration System

Water recirculation rate	2.75 LPM
Water temperature	20°C
Ozone gas flow rate	100 mL/min
TMP	0.5 bar
Ozone dose	2.5 g/m^3

5.4 RESULTS AND DISCUSSION

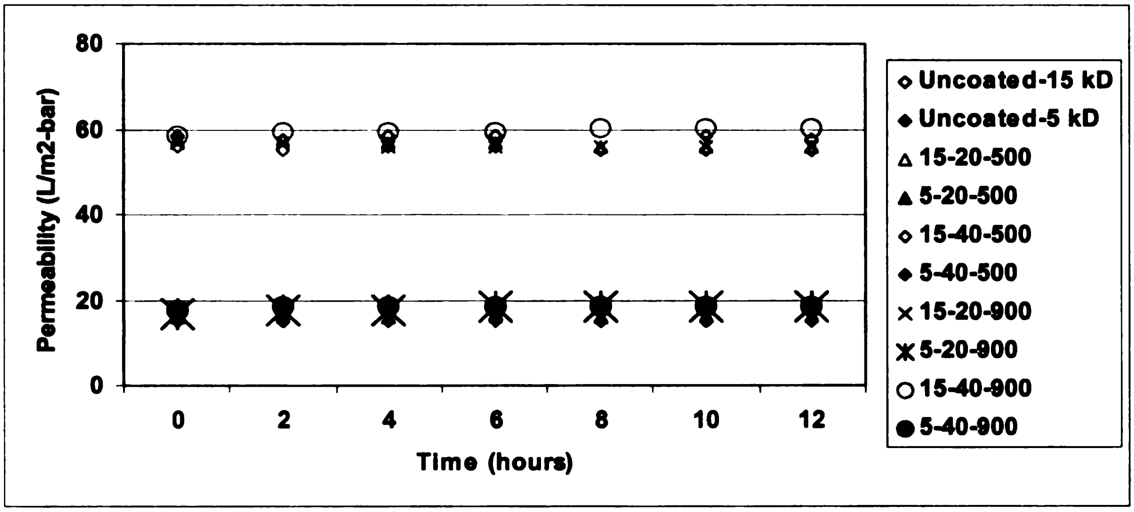

Figure 5.3 Permeate flux for different membrane coating modifications.
Experimental setup: Fig. 5.2. Operating Conditions: Table 5.1.Membrane Size: 5 or 15 kD
**All values are average of triplicates within experiments and duplicate experiments. The values have a maximum std. deviation of 5%. For the coated membranes the first number in the legend corresponds to MWCO of the membrane, the second number is the number of coatings and the third number is the sintering temperature. For example, 15-20-500 is a membrane with 15 kD MWCO coated 20 times with the catalyst and sintered at 500 °C. All values are average of triplicates within experiments.*

Our earlier work showed no significant decrease in the permeate flux when using ozone at gas phase concentrations greater than 2.5 g/m^3 (Karnik et al., 2005a). Experiments were conducted to determine the effect of the coating procedure on membrane permeability. As shown in Figure 5.3, stable fluxes were maintained throughout the course of each experiment. The coating of the membrane had little effect on its permeability, suggesting that processing did not damage the integrity of the membrane and that the resistance of the iron oxide coating is comparatively small.

Figures 5.4-5.7 compare the results obtained for the coated and uncoated membranes. The results for the 15 kD membrane are shown in Figures 5.4 and 5.5 and Figures 5.6 and 5.7 show the results for the 5 kD membrane.

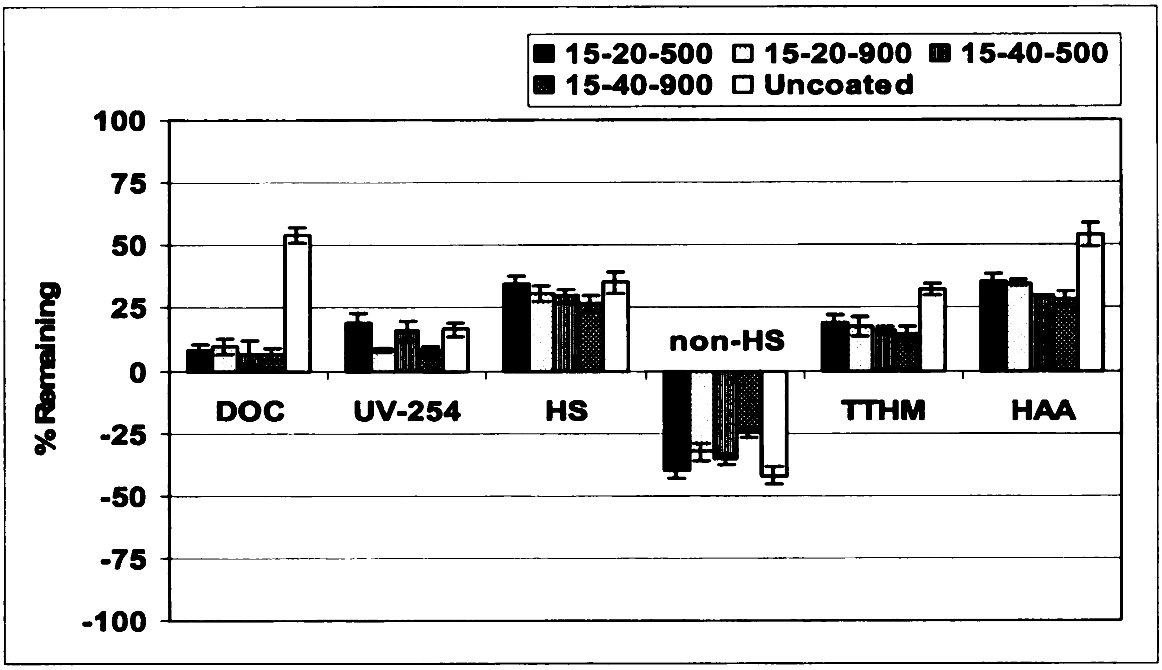

Figure 5.4 Water quality results for two different sintering temperatures.
Experimental setup: Fig. 5.2. Operating Conditions: Table 5.1. Membrane Size: 15 kD, Coating: 20 or 40 coatings, Sintering temperature: 500 °C or 900 °C. All values are average of triplicates within experiments. Explanation of the legend is given in the caption of Fig.5.3

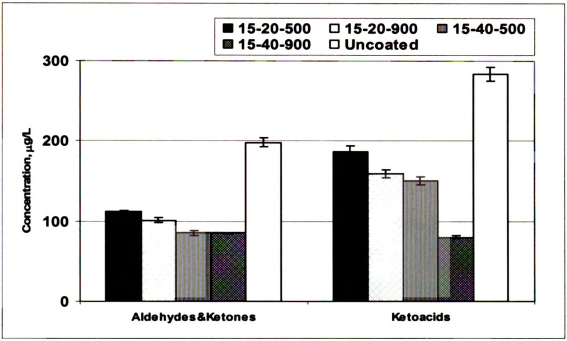

Figure 5.5 Concentrations of ozonation by-products in the permeate for two different sintering temperatures.
Experimental setup: Fig. 5.2. Operating Conditions: Table 5.1. Membrane Size: 15 kD, Coating: 20 or 40 coatings, Sintering temperature: 500 °C or 900 °C. All values are average of triplicates within experiments. Explanation of the legend is given in the caption of Fig.5.3

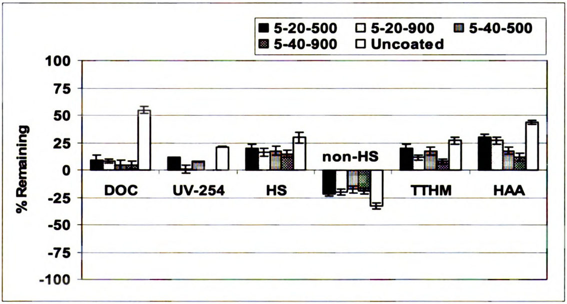

Figure 5.6 Water quality results for two different sintering temperatures.
Experimental setup: Fig. 5.2. Operating Conditions: Table 5.1. Membrane Size: 5 kD, Coating: 20 or 40 coatings, Sintering temperature: 500 °C or 900 °C. All values are average of triplicates within experiments. Explanation of the legend is described in the caption of Fig.5.3

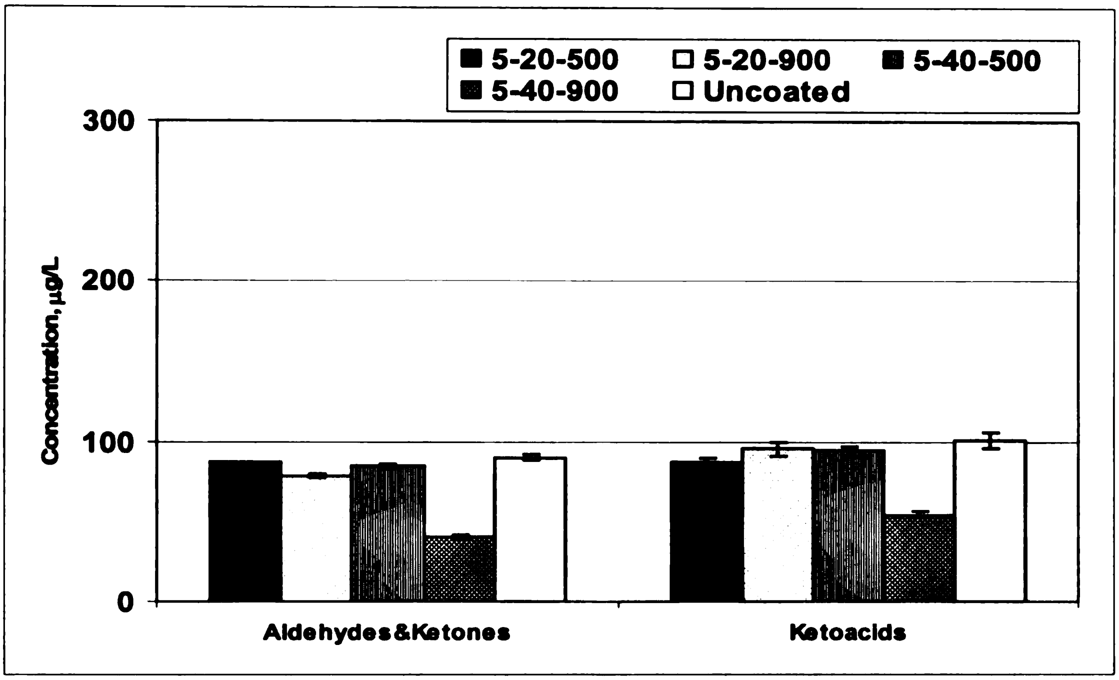

Figure 5.7 Concentrations of ozonation by-products in the permeate for two different sintering temperatures.

Experimental setup: Fig. 5.2. Operating Conditions: Table 5.1. Membrane Size: 5 kD, Coating: 20 or 40 coatings, Sintering temperature: 500 °C or 900 °C. All values are average of triplicates within experiments. Explanation of the legend is described in the caption of Fig.5.3

As shown in Figure 5.4, the permeate fluxes are different for the 15 and 5 kD MWCO membranes. Thus, due to the different ozone contact times, a direct comparison of the results for the membranes with different MWCOs is impossible.

Figures 5.4 and 5.6 show that the reduction in the DOC concentration in the P2 samples is greater for the coated membranes than for the uncoated membrane. This reduction in DOC concentrations suggests that the iron oxide coating catalyzes the degradation of ozone to produce radical species at the membrane surface, which degrade the NOM. Losses due to sorption of NOM on the iron oxide coating are expected to be very small, since the iron oxide coatings are extremely thin. Based on the observed thickness of the coating (using TEM) the total quantity of iron oxide deposited on the membrane is estimated to be less than 0.1 μg. The quantity of DOC removed is > 4 mg C. To remove this amount of NOM via sorption, the sorptive capacity of the iron oxide would have to be of the order of 4 x 10^7g/kg. This figure is too large to be reasonable, even for nanoparticles, so we conclude that sorption to the iron oxide particles cannot explain the enhanced NOM removal seen with the coated membranes. As with all parameters measured, the results for NOM removal in the P1 samples follow the same trends as observed with P2 samples. As such, only the data for P2 samples is presented in the figures. The data for P1 samples is available in Fig 5.8 to 5. 15.

There is a little difference between the coated and uncoated membranes in the extent to which the absorbance of the UV-254 absorbing compounds is reduced. In our earlier work, we showed that the removal of the UV-254 absorbing compounds is due predominately to the reaction of ozone with these substances and not due to filtration (Karnik et al., 2005b). Together, these results suggest that the reduction in UV absorbing compounds is due to solution phase ozonation rather than surface catalytic reactions.

Similarly, no statistically significant differences were observed in the concentrations of the humic substances found in the permeate after combined treatment of ozonation-membrane filtration using either the coated and uncoated membranes. Consistent with these results for the removal of humic substances, the concentrations of non-humic substances formed were also similar in the permeates from all membranes studied (see Figures 5.4 and 5.6). The behavior of HS and non-HS in the ozone membrane filtration system is discussed in detail in our earlier work where we studied the destruction of HS and formation of the non-HS during ozonation alone, membrane filtration alone, and in the hybrid process (Karnik et al., 2005b). The concentration of HS remaining in the P2 samples after ozonation/membrane filtration was less than 50% of that in the raw water. This reduction is, in part, due to the reaction of NOM with either ozone or OH radicals, since an increase in the non-humic substance (non-HS) concentration after ozonation/filtration was observed. The increase in non-HS concentration could only be caused by the conversion of HS to non-HS. Filtration would not have resulted in such a conversion. This conclusion is substantiated by results presented by Karnik et al. (2005b), which show that the percent removal of HS using ultrafiltration was 13% for P2, while 50% of the HS was removed by ozonation.

The concentrations of non-HS measured in the P2 samples increased by approximately 20% compared to that in the P1 samples, indicating that the reaction of HS to form non-HS continued throughout the course of the experiment. If the humic substances were removed purely by filtration, the extent of removal would not likely have increased with ozonation time.

Despite the results for HS, the extent to which the DBPs precursors were removed was greater with the coated membranes than with the uncoated membrane (see Figures 5.4 and 5.6). The concentrations of TTHMs and HAAs were reduced by up to 90% and up to 85%, respectively, with ozonation combined with an iron oxide coated 5 kD membrane. The membrane surface coated with iron oxide appears to catalyze reactions that lead to a reduction in DBPs and DBP precursors. For the 15 kD membranes, the concentrations of aldehydes, ketones, and ketoacids in the permeate following treatment using the coated membranes were less than that obtained with the uncoated membrane (see Figure 5.5). Ozone may decompose on the active metal sites of the iron oxide surface, resulting in increased rates of hydroxyl radical production (Ernst et al., 2004; Ma et al., 2000; 1999), which in turn leads to a concomitant decrease in the concentration of disinfection by-products and their precursors. To improve the adhesion of the coating to the membrane, several coated membranes were sintered at 900 °C. The results for the coated membranes treated at 500 °C and 900 °C are compared in Figures 5.3 to 5.6. A small decrease in the concentration of ozonation by-products was found when the higher sintering temperature was used. It appears that sintering at higher temperatures alters the properties of the ceramic membrane surface, which further enhances its catalytic properties.

Ongoing studies are being conducted using scanning electron microscopy (SEM) and TEM imaging of these sintered surfaces along with chemical and phase analysis of the membrane surface to better understand the changes that occur during sintering.

As seen in Figures 5.4 to 5.7, increasing the number of coatings of iron oxide did not result in a significant improvement in the system performance, except for the ozonation by-products. The lowest concentrations of aldehydes, ketones, and ketoacids were achieved using the membrane that was coated 40 times and sintered at 900 °C. The 5 kD membrane performed better than the 15 kD membrane. A statistical analysis of the data presented in Figures 5.4-5.7 using ANOVA indicates that at the 95% confidence level, with the exception of the results for HAAs with a 5 kD membrane (see Figure5.6) and the ozonation by-products with a 15 kD membrane (see Figure 5.5), there is no statistically significant difference for the removal of NOM, DBPs or DBP precursors using the membranes coated 20 or 40 times.

The US EPA, under the Stage 2 Disinfection/Disinfection By-Product (D/DBP) Rule, sets standards for maximum DBP concentrations in drinking water. The maximum contaminant levels for TTHMs and HAAs are 80 μg/L and 60 μg/L, respectively. Catalytic ozonation membrane filtration met regulatory limits for both contaminants. Using a 5 kD MWCO membrane, coated 20 times and sintered at 900°C, the concentrations of TTHMs and HAAs after chlorination were approximately 25 to 30 μg/L and 20 to 25 μg/L, respectively. Even better quality water was achieved using a 5 kD MWCO membrane, coated 40 times and sintered at 900°C. After chlorination the concentration of TTHMs was approximately 15 to 20 μg/L and the concentration of HAAs was approximately 7 to 15 μg/L. These results are especially significant because these limits are difficult to meet with poor quality waters, such as those used in this work.

Previous work has demonstrated we can meet the regulatory requirements for DBPs using a 1 kD membrane and a gaseous ozone concentration of 2.5 g/m^3 (Karnik et al., 2005b). Comparable results could be obtained using iron oxide coated 5 kD membranes. As the permeability of the 5 kD membrane is three times greater than that of the 1 kD membrane, a significant decrease in the costs associated with the process can be achieved using the coated membrane while still producing high quality water that meets the pertinent regulatory requirements of the Stage 2 D/DBP Rule.

5.5 SUPPLEMENTAL INFORMATION

This data is included in Appendix A, showing water quality for permeate 1 (P1) of the 15kD and 5kD MWCO is available in supplemental information Figures A1 to A4. The effect of sintering temperatures on the permeates of 15 and 5 kD MWCO is shown in Figures A5 to A8.

5.6 ACKNOWLEDGEMENTS

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CHAPTER SIX

Karnik, Bhavana S.; Davies, Simon H.; Baumann, Melissa J.; Masten, Susan J. (2006). AFM and SEM Characterization of Iron Oxide Coated Ceramic Membranes. Accepted for publication in Journal of Materials Science.

CHAPTER SIX

AFM and SEM Characterization of Iron Oxide Coated Ceramic Membranes

6.1 ABSTRACT

Alumina-zirconia-titania (AZT) ceramic membranes coated with iron oxide nanoparticles have been shown to improve water quality by significantly reducing the concentration of disinfection by-product precursors, and in the case of membrane filtration combined with ozonation, to reduce ozonation by-products such as aldehydes, ketones and ketoacids. Commercially available ceramic membranes with a nominal molecular weight cut-off of 5 kilodaltons (kD) were coated 20, 30, 40 or 45 times with sol suspension processed Fe_2O_3 nanoparticles having an average diameter of 4-6 nm. These coated membranes were sintered in air at 900 °C for 30 minutes. The effects of sintering and coating layer thickness on the microstructure of the ceramic membranes were characterized using atomic force microscopy (AFM), scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS). AFM images show a decreasing roughness after iron oxide coating with an average surface roughness of ~ 161 nm for the uncoated and ~ 130 nm for the coated membranes. SEM showed that as the coating thickness increased, the microstructure of the coating changed from a fine grained (average grain size of ~ 27 nm) morphology at 20 coating layers to a coarse grained (average grain size of ~ 66 nm) morphology at 40 coating layers with a corresponding increase in the average pore size from ~ 57 nm to ~ 120 nm. Optimum water quality was achieved at 40 layers, which corresponds to a surface coating morphology consisting of a uniform, coarse-grained structure with open, nano-sized interconnected pores.

Keywords: ceramic membrane, nanosized, iron oxide, catalytic coating, scanning electron microscopy, atomic force microscopy, nanofiltration

6.2 Introduction

In the United States there is an increasing interest in the application of both ozone and membrane filtration for disinfection by-products (DBPs) and DBP precursor removal in order to meet the requirements of the US Environmental Protection Agency's (US EPA) Surface Water Treatment Rule (SWTR), the Disinfectant and Disinfectant By-products Rule (D/DBPR) and the Long Term 1 Enhanced Surface Water Treatment Rule (LT1ESWTR). During the last decade, researchers have attempted, with limited success, to combine ozonation and polymeric membrane filtration as a water and wastewater treatment option (Hashino et al., 2000; Shanbhag et al., 1998; Castro and Zander, 1995; Shen et al., 1990). The increasing severity of operating parameters, including higher temperatures and pressures, higher resistance to chemicals and overall durability, made ceramic membranes the natural choice in spite of their much higher costs (Zuzek et al., 2001). Potential applications for ceramic membranes include separation, purification, catalysis and chemical sensors at high temperatures as well as use in chemically reactive environments (Zeng et al., 1997). Ceramic membranes are ozone resistant and when used in combination with ozone, can achieve stable permeate fluxes without membrane damage (Karnik et al., 2005a; Schlichter et al., 2004; Kim and Somiya, 2001; Kim et al., 1999; Allemane et al., 1993).

Our earlier work showed that stable fluxes could be obtained with ozonation in combination with ceramic membrane filtration (Karnik et al., 2005a; 2005b). Catalytic degradation of ozone at the membrane surface is thought to oxidize foulants that accumulate at the membrane surface, thereby preventing membrane fouling. Ozonation-filtration resulted in a reduction of 50% in the dissolved organic carbon (DOC) concentration. It also resulted in the formation of partially oxidized compounds from natural organic matter (NOM) that were less reactive with chlorine, decreasing the concentration of carcinogenic compounds such as trihalomethanes and haloacetic acids. The formation of simulated distribution system total trihalomethanes (SDS TTHMs) and simulated distribution system halo acetic acids (SDS HAAs) were decreased by up to 80% and 65%, respectively (Karnik et al., 2005a; 2005b).

Based on extensive research involving various ozonation methods for drinking water treatment, catalytic ozonation has been determined to be one of the best alternatives for oxidizing NOMs and reducing the demand for chlorine, a common disinfectant used in water purification (Volk et al., 1997; Allemane et al., 1993). In the presence of different metal oxide catalysts, such as iron oxide, manganese oxide, titania, alumina and zirconia, ozone degrades organic compounds, including known harmful and potential carcinogens like saturated carboxylic acids, phenols, aromatic hydrocarbons, dyes, humic substances and herbicides (Karnik et al., 2005c). We have developed a novel procedure based on a layer-by layer method (McKenzie et al., 2002) for coating alumina-zirconia-titania (AZT) nano-crystalline ceramic membranes. Iron oxide coated membranes reduced the concentration of DOCs by >85% and the concentrations of SDS TTHMs and SDS HAAs by up to 90% and 85%, respectively, compared to that found with untreated water (Karnik et al., 2005c). Similarly, the iron oxide coated AZT membrane reduced the concentrations of ozonation disinfection by-products (aldehydes, ketones, and ketoacids) in the permeate by >50%, as compared to that obtained using uncoated membranes (Karnik et al., 2005c).

Surface modification is significantly affected by surface morphology; it is an important way to enrich the functionality of the ceramic membranes. Atomic force microscopy (AFM), scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS) have been used to examine ceramic membrane surfaces. Researchers have successfully characterized the fabrication and microstructure of ceramic membranes derived from alumoxane, ferroxane nanoparticles and Al_2O_3 - Al nano-composite powders (Lu et al., 2005; Cortalezzi et al., 2003 ; 2002). AFM, SEM and EDS have been used to characterize these coatings on titania membranes, composites of alumina-titania, metal doped ceramics and similar ultra and nanofiltration membranes (Lu et al., 2005; Siriwardane et al., 2000; Chou et al., 1999; Bae et al., 1998; Pedersen et al., 1997).

In this work, AFM, SEM and EDS were used to investigate the surface characteristics of the iron oxide nanolayered coated AZT ceramic membranes. A suspension of iron oxide nanoparticles was passed over the AZT membrane surface 20, 30, 40 or 45 times followed by sintering at 900 °C. The water quality analysis performed on the permeate of different membrane coatings did not show any significant improvement in the reduction of DBPs concentrations neither was there increased removal of DBP precursor with the increase in the number of catalyst coatings (Karnik 2005c). However, the ozonation by-products monitored in the permeate showed a significant reduction in concentration with increasing number of catalyst coatings from

20 to 40. No significant reduction in the concentrations of the ozonation by-products was reported for 60 coating layers making 40 coatings the optimum choice in terms of water quality performance and biological stability.

6.3 MATERIALS AND METHOD

6.3.1 Membrane Preparation

Tubular AZT (a mixture of alumina, zirconia and titania) ceramic membranes (Clover-leaf design (containing three channels), CéRAM Inside, TAMI North America, St. Laurent, Québec, Canada) with nominal molecular weight cut-offs of 5 kilodaltons (kD) were used as a support for the iron oxide catalytic coatings. The external diameter of each membrane was 10 mm and the active membrane length was 8 cm. The total filtering area of each membrane was approximately 11 cm^2 with each membrane operational from pH 0-14. The initial permeability of the membranes was tested using distilled deionized (DDI) water (Karnik 2005a).

A detailed description of the membrane preparation is available in our earlier published work (Karnik 2005c). The colloidal particles used for coating the membranes were prepared using Sorum's method (McKenzie et al., 2002). Transmission electron microscopy (TEM) characterization showed that the average particle diameter was 4 to 6 nm. The layer-by-layer technique used to coat the membranes is based on a protocol described by McKenzie et al. (2002) for coating doped tin oxide electrodes. The membrane was immersed in the colloidal suspension for one minute and then rinsed with DDI water. Then, the membrane was immersed in aqueous phytic acid (40 mM) for one minute and rinsed with DDI water. This sequence was repeated the desired number of times (20, 30, 40 or 45). After coating, the membrane was sintered at 900 °C for 30 minutes. This temperature was chosen to produce membranes on which the iron oxide particles were completely sintered to each other and to the membrane surface. These sintered membranes were then examined using AFM, SEM and EDS.

6.3.2 Characterization of Membranes

To obtain images of the coated surface of the tubular ceramic membranes, the membrane was first sliced into circular discs of 1 mm thickness using a diamond-wafering saw. Subsequently, these sections were cut to form small arcs of length 3 mm and width 1 mm. These arcs were then mounted on aluminum discs for AFM and aluminum mounting stubs for SEM using carbon adhesive tape. The schematic representation of this procedure is shown in Figure 6.1. The samples were then imaged and data collected using AFM, SEM and EDS.

AFM images of the uncoated and coated membranes were obtained using a Nanoscope IV Multimode Atomic Force Microscope (Digital Instruments Inc.), in ambient air in contact mode, which is ideal for examination of textured samples like ceramics. Silicon nitride (Si_3N_4) NP triangular cantilever probes were used to image the iron oxide coated membranes along with uncoated membranes for comparison purposes (Digital Instruments, Veeco Metrology group, CA) with a cantilever spring constant of 0.12 N/m and a frequency of 20 kHz. The tip has a nominal radius of curvature of 20 nm with a height 2.5-3.5 µm and a side angle of 35°. Scans of 20 µm × 20µm were taken at a scanning rate of ~ 0.5 Hz. Height and deflection data was taken simultaneously for the same scan area. The 3D surface plot and roughness analysis using the height data were performed on the images to study the surface morphology.

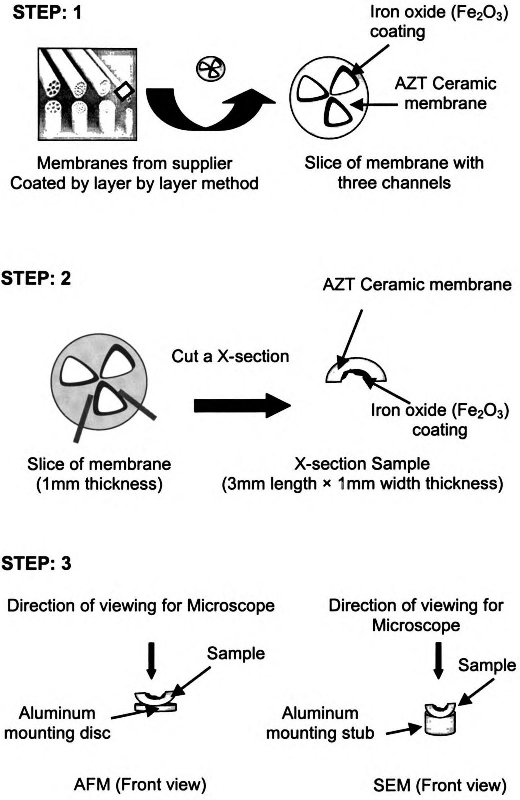


Figure 6.1 Schematic Representation of sample preparation for SEM and AFM imaging

SEM images of the membranes were obtained using a JEOL 6400V scanning electron microscope equipped with a LaB_6 emitter operated at an accelerating potential of 15 kV at magnifications from 5,000X to 60,000X. The mounted samples were gold coated using an Emscope SC 500 sputter coater at a rate of 7 nm/min with 20 mA current. EDS microanalysis was performed on the samples using a Noran EDS analyzer (Noran Instruments Inc.) at accelerating potential of 20 kV and magnifications ranging from 100X to 5000X. Samples were carbon coated using an EFFA Mk II carbon coater (Ernest Fullam Inc., Latham NY) in preparation for EDS analysis.

EDS microanalysis has a in built software module to measure the average grain size using the line intercept method. The grain sizes are measured using the average calculated from five micrographs for each sample where on average; 200 grains were measured per micrograph. ANOVA testing was performed on the grain size data within 90% confidence intervals to determine if the differences in the measurements were significant. An identical procedure was followed for the pore size measurements, however instead of grain size module; arbitrary distance was measured between the grains to determine the pore size.

The natural organic matter (NOM) and the DBP precursors were monitored in terms dissolved organic carbon concentrations (DOC) (Standard Methods, 1998). The DBPs total trihalomethanes (TTHMs) and halo acetic acids (HAAs) were measured using standard methods and reported elsewhere (Karnik 2005b; 2005c). Similarly, ozonation by-products (aldehydes, ketones and ketoacids) were measured using USEPA standard methods (Munch et al., 1998).

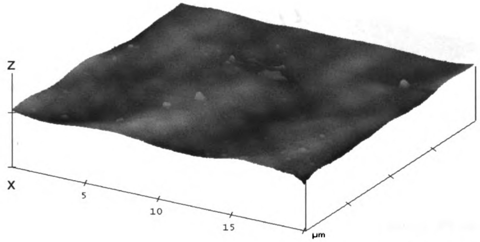
6.4 RESULTS AND DISCUSSION

6.4.1 AFM imaging

AFM analysis provided data on the surface morphology and surface roughness. The manner in which these properties correlate with the surface porosity and filtration performance provide insight into the structure of the filtration membrane. The surface roughness from AFM measurements can be correlated to the grain size found using SEM. Figure 6.2 a-c shows AFM images of a typical 5 kD uncoated AZT membrane, an uncoated AZT membrane sintered at 900 °C and an AZT membrane coated 40 times with the iron oxide nanoparticle suspension and sintered in air at 900 °C.

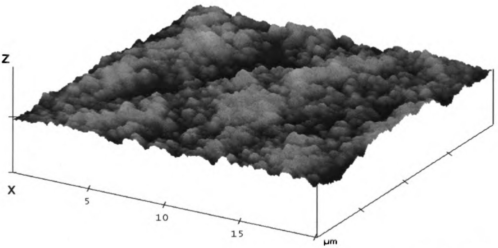
For each AFM image, the area in view represents a 20 μm × 20 μm square. The features within any given sample are relatively uniform throughout the sample. With sintering, the surface of the AZT uncoated membrane (Figure 6.2a) undergoes a gradual transition from flat featureless regions of ~ 2.5μm (± 0.2) height to more sharp surface features of ~ 3 μm (± 0.08) height (Figure 6.2b). With coating and sintering (Figure 6.2c), the height of these features reduces to ~ 1.5 μm (± 0.1). When comparing membranes coated for 20, 30 and 40 times followed by sintering, the respective AFM height data (plotted in Figure 6.3) show no statistical difference between membranes coated 30 and 40 times. However, both are significantly decreased in comparison to the membranes coated 20 times.

a) 5kD uncoated



X axis- 5.000 µm/div
Z axis- 2000.000 nm/div

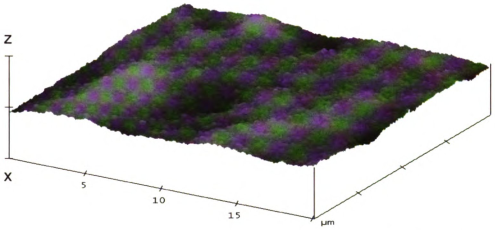
b) 5kD uncoated- sintered (900°C)



X axis- 5.000 µm/div
Z axis- 3000.000 nm/div

Figure 6.2 AFM images of the AZT ceramic membranes: a) 5kD MWCO AZT membrane uncoated, b) 5kD AZT membrane uncoated, sintered at 900 °C for 30 minutes

c) 5kD - 40 coatings- sintered (900°C)



X axis- 5.000 µm/div
Z axis- 1500.000 nm/div

Figure 6.2 c) AFM images of the AZT ceramic membranes: 5kD AZT membrane with 40 coatings of iron oxide, sintered at 900 °C for 30 minutes

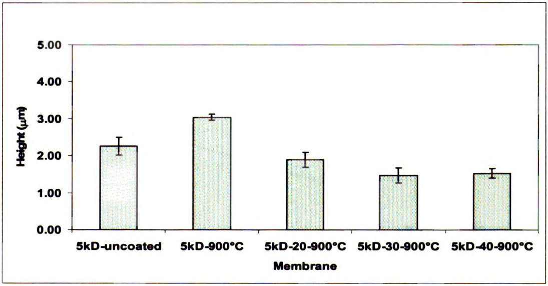


Figure 6.3 Height data for AFM images of membranes with different number of coatings

However, while the height of each feature is not significantly reduced as the number of coats increases (Figure 6.4), there is an increase in the number of these features. This result is substantiated by AFM roughness analysis which shows a significant decrease in roughness from ~ 161 nm to ~ 78 nm upon sintering of the uncoated AZT membrane. There is also a reduction in the surface roughness from ~ 161 nm for the uncoated membrane to an average of ~ 130 nm for the coated membranes, with no statistical difference in the roughness with an increase in the number of coats.

a) 5kD - 20 coatings

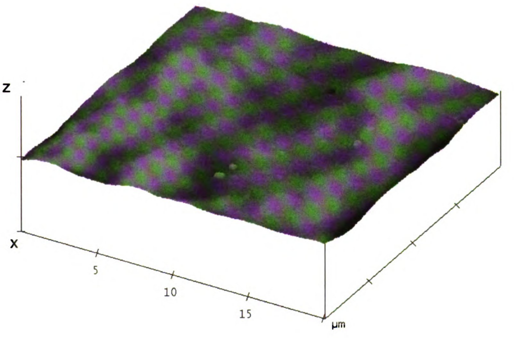
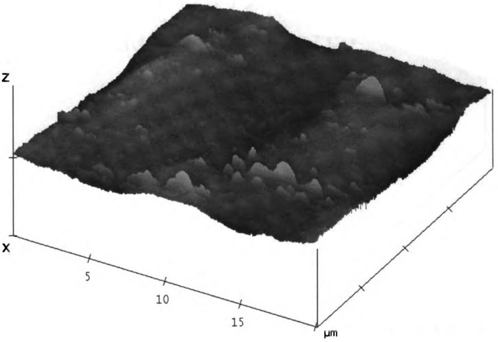


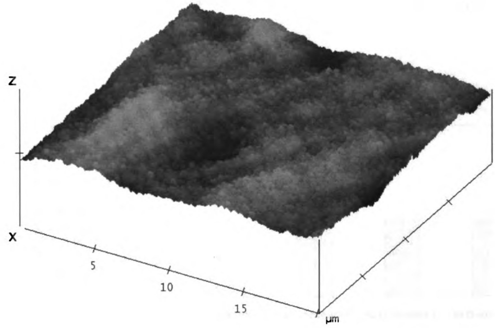
Figure 6.4 a) AFM image of an AZT ceramic membrane with iron oxide coating: 5kD AZT membrane with 20 coatings of iron oxide, sintered at 900 °C for 30 minutes



b) 5kD - 30 coatings

X axis- 5.000 µm/div
Z axis- 1500.000 nm/div

Figure 6.4 b) AFM image of an AZT ceramic membrane with iron oxide coating: 5kD AZT membrane with 30 coatings of iron oxide, sintered at 900 °C for 30 minutes



c) 5kD - 40 coatings

X axis- 5.000 µm/div
Z axis- 1500.000 nm/div

Figure 6.4 c) AFM image of an AZT ceramic membrane with iron oxide coating: 5kD AZT membrane with 40 coatings of iron oxide, sintered at 900 °C for 30 minutes.

For all membranes tested, the observed magnitude of the roughness, shown in Figure 6.5, is much greater than the size of the original iron oxide particles (4-6 nm). As shown in the SEM micrographs in Figure 6.6, this increase in roughness is due to interparticle sintering between the iron oxide nanoparticles and, given the integrity of the iron oxide nanocoating, a result of the coating sintering to the underlying porous ceramic AZT membrane.

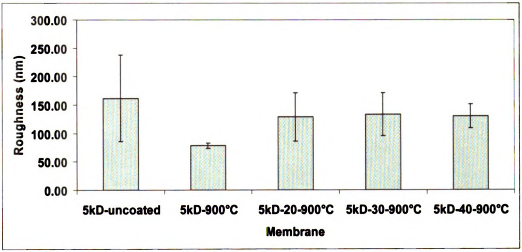


Figure 6.5 Roughness data for AFM images of membranes with different number of coatings

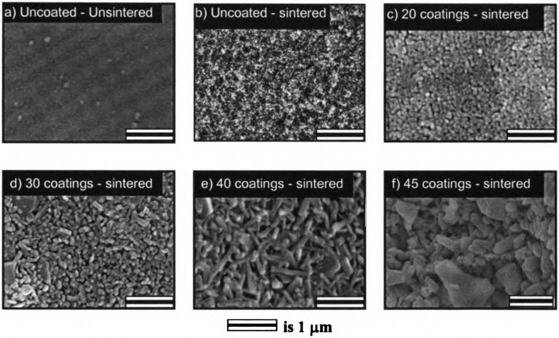


Figure 6.6 SEM images of an AZT ceramic membrane: a) 5kD MWCO AZT membrane uncoated, b) 5kD AZT membrane uncoated, sintered at 900°C for 30 minutes and c – f) 5kD AZT membrane with 20, 30, 40, 45 coatings, respectively, of iron-oxide, sintered at 900°C for 30 minutes.

6.4.2 SEM imaging

The SEM micrographs (Figure 6.6) of the coated AZT ceramic membranes exhibit a similar coarsening behavior of the membrane surface with increases in the size and number of surface grains with number of coats, as was found using AFM (Figure 6.4 a-c). The nanoparticles on the surfaces have sintered together and there is an overall coarsening of the surface (increase in the average grain size) as the number of coatings increases from 20 to 40.

The average grain size for the membrane surfaces are plotted in Figure 6.7. After sintering for 30 minutes, the average grain size increased from ~ 21 nm (± 0.24), for the uncoated membranes, to ~ 66 nm (± 20.0) for the coated membranes. Further increasing the number of coatings from 20 to 30 and subsequently 30 to 40, resulted in a significant increase in the average grain size from ~ 27 nm (± 10) to ~ 31 nm (± 11) to ~ 66 nm (± 23) respectively. This particle growth is likely a result of the large driving force for sintering posed by the high surface area of these nanosized particles, whereby agglomerated regions of nanoparticles rapidly sinter and are separated by larger pores (Barsoum, 2003). This finding is verified by noting that both the average *grain* size for the sintered membranes coated 40 times (Figure 6.7, 5 kD-40-900 °C) and the average *pore* size following sintering (Figure 6.8, 5 kD-40-900 °C) have both increased over those average grain and pore sizes reported for 20 and 30 coatings. This indicates that a greater degree of agglomeration of the iron oxide particles has occurred for membranes coated 40 times.

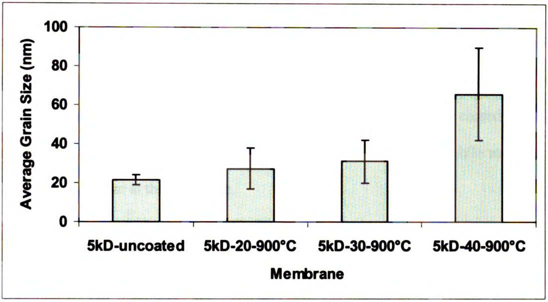


Figure 6.7 Grain size measurements of AZT ceramic membrane: Membranes: 5kD MWCO uncoated, 5kD with 20, 30, 40 coatings of iron oxide sintered at 900 °C for 30 minutes.

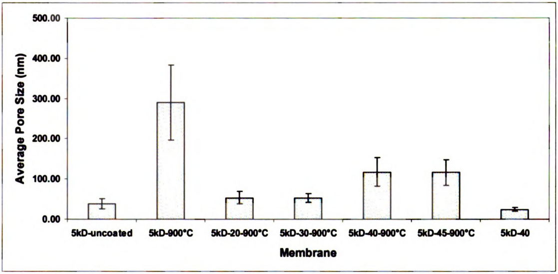


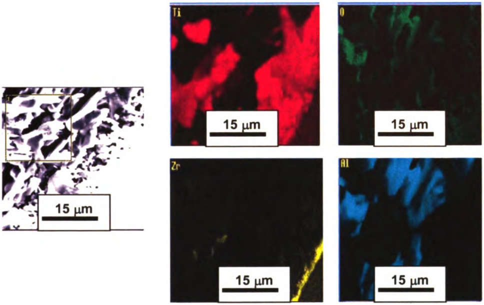
Figure 6.8 Average pore size measurements for the AZT membranes: 5kD MWCO uncoated, 5kD sintered at 900 °C for 30 minutes, 5kD with 20, 30, 40, 45 coatings of iron oxide sintered at 900 °C for 30 minutes and 5kD with 40 coatings of iron oxide unsintered.

With 45 coatings, no significant increase in porosity is observed, and more importantly, no water quality improvements were found, making 40 coatings a critical processing parameter. So, while the average surface pore size has increased from 40 nm (± 10) for the uncoated membrane to 120 nm (± 40) for the membranes coated 40 times, the more open porosity has significantly increased the water quality while maintaining the average pore size at the nanoscale.

SEM micrographs (Figure 6.6) show a clear evidence of uniform coverage of coating and sintering as verified by AFM results shown in Figures 6.2 and 6.4. Also the coarsening of the membrane surface explains the decrease in roughness value from uncoated membranes to coated and sintered membranes.

Energy dispersive x-ray microanalysis (EDS) mapping was done for Ti, Al, Zr, O and Fe. EDS mapping of the uncoated AZT membrane (Figure 6.9a) showed a uniform distribution of titania and zirconia over a porous alumina matrix. The skin of the as-received uncoated membrane was therefore a mixture of titania and zirconia which formed an ultrafiltration layer (ultrafiltration occurs between microfiltration (10^{-6} m) and nanofiltration (10^{-9} m)). EDS mapping of a coated and sintered membrane (Figure 6.9b) confirmed the morphology and composition of the uncoated membrane with the addition of an iron oxide layer predominantly present at the surface, with a uniformly diffused iron oxide presence into the membrane surface. This uniform distribution of iron oxide into the membrane could be a result of capillary action during the coating process and/or a result of the diffusion of iron oxide nanoparticles in the sintering process.

a) 5kD uncoated



b) 5kD - 40 coatings- sintered (900°C)

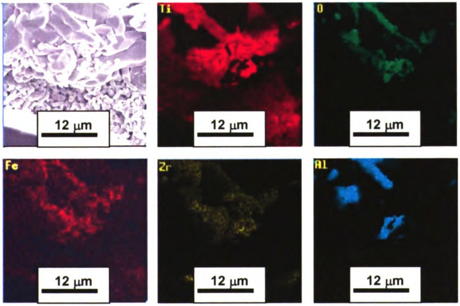


Figure 6.9 EDS mapping of the membranes: a) EDS mapping of uncoated membrane and b) EDS mapping of membrane with 40 coatings and sintered at 900 °C for 30 minutes.

As expected, EDS line scans for the membranes coated 20, 30 and 40 times revealed a corresponding increase in the concentration of iron (Fe) present in the membrane surface. The Fe concentration was proportional from 20 to 30 to 40 coatings (Figure 6.10).

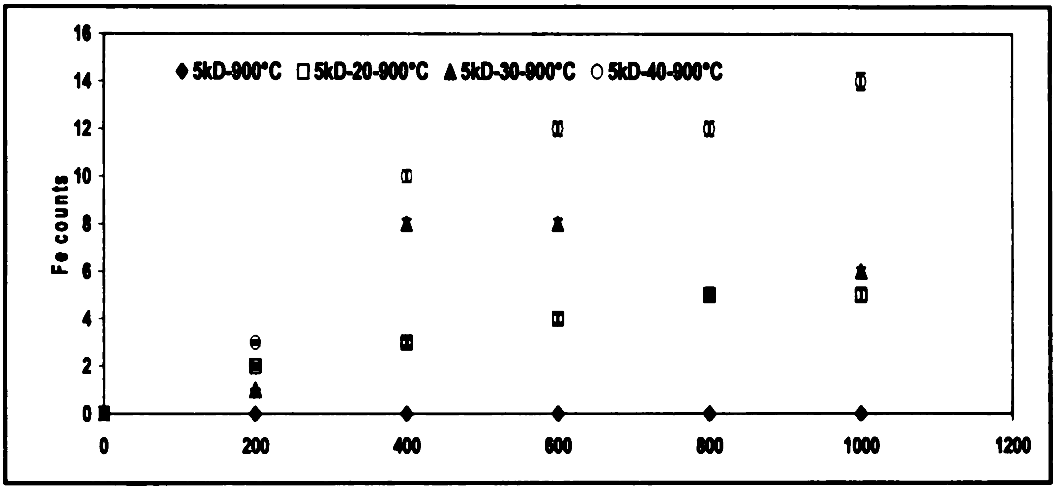


Figure 6.10 Relative Fe concentration from EDS scans.
The graph represents relative Fe concentrations measured as Fe counts in the EDS scans

The water quality data shown in Figure 6.11 gives evidence as to how the catalyst coating has improved water quality performance in terms of reducing DBP precursors when compared to uncoated membranes. Iron oxide coated ceramic membranes were superior in terms of performance as compared to uncoated ceramic membranes in terms of DBP precursors as well as DBPs as shown in Figure 6.11. DOC concentrations showed a significant decrease for the Fe_2O_3 catalyst coated ceramic membranes with increasing Fe_2O_3 coating layers when compared to uncoated membranes. Our earlier work details the improvement in water quality for Fe_2O_3 catalyst coated ceramic membranes with different treatment processes in comparison to the uncoated ceramic membranes (Karnik et al., 2005c).

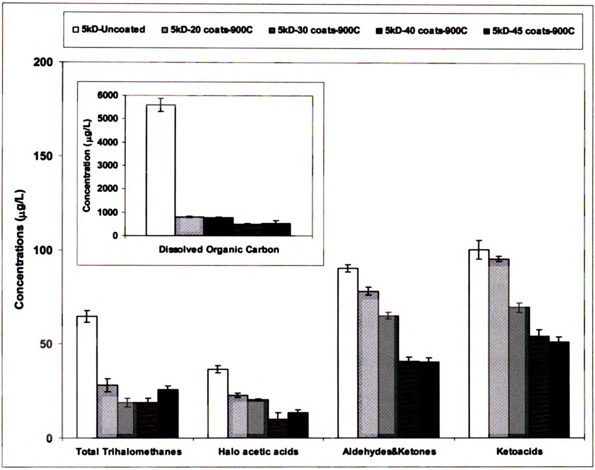


Figure 6.11 Water Quality data for the permeate after combined ozonation membrane treatment process

The data for water quality parameters for a 5kD AZT membrane uncoated, unsintered, with 20, 30, 40, 45 coatings of iron-oxide, sintered at 900°C for 30 minutes. The insert in the graph is the plot of dissolved organic carbon concentrations for the same membranes. Experiment details (Karnik et al., 2005c).

Fe_2O_3 catalyst coated ceramic membranes are a promising tool for reducing the ozonation by-products which serve as substrates for growth of microorganisms. This reduces their regrowth potential in the permeate making the water more biologically stable and safe for consumption. Further, the figure shows no significant changes in the water quality in terms of measured concentration of DBPs like TTHMs and HAAs with increasing Fe_2O_3 catalyst coating layers from 20 to 40 coats. A concomitant decrease in the ozonation by-products was seen with increasing number of Fe_2O_3 coating layers, however, no significant changes in the concentrations were reported beyond 40 coating layers.

AFM characterization showed a decrease in the surface roughness of the ceramic membrane with Fe_2O_3 coating which led to an improved effective filter separation layer most likely comprised of nanosized iron oxide grains. SEM micrographs show a nanoscale average pore size and uniform coverage of the coating layers, not only across the ceramic membrane surface, but also into the membrane itself. This has likely led to the catalytic reactions that resulted in a significant improvement of water quality in terms of removal of disinfection by-products and ozonation by-products shown in Fig.11. The increased Fe concentration into and away from the outer membrane surface, as measured by EDS, further supports the explanation given for the improved water quality data for the ceramic membranes coated with 40 layers of Fe_2O_3 nanoparticles.

6.5 CONCLUSIONS

Coating and sintering of AZT membranes with nanoscale iron oxide particles resulted in significant changes in the membrane surface morphology as a result of sintering and coarsening of the coating nanoparticles. SEM details the changes in surface morphology of the coated membrane where the surface morphology changes from a fine grained uniform structure at 20 coats to a coarser grain uniform structure at 40 coats. SEM also captured the change in the average pore size, from the micropores in the underlying AZT membrane to the nanopores within the iron oxide surface layer of the coated membrane. This decrease in porosity into the nanopores regime is one possible reason for the improved performance of these iron oxide coated ceramic membranes over uncoated membranes. AFM and SEM data are consistent, where decreasing surface roughness correlates with a coarsened average grain size on both the sintered uncoated and coated membranes, with the smoothest and coarsest surface existing at 40 coats, which is the optimum in terms of water filtration (Karnik et al., 2005c). It is at 40 layers that we have the largest average pore size (although still in the nanopores range at 120 nm (± 40)) and largest average grain size that results from the greater degree of agglomeration of the iron oxide particles during the coating process. Capillary action during the coating process, and/or diffusion during sintering, results in the uniform distribution of iron oxide particles throughout the membrane interior. This further enhances water filtration because of the increased exposure to the catalytic iron oxide, not only at the membrane surface, but into the membrane itself. Ongoing studies using SEM of coated and unsintered membranes will determine whether capillary forces during the coating application process are sufficient to drive the iron oxide nanoparticles into the interior of the membrane. We have found that 40 coats of the nanosized iron oxide particles on the underlying AZT ceramic membrane is the optimum coating in terms of water quality performance which meets the stringent EPA regulatory requirements, while still in the regime of nanofiltration. Future research will examine the mechanisms for the degradation of NOM and the removal of harmful DBPs by the iron oxide coated AZT ceramic membranes.

6.6 ACKNOWLEDGEMENTS

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CHAPTER SEVEN

TEM CHARACTERIZATION OF IRON OXIDE COATED CERAMIC MEMBRANES

7.1 ABSTRACT

Commercially available porous alumina-zirconia-titania ceramic (AZTC) membranes having a titania surface coating were characterized using transmission electron microscopy (TEM). TEM photomicrographs showed the as-received AZTC membrane to be a multi-layered structure consisting of a porous alumina-zircona-titania core having ultrafine pore sizes, coated by an additional layer of micro porous titania. Electron diffraction studies revealed an amorphous surface titania layer while the underlying AZTC membrane was crystalline. The AZTC membranes were coated with iron oxide (Fe_2O_3) nanoparticles, synthesized from a colloidal sol suspension 20, 30, 40, 45 or 60 times using a layer-by-layer procedure after which the membranes were sintered in air at 900 °C for 30 minutes. Following Fe_2O_3 coating and sintering, TEM revealed relatively uniform Fe_2O_3 coverage, with nanoporosity in the Fe_2O_3 layer, where the Fe_2O_3 coating thickness increased with increasing number of layers. Electron diffraction patterns showed the Fe_2O_3 coating to be crystalline in nature, verified by x-ray diffraction (XRD) results showing the structure to be α-Fe_2O_3. The average pore size of the underlying AZTC membrane increased after the Fe_2O_3 coated membrane was sintered. However, no significant increases in the average pore size were observed beyond 40 layers of Fe_2O_3. Coating the membrane with iron oxide particles improved the catalytic properties of the

membrane when used in water treatment applications, where the maximum benefit, in terms of water quality improvements, were found at 40 layers of Fe_2O_3.

Keywords: ceramic membrane, nanoparticles, iron oxide, catalytic coating, transmission electron microscopy (TEM), x-ray diffraction (XRD), nanofiltration

7.2 INTRODUCTION

The use of ceramics as catalyst materials is a well accepted practice (Keane, 2003) and has led to the development of ceramic materials that are effective catalyst supports and catalytic agents. Recent advances in our ability to manipulate structures at the molecular and atomic levels have further advanced the use of nanosized ceramics as catalytic materials (Keane, 2003; Trudeau and Ying, 1996). Ceramic catalysts are used in the production of commodity chemicals and pharmaceuticals, as well as finding increasing application in environmental pollution control and abatement (Keane, 2003). Mixed metal oxides have displayed promising catalytic properties in addition to improved structural and acid-base properties (Neri et al., 2004).

Membrane filtration is an effective technique in water treatment for the removal of particulate matter, micro-organisms and organic matter (US EPA, 2001). During recent years, there has been increasing interest in the application of micro porous ceramic membranes because of their chemical, mechanical and thermal stability (Puhlfürβ et al., 2000). A combined water treatment process of ozone disinfection and polymeric membrane filtration has been attempted by several researchers with very little limited success (Hashino et al., 2000; Shanbhag et al., 1998; Castro and Zander, 1995; Shen et al., 1990). In contrast to polymeric membranes, ceramic membranes are ozone resistant and when these membranes are used in combination with ozone, stable permeate fluxes can be achieved without membrane damage (Karnik et al., 2005a; Schlichter et al., 2004; Kim and Somiya, 2001; Kim et al., 1999; Allemane et al., 1993).

Our earlier work showed stable permeate fluxes could be maintained using uncoated AZTC membranes in a combined ozonation-membrane filtration process (Karnik et al., 2005a). Further combined ozonation and membrane filtration resulted in a decrease in the concentration of disinfection by-products (DBPs), such as total trihalomethanes (TTHMs) and halo acetic acids (HAAs), of up to 80% and 65%, respectively. This results from the formation of partially oxidized compounds from naturally organic matter (NOM) that were less reactive with chlorine (Karnik et al., 2005b). When the removal of ozonation by-products was investigated using a combined ozonation-membrane filtration system, where now the AZTC membranes were coated with Fe_2O_3 nanoparticles, a further reduction of at least 50% was measured when compared to the combined ozonation and uncoated AZTC membrane filtration system alone. A 5 kilodalton (kD) nominal molecular weight cut off (MWCO) AZTC membrane, coated with 40 layers of Fe_2O_3 nanoparticles and sintered in air at 900 °C, combined with ozonation (at a gaseous ozone concentration of 2.5 g/m^3) produced a permeate water that met the US EPA regulatory requirements for TTHMs of 80 μg/L and HAAs of 60 μg/L set under Stage 2 D/DBPs Rule for drinking water (Karnik et al., 2005c).

The effects of sintering temperature and coating layer thickness on the microstructure of the commercially available AZTC membranes coated with sol suspension processed Fe_2O_3 nanoparticles have previously been characterized in our laboratory using atomic force microscopy (AFM), scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS) (Karnik et al., 2006). Our results showed decreasing surface roughness after Fe_2O_3 coating, while an increase in the Fe_2O_3 coating thickness caused a change in the microstructure from a fine-grained morphology at 20 coating layers (average grain size 27 ± 10 nm) to a coarser grained morphology at 40 coating layers (average grain size 66 ± 23 nm) with a corresponding increase in the average pore size from 57 ± 15 nm to 120 ± 40 nm. Optimum water quality was achieved at a coating of 40 layers of Fe_2O_3, corresponding to a surface having a uniform, coarse-grained (average grain size 66 ± 23 nm) structure with open, nano-sized (66 ± 23 nm) interconnected pores (Karnik et al., 2006).

In this work, transmission electron microscopy (TEM) and x-ray diffraction (XRD) were used to further investigate the characteristics of the Fe_2O_3 nanoparticle coated AZTC membranes. A suspension of Fe_2O_3 nanoparticles was layered onto the AZTC membrane surface 20, 30, 40, 45 or 60 times followed by sintering in air at 900 °C. The surface area measurements and average pore size of the AZTC membrane were measured using Brunauer-Emmett-Teller (BET) and the Barett, Joyner and Halenda (BJH) methods, respectively.

7.3 MATERIALS AND METHODS

7.3.1 Membrane Preparation

Tubular AZTC (a mixture of alumina, zirconia and titania) membranes (CéRAM Inside, TAMI North America, St. Laurent, Québec, Canada, shown in Figure 7.1) with a clover-leaf design (containing three channels), with nominal molecular weight cut-offs of 5 kilodalton (kD) were used as a support for the Fe_2O_3 catalytic coatings. The external diameter of each membrane was 10 mm and the active membrane length was 8 cm. The total filtering area of each membrane was approximately 11 cm^2. The initial permeability of the membranes was determined using distilled deionized (DDI) water (Karnik et al., 2005a).

A detailed description of the membrane preparation is available in our earlier published work (Karnik et al., 2005c). Briefly, the colloidal Fe_2O_3 nanoparticles used for coating the AZT ceramic membranes were prepared using Sorum's method (McKenzie et al., 2002). Transmission electron microscopy (TEM) characterization of the Fe_2O_3 nanoparticles showed that the average particle diameter was 4 to 6 nm (Figure 7.2). The layer-by-layer technique used to coat the AZTC membranes is based on a protocol described by McKenzie et al. (McKenzie et al., 2002) for coating doped tin oxide electrodes. The AZTC membranes were immersed in the colloidal suspensions for one minute and then rinsed with DDI water. Then, the membranes were immersed in aqueous phytic acid (40 mM) for one minute and again rinsed with DDI water. This sequence was repeated for the desired number of layers (20, 30, 40, 45 or 60). After coating, the Fe_2O_3 coated AZTC membranes were sintered in air at 900 °C for 30 minutes. This temperature was chosen to produce membranes on which the Fe_2O_3 particles were sintered together as well as to the underlying AZTC membrane surface. These sintered membranes were then prepared for examination using TEM and XRD.

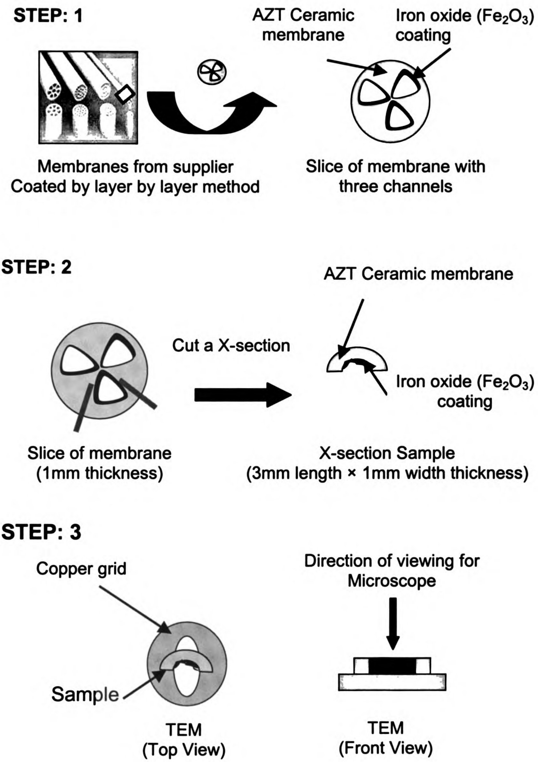

Figure 7.1 Schematic Representation of sample preparation for TEM imaging

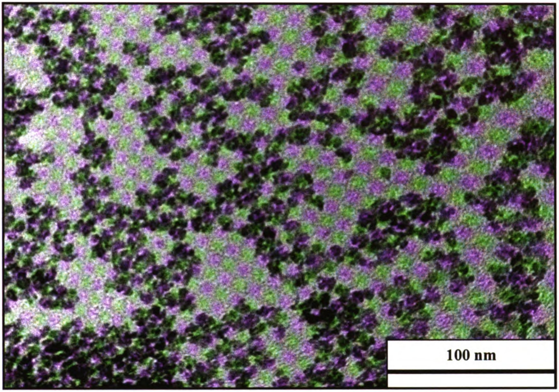

Figure 7.2 TEM image of Fe_2O_3 nanoparticles processed from sol

7.3.2 Membrane Characterization

The schematic representation of the procedure used to obtain images of the coated surface of the tubular Fe_2O_3 coated AZTC membranes is given in Figure 7.1. The membrane was first sliced into circular discs of 1 mm thickness using a diamond-wafering saw. Subsequently, these 1 mm sections were sliced with a razor blade to form small arcs, 3 mm in length and 1 mm in width. These arcs were then mounted onto slotted copper grids, (3 mm inner diameter) perpendicular to the slot. These grids were then subsequently mounted on stubs for further preparation.

The grids were next prethinned with hand polishing using 15, 6, 3 and then 1 μm diamond paste to obtain a slice with a final thickness of approximately 70-100 μm. The sample was then dimpled (GATAN Precision Dimple Grinder, Model 656) to thin the center of the disk while minimizing the damage to the sample surface. The dimpler load was controlled and approximately 40 μm of sample removed, making the final thickness of the sample approximately 40 to 60 μm. The final thinning of the Fe_2O_3 coated ceramic membranes was done by ion milling, at an accelerating voltage of 4.5 keV with ion beam inclination of 4°, to avoid preferential thinning, using a commercial ion mill (GATAN Precision Polishing System Model 691). The thinned specimens were examined using TEM on a JEOL 100CX at accelerating voltage of 100 kV and photomicrographs collected using a Megaview III digital camera. Electron diffraction patterns were collected at a camera length of 100 cm in order to distinguish between amorphous and crystalline particles.

XRD analysis using Cu Kα radiation was carried out on a Rigaku Rotaflex 200B diffractometer with an accelerating voltage of 45 kV and a current of 100 mA. Samples were scanned at angles ranging from 20° to 80°, with a scanning angle speed of 2°/min and a step size of 0.02° and the results analyzed using MDI Jade 6.5 XRD software.

Nitrogen adsorption-desorption isotherms were recorded on a NOVA 2000. The samples of size 1 cm × 1 cm weighing 1.2 ± 0.05 g were dried at 150 °C under vacuum overnight, prior to N_2 sorption measurement. The specific surface area was calculated using the multipoint Brunauer-Emmett-Teller (BET) method (Brunauer et al., 1938). Pore size distributions were calculated by the Barrett, Joyner and Halenda (BJH) method (Barrett et al., 1951).

7.4 RESULTS AND DISCUSSION

Figure 7.3a is a TEM photomicrograph of a cross section of an AZTC membrane supplied by the manufacturer. This micrograph reveals a multi-layered structure showing the underlying alumina-zirconia-titania ceramic membrane with a non-uniform TiO_2 filtration coating of thickness ~ 30 nm - 100 nm. An electron diffraction pattern of this surface shows the amorphous nature of the titania coating (shown in the insert of Figure 7.3a). After coating the AZTC membranes with 40 layers of Fe_2O_3 nanoparticles, TEM photomicrographs clearly show a second distinct surface layer having an average thickness of 50 nm ± 5 nm (Figure 7.3b). The electron diffraction pattern of this coating (shown in the insert of Figure 7.3b) demonstrates the crystalline nature of the hexagonal closed packed (hcp) α-Fe_2O_3 coating.

While not clear from the TEM micrographs, evidence of Fe_2O_3 diffusion into the porous AZTC membrane was collected in the SEM, using EDS mapping which clearly showed that iron had diffused into the membrane to a depth of at least 500 μm (Karnik et al., 2006).

The scale on the bar represents 100 nm.

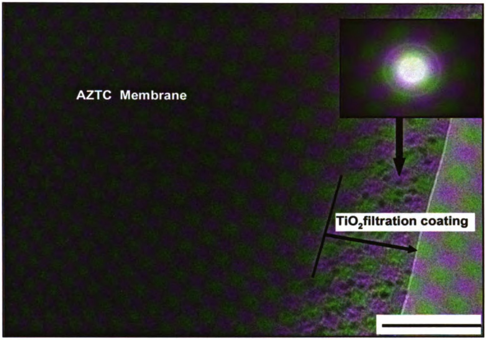

Figure 7.3 a) TEM cross section of the micro porous AZTC membrane supplied from the manufacturer. The insert is electron diffraction pattern of the TiO_2 coating on the AZTC membrane

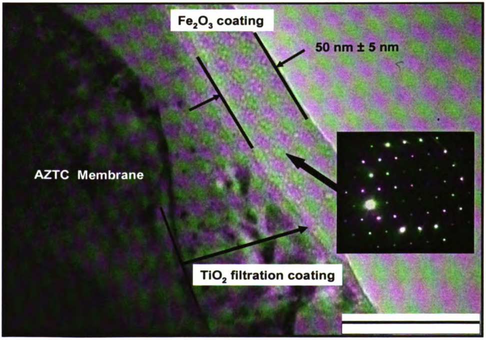

Figure 7.3 b) TEM cross section of micro porous AZTC membrane with 40 coatings of iron oxide sintered at 900 °C for 30 minutes

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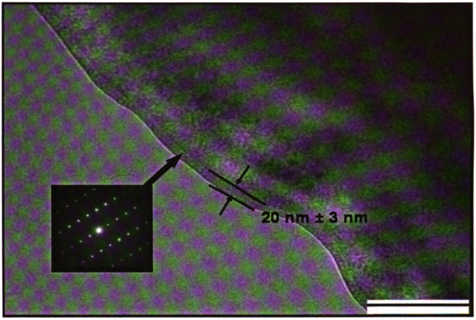

Figure 7.4 a) TEM cross section and Electron diffraction patterns of a 5kD AZTC membrane with 20 coatings of iron oxide, sintered at 900 °C for 30 minutes

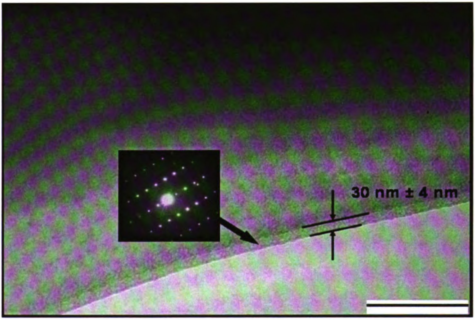

Figure 7.4 b) TEM cross section and Electron diffraction patterns of a 5kD AZTC membrane with 30 coatings of iron oxide, sintered at 900 °C for 30 minutes

The scale on the bar represents 100 nm.

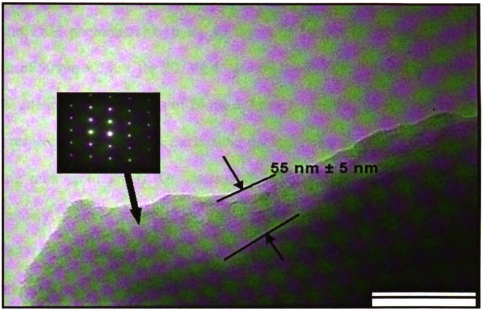

Figure 7.4 c) TEM cross section and Electron diffraction patterns of a 5kD AZTC membrane with 45 coatings of iron oxide, sintered at 900 °C for 30 minutes

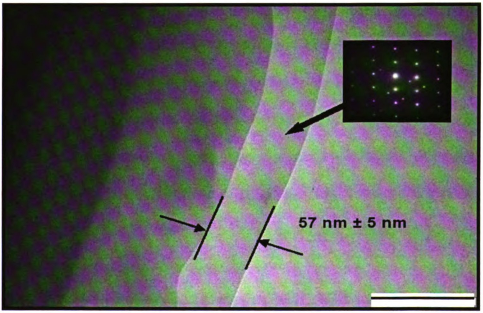

Figure 7.4 d) TEM cross section and Electron diffraction patterns of a 5kD AZTC membrane with 60 coatings of iron oxide, sintered at 900 °C for 30 minutes

Figures 7.3b, 7.4a, 7.4b, 7.4c and 7.4d illustrate the relationship between the number of Fe_2O_3 layers applied and the resulting thickness of the sintered Fe_2O_3 coating. While the TEM photomicrograph for 40 layers of Fe_2O_3 (Figure 7.3b) shows a layer thickness of 50 nm ± 5 nm, the 20, 30, 45 and 60 layers of Fe_2O_3 coating (Figure 7.4a-d) yielded a coating layer thickness of 20 nm ± 3 nm, 30 ± 4 nm, 55 nm ± 5 nm, and 57 nm ± 5 nm respectively. In general, the coating thickness was found to have increased with increasing number of layers. On average, the thickness of the coating increased by approximately 10 nm of sintered Fe_2O_3 for every 10 layers applied. This rate of increase in the Fe_2O_3 layer thickness is not what would be expected if each coating resulted in the deposition of a Fe_2O_3 monolayer, given the 4-6 nm particle size of the Fe_2O_3 that could result in a Fe_2O_3 layer thickness of 28 to 42 nm for every 10 layers applied. However, because of the aforementioned diffusion of iron into the AZTC membrane itself, we know that some of the Fe_2O_3 penetrated into the membrane surface (Karnik et al., 2006). It is thought that capillary action through the abundant surface connected porosity during the coating process, as well as diffusion during sintering, results in the uniform distribution of iron oxide particles into the membrane to a depth of at least 500 μm. Further, as is typical for ceramics, upon sintering, shrinkages of 40-50% are common (Barsoum, 2003). Therefore, it is reasonable to achieve only a 50 nm thick coating layer, for 40 applied layers of Fe_2O_3, after taking into account the combined effects of diffusion into the interior of the membrane and sintering.

The increase in the Fe_2O_3 coating layer thickness improved the AZTC membrane performance in terms of water quality. This may occur because as the Fe_2O_3 layer thickness increased, a greater surface area is available to facilitate surface catalytic reactions that result in the degradation of contaminants in the treated water. The corresponding water quality data for AZTC membranes with 0, 20, 30, 40, 45 and 60 layers of Fe_2O_3 are shown in Figure 7.5. More detailed presentations of these water quality results have been published elsewhere (Karnik et al., 2005a; 2005b; 2005c). Comparing water quality data for the AZTC membranes receiving 20 and 30 Fe_2O_3 layers shows no statistically significant differences in terms of water quality, which is linked to a similar thickness of the Fe_2O_3 surface coating. Once the Fe_2O_3 layers were increased to 40, the resulting sintered Fe_2O_3 surface layer thickness begins to increase again, and we find a corresponding improvement in water quality. However, 40 Fe_2O_3 layers was found to be the optimum in terms of water quality improvements, as continuing to deposit Fe_2O_3 at 45 layers, found no further gains in water quality as once again no significant increases in Fe_2O_3 surface layer thickness were found. In fact, water quality from the AZTC membranes coated with 60 Fe_2O_3 layers (Figure 7.5) also showed no gain in water quality as the increase in the Fe_2O_3 surface thickness was small compared to that for the membrane coated 45 times (Figure 7.4d).

Diffusion of Fe_2O_3 into the AZTC membrane also has long term implications for the successful commercialization of this technology because over time, as the ceramic membrane gradually erodes, the benefits of the catalytic action of the Fe_2O_3 would be expected to continue beyond the water quality improvements that result from just the initial Fe_2O_3 coating layer.

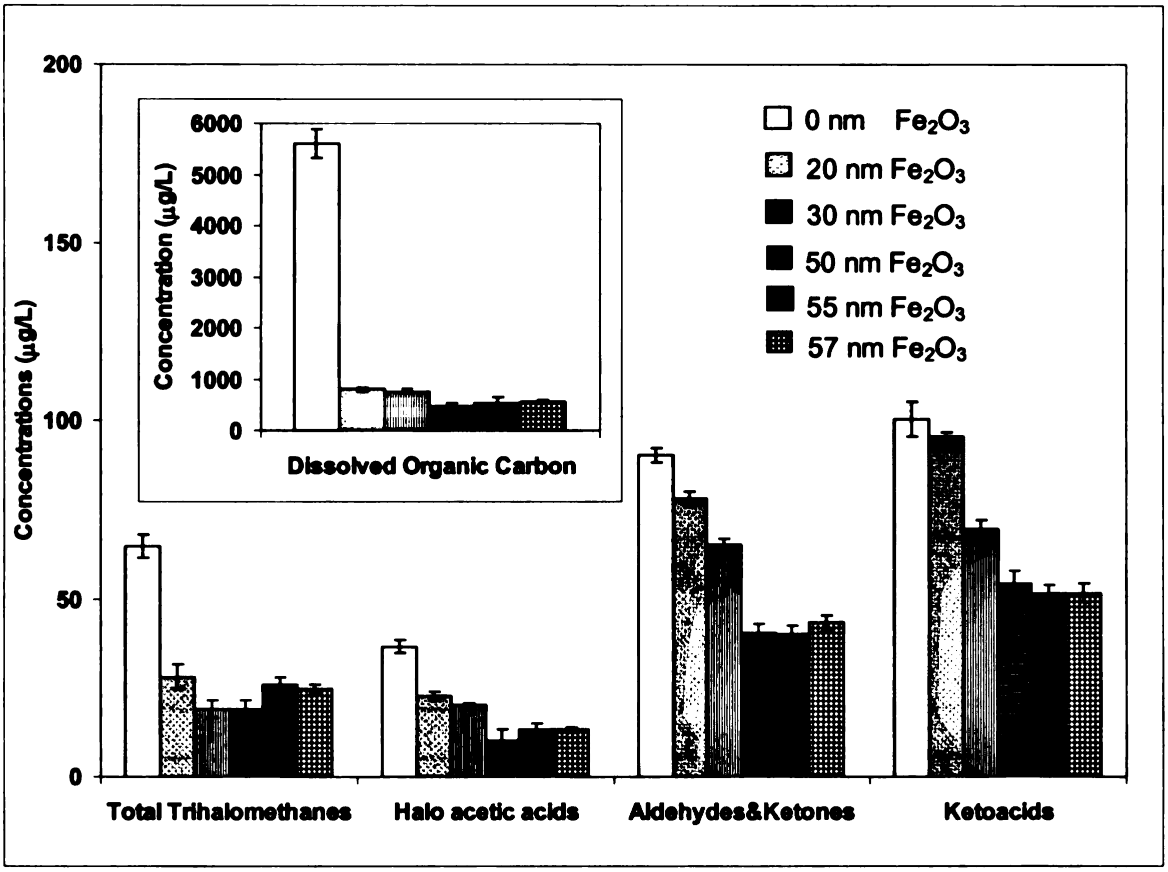

Figure 7.5 Water Quality data for the permeate after combined ozonation membrane treatment process.

The data for water quality parameters for a 5kD AZT membrane uncoated, unsintered (0 nm coating thickness), with 20, 30, 40, 45 and 60 coatings of iron-oxide, sintered at 900°C for 30 minutes with respectively, 20, 30, 50, 55, 57 nm coating thickness. The insert in the graph is the plot of dissolved organic carbon concentrations for the same membranes. Experiment details (Karnik et al., 2005c)

XRD characterization (Figure 7.6) of the samples showed that the uncoated, unsintered AZTC membrane samples were a mixture of the anatase and rutile phase of TiO_2 as well as ZrO_2 and corundum, Al_2O_3. Following coating, XRD scans showed the presence of α-Fe_2O_3 with no changes observed after sintering in air at 900 °C with a preferred (111) orientation along the [111] direction aligned perpendicular to the membrane surface. All XRD peaks were indexed as hcp α-Fe_2O_3 with a least squares best fit lattice parameter of 0.50361 ± 0.00015 nm, 0.503631 ± 0.00020 nm, 1.37524 ± 0.00018 nm.

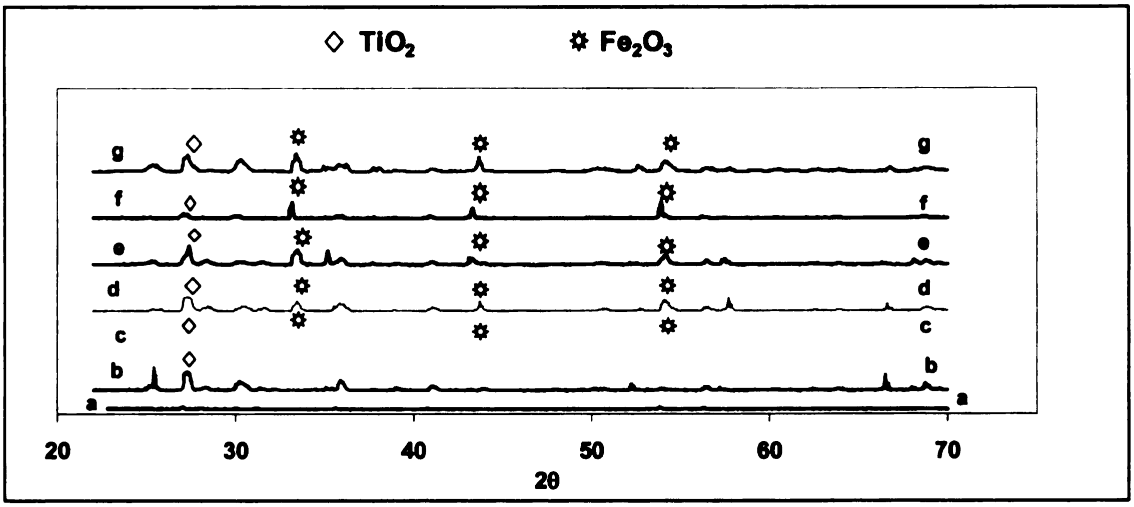

Figure 7.6 X-ray diffraction patterns of AZTC membrane

a) 5kD MWCO AZTC membrane uncoated, b) 5kD AZTC membrane uncoated, sintered at 900°C for 30 minutes c) 5kD AZTC membrane with 40 coatings of iron-oxide unsintered and d-g) 5kD AZTC membrane with 20, 30, 40 or 45 coatings of iron oxide, sintered at 900 °C for 30 minutes.

The surface area and pore size measurements for the as received and the Fe_2O_3 coated AZTC membranes are tabulated in Table 7.1. The BET surface area measurements did not show any statistically significant difference in surface area measured for the samples. The pore size distributions showing the average pore size of the as-received AZTC membranes ranged from 4.6 nm ± 0.02 for the uncoated and unsintered membrane, to 4.8 nm ± 0.03 for both the 20 and 30 Fe_2O_3 layer coated AZTC membranes. Beyond 30 Fe_2O_3 layers, the average pore size increased to 5.2 nm ± 0.03 for 40 Fe_2O_3 layers, remaining constant at 45 and 60 Fe_2O_3 layers. It should be further noted that the additional heat treatment required to sinter the Fe_2O_3 layers also serves to coarsen the pores in the underlying AZTC membrane. These results suggest that increasing the number of Fe_2O_3 layers yields a corresponding increase in coarsening of the AZTC membrane which also serves to facilitate the catalytic performance that was optimized at 40 Fe_2O_3 layers, as well as to transform the surface from a relatively flat surface, to one having surface undulations on the micron scale. This confirms our earlier AFM results showing a decrease in submicron scale surface roughness with sintering and Fe_2O_3 coating (Karnik et al., 2005c; Karnik et al., 2006). Further increasing the number of coats Fe_2O_3 does not improve the water quality which corresponds to no statistical increase in the coating thickness at 45 or 60 layers of Fe_2O_3 (Figure 7.4c and 7.4d), nor did we find any statistical significant decrease in AFM roughness beyond 40 layers, as shown in our previous AFM analysis (Karnik et al., 2006). Further these TEM photomicrographs confirm, as do our other findings that the sintered Fe_2O_3 coated AZTC membranes used in our hybrid nanofiltration-ozonation study are indeed still operating in the nanofiltration domain.

Table 7.1
Summary of surface area and average pore size

Sample	Surface area (m^2/g)	Average pore size (nm)
5 kD-uncoated-unsintered	4.985	4.6 (± 0.02)
5 kD - 20 coats-900 °C	5.117	4.8 (± 0.03)
5 kD - 30 coats-900 °C	5.171	4.8 (± 0.02)
5 kD - 40 coats-900 °C	4.452	5.2 (± 0.03)
5 kD - 45 coats-900 °C	4.523	5.2 (± 0.01)
5 kD - 60 coats-900 °C	4.589	5.2 (± 0.02)

7.5 CONCLUSIONS

TEM observations revealed that coating the AZTC membrane with iron oxide nanoparticles followed by sintering at 900 °C in air led to a transformation of the outer most amorphous TiO_2 filtration layer on the as received AZTC membrane to a crystalline TiO_2 structure coated by a crystalline α-Fe_2O_3 surface layer. Increasing the number of Fe_2O_3 layers did not produce a one to one corresponding increase in the thickness of the Fe_2O_3 surface. The fact that the thickness of the coating is less than might be expected is a result of both diffusion of the Fe_2O_3 nanoparticles into the membrane by capillary action and subsequent densification of the porous Fe_2O_3 layer during sintering.

In general the porosity of the AZTC membranes having a nanoscale Fe_2O_3 coating, led to changes in the surface morphology and average pore size of the Fe_2O_3 surface layer as a result of sintering and coarsening of the Fe_2O_3 nanoparticles, while maintaining nanoscale pore filtration capabilities. Capillary action during the coating process, and/or diffusion during sintering, resulted in a uniform distribution of iron oxide particles into the membrane to a depth of at least 500 μm (Karnik et al., 2006). The synergy of the catalytic effect of the Fe_2O_3 nanoparticle coating on the membrane surface and the diffused Fe_2O_3 layer into the membrane enhances water filtration because of the increased exposure to the catalytic iron oxide, not only at the membrane surface, but into the membrane itself. The AZTC Fe_2O_3 coated membrane exceeds the current EPA regulatory requirements (US-EPA), while still in the nanofiltration regime. Future research will examine the mechanisms for the degradation of NOM and the removal of harmful DBPs by the iron oxide coated AZTC ceramic membranes.

7.6 LIMITATIONS-PROBLEMS

The diameter of the smallest diffraction aperture size on the JEOL 100CX is 100nm. The edge surface regions being imaged for electron diffraction patterns are obtained by carefully positioning the aperture at the extreme edge. However there are limitations to the technique. A diffraction patterns could have emerged from the regions other the edge surface of the sample. So the electron diffraction patterns obtained cannot be positively said to come from only the outer surface. However the TEM images illustrating the morphology and coating thickness of the samples are valid. However it should be noted that while the surface region cannot definitely be said to be only Fe_2O_3, an Fe_2O_3 surface layer is not ruled out. Research is ongoing to obtain nano beam diffraction patterns using JEM-2200FS which is a high resolution TEM with a resolution limit of 1 nm. This study will help us confirm the electron diffraction patterns obtained for the ceramic membranes and the catalyst coating on the lower resolution JEOL 100CX.

7.7 ACKNOWLEDGEMENTS

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CHAPTER EIGHT

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CHAPTER EIGHT

REMOVAL AND SURVIVAL OF *ESCHERICHIA COLI* AFTER TREATMENT USING OZONATION-ULTRAFILTRATION WITH IRON OXIDE COATED MEMBRANES

8.1 ABSTRACT

The effect of membrane filtration, ozonation, and combined ozonation-membrane filtration on the removal of bacteria was studied. Commercially available ceramic membranes with a molecular weight cutoff (MWCO) of 5kDa were used as is, and also coated with iron oxide nanoparticles and sintered at 900°C. With membrane filtration and ozonation-membrane filtration using the uncoated membrane, 7 log removal of bacteria was achieved, as compared to 7.5 log removal with ozonation-membrane filtration with the coated membrane. Only 4 log removal was achieved with ozonation alone. A Live-Dead assay indicated that the mortality of bacteria in the product water was ~50%, ~85%, and >99% with ozonation, combined ozonation-membrane filtration with the uncoated membrane, and ozonation-membrane filtration with the coated membrane, respectively. With the coated membrane, the concentration of assimilated organic carbon (AOC) was reduced by up to 50% more than with the uncoated membrane filtration (both, with systems operated with ozonation). It appears that the catalyst-coated membranes enhance surface catalytic reactions that degrade microbial substrates, such as aldehydes and ketoacids, thereby reducing the potential for microbial regrowth in the water distribution system. Scanning electron micrographs (SEM) of the membrane surface show that the

surface morphology is changed as a result of the coating the membrane. The SEM results also show that the adhesion of particles found in the water to the membrane surface is affected by the coating on the membrane.

Keywords: ceramic membranes, ozonation, nanofiltration, iron oxide, bacteria, catalytic ozonation, nanofilm, membrane filtration, scanning electron microscopy (SEM), assimilated organic carbon (AOC)

8.2 INTRODUCTION

The implementation of sand filtration and disinfection for water treatment in the early twentieth century significantly reduced the number of outbreaks of waterborne diseases transmitted through drinking water. The effect was so great that by the early 1980's the drinking water community assumed that problems related to microbial contamination were essentially solved. This perspective changed when the Milwaukee *Cryptosporidium* outbreak in 1993 resulted in an estimated 400,000 cases of cryptosporidiosis and at least 50 deaths. More recently, in Walkerton, Ontario, at least 2,300 cases of gastroenteritis and seven deaths were attributed to drinking water contaminated with *E. coli* 0157 (Finstein, 2004, Hrudey et al., 2003). The severe consequences of accidental, as in these cases, or (potentially) deliberate, contamination of drinking waters by pathogenic organisms has made it clear that better water treatment technologies must be developed and implemented to reliably eliminate pathogens from drinking water supplies.

Ozone, a strong oxidant and a powerful disinfectant, is very effective for the inactivation of bacteria, protozoa and viruses (e.g., see, Lee et al., 1999, Owens et al., 1999, Liltved et al., 1995, Helmer et al., 1993). Membrane technology is considered to be an effective alternative to conventional water treatment for the removal of particles, microorganisms and organic matter (Cleveland, 1999, Nakatsuka et al., 1996). Several researchers have reported greater than 4 log reduction for bacteria, viruses, and protozoa (i.e., *Cryptosporidium* and *Giardia)* using membrane filtration (Hsu et al., 2003, Hagen, 1998, Otaki et al., 1998, Oe et al., 1996, Dumoutier et al., 1996, Madaeni et al., 1995). However, the decrease in permeate flux resulting from membrane fouling remains a major problem (e.g., see Lee et al., 2001; Cho et al., 2000a, 2000b; Field, 1996).

Ceramic membranes are ozone resistant and when combined with ozonation, generate very high and stable permeate fluxes without causing membrane damage (Karnik et al., 2005a, Schlichter et al., 2004, Kim et al., 2001, Kim et al., 1999). These membranes have proved effective for the control of disinfection by-products (DBPs) (Karnik et al., 2005a, Lee and Cho 2004, Benfer et al. 2004). A decrease in the concentration of Simulated Distribution System total trihalomethanes (SDS TTHMs) and Simulated Distribution System halo acetic acids (SDS HAAs) of up to 80% and 65% (as compared to generated by ozonation alone), respectively, was reported with the application of the ozonation-membrane filtration process (Karnik et al., 2005b). The ceramic membranes when used for drinking water treatment also showed complete removal of microorganisms, when measured for fecal coliforms, total coliforms and *E.coli,* thus having tremendous potential for the application in drinking water treatment process to improve the water quality (Bottino et al., 2001).

Ozone has been used in the presence of different metal oxide catalysts, including manganese oxide, titania, alumina, and zirconia, to degrade refractory compounds, including saturated carboxylic acids, phenols, aromatic hydrocarbons, dyes, humic substances and herbicides (Beltran et al., 2003a, 2003b, Radhakrishnan and Oyama, 2001, Ni and Chen, 2001, Gracia et al., 1996, 2000a, 2000b, Legube and Karpel Vel Leitner, 1999). Catalytic ozonation is a promising technology as the ·OH and oxygen radicals generated at the surface can potentially react with both living and non-living organic substrates, including bacteria and viruses, which would be killed or inactivated on contact by the oxidants (Legube and Karpel Vel Leitner, 1999, Heinig, 1993). In our earlier work with ozonation-membrane filtration, we showed that the catalyst (iron oxide) coated membrane enhanced the degradation of the sorbed or trapped ozone byproducts, such as aldehydes and ketoacids, which facilitate the regrowth of bacteria in water distribution systems. When the coated membrane was used, the concentrations of aldehydes, ketones, and ketoacids in the membrane permeate were reduced by >50% as compared to those obtained with the uncoated membranes (Karnik et al., 2005c).

Metal oxides, such as iron oxide, have been shown to retard the transport of bacteria (Penn et al., 2002, Silliman et al., 2001, Johnson et al., 1996, Scholl et al., 1990, DeFlaun et al., 1997, Knapp et al., 1997). Bacteria adhere to metal oxides, reducing the levels of the bacteria in the aqueous phase (Silliman et al., 2001). As such, it is expected that adhesion to the iron oxide surface will increase the retention of bacteria at the membrane surface, prolonging the contact of the bacteria with ozone, and, as a result, will improve disinfection.

In this work we hypothesize that catalyzed ozonation and membrane filtration will act synergistically, resulting in improved inactivation of and/or removal of bacteria from the filtrate. We have studied the removal and survival of bacteria in these treatment systems. The assimilated organic carbon concentrations (AOCs), a measure of bacterial regrowth potential of heterotrophic bacteria, were also monitored. Scanning electron microscopy was used to study the membrane surface before and after treatment.

8.3 MATERIALS AND METHODS

Experiments were carried out using samples taken from Lake Lansing (Haslett, MI), which is a borderline eutrophic lake (*Lake Lansing Watershed Advisory Committee Progress Report*, 1998). The samples were collected at the boat ramp at the Lake Lansing Park-South, Haslett, MI in five-gallon polyethylene carboys and stored at 4°C for a maximum storage period of seven days. The typical characteristics of Lake Lansing water are given in Table 8.1.

Table 8.1
Typical Characteristics of Lake Lansing Water (Haslett, MI) [a]

Parameters	Lake Lansing
TOC (mg/L)	8.6 to 11.6
pH	7.7 to 8.6
Alkalinity (mg/L as $CaCO_3$)	145 to 157
UV-254 (abs.)	0.160 to 0.180
SDS THM[b] (µg/L)	240
SDS HAA[b] (µg/L)	75
BDOC (mg/L)	1.0 to 4.1
Nitrate (mg/L)	0.44
Total Phosphate (mg/L)	0.06
Hardness (mg/L as $CaCO_3$)	190 to 198

[a] *All data reported is obtained from the Lake Lansing Watershed Advisory Committee Report (1998) except for SDS THM and SDS HAA, which were measured as part of this study*
[b] *SDS THM and SDS HAA were measured using Standard Method 5710 and USEPA Method 552.2, respectively.*

A protocol was developed to challenge the treatment system using *E.coli* strains (*E. Coli - DH1* obtained from Department of Cell and Molecular Biology, Michigan State University). Cultures of *E. Coli* (100 mL) were grown to late log phase in deionized water that contained reagent grade NaCl (10 g/L), Bactotryptone (10 g/L), and Difco yeast extract (5 g/L). The pH of the media was adjusted to 7.2 using 1 M NaOH before being spiked with *E. Coli.*

Once the bacteria reached late log phase (1×10^8 bacteria/mL for *E.coli* corresponding to an OD_{570} of ~0.03), 30 mL of this culture were concentrated by centrifugation at 10,000× g for 10-15 minutes. The supernatant was discarded and the pellet was suspended in 10 mL of the deionized water that had previously been filtered through a 0.2 μm pore size filter to remove bacteria and particulate matter.

The untreated feed raw water sample was spiked with 100 mL of this bacterial suspension per 3.5 liters of the feed raw water sample.

8.3.2 Experimental Methods

The experimental setup used for the combined ozone membrane filtration is shown in Figure 8.1. A tubular ceramic membrane in a stainless steel filter holder was used in these experiments. Teflon® tubing and stainless steel or Teflon® joints and valves were used throughout the system. Other components included: 3.5-liter and 1.5-liter water-jacked glass reservoirs made of Pyrex® glass, and a simple Y inline mixer (Ozone Service, Burton, B.C., Canada). Ozone gas was added into the water stream through the simple Y inline mixer just before the feed water entered the membrane module. The water level in the 3.5-liter reservoir was maintained at a constant level during the experiments using a peristaltic pump (Masterflex Model 7520-35, Cole-Parmer Co., Chicago, Illinois) to transfer water from the 1.5-liter reservoir into the 3.5-liter reservoir. A constant water temperature of 20°C was maintained using a recirculating water bath. The operating conditions used are given in Table 8.2. The gaseous ozone concentration was 2.5 g/m^3. The experiments were performed with membrane cross flow velocity of 0.6 m/s; the flow was turbulent with Reynolds number of approximately 6000.

Table 8.2

Operating Conditions for the Ozone –Membrane Filtration System

Water recirculation rate	2.75 LPM
Water temperature	20°C
Ozone gas flow rate	100 mL/min
TMP	0.5 bar

Permeate samples were collected in bottles covered with Parafilm® and stored in an ice-bath for the duration of the experiment. The experiments were performed included ozonation alone, membrane filtration alone, combined ozonation-nanofiltration using the uncoated/unsintered membranes.

The membrane used in these experiments was a Clover-leaf design (containing three channels) CéRAM membrane (TAMI North America, St. Laurent, Québec, Canada) with a molecular weight cut-off of 5 kDa. The external diameter of the membrane was 10 mm and the active membrane length was 25 cm. The membrane had a total filtering area of 41.2 cm^2. The membrane was used uncoated (as supplied by the manufacturer) and it was also used coated with iron oxide.

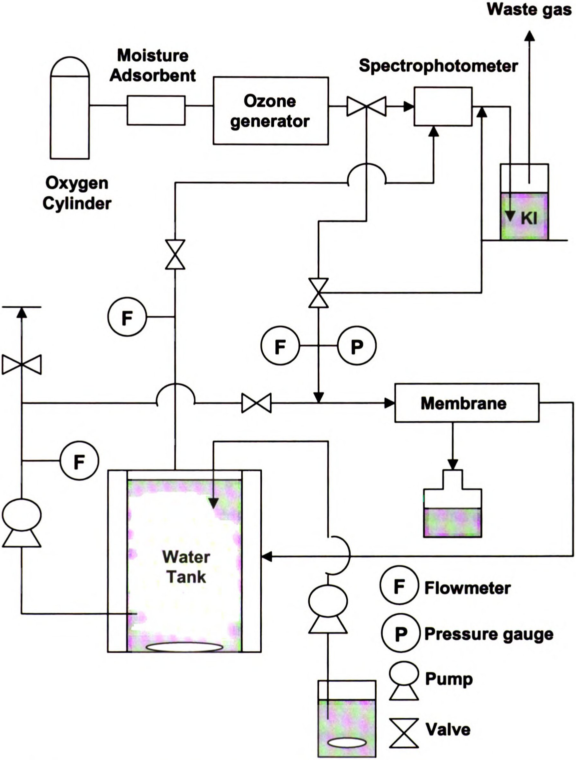


Figure 8.1 Schematic representation of the ozone-membrane filtration system
(Karnik et al., 2005a)

The layer-by-layer technique used to coat the membranes is based on a protocol described by McKenzie et al. (McKenzie et al., 2002) for coating doped tin oxide electrodes. The membrane was coated with 40 layers of iron oxide nanoparticles and sintered at 900°C. A detailed description of the method used to prepare the iron oxide coated membrane is available in our earlier work (Karnik et al., 2005c). The colloidal particles used for coating the membranes were prepared by Sorum's method. Transmission electron microscopy (TEM) characterization showed that the average particle diameter was 4 to 6 nm. The choice of the conditions for coating and sintering were based on results obtained in previous work on the removal of disinfection by-products and on evidence obtained by microscopy regarding the morphology of the membrane surface (Karnik et al., 2005b, c).

To generate ozone, pure oxygen gas (99.999%) from a pressurized cylinder was dried using a molecular sieve trap, and then fed to an ozone generator (Model OZ2PCS, Ozotech Inc., Yreka, Calif.). The gaseous ozone concentration was controlled by varying the voltage applied to the ozone generator. The excess gas was vented after passing the gas through a 2% potassium iodide (KI) solution to destroy any residual ozone gas.

The experiments were performed for ozonation alone, membrane filtration alone, ozonation membrane filtration and ozonation using catalyst coated membrane filtration. All the experiments were carried out for eight hours. A gaseous ozone concentration of 2.5 g/m^3 was used for all ozonation experiments, so the ozone dosage was the same for all experiments.

Samples of the feed water, permeate and reject streams (for the filtration experiments) and ozonated water (for the ozonation experiment) were analyzed using fluorescence microscopy to determine the ratio of live:dead bacteria. Samples were also taken to determine the concentration of assimilable organic carbon (AOC) in the water.

8.3.3 Analytical Methods

8.3.3.1 Bacterial analysis by fluorescence microscopy

A commercially available molecular probe kit (L-7012 LIVE/DEAD® BacLight, Bacterial Viability Kit, Molecular Probes, Eugene, OR.) was used for the characterization of bacteria as live or dead by fluorescence spectroscopy. The kit is used for monitoring the viability of bacterial populations as a function of the membrane integrity of the cell. Under the experimental conditions and the range of excitation wavelengths used, cells with a compromised membrane, those are considered to be dead or dying, will stain fluorescent red, whereas cells with an intact membrane will stain fluorescent green.

An aliquot (10 mL) of the water sample from the challenge experiments was prepared for fluorescence microscopy by concentrating the bacteria using centrifugation at 10,000× g for 10–15 minutes. The supernatant was then removed and the pellet was resuspended in 2 mL deionized water. One (1) mL of this suspension was added to each of the 1.5 mL microcentrifuge tubes and centrifuged for 10 minutes. The supernatant was decanted and resuspended in either 1 mL of filtered water for LIVE or 1 ml 70% ethyl alcohol for DEAD cell counts. The samples were incubated at room temperature for 1 hour, with mixing accomplished every 15 minutes. The samples were then centrifuged at 10,000× g for 10-15 minutes. Each pellet was resuspended in 1 mL of filter sterilized water.

Bacteria were stained with the dye available in the L-7012 kit in proportions given by the manufacturer. One volume of SYTO 9 dye was combined with one volume of propidium iodide stain in a 1.5 mL microcentrifuge tube and mixed thoroughly. For each 1 mL of the bacterial suspension, 3 μL of the dye mixture were added. When used at the recommended dilutions, the reagent mixture contributed 0.3% dimethyl sulfoxide (DMSO) to the staining solution. Higher DMSO concentrations were not used as these may adversely affect staining. The suspension was mixed thoroughly and incubated at room temperature in the dark for 15 minutes. The stained bacterial suspension was pipetted in volumes of 5 □L onto an ethanol cleaned slide and covered with an 18 mm square coverslip. Live and dead bacteria were then observed simultaneously using a fluorescence microscope (Leica DM4000 digital microscope) equipped with a standard fluorescein longpass filter set (Filter I3). For each sample, three slides were prepared and data from 10 fields were recorded. Digital images of the bacteria were also recorded.

To quantify the bacteria counts, fluorescence was measured using an excitation wavelength of 470 nm, and emission wavelengths within range of 490-700 nm and compared to a calibration curve prepared from known densities of a stained cell suspension. The calibration curve was prepared by measuring the ratio of the integrated intensity of the portion of each spectrum between 510–540 nm (emission for green) to the intensity of the portion between 620–650 nm (emission for red) for each bacterial suspension. This ratio of integrated green fluorescence to integrated red fluorescence ($R_{(G/R)}$) versus percentage of live cells (% Bacteria counts) in the *E. coli* suspension was plotted to give the calibration curve. The calibration equation obtained was

$R_{(G/R)} = 0.043 \times$ percentage of live bacteria counts $+ 0.6466$

where $R_{(G/R)}$ is the ratio of green fluorescence to red fluorescence and bacteria counts are measured for live bacteria detected in fluorescence spectrophotometer (SpectraMax M2, Molecular Devices). The results for the feed raw water sample showed that only 90% of the bacteria in this water were alive. The results reported here do/do not account for the number of bacteria that were dead in the raw water.

8.3.3.2 Regrowth potential of heterotrophic bacteria

The biodegradability of organics present in water was assessed using AOC (Van der kooij et al., 1982). The concentration of AOC was measured using Method 9217 (Clesceri et al., 1998). Water samples were collected in organic-carbon-free glass bottles. After the samples were mixed well, aliquots were decanted into test tubes. The test tubes were capped immediately and pasteurized in a 70°C water bath for 30 minutes to inactivate bacteria originally present in the sample. After pasteurization, samples were cooled to room temperature and inoculated with 1 mL of *Pseudomonas fluorescens* strain P17 and *Spirillum* strain NOX (each, at 500 colony-forming units (CFU)/mL). The samples were then incubated at room temperature (20 °C) for seven days. Following this, the Heterotrophic Plate Count (HPC) was determined by distributing aliquots of the sample on predried R2A agar plates (Clesceri et al., 1998). The colonies were counted on the plates after three days of incubation at room temperature and the concentration of AOC was determined.

8.3.3.3 Microscopic observation of the membrane surface

To obtain the images of the membrane surface, the tubular ceramic membrane was first sliced into circular disc sections of 1 mm thickness using a diamond wafering saw. Subsequently, these sections were cut to form small arcs of length 3 mm and width of 1 mm. These arcs were then mounted, using carbon adhesive tape, on aluminum mounting stubs for SEM examination.

To image the membrane surfaces after treatment, the bacteria and biomass present were immobilized by immersing the membrane surface in 4% glutaraldehye, a standard fixative, and 0.1M phosphate buffer for 45 minutes. These samples were next rinsed with 0.1M sodium phosphate buffer (pH 4) for 30 minutes and subsequently dehydrated in 25% ethanol (in water) by soaking for 15 minutes. Next, the samples were immersed in 50% ethanol for 15 minutes, sliced in rings of 1 cm thickness and placed in critical point dryer baskets, standard practice when fixing biological samples for SEM analysis. The dehydration was continued using 75, 95 and 100% ethanol, where samples were then allowed to stand for 15 minutes after each step. The samples were finally dried using a critical point dryer (Blazers Inc.). The dried samples were cut in arcs having a length of 3 mm and a width of 1 mm. These arcs were mounted, using carbon adhesive tape, on aluminum mounting stubs for SEM examination.

SEM images of the mounted samples were obtained using a JEOL 6400V scanning electron microscope with a LaB_6 emitter at an accelerating potential of 15 kV and magnifications ranging from 5,000X to 60,000X. The mounted samples were coated with gold using Emscope SC 500 sputter coater at a rate of 7 nm/min with a 20 mA current. The resulting digital micrographs were recorded using the AnalySIS® imaging system.

8.4 RESULTS AND DISCUSSION

A statistical analysis of the data presented was carried out using one way ANOVA at the 95% confidence level ($p<0.05$).

8.4.1 Bacterial analysis by fluorescence microscopy

Comparison of the images obtained from fluorescence microscopy (see Figure 8.2) reveal that ozonation resulted in a decrease in the number of live bacteria (those that

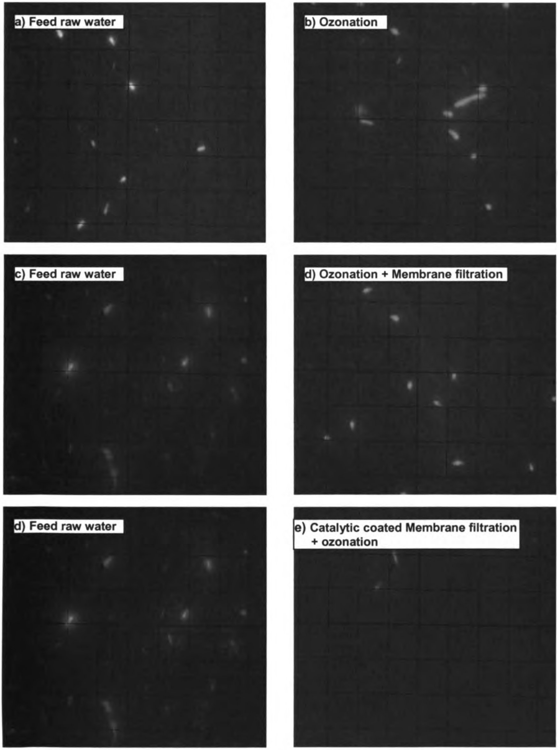


Figure 8.2 Fluorescence images indicating bacteria presence in the permeate after different treatments.

Experimental setup: see Fig. 8.1 Operating Conditions: see Table 8.2. Membrane Size: 5 kDa, Gaseous ozone concentration 2.5 g/m^3, catalyst coated membrane: coated with 40 times with iron oxide nanoparticles, and then sintered in air at 900°C.

stained green) as compared to that observed in the feed raw water from Lake Lansing prior to ozonation treatment. In the combined ozonation-membrane filtration experiment, the number of live bacteria in the permeate was further decreased, suggesting a synergy between ozonation and membrane filtration. Further improvements were obtained when using the iron oxide catalyst-coated membrane (see Figure 8.2e).

The mortality of the bacteria in the product water (permeate or ozonated water) after treatment using ozonation, combined ozonation-membrane filtration, and ozonation-membrane filtration process with an iron oxide coated membrane was 50%, 85%, and >99%, respectively (as shown in Table 8.3, Figure 8.3).

Table 8.3
Live-Dead bioassays using fluorescence spectroscopy
The precision of the analytical procedure is within 5 %.

Live-Dead assays using Fluorescence Spectroscopy Method				
Treatment Process	Permeate Stream		Removal	
	R(G/R)	LIVE*	R(G/R)	LIVE*
		(% Bacteria counts)		(% Bacteria counts)
Membrane filtration	4.29	85	4.60	92
Ozonation	2.78	49.5	3.87	75
Ozonation-Membrane filtration	1.23	13.5	2.15	35
Catalytic Ozonation-Membrane filtration	0.69	1	1.16	12

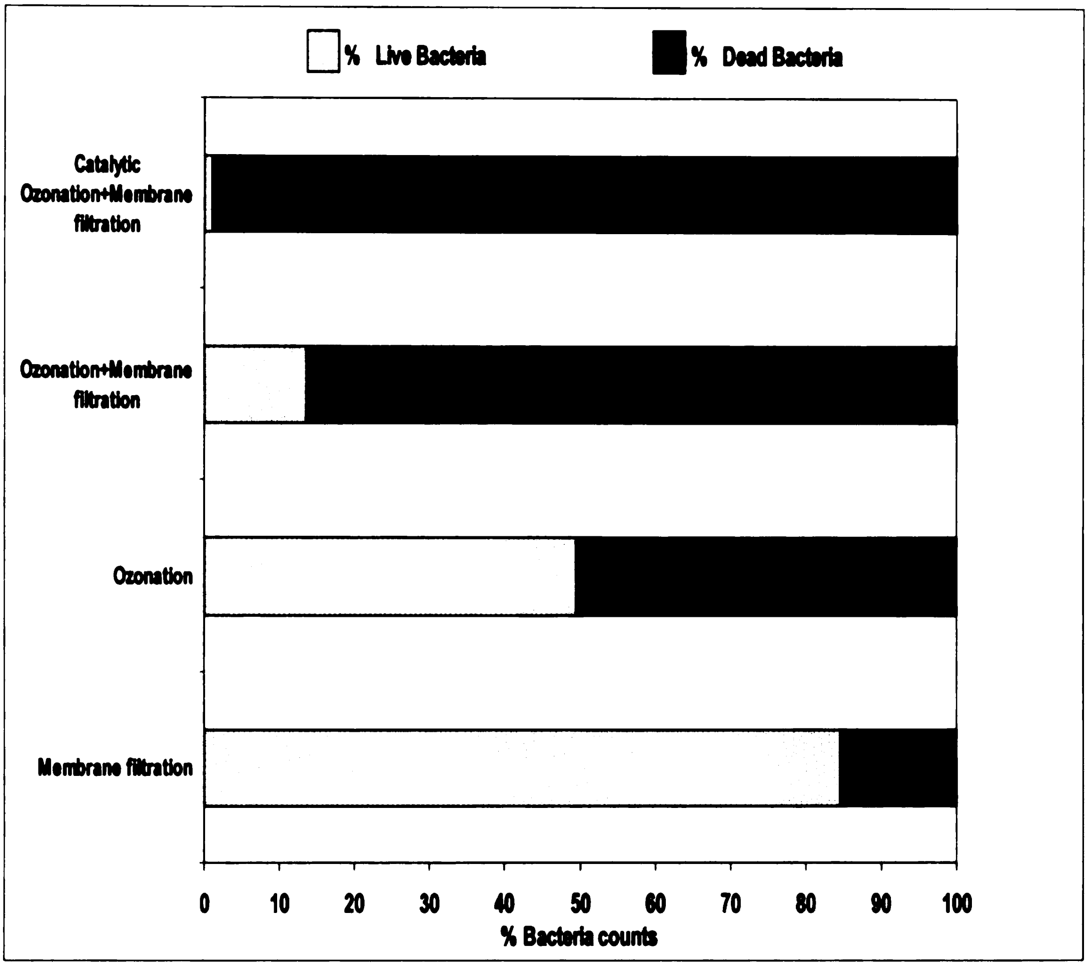


Figure 8.3 Percent of live – dead bacteria in the permeate after different treatments.

Experimental setup: see Figure 8.1 Operating Conditions: see Table 8.2. Membrane Size: 5 kDa, Gaseous ozone concentration 2.5 g/m^3, catalyst coated membrane: coated with 40 times with iron oxide nanoparticles, and then sintered in air at 900°C. The results were determined using fluorescence spectroscopy after staining with molecular probes. All values are the average of triplicates within experiments.

The mortality of the bacteria in the reject stream was 25%, 65%, and 88% for ozonation, combined ozonation-membrane filtration, and catalytic ozonation-membrane filtration, respectively. It is evident that mortality of the bacteria was significantly higher in combined ozonation-filtration experiments than that obtained in the ozonation experiments and that the mortality of the bacteria is highest when the coated membrane was used.

As the same ozone dosage was used in all experiments, it is apparent that disinfection is more effective using ozonation-membrane filtration. The improved disinfection observed using the combined process may be explained by the catalytic decomposition of ozone at the iron oxide surface, which results in the formation of ·OH or other radical species that inactivate the bacteria near the surface. Bacteria have been shown to adhere strongly to iron oxide surfaces (Knapp et al., 1997). The adhesion of bacteria to the iron oxide surface may also improve performance. The lower mortalities found in the reject stream are also consistent with this explanation, since the bacteria in permeate are more likely to have been at the membrane surface (and passed through imperfections in the membrane) than the bacteria in the reject stream (which are in the recirculating water stream).

The bacteria counts measured as HPC in the permeate stream are tabulated in Table 8.4. The higher bacteria counts were found in the permeate for the membrane filtration alone (2 CFU/mL) when compared to that observed in the permeates from the hybrid process using ozonation and membrane filtration with the uncoated membrane (1.67 CFU/mL) and also the hybrid process using ozonation and iron oxide coated membranes (0.67 CFU/mL). These results show that removal of bacteria by filtration is at least 3 logs better than that obtained with ozonation alone. For the ozonation-membrane filtration experiment using the uncoated membrane the removal of bacteria is only slightly higher than that observed in the filtration experiment. However, for the ozonation-membrane filtration experiment using the coated membrane the removal of bacteria is significantly higher. The higher removal found using the coated membrane is consistent with higher mortality found using the Live-Dead assay.

Table 8.4

Reduction in *E. coli* Counts Using Heterotrophic plate count method

Heterotrophic Plate Count Method				
Treatment Process	Concentration in feed (C_f)*	Concentration in product water (C_p)*	Removal	Log Removal (R_{LOG})
	(CFU/mL)	(CFU/mL)	$R=1-C_P/C_R$	$R_{LOG=}$-log(1-R)
Membrane filtration	1.86E+07	2.00	0.99999989	6.97
Ozonation	1.83E+07	1670.00	0.99990891	4.04
Ozonation-Membrane filtration	1.83E+07	1.67	0.99999991	7.04
Catalytic Ozonation-Membrane filtration	190E+07	0.67	0.99999996	7.45

******All values are with 5% std.deviation*

8.4.2 Regrowth Potential of Heterotrophic Bacteria

As shown in Figure 8.4, the measured AOC concentrations decreased significantly in the permeate using membrane filtration-ozonation compared to that obtained in the product water when using ozone alone. AOC concentrations of 0.089 (± 0.0005) mg/L, 5.05 (± 0.04), and 3.75 (± 0.03) mg/L were observed in the permeate samples from membrane filtration alone, ozonation/ membrane filtration using uncoated membranes, and ozonation/filtration using coated membranes.

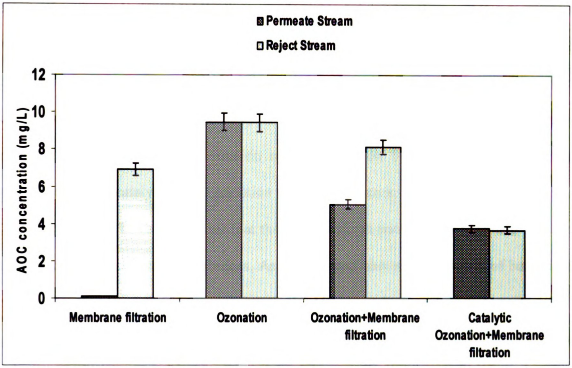


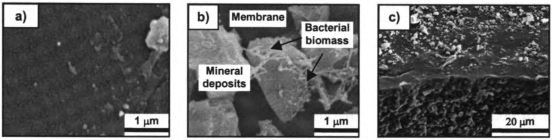
Figure 8.4 Assimilated Organic Carbon (AOC) concentration after different treatments for the permeate and reject streams.
*Experimental setup: Fig. 8.1 Operating Conditions: Table 8.2. Membrane Size: 5 kDa, Gaseous ozone concentration 2.5 g/m^3, catalyst coated membrane: coated with 40 times with iron oxide nanoparticles, and then sintered in air at 900°C. *All values are the average of triplicates within experiments.*

This compares to an AOC concentration in the ozonated water of 9.44 (± 0.05) mg/L. The AOC concentrations measured for the reject stream were 6.19 (± 0.008), 8.14 (± 0.004), and 3.67 (± 0.03) mg/L, respectively, for membrane filtration alone, combined ozonation-(uncoated) membrane filtration, and catalytic ozonation-membrane filtration.

For the iron oxide coated membrane experiments, the AOC concentrations in the permeate were <50% of that that obtained in the experiments with the uncoated membrane. This confirms our earlier work where it was found that the concentrations of ozonation byproducts in the permeate were lower when ozonation-membrane filtration was used as compared to the concentrations observed in the treated water with ozonation alone (Karnik et al., 2005b). Work in our laboratory has also shown that a significant reduction in the concentration of ozonation byproducts in the permeate occurs when the membrane is coated with iron oxide (when compared to uncoated membranes) (Karnik et al., 2005c). The membrane surfaces appear to serve as a catalyst for the degradation of ozone, thereby reducing the formation of the ozonation byproducts. The membrane surface may also catalyze the degradation of some ozonation by-products (Karnik et al., 2005b, 2005c). The data indicates that there is a reduced potential for regrowth in water treatment using the coated membranes. As is discussed above, the survival of bacteria is also lower when these membranes are used. The lower survivals and AOC concentrations observed using combined catalytic ozonation-membrane filtration suggest it is likely to be a very effective process to both disinfect the water and control bacterial regrowth in the distribution system.

8.4.3 Microscopic observation of the membrane surface

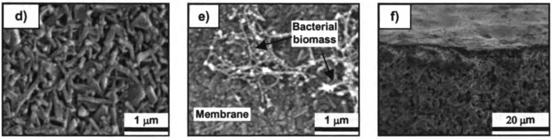
Figure 8.5 shows SEM micrographs for an uncoated membrane with 5 kDa MWCO and a 5 kDa membrane coated 40 times with iron oxide particles and sintered at 900°C. Images are shown for the membrane both before and after the membranes were used in the ozonation-membrane filtration treatment process. The SEM micrographs clearly show that the morphology of the surface is altered as a result of the coating procedure. The surface morphology changed from a fine-grained microstructure for the uncoated membrane (Figure 8.5a) to a coarse-grained morphology with uniformly interconnected pores on the iron oxide coated and sintered membrane (Figure 8.5d). As can be seen in Figures 8.5b and 8.5c, there are mineral deposits and possibly organic detritus on the uncoated-unsintered membrane surface that had been used to filter water.



Uncoated-Unsintered-pretreatment

Uncoated-Unsintered-post treatment

post treatment-cross sectional view



5kD-40 layers-900°C-pretreatment

5kD-40 layers-900°C-post treatment

post treatment-cross sectional view

Figure 8.5 SEM images of membrane surface before and after treatment

SEM JEOL 6400V, accelerating voltage 15 kV, a-c) SEM images of an uncoated-unsintered membrane from the manufacturer, d-f) SEM images of a membrane coated with 40 times with iron oxide nanoparticles, then sintered in air at 900°C. Pretreatment and post-treatment refers to samples before and after ozonation-membrane filtration hybrid process treatment

Mineral grains in the micron size range are found on this surface. However, there is no evidence of such mineral deposits on the iron oxide coated-sintered membrane surface (see Figures 8.5e and 8.5f). The lack of mineral deposits may be a result of the alteration in the surface charge or morphology of the membrane surface, which does not allow mineral deposition onto the membrane surface. It appears that there is more organic detritus on the coated membranes than on the uncoated membrane (compare Figure 8.5b with Figure 8.5e). Further research will be conducted to study the deposition of this material on the membrane surface.

8.5 ACKNOWLEDGEMENTS

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CHAPTER NINE

USE OF SALICYLIC ACID AS A MODEL COMPOUND TO INVESTIGATE HYDROXYL RADICAL REACTION IN OZONATION-MEMBRANE FILTRATION HYBRID PROCESS

9.1 ABSTRACT

In this paper, we report on an investigation of the reaction mechanism which occurs in the ozone-membrane filtration hybrid process. In this study experiments were conducted using salicylic acid (SA) as a hydroxyl radical probe. Four processes were investigated: ozonation alone, membrane filtration alone, the ozonation-ceramic membrane filtration hybrid process and ozonation-iron oxide coated ceramic membrane filtration. Experiments were conducted at two different pH values: pH ca. 2.5 and pH ca. 7.0. There was no change in concentration of SA at pH below 3.0. The results show SA was not removed by either molecular ozone reactions, filtration (including sorption), or the combined processes at pH values less than 3.0 and that the reaction rates increase significantly at pH values >7.0, demonstrating that hydroxyl radical reactions control the reaction mechanism. The results also showed that the salicylate ion sorbed to the membrane whereas salicylic acid did not. At pH above 7.0 in the hybrid process, there is continuous decline in the concentration of SA suggesting a strong surface catalytic reaction dominating the process. The iron oxide coated membranes combined with ozonation result over 95% removal of SA after 240 minutes at an ozone dosage of 2.5 g/m^3, compared with 80% percentage with the uncoated membrane. The presence of 2, 3-dihydroxy benzoic acid (2, 3-DHBA) and 2, 3-dihydroxy benzoic acid (2, 5-DHBA) in the permeate was confirmed using GC/MS. 2,3-DHBA was found to be the predominate byproduct and is known to form as a result of hydroxyl radical reaction with SA. A reaction mechanism is suggested to explain the enhanced SA removal in the hybrid process.

Keywords: ceramic membrane, iron oxide, catalytic coating, ozonation, catalytic ozonation, salicylic acid, membrane filtration, high perform liquid chromatography (HPLC), GC-MS

9.2 INTRODUCTION

Over the last decade there has been increasing interest in combining ozonation with membrane technology for drinking water treatment. Few studies have investigated effect of ozone on organic membranes as these membranes are not resistant to ozone and are damaged during operation (Hashino et al., 2000; Shanbag et al., 1998; Castro and Zander 1995; Shen et al., 1995). An alternate solution is to combine ozone with ceramic membranes, as these membranes are ozone resistant and have demonstrated stable permeate fluxes without membrane damage (Karnik et al., 2005a; Schlichter et al., 2004; Kim et al, 2001, 1999; Allemane, 1993). Recent studies have shown that permeability rates obtained with ceramic membranes are superior to those from polymeric membranes. Ceramic membranes have also been found to be to be more effective than polymeric membranes for the treatment of textile waste water and in alkaline and acidic solutions (Weber et al., 2003). Lee and Cho (2004) found a ceramic tight-ultrafiltration membrane had the same potential as a nanofiltration polymeric membrane, in terms of reducing the formation of haloacetic acid formation, and were comparable to polymeric membranes with similar molecular weight cut-off (MWCO) for the removal of natural organic matter (NOM). Several researchers (Karnik et al., 2005b, 2005c; Schlichter, 2004; Shioyama et al., 2001) found that the combined process involving ceramic membrane filtration with ozonation was more efficient for the elimination of disinfection byproducts (DBPs) and other organic contaminants in raw water without membrane damage. Ceramic membranes have robust performance when compared to polymeric membranes in terms of increasing severity of operating parameters, including higher temperatures and pressures, as well as a higher resistance to chemicals and overall durability, thus making ceramic membranes a natural choice in spite of their higher initial costs (Benfer et al. 2004; Zuzek et al., 2001). The metal oxide that makes up the base material for the ceramic membrane matrix also acts as a catalyst and assists in the degradation of ozone on the membrane surface. The ozone gas is adsorbed on the catalyst surface, resulting in its decomposition and subsequent formation of ·OH radicals (Acero et al., 1999). In the presence of different metal oxide catalysts, such as iron oxide, manganese oxide, titania, alumina and zirconia, ozone degrades NOM, recalcitrant organic compounds, including saturated carboxylic acids, phenols, aromatic hydrocarbons, dyes, humic substances and herbicides (Beltran et al., 2005, 2003a, 2003b; Trapido et al., 2005; Ni and Chen 2001; Radhakrishnan and Oyama, 2001; Gracia et al., 2000a, 2000b, 1996). The enhanced degradation of ozone on the metal oxide surface is thought to result from the adsorption of organic compounds on the metal oxide and the subsequent decomposition of ozone, resulting in the formation of hydroxyl radicals which further assist in the degradation of these refractory organic compounds (Ernst et al., 2004; Pines and Reckhow, 2003; Ma et al., 2000, 1999; Andreozzi et al., 2000, 1998a, 1998b, 1992).

Several researchers have attempted to study hydroxyl radical reactions in water with the use of probe compounds, electron paramagnetic resonance (EPR) spectroscopy, and ultrasound irradiation process (Han et al., 2002). The most commonly used probe chemicals include *para* chlorobenzoic acid, salicylic acid, dimethyl sulfoxide (Park et al., 2004; Xi et al., 2004; Stiener and Babbas, 1990). Since the ideal probe will react only with OH radicals and not to an appreciable extent with ozone, the disappearance of the probe is a measure of the OH radical concentration. While a number of probes may be used, salicylic acid (SA) is preferred over other probe compounds because of i) its high reaction rate with the OH radical (5×10^9 $M^{-1}s^{-1}$), ii) its use at concentrations sufficient to compete with other scavengers present in the solution and iii) the stability of the resulting products, which allows for their analysis and quantification (Punchard and Kelly, 1996). The major products formed as a result of hydroxyl reactions with SA are 2, 3-dihydroxy benzoic acid (2,3-DHBA), 2, 5-dihydroxy benzoic acid (2, 5-DHBA) and catechol (Albarran and Schuler, 2003). This paper reports on our investigations into the catalytic reaction in the ozone-membrane filtration hybrid process using salicylic acid as a probe compound to quantify hydroxyl radicals and to determine the reaction mechanism in the hybrid process.

9.3 MATERIALS AND METHODS

9.3.1 Ozone-Membrane Filtration Experiments

The experimental setup used for the combined ozone membrane filtration is shown in Figure 9.1. Ozone gas was added into the water stream through the simple Y inline mixer (Ozone Service, Burton, B.C., Canada) just before the feed water entered the membrane module. The water level in the 3.5-liter reservoir was maintained at a constant level during the experiments using a peristaltic pump (Masterflex Model 7520-35, Cole-Parmer Co., Chicago, Illinois) to transfer water from the 1.5-liter reservoir into the 3.5-liter reservoir. The operating conditions used are given in Table 9.1. The experiments were performed with membrane cross flow velocity of 0.6 m/s; the flow was turbulent with Reynolds number of approximately 6000.

Table 9.1

Operating Conditions for the Ozone –Membrane Filtration System

Water recirculation rate	2.75 LPM
Water temperature	20 °C
Ozone gas flow rate	100 mL/min
TMP	0.5 bar

To generate ozone, pure oxygen gas (99.999%) from a pressurized cylinder was dried using a molecular sieve trap, and then fed to an ozone generator (Model OZ2PCS, Ozotech Inc., Yreka, Calif.). The gaseous ozone concentration was controlled by varying the voltage applied to the ozone generator. The excess gas was vented after passing the gas through a 2% potassium iodide (KI) solution to destroy any residual ozone gas. Teflon® tubing and stainless steel or Teflon® joints and valves were used throughout the system.

A tubular ceramic membrane in a stainless steel filter holder was used in these experiments. The membrane used in these experiments was a Clover-leaf design (containing three channels) CéRAM membrane (TAMI North America, St. Laurent, Québec, Canada) with a molecular weight cut-off of 5 kDa. The external diameter of the membrane was 10 mm and the active membrane length was 25 cm. The membrane had a total filtering area of 41.2 cm^2.

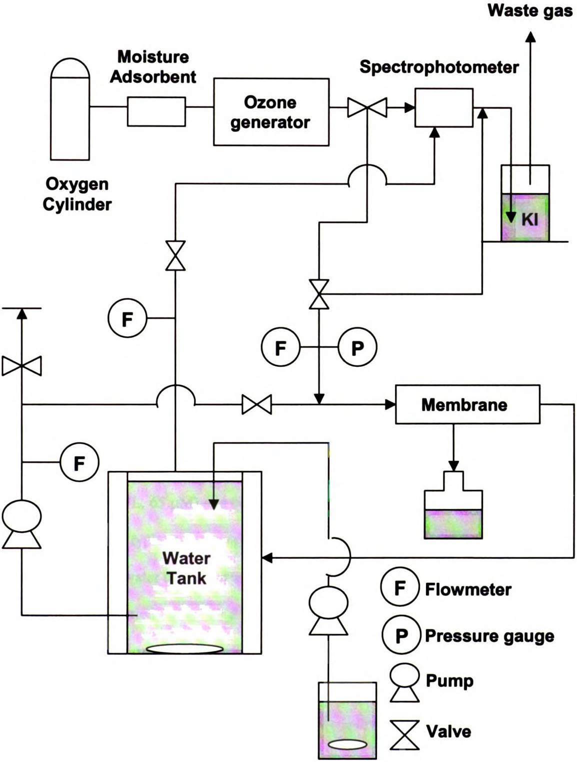


Figure 9.1 Schematic Representation of the Ozone-Membrane Filtration System *(Karnik et al., 2005a)*

The membrane was used uncoated (as supplied by the manufacturer) and it was also used after being coated with iron oxide. Colloidal iron oxide particles, having an average particle diameter of 4 to 6 nm, were prepared by Sorum's method and used for coating the membranes following the layer-by-layer technique developed by McKenzie et al. (2002) for coating doped tin oxide electrodes (Karnik et al., 2005c). The membranes were coated with 40 layers of iron oxide nanoparticles and sintered at 900 °C. The conditions for coating and sintering were determined based on results obtained for the removal of disinfection byproducts (Karnik et al., 2005b,c) and on the changes in the morphology of the membrane surface as detected by electron microscopy (Karnik et al., 2006).

In this study, the treatment processes evaluated included membrane filtration, ozonation, and combined ozonation-membrane filtration using both uncoated/unsintered membranes and iron oxide coated/sintered membranes. Deionized water was spiked with salicylic acid (17 mg/L, 65 μM) at a concentration equivalent to the total organic carbon (TOC) concentration typically present in Lake Lansing, MI a border line eutrophic lake which served as the water source for all our earlier work (Karnik et al., 2005a, b, c). All experiments were carried out for four hours with a constant water temperature of 20 °C and constant gaseous ozone concentration of 2.5 g/m^3. Permeate samples were collected in bottles covered with Parafilm® and stored on ice for the duration of the experiment. The permeate was collected and analyzed to determine the concentrations of salicylic acid, 2,3-DHBA, 2,5-DHBA and catechol. The experiments were performed at pH 2.5-

3.0 and pH 7.9-8.1. Where pertinent t-butyl alcohol (t-BuOH) (ACS grade, 15.5 mg/L) was added as an •OH radical scavenger to study the reaction mechanism.

9.3.2 Quantification of salicylic acid and its byproducts

Salicylic acid (SA), 2,3-dihydroxy benzoic acid (2,3-DHBA), and 2,5-dihydroxy benzoic acid (2,5-DHBA) were acquired from Sigma-Aldrich Corp. (St. Louis, MO, USA). A stock solution of SA (20 mg/L) was prepared weekly and stored in the dark at 4 °C. The concentration of SA, 2,3-DHBA , 2,5-DHBA and catechol was measured using high performance liquid chromatography (HPLC).

HPLC analysis was carried out using a Perkin Elmer (Wellesley, MA, USA) Binary LC 250 pump, Waters Millipore Lambda-Max Model 480 LC (Bedford, MA,USA) spectrophotometer detector and PE series 200 autosampler. The wavelength was set to 234 nm.

Separation of SA and its byproducts was achieved using a LiChrospher 100 C18 RP, 250×4.6 mm I.D., 5 μm (Merck – 5 μm). Elution of the compounds was performed at 1 mL/min. The mobile phase was a solution of HPLC-grade water (supplier) containing 0.1 % phosphoric acid and HPLC-grade acetonitrile (supplier) prepared at a ratio 60:40. Under these conditions, the retention times of SA, 2,3-DHBA, 2,5-DHBA and catechol were 8.7, 3.4, 4.5 and 5.2 minutes, respectively. All samples were adjusted to pH 2.9 with ACS reagent grade phosphoric acid before analysis. Calibration curves were obtained following the analysis of five standards prepared from stock solution.

9.3.3 Confirmation of the identity of byproducts using GC-MS

The permeate samples were evaporated under helium and the residue was dried over P_2O_5 in a vacuum desiccator for one hour. The completely dried sample was derivatized by silylation using bis(trimethylsilyl)trifluoroacetamide (BSTFA) + 1% trimethylchlorosilane (TMCS) (Regis, Morton Grove, IL) at 100 °C for 20 min to convert all free -OH and -COOH groups into their volatile TMS-ether (-$OSiMe_3$) and TMS-ester (-CO_2SiMe_3) derivatives, respectively. GC-MS was performed using a JEOL AX-505H double-focusing mass spectrometer coupled with a Hewlett-Packard 5890J GC (Norwalk, CT). The mass spectrometer was operated in electron impact mode and a 30 m × 0.32 mm I.D., 0.25 μm DB-1ms column (J&W Scientific, Folsom, CA) was used for the analysis. The oven temperature was ramped from 150 °C to 299 °C at a rate of 10 °C/min. The injector temperature and separator temperature were 299-300 °C and 280 °C, respectively. The flow rate of the carrier gas (N_2) was 20.0 mL/min.

9.4 RESULTS AND DISCUSSION

As shown in Figure 9.2, neither ozonation, neither membrane filtration-ozonation, nor membrane filtration alone resulted in a significant decrease in the SA concentration (within 5% std. deviation) after up to 240 minutes of treatment. As membrane filtration (alone) did not result in a significant reduction in the SA concentration, it appears that at low pH, SA is not sorbed within the system to any appreciable over the period of experiment. It is also apparent that SA does not react with molecular ozone under these experimental conditions. Removal of SA did not occur to any appreciable extent with the ozone-filtration process, suggesting that significant decomposition of ozone and formation of OH radicals did not occur with the uncoated membrane at a pH of 2.5-3.0. This further substantiates our choice of SA as a model compound as it neither substantially sorbs to the membrane surface nor undergoes direct reactions with molecular ozone, thus the decrease in concentration of SA can be correlated to the hydroxyl radical concentration.

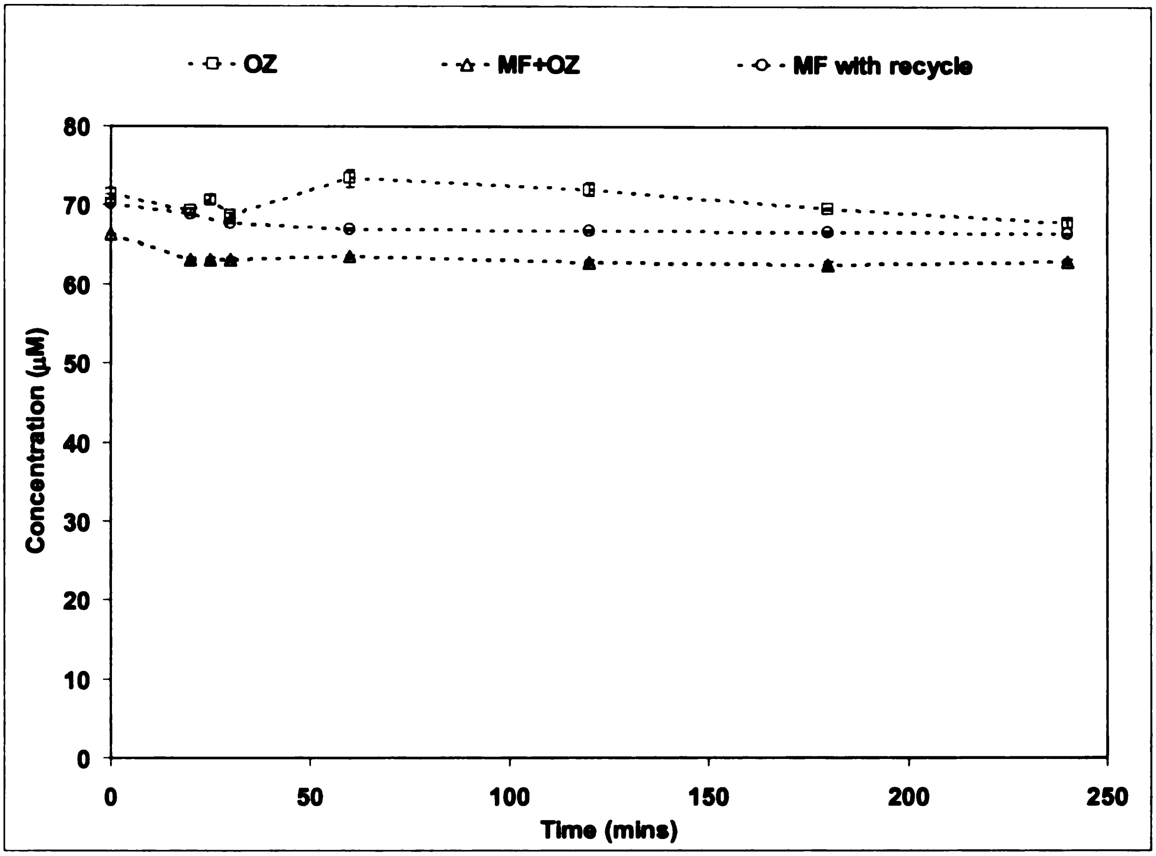


Figure 9.2 Disappearance of salicylic acid at pH 2.5-3 with different treatment processes

Experimental Setup: Fig 9.1, Operating Conditions: Table 9.1

Membrane filtration (MF), Ozonation (OZ), Ozone-uncoated unsintered Membrane filtration (MF+OZ)

As shown in Figure 9.3, at pH values in the range of 7.9 to 8.1, membrane filtration with recycle resulted in the sorption of SA on the membrane surface over the first 50 minutes of treatment. The concentration of SA gradually reached steady state and concentration of SA remained constant for the remainder of the experiment. When the same treatment was repeated but without recycle of the reject stream, the capacity for SA appeared to increase, although steady-state conditions were still reached after approximately 30 minutes and further reductions in the SA concentration beyond the initial loss did not occur.

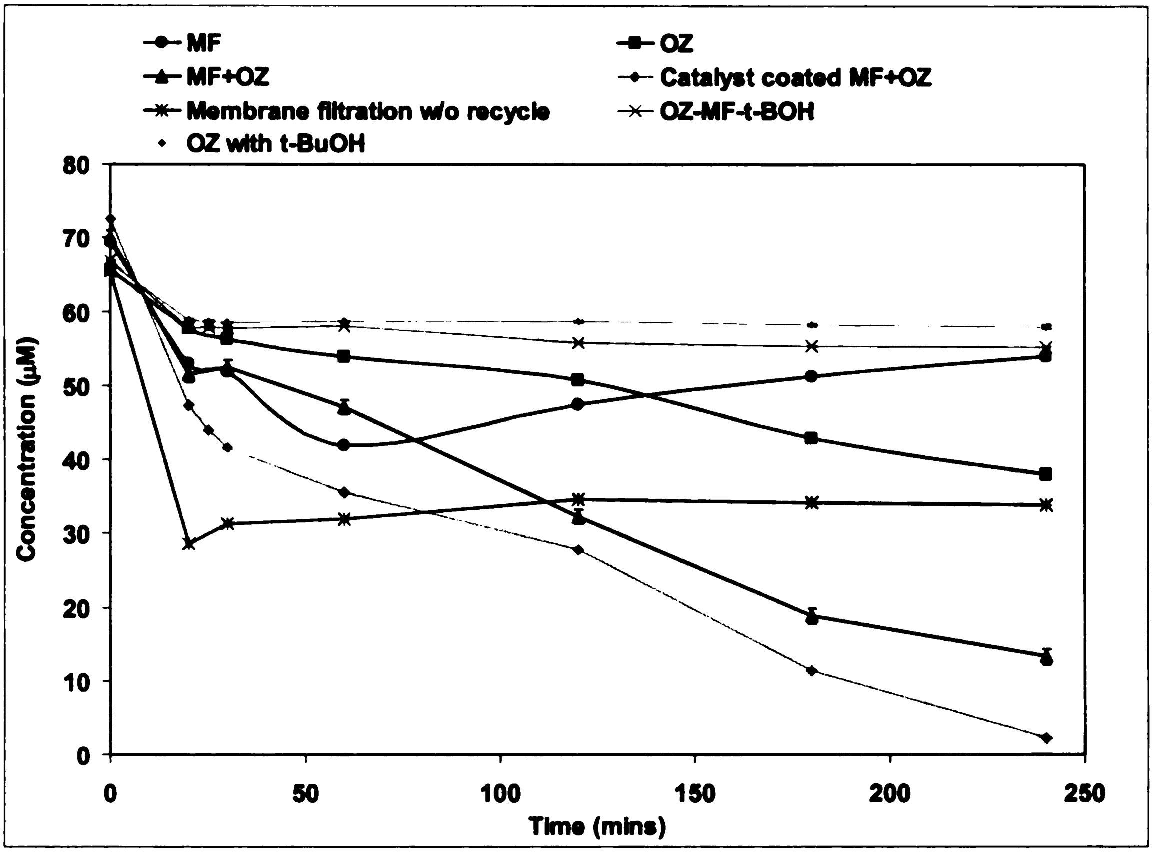


Figure 9.3 Disappearance of salicylic acid at natural pH with different treatment processes
Experimental Setup: Fig 9.1, Operating Conditions: Table 9.1, pH 7.0-8.1
Membrane filtration (MF), Ozonation (OZ), Ozone-uncoated unsintered Membrane filtration (MF+OZ), Iron oxide catalyst coated membrane filtration combined with ozonation (Catalyst coated MF+OZ)

Comparing these results to those obtained with membrane filtration at pH 2.5-3.0, it appears that the salicylate ion more effectively sorbs to the membrane surface than does the protonated form (the *pK_a for salicylic acid is 2.9*). At the higher pH, SA was degraded by ozone to a greater extent than that observed at pH 2.5-3.0 (40% at pH 8 vs.

<5% at pH 2.8 after 240 minutes). The combination of ozonation and membrane filtration resulted in further removals (>80% after 240 minutes), with combined ozonation and membrane filtration using the iron oxide coated membrane being the most effective of the processes studied (up to 95% after 240 minutes). In order to elucidate the mechanism of the reaction, t-BuOH was added as an OH radical scavenger. The addition of t-BuOH to the ozonation process alone and the ozonation–uncoated membrane filtration system, resulted a significant decrease in the reactivity of SA even at higher pH (<15% removal after 240 minutes), suggesting the importance of indirect oxidation reactions rather than the effect of pH being the result of a greater reactivity of the salicylate ion with ozone than salicyclic acid. The indirect reaction pathways result in the formation of hydroxyl, super oxide and other radicals, which appear to accelerate the decomposition of SA. The synergy between sorption and reactions involving the hydroxyl radical appears to lead to a greater decrease in SA concentration in the hybrid process than in the ozonation process (at the same ozone dose), This enhanced removal of SA with the iron oxide coated membranes is believed to be a result of changes in the surface morphology (Karnik et al., 2006), which affect the performance of the system by improving surface catalytic properties of the membrane surface. This improved performance with coated membranes when compared to uncoated membranes suggest a strong correlation of surface chemistry and hydroxyl reaction in the hybrid process.

To substantiate our claims of the importance of hydroxyl radical reactions in the process, we analyzed the permeate from different experiments for the products formed from the reaction of SA with hydroxyl radicals. These products include 2, 3 DHBA, 2, 5-

DHBA and catechol. In these experiments we detected only two byproducts 2, 3 DHBA and 2, 5-DHBA, there was no evidence of catechol in any of the experiments conducted.

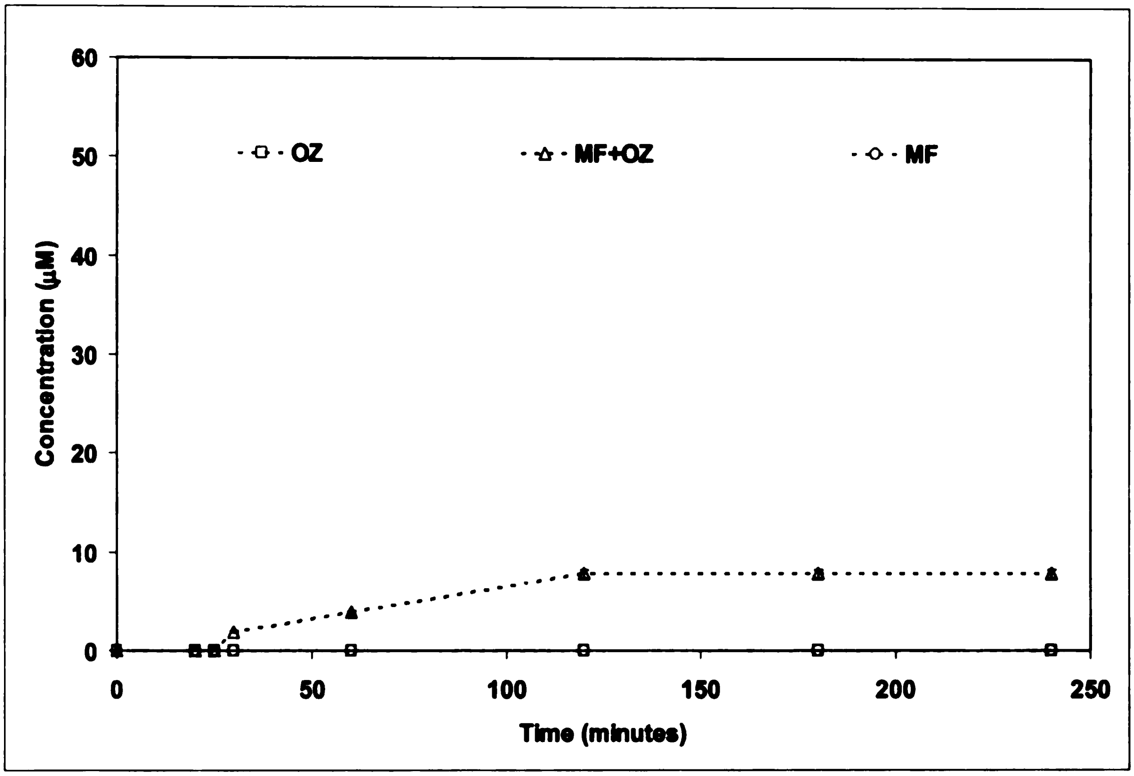


Figure 9.4 Formation of oxidation byproducts at pH 2.5-3 with different treatment processes

Experimental Setup: Fig 9.1, Operating Conditions: Table 9.1

Membrane filtration (MF), Ozonation (OZ), Ozone-uncoated unsintered Membrane filtration (MF+OZ)

Further the by products concentration are reported as a total by products concentration by adding the molar concentration of the individual compounds. The individual concentration of these compounds is reported in Table 9.2. At pH 2.5-3.0, there was no evidence of SA byproducts in the treated stream from either ozonation or membrane filtration alone (Figure 9.4). However, with the hybrid process SA byproducts were formed at concentrations <7.8 µM, supporting the suggested mechanism that adsorption followed by the decomposition of ozone on the membrane surface leads to the formation of hydroxyl radical, which react with SA to form the observed byproducts.

Table 9.2

Total molar concentration (μM) of the by-product in individual treatment process

Time (mins)	OZ pH 2.5-3.0	MF pH 2.5-3.0	MF+OZ pH 2.5-3.0	MF w/o recycle pH 8.1	MF w/recycle pH 8.1	MF+OZ w/ t-BuOH	OZ pH 8.1	MF+OZ pH 8.1	Catalyst coated MF+OZ pH 8.1
0	ND	ND	ND	ND	ND	ND	ND	ND	ND
20	ND	ND	ND	ND	ND	4.54	13.60	12.33	24.66
25	ND	ND	ND	ND	ND	4.54	14.30	22.06	24.33
30	ND	ND	1.95	ND	ND	4.54	14.20	22.06	30.17
60	ND	ND	3.89	ND	ND	4.54	20.71	35.66	33.74
120	ND	ND	7.79	ND	ND	4.54	20.30	36.98	35.04
180	ND	ND	7.79	2.6	ND	4.54	21.60	[‡]40.36	45.09
240	ND	ND	7.79	2.6	ND	[‡]7.85	21.62	37.63	55.15

[‡] *All concentrations are molar concentrations of 2,3-DHBA expect in these cases where it is the sum of 2,3-DHBA and 2,5-DHBA. There was no detection of catechol in any of the experiments.*
For MF+OZ pH pH 8.1 at time 180 minutes, *[2,5-DHBA]=2.78 μM and*
For MF+OZ w/ t-BuOH at time 240 minutes, *[2,5-DHBA]=3.32 μM*

Again, comparison of Figures 9.4 and 9.5 for hybrid process at lower pH < 3 and the hybrid process with t-BuOH at pH > 7.0 respectively show similar concentration (~ 7.8 μM) of SA byproducts, supporting the theory that the reaction was the result of hydroxyl radical initiated decomposition rather than sorption alone. Also we found in experiment where t-BuOH was added to ozonation alone, there was no significant concentration of the by-products concentration reported further supporting our hypothesis of hydroxyl radical reaction mechanism.

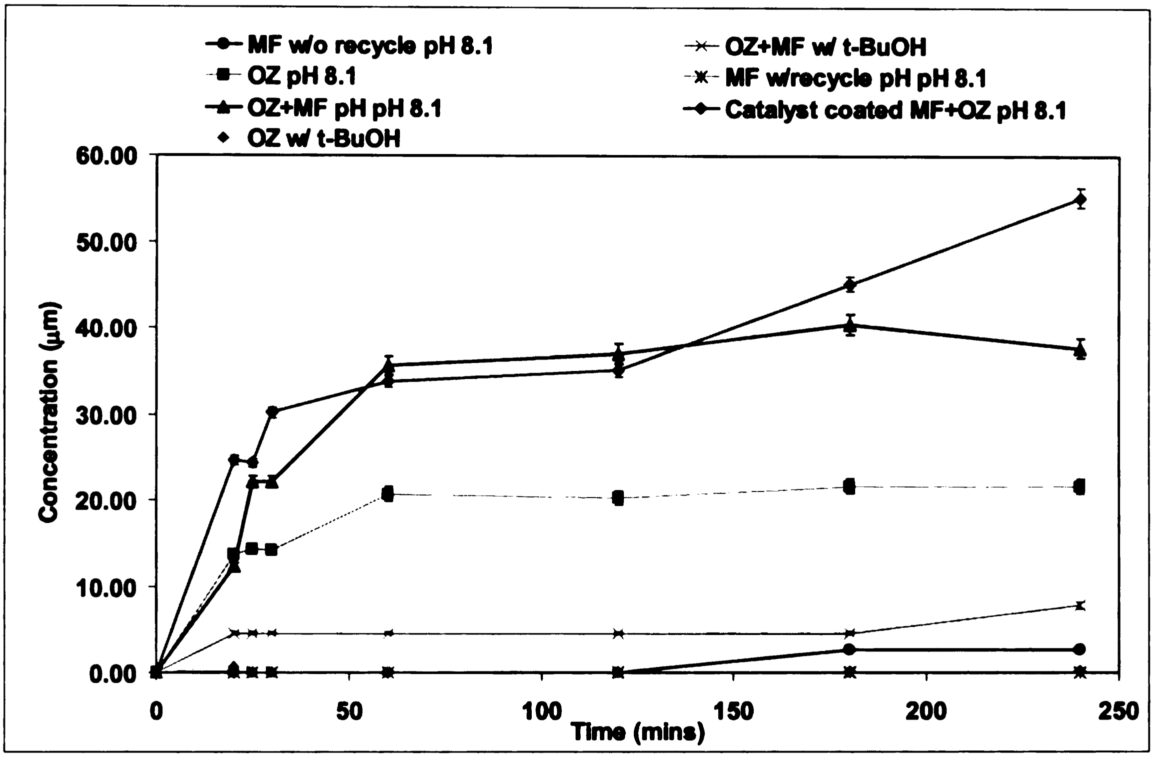


Figure 9.5 Formation of byproducts at pH 8 with different treatment process
Experimental Setup: Fig 9.1, Operating Conditions: Table 9.1, pH 7.0-8.1
Membrane filtration (MF), Ozonation (OZ), Ozone-Membrane filtration (MF+OZ), Iron oxide catalyst coated membrane filtration combined with ozonation (Catalyst coated MF+OZ)

From Figure 9.5, we can see there is a significant decrease in SA byproducts formed from membrane filtration alone with or without recycle than with ozonation where we have reported. With the hybrid process with uncoated/unsintered or coated/sintered membranes the concentration of SA byproducts increased to ~ 40 µM and ~ 55 µM, respectively compared to ~21. µM with ozonation.

GC-MS analysis verified the identity of the SA byproducts as 2,3–DHBA and 2,5–DHBA. There was no evidence of any catechol formed in the process. The concentrations of these compounds were verified with HPLC and indeed coincided with the results of GC-MS. There was no evidence of 2,5–DHBA in any of the experiments except for the hybrid process and the concentration was detected only after two hours of experiment, making 2,3–DHBA the most dominant byproduct obtained in this study. Figure 9.6a shows the total ion chromatogram obtained from the feed water, containing SA acid. Figures 9.6b and 9.6c show the results of the permeate analysis after treatment with the ozonation-membrane filtration and ozonation-iron oxide coated membrane filtration. There are clear peaks of SA marked as 457, 2, 3-DHBA marked as 625 and 2, 5-DHBA marked as 649. The mass spectra (Figure 9.7 a-c) confirm the identity of these compounds. Quantification of these compounds using HPLC analysis confirmed the dominance of 2, 3-DHBA isomer as the major reaction product in the permeate.

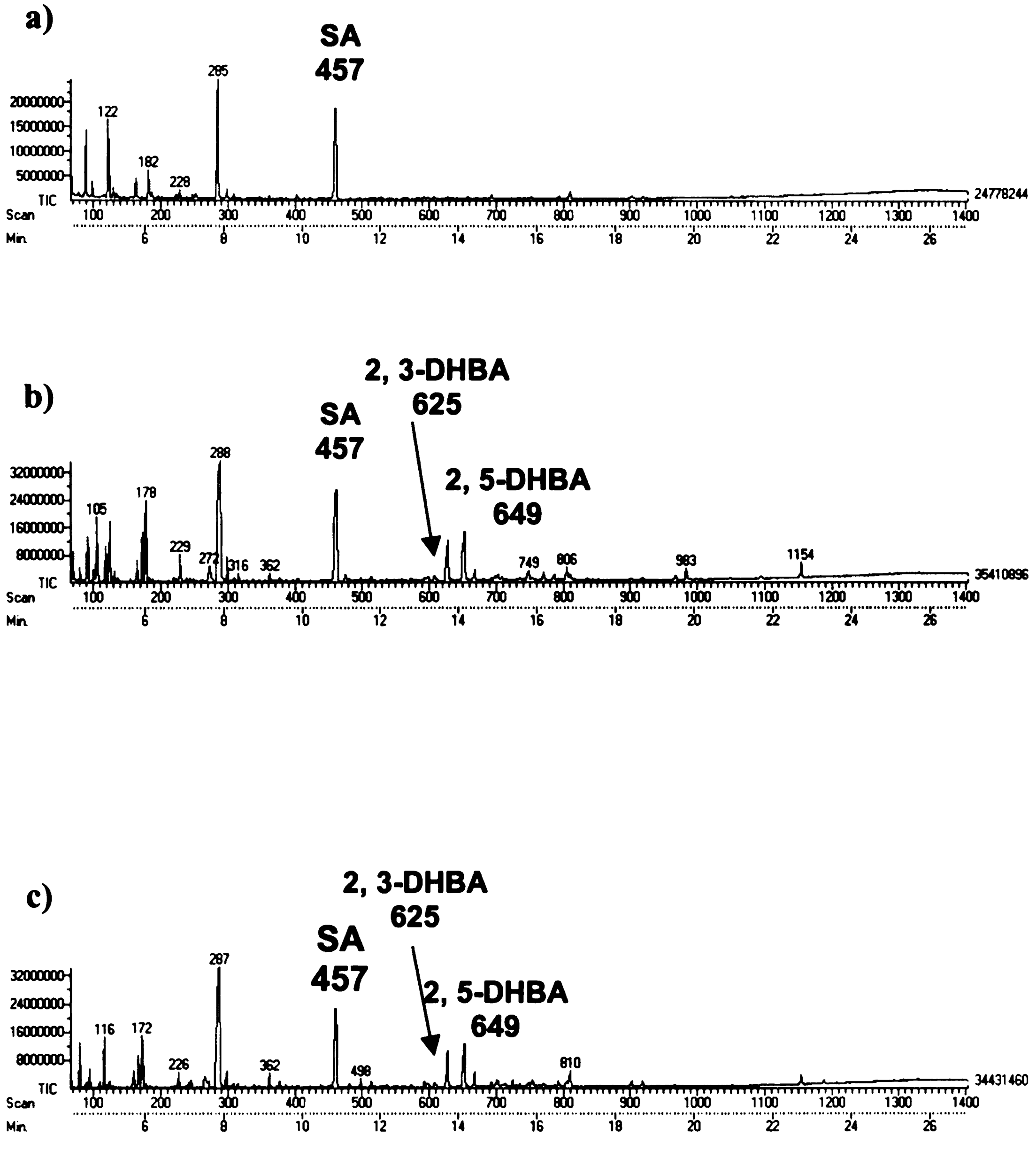
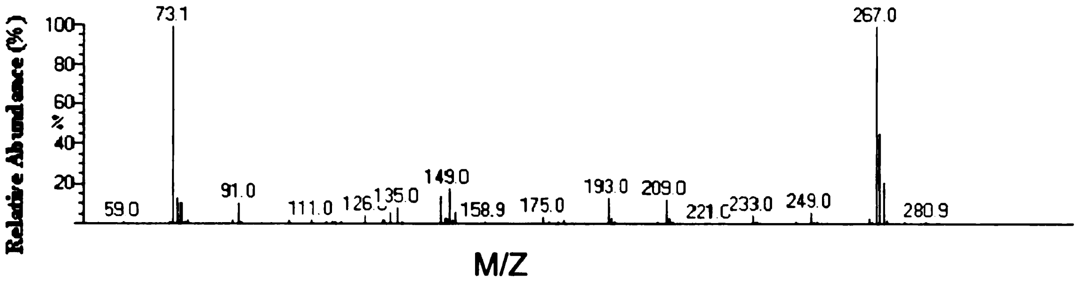


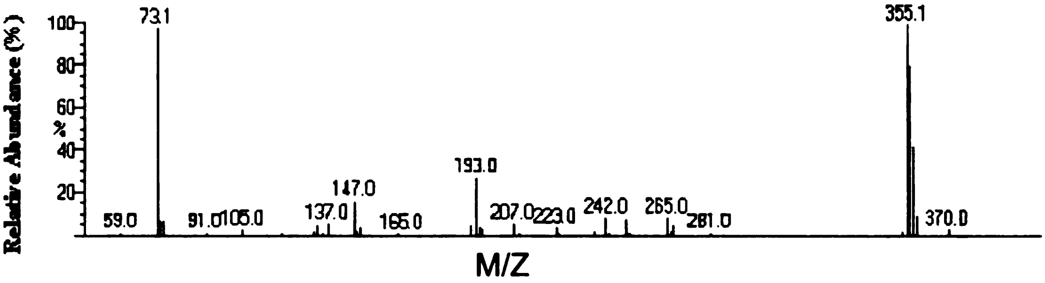
Figure 9.6 Total ion chromatograms (TIC) for Salicylic acid (SA), 2, 3- dihydroxy benzoic acid (2, 3-DHBA), and 2, 5- dihydroxy benzoic acid (2, 5-DHBA) derivatized by BSTFA+ TMCS.

a) TIC obtained from the sample before treatment, b) TIC obtained from the permeate from ozone-membrane filtration process and c) TIC obtained from the permeate from ozone-catalyst coated membrane filtration process

a) Salicylic acid derivative



b) 2,3 DHBA derivative



c) 2,5 DHBA derivative

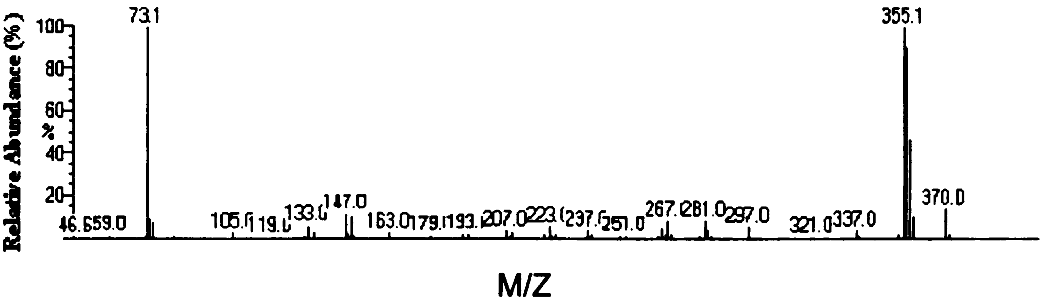


Figure 9.7 Mass spectra (MS) for compounds derivatized by BSTFA+ TMCS.

a) Mass Spectra for Salicylic acid, b) Mass spectra for 2,3-DHBA and c) Mass spectra for 2,5-DHBA

From our results we can suggest that the probable mechanism occurring in the ozone-membrane filtration hybrid process is a heterogeneous phase reaction involving the enhanced removal of SA by the adsorption of SA to the membrane followed by the decomposition of ozone at the membrane surface resulting in the formation of OH radicals which then react with the sorbed SA. It is thought that the active sites on the ceramic membrane surface or the modified surface morphology (pore size, grain size, surface area) and properties (surface charge, hydrophobicity) resulting from coating and sintering (Karnik et al., 2006) accelerates the decomposition of ozone and the reaction of these radicals, thereby promoting the reaction of SA. This could possibly explain the decrease in the dissolved ozone concentration in the treated Lake Lansing water for ozonation alone and the hybrid process with uncoated/unsintered membranes and coated sintered membranes combined with ozonation. The results are tabulated in Table 9.3; we found a decrease in dissolved ozone concentration in hybrid process when compared to ozonation alone. In addition with coated membranes the dissolved ozone concentration decreased more than 40 (± 1.0) % when compared to the uncoated membranes.

Table 9.3
Dissolved ozone concentration in the permeates of Lake Lansing water for different treatment processes.

Treatment Process	**Dissolved ozone concentration (mg/L)**
Ozonation alone	0.15 (± 0.01)
Uncoated-unsintered membrane filtration + ozonation	0.12 (± 0.03)
Coated-sintered membrane filtration + ozonation	0.07 (± 0.01)

The suggested mechanism is depicted in Figure 9.8. When the system is operated in the continuous recirculation operation mode, the dissolved ozone adsorbs on the ceramic membrane surface and rapidly decomposes due to the presence of reactive surface groups. It is known that ozone in gaseous phase rapidly decomposes on metal oxide surface (e.g., Ernst et al., 2004, Acero et al., 1999). The decomposition of ozone is well documented (Bablon et al., 1991). Based on the published mechanisms for the decomposition of ozone, we hypothesize the decomposition of ozone generates active atomic oxygen and reacts with the membrane surface (TiO_2 in case of uncoated membranes and TiO_2-Fe_2O_3 in case of coated ceramic membranes) to produce O_2H^- anions which subsequently react with the dissolved O_3 molecule to generate the ozonide anion (O_3^-) radical. This radical further decomposes to form the hydroxyl radical which can oxidize the SA. However, further investigations are necessary to confirm the oxidation mechanism.

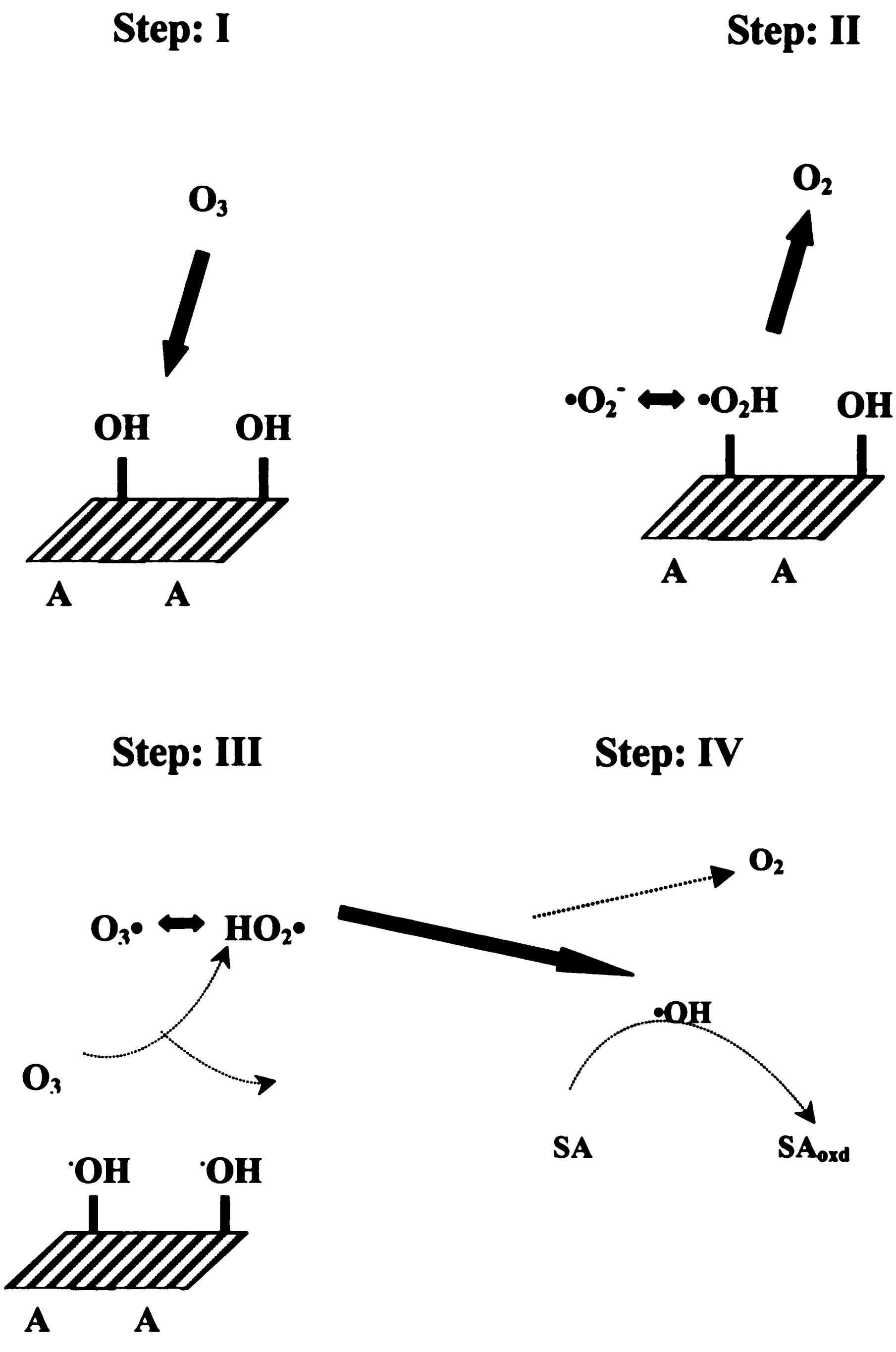


Figure 9.8 Schematic of the suggested mechanism during ozonation membrane filtration hybrid process.

A: is TiO_2 *in case of uncoated/unsintered membranes and is* TiO_2*-*Fe_2O_3 *in case of iron oxide coated sintered membrane.*

9.5 ACKNOWLEDGMENTS

The authors would like to acknowledge the US Environmental Protection Agency (US EPA) Science To Achieve Results (STAR) Program (Grant No. RD830090801) for financial support of this work. We acknowledge Ms. Beverly Chamberlain from the Mass Spectrometry Core of the Research Technology Support Facility, Michigan State University for her assistance in the GC-MS analysis and Mr. Cun Liu from the Department of Crops and Soil Sciences for generously allowing us to use the HPLC facility in his lab. We would also like to thank Mr. David Jackson for his assistance with the membrane coating process.

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CHAPTER TEN

CONCLUSIONS AND RECOMMENDATIONS

10.1 CONCLUSIONS

1. For the experimental setup described in this work increases in gaseous ozone concentration beyond a particular ozone gas concentration (5 g/m^3), had no effect on the level of permeate flux recovery, thus a minimum threshold concentration could achieve complete recovery.
2. The pH of the feed water affected the permeate flux. The improved permeate flux recovery at lower pH is a result of higher dissolved ozone concentration under these conditions, leading to increased ozone reaction with the NOM species that are responsible for fouling.
3. Use of the combined ozonation/filtration treatment system resulted in significant improvements in water quality compared to the filtered raw water and to that using either ozonation or membrane filtration alone.
4. Using a membrane with a 1kD MWCO, the minimum gaseous ozone concentration required to bring about effective NOM degradation and meet regulatory requirements for chlorinated DBPs was 2.5 g/m^3.
5. With iron oxide coated ceramic membrane, the concentration of dissolved organic carbon was reduced by >85% and the concentrations of simulated distribution system total trihalomethanes and simulated distribution system halo acetic acids decreased by up to 90% and 85%, respectively. In addition the concentrations of aldehydes,

ketones, and ketoacids in the permeate were reduced by >50% as compared to that obtained with the uncoated membranes. Also on coating the membranes a 5kD MWCO membrane can produce water quality to meet pertinent regulatory standards.

6. With coating and sintering the membrane surface there is an evidence of change in surface morphology, which leads to changes in the surface properties, like changes in pore size, roughness, grain size which subsequently led to improvement in surface properties of the membrane which enhanced the catalytic reactions on the membrane surface thereby leading to improvements in water quality.
7. With coating and sintering the membranes led to modification in surface morphology which accelerated decomposition of ozone on the membrane surface and reaction of radicals formed as a result of this decomposition, this was demonstrated by decrease in dissolved ozone concentration for the permeates of coated-sintered membranes when compared to the uncoated-unsintered membranes.
8. Surface characterization demonstrated beyond 40 coats of iron oxide on the membrane there is no evidence of significant decrease in surface roughness, or increase in the thickness of the catalyst coating, make the 40 coats the optimum.
9. Diffusion and capillary action during the coating process not only leads to uniform coating on the membrane surface but also results in distribution of iron oxide nanoparticles into the membrane surface.
10. The catalyst coated membrane filtration results in greater 7 log removal for bacteria, and also reduces the risk of potential regrowth of bacteria in the distribution system after treatment.

11. The changes in the surface properties of the membrane degrade the ozone on the membrane surface and accelerate the hydroxyl radical reactions which further degrade organic compounds on the membrane surface consequently reducing the extent the membrane fouling, maintain stable permeate fluxes and giving improved performance in terms of water quality to meeting US-EPA regulatory standards for drinking water.

10.2 RECOMMENDATIONS FOR FUTURE RESEARCH

1. The current system was operated at low transmembrane pressure, thus it is necessary to upgrade the ozone nanoceramic system to high pressure system and evaluate its performance in terms of permeate flux, water quality and membrane fouling if present.
2. The system should be scaled to pilot-scale to evaluate the performance of the ozonation nano ceramic membrane filtration system. The study should be carried out to evaluate the performance by varying operating parameters like higher flow rates, higher pressures, temperatures and ozone dosage.
3. Ceramic membranes coatings tested in this work were commercially available and TiO_2 membranes coated with iron oxide nano particles. Different metal oxide coatings like MnO_2 and ZrO_2 should be investigated to determine their effect on the treated water quality.
4. The economic analysis and feasibility studies need to be conducted to investigate application of this system as an option to conventional treatment methods for drinking water.

5. Further studies should be done to investigate the mechanism involved in catalytic oxidation.
6. The experiments should be carried out with different coating and sintering conditions for different metal oxide coatings. Specifically effort could be directed to investigate how porosity, average grain sizes and microstructure of the coating affect the performance of the membranes. If there is a possibility of microcracking with different coating materials that could possibly affect the performance of the system.
7. This work found increased removal of ozonation by-products with increase in the number of coatings; however there was no enhanced removal of disinfection by-products with increase in number of coatings, a study is required to investigate this different removal efficiency with different number of coats.
8. The surface charge of the membrane affects the performance of the membrane in terms of catalytic reactions and membrane fouling. A study should be carried out to modify the surface charge and surface properties and evaluate the performance of the system to these conditions.
9. The Lake Lansing water contains low bromide concentration. As bromide not only reacts with ozone and forms bromate, but also affects the formation of other DBPs, it is important to investigate the applicability of this system on waters containing high bromide concentrations.
10. A study should be carried out to investigate the efficiency of the system for the control and removal of existing or potential contaminants having an effect on human health and environment.

APPENDIX A

The Supporting Information section consists of five pages, including eight figures showing water quality data for permeate 1 showing effect on number of coatings on the permeate of 15 kD and 5kD molecular weight cut off membranes, the effect of sintering at two different temperatures on the permeate water quality.

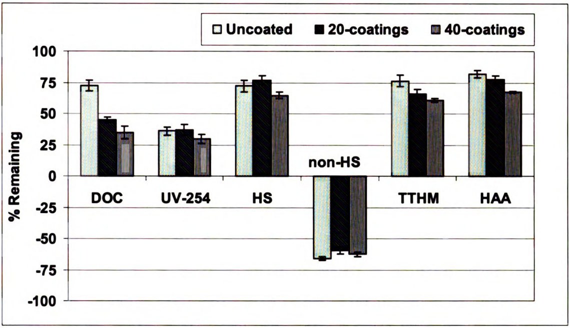

Fig.A1 Effect of the number of catalyst coatings on the water quality of P1
*Experimental setup: Fig. 5.2. Operating Conditions: Table 1. Membrane Size: 15 kD, 20 or 40 layers, oven baked at 500°C. *All values are averages of triplicates within experiments.*

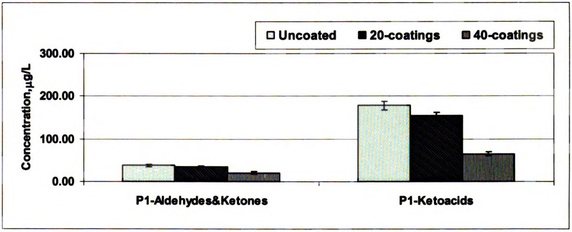

Fig.A2 Effect of the number of catalyst coatings on the concentrations of ozonation by-products in the permeate P1
*Experimental setup: Fig. 5.2. Operating Conditions: Table 1. Membrane Size: 15 kD, 20 or 40 layers, oven baked at 500°C. *All values are average of triplicates within experiments.*

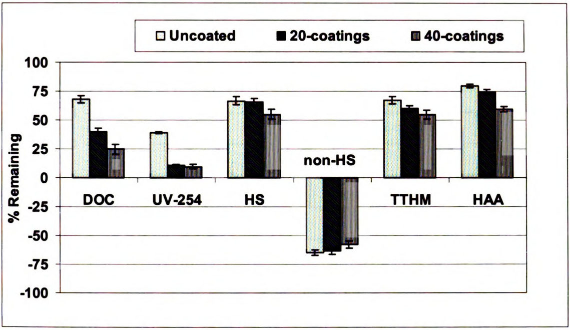

Fig.A3 Effect of the number of catalyst coatings on the water quality of P1
*Experimental setup: Fig. 5.2. Operating Conditions: Table 1. Membrane Size: 5 kD, 20 or 40 layers, oven baked at 500°C. *All values are averages of triplicates within experiments.*

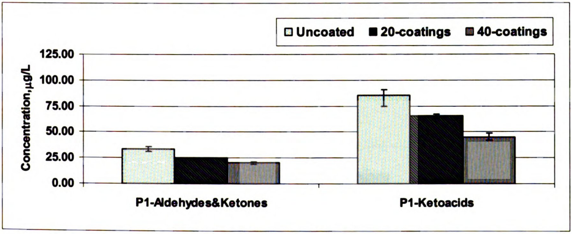

Fig.A4 Effect of the number of catalyst coatings on the concentrations of ozonation by-products in the permeate P1
*Experimental setup: Fig. 5.2. Operating Conditions: Table 1. Membrane Size: 5 kD, 20 and 40 layers, oven baked at 500°C. *All values are average of triplicates within experiments.*

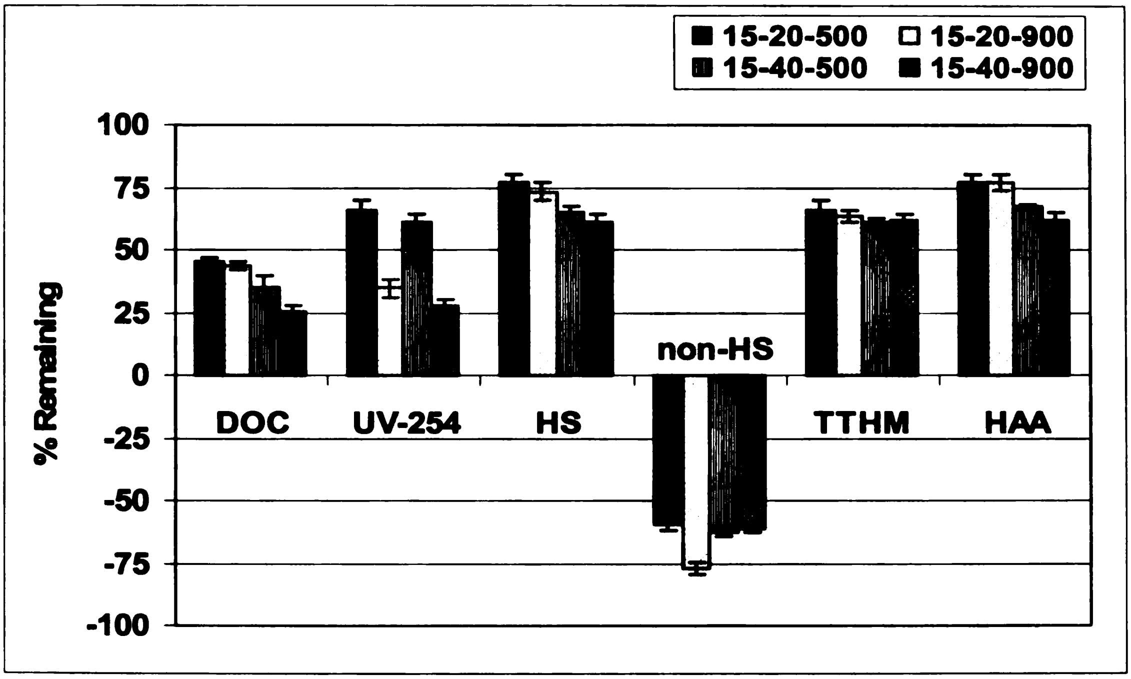

Fig.A5Water quality for P1 for two different sintering temperatures *Experimental setup: Fig. 5.2. Operating Conditions: Table 1. Membrane Size: 15 kD, 20 or 40 coatings, oven-baked at 500°C or sintered at 900°C. *All values are average of triplicates within experiments. Explanation of the legend is described in the caption of Fig.1*

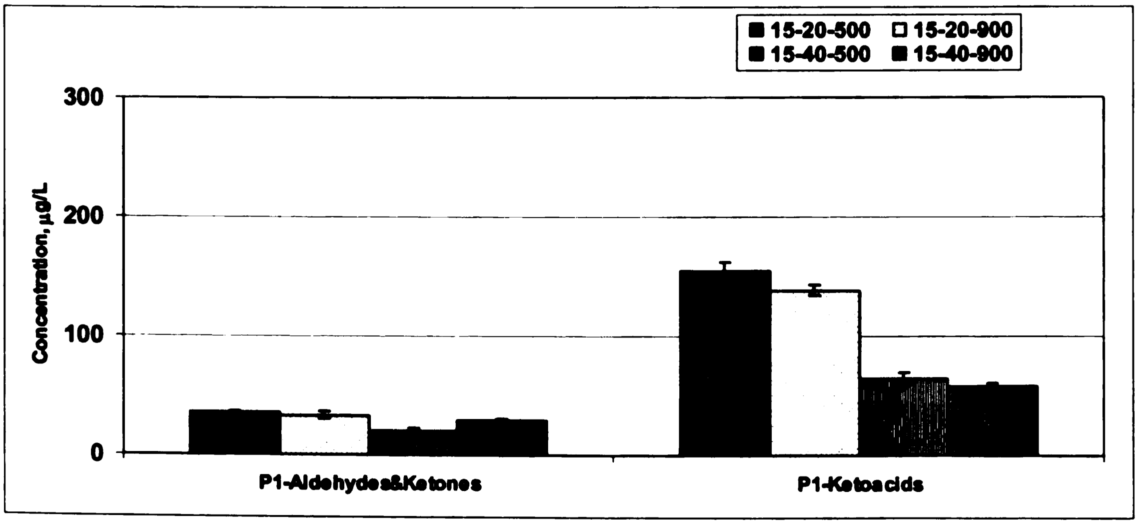

Fig.A6 Concentrations of ozonation by-products in P1 for two different sintering temperatures

*Experimental setup: Fig. 5.2. Operating Conditions: Table 2. Membrane Size: 15 kD, 20 or 40 coatings, oven-baked at 500°C or sintered at 900°C. *All values are average of triplicates within experiments. Explanation of the legend is described in the caption of Fig.1*

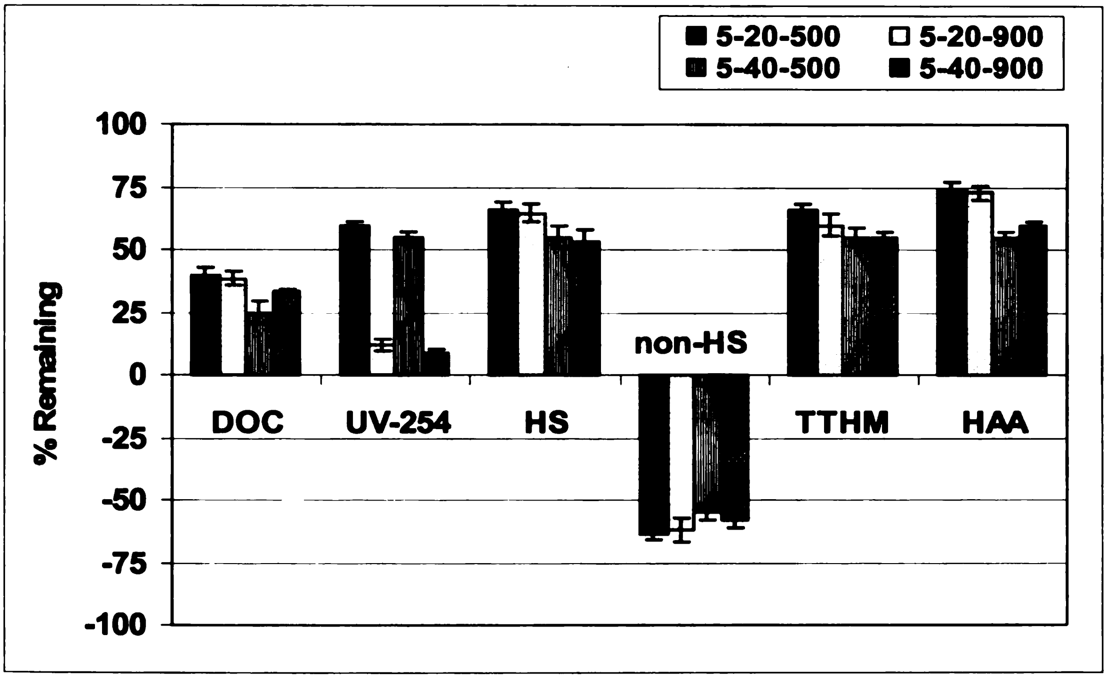

Fig.A7 Water quality for P1 for two different sintering temperatures

*Experimental setup: Fig. 5.2. Operating Conditions: Table 1. Membrane Size: 5 kD, 20 or 40 layers, oven-baked at 500°C or sintered at 900°C. * All values are average of triplicates within experiments. Explanation of the legend is described in the caption of Fig.1*

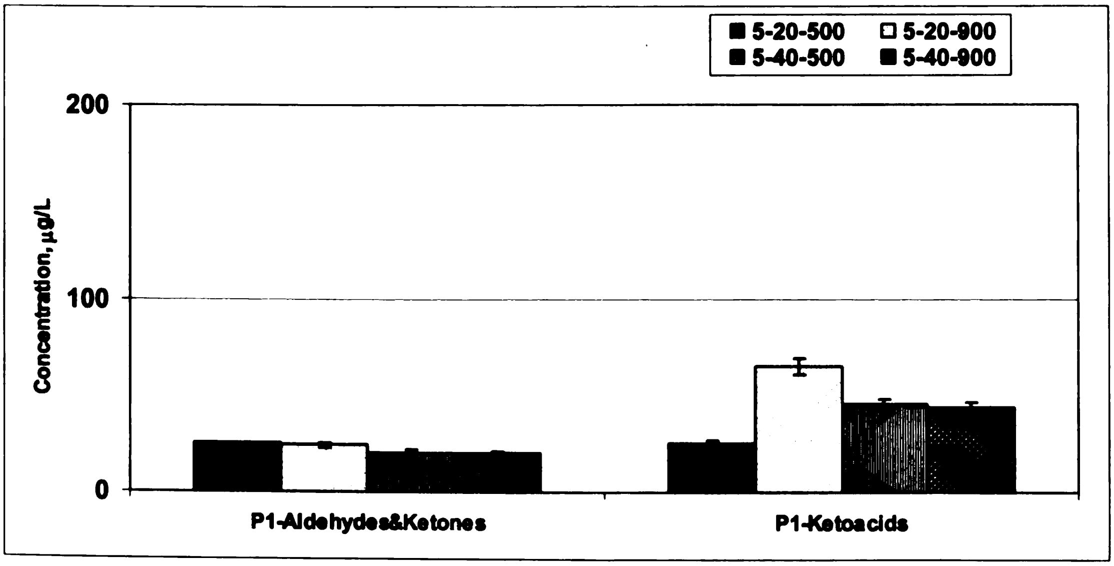

Fig.A8 Concentrations of ozonation by-products in P1 for two different sintering temperatures

*Experimental setup: Fig. 5.2. Operating Conditions: Table 1. Membrane Size: 5 kD, 20 or 40 layers, oven-baked at 500°C or sintered at 900°C. *All values are average of triplicates within experiments Explanation of the legend is described in the caption of Fig.1*