The effect of ozone on ceramic membranes for application to secondary treated effluent

By

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To my wife, Rabita
for her kindness and love, and
for her endless support and encouragement
Abstract

As the global warming and population growth in urbanized areas lead to pressures on the accessibility of potable water resources, water recycling is regarded as one of the most viable solutions in Australia and overseas. Recycling wastewater can help in relieving the demand on existing high quality potable water supplies while at the same time protecting remaining water sources from contamination. Among the different wastewater treatment processes to raise wastewater quality to a suitable standard for recycling, membrane filtration has become a common operation due to its ability to provide high quality water at high efficiency. Despite the wide spread application of membranes made of polymeric materials, membranes made instead from ceramic materials can be operated with lower maintenance and operational requirements because of their stronger mechanical structure, superior chemical durability and better physical strength. In practice, these translate to their ability to be operated under high temperature, pressure and pH condition without concern for compaction, delamination, damage or swelling of the membrane. Such benefits are known to offset the higher material cost of ceramics, but are also useful in water recycling where the membrane functions as a reliable barrier to water-borne pathogens. Meanwhile, the material robustness enables ceramic membranes to be operated in combination with more effective pretreatment options like ozonation.

However, in combining ozonation with ceramic membrane filtration (CMF), several additional advantages have been found over the usual individual functions. In the combined ozone-ceramic membrane system, membrane fouling is reduced significantly, resulting in significantly higher permeate flux across the membrane which plays a key role in plant capital cost reduction. The flux enhancement of ceramic membrane by ozone pre-treatment is hypothesized to be due to the decomposition of ozone to hydroxyl (·OH) or other radicals at the membrane surface which are powerful oxidants to organic membrane fouling material. This understanding is based on numerous studies on similar materials to those which make ceramic membranes (i.e., metal oxides), which show ozone decay and ·OH radical formation. However, the formation of ·OH radicals on commercially available ceramic membranes, and its significance under typical membrane operating conditions, has
not been investigated and the effect remains unconfirmed. This thesis therefore focuses primarily on the behavior of ozone through ceramic membranes, and the formation of \( ^{\cdot}\text{OH} \) radicals under practical operation conditions and in the presence of wastewater or its components (organic and mineral).

The thesis also studied the effect of a process that is often followed from ozone treatment, biological activated carbon (BAC), as a pretreatment in combination with ozonation prior to CMF using real secondary effluent (RSE). The effect on ceramic membrane fouling when fed with wastewater treated first by ozone and BAC has been analyzed using unified membrane fouling index (UMFI). Ozone alone was found to be the most effective pretreatment for ceramic membrane performance than the BAC and combined ozone-BAC pretreatment. This finding shows that if BAC was to be applied with ozone in this case, it should follow CMF.

In investigating the components in wastewater that foul ceramic membranes and control flux, it was found that the higher molecular weight (MW) biopolymers and low MW humic substances (HS) in RSE are captured and accumulate on the ceramic membrane. Their role in membrane flux resistance was investigated using 0.1 µm cellulose membrane discs with either raw or ozone treated RSE. The captured solids after ozone treatment were found to be weaker in structure and showed cracking under SEM analysis. Rising permeability with increasing pressure observed from stepped permeability testing indicated the possibility that some of the fouling material broken down by ozone may be able to penetrate the membrane pores with increased pressure, opening the fouling layer to enable higher flux. This investigation provided evidence that the bulk reaction with ozone on the organic matter accumulated on the membrane could be responsible for the high flux effect. However the significance of \( ^{\cdot}\text{OH} \) radicals was confirmed later in the study.

In order to investigate the role of the ceramic membrane properties in high flux, the membrane’s physical characteristics (pore size, porosity, and thickness of the filtration layer) were measured. The flow of water through a 100 nm and a 200 nm ceramic membrane was then investigated under different salinity, temperature and pH range. With these properties, the experimental permeability followed the Hagen-Poiseuille model under
different NaCl concentration and temperature. The permeability decreased slightly (6%) with increasing salt concentration (0.5 g/L to 30 g/L) and increased gradually (225%) with increasing temperature (0°C to 50°C). However, at a salt concentration below 0.5 g/L the permeability has shown to be decreased possibly due to the electro-viscous effect. The effect of pH on permeability (pH 2 to pH 10) was observed to be insignificant. This investigation showed that these changes in basic properties of water can alter flux, but only in a major way with temperature. However under typical operating conditions, these effects are minor and changes from the fouling effect is the most significant contributor to the well-known high flux effect.

The next stage was to investigate the reaction of ozone with the individual and combined components (organics and minerals) of synthetic secondary effluent (SSE). The decay of ozone after 10 minutes of ozone dosing in the presence of SSE has shown a rapid reaction phase of and a comparatively slower ozone decay phase. However, the organics on their own did not show any effect in the decomposition of ozone after 10 minutes of dosing. This was attributed to the consumption of ozone by very fast initial reactions between organics and ozone. The minerals however, have shown to fit a first order kinetic model after 10 minutes of ozone exposure. In order to explore the role of ozone in the presence of ceramic membrane materials, the decomposition of ozone in the presence of common ceramic membrane materials Al₂O₃, TiO₂ and SiC has been investigated. TiO₂ powders have shown significantly stronger catalytic effect on the decomposition ozone where the common Al₂O₃ membrane substrate material has shown only a slight effect. The SiC powders have shown even lower effect than the Al₂O₃. The catalytic degradation of ozone by ceramic materials to 'OH radicals was studied using para-chlorobenzoic acid (pCBA) as a probe for 'OH formation. The formation of 'OH radicals has been quantified by the calculation of the $R_{ct}$ value. The higher $R_{ct}$ value observed for the TiO₂ powders indicated higher formation of 'OH radicals, hence higher catalytic effect. This would be expected from the TiO₂ used, being a commercially available nanoparticle catalyst (Degussa P25) with a high catalytically enhanced anatase phase. However, very slight catalytic effect was observed for the Al₂O₃ powders, a material widely used in the manufacturing of ceramic membranes. At this point in the study, it appeared that if 'OH radicals can form as a result of combining
ozone with ceramic membranes; it would not be a major contributor to ozone demand compared to other components in wastewater.

To confirm the ozone decay and \(^{\cdot}\)OH radical formation potential on actual membranes, the decomposition of ozone in the presence of separate components (organics and minerals) of SSE and the full composition of SSE was analyzed on two commercially available membranes, where one is well known for application to water treatment practice (Metawater). Ozone concentration consistently dropped across the ceramic membranes when total pressure drop was high (27 kPa), while did not show consistent decay at low total pressure drop (6.5 kPa). Since it was already confirmed that ozone decay in ceramic membrane materials was not significant, the rapid decay observed at higher pressures was instead attributed to a depressurizing effect of the ozonized solution (ozone degassing). Investigating \(^{\cdot}\)OH radical formation of water filtered through the membrane showed only a very small amount, particularly during the first minutes of ozone exposure or at a higher applied ozone dosage. Despite the slight catalytic activities measured, bromate (a well-known toxic byproduct of ozone use in waters containing bromide) formation was greatly reduced as a result of permeating through the membrane. This was attributed to the suppression of the oxidation of Br\(^{-}\) and \(\text{HOBr/BrO}^{\cdot}\) to \(\text{BrO}_3^{-}\) due to the decomposition of ozone and possible very slight enhancement of \(^{\cdot}\)OH radicals.

This study has therefore revealed key findings in the synergistic merger of ozone with ceramic membranes. The contributions to industry include demonstrating uniquely that ozone prior to ceramic membranes (and not applying BAC prior to ceramic membranes) contributes to reduced membrane fouling and higher flux performance potential. Also, the results obtained from the permeability of ceramic membrane under simple water conditions showed effects that are related to these conditions, while the remaining changes would be due to the more complex effects from the wastewater component matrix. The contribution to science from this investigation include, identifying the major foulants (\(i.e.,\) high MW biopolymers and low MW HS) of ceramic MF membrane during filtration of secondary effluent. The effect of ozone on the properties of the cake fouling layer revealed that, ozone creates a weaker cake fouling layer structure by breaking down higher MW components into smaller particles. The smaller particles appeared to be forced through the MF
membrane pores resulting in higher permeate flux by ozonized solution. When filtering a very low salt concentration (< 0.0005 g/L (0.5 mg/L)) of solution, the pores of the ceramic MF membrane can also be affected by the electro-viscous effect, resulting in decrease in the permeability with reducing salinity. The Metawater ceramic membrane has shown very slight catalytic effect to decompose ozone in the presence of organic molecules. The effect is stronger during the first minute of ozone exposure or with higher initial ozone residual concentrations. However, degassing of ozone may also reduce the residual ozone concentration across the ceramic membrane. Bromate formation during the ozonation of bromide containing water can be reduced when ozone and ceramic membrane are used in combination. The reduction in the bromate formation is attributed to the degassing of ozone through ceramic membrane resulting in reduction in residual ozone concentration across the membrane.

Future works require pilot scale analysis of the ozone-BAC-CMF test in order to obtain scalable and reproducible data during longer filtration operation. More detailed analysis of the RSE can be done by liquid chromatography-organic carbon detection (LC-OCD) technique to quantify the DOC and separate them into biopolymers, HS, building blocks, low MW acids and low MW neutrals. As the conventional pore size measurement methods (i.e., gas permeation and porometry) are not suitable for ceramic membranes, future work is also suggested to develop a more rapid approach which can provide accurate pore sizes of the membrane. The ceramic membrane has shown very slight catalytic activity in ozone decomposition. However, combined ozone and coagulation prior to ceramic membrane have already been applied in industry to achieve high flux. Therefore, further work is needed to develop a fouling model for the combined ozonation and coagulation prior to ceramic membrane. The model could be developed based on the interaction forces between the fouling particles and a membrane surface which will be obtained by measuring the surface tensions of fouling particles and zeta-potential data of the ceramic membrane.
Declaration

“I, Khaled Ibn Abdul Hamid, declare that the PhD thesis entitled ‘The effect of ozone on ceramic membranes for application to secondary treated effluent’ is no more than 100,000 words in length including quotes and exclusive of tables, figures, appendices, bibliography, references and footnotes. This thesis contains no material that has been submitted previously, in whole or in part, for the award of any other academic degree or diploma. Except where otherwise indicated, this thesis is my own work”.

Signature: Date: 3rd January 2017
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3rd January 2017
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<th>Full Form</th>
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<tbody>
<tr>
<td>AER</td>
<td>Anion exchange resin</td>
</tr>
<tr>
<td>AMWD</td>
<td>Apparent molecular weight distribution</td>
</tr>
<tr>
<td>ATR-FTIR</td>
<td>Attenuated total reflection-Fourier transform infrared</td>
</tr>
<tr>
<td>BAC</td>
<td>Biological activated carbon</td>
</tr>
<tr>
<td>BDOC</td>
<td>Biodegradable dissolved organic carbon</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer–Emmett–Teller</td>
</tr>
<tr>
<td>BJH</td>
<td>Barrett–Joyner–Halenda</td>
</tr>
<tr>
<td>BOD</td>
<td>Biological oxygen demand</td>
</tr>
<tr>
<td>C–C</td>
<td>Carbon-carbon</td>
</tr>
<tr>
<td>CEB</td>
<td>Chemically enhanced backwash</td>
</tr>
<tr>
<td>CFV</td>
<td>Cross flow velocity</td>
</tr>
<tr>
<td>CHA</td>
<td>hydrophilic charged</td>
</tr>
<tr>
<td>CIP</td>
<td>Cleaning in place</td>
</tr>
<tr>
<td>CMF</td>
<td>Ceramic membrane filtration</td>
</tr>
<tr>
<td>CN</td>
<td>Cellulose nitrate</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical oxygen demand</td>
</tr>
<tr>
<td>D</td>
<td>Dialysis</td>
</tr>
<tr>
<td>DI</td>
<td>De-ionized</td>
</tr>
<tr>
<td>DOC</td>
<td>Dissolved organic carbon</td>
</tr>
<tr>
<td>DOM</td>
<td>Dissolved organic matter</td>
</tr>
<tr>
<td>EBCT</td>
<td>Empty bed contact time</td>
</tr>
<tr>
<td>ED</td>
<td>Electro-dialysis</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>EEM</td>
<td>Excitation-emission matrix</td>
</tr>
<tr>
<td>Em</td>
<td>Emission</td>
</tr>
<tr>
<td>EU</td>
<td>European Union</td>
</tr>
<tr>
<td>Ex</td>
<td>Excitation</td>
</tr>
<tr>
<td>FBP</td>
<td>First bubble point</td>
</tr>
<tr>
<td>HAA</td>
<td>Halo acetic acid</td>
</tr>
<tr>
<td>HP</td>
<td>Hagen Poiseuille</td>
</tr>
<tr>
<td>HPLC-SEC</td>
<td>High performance liquid chromatography – size exclusion chromatography</td>
</tr>
<tr>
<td>HPSEC</td>
<td>High performance size exclusion chromatography</td>
</tr>
<tr>
<td>ICP</td>
<td>Inductively Coupled Plasma</td>
</tr>
<tr>
<td>IEP</td>
<td>Iso-electric point</td>
</tr>
<tr>
<td>LC</td>
<td>Liquid Chromatography</td>
</tr>
<tr>
<td>LOD</td>
<td>Limit of detection</td>
</tr>
<tr>
<td>MC</td>
<td>Membrane contactors</td>
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<tr>
<td>MD</td>
<td>Membrane distillation</td>
</tr>
<tr>
<td>MF</td>
<td>Microfiltration</td>
</tr>
<tr>
<td>MFI</td>
<td>Membrane fouling index</td>
</tr>
<tr>
<td>MFP</td>
<td>Mean flow pore</td>
</tr>
<tr>
<td>MW</td>
<td>Molecular weight</td>
</tr>
<tr>
<td>MWCO</td>
<td>Molecular weight cut-off</td>
</tr>
<tr>
<td>NEU</td>
<td>Hydrophilic neutral</td>
</tr>
<tr>
<td>NF</td>
<td>Nano-filtration</td>
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<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>NOM</td>
<td>Natural organic matter</td>
</tr>
<tr>
<td>OM</td>
<td>Organic matter</td>
</tr>
<tr>
<td>PAC</td>
<td>Powdered activated carbon</td>
</tr>
<tr>
<td>pCBA</td>
<td>Para-chlorobenzoic acid</td>
</tr>
<tr>
<td>PDA</td>
<td>Photodiode array detector</td>
</tr>
<tr>
<td>PP</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>PVDF</td>
<td>Polyvinylidenefluoride</td>
</tr>
<tr>
<td>RO</td>
<td>Reverse osmosis</td>
</tr>
<tr>
<td>RSE</td>
<td>Real secondary effluent</td>
</tr>
<tr>
<td>SDI</td>
<td>Silt density index</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>SHA</td>
<td>Slightly hydrophobic acids</td>
</tr>
<tr>
<td>SP</td>
<td>Smallest pore</td>
</tr>
<tr>
<td>SSE</td>
<td>Synthetic secondary effluent</td>
</tr>
<tr>
<td>SUVA</td>
<td>Specific ultra-violete absorbance</td>
</tr>
<tr>
<td>TDS</td>
<td>Total dissolved solid</td>
</tr>
<tr>
<td>TMP</td>
<td>Trans-membrane pressure</td>
</tr>
<tr>
<td>TOC</td>
<td>Total organic carbon</td>
</tr>
<tr>
<td>TrOC</td>
<td>Trace organic chemical</td>
</tr>
<tr>
<td>UF</td>
<td>Ultrafiltration</td>
</tr>
<tr>
<td>UK</td>
<td>United Kingdom</td>
</tr>
<tr>
<td>UMFI</td>
<td>Unified membrane fouling index (m2/L)</td>
</tr>
</tbody>
</table>
UMFI_C  Chemically irreversible fouling potential
UMFI_I  Hydraulically irreversible fouling potential
UMFI_R  Reversible fouling potential
UMFI_T  Total fouling index
USEPA   United States Environmental Protection Agency
UV      Ultra violate
VHA     Hydrophobic acids
WHO     World Health Organization
WTP     Melbourne water western treatment plant
### List of symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>( \cdot {\text{OH}} )</td>
<td>Hydroxyl radical</td>
</tr>
<tr>
<td>( R_{ct} )</td>
<td>The ratio of hydroxyl radical exposure vs. ozone exposure</td>
</tr>
<tr>
<td>( \text{UVA}_{254} )</td>
<td>Ultra violate absorbance at 254 nm wavelength</td>
</tr>
<tr>
<td>( R(\phi) )</td>
<td>Hindered settling function</td>
</tr>
<tr>
<td>( \text{Da} )</td>
<td>Dalton</td>
</tr>
<tr>
<td>( j )</td>
<td>Flux (L/m(^2)·h)</td>
</tr>
<tr>
<td>( \Delta P )</td>
<td>Pressure drop (Pa)</td>
</tr>
<tr>
<td>( d_m )</td>
<td>Pore size (m)</td>
</tr>
<tr>
<td>( \varepsilon )</td>
<td>Porosity</td>
</tr>
<tr>
<td>( \mu )</td>
<td>The dynamic viscosity (N·s/m(^2))</td>
</tr>
<tr>
<td>( \tau )</td>
<td>Tortuosity</td>
</tr>
<tr>
<td>( L )</td>
<td>Thickness of the membrane material (m)</td>
</tr>
<tr>
<td>( j/\Delta P )</td>
<td>Permeability (L/m(^2)·h·kPa)</td>
</tr>
<tr>
<td>( P_s(\phi) )</td>
<td>Compressive yield stress</td>
</tr>
<tr>
<td>( \phi_r )</td>
<td>Gel point</td>
</tr>
<tr>
<td>( \phi )</td>
<td>Solids volume fraction</td>
</tr>
<tr>
<td>( V )</td>
<td>Volume (m(^3))</td>
</tr>
<tr>
<td>( t )</td>
<td>Time (s)</td>
</tr>
<tr>
<td>( \phi_f )</td>
<td>Equilibrium volume fraction at certain pressure</td>
</tr>
<tr>
<td>( \beta^2 )</td>
<td>Filtration parameter (m(^2)/s)</td>
</tr>
<tr>
<td>( \phi_0 )</td>
<td>Initial solid volume fraction</td>
</tr>
<tr>
<td>( P )</td>
<td>Pressure (Pa)</td>
</tr>
</tbody>
</table>
$V_s$ Specific permeate volume (L/m²)

$J_s$ Normalized specific flux

$OM_d$ Component of organic matter that may consume ozone by a direct reaction

$OM_i$ Component of organic matter that may act as initiator of the hydroxyl radical chain reaction

$OM_p$ Component of organic matter that may act as promoter of the hydroxyl radical chain reaction

$OM_s$ Component of organic matter that may act as inhibitor of the hydroxyl radical chain reaction

$k$ First order reaction rate constant (s⁻¹)

$C$ Concentration

$pH_{PZC}$ The pH at which the net surface charge is zero

$N_{K-P}$ Steady-state gas permeation flux (kmol⋅m⁻²⋅s⁻¹)

$r$ Pore radius of the membrane (m)

$R$ Gas constant (8.314 J⋅mol⁻¹⋅K⁻¹)

$M$ Molar mass (kg/mol)

$T$ Temperature (K)

$\eta$ Kinematic viscosity (Pa⋅s)

$P_m$ Average pressure within the membrane pores (Pa)

$J_{K-P}$ Gas permeability (kmol⋅m⁻²⋅s⁻¹⋅Pa⁻¹)

$A_0$ Gas permeation parameter

$B_0$ Gas permeation parameter

$\gamma$ Surface tension of liquid

$D$ Pore diameter (m)

XXX
$\theta$ Contact angle

$W_1$ Weight of dry membrane (g)

$W_2$ Weight of wet membrane (g)

$\rho$ Density (kg/m$^3$)

$V_V$ Volume of void (m$^3$)

$V_T$ Total volume (m$^3$)

$P_{T=20}$ Pressure at 20°C (Pa)

$P_{abs}$ Absolute pressure (Pa)

$\mu_{T=20}$ Viscosity of water at 20°C (N·s/m$^2$)

$\mu_T$ Viscosity of water at temperature $T$ (N·s/m$^2$)

$R_j$ Rejection (%)

$C_{perm}$ Concentration in the permeate (mg/L)

$C_{reject}$ Concentration in the reject (mg/L)

$\Delta P_{f(gas)}$ Pressure drop across the filtration layer of the membrane during gas flow (Pa)

$d_{mf}$ Average pore size of the filtration layer (m)

$L_f$ Thickness of the filtration layer (m)

$\mu_N$ Dynamic viscosity of nitrogen gas used in the gas permeability test (N·s/m$^2$)

$j_N$ Gas permeate flux (m/s)

$\Delta P_{t(gas)}$ Total pressure drop (Pa)

$\Delta P_{s(gas)}$ Pressure drop across the support layer of the membrane during nitrogen gas flow (Pa)

$d_{bulk}$ Bulk pore diameter

$\mu_a$ Apparent viscosity (N·s/m$^2$)
\( \zeta \)  
Zeta potential

\( \kappa \)  
Debye constant (m\(^{-1}\))

\( 1/\kappa \)  
Debye length (m)

\( \beta \)  
Dimensionless parameter describing the properties of the electrolyte

\( G \)  
Ratio of mean electrostatic potential across the capillary to the zeta potential

\( F \)  
Electric field strength

\( A \)  
Conductivity (\( \Omega^{-1} \) cm\(^2\) mol\(^{-1}\))

\( I \)  
Ionic strength (mole/m\(^3\))

\( \varepsilon_0 \)  
Permittivity of free space (F/m)

\( \varepsilon_r \)  
Dielectric constant

\( k_B \)  
Boltzmann’s constant (1.381 \( \times \) 10\(^{-23}\) JK\(^{-1}\))

\( N_A \)  
Avogadro’s number (6.022 \( \times \) 10\(^{23}\) mol\(^{-1}\))

\( e \)  
Elementary charge (Q)

\( k \)  
Reaction rate constant (s\(^{-1}\))

\( k_{Tot} \)  
Total ozone decomposition rate (s\(^{-1}\))

\( k_B \)  
First order reaction rate constants of ozone inside the beaker (s\(^{-1}\))

\( k_{Mem} \)  
First order reaction rate constants of ozone inside the membrane (s\(^{-1}\))

\( k_{Mod} \)  
First order reaction rate constants of ozone inside the module (s\(^{-1}\))
Chapter 1

Introduction
1.1 Background

Australia is one of the driest populated continents on earth with extremely varying rainfall. Climate change and population growth (urbanization) has led to pressures on the availability of Australian freshwater resources [1]. By the year of 2030, the population of Australia will reach up to 28 million [2], while population stresses and water shortages are an issue worldwide. Water recycling is therefore considered as one of the most viable solution in Australia and overseas. This can help in alleviating the pressure on existing water supplies, while on the other hand protects remaining water sources from becoming polluted [3]. Therefore, current wastewater treatment technologies are not only focusing on meeting permissible discharge limits but also on meeting requirements for reuse, both for industry and even potable applications [4]. Conventional methods, such as coagulation/flocculation, biological treatment, and sand filtration can be used, but advanced techniques may also be required. Among the different advanced wastewater treatment processes, membrane filtration has become popular. Membrane filtration can provide high quality water at high efficiency, with minimal maintenance and operational requirements compared to many conventional physical and chemical purification methods [4, 5].

Pressure driven membrane processes (microfiltration, ultrafiltration, nano-filtration, reverse osmosis) are among the most promising membrane filtration techniques. These processes can be used to remove a wide range of components, ranging from suspended solids (microfiltration) to small organic molecules and ions (reverse osmosis). However selecting the appropriate process is very important, as it determines not only water quality, but also the treatment costs and energy requirement. Microfiltration (MF) membranes have a high permeability, where suitable water flux is obtained at a low applied hydraulic pressure. The pore size ranges from 0.1 µm to 10 µm. Suspended solids, colloids and bacteria are retained in MF by a sieving mechanism [5].

The application of MF membranes to treat secondary effluent (SE) from wastewater treatment plant has focused on membranes made of polymeric materials as this has been a key part in the practical success of their adoption to water treatment [6]. Recently however, the application of membranes made of ceramic materials in wastewater treatment is growing popularity. Although the price per square meter of the active filtration layer of the ceramic membranes are typically higher than that of the polymeric
membranes [7], the ability of ceramic membrane to effectively pair with different pretreatment options have made them an emerging concept in the wastewater treatment technology to offset this higher material cost [8]. One well known merger is with ozone as a pretreatment, which can provide higher permeate flux while filtering SE without any damage of ceramic membrane [6]. Higher flux leads to lower capital cost and therefore is a key part in the affordability of ceramic membranes for water treatment. Ozone is known to react with organic material in the wastewater either directly, or indirectly via free hydroxyl (’OH) radicals produced during its decomposition. It is also known that the material used to make ceramic membranes, will catalyse the breakdown of ozone to ’OH radicals [9]. However there is no work that has actually measured and analysed the role of ’OH radicals in the reported high flux of ceramic membranes operated with ozone. Also, despite all these benefits of ozone as a water treatment operation either on its own, or with catalytic materials, bromate is well documented to be formed as a by-product during ozonation of bromide containing water [10]. This highly undesirable by-product is a major issue in the implementation of ozone in water treatment, as bromate is more toxic than its precursor, bromide. A study on the behaviour of ozone within ceramic membranes and formation of this by-product would be of value to industry while also yielding interesting scientific outcomes.

Another feature of ozone application in water treatment that must be considered when operated in conjunction with ceramic membranes is its typical merger with a downstream biological activated carbon (BAC) process. BAC is often used after ozonation of SE as it adsorbs bio-refractory compounds, as well as contributes to the bio-oxidation of biodegradable organic matter coming from ozone reaction with wastewater organics [11]. However, application of ozone and BAC with ceramic membranes has not been investigated for advanced treatment of secondary wastewater effluents [12].

The key to investigating how ceramic membranes can achieve high fluxes with ozone is to analyse the relative differences in membrane fouling. Fouling is considered as the major constraint for any membrane filtration process, determining the physical properties of the fouling layer accumulated on the membrane surface is important. Determining the characteristics of the membrane (e.g., pore size, porosity and thickness of the filtration layer) is also important in order to understand the filtration performance of an MF ceramic membrane. Measuring the filtration behaviour of ceramic membranes
at different salinity, temperature and pH conditions must first be conducted to observe their significance prior to assessing the impact of fouling from wastewater components. Exploring the decomposition of ozone in the presence of minerals and organic components of synthetic secondary effluent (SSE) will provide the foundation to further investigate the decomposition of ozone along with formation of OH radicals.

### 1.2 The ozone and ceramic membrane filtration process

Ceramic materials can provide potential benefits over the conventional polymeric MF membranes [13]. The combined process of ozonation and ceramic membrane filtration (CMF) was found to offer several advantages. Schlichter et al. (2004) found that a minimum concentration of 0.05 mg ozone per litre was needed to maintain stable and high permeate fluxes during MF and UF of river water without back-flushing [14]. Another study conducted by Kim et al. (2008) showed that, the hybrid ozonation–ceramic membrane system can significantly reduce membrane fouling and the fouling behavior is strongly dependent upon ozone concentration and hydrodynamic conditions [15]. Park et al. (2012) investigated the characteristics of natural organic matter (NOM) treated by the hybrid ceramic membrane process. The changes in permeate flux against filtration time was observed for the cross flow membrane filtration system at a flux of 44 L/m²·h. A noticeable increase (25%) was observed for the flux of hybrid ceramic membrane ozonation process. The reduction in fouling was attributed to the reaction by ozonation or catalytic ozonation to enhance the decomposition of NOM efficiently [16]. Lehman et al. (2009) studied the effect of ozonation and ceramic membrane on the SE of a pilot plant located in Chino, California. They found that, the ozone treatment is effective at degrading colloidal NOMs which are likely responsible for the majority of membrane fouling [6]. While it is understood this is because of the reduced diffusion resistance in the cake layer [8], the mechanism of ozone giving rise to the benefits is not well understood.

Karnik et al. (2005) investigated the samples taken from Lake Lansing (Haslett, Michigan). The permeate flux through a titania coated ceramic membrane was found to be significantly affected by ozonation and the pH of the feed water in the system. The effect of ozone was attributed to the decomposition of ozone, resulting in the formation
of 'OH or other radicals at the membrane surface and reduce the extent of membrane fouling [17]. Despite attributing the performance enhancements to 'OH radical formation, no actual measurement of the 'OH radicals has been conducted in this application to prove they have this role. Therefore to better understand the well-known flux enhancement via ozone’s contact with the ceramic membrane, analysis of 'OH radical formation that is expected to be accelerated within the continuous filtration of the ceramic membrane, would offer some insight. 'OH radical formation potential and kinetics can then be determined by a reaction kinetics model to quantify the ozone reaction mechanisms within the membrane and conclude their significance and possibly the role in understood high performance benefits.

1.3 Research objectives

The goal of this study is therefore to address the gap in understanding of ozone interactions with ceramic membranes, and investigate the mechanism of ozone and 'OH radicals on giving rise to the benefits in combined ozone ceramic membrane treatment process of SE. To achieve this goal, ceramic membrane must be first ascertained by its physical characteristics such as pore size, porosity and filtration layer thickness. The effect of salinity, temperature and pH on the permeability of ceramic membrane will provide some basic understanding. The effect of powdered ceramic materials on the decomposition of ozone will form the base of the principal goal. In achieving the objective to understand the role of ozone in application to ceramic membranes, the approaches in this thesis include:

- Investigate the effect of BAC filtration and ozonation on the fouling of MF ceramic membrane while filtering secondary treated effluent;
- Capture membrane foulants and measure the filtration properties of the cake fouling layer;
- Measure the characteristics (e.g., pore size, porosity and thickness of the filtration layer) of a commercially available MF ceramic membrane;
- Study the effect of basic water quality parameters such as salinity, temperature and pH on the permeability of ceramic membrane;
- Study the decomposition of ozone in the presence of minerals and organics and different ceramic materials;
- Quantify the •OH radical formation potential during filtering ozonized solution through ceramic membrane;
- Analyse bromate formation during ozonation of bromide containing water treated by CMF.

1.4 Outline of the thesis

Chapter 1 – Introduction
The purpose of this chapter is to introduce the problem associated with the scarcity and the demand for high performance membranes to enable utilisation of existing wastewaters. The requirement for a durable low cost treatment process is explained followed by the importance of ceramic MF membrane process. The benefits of combined ozone-CMF in treating surface water and wastewater is presented. The objectives of this research and the approach of this thesis are summarised.

Chapter 2 – Literature review
The review contains a summary of the low pressure membrane processes. The superiority of ceramic MF membranes over conventional polymeric membranes is described. Fouling which is known as the major problem in membrane filtration process is explained. The techniques to characterize fouling and the ways to mitigate fouling are also presented. The theory of decomposition of ozone in the presence of different catalytic metal oxides are described followed by an effective •OH radical measurement technique (the \(R_{ct}\) concept).

Chapter 3 – Materials and methods
This chapter covers the experimental setup used in this research. The basic membrane filtration setup include the investigation of the effect of basic filtration parameters (salinity, temperature and pH) on the permeability, the BAC filtration setup, the cake layer percolation test, the ozone decomposition experiments in the presence of minerals, organics and different ceramic materials and the ozone and •OH radical measurement during combined ozone-ceramic membrane process are all explained. Analytical techniques for measuring the membrane properties (pore size, porosity and thickness of filtration layer) and the water quality (pH, DOC, colour, turbidity, conductivity, TDS) are also explained.
Chapter 4 – Effect of pre-treatment processes on ceramic membrane performance

In this chapter results from experiments conducted using ozone and BAC filtration method prior to ceramic MF are presented. Results have compared in terms of general water quality parameters (DOC, UVA$_{254}$ and colour) and the permeability across the membrane. The unified membrane fouling indexes (UMFI) of different pre-treatment options along with reversible and irreversible fractions are explained as well. The goal of this chapter is to present performance of ceramic membranes under real water treatment scenarios and align their performance with well-known findings by industry and researchers prior to commencing the detailed study of mechanisms.

Chapter 5 – Analysis of fouling layer filtration properties

In this chapter results from the cake layer permeability tests are presented and discussed. SEM images were used to show the texture and porosity of the fouling layers on top of a 0.1 µm cellulose disc filters. Deposited fouling layers of the raw real secondary effluent (RSE) and ozone pre-treated RSE have been compared using hindered settling function, $R(\phi)$. The purpose of this chapter is to explore the effect of ozone on fouling layers to assess the role in the fouling layer property on altering the filtration resistance that could potentially explain the high flux effects.

Chapter 6 – Ceramic membrane physical structure and filtration behaviour under simple process conditions

Results for the characterisation techniques applied to identify the physical properties (pore size, porosity and thickness of the filtration layer) of membrane are presented and discussed. SEM images are used to explore the thickness of the membrane. Pressure drop across the membranes was measured over varying salinity, temperature and pH conditions. The observed experimental permeability was then compared with viscous flow theory, which was obtained using Hagen-Poiseuille equation. The goal of this chapter is to explore the physical characteristics of ceramic membrane and understand performance under different salinity, temperature and pH conditions. These findings establish the baseline performance prior to moving to more complex water solutions.
Chapter 7 – Effect of ozone on ceramic membrane materials

Ozone decomposition tests were conducted in the presence of typical wastewater organics, minerals and SSE. Ozone decomposition in the presence of different ceramic materials (Al₂O₃, TiO₂, SiC) have also been conducted. The •OH radical formation potential was quantified by measuring the $R_{eq}$ value. The results of these experiments have been presented and discussed in this chapter. This chapter was aimed to explore the mechanism of ozone decomposition in the presence of different organic components and minerals present in the SSE. The influence of different ceramic materials to generate •OH radicals during ozonation was also explored.

Chapter 8 – Decomposition of ozone through ceramic membranes

Ozone decomposition across the membranes was conducted to quantify the formation of •OH radicals. Bromate formation during ozonation of bromide containing water has also been quantified. The results have been presented in this chapter with discussion. The purpose of this chapter is to explore the behaviour of ozone within the ceramic membranes, and its potential to influence water treatment by formation of •OH radicals. Bromate formation during ozonation of bromide containing water has also been explored, where the unique ozone-membrane interactions may influence the formation of this well-known by-product formed when ozone is applied to treat water.

Chapter 9 – Conclusions and recommendations for future work

The major conclusions of all the results are summarized in this chapter, including a summary of the contributions to industry and science. This is followed by the recommendations for future work.

1.5 References

2. Young, R., National trends in urban water resource management. Address to Gold Coast Water Future Advisory Communities, 2005.


Chapter 2

Literature review
2.1 Introduction
A detailed review of literature is presented in this chapter describing the benefits of ozonation in catalytically enhancing flux of the ceramic membrane filtration (CMF) for the treatment of secondary effluent (SE) wastewater. Previous research on the catalytic activity of ozone in the presence of ceramic membrane is then presented, explaining the requirement for an ongoing research that explores the mechanism and significance of the catalytic effect. The literature review commences by explaining the benefits of microfiltration (MF) ceramic membrane over the conventional widely used polymeric membranes. As fouling is the major performance limitation in membrane filtration, the various factors influencing fouling have been reviewed. Subsequently, several ways to mitigate performance loss from fouling has been discussed. The effect of ozonation as a pre-treatment prior to CMF is then discussed. Biological activated carbon (BAC) filtration after ozonation can be significant in order to reduce the bacterial regrowth in the ozone residual. The decomposition of ozone into hydroxyl (•OH) radicals which are known as the strongest oxidants are briefly explained with an effective technique for the •OH radical measurement. The catalytic effect of ceramic materials during ozonation has been described. Finally, the mechanism of bromate formation during ozonation of bromide containing water has been explained. The purpose of this chapter is therefore to describe, summarize, evaluate and clarify the literature related to this study and to identify gaps in knowledge in this nature of research.

2.2 Membrane filtration
A membrane is a thin film of permeable or semi-permeable material. Membrane filtration is a physical separation process where a feed stream is divided by a membrane into a retentate (or concentrate) and a permeate fraction. Membrane filtration can be used as a pre-treatment option for reverse osmosis or to take out specific particulate species like bacteria, virus or organic compounds like proteins, fats in industries and/or in many more applications [1]. Recently membrane filtration has become popular in different wastewater treatment processes, because of its high efficiency to provide high quality water with minimal maintenance and operational requirements compared to many conventional physical and chemical purification methods [2, 3].
2.2.1 Membrane classification

Membrane filtration processes can be classified by applied driving force. When a pressure serves as a driving force to separate permeates and retentate, it is called pressure driven membrane process. Based on the molecular weight cut-off (MWCO) and applications, pressure driven membranes processes can be classified into reverse osmosis (RO), nano-filtration (NF), ultrafiltration (UF) and microfiltration (MF) [3]. Characteristics of all these processes are summarized in Table 2.1.

Table 2.1: Overview of pressure driven membrane processes and their characteristics [1, 3, 4].

<table>
<thead>
<tr>
<th>Process</th>
<th>Microfiltration (MF)</th>
<th>Ultrafiltration (UF)</th>
<th>Nano-filtration (NF)</th>
<th>Reverse osmosis (RO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore size (nm)</td>
<td>100 – 10000</td>
<td>2 – 100</td>
<td>0.5 – 2</td>
<td>&lt; 0.5</td>
</tr>
<tr>
<td>Operating pressure (bar)</td>
<td>0.1 – 2</td>
<td>0.1 – 5</td>
<td>3 – 20</td>
<td>5 – 120</td>
</tr>
<tr>
<td>Permeability (L/m²·h·bar)</td>
<td>&gt; 1000</td>
<td>10 – 1000</td>
<td>1.5 – 30</td>
<td>0.05 – 1.5</td>
</tr>
<tr>
<td>Mechanism of separation</td>
<td>Sieving</td>
<td>Sieving</td>
<td>Sieving, Charge effects</td>
<td>Solution-diffusion</td>
</tr>
<tr>
<td>Species passed</td>
<td>Solvent (water) and dissolved solutes</td>
<td>Solvent (water) and low molecular weight (MW) solutes (&lt; 1000 Da)</td>
<td>Solvent (water), low molecular weight solutes, monovalent ions</td>
<td>Solvent (water)</td>
</tr>
<tr>
<td>Species retained</td>
<td>Suspended solids, fine particulars, some colloids</td>
<td>Macro-solutes and colloids</td>
<td>Molecular weight compounds (&gt; 200 Da), multivalent ions</td>
<td>Dissolved and suspended solids</td>
</tr>
<tr>
<td>Applications</td>
<td>Clarification, pre-treatment, removal of bacteria</td>
<td>Removal of macromolecules, bacteria and viruses</td>
<td>Removal of (multivalent) ions and relatively small organics.</td>
<td>Ultra-pure water, desalination</td>
</tr>
</tbody>
</table>
Among the different types of membranes, MF and UF (known often as low pressure membrane processes) are gaining popularity as a result of increasingly rigid discharge standards and increased water recovery demand. The use of MF/UF to treat secondary or tertiary treated effluent offers improved water quality compared to the conventional treatment processes [5].

2.2.2 Membrane materials

Commercial MF/UF membranes used for water and wastewater separations are made from a wide range of organic and inorganic materials [3]. Organic MF membranes can be produced from different polymeric materials like: polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), polypropylene (PP), polyethylene (PE), cellulose esters, polycarbonate, polysulfone (PS), polyethersulfone (PES), polyimide (PI), polyetherimide (PEI), aliphatic polyamide and polyetheretherketone (PEEK). The first four polymers are hydrophobic whilst the remainder are hydrophilic [6]. In terms of price per unit square meter, chemical resistance, thermal stability and biodegradability each membrane material has benefits and drawbacks [7, 8]. However, there are certain limitations that restrain performance of polymeric membranes. First, polymeric membranes cannot be used at high temperature, either due to the limitation of the membrane material itself, and/or the sealing material within the membrane module [9]. This limits use to ambient temperature operations, in particular cleaning and sterilization. Second, polymeric membranes or their sealants can be destroyed by repeated cleaning to reverse fouling or pre-treatment operations like advanced oxidation or ozonation. Last, softer polymer materials are less resistant to abrasive particles [10]. As a result, polymeric membranes have a shorter operating life span than some non-polymeric alternatives [11]. Cleaning and membrane replacement costs are significant and are responsible for about 60% of the total operating costs of secondary wastewater membrane filtration [12]. This limits the performance of polymeric membranes. Ceramic materials are an alternative membrane material, that have benefits relative to these polymer membrane limitations [13].

Ceramic membranes, which can be used in MF and UF are made from materials of alumina (Al₂O₃), titania (TiO₂), silica (SiO₂) and zirconia (ZrO₂) [3]. These membranes have stronger mechanical structure and better physical strength than polymeric membranes [5]. They can be operated under high temperature, pressure and pH without
concern of compaction, delamination, breakage or swelling of the membrane [2, 3, 5]. A wide range of pore sizes of ceramic membranes can be easily manufactured using sintering and sol-gel methodologies [3]. Bas et al. (2011) have shown that, ceramic membranes have an enhanced ability to remove UV active compounds, turbidity and organic carbon from water compared to their polymeric counterparts under the same flux conditions [14]. They also have a greater potential for natural organic matter (NOM) removal as well as the minimization of halo acetic acid (HAA) [13]. The reason for the higher rejection performance and improved flux behaviour of ceramic membranes are due to the differences in the surface groups of ceramic and polymeric membranes. Specially the solute-membrane surface interaction has been frequently correlated to NOM fouling characteristics [15]. The material robustness also enables more effective cleaning methods like chemical enhanced back-flushing for a longer time at higher chemical concentration or higher pressure [2, 5]. All these advantages of ceramic membrane over polymeric membrane permit them to operate under high operating flux with sufficient separation characteristics [14].

2.2.3 Membrane configuration

In order to achieve greater filtration performance in the MF membranes, the membrane configuration and the membrane module are highly significant. Commonly used MF membrane configurations include plate and frame, spiral wound cylinder, hollow fiber, tubular, and rotating flat plate [8]. Ceramic MF membranes are generally shaped into two main configurations: flat plate, single channel tubular membranes and multi-channel membranes. In the flat plate membrane unit, a supporting plate maintains module integrity. Within the module, multiple supporting plates are placed with specific distances between them [16, 17]. The single channel tubular membranes are located on the inside of a tube. The active filtration layer of the membrane is coated on a thicker support layer. The feed generally flows toward inside out direction. A multi-channel ceramic membrane contains multiple parallel channels. The surface of the channels is coated with membrane filtration material. A feed is introduced through the inlet of the channel and flows through the channel over the membrane [16, 17].

2.2.4 Operational mode of membrane filtration

Two operational modes can be used in MF membrane processes: dead end mode and cross flow mode [6]. Figure 2.1 shows the dead end and cross flow filtration operations.
In the dead-end approach, the pressure applied to the liquid flow is applied vertical to the membrane surface. The feed solution is forced to flow through the membrane wall so that rejected particles accumulate by the filtration layer of the membrane. This accumulation of rejected particles forms a cake layer on the membrane surface. The thickness of the cake layer increases with the filtered volume [8]. To remove accumulated cake layer, a routine backwash system is usually employed lasting from minutes to hours for each backwash routine. In cross flow filtration system, the feed flows in a direction parallel to the membrane surface and vertical to the direction of permeate flow. The deposition of the particles present in the feed may form thin cake layer on the membrane surface. The cake layer is washed away using high liquid velocity. Thus fouling is reduced by preventing any buildup of cake layer on the membrane surface [6]. A part of the feed (concentrate) is recycled, while the remaining part can be bled from the system leading to a continuous process that doesn’t rely on backwash. The dead end systems are more prone to fouling than cross flow systems, however their advantage is lower energy consumption [18]. Water treatment widely uses dead-end filtration, while cross flow systems are more popular in other applications including food processing, where the higher energy cost and equipment requirement (large pumps and piping) from cross flow can be justified.

![Figure 2.1: Dead end and cross flow modes for membrane filtration (Figure taken from Poirier et al. (2001) [19]).](image)

### 2.3 Membrane fouling

Fouling is considered as the major limitation for the operation of any membrane filtration process. Fouling reduces the performance of a membrane by depositing particles or compounds on the external surface, at the pore openings or within its pores. This consequently increases the operational costs due to added pumping energy (pressure), cleaning and operational procedures [20-23]. There are two types of fouling layer: a ‘reversible’ type removed by simple stages like hydraulic backwash, scrubbing,
periodic chemical cleaning; and an ‘irreversible’ type that is never removed and contributes to the need for membrane replacement [2]. There are different material features of the membrane that influence fouling. In order to achieve a better flux performance of MF and UF ceramic membrane, the factors which influence the fouling are important to understand.

Barger et al. (1999) reported that there are several ways in which membranes can become fouled. Colloidal particulates existing in the feed water can be deposited on the membrane surface (particulate fouling). Dissolved organic matter (DOM) can be precipitated on the membrane surface or in membrane pores (organic fouling). Biological growth can be accumulated on the system and/or its attachment to the membrane (bio-fouling). Physical and chemical reactions of some feedwater components with membrane surface may also cause fouling [24]. However, in MF and UF membranes, organic matters are considered as the main reason of membrane fouling. Especially the DOM present in the feed can accumulate in the membrane pore or on the membrane surface, resulting in organic fouling. There are several issues that influence the quality and extent of the membrane fouling. The key issues are the characteristics of the feed solution, material properties of the membrane, configurations of the membrane and working conditions [8].

2.3.1 Effect of feed water characteristics

Different feed water content like dissolved organic matter (DOM), microorganisms, inorganic materials and suspended solids are found to be potential foulants during MF of wastewater. DOM is a major component in wastewaters and generally is comprised of humic substances (HS), polysaccharides, amino acids, proteins, fatty acids, phenols, carboxylic acids, quinines, lignins, carbohydrates, alcohols, resins [25]. The presence of higher DOM concentrations in the feed water does not always found to generate more severe fouling. This indicates that, some organic fractions may have higher fouling potential than others [26].

The fouling generated by DOM can be affected by the inorganic particles too. Inorganic compound includes silica, alumino-silicates, iron, aluminium and suspended solids. The presence of clay minerals can significantly compete with DOM to adsorb on the membrane surface or in the pores. Contrary to this, high surface area of inorganic materials may enhance the adsorption of organic on clay minerals. This results in a
decrease in the sorption of DOM on to the membrane, which results in increase in the membrane permeability [25]. Mallevialle et al. (1989) showed that, fouling layer comprising of an organic matrix can be served as a glue for the inorganic components [27]. Kaiya et al. (1996) investigated the fouling of an MF hollow fiber membrane. The Lake Kasumigaura (Japan) water was used as the feed of their study. It was observed that, major fouling on the MF membrane was caused by organic matter and manganese [28]. Schäfer et al. (2000) found that the DOM fouling on the MF membrane surface was the result of the precipitation of calcium-organic complex [29]. Mo et al. (2003) analyzed the properties of the fouling while treating the micro-polluted raw water. It was found that, the microorganisms, low molecular organic matters and inorganic matters (mainly calcium) caused the fouling on the exterior surface. However, the main cause of fouling on the inner surface was bio-fouling [30].

2.3.2 Effect of solution chemistry

Fouling can be significantly affected by the different chemical properties of the solution. The fouling can significantly be affected by the pH of the feed, concentration of multivalent cations present in the feed, ionic strength of the solution, and water hardness [8]. Fouling by natural organic matter (NOM) can be increased by ionic strength, pH and divalent cations [31]. At higher multivalent cations concentration and lower pH value, NOM particles are found to agglomerate more. Contrary to this, the particles expand to more linear chains at low ionic strength and neutral pH [32]. It is hypothesized that, the coiling and aggregation of the solute molecules are assisted by protecting the charges of the molecules by increasing ionic strength. Thus accumulation of these molecules result in fouling on the membrane surface [25]. Ghosh et al. (1980) measured the surface pressure and viscosity of the HS at different ionic strength and pH values. It was observed that, at high multivalent cation concentration and low pH value more aggregation of HS occurs. Opposite to this, the molecules expand to more linear forms at low ionic strength and neutral pH value [33].

2.3.3 Effect of structural parameters

The structural features of the membrane including porosity, roughness, pore size, pore shape and pore size distribution are crucial factors affecting the performance of membrane fouling. Hwang et al. (2008) investigated two different pore sized membranes made of polycarbonate with a hydrophilic surface. It was found that, fouling
of 0.15 µm polymethyl methacrylate (PMMA) in the 0.4 µm pore sized membrane was greater than that of a 0.2 µm membrane under the same pressure and filtration flux conditions. It was inferred that, the PMMA particles penetrated into and accumulated in the larger pore sized membrane more easily. This resulted in larger pore blocking in the 0.4 µm pore sized membrane than that of a 0.2 µm membrane [34]. In contrast, Zhao et al. (2002) found that the total resistance for a 0.2 µm fouled ceramic membrane is double than that of a 1 µm membrane during the filtration of acid waste-streams [35]. Clearly fouling varies with pore size, but many other features of both the membrane and the water are to be treated.

2.3.4 Effect of operating condition

The extent of membrane fouling can be influenced by the operating conditions (i.e., operating pressure, flux, back-wash frequency and cross-flow velocity) of the filtration system [8, 21, 36]. In dead end configuration, quick deposition of a cake layer results in rapid fouling, where in cross flow mode deposition of cake layer is greatly reduced by the velocity of liquid. The initial flux in MF also affects the permeability reduction. Field et al. (1995) attributed the rapid fouling in the MF membrane to the higher operating flux [37]. However achieving high fluxes is important to reducing the total membrane area requirement, which is directly associated with the capital and operating costs of the plant. Understanding the membrane chemistry, solution component chemistry and the fouling properties is important to developing economically viable membrane treatment systems.

2.4 Fouling mitigation

Longer membrane life requires application of suitable fouling mitigation techniques. Fouling can be controlled by different techniques: properties of membrane can be modified; configuration of membrane module and operating parameters can be optimized; membranes can be cleaned periodically and feed water can be treated prior to membrane filtration [8].

2.4.1 Membrane properties modification

Fouling can be controlled by suitably selecting the membrane and/or modifying surface properties of membrane. The property of attracting or repelling water by the membrane surface is an important factor on mitigating fouling. For example, fouling can be
mitigated by hydrophilic membranes while filtering feed containing proteins. This is because proteins can be adsorbed more strongly on the surface of the hydrophobic membranes [38]. Also, negatively charged membranes are useful to reduce fouling while filtering feed containing charged colloids as most colloids are charged negatively [8].

2.4.2 Optimisation of membrane module configuration and operating conditions

Fouling can be mitigated by correctly selecting the membrane module configuration and operating conditions. Decreasing module length and/or increasing hydraulic diameter can increase the mass transfer coefficient [8]. Operating the membrane at high cross flow velocity (CFV) and low flux also increases the mass transfer coefficient. Though higher CFV consumes more energy, it can reduce the concentration polarization and the membrane fouling [6, 39]. Operating the membrane below critical flux can reduce fouling to zero or negligible [37, 40]. In order to increase the water productivity in the water purification plants, filtration process is run above the critical flux. Thus fouling is occurred on the membrane surface [8]. Back-washing with frequent interval or relieving the pressure that is holding the cake layer to the membrane surface can be applied to eliminate fouling [40]. Howell et al. (2002) observed that, regular intermittent flux can reduce long-term fouling [41].

2.4.3 Membrane cleaning

In dead-end filtration configuration, backwashing can be applied as a hydraulic cleaning method of MF membrane. In backwashing, DI water or filtrate itself is used to flush from the filtrate side of the MF membrane to feed side. Thus the deposited cake fouling layer can be detached from the membrane surface. In the drinking water treatment plants in United Kingdom (UK), the rate of back-washing varies from 5 to 96 per day, which usually lasts for 10 seconds to 10 minutes [42]. In MF and UF of SEs, back-wash is conducted in every 15 to 30 minutes [43, 44].

Chemical enhanced backwash (CEB) can be applied if hydraulic backwash is not adequate. In CEB, backwash water is mixed with very low concentrated cleaning chemicals. At ambient temperature, CEB is carried out for a short period of time and is automatically scheduled daily to weekly [8]. After certain period of operation if the permeability of the membrane falls below a standard value, cleaning in place (CIP) is
required to recover the flux [45]. Normally, CIP is conducted with higher concentration of cleaning agent, longer soaking time and at higher temperature. The rate of CIP varies from 0.2 to 50 per year in the drinking water treatment plants in UK [42].

Cleaning agents should be selected on their compatibility with the membranes to avoid membrane damage. Maintaining the quality of product water should be highly considered while evaluating the cleaning performance [46]. The efficiency of cleaning is influenced by the concentration of cleaning agents, working temperature, cleaning time and hydrodynamic conditions [47].

2.4.4 Feed water pre-treatment

In order alleviate membrane fouling several pre-treatment options can be adopted: ion-exchange resins, activated carbon adsorption, electro-flocculation, coagulation, ozonation, BAC filtration etc.

*Ion exchange resins*

Ion exchange resins (cationic or anionic) are resins or polymers which usually work as ion exchangers [8]. In water and wastewater treatment processes, the application of anion exchange resins (AERs) has become broad [48]. Especially in wastewater, DOM and color can be effectively removed by the AERs.

The negatively charged DOM molecules displace the anionic groups to attach to the cationic functional group of the AER. Many AERs have the advantage of easy regeneration. Those with higher water contents have been found to be more efficient in DOC removal due to the presence of more active sites. Strong base resins tend to be more effective for DOM removal than weak base resins [49].

*Powder activated carbon*

The deposition of cake fouling layer can be reduced by powdered activated carbon (PAC). The dissolved foulants can be adsorbed rapidly by the PAC resulting in reduced DOC adsorption [25]. PAC can increase the permeability of cake fouling layer and reduce its compressibility. Thus PAC improves the hydraulic properties of the cake fouling layer. PAC has been used widely in many water treatment plants as a pre-treatment to remove DOM, taste, odor and synthetic organic chemicals. In those treatment plants, MF and UF membrane systems are used to remove the spent PAC, micro-organisms and other particulate matters [42].
In most studies, PAC has been found to decrease the hydraulic resistance and irreversible fouling [50, 51]. Konieczny et al. (2002) observed an improvement in MF and UF flux with PAC pre-treatment using surface water [52]. Haberkamp et al. (2007) studied the effect of pre-treatment with PAC on SE. An increase in the permeate flux was observed by the PAC. This was attributed to the removal of biopolymers containing proteins and polysaccharides by the PAC [53]. However, Nilson et al. found that the adsorption of PAC resulted in large and more hydrophobic residuals in the membrane feed which were destructive to membranes [54]. Similar results were observed by Lin et al. (2000) who reported that, adsorption of PAC leaves small particles which causes flux reduction [55]. The contradictory effects found in these studies can be attributed to the properties (e.g., particle size, pore size, surface charge and dosage) of different PAC used in different studies. Moreover, the properties of the membrane and the characteristics of the feed solution may also influence the result [8].

**Coagulation**

Aluminium-based and iron-based coagulants can generate positive charges which invalidate the negative charges on the particles of NOM [21]. This allows the particles of NOM to accumulate and form larger particles which can be removed by MF membranes more easily. The higher MW compounds and those with more hydrophobicity can be effectively removed by coagulation [56]. After coagulation, the small MW components and the neutral or hydrophilic components are left in the NOM. Thus, the permeate quality in the MF system is enhanced by coagulation pretreatment [30, 57-60]. Combination of coagulation and membrane filtration can improve not only the permeability of membrane but also the quality of produced water [61]. Mallevialle et al. (1996) stated that, coagulation pretreatment in combination with ceramic MF reduced the rate of cleaning operations [62].

However, it was observed in a study conducted by Lahoussine-Turcaud et al. (1990) that, the irreversible fouling of low MW polysaccharide compounds cannot be reduced by coagulation [63]. Mallevialle et al. (1996) found that, unfavorable results may occur when coagulation is applied prior to polymeric MF membranes [62]. Thus partial removal of NOM by adding coagulant chemicals result in suppressing fouling in MF membranes. However, especially in case of potable water production, minimizing
chemical residuals is required to ensure the water is safe and drinkable. Therefore, incorporation of ozonation can be an alternative solution to reduce membrane fouling.

**Ozonation**

The role of ozone to reduce fouling on membrane has been demonstrated by many researchers [64-66]. Much of the NOMs present in the surface water can be oxidized and decomposed by ozone [64]. In ozone-ceramic membrane hybrid system, ozone reacts with the NOM deposited on the membrane surface or attached to the pore walls, resulting in a decrease of its bond with membrane surface. The partly dissociated foulants can be flushed away from the membrane surface and pore walls by the back wash process. Recovering the permeable membrane surface allows initial clean water permeate flux. Since ozone is a very high oxidizer, the membranes have to be adequately capable of withstanding reaction with ozone.

Ceramic tubular membranes are made of metal oxides, such as alumina, titania and zirconia are believed to be ozone resistant [65]. Karnik et al. (2005) investigated the hybrid ozonation/ceramic ultrafiltration membrane system. The found 100% permeate flux recovery as a cross-flow configuration under a constant trans-membrane pressure (TMP) [65]. They also showed that, ozonation at reasonably low dosages (1.5 g/L) allows for continuous filtration without need for frequent chemical cleaning. Other researchers also investigated the hybrid ozonation/CMF system [64, 67]. They also found that, continuous filtration operation at comparatively high permeate flux (more than 90%) can be maintained by keeping a minimum ozone concentration in the water. Furthermore, the other cleaning procedures can be eliminated too. Beside this improvement in permeate flux of MF system, ozone offers several side advantages.

Ozone oxidizes electron-rich compounds containing carbon-carbon (C–C) double bonds and aromatic alcohols [68]. It removes color, tastes and odors in drinking water production. Though, the application of ozone in the SE treatment is reasonably limited [69]. Paraskeva et al. (1998) found that ozone removed BOD, COD and color and increased the dissolved oxygen concentration (DOC) in SE deprived of causing any detrimental effects [70]. Contrary to these benefits, ozone was found to worsen the fouling of SE through a ceramic membrane (0.1 μm) in dead end configuration. The negative effect of ozone was attributed to the increase in the quantity of large organic molecules after ozonation [71].
The potential of ozone to kill microorganisms can release biodegradable substances from broken bacterial cells. Moreover, the high MW DOM can be broken down to low MW components [8]. Consequently, bacterial regrowth can be facilitated resulting in accelerated membrane bio-fouling [72, 73]. In order to overcome this problem, BAC filtration can be introduced between the ozone and membrane filtration system.

**BAC filtration**

Ozonation followed by BAC is widely used for drinking water treatment [74]. However, very few researches are found on the ozonation followed by BAC filtration prior to CMF for the treatment of secondary wastewater effluents. In the ozone-BAC process the biodegradable materials in the ozonated water can be consumed by the microbial flora attached to the activated carbon of BAC column [75, 76]. Combination of ozonation and BAC filtration was found to achieve 50% removal of DOC, more than 90% removal of a wide range of trace organic chemicals (TrOCs), 70% removal of non-specific toxicity and more than 95% reduction of estrogenicity [77]. Pramanik et al. (2014) investigated the performance of BAC as a pretreatment for reducing the organic fouling of a PVDF MF membrane in the treatment of secondary treated effluent. It was found that, BAC treatment reduced the high MW molecules such as biopolymers and humic substances (HS) through biodegradation and adsorption respectively. Thus the flux of the MF membrane increased remarkably [78].

### 2.5 Fouling characterization techniques

#### 2.5.1 Characterization of constituents in feed and permeate

The constituents present in the feed and permeate of a membrane filtration system can be characterized using different methods. The analyses commonly used to measure DOM to analyze fouling of MF membranes. Simple methods like measurement of the dissolved organic carbon (DOC) and UV absorbance at 254 nm can be used to quantify DOM. The ratio of the UV absorbance at 254 nm to the DOC is defines as the specific UV absorbance (SUVA). SUVA quantifies the proportion of humic and non-humic fractions in the wastewater [79]. However, lower DOC does not always correspond to less fouling in the membrane. Therefore DOC in a particular wastewater cannot always be a true index of its fouling potential [80]. This implies that, some specific proportion of DOC is causing membrane fouling. This particular fraction of DOC can be varied from one water source to another [8]. Therefore, to achieve more information on the
membrane fouling (such as, size and structure of the fouling layer and functionality of fouling materials on the membrane surface), advanced characterization technique is required. The apparent molecular weight distribution (AMWD) of the wastewater sample can be determined using high performance size exclusion liquid chromatography (HPLC). The quantity of different MW range can also be determined by the HPLC [81]. The biodegradability of the dissolved organic matter in the wastewater can be evaluated using the parameter called biodegradable dissolved organic carbon (BDOC). The potential of bio-fouling and the formation of biofilm can be estimated by the BDOC [8, 82, 83].

2.5.2 Characterization of foulant materials on membrane surface

Scanning electron microscope (SEM) can provide images of clean and fouled membrane surfaces and cross sections with high resolution [8]. An SEM is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons [84]. The electrons interact with atoms in the sample, producing several signals that comprise information about the sample’s surface topography and composition. Low-voltage field emission can offer images with as high resolution as 7Å [85]. However SEM only gives a visual understanding of the fouling layer properties, particularly the physical structure which leads to its resistance to water flow. A suitable complement to the visual appearance from SEM is from the direct measurement of flow resistance represented by the hindered settling function which can be measured by the stepped permeability test.

Fouling layer on the MF membrane surface can be analysed physically by the stepped permeability test that is used to characterize the dewaterability of flocculated suspension [86]. Buscall et al. (1987) established that the dewaterability of a suspension can be characterised by three physical parameters, namely the gel point, $\phi_g$, the compressive yield stress, $P_y(\phi)$, and the hindered settling factor, $R(\phi)$ [87]. The solid concentration at which a continuous network structure is formed is called the gel point. The compressive yield stress, $P_y(\phi)$, represents the compressibility and is defined as the minimum compressive stress required for the network structure to yield and compress irreversibly for a given solids volume fraction $\phi$. As a continuous particle network structure is required for the transmission of stress, the compressive yield stress can be determined at a solid concentration above the gel point. The hindered settling factor, $R(\phi)$, represents
the hydrodynamic resistance to flow through the suspension network structure as a function of solids volume fraction $\phi$. The rate and extent of the dewatering can be characterized by the hindered settling factor, $R(\phi)$, and the compressive yield stress, $P_y(\phi)$, respectively [88, 89].

The inter-particle network of the suspension will remain in its original form until an applied stress $\Delta P$ on the network exceeds the compressive yield stress, $P_y(\phi)$. At this point, the network structure will breakdown, irreversible particle consolidation will take place, and the local volume fraction will increase [87]. $P_y(\phi)$ will increase with $\phi$ as the number of inter-particle linkages increases so dewatering occurs until $\phi$ is such that $P_y(\phi) = \Delta P$. Also, $P_y(\phi)$ can only be traced in a regime where $\phi$ is greater than $\phi_g$. Below this limit ($\phi < \phi_g$), the particle concentration is too low to permit a particle network to generate and thus the compressive yield stress is zero (neglecting the suspension osmotic pressure). The hindered settling factor accounts the hydrodynamic interactions between the particles. These particle interactions increase drag on any particle in the concentrated dispersions [90]. These particle interactions hinder the relative movement of solids and liquid and thus $R(\phi)$ increases in a nonlinear mode with volume fraction $\phi$. Notably, the dewatering in settling is explained by the $R(\phi)$. The drag force on a particle moving through a liquid is quantified by the $R(\phi)$. Moreover, in a bed with a continuous network, it measures the drag experienced by liquid moving through a network of solids. Thus, $R(\phi)$ may be used in the modelling of filtration behaviour [88]. There are a few methods available for the determination of $P_y(\phi)$ and $R(\phi)$ [91].

During cake formation, the relationship between time $t$ and the specific volume of filtrate (volume expressed per unit area of membrane) follows a quadratic relationship such that a plot of $t$ vs. $V^2$ is linear. The inverse of the slope of this linear portion is designated as $\beta^2$ and can be used in the determination of $R(\phi)$ [88]. Landman et al. (1995) explained the theory which allows a more mathematically exact determination of $R(\phi)$ according to the following equation [88, 90, 92]:

$$R(\phi) = \frac{2}{dP^2} \left( \frac{1}{\phi_f} - \frac{1}{\phi_0} \right) (1 - \phi_f)^2$$

(2.1)
Where, $\phi_0$ is the initial solid volume fraction, $\phi_f$ is the equilibrium volume fraction at pressure $P$ and $\beta^2$ is the filtration parameter (m$^2$/s). As per Equation 2.1, $R(\phi)$ is inversely proportional to $\beta^2$ indicates hydrodynamic resistance decreases with increasing $\beta^2$. Thus experimentally measuring the resistance of the cake layer may represent the filtration resistance in the actual membrane filtration system. However, specific indices are required to evaluate potential of fouling on the surface of the MF membranes.

2.6 Fouling modelling

During dead end mode in the MF and UF filtration system, fouling can be generated by the following consecutive stages [93]:

- The smallest pores of the membrane can be blocked by the particles reaching to them;
- The inner surface of the bigger pores can be covered by the some particles;
- The particles that are already attached to the membrane can attach some newly arrived particles; and
- Cake layer starts to generate.

Based on the pore sizes of the membrane and size of the particles present in the feed solution, the mechanism of fouling in MF filtration can be explained by four distinct methods (Figure 2.2): complete pore blocking, intermediate blocking, standard blocking and cake layer formation. When the particles are dimensionally similar to the mean pore size of the membrane, complete pore blocking occurs. When some pores are blocked by the particles, flow is directed to other pores which are blocked successively. In intermediate blocking, the particles can block some of the membrane pores or attached to some other particles previously blocked some other pores. Standard pore blocking occurs when the particles are dimensionally smaller than the mean pore size of the membrane. The particles of the feed adhere to the inner pore walls resulting in pore narrowing. After certain period of time the decreased pore diameter leads to complete pore blocking. If the particles are larger than the mean average pore size of the membrane cake layers are formed. Cake layers increase with filtration volume and thus creates additional porous barrier for the feed [94, 95].
Figure 2.2: Schematic representation of the distinct fouling mechanism: (a) complete pore blocking; (b) intermediate blocking; (c) standard blocking and (d) cake layer formation (Figure taken from Abbasi et al. (2012) [94]).

If the pore size of the membrane is uniform and on average it is larger than the particle size in the feed, the membrane fouling is hypothesised to start with a standard blocking step followed by a complete pore blocking, and intermediate blocking and a cake layer formation. If the particles are much larger than the mean pore size of the membrane, complete pore blocking will start followed by intermediate blocking and then cake filtration [93]. In MF/UF system, the initial rapid flux decline by the biologically treated SE is attributed to the complete pore blocking and standard blocking due to the adsorption of effluent organic matters in the membrane inner pores. The subsequent slower flux decline is attributed to the cake layer formation on the membrane surface [96, 97].

As the flux in the MF system is contributed by different factors like pore blocking, standard blocking, cake layer formation, the fouling model can be presented by a series of resistances:

\[
J = \frac{\Delta P - \Delta \pi}{\mu (R_m + R_a + R_p + R_c)}
\]

(2.2)

In Equation 2.2, \( \Delta \pi \) is the osmotic pressure difference across the membrane. \( \mu \) is the dynamic viscosity. \( R_m, R_a, R_p \) and \( R_c \) are the resistances exerted by the membrane, adsorption of foulants, pore blocking and cake layer formation respectively (\( \text{m}^2 \cdot \text{h} \cdot \text{kPa}/\text{L} \)). \( R_m \) can be obtained by experimentally measuring the flux of the pure water feed.
The flow resistance within a porous ceramic MF membrane can be expressed by the Hagen Poiseuille’s law [3]. The relationship between pressure drop and flow rate of a fluid through capillaries relevant to the MF application can be described by Equation 2.3 [98, 99], which assumes viscosity as the main influencing parameter of the fluid on permeation. According to the Hagen-Poiseuille (HP) model, the permeability, \( J/\Delta P \), (L/m\(^2\)·h·kPa) can be expressed as:

\[
\frac{J}{\Delta P} = \frac{d_m^2 \varepsilon}{32 \mu L \tau}
\]  

(2.3)

Where \( J \) is the flux (L/m\(^2\)·h), \( \Delta P \) is the pressure drop (Pa), \( d_m \) is the average pore size (m), \( \varepsilon \) is the porosity (defined as the fractional pore area at the membrane surface), \( \mu \) is the dynamic viscosity (N·s/m\(^2\)) obtained from viscosity and salinity relationships [100], \( \tau \) is the tortuosity (defined as the ratio of the length of the pores compared to cylindrical pores perpendicular to the membrane surface) and \( L \) is the thickness of the membrane material (m). Thus, the flux \( J \) depends on water characteristics (the viscosity \( \mu \)), on the applied pressure (\( \Delta P \)), and on membrane properties (the pore size \( d_m \), the surface porosity \( \varepsilon \), the tortuosity \( \tau \) and the membrane thickness \( L \)). Therefore correlating the water flow rate through the membrane with the operation temperature and salinity should be represented by this model. The permeability determined by the HP model can be conveniently used to represent the membrane resistance in a resistance in series model (Equation 2.2), as \( R_m \) is simply the inverse of permeability. Therefore can be expressed as,

\[
R_m = \frac{32 \mu L \tau}{d_m^2 \varepsilon}
\]  

(2.4)

### 2.7 Evaluating fouling potential

Many fouling indices have been proposed to quantify the membrane fouling to date. Among those indices, the silt density index (SDI, ASTM D4189–95) and the membrane fouling index (MFI) account the fouling potential of specific feed solution [101]. Unfortunately, they do not allow determining the fouling potential of a particular combination of water and membrane operational conditions [102]. Huang et al. (2007) developed the unified membrane fouling index (UMFI) which can quantitatively
compare membrane fouling for a given type of water regardless of the membrane operational conditions [103, 104]. Interestingly, the UMFI was found to distinguish hydraulically and chemically reversible fouling from irreversible fouling [105]. Huang et al. (2009) reported that, the characteristics of the feed and the properties of the membrane are responsible for the inconsistency observed in fouling [106]. Higher variations were observed in the irreversible fouling, that was evaluated by the UMFI [102].

The concept of UMFI was developed based on a revised Hermia model [95] by covering the mathematical relationship for cake layer formation, but included a potential contribution from both cake layer formation and pore blocking [106]. The model is written using the following relationship:

\[
\frac{1}{J_s} = 1 + (UMFI) \times V_s
\]  

(2.5)

Where \(J_s\) is the normalized membrane specific flux, UMFI is an estimate of the extent of fouling \((m^2/L)\) and \(V_s\) \((L/m^2)\) is the specific permeate volume. In Equation 2.5, a greater UMFI value indicates a faster decrease in the normalized specific flux. UMFI can be determined experimentally by obtaining normalized specific flux at given specific permeate volume. It has been observed that, hydraulically reversible fouling and chemically reversible fouling can be differentiated by the UMFI [105]. The variability of fouling can be attributed to the combination of water and membrane properties. Higher variability was observed in the irreversible fouling when the fouling evaluation has been conducted using UMFI [106]. Total fouling can be influenced by the type of the membrane, hydraulically irreversible fouling by both the membrane type and feed composition and chemically irreversible fouling only by the feed composition [102, 105].

### 2.8 Ozone decomposition

When ozone is used for disinfection or oxidation, the life time of ozone has to be considered [107]. The half-life (seconds to hours) of ozone depend on the quality of water [108, 109]. Specially the pH of water, the type of NOM content and the alkalinity of water are very important [108]. The pH is important as the hydroxide ions may
initiate the decomposition of ozone [110-112]. Ozone can be decomposed into \( \cdot OH \) radicals which are known as the strongest oxidants in water [113]. Therefore, the analysis of ozonation processes always involves the two kinds ozone and \( \cdot OH \) radicals. However, for different applications of ozone the two kinds are of different significance. During disinfection through ozonation, both ozone and \( \cdot OH \) radicals may oxidize the disinfectants [108, 114, 115]. Ozone is a very selective oxidant however; \( \cdot OH \) radicals can react with many dissolved components rapidly.

It has been reported that organic compounds with different components can either initiate or inhibit ozone decomposition via their direct reactions with ozone and engagement in the \( \cdot OH \) chain reactions [113]. A compound is categorized as the initiator if it can react with ozone to produce radical intermediates such as \( \cdot O_2 \) or \( \cdot O_3 \) that leads to the formation of \( \cdot OH \). The promoter is a compound that can react with \( \cdot OH \) to form an organic radical intermediate that propagates the \( \cdot OH \) chain reactions with additional ozone to eventually produce another \( \cdot OH \). A compound is categorized as the inhibitor if it reacts with \( \cdot OH \) to produce an end product that ceases the chain reactions [113, 116].

To describe the ozone decomposition in the presence of organic matters (OM) of SE the following possible reactions can be considered [117, 118]:

\[
O_3 + OM_d \rightarrow \text{products} \\
k_d = \text{direct reaction rate constant}
\]

\[
O_3 + OM_i \rightarrow OH^* + \text{products} \\
k_i = \text{initiation reaction rate constant}
\]

\[
OH^* + OM_p \rightarrow O_2^* + \text{products} \\
k_p = \text{promotion reaction rate constant}
\]

\[
OH^* + OM_s \rightarrow \text{products} \\
k_s = \text{scavenging reaction rate constant}
\]

Where, \( OM_d \) is the component of organic matter (OM) that may consume ozone by a direct reaction. \( OM_i \), \( OM_p \), and \( OM_s \) are other components that may act as initiators,
promoters, and inhibitors of the 'OH chain reaction, respectively [107]. There are several methods (i.e., electrochemical, optical or colorimetric method) for directly measuring the ozone concentration. Research shows that, ozone oxidation reaction follows first order kinetics when ozone was reacted with biologically treated wastewater of aniline dye production [119]. The first order reaction rate constant, \( k \) (s\(^{-1}\)), was calculated according to:

\[
  k = -\frac{1}{t} \times \ln \left( \frac{C}{C_0} \right)
\]  

(2.10)

Where, \( C \) is the concentration of ozone remaining in the reactor (mol/L) at the given time \( t \). In contrast, the direct measurement of 'OH radicals are very difficult. To quantify the transient concentration of 'OH radicals during ozonation, a method was developed based on the measurement of the disappearance of an ozone resistant probe for 'OH radicals. This provides an indirect measurement of the concentration of 'OH radicals by observing the decrease in the concentration of the probe compound [120].

2.8.1 Concept of \( R_{ct} \)

This method is based on the measurement of the disappearance of an ozone-resistant probe compound during ozonation with a known second-order rate constant for 'OH. The concept of the ideal 'OH probe compound is that it reacts only with 'OH radicals, and not significantly with O\(_3\) or secondary oxidants. Thus, the disappearance of the probe is an indirect measure of the 'OH concentration [120]. Moreover, the probe compound should be easy to measure. Taking these requirements into consideration, para-chlorobenzoic acid (pCBA) has been selected as a probe compound because it has a very low reactivity with O\(_3\) \((k_{O_3,pCBA} < 0.15 \text{ M}^{-1} \text{s}^{-1})\) [121] but reacts readily with 'OH \((k_{\cdot OH,pCBA} = 5 \times 10^9 \text{ M}^{-1}\text{s}^{-1})\) [122]. A low detection limit of about 0.025 mM (4 mg/L) can be achieved by HPLC. Thus, a spiked low concentration of pCBA can prevent a significant contribution to the overall scavenging of 'OH [120]. With these advantages, pCBA has created considerable interest and has been widely used in recent years.

To explore the breakdown more closely, 'OH radical formation can be analysed via measure of the pCBA probe. Since the probe compound pCBA has a very low reactivity
with O₃ but reacts rapidly with 'OH, the rate of decomposition in ozonation in the presence of 'OH-probe compound can be expressed as [123]:

\[
\frac{d[pCBA]}{dt} = -k_{O,H,pCBA}[pCBA] \cdot [\cdot OH]
\] (2.11)

Equation 2.11 can be rearranged and integrated as:

\[
ln\left(\frac{[pCBA]}{[pCBA]_0}\right) = -k_{O,H,pCBA} \int [\cdot OH]dt
\] (2.12)

Where the term \(\int [\cdot OH]dt\) represents the time integrated concentration of 'OH, which is synonymous with the 'OH-exposure. Equation 2.12 shows that the relative decrease in concentration of a probe compound at any time \(t\) is an indirect measurement of the 'OH-exposure for the reaction period from time \(t = 0\) until that reaction time. Elovitz and von Gunten [120] proposed the term \(R_{ct}\), as the ratio of 'OH radical exposure vs ozone exposure. Therefore, \(R_{ct}\) can be expressed as:

\[
R_{ct} = \frac{\int [\cdot OH]dt}{\int [O_3]dt}
\] (2.13)

Where the time-integrated ozone concentration, \(\int [O_3]dt\) is the ozone exposure. The ozone exposure can be calculated from the integral of the ‘ozone concentration versus time’ data. 'OH radical exposure can be obtained from Equation 2.14:

\[
\int [\cdot OH]dt = -ln\left(\frac{[pCBA]}{[pCBA]_0}\right)/k_{O,H,pCBA}
\] (2.14)

Substituting Equation 2.13 into 2.12 leads to:

\[
ln\left(\frac{[pCBA]}{[pCBA]_0}\right) = -R_{ct} k_{O,H,pCBA} \int [O_3]dt
\] (2.15)

When the \(pCBA\) concentration is plotted with respect to O₃ exposure (product of ozone concentration and time) the slope represents the \(R_{ct} \times k_{O,H,pCBA}\) value. Since \(k_{O,H,pCBA}\) is well known to be \(5 \times 10^9\) M\(^{-1}\)s\(^{-1}\) [120], the \(R_{ct}\) value can be obtained from this slope. As
the ozone concentration can be easily measured, the constant $R_{ct}$ value allows the calculation of the \( ^\cdot \text{OH} \) concentration in the ozonation process. During the ozonation of natural water, the $R_{ct}$ has been found to follow a two stage pattern. An initial stage can be observed within the first 20 seconds and a comparatively slower stage can be observed at a constant rate during the process of ozonation [120]. The initial high $R_{ct}$ stage is attributed to the initiation reactions involving the natural organic matter present in all kind of water. The initial higher $R_{ct}$ stage was found to vary as a function of time. The value of higher $R_{ct}$ was found to be about 2 to 3 orders of magnitude higher than that of the later slower stage [124]. The concept of $R_{ct}$ has become beneficial to model the degradation of micro-pollutants during the treatment of natural water or wastewater by ozonation [120]. Since $R_{ct}$ is a useful tool to indirectly quantify the concentration of \( ^\cdot \text{OH} \) radicals in ozonation system, the catalytic effect of combined ozonation and CMF to generate \( ^\cdot \text{OH} \) radicals during the treatment of SE can be quantified by this concept.

### 2.8.2 Catalytic effect of ceramic oxides

The catalytic activity of the catalysts mentioned is mainly based on the catalytic decomposition of ozone and the enhanced generation of \( ^\cdot \text{OH} \) radicals. 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 \( ^\cdot \text{OH} \) or other radicals [65, 125-127]. \( ^\cdot \text{OH} \) radicals contain an unpaired electron, which gives them unusually fast reactivity. The surface properties of the catalyst and the pH of the solution are the major factors that influence the efficiency of the catalytic ozonation process [128].

The catalysts have several physical and chemical parameters which may influence their catalytic effect. The main physical parameters are: surface area, density, pore size, pore volume, porosity, purity and commercial availability. The major chemical parameters are: chemical stability and especially the presence of active surface sites such as Lewis acid sites, which are responsible for catalytic reactions. However, the acidity and the basicity are the key parameters that determines the catalytic properties of the metal oxides [128]. If a metal oxide surface is exposed to water, it becomes hydrated. When the surface is in contact with polar liquids, the amphoteric MOH groups (M = metal cation, e.g., Al\(^{3+}\), Zr\(^{4+}\) or Ti\(^{4+}\)) will dissociate. This causes the amphoteric groups to become either negatively or positively charged [129, 130].
As $H^+$ and $OH^-$ are the potential determining ions, the surface charge will depend on the excess of one type of charged site over the other and is a function of solution pH. The point of zero charge, which is the pH at which the net surface charge is zero depends on ionization reactions and is related to the ionization constants [131]:

$$pH_{PZC} = 0.5(K_1 + K_2)$$

At pH $< pK_1$ metal oxide will act as an anion exchanger while at pH $> pK_2$ it will act as cation exchanger [131]. It has to be emphasized that at pH values between $pK_1$ and $pK_2$ the amount of un-dissociated hydroxyl groups is approximately constant. The surface charge increase starts from the pH$_{PZC}$ in both acidic and basic directions and above $pK_2$ and below $pK_1$ the surface hydroxyl groups are in the ionized forms [131].

Several metal oxide catalysts such as TiO$_2$ [132, 133], MnO$_2$ [134, 135] and Al$_2$O$_3$ [136, 137] were studied as possible means for ozonation process. The O$_3$/TiO$_2$ system was found to be efficient for oxalic acid degradation in water at acidic pH [132, 133]. Metal oxides TiO$_2$, Fe$_2$O$_3$, MnO$_2$ immobilized on supports such as, silica gel, clay, Al$_2$O$_3$ and TiO$_2$ were found to be effective for organic compounds removal from water [125, 126, 138]. The TiO$_3$/Al$_2$O$_3$/O$_3$ process was also effective for the removal of natural organic matter from the Ebro River [125, 126].

### 2.9 Ozone disinfection by product (DBP) formation

Ozone has become an excellent disinfectant because of its ability to inactivate more resistant microorganisms (i.e., protozoa) over the conventional (i.e., chlorine, chlorine dioxide). However, very high ozone exposure is required to inactivate these microorganisms. This causes the formation of surplus concentrations of unsought disinfection by products such as aldehydes, ketones and carboxylic acids and one main inorganic byproduct, bromate ($BrO_3^-$) [139]. This human carcinogenic by product is problematic as it cannot be biodegraded in the biological filters [140]. Bromate was declared as a potential human carcinogen as it was found to be a genotoxic carcinogen.
inducing (e.g., renal cell tumors in rats) [141]. The guideline value of bromate issued by
the World Health Organization (WHO) is 25 µg/L. Moreover, a maximum contaminant
level of 10 µg/L bromate concentration is established by both the European Union and
the USEPA [142, 143].

Bromate is formed by the reaction of hypobromous acid with NOM. Hypobromous acid
is a product of the reaction between bromide and ozone [144]. In natural waters,
bromide levels are highly variable in a range of 10 – 1000 µg/L [140]. Though bromide
itself is not toxic [145], the formation of bromate can become a serious issue for
bromide concentrations above 100 µg/L based on the specific treatment goals [140].
The formation of bromate is a result of the oxidation of bromide by both the ozone and
 OH radicals. Initially, ozone oxidizes bromide via an oxygen atom and transfer to
produce hypobromite (OBr`). Subsequently, hypobromite (OBr`) reacts with ozone to
form bromite ion (BrO2-), which further reacts with molecular ozone to form bromate
(BrO3`). Equations 2.19 – 2.24 show the direct reaction pathways to generate bromate
during ozonation of bromide bearing water [146]:

\[
Br^- + O_3 \rightarrow OBr^- + O_2 \quad k = 160 \ M^{-1}s^{-1} \quad (2.19)
\]
\[
O_3 + OBr^- \rightarrow BrO_2^- + O_2 \quad k = 100 \ M^{-1}s^{-1} \quad (2.20)
\]
\[
O_3 + OBr^- \rightarrow Br^- + 2O_2 \quad k = 330 \ M^{-1}s^{-1} \quad (2.21)
\]
\[
HOBr + O_3 \rightarrow BrO_2^- + O_2 + H^+ \quad k = 0.01 \ M^{-1}s^{-1} \quad (2.22)
\]
\[
O_3 + BrO_2^- \rightarrow BrO_3^- + O_2 \quad k \geq 10^5 \ M^{-1}s^{-1} \quad (2.23)
\]
\[
HOBr \rightleftharpoons H^+ + OBr^- \quad (2.24)
\]

Bromide can also react with the 'OH to form the bromine radical ('Br), which then
reacts with molecular ozone in a complex set of reactions to form bromate. As such,
both direct and indirect pathways play a role in bromate formation (Figure 2.3).
Equations 2.25 – 2.35 show the indirect reaction pathways [146].

\[
Br^- + HO' \rightleftharpoons Br' + OH^- \quad k = 10^{10} \ M^{-1}s^{-1}; \ 3.3 \times 10^7 s^{-1} \quad (2.25)
\]
\[
BrOH^- \rightarrow Br' + OH^- \quad k = 4.2 \times 10^6 s^{-1} \quad (2.26)
\]
Figure 2.3: Bromate formation during ozonation of bromide containing water: (a) reactions with ozone and (b) reactions with ozone and \( ^\cdot OH \) radicals (Figure taken from Urs von Gunten (2003) [140]).

Croué et al. (1996) investigated the effect of pH, bromide concentration, ozone dose, bicarbonate ion and ammonia on the formation of bromate during ozonation of bromide containing water [147]. Linear relationships were established between the formation of bromate and the ozone/DOC ration. The formation of bromate was also linearly proportional to the initial concentration of bromide ion.
2.10 Scope of research

Despite the broad application of conventional polymeric membranes in the industries, ceramic membranes are superior in terms of better physical strength and stronger mechanical structure. The material robustness of ceramic membranes permits them to operate under high pressure, temperature and operating flux with adequate separation characteristics. However, pre-treatment is required prior to CMF in order to minimise and maintain suitable control of membrane fouling and avoidance of frequent back-flushing. Ozone is an effective pre-treatment prior to CMF when filtering SE. BAC filtration along with ozone can reduce the fouling potential in the ceramic membrane. Research has only looked at the effect of BAC and ozone pre-treatment in the improvement of drinking water quality by CMF. The SE wastewater could also be benefited by BAC and ozone pre-treatment.

The ceramic materials are known to affect the catalytic ozonation by generating \( ^\cdot \)OH radicals. \( ^\cdot \)OH radicals are considered widely in the literature as playing a role in the beneficial features of ceramic membranes in contact with ozone. However, it is not clear how the application of ozone improves ceramic membrane flux when filtering SE. Measurement of \( ^\cdot \)OH radicals using the \( R_c \) concept could provide useful information on the mechanism of ozone decomposition. Moreover, ozone is responsible for the formation of bromate during ozonation of bromide containing water. Tracing bromate formation along with \( ^\cdot \)OH radicals could be beneficial to clearly understand the mechanism. Based on the above literature survey, several questions are presented in order to identify the optimal use and better implication of combined ozone CMF system for the SE treatment:

- Is there any beneficial effect of combined ozonation and BAC filtration prior to MF ceramic membrane system for the treatment of SE wastewater?
- How the fouling layer formed on the membrane appears physically and how does its resistance contribute to the ability for ceramic membranes to operate at higher fluxes when ozone is used prior to the membrane?
- How do basic water properties of salinity, temperature and pH affect the permeability of MF ceramic membrane?
- How the presence of minerals and organics of synthetic SE affect the decomposition of ozone?
• How the presences of different ceramic materials affect the decomposition of ozone?
• What is the mechanism of ’OH radical formation during filtering ozonized solution through ceramic membrane?
• What is the potential for bromate formation during ozonation of bromide containing water, a major issue in ozone treatment of water, in the context of ozone use in conjunction with CMF?

2.11 References

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Chapter 3

Materials and methods
3.1 Introduction

In this chapter, the equipment and experiments carried out in this project are described. The main sections relate to the measurement of membrane properties that is relevant to understanding their performance. The setups of the various membrane testing experiment and the water quality analysis techniques are also shown.

3.2 Materials

3.2.1 Membranes

Two different pore sized (100 nm and 200 nm) tubular ceramic membranes (Figure 3.1(left)) were purchased from Pall Corporation (Australia). Each single membrane element had dimensions of 25 cm in length and a single channel. The outer diameter and channel diameter are 10 mm and 7 mm respectively. The total filtration surface area of the membranes is 0.0055 m². The inside-out membranes have similar support material (α-Al₂O₃). However, the membrane material of the 100 nm and 200 nm are ZrO₂ and α-Al₂O₃ respectively. The properties of both the membranes are given in Table 3.1.

<table>
<thead>
<tr>
<th>Properties</th>
<th>100 nm membrane</th>
<th>200 nm membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manufacturer</td>
<td>Pall Corp. (Australia)</td>
<td>Pall Corp. (Australia)</td>
</tr>
<tr>
<td>Length (cm)</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Outer diameter (mm)</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Channel diameter (mm)</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>Number of channel</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Support material</td>
<td>α-Al₂O₃</td>
<td>α-Al₂O₃</td>
</tr>
<tr>
<td>Membrane material</td>
<td>ZrO₂</td>
<td>α-Al₂O₃</td>
</tr>
<tr>
<td>Cross-sectional area of channels (cm²)</td>
<td>0.39</td>
<td>0.39</td>
</tr>
<tr>
<td>Membrane surface area (m²)</td>
<td>0.0055</td>
<td>0.0055</td>
</tr>
<tr>
<td>Element per m² (pcs)</td>
<td>45.5</td>
<td>45.5</td>
</tr>
<tr>
<td>Molecular weight cut-off (kDa)</td>
<td>200</td>
<td>400</td>
</tr>
</tbody>
</table>

In addition to the Pall membranes, a multi-channel ceramic membrane was obtained from Metawater Co., Ltd (Figure 3.1(right)). The 100 nm membrane is the scaled down version of the Metawater commercial unit which is commonly applied to water treatment applications. The 10 cm long membrane has 55 channels with 2 mm channel
diameter. The total filtration surface area of the membrane is 0.04 m². The properties of the membrane are given in Table 3.2.

**Table 3.2:** Properties of the multi-channel Metawater ceramic membrane.

<table>
<thead>
<tr>
<th>Properties</th>
<th>100 nm membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manufacturer</td>
<td>Metawater Co., Ltd.</td>
</tr>
<tr>
<td>Length (cm)</td>
<td>10</td>
</tr>
<tr>
<td>Outer diameter (mm)</td>
<td>18</td>
</tr>
<tr>
<td>Channel diameter (mm)</td>
<td>2</td>
</tr>
<tr>
<td>Number of channels</td>
<td>55</td>
</tr>
<tr>
<td>Support material</td>
<td>α-Al₂O₃</td>
</tr>
<tr>
<td>Membrane material</td>
<td>Titania based</td>
</tr>
<tr>
<td>Membrane surface area (m²)</td>
<td>0.04</td>
</tr>
</tbody>
</table>

**Figure 3.1:** Mono channel tubular ceramic membranes from Pall Corporation, Australia (left), Metawater ceramic membrane from Metawater Co., Ltd (right).

### 3.2.2 Chemicals

Real secondary effluent (RSE) was collected from Melbourne Water’s Western Treatment Plant (WTP), Werribee, Victoria, Australia, where more than 50% of Melbourne’s sewage is treated by an activated sludge-lagoon process.

The biological activated carbon (BAC) particles (Acticarb BAC GA1000N) were obtained from an operating ozone – BAC system in Castlemaine water reclamation plant, Castlemaine, Australia [2]. Other chemicals and reagents used in this study are given in Table 3.3.
Table 3.3: Summary of the major chemicals and reagents used in this study.

<table>
<thead>
<tr>
<th>Chemicals or reagents</th>
<th>Supplier / manufacturer</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beef extract</td>
<td>OXOID</td>
<td>To prepare synthetic secondary effluent (SSE)</td>
</tr>
<tr>
<td>Peptone</td>
<td>OXOID</td>
<td>To prepare SSE</td>
</tr>
<tr>
<td>Nitro humic acid</td>
<td>Sigma Aldrich</td>
<td>To prepare SSE</td>
</tr>
<tr>
<td>Tannic acid</td>
<td>BDH</td>
<td>To prepare SSE</td>
</tr>
<tr>
<td>Sodium lignin sulfonate</td>
<td>Sigma Aldrich</td>
<td>To prepare SSE</td>
</tr>
<tr>
<td>Sodium lauryle sulphate</td>
<td>Sigma Aldrich</td>
<td>To prepare SSE</td>
</tr>
<tr>
<td>Arabic gum powder (NH₄₂SO₄)</td>
<td>Sigma Aldrich</td>
<td>To prepare SSE</td>
</tr>
<tr>
<td>K₂HPO₄</td>
<td>BDH</td>
<td>To prepare SSE</td>
</tr>
<tr>
<td>NH₄HCO₃</td>
<td>AJAX Chemicals</td>
<td>To prepare SSE</td>
</tr>
<tr>
<td>MgSO₄</td>
<td>Sigma Aldrich</td>
<td>To prepare SSE</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>Sigma Aldrich</td>
<td>To prepare SSE</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>MERCK</td>
<td>To prepare SSE</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>Sigma Aldrich</td>
<td>Investigate the catalytic effect</td>
</tr>
<tr>
<td>TiO₂ (P25)</td>
<td>Degussa</td>
<td>Investigate the catalytic effect</td>
</tr>
<tr>
<td>SiC</td>
<td>Sigma Aldrich</td>
<td>Investigate the catalytic effect</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>Sigma Aldrich</td>
<td>Investigate the catalytic effect</td>
</tr>
<tr>
<td>Para-chlorobenzoic acid</td>
<td>Supelco</td>
<td>To measure 'OH radical formation</td>
</tr>
<tr>
<td>Tert-Butanol</td>
<td>Sigma Aldrich</td>
<td>To inhibit 'OH radical formation</td>
</tr>
<tr>
<td>KH₂PO₄</td>
<td>Sigma Aldrich</td>
<td>To prepare mobile phase for the SSE and phosphate buffer</td>
</tr>
<tr>
<td>Na₃HPO₄</td>
<td>Sigma Aldrich</td>
<td>To prepare mobile phase for the SSE</td>
</tr>
<tr>
<td>Methanol</td>
<td>Sigma Aldrich</td>
<td>To prepare mobile phase for the pCBA</td>
</tr>
<tr>
<td>H₃PO₄</td>
<td>Sigma Aldrich</td>
<td>To prepare mobile phase for the pCBA and to prepare indigo reagent</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>Sigma Aldrich</td>
<td>To prepare mobile phase for the pCBA</td>
</tr>
<tr>
<td>Potassium indigo trisulfonate</td>
<td>Sigma Aldrich</td>
<td>To prepare indigo reagent which will measure residual ozone</td>
</tr>
<tr>
<td>K₂HPO₄</td>
<td>Sigma Aldrich</td>
<td>To prepare phosphate buffer</td>
</tr>
<tr>
<td>KBr</td>
<td>MERCK Pty limited</td>
<td>To prepare Br⁻ stock solution</td>
</tr>
<tr>
<td>NaBrO₃</td>
<td>MERCK Pty limited</td>
<td>To prepare BrO₅⁻ stock solution</td>
</tr>
<tr>
<td>NaCl AR grade</td>
<td>MERCK Pty limited</td>
<td>Permeability of membrane in different salinity</td>
</tr>
<tr>
<td>NaCl (high purity)</td>
<td>Sigma Aldrich</td>
<td>Permeability of membrane in different salinity</td>
</tr>
<tr>
<td>HCl</td>
<td>Sigma Aldrich</td>
<td>To clean the used membranes</td>
</tr>
<tr>
<td>NaOH</td>
<td>Sigma Aldrich</td>
<td>To clean the used membranes</td>
</tr>
</tbody>
</table>
3.3 Membrane properties measurement

3.3.1 Pore size by gas permeation method

Determining the pore size and pore size distribution is the common means to characterize the membrane filters. The significance of the pore size and pore size distribution of membranes are understandable as the liquid flows through the pores and the suspended particles are retained at the pores. In this method, the pore size of the membranes were estimated by a gas permeability test [3]. The permeation of single gas driven by a total pressure across a porous membrane will be regulated by Knudsen diffusion – Poiseuille flow mechanism. The total mass flux can be obtained from the following Equation:

\[ N_{K-P} = \left( -\frac{8 \rho \varepsilon}{3 \tau} \sqrt{\frac{1}{2\pi R M T}} - \frac{\varepsilon r^2}{\tau 8\eta} \right) \nabla P \]  

(3.1)

Where, \( N_{K-P} \) is the steady-state gas permeation flux (kmol\( \cdot \)m\(^{-2}\)\( \cdot \)s\(^{-1}\)), \( r \) is the pore radius of the membrane (m), \( \varepsilon \) is porosity, \( \tau \) is the tortuosity, \( R \) is the gas constant (8.314 J\( \cdot \)mol\(^{-1}\)\( \cdot \)K\(^{-1}\)), \( M \) is the molar mass (kg/mol), \( T \) is temperature (K), \( \eta \) is viscosity (Pa\( \cdot \)s), \( P \) is the applied pressure (Pa). Integrating over the membrane thickness, the steady-state gas permeation flux is obtained:

\[ N_{K-P} = \left( \frac{8 \rho \varepsilon}{3 \tau \delta} \sqrt{\frac{1}{2\pi R M T}} + \frac{\varepsilon r^2}{\tau \delta 8\eta} \frac{1}{R T} \right) \Delta P \]  

(3.2)

In Equation 3.2, \( P_m \) (Pa) is the average pressure within the membrane pores. In another form,

\[ J_{K-P} = A_0 + B_0 P_m \]  

(3.3)

Where,
In order to obtain $A_0$ and $B_0$, gas permeation experiments are carried out at various $P_m$, while keeping the pressure difference across the membrane constant. Under this condition the gas permeation fluxes $N_{K-P}$ (kmol·m$^{-2}$·s$^{-1}$) through the membrane are measured. In terms of Equation 3.3, by plotting the curve of $J_{K-P}$ (kmol·m$^{-2}$·s$^{-1}$·Pa$^{-1}$) with $P_m$, the intercept with y-axis is $A_0$ and the slope is $B_0$. On this basis the membrane characteristics can be obtained from $A_0$ and $B_0$ by the following Equations:

\[
J_{K-P} = \frac{N_{K-P}}{\Delta p}
\]

\[
A_0 = \frac{8 \epsilon \tau}{3 \delta} \sqrt{\frac{1}{2\pi RMT}}
\]

\[
B_0 = \frac{\epsilon \tau^2}{\delta \eta R T}
\]

The test involves the porous membrane and a single gas such as nitrogen. The gas was forced to diffuse through the membrane by a total pressure difference exerted between the two sides of the membrane. The applied pressure on the membrane was varied in the range of 5–120 kPa while the pressure difference across the membrane was maintained constant at 1.00±0.01 kPa. Pressure difference across the membrane and the applied pressure were monitored using a digital manometer (TPI 665). A soap bubble meter was attached to the module to measure the flow rate of the gas passing through the membrane. A stop watch was used to record the time of the soap bubble passing through the soap bubble meter. A schematic diagram of the experimental setup is shown in Figure 3.2.
3.3.2 Pore size by porometry

In this method, a porometer (POROLUX™ 1000 series) was used to investigate the pore size of the membranes. The principle of capillary flow porometry is the displacement of a wetting liquid from the pores of the samples by applying a gas flow at increasing pressure [4, 5]. The pressure is used to calculate the pore size diameter with the Young-Laplace Equation 3.9.

$$P = \frac{4\gamma \cos \theta}{D} \tag{3.9}$$

Where $P$ is the pressure required to displace the liquid from the pore, $\gamma$ is the surface tension of liquid, $\theta$ is the contact angle and $D$ is the pore diameter. The method involves impregnation the sample with a wetting liquid. Porefil was used as a wetting liquid as it is inert and it has relatively low surface tension and vapour pressure. This allows obtaining a good wetting of the sample. The pressure builds up inside the pressure chamber starting from ambient pressure and the pores start to open gradually, starting with the largest pore, and the flow of gas through the sample is measured. The pressure increases until the wetting liquid is out of all pores resulting in the sample to be completely dried. This measurement is known as wet curve. The instrument deflates and a second run (dry run) is performed, in which the flow rate through the sample is measured. This measurement is known as the dry curve. From these measurements it is possible to obtain information on the largest and smallest pores, mean flow pore size,
and the distribution of pore sizes in the sample. The pressure is increased in different steps. At each pressure step, both pressure and flow are monitored and a data point is taken when stabilization criteria are met. This pressure step/stability method provides more accurate information, and can also be used at increased pressures [5].

### 3.3.3 Membrane material porosity
The porosity of the membranes was measured by the solvent displacement method. The weight of the membrane was measured in completely dry condition and after soaking the membrane in to deionized (DI) water for 2 hours.

\[
V_v = \frac{W_2 - W_1}{\rho V_T}
\]  

(3.10)

Where, \( V_v \) is the volume of void (m\(^3\)), \( W_1 \) and \( W_2 \) are the weight of membrane before and after the immersion in DI water respectively, \( \rho \) is the density of DI water and \( V_T \) is the total volume (m\(^3\)). The porosity is calculated using Equation 3.11,

\[
\varepsilon = \frac{V_v}{V_T} \times 100
\]  

(3.11)

Where, \( \varepsilon \) is porosity of the membrane. To reduce the effect of the air trapped in the scrim opening, the submerged membranes were also subjected to a deionised water flushing process for 2 min.

### 3.3.4 Membrane thickness
Scanning electron microscopy (SEM) was performed using a Jeol Neoscope to observe the cross section and the surface of the ceramic membrane. SEM samples were prepared by fracturing a membrane cross-section and then coated with gold (16-20 nm).

### 3.4 Lab-scale experimental apparatus

#### 3.4.1 Basic membrane filtration setup
Two different pore sized (100 nm and 200 nm) tubular ceramic membranes were purchased from Pall Corporation (Australia). Each single membrane element had dimensions of 250 mm in length, 10 mm outer diameter and 7 mm inner diameter. The
total filtration surface area was 0.0055 m$^2$. The inside-out membranes were operated in a conventional pressurized configuration using a direct filtration (dead-end) mode. A stainless steel Schumasiv membrane module was used to house the membranes. The specifications of the membranes are given in Table 3.1. Stainless steel fittings (Swagelok) and high pressure tubes were used for connecting the membrane rig. The feed was pumped using a low speed piston pump (Fluid Metering, Inc, QG 150). Pressure was monitored using a digital manometer (TPI 665). A schematic diagram of the experimental setup is shown in Figure 3.3. Each filtration was run for about 30 minutes at a constant flow rate of 20 mL/min. After each set of experiments, the ceramic membrane was rinsed with DI water using method described in Section 3.6.1 and the permeability of the DI water was measured again under the same experimental condition.

To investigate the effect of salinity on ceramic membranes, experiments were performed using different concentrations (0 – 30,000 mg/L) of sodium chloride (NaCl) ≥ 99.999% (metals basis) from Sigma-Aldrich. Ultra-high purity NaCl was used in order to avoid the effect of impurities present in the standard AR grade NaCl, (i.e., 6 mg/L Ca and 1.5 mg/L Mg in a 30,000 mg/L solution, as per supplier’s information). DI water was produced using a Millipore filter system. Before each filtration experiment, the permeability of the membrane was measured using DI water at a constant flow rate of 20 mL/min until a steady state was attained. During filtration, the pressure rise and the temperature were recorded. The rise in pressure was temperature corrected to a reference temperature of 20°C using Equation 3.12 and Equation 3.13 [6],

\[
P_{T=20} = P_{abs} \times \frac{\mu_{T=20}}{\mu_T}
\]

\[
\mu_T = 1.784 - (0.0575 \times T) + (0.0011 \times T^2) - (10^{-5} \times T^3)
\]

Where, $P_{T=20}$ is the pressure at 20°C (Pa), $P_{abs}$ is the absolute pressure (Pa), $\mu_{T=20}$ is the viscosity of water at 20°C and $\mu_T$ is the viscosity of water at temperature $T$.

The effect of temperature on ceramic membrane performance was investigated using 500 mg/L ultra-high purity NaCl solution at 0°C, 20°C, 30°C and 50°C. The feed tank along with the stainless steel membrane module was submerged into a water bath. The
temperature was maintained using an immersion heater circulator. To investigate the 0°C case, an ice slurry was used for the water bath.

The effect of pH in the range 2 - 10 was investigated using DI water, 500 mg/L, 5,000 mg/L and 15,000 mg/L ultra-high purity NaCl solutions. The pH was altered using 0.1 M HCl and 0.1 M NaOH solutions. During each filtration, the pressure rise and the temperature were recorded. The rise in pressure was temperature corrected to a reference temperature of 20°C using Equation 3.12 and Equation 3.13 [6]. The rejection of Na was calculated using Equation 3.14,

$$R_j = 100 \times \left(1 - \frac{C_{perm}}{C_{reject}}\right)$$  \hspace{1cm} (3.14)

Where, $R_j$ is the rejection (%), $C_{perm}$ is the concentration of Na in the permeate (mg/L) and $C_{reject}$ is the concentration of Na in the reject (mg/L).

### 3.4.2 Ozonation, BAC and ceramic membrane filtration setup

A BAC column with a height of 180 mm and diameter of 50 mm has been used in this test. The BAC feed was pumped at a flow rate of 15 mL/min. The empty bed contact time (EBCT) of the column was 20 min. A 100 nm tubular ceramic membrane was used as an MF unit. The specification of the membrane is given in Table 3.1. A stainless steel Schumasiv membrane module was used to house the membrane. Stainless steel fittings
(Swagelok) and high pressure tubes were used for connecting the membrane rig together. The membrane feed was pumped using a low speed piston pump (Fluid Metering, Inc, QG 150) at a flow rate of 15 mL/min. Pressure was monitored using a digital manometer (TPI 665). The schematic of the experimental setup is shown in Figure 3.4.

![Figure 3.4: Ozone-BAC-Ceramic membrane filtration rig.](image)

An A2Z ozone generator was used to generate ozone. Pure oxygen was supplied to the generator at a flow rate of 2 L(NTP)/min. In a beaker, 1.5 L of 500 mg/L NaCl solution was prepared. Ozone was injected in the feed sample at a flow rate of 1.4 L(NTP)/min. During Ozone – BAC – ceramic membrane experiment, measured residual ozone was 0.3 ~ 0.5 mg/L prior to BAC column. During Ozone – ceramic membrane experiment, measured residual ozone was 2 ~ 3 mg/L prior to ceramic membrane. RSE as mentioned in Section 3.3.2 was used as the feed of these tests. RSE sample was pre-filtered by 10 micron filters. The RSE was fed to the ceramic membrane in four different arrangements:

A. ceramic membrane only;
B. BAC followed by ceramic membrane;
C. Ozone followed by ceramic membrane; and
D. Ozone followed by BAC then followed by ceramic membrane.
The membrane was operated in an inside-out mode (membrane coating is on the inside channel) in a conventional pressurized configuration using a direct filtration (dead-end) mode. This replicates the operation of real plants by the water industry. Each filtration was conducted for at least four hours. Hydraulic (liquid) backwashing was performed periodically via pressurized DI water and a series of valves. The backwash was set to occur after every 30 min of filtration at a backwash pressure of 4 bar. Samples were collected before and after each filtration steps to investigate different water quality parameters. Prior to each experiment the membrane was cleaned using a prescribed cleaning method in Section 3.6.2. The effectiveness of the cleaning procedure was confirmed by performing clean water test at 180 L/m²·h for a minimum of one hour and achieving a TMP of 15 kPa ± 2 kPa.

### 3.4.3 Vacuum filtration test

To be able to capture and study the nature of cake layer formed during MF of RSE, Millipore MF nitrocellulose membrane filters (100 nm) were used in this test instead of 100 nm ceramic membrane. This 47 mm diameter membrane is composed of mixed cellulose acetate & cellulose nitrate. The membrane has a thickness of 100 µm and is hydrophilic in nature. The membrane filters have the same simple pore size feature of the 100 nm tubular ceramic membrane described in Section 3.3.1. The experiment has been conducted in Victoria University, Melbourne using the sample RSE, mentioned in Section 3.3.2. The schematic of the experimental setup is shown in Figure 3.5.

**Figure 3.5: Vacuum filtration test unit.**

A Büchner funnel filtration apparatus was connected to a motorized vacuum pump (Rocker 600) using rubber tubes. The pump operates a vacuum with a constant pressure of 80 kPa. An HD webcam (Logitech C270) was used to monitor the level of liquid above the membrane. The membrane filter was loaded into the filtration apparatus. 150 mL of RSE was passed through the membrane filter to form cake layer on the filter. The
HD webcam was used to take photos to accurately measure the exact amount of filtrate volume with time. In another batch of experiment, RSE was treated with ozone for 30 seconds using a diffuser. Ozone was supplied from an A2Z ozone generator which was described in Section 3.4.2. The ozone pre-treated sample was loaded into the membrane filter and the filtration test was repeated. All the membrane filters and filtrates for direct RSE and pre-treated RSE runs were collected to use in stepped permeability test as described in Section 3.4.4.

### 3.4.4 Stepped permeability test

This test was conducted in the lab of The University of Melbourne. Membrane filters containing cake layers produced by direct RSE and ozone pre-treated RSE (Section 3.4.3) were used in this experiment. The schematic of the experimental setup is shown in Figure 3.6. The membrane filters were loaded onto a filtration plate and secured in place by a cylinder and an o ring. 125 mL of solution which was collected previously in vacuum filtration experiment (Section 3.4.3) was loaded onto the apparatus. A piston was activated to pressurise the solution at a controlled pressure, forcing the liquid through the membrane filter and out into the filtrate receiving container. A computer was used to set pressures utilising a pressure transducer to feedback the pressure to the piston control system using the LabVIEW program. The computer applied these pressures by communicating to a pressure controller, which was also connected to a pressurized airline and linear encoder (which is connected to the piston).

Once a set pressure had been established, the next pressure begins. A tolerance level of 1-3% was used, for when the program considers that test complete and proceeds to the next step pressure. The run was completed if one of two conditions were met: either if all the set pressures were achieved, or if volume of solution loaded into the cylinder runs out. The filtration rig experiment was carried out using step pressures of 10, 20, 50, 100, 150, 200 and 300 kPa (gage pressure). These reflect the range within a typical ceramic membrane filtration process (up to 300 kPa TMP). The LabVIEW program also logs and manipulates the basic data, and controls the experimental pressure in addition to monitoring the criteria used to evaluate when to step between pressures. A graphical interface allows to view the progress of the experiment, monitoring transient behaviour of the \( t \ vs \ V^2 \) data and the slope is calculated [7].
3.4.5 Effect of minerals and organics on ozone decomposition

This experiment was conducted in the lab of Victoria University, Melbourne. In a beaker, 1.5 L of working solution was prepared by mineral components of the synthetic secondary effluent (SSE, details given in Table 7.1). A schematic diagram of the experimental setup is shown in Figure 3.7.

![Figure 3.6: Stepped pressure permeability test unit.](image)

**Figure 3.6:** Stepped pressure permeability test unit.

![Figure 3.7: Schematic of the experimental setup for the effect of minerals and organics on ozone decomposition.](image)

**Figure 3.7:** Schematic of the experimental setup for the effect of minerals and organics on ozone decomposition.
An A2Z ozone generator was used to generate ozone. Pure oxygen was supplied to the generator at a flow rate of 2 L/min (NTP). Ozone was applied into the prepared working solution using a bubble diffuser at a flow rate of 1.4 L(NTP)/min. After 10 minutes of ozonation, the generator was stopped and immediately after that samples have been collected with frequent time interval. The samples have been directly stored into pre-prepared centrifuge tubes containing indigo reagents. The residual concentration was measured using the method detailed in Section 3.5.8. Duplicate experiments were conducted by replacing the minerals of SSE with the organics of SSE and only SSE.

### 3.4.6 Effect of ceramic materials on ozone decomposition

This test has been conducted in the lab of Victoria University, Melbourne. Al₂O₃, SiC and TiO₂ (Table 3.4) powders were rinsed thoroughly with DI water until they give a stable pH of 7. The powders were dried in a desiccator. An A2Z ozone generator was used to generate ozone. Pure oxygen was supplied to the generator at a flow rate of 2 L(NTP)/min. In a beaker, 1.5 L of 500 mg/L NaCl solution was prepared. Ozone was applied into the NaCl solution using a bubble diffuser at a flow rate of 1.4L(NTP)/min. After 10 minutes of ozonation, the ozone generator was stopped and immediately after that an overhead stirrer was turned on to mix the solution homogeneously. Samples were collected to measure residual ozone concentration with frequent time interval into centrifuge tubes containing indigo reagents. The residual concentration was measured using the method detailed in Section 3.5.8. A schematic diagram of the experimental setup is shown in Figure 3.8. The decomposition of ozone in the NaCl was used as the background test.

#### Table 3.4: Specification of the used ceramic materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Manufacturer / supplier</th>
<th>BET (m²/g)</th>
<th>Pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>Sigma Aldrich</td>
<td>253.6</td>
<td>342</td>
</tr>
<tr>
<td>SiC</td>
<td>Sigma Aldrich</td>
<td>0.26</td>
<td>0.72</td>
</tr>
<tr>
<td>TiO₂ P25</td>
<td>Degussa</td>
<td>51.5</td>
<td>5560</td>
</tr>
</tbody>
</table>

In separate tests, 30 g of each powder was added into the ozonized solution immediately after stopping ozonation. Ozonized samples containing the powders were filtered before collecting into the centrifuge tubes using 0.45 micron syringe filters.
3.4.7 Ozone decomposition by Al$_2$O$_3$ and TiO$_2$ powders in the presence of pCBA

This test has been conducted in the lab of Curtin University, Perth. Oxygen was supplied to an ozone generator (American Ozone Systems Inc) to generate ozone. Stock solutions of ozone were prepared by continuously bubbling the generated ozone into ice-cooled MQ water through a Dreschel bottle as described by Bader and Hoigne (1981) [8]. The concentrations of the stock solutions were approximately 50 mg/L, which were standardised by measurement of the UV absorbance ($\varepsilon_{258\text{ nm}} = 3000 \text{ M}^{-1}\text{cm}^{-1}$). In a beaker, 500 mL of a mixture containing para-chlorobenzoic acid (pCBA), tert-butanol and phosphate buffer was mixed together. pCBA was added to the solution as an ozone-resistant probe compound for hydroxyl radical (•OH) measurement [9]. pCBA was selected as an •OH-probe compound because it has a very low reactivity with molecular ozone [10] but reacts readily with •OH [11-13]. Tert-butanol was added to stabilize the decay of ozone in the solution [14]. The final concentrations of pCBA and tert-butanol in the mixture were 10 µM and 25 µM respectively. The beaker was placed on a magnetic stirrer and the solution mixed under moderate stirring. A schematic diagram of the experimental setup is shown in Figure 3.9.

Stock ozone solution was spiked into the beaker using a glass syringe so that the effective ozone concentration in the beaker reached 5 mg/L approximately. Samples were collected to measure residual ozone and pCBA concentration with frequent time interval into centrifuge tubes. The centrifuge tubes have been prefilled with indigo reagents. The residual ozone concentration was measured using the method detailed in Section 3.5.8. The pCBA concentration was measured using the method detailed in Section 3.5.9. The decomposition of ozone in the MQ was used as the background test.
In order to investigate the effect of powders on ozone decay, Al₂O₃ and TiO₂ powders were washed and rinsed multiple times until the solution reached a stable pH of 7. The washed powders were dried in a desiccator. In separate tests, 30 grams of each powder was added into the mixture solution of pCBA and tert-butanol. Stock ozone solution was spiked immediately into the beaker containing the mixture and powder using a glass syringe to achieve an effective ozone concentration of approximately 5 mg/L. Samples have been collected into prefilled centrifuge tubes containing indigo reagents. Samples were filtered using 0.45 micron syringe filters prior to measure the ozone concentration using method described in Section 3.5.8. The pCBA concentration was measured using the method detailed in Section 3.5.9.

3.4.8 Ozone decomposition through Pall ceramic membrane

The experiments have been carried in the lab of Victoria University, Melbourne. A 200 nm tubular ceramic membrane purchased from Pall Corporation (Australia) was used to investigate the ozone decay across the membrane. The detail of the membrane is given in Table 3.1. An A2Z ozone generator was used to generate ozone. Pure oxygen was supplied to the generator at a flow rate of 2 L(NTP)/min. In a beaker 1.5 L of DI water was added. Ozone was continuously bubbled into the beaker using a bubble diffuser. The membrane was held in a horizontal position with clamps in its two ends. A low speed piston pump (Fluid Metering, Inc, QG 150) was set to feed the ozonized solution into the membrane at a flow rate of 20 mL/min.

A schematic diagram of the experimental setup is shown in Figure 3.10. To measure the residual ozone concentration, samples were collected from different locations into some previously prepared centrifuge tubes containing indigo reagents. A stainless steel three
way valve (Swagelok) was connected to the entrance of the membrane in a way so that samples can be collected from the feed of the membrane easily. Permeate was taken by collecting the solutions dripping directly from the membrane tube’s outer surface into the centrifuge tubes. The reject was collected by opening the end valve quickly and then closing it immediately to continue the permeation of ozonized solution across the membrane. The residual ozone concentration was measured using the method detailed in Section 3.5.8.

![Figure 3.10: Schematic of the experimental setup for the ozone decay across Pall ceramic membrane.](image)

In separate experiments, DI water was replaced by 500 mg/L NaCl solution, minerals of SSE, organics of SSE components and complete SSE. The components of SSE are given in Table 7.1. The residual ozone concentration was measured using the method detailed in Section 3.5.8.

### 3.4.9 Ozone decomposition through Metawater ceramic membrane

This test has also been conducted in Victoria University, Melbourne. All the above tasks in Section 3.4.8 were repeated by replacing the tubular ceramic membrane with a multichannel ceramic membrane obtained from Metawater Co. Ltd. The membrane element had dimensions of 10 cm in length and 0.04 m² of total filtration surface area (Table 3.2). A stainless steel membrane module (Metawater) was used to house the membrane. Stainless steel fittings (Swagelok) and high pressure tubes were used for connecting the membrane rig together. The feed was pumped using a low speed piston pump (Fluid Metering, Inc, QG 150) at a flow rate of 47 mL/min (70 L/m²·h). Feed and reject was collected following the similar method used for the Pall ceramic membrane. The permeate was collected from the permeate line of the stainless steel module. A schematic diagram of the experimental setup is shown in Figure 3.11.
3.4.10 Hydroxyl radical formation through Pall ceramic membrane

This experiment has been conducted in Curtin University, Perth. The experiments have been conducted in batch mode by recirculating an ozonized sample through a stainless steel Pall membrane empty module, Al$_2$O$_3$ membrane (200 nm), ZrO$_2$ membrane (100 nm) and TiO$_2$ membrane (5 nm). Stock ozone solution was generated by the method described in Section 3.4.7. The inlet and outlet of the membrane rig were connected to a glass beaker so that the feed solution can be directed through the membrane rig and the permeate returns to the beaker. A schematic diagram of the experimental setup is shown in Figure 3.12.

200 mL of tap water (0.29 mg/L DOC; 220 µS/cm conductivity; 0.34 NTU turbidity) was added to the glass beaker (250 mL). $p$CBA and Br$^-$ were spiked into that tap water, so that the final concentration of $p$CBA and bromide were 0.5 µM and 6.25 µM respectively. The measured pH value was always 7.5. The beaker was covered with para-film and placed on a magnetic stirrer. First the solution was stirred vigorously for 10 sec to ensure a good homogeneity. Then the stirring was stopped and stock ozone solution was spiked into the beaker using a glass syringe so that the effective ozone concentration in the beaker reached 5 mg/L approximately. The pump was turned on immediately. After each specified reaction time, the recirculated samples (3 mL) have been collected into a tube containing buffered indigo tri-sulphonate to quench the ozone reaction. Ozone was analysed using the method detailed in Section 3.5.8 and $p$CBA was analysed using the method detailed in section 3.5.9. After 15 minutes, a sample (3.5
mL) was collected for bromide and bromate analysis using the method detailed in section 3.5.10.

![Diagram](image)

**Figure 3.12**: Schematic of the experimental setup for investigating the $^\cdot$OH radical formation across ceramic membranes in sample recirculating mode.

### 3.4.11 Hydroxyl radical formation through Metawater ceramic membrane with recirculating solution

The experiments described in Section 3.4.10 were conducted using the Metawater empty module (no membrane inside the module) and Metawater ceramic membrane instead of Pall tubular membranes.

### 3.4.12 Hydroxyl radical formation through Metawater ceramic membrane with single-pass solution

This experiment has been conducted in Curtin University, Perth. The experiments have been conducted in batch mode by recirculating an ozonized sample through a stainless steel Metawater membrane empty module and 100 nm Metawater ceramic membrane. Stock ozone solution was generated by the method described in Section 3.4.7. A schematic diagram of the experimental setup is shown in Figure 3.12.

1000 mL of tap water (0.29 mg/L DOC; 220 μS/cm conductivity; 0.34 NTU turbidity) was added to the glass beaker (1200 mL). pCBA and Br were spiked into that tap water, so that the final concentration of pCBA and bromide were 0.5 μM and 6.25 μM respectively. The measured pH value was always 7.5. The beaker was covered with para-film and placed on a magnetic stirrer. First the solution was stirred vigorously for 10 sec to ensure a good homogeneity. Then the stirring was stopped and stock ozone
solution was spiked into the beaker using a glass syringe so that the effective ozone concentration in the beaker reached approximately 10 mg/L. The pump was turned on immediately. The ozonized tap water sample was pumped into the module for a period of time to ensure a complete fill of fresh feed. After a sufficient time, the pump was stopped and the sample held inside the membrane rig. This was done for four different contact times (1 min, 3 min, 5 min and 7 min) over the course over a single ozonated water feed run. Ozone was analysed using the method detailed in Section 3.5.8 and pCBA was analysed using the method detailed in section 3.5.9.

![Figure 3.13: Schematic of the experimental setup for investigating the •OH radical formation across Metawater membrane in single pass mode.](image)

In duplicate tests, the pCBA was replaced by 50 mM tert-BuOH. Tert-BuOH was used in order to determine whether ozone was transformed into •OH, as it is an effective scavenger with stronger radical capturing ability. The reaction rate constants between tert-BuOH and either •OH or O₃ has been reported as $k_{OH} = 5.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{O₃} = 3.0 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ respectively [15-18], highlighting the substantial ability for tert-BuOH to rapidly consume •OH radicals and remove their function from the investigation into the reaction. After each specified reaction time, samples (11 mL) from the feed beaker and the permeate outlet have been collected into a tube containing buffered indigo trisulphonate. While taking sample from the permeate outlet, permeate for at least 40 seconds have been allowed to dispose. After that, sample was collected into the tube containing indigo reagent. This was to confirm the collection of sample that was in contact with the membrane material. Ozone was analysed using the method detailed in
Section 3.5.8. Bromide and bromate analysis have been conducted using the method detailed in section 3.5.10.

### 3.5 Analytical methods

In this section, all the analytical techniques used in this research for different water quality parameters are briefly described. Molecular weight analysis of SSE was conducted by high performance liquid chromatography (HPLC). Analysis of residual ozone concentration, pCBA concentration and bromate analysis are also detailed in this section. Nitrogen porosimetry analysis was conducted to measure the BET surface area of ceramic powders.

#### 3.5.1 pH

A standard WTW pH meter (inoLab pH 7110) was used to measure the pH of the solution. The pH meter probe was wiped with Kimwipes followed by a DI water rinse. The calibration was performed regularly with buffer solutions at pH 4, 7 and 10.

#### 3.5.2 UVA$_{254}$

UVA$_{254}$ was measured using a HACH spectrophotometer (DR 5000) with a 1 cm quartz cell. Background measurement was performed using DI water.

#### 3.5.3 Dissolved organic carbon (DOC)

DOC was measured using a SHIMADZU Total Organic Carbon Analyzer (TOC-VCSH), which was equipped with an auto-sampler. DOC concentration was indirectly obtained by subtracting the two directly measured parameters: the total carbon (TC) and the inorganic carbon (IC). All samples were filtered through 0.45 µm membrane filter prior to analysis.

#### 3.5.4 Colour

Colour was measured using HACH spectrophotometer (DR 5000) with a 10 cm quartz cell. Background measurement was performed using the DI water.

#### 3.5.5 Turbidity

Turbidity was measured using a Hanna Turbidimeter (HI88703). Background measurement was performed using the DI water. The instrument was regularly calibrated with standard calibration kit (Hanna).
3.5.6 Conductivity and total dissolved solid (TDS)

The electrical conductivity and total dissolved solid (TDS) of the samples were measured using a TPS conductivity-salinity meter (WP-84 conductivity-Salinity). The instrument was calibrated using a KCl standard solution (0.01M).

3.5.7 Apparent molecular weight distribution (AMWD)

Molecular weight distributions of the wastewater components by Liquid Chromatography (LC) analyses were performed with a PDA and fluorescence detector in series. LC Method was performed using a TSK gel column (G3000 SW, C-No.SW3600482) at room temperature with a phosphate buffer (10 mM KH$_2$PO$_4$ + 10 mM Na$_2$HPO$_4$) as the mobile phase. The column was operated with a flow-rate of 0.5 mL/min and a 50 mL injection volume. This was coupled with sequential on-line detectors consisting of a UV visible photodiode array (λ = 200 - 800 nm) and a fluorescence detector (RF-10AXL). The response of the on-line fluorescence detector depends on the chosen excitation and emission wavelengths. In this study, fluorescence excitation and emission wavelengths of 295 nm/350 nm (ex/em) were applied, since such wavelengths were known to be specific for protein-like compounds. Polystyrene sulphonate (PSS) molecular weight standards of 3420, 4600, 6200, 15,650 and 39,000 Da were used to calibrate the LC column.

3.5.8 Ozone concentration

The concentrations of dissolved ozone in the experimental reaction solutions were determined by the Indigo Method [8]. The method is based on decolourization of the indigo reagent by ozone, where the loss of colour is directly proportional to the ozone concentration. High purity indigo trisulfonate (>80%) was used as the indigo reagent which has a molar absorptivity of about 20000 M$^{-1}$cm$^{-1}$ at 600 nm. To measure the residual ozone the absorbance of indigo trisulfonate after reaction with sample was subtracted from that of an ozone free blank. The absorbance at 600 nm has been measured using a DR 5000 spectrophotometer (HACH) and an UVmini-1240 UV-vis spectrophotometer (Shimadzu) in the lab of Victoria University and Curtin University respectively.
3.5.9 pCBA concentration

pCBA was quantified by high performance liquid chromatography (HPLC) (Agilent Technologies 1200 Series) with UV detection at 240 nm. The flow rate and eluent were 0.7 mL/min of 70% methanol and 30% 10 mM phosphoric acid. The column was a 4.6 mm × 250 mm Kinetex XB-C18 (Phenomenex) 5μm particle size, with a pre-column attachment.

3.5.10 Bromide and bromate concentration

Bromide and bromate ions were measured simultaneously via ion chromatography using a Dionex ICS3000 (AG9HC/AS9HC) followed by a post-column reaction, according to the standard operating procedure for an existing method previously reported by Salhi and von Gunten (1999) [19]. All samples were measured in duplicate and blank analyses were performed. The limits of detection (LODs) were calculated for every analytical batch using the EPA Method Detection Limit method (US-EPA 2004). The average LOD for bromide was 2 μg L⁻¹ (25 nM) and for bromate was 0.5 μg L⁻¹ (4 nM).

3.5.11 Nitrogen porosimetry

The physicochemical properties of ceramic powder samples (Al₂O₃, SiC and TiO₂) and BAC particles were measured by adsorption–desorption isotherms of nitrogen (Micromeritics ASAP2000, USA). Prior to the measurements, the samples were degassed at 250°C for 12 h under vacuum to remove moisture. The specific surface area and pore size distribution of the powers were determined by the Brunauer–Emmett–Teller (BET) and the Barrett–Joyner–Halenda (BJH) equations, respectively. Both were determined by the software provided by the supplier.

3.6 Membrane cleaning methods

3.6.1 Cleaning with MilliQ water

When only ozone or minerals were applied on the membranes, only MilliQ was used to rinse the membranes. Rinsing was continued until a steady state TMP was achieved.

3.6.2 Membrane chemical clean

To remove accumulated organic and inorganic materials from the membrane, the following chemical rinsing steps were adopted [1]:
- Rinse with clean, hot water for 10 min;
- Clean with sodium hydroxide (2% w/v) for 20-30 min (the temperature should be 75-80°C);
- Rinse with clean, hot water for 10 min;
- Clean with nitric acid (2% w/w) for 20-30 min, (the temperature should be 75-80°C); and
- Rinse with clean water until pH is neutral

3.7 References


Chapter 4

Effect of pre-treatment processes on ceramic membrane performance
4.1 Introduction

This chapter investigates the effect of the widely used ceramic membrane pre-treatment processes, ozonation and biological activated carbon (BAC), on the permeability of real secondary effluent (RSE) through a ceramic microfiltration (MF) membrane. The RSE was fed to the ceramic membrane after different pre-treatment arrangements: membrane only (no pre-treatment), BAC – membrane, Ozone – membrane and Ozone – BAC – membrane. The membrane used in this study was a 0.1 µm tubular ceramic membrane (Pall Corporation). The membrane has a dimension of 250 mm in length, 10 mm outer diameter and 7 mm inner diameter with a ZrO₂ filtration layer on top of an Al₂O₃ support layer. Multi-cycle filtration tests (30 min filtration followed by 1 min backwashing) were conducted to correlate the bench scale filtration tests with the full scale plants. General water quality parameters like dissolved organic carbon (DOC), UVA₂₅₄ absorbance and colour are then presented for individual treatment methods (i.e., ozonation, BAC filtration and ceramic membrane filtration (CMF)) and for all different pre-treatment options with ceramic membranes. Apparent molecular weight distribution (AMWD) was presented to explain the characteristics of the RSE during each treatment method. The unified membrane fouling index (UMFI) was used to evaluate the relative effectiveness of the different pre-treatment methods on fouling reduction. The goal of this investigation in the thesis was to explore the impact to the flux performance of the ceramic membrane as a result of the influences of these pre-treatment approaches on model real wastewater quality.

4.2 Characterization of RSE

RSE was collected from the Melbourne Water Western Treatment Plant (WTP), Werribee, Victoria, Australia. The RSE was collected from the maturation lagoon overflow of WTP before the UV disinfection and chlorination, which corresponds to the water that would be fed to a membrane plant for reuse. The sample wastewater was pre-filtered by 10 µm paper filters in order to remove the particulate matters from it. This water is referred as RSE throughout the following chapter. The characteristics of the sample water along with the properties of RSE found in literature are given in Table 4.1. It can be seen that, the quality of the RSE given in literature have a wide range of values. The pH, UVA₂₅₄, conductivity and chemical oxygen demand (COD) of the sample RSE used in this study are very similar to what was given in the literature (Table
The colour, turbidity, total dissolved solid (TDS) and dissolved organic carbon (DOC) of the sample RSE are found to be dissimilar. This is due to the different types of secondary treatment in different treatment plant.

**Table 4.1:** Characteristics of RSE used in this work, and comparison to other studies reported in literature.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
<th>Other studies</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.7-7.9</td>
<td>7.3 [1], 7.8 [2], 7.4-8 [3]</td>
</tr>
<tr>
<td>UV A$_{254}$, cm$^{-1}$</td>
<td>0.218±0.02</td>
<td>0.14 [4], 0.22 [2], 0.34 [5]</td>
</tr>
<tr>
<td>Colour, Pt-Co</td>
<td>35-37</td>
<td>109 [5], 56-85 [3]</td>
</tr>
<tr>
<td>Turbidity, NTU</td>
<td>0.9±0.1</td>
<td>7.3 [4], 1.5 [1]</td>
</tr>
<tr>
<td>Conductivity, μS/cm</td>
<td>1665±35</td>
<td>1065 [5], 1620-1950 [3]</td>
</tr>
<tr>
<td>Total dissolved solid (TDS), ppm</td>
<td>883±5</td>
<td>1038 [6]</td>
</tr>
<tr>
<td>Dissolved organic carbon (DOC), mg/L</td>
<td>13±0.5</td>
<td>11.7 [1], 11.4 [2]</td>
</tr>
<tr>
<td>Chemical oxygen demand (COD), mg/L</td>
<td>27.9±1</td>
<td>27 [6], 52.5 [7]</td>
</tr>
</tbody>
</table>

Fluorescence excitation-emission matrix (EEM) spectra of the RSE are shown in Figure 4.1. The RSE has shown at least two peak locations (280 nm/352 nm, 330 nm/425 nm, Ex/Em). Fluorescence peaks with Em < 380 nm represent protein-like substances (tyrosine and tryptophan), and fluorescence peaks with Em > 380 nm represent humic-like substances [8-11]. Her et al. (2003) used two pairs of excitation and emission wavelengths specific to protein like and fulvic like humic substances (HS) at Ex: 278 nm/Em: 353 nm and Ex: 337 nm/ Em: 423 nm respectively for the fluorescence detector [12]. Additionally, Salanis et al. (2011) has shown that tryptophan-like proteins fluoresce at Ex: 278-280 nm/Em: 320-350 nm [13]. Therefore, in this study peak location with excitation and emission wavelengths of 278 and 353 nm was selected for detecting protein-like substances and excitation and emission wavelengths of 330 and 425 nm was selected for detecting fulvic like substances.
4.3 Treatment of RSE by different processes

Table 4.2 shows the operating conditions of hybrid ozone-BAC-CMF system. The detail of the experiment is given in Section 3.4.2. Figure 4.2 shows the average removal percentages of DOC, UVA$_{254}$ and colour individually by CMF, BAC filtration and ozonation. It is evident from Figure 4.2 that both BAC and ozone were very effective for the removal of colour and UVA$_{254}$ absorbance compared to the CMF. Ozone removed colour by oxidizing the colour transmitting compounds of the RSE (i.e., compounds with conjugated C–C double bonds or aromatic rings, particularly HS) and producing more colourless materials. Removal of double bonds and aromatic rings is also shown by the 52% reduction in the UVA$_{254}$ [5, 14]. This finding confirms a well-known effect for improving treated water aesthetics [5, 14-16]. The significant UVA$_{254}$ reduction (approximately 47%) by BAC filtration indicated the removal of HS [17]. However, DOC reduction was consistently low (4~5%) for all processes. BAC filtration potentially removed the highest DOC (average 10%). Li et al. (2005) studied two parallel BAC filters to treat secondary effluent and observed an average DOC removal efficiency of 14% [18]. From these results, it can be observed that, both BAC and ozone are effective in terms of removing UVA$_{254}$ and colour from the RSE. Therefore, these pre-treatment options can be effectively used to improve the feed water quality of the CMF process.
**Table 4.2:** Operating conditions of different treatment steps.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane</td>
<td></td>
</tr>
<tr>
<td>Filtration area</td>
<td>0.0055 m²</td>
</tr>
<tr>
<td>Pore size</td>
<td>100 nm</td>
</tr>
<tr>
<td>Filtration mode</td>
<td>Dead end</td>
</tr>
<tr>
<td>Pump flow rate</td>
<td>15 mL/min</td>
</tr>
<tr>
<td>Flux</td>
<td>180 L·m⁻²·h⁻¹</td>
</tr>
<tr>
<td>Backwash frequency</td>
<td>30 min</td>
</tr>
<tr>
<td>Backwash pressure</td>
<td>4 bar</td>
</tr>
<tr>
<td>Ozone</td>
<td></td>
</tr>
<tr>
<td>Gas flow rate</td>
<td>1.4 L/min</td>
</tr>
<tr>
<td>Mass concentration</td>
<td>0.11 g/L</td>
</tr>
<tr>
<td>Production rate</td>
<td>13.05 g/L</td>
</tr>
<tr>
<td>BAC</td>
<td></td>
</tr>
<tr>
<td>Empty bed contact time</td>
<td>20 min</td>
</tr>
<tr>
<td>Flow rate</td>
<td>15 mL/min</td>
</tr>
<tr>
<td>BET surface area</td>
<td>502 m²/g</td>
</tr>
<tr>
<td>Depth of bed</td>
<td>180 mm</td>
</tr>
</tbody>
</table>

**Figure 4.2:** Removal of DOC, UVA₂₅₄ and colour of RSE by CMF, BAC filtration and ozonation (Temperature: 22±1°C).

### 4.4 Pre-treatment effect on ceramic membrane performance

#### 4.4.1 Effect on the water quality

Figure 4.3(a) shows the removal percentages of DOC, UVA₂₅₄ and colour from RSE by CMF alone, BAC-CMF, ozone-CMF and ozone-BAC-CMF. Overall, the ozonation followed by CMF (even with BAC) was the most efficient in removing UVA₂₅₄ (63%)
and colour (97%). With BAC only before CMF was found to be most efficient in removing DOC.

Figure 4.3b shows the removal percentages of DOC, UVA$_{254}$ and colour from RSE by the unit contribution of each stage in the BAC-CMF system. Higher percentages (43%) of UVA$_{254}$ reduction has been observed by BAC filtration compared to CMF. This implied that, BAC reduced greater HS than the CMF [17]. The DOC and colour removal by BAC filtration was 13% and 69% respectively. Pramanik et al. (2014) studied the BAC filtration as a pre-treatment for reducing the organic fouling of a MF membrane in the treatment of secondary effluent and found the reduction in DOC and colour by just the BAC were 32% and 78% respectively [17]. The removal of DOC can be attributed simultaneously to the adsorption of bio-refractory compounds and bio-oxidation of biodegradable organic matter by the BAC particles.

Figure 4.3c shows the removal percentages of DOC, UVA$_{254}$ and colour from RSE by ozonation and ozonation followed by CMF. The reduction of DOC by ozonation was not significant (7%) however, ozonation effectively reduced UVA$_{254}$ (63%) and colour (88%) from the RSE as observed by others before. Dow et al. (2013) investigated the performance of ceramic MF membrane to treat RSE with ozone and/or coagulation pre-treatment [15]. It was found that ozone reduced DOC, colour and UVA$_{254}$ by 5%, 52% and 85% respectively. Compared to the results obtained by Dow et al. (2013), the effect of ozonation on the quality of RSE is found slightly better in this study. This indicates that ozone has been playing a significant role in improving quality of RSE prior to entering the CMF.

Figure 4.3d represents the removal percentages of DOC, UVA$_{254}$ and colour from RSE by the full process train consisting of ozonation, BAC filtration then CMF. The negative value in the removal percentages of UVA$_{254}$ for the ozonized RSE through BAC filtration was due to the increase in UVA$_{254}$. The rises in the UVA$_{254}$ are assumed to be due to the improved clarity of the RSE sample by ozonation which enables better light absorbance [15]. Again, ozone played a key role in removal of UVA$_{254}$ and colour, and since BAC followed ozone, its removal contribution was not as strong as compared to when BAC is used without ozone (Figure 4.3b).
From these results, it can be seen that, with any pre-treatment option prior to CMF the UVA\textsubscript{254} was reduced more than 48% where DOC was reduced 13% at most. Therefore to obtain a better understanding of the removal efficiencies of different pre-treatments, AMWD of the samples needs to be explored. High performance liquid chromatography – size exclusion chromatography (HPLC-SEC) is a good indicator of chemical and physical changes in the properties of the organics at molecular level.

\textit{Figure 4.3:} Removal of DOC, UVA\textsubscript{254} and colour of RSE by \textbf{a.} all four sequences using ceramic membrane; unit contribution for each stages of \textbf{b.} BAC-CMF; \textbf{c.} Ozone-CMF; \textbf{d.} Ozone-BAC-CMF system (Temperature: 22±1°C; Flux: 180 L·m\textsuperscript{-2}·h\textsuperscript{-1}).

Figures 4.4(a-d) and 4.5(a-d) represent the fluorescence spectrum at 280 nm/352 nm (Ex/Em) and 330 nm/425 nm (Ex/Em) respectively of the RSE through all different treatment sequences with ceramic membrane. The fluorescence spectrum at 280 nm/352 nm (Ex/Em) in Figures 4.4(a-d) was selected for protein like substances. A small peak is observed for the RSE at approximately 43 kDa (Figures 4.4(a-d)). Generally the biopolymers have a molecular weight (MW) range of greater than 20 kDa [5, 19]. Moreover, Myat \textit{et al.} (2012) observed a peak at 50 kDa (fluorescence spectrum at 278 nm/304 nm (Ex/Em)) indicated the presence of protein like biopolymers [20]. Therefore, the peak detected at 43 kDa can be indicated as the presence of biopolymers. The fluorescence spectrum at 280 nm/352 nm (Ex/Em) in Figures 4.5(a-d) was selected.
fulvic like HS. In Figures 4.5(a-d), multiple peaks are observed in the range of 0 to 5000 Da. Generally, the HS are ranged from 0 to 5000 Da [21]. Therefore, the peaks observed in Figures 4.5(a-d) are indicating the presence of HS in the RSE.

The rejections of biopolymers and HS by the different steps of CMF are shown in Table 4.3. As shown in Figure 4.4a, the biopolymers detected at 280 nm/352 nm (Ex/Em) were significantly removed by the CMF (97% rejected, Table 4.3) where, HS (Figure 4.5a) detected at 330 nm/425 nm (Ex/Em) were only slightly removed by the membrane (only 7% removed, Table 4.3). Pramanik et al. (2015) found that biopolymers were rejected more (20%) than HS (10%) using a 0.1 µm hydrophilic PVDF membrane [22]. The higher rejection of biopolymers by the CMF in this study can be attributed to the narrower pore size of the ceramic membrane. As ceramic membranes have higher proportions of smaller pores and less larger pores, greater quantity of high MW biopolymers can be rejected by CMF. In the BAC-CMF process, a partial reduction of biopolymers (Figure 4.4b) and HS (Figure 4.5b) were observed by BAC filtration. The high MW biopolymers were biodegraded by microorganisms formed in the BAC and the HS were adsorbed by the activated carbon of the BAC [3, 17]. Following the BAC, CMF effectively removed biopolymers but added little additional removal to HS. Pramanik et al. (2016) studied the effect of BAC prior to 0.1 µm hydrophilic PVDF membrane while treating biologically treated secondary effluent (BTSE) [3]. It was observed that, for the BAC treated BTSE high MW biopolymers and HS were retained by the membrane. These indicate that biopolymers and HS played an important role in membrane fouling.

In the O3-CMF process (Figure 4.4c), a significant amount of biopolymers were removed by ozonation. This was found in some previous studies [23]. The removal effect of ozone is attributed to the transformation of biopolymers into smaller compounds [24]. However, ozonation also reduced significant quantity of HS (Figure 4.5c). The high aromaticity of HS justifies the significant removal of this fraction [25]. Following ozonation, no further removal of organics was observed by CMF. In the O3-BAC-CMF process (Figure 4.4d), biopolymers and HS were removed significantly by the ozonation. Following ozonation, a very slight increase in the biopolymer and clear increase in the HS quantities were observed in the BAC effluent. Biopolymers were reduced by the following CMF where the HS remained unchanged. It is interesting to
note that, HS increased after BAC filtration which is similar to the increase of UVA\textsubscript{254} shown in Figure 4.3d. Ozone was known to decompose the HS into low MW substances, therefore increase the biodegradability of HS [26-28], which normally leads to organic degradation by the biological community present on the BAC. However in this study, HS was increased by 34% after BAC indicating that the activity in the BAC contributed some lower MW organics back to the solution. The increase in HS can be explained by the regeneration processes in the BAC column. Regeneration in BAC is a process of increasing the adsorptive capacity of the carbon by chemical oxidation of adsorbed material, steam to drive off the adsorbed material, solvents and biological conversion [29]. The presence of ozone (0.34 mg/L) prior to BAC filtration oxidized the biofilm generated on the BAC particles and thus increased the HS quantity in the BAC effluent. Following CMF, a slight increase in the HS has been observed too. This could be the result of the contamination of HS existing in the membrane rig.
Figure 4.4: Fluorescence spectrum at 280 nm/352 nm (ex/em) for RSE treated by a. CMF alone; b. BAC-CMF; c. ozone-CMF; d. ozone-BAC-CMF system (Flux: 180 L·m⁻²·h⁻¹; Temperature: 22±1°C).
Figure 4.5: Fluorescence spectrum at 330 nm/425 nm (ex/em) for RSE treated by a. CMF alone; b. BAC-CMF; c. ozone-CMF; d. ozone-BAC-CMF system (Flux: 180 L·m$^{-2}$·h$^{-1}$; Temperature: 22±1°C).
Table 4.3: Biopolymers and HS present in RSE during different treatment steps of CMF considering the RSE as 100% (calculated by peak area from Figures 4.4(a-d) and 4.5(a-d) respectively).

<table>
<thead>
<tr>
<th>Process</th>
<th>Steps</th>
<th>Biopolymers (%)</th>
<th>HS (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(40 kDa-45 kDa)</td>
<td>(100 Da-5.5kDa)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ex/Em : 280/352 nm</td>
<td>Ex/Em : 330/425 nm</td>
</tr>
<tr>
<td>Ceramic</td>
<td>CMF</td>
<td>3</td>
<td>93</td>
</tr>
<tr>
<td>BAC-Ceramic</td>
<td>BAC</td>
<td>41</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>BAC + CMF</td>
<td>1</td>
<td>45</td>
</tr>
<tr>
<td>O3-Ceramic</td>
<td>O3</td>
<td>0</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>O3 + CMF</td>
<td>14</td>
<td>16</td>
</tr>
<tr>
<td>O3-BAC-Ceramic</td>
<td>O3</td>
<td>0</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>O3 + BAC</td>
<td>25</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>O3 + BAC + CMF</td>
<td>4</td>
<td>34</td>
</tr>
</tbody>
</table>

4.4.2 Effect on the permeability of CMF

Figures 4.6a and 4.6b represent the normalized permeability with time and total fouling index (UMFI_T) respectively for the RSE by all four different filtration options. The normalized permeability was highest for the O3-CMF process. After 1st cycle the normalized permeability of the O3-CMF test was reduced to 68%. After 7 successive cycles of operation the normalized permeability was reduced to 50%. However in the CMF, BAC-CMF and O3-BAC-CMF tests the normalized permeability after first cycle was 29%, 25% and 24% respectively. After 7 successive cycles of operation, the normalized permeability of the CMF, BAC-CMF and O3-BAC-CMF tests were 7%, 9% and 9% respectively. The total unified membrane fouling index (UMFI_T) for the raw RSE has been increasing gradually and after 7 successive filtration cycles it was greatest (0.73 m²/L). The BAC and ozone-BAC pre-treated RSE feed have been shown a similar UMFI_T (0.34 m²/L), after completing 7 successive filtration cycles. However the UMFI_T of the ozone pre-treated RSE feed was always less than 0.03 m²/L. This further strengthens the ability of ozone pre-treatment to improve the quality of RSE prior to CMF.
Figures 4.7(a-d) show the reversible fouling index (UMFI_{R}) and irreversible fouling index (UMFI_{I}) for all four different filtration options. In the direct CMF test, the reversible fouling index (UMFI_{R}) was higher than the irreversible fouling index (UMFI_{I}) (Figure 4.7a), revealed that the majority of foulants were loosely attached to the membrane surface to form cake layers [22] and could be removed by the backwashing procedure. The role of biopolymers to form cake layers on the membrane surface was found in other studies [17, 30] since the organics mostly rejected by the membrane are biopolymers (Figure 4.4) and would logically accumulate on the surface. However in-pore fouling can also occur from materials that pass through the membrane [31].
It is clearly shown in Figure 4.6a that BAC pre-treatment improved the filterability of ceramic membrane, but only after an initial permeability decline similar to that of direct filtration. The irreversible fouling index was reduced by the BAC pre-treatment (Figure 4.7b), resulting into an improvement in the normalized permeability after completion of 7 filtration cycles. This improvement can be attributed to the partial removal of biopolymers by the BAC (Figure 4.4b) but more substantially HS (Figure 4.5b) from RSE. Similar results were found in a previous study where BAC pre-treatment improved the flux of a 0.1 µm poly-vinylidene fluoride membrane by removing organic foulants from the biologically treated secondary effluent [17]. The results in this study indicate that, HS are smaller and not rejected by the membrane. Therefore, HS enters into the pores of the membrane and contribute to in-pore fouling [31].

Ozonation prior to the CMF was found to achieve highest normalized permeability after 7 successive filtration cycles. With the data so far of water quality changes, this can be attributed to the removal of biopolymers (Figure 4.4c) and HS (Figure 4.5c) from RSE by ozonation. The UMFI$_T$ was lowest for the ozonized RSE through CMF (Figure 4.6b), indicating that, both reversible and irreversible fouling of the membrane were reduced by breaking down of fouling substances (biopolymers and HS) due to ozonation [5]. Ozone was found to improve the permeability of ceramic membrane in other studies using ozone combined with ceramic membranes to treat secondary effluent [16, 32-34]. However in these cases, the effect of increased flux has also been attributed to ozone breakdown to hydroxyl radicals due to a catalytic effect of the ceramic membrane. However, evidence of this effect has not been confirmed. Therefore in order to fully explain the increased permeability as a result of ozone pre-treatment, further investigation is required on the ozone interaction with the ceramic membrane materials.

For the O$_3$-BAC-CMF train, the normalized permeability (Figure 4.6a) and UMFI$_T$ (Figure 4.6b) is similar to the less favourable values of the original BAC-CMF sequence. This can be explained by the increase in HS (Figure 4.5d), and a very slight increase in biopolymers (Figure 4.4d) by BAC filtration in the O$_3$-BAC-CMF train. The increase in HS is explained in Section 4.4.1 by the regeneration process in the BAC column. The irreversible fouling index has been reduced whereas the reversible fouling index increased gradually by the ozone-BAC pre-treatment (Figure 4.7d). This resulted in almost similar UMFI$_T$ increasing trends for both BAC and ozone-BAC pre-treatment prior to CMF (Figure 4.6b). Thus the effluents of the
BAC column for both the BAC-CMF and O₃-BAC-CMF were similar in terms of water quality parameters (Section 4.4.1) and membrane filtration performance (Figure 4.6a).

![Graphs showing reversible fouling (UMFIᵣ) and irreversible fouling (UMFIᵢ) for a. Raw RSE feed, b. BAC-CMF, c. ozone-CMF, and d. ozone-BAC-CMF.]

**Figure 4.7:** Reversible fouling (UMFIᵣ) and irreversible fouling (UMFIᵢ) of a. CMF; b. BAC-CMF; c. ozone-CMF; d. ozone-BAC-CMF (Flux: 180 L·m⁻²·h⁻¹; Temperature: 22±1°C).

### 4.5 Discussion

In the MF of RSE collected from a local WTP, the larger MW biopolymers and the smaller MW HS are appeared to be the major foulants. From the flux data, the reversible fouling index (UMFIᵣ) for the ceramic membrane was much higher compared to the irreversible fouling index (UMFIᵢ), indicating that cake layer was formed on the membrane surface by loosely attached organics [22]. Laine et al. (1989) showed that high MW biopolymers are known to be the major component of the cake layer [35]. HPLC analysis of the RSE feed and permeate showed that biopolymers were removed completely from permeate whereas, HS was completely passed through the membranes. These results indicate that, the biopolymers formed cake layer on the membrane surfaces and thus reduced the performance of the membranes. However pore constriction by HS that are allowed to enter the pores can also occur due to strong interactions between HS and the membrane material [31].
BAC filtration improved the permeability of the ceramic membranes. The BAC column retained the biopolymers and HS from the RSE. This was attributed to the breakdown of the biopolymers by the microorganisms, and possible retention of those organic molecules by the biofilm attached to the carbon particles in the BAC column. The biofilm consumes the organics by the microbiological activity [17]. Removal of these organics gave greater flux improvement for the CMF systems. However, the permeability of the membrane was not improved further, due to the small amount of removal of biopolymers and HS by the BAC column. There was reduction of UVA$_{254}$ and colour by BAC pre-treatment prior to ceramic membranes as well.

Ozonation removed the biopolymers and improved the permeability higher than BAC filtration prior to the membranes. The effectiveness of ozone to improve the permeability of membranes is well known [16, 32-34]. Generally high MW compounds are most reactive with ozone [36, 37]. Ozonation transformed the higher MW biopolymers into smaller compounds [24]. Ozone is also known to decompose the HS into low MW substances [26-28]. Although, the increase in low MW compounds by ozonation was found in a study conducted by Gonzalez et al. [25], in this study the increase in low MW compounds was not observed. This is probably because the HPLC was not able to detect the low MW compound with the PDA and fluorescence detector used in this experiment. On the other side, in the study conducted by Gonzalez et al., an organic carbon detector has been used [25]. However, ozone significantly removed UVA$_{254}$ and colour from RSE prior to CMF. However, the addition of coagulant prior to ozonation led to enhanced sustainable fluxes in CMF, which has been shown in the study conducted by Dow et al. (2013) [15]. It was observed that, coagulant assisted TMP reversibility during backwash, while ozone reduced the TMP rate between backwashes. Thus coagulant and ozone together yielded to achieve higher fluxes. More over the combined effect of coagulant and ozone can also reduce the frequency of chemical enhanced backwash (CEB) when operating at moderate of low flux. However, this Chapter has put a focus on the ozone behaviour as it also assists in achieving high ceramic membrane fluxes and little is understood on the role of ozone in interacting with the membrane. In this study, the physical and chemical properties of the fouling material play a major role in giving the high flux effect due to reduced resistance through the cake layer.
4.6 Summary

This study gave some new insights into the ozone, BAC and ozone-BAC pre-treatments prior to ceramic MF membranes. In terms of permeability, ozone pre-treatment had shown highest normalized permeability (67%) after 100 minutes of filtration of RSE through the ceramic MF membrane. Ozone-BAC pre-treatment did not show much improvement in the permeability because of the regeneration effect of the BAC column. The normalized permeability of the ceramic membrane for the no pre-treatment, BAC alone, ozone alone and ozone-BAC were dropped to 7%, 9%, 9% and 50% respectively after 200 minutes of operation.

The UMFI of ozone, BAC and ozone-BAC pre-treatments prior to ceramic MF membranes have also been studied. The properties of the fouling material played a major role on the permeability of the MF ceramic membrane. The higher MW biopolymers and low MW HS are found to cause fouling while filtering RSE by ceramic membrane. The lowest UMFI was found for the pre-treatment with ozone alone. Further work presented in Chapter 5 shows the physical effect of ozone on fouling layers. Thus the role of ozone to alter the filtration resistance by changing fouling layer property would be understood.

4.7 References

Chapter 5

Analysis of fouling layer filtration properties
5.1 Introduction

In this chapter, the permeability properties of the fouling layers on a 0.1 µm pore size cellulose disc filter (Millipore) are presented and discussed using the hindered settling function, \( R(\phi) \), as an indicative permeability parameter. Vacuum filtration tests were conducted using cellulose disc filters to observe the formation of cake layers generated by real secondary effluent (RSE) and ozone pre-treated RSE on the membrane surfaces. The surface images of the fouled membranes were analysed using scanning electron microscope (SEM) to see the texture and porosity of the fouling layers on top of cellulose disc filters. Step permeability tests were conducted to physically characterize the deposited fouling layers of raw RSE and ozone pre-treated RSE samples on the cellulose membrane. As the properties of the fouling layer can affect the filtration resistance, this chapter aims to explore the effect of ozone on changing the properties of fouling layers. It is anticipated that, this will provide useful information on how ozone helps retain a high permeability of the membrane.

5.2 Vacuum filtration of various treated wastewaters

The properties of the fouling layer are important in its role in the overall water flow path in water treatment applications. As true properties of wet fouling layers are difficult to measure, understanding water flow resistance and compaction under pressure is more relevant. The results in Figure 5.1 show the volume filtered with time for the tests described in Section 3.4.3.

![Figure 5.1: Fixed volume (150 mL) of DI water, raw RSE and ozonized RSE through 0.1 µm cellulose filter using vacuum filtration.](image-url)
DI water was used as a benchmark for comparison to the raw RSE and ozonized RSE. Under standard pressure conditions, a fixed volume of 150 mL DI water took 14.6 minutes to pass through the cellulose membrane where the raw RSE and ozonized RSE took 33.4 minutes and 29.7 minutes respectively (Table 5.1). The DI water therefore took less than half the time to filter the 150 mL volume compared to the raw RSE and the ozonized RSE. As expected, DI water does not contain any particulate matter which may build up a fouling layer on the membrane. A noticeable difference is observed between the time required to filter a fixed volume of raw RSE and the ozonized RSE, where the raw RSE took 12.5% more time to filter the same volume of water. This preliminary result indicates the ozone treated solids captured on the filter paper are less resistive to water flow compared to raw solids. This supports the findings of less flow resistance through the membrane which enabled retention of high flux for longer periods in pilot trials on ozone/ceramic membrane systems [1, 2]. However, real systems operate under constant flux conditions (variable pressure), and therefore the study needs to be extended to constant flow and accommodate changing pressures. The permeate and the fouled membranes of this test were preserved for testing in a stepped permeability test.

Table 5.1: Time required to pass fixed volume (150 mL) of sample through cellulose disc filters.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time required (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DI water</td>
<td>14.6</td>
</tr>
<tr>
<td>Raw RSE</td>
<td>33.4</td>
</tr>
<tr>
<td>Ozonized RSE</td>
<td>29.7</td>
</tr>
</tbody>
</table>

Figure 5.2 shows the appearance of a pristine cellulose membrane (PLAIN MEMBRANE), a raw RSE filtered membrane (SEC. EFFLUENT) and an ozonized RSE filtered membrane (SEC. EFFLUENT + OZONE). The raw RSE filtered membrane became green in colour indicating that a fouling layer has been deposited on the membrane surface. The ozonized RSE filtered membrane showed much less colour, where only a light green colour could be observed. The loss of colour is related to the effect of ozone to reduce colour of the organics. It was observed in Chapter 4 that, ozonation effectively reduced UVA_{254} (63%) and colour (88%) from the RSE. Dow et al. (2013) also observed reduction of colour (52%) and UVA_{254} (85%) by ozonation of RSE [1]. The removal of colour by ozone can be attributed to the oxidizing effect of ozone on the colour transmitting compounds of the RSE (i.e., compounds with
conjugated C–C double bonds or aromatic rings, particularly HS) and producing more colourless materials [3, 4]. However, the particulate content of the fouling is expected to be similar to the RSE as the wastewater total solids and organics were not greatly affected by ozone.

Figure 5.2: Images showing appearance of an unused ‘plain’ membrane, RSE ‘sec. effluent’ filtered membrane and an ozone pre-treated RSE filtered ‘sec. effluent + ozone’ membrane.

5.3 Stepped pressure permeability test

A stepped pressure permeability test was performed on the membranes using a raw RSE feed and ozonized RSE feed. The cellulose membranes used in vacuum filtration test (Section 5.2) were used for the test (method described in Section 3.4.4). During the vacuum pressure test, the membranes were fouled at a pressure of 80 kPa, so that the differences between the permeability of raw RSE sample and ozonized RSE sample can be identified above this pressure. The permeate collected from the vacuum filtration test was used as the solution in the stepped pressure permeability test. The reason of using the permeate from vacuum filtration test (not DI water) is to use of similar solution matrix that would be present in the real system to ensure the results are more aligned to the actual filtration operation. Moreover, the cake layer composition of the RSE can be hydrophilic in nature. Therefore, to avoid the dissolution of the fouling layer by DI water, solutions from the vacuum filtration test were considered more appropriate. The solutions used in this test were named as ‘filtered RSE’ and ‘ozonized + filtered RSE’.

The permeability of the fouling layers can be quantified using the hindered settling factor $R(\phi)$, which is defined as the hydrodynamic resistance to flow through the
suspension network structure as a function of solids volume fraction $\phi$ [5]. $R(\phi)$ can be determined by the following equation [6, 7]:

$$R(\phi) = \frac{2}{d\phi^2/dP} \left( \frac{1}{\phi_0} - \frac{1}{\phi_f} \right) (1 - \phi_f)^2$$

(5.1)

Where, $\phi_0$ is the initial solid volume fraction of the fouling layer, $\phi_f$ is the equilibrium volume fraction at pressure $P$ and $\beta^2$ is the filtration parameter (m$^2$/s). $\beta^2$ is derived from the stepped permeability experiment using an automated analysis system. As per Equation 5.1, $R(\phi)$ is inversely proportional to $\beta^2$ which indicates hydrodynamic resistance decreases with increasing $\beta^2$. The $\beta^2$ vs. pressure plots for filtered RSE and ozonized + filtered RSE are given in Figure 5.3.

![Figure 5.3: $\beta^2$ value with increasing pressure for the filtered RSE and ozonized + filtered RSE.](image)

The term $\beta^2$ is proportional to the permeability [7]. It can be seen in Figure 5.3 that no significant difference is observed between the permeability of the filtered RSE and ozonized + filtered RSE below the pressure value of 80 kPa. This may be because the two membranes were loaded with the same organic load (150 mL) at the same pressure (80 kPa) during the vacuum filtration experiment. The cake layers for both samples have been compressed to a similar extent of 80 kPa. Once the filtration rig increases the applied pressure onto the cake layer above 80 kPa, the difference in behaviour was noticed between the filtered RSE and ozonized + filtered RSE. Thus a significant
increase in the permeability above the pressure of 80 kPa was observed in the ozonized + filtered RSE sample relative to the filtered RSE. At 300 kPa, the ozonized + filtered RSE showed nearly double the permeability value than that of the filtered RSE. The rate at which the two samples vary in permeability value with respect to increase in pressure is also noticeably different. The ozonized + filtered RSE appears to be increasing in permeability at a steady rate with increasing pressure. The filtered RSE on the other hand is less sensitive to pressure increase. However, the permeability usually decreases with increasing pressure during the dewatering of municipal sludge [8]. In this study, the cake layer formed on the cellulose membrane may contain such low solid volume fraction that it is below the gel point $\phi_g$. Gel point is the solids concentration at which a continuous structure is formed. Below the gel point, the particle concentration is too small to allow an inter-connected particle network to develop [6]. Therefore, the fouling layer on the cellulose membrane did not behave like conventional sludge dewatering theory. The results of this test are further discussed in Section 5.4.

The fouling layers generated on the cellulose membrane samples were further analysed by scanning electron microscopy (SEM). Figures 5.4(a-e) shows the SEM images of plain membrane, RSE filtered membrane at pressure 80 kPa, ozonized RSE filtered membrane at 80 kPa, RSE filtered membrane used in the stepped permeability test up to a pressure of 300 kPa and ozonized RSE filtered membrane used in the stepped permeability test up to a pressure of 300 kPa. Some diatoms were observed on the membrane surfaces filtered with raw RSE and ozonized RSE. To exclude the diatoms, the SEM images were cropped and expanded in size.

The pristine membrane surface (Figure 5.4a) appeared to be clear with distinct pore openings. The larger pores are approximately 0.4 µm and the smaller pores are 0.05 µm. The pore size provided by the supplier is 0.1µm which is clearly between the ranges of pore size observed by SEM. The SEM of the raw RSE filtered membrane and the ozonized RSE filtered membrane at 80 kPa are given in Figure 5.4b and Figure 5.4c respectively. The surfaces of both the RSE filtered membrane and the ozonized RSE filtered membrane at 80 kPa appeared to be completely covered with fouling layers. However, the fouling layer on the ozonized RSE filtered membrane (Figure 5.4c) had a grainy appearance. This indicates the probable removal of specific components (high molecular weight (MW) aromatic compounds [9-11]) of the RSE by ozonation. The
SEM of the raw RSE filtered membrane and the ozonized RSE filtered membrane used in the stepped permeability test up to a pressure of 300 kPa are given in Figure 5.4d and Figure 5.4e respectively. Similar to the surfaces of the membranes filtered at 80 kPa, the surfaces of the membranes used in the stepped permeability test are completely covered with fouling layer. However, the membranes used in the stepped permeability tests had a cracked opening on the fouling layers. Moreover, the ozonized RSE filtered membrane (Figure 5.4e) had very clear cracked openings compared to the raw RSE one (Figure 5.4d). This can be attributed to the ability of ozone to convert high MW aromatic compounds [9-11] into smaller ones in the RSE. The gel-like structure is converted to a grainier, less elastic structure due to the breakdown of the polymeric properties by ozone. The cracking is almost certainly the result of drying of the fouling layer for SEM analysis but is suggestive that the fouling layer is less integral in the ozonized case.
Figure 5.4: SEM images of pristine membrane surface (a); RSE filtered membrane at 80 kPa (b); ozonized RSE filtered membrane at 80 kPa (c); RSE filtered membrane after stepped permeability test up to 300 kPa (d); ozonized RSE filtered membrane after stepped permeability test up to 300 kPa (e).
5.4 Discussion

In order to quantify the permeability of DI water, raw RSE and ozonized RSE across the cellulose membrane during the vacuum filtration test, linear regressions of the first three data points (where water recovery is relatively low and the line is linear) are taken from Figure 5.1 for the three above mentioned solutions. Figure 5.5 shows the linear regression of the DI water, raw RSE and ozonized RSE. The calculated permeability using the linear regression is given in Table 5.2.

![Graph showing linear regressions for DI water, ozonized RSE, and raw RSE](image)

**Figure 5.5**: Volume filtered vs. time for the DI water, ozonized RSE and raw RSE to calculate permeability.

In Table 5.2, the permeability of the DI water, ozonized RSE and raw RSE are 1.29 L·m⁻²·h⁻¹·kPa⁻¹, 0.75 L·m⁻²·h⁻¹·kPa⁻¹ and 0.64 L·m⁻²·h⁻¹·kPa⁻¹ respectively. The ozonized RSE was 17% higher in permeability than that of the raw RSE. The effect of ozone pre-treatment on achieving greater normalized permeability of microfiltration (MF) ceramic membrane was observed in Chapter 4 as well. In Chapter 4, the initial permeability of the raw RSE across the ceramic membrane was 11.5 L·m⁻²·h⁻¹·kPa⁻¹ and it reduced to 7.8 L·m⁻²·h⁻¹·kPa⁻¹ after completing one filtration cycle of 30 minutes. However, for the ozonized RSE, the initial permeability was 10.4 L·m⁻²·h⁻¹·kPa⁻¹ and it reduced to 2.7 L·m⁻²·h⁻¹·kPa⁻¹ after completing the first filtration cycle. The increase in permeability for the ozonized RSE in this study is less than the result obtained in Chapter 4. This is probably because ozone was mixed at a flow rate of 1.4 mg/L in the study conducted in Chapter 4. In this study, the concentration of applied ozone was less than 0.5 mg/L. Despite these differences in magnitude, the permeability still increased after ozonation, which is also consistent with literature. Kim et al. (2008) studied the effect of ozone dosage and hydrodynamic conditions on permeate flux in a hybrid ozonation-ceramic UF membrane system treating natural water. The application of
ozone prior to the ceramic membrane resulted in an increase in the permeate flux over a wide range of operational conditions [12]. Karnik et al. (2005) also investigated the application of ozone prior to a titania membrane with a molecular weight cut-off of 15 kDa while treating water from Lake Lansing. The application of ozone gas prior to filtration resulted in a significant increase in membrane flux. This was attributed to the reaction of ozone with potential foulants [13]. Therefore, substances that are responsible for fouling generation on MF membrane are required to be explored.

**Table 5.2:** Permeability of the DI water, ozonized RSE and raw RSE through 0.1 µm cellulose disc filters.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Permeability (L/m²·h·kPa)</th>
</tr>
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<tbody>
<tr>
<td>DI water</td>
<td>1.29</td>
</tr>
<tr>
<td>Ozonized RSE</td>
<td>0.75</td>
</tr>
<tr>
<td>Raw RSE</td>
<td>0.64</td>
</tr>
</tbody>
</table>

Pramanik et al. (2014) investigated the effect of biological activated carbon (BAC) filtration as a pre-treatment for reducing the organic fouling of a MF membrane (0.1 µm polyvinylidene fluoride) in the treatment of a biologically treated secondary effluent (BTSE) from a municipal wastewater treatment plant [14]. They also used a granular activated carbon (GAC) treatment which was used as a control. Their data showed that both the diluted BTSE and the GAC treated sample, which had lower DOC than the BAC treated sample, led to greater flux decline than the BAC treated sample. This indicated that the characteristics of the organic molecules present, rather than simply the DOC concentration, played an important role in the membrane fouling [14]. Therefore understanding the molecular characteristics of the RSE used in this study would be useful to understand the properties of the fouling layer.

The RSE used in this study has been characterized in Chapter 4 (Section 4.2), where it shows that the humic substances (HS) and biopolymers are major constituents of the raw RSE. The biopolymers accumulate on the surface of the MF ceramic membrane to form cake layers on the membrane surface. Laine et al. (1989) showed that high MW biopolymers are known to be the major component of the cake layer [15]. In a study conducted by Pramanik et al. (2016), it was observed that biopolymers and HS played an important role in 0.1 µm hydrophilic PVDF membrane fouling [16]. The results of Chapter 4 (Section 4.4) also show that HS are smaller in size and are not rejected by MF
membrane. In this study, therefore, the biopolymers present in the RSE are likely responsible for generating cake layer on the membrane surface. HS are responsible for the pore blocking as they can enter into the pores of the membrane and strongly interact with the membrane material [17]. Thus, the flux of ozonized RSE, which is lower in high MW biopolymers, was observed to be higher compared to that of raw RSE.

In the filtration of ozonized RSE through the cellulose membrane, ozone played an important role on achieving higher flux than the raw RSE. In Chapter 4, it was found that, significant amount of biopolymers were removed by ozonation (Section 4.4). This was similar to the study of Filloux et al. (2012), where the effect of ozonation on the effluent organic matter (EfOM) matrix of the biologically treated wastewater was investigated. Ozonation was found to induce a large reduction of the biopolymer concentration [18]. Stüber et al. (2013) also found that ozonation transformed the higher MW biopolymers into smaller compounds [11]. The results of Chapter 4 also showed that ozone reduced the HS from the raw RSE (Section 4.4). González et al. (2013) studied the reaction of ozone with dissolved organic matter (DOM) present in two different secondary treated effluents and quantified the biopolymers, HS, building blocks, low molar mass (LMM) neutrals and LMM acids. The molecular ozone was found to induce a large reduction of the biopolymers and aromatic HS [19]. In this study, the reduction of biopolymers and HS by ozonation was deemed responsible for the increased flux of the ozonized RSE.

During the stepped pressure permeability tests, the $\beta^2$ value of the filtered RSE and the ozonized + filtered RSE indicated an increasing tendency with pressure (Figure 5.3). The fouling layer generated on the cellulose membrane has some discrete flocs or particles which come into contact to form a continuous network structure. However, the ozonized + filtered RSE has shown a significantly higher $\beta^2$ value than the filtered RSE. The higher $\beta^2$ value in the ozonized + filtered RSE and hence higher permeability implies the effect of ozone to create more numbers of porous channels in the fouling layer [6]. Stüber et al. (2013) investigated the feasibility of pre-ozonation combined with coagulation and ceramic membrane filtration for tertiary treatment. They found that ozonation transformed the higher MW biopolymers present in the secondary effluent (SE) into smaller compounds [11]. Park et al. (2012) studied the changes in the physical and structural properties of natural organic matter (NOM) during hybrid
ceramic membrane processes that combined ozonation with ultrafiltration ceramic membrane. The results of their study revealed that high MW compounds are the most reactive with ozone [10]. It was also found in another study that ozone breaks down the higher MW compounds of SE into smaller compounds [9]. Based on this, there appears to be a possible effect whereby the smaller MW compounds of the ozonized RSE passes through the porous membrane walls, the ozonized + filtered RSE resulting in a significantly higher permeability than the filtered RSE.

5.5 Summary

Vacuum filtration was been conducted to generate a fouling layer on the surface of MF cellulose membranes with raw RSE and ozonized RSE. The permeability of the two different samples was then compared. The ozonized RSE sample filtered at a higher permeability (0.75 L/m²·h·kPa) through the cellulose membrane than the raw RSE (0.64 L/m²·h·kPa). The higher permeability obtained by the ozonized RSE can be attributed to the ability of ozone to remove high MW organic compounds from the RSE.

Stepped pressure permeability testing was then conducted using the membranes pre-fouled during the vacuum filtration test. The solution used here was the permeate collected during the vacuum filtration test. The ozonized + filtered RSE indicated higher permeability across the pre-fouled membrane compared to the filtered RSE. The higher permeability was attributed to the effect of ozone to create more porous channels and openings in the fouling layer by removing high MW organic components from the RSE. The mechanism is not clear but could be due to the forcing of lower MW components produced from ozone reaction with larger organics (e.g., biopolymers) through the membrane pores. The SEM of the fouled membranes further strengthens this statement. The result obtained from this study depicts the physical characteristics of the cake layer during ozonation of hybrid ozone-MF process in order for achieving higher permeate flux. However, the chemical interaction of ozone with the RSE components responsible for generating cake layer in the hybrid ozone-ceramic membrane process is yet to be explored. In order to explore the role of ozone in achieving higher permeate flux in the combined ozone-ceramic membrane process, the permeability of ceramic membrane under varying simple water properties of salinity, temperature and pH conditions will be analysed in the following chapter. Subsequent chapters will then explore in more
detail the interaction of ozone with wastewater components and ceramic materials and membranes.

5.6 References

Chapter 6

Ceramic membrane physical structure and filtration behaviour under simple process conditions
6.1 Introduction

This chapter looks into the characterization techniques applied to identify the physical properties (pore size, porosity and thickness of the filtration layer) of the commercial ceramic membrane. Pore size was measured using gas permeation method and the porometry method. Scanning electron microscopy (SEM) images are used to explore the thickness of the membrane. The chapter also looks into the total flux under simple water conditions including salinity, temperature and pH. The experiments were performed in a conventional pressurized configuration using a direct filtration (dead-end) mode. Pressure drop across the membranes was measured over varying salinity, temperature and pH conditions. The observed experimental permeability was then compared with theoretical permeability. The theoretical permeability was obtained using Hagen-Poiseuille equation which describes the relationship between the pressure drop and flow rate of a fluid through capillaries. The purpose of this chapter is to understand the physical properties of the commercial ceramic membranes and to observe the permeability of ceramic membrane under different salinity, temperature and pH conditions. These findings establish the baseline performance prior to moving to more complex water solutions.

6.2 Theory of filtration

The relationship between pressure drop and flow rate of a fluid through capillaries relevant to the MF application in this study can be described by the Hagen-Poiseuille equation [1, 2], which assumes viscosity as the only influencing fluid property on permeation. According to the Hagen-Poiseuille model, the permeability, \( \frac{J}{\Delta P} \), (L/m²·h·kPa) can be expressed as:

\[
\frac{J}{\Delta P} = \frac{d_m^2 \varepsilon}{32 \mu L \tau}
\]  

(6.1)

Where \( J \) is the flux (L/m²·h), \( \Delta P \) is the pressure drop (Pa), \( d_m \) is the average pore size (m), \( \varepsilon \) is the porosity, \( \mu \) is the dynamic viscosity (N·s/m²) obtained from viscosity and salinity relationships [3], \( \tau \) is the tortuosity and \( L \) is the thickness of the membrane material (m). On the right hand side of Equation 6.1, all the parameters except viscosity are assumed to be constant for a particular membrane with changing salinity,
temperature and/or pH [4]. Pore size can be considered constant, but can vary in effective size depending on the chemistry of the surface, for example due to surface hydration. Such effects will have a stronger impact to the calculated flux due to the relation to pore diameter to the second power. This will be of relevance in this work where variations in experimental flux fitted with Equation 6.1 will be most sensitive to uncertainties in the pore size as compared to the other parameters. In order to understand the flux behaviour of the membranes, the physical properties (e.g., pore size, porosity and thickness of filtration layer) need to be quantified.

**6.3 Measurement of commercial ceramic membrane thickness**

The overall thicknesses of the Pall 100 nm and 200 nm membranes were calculated using Vernier callipers. The thicknesses of the 100 nm and 200 nm membranes were 1.72 mm and 1.68 mm respectively (Table 6.1). However ceramic membranes are often coated and the rate determining layer is much thinner. In order to observe the thinner coatings, the SEM images of the 100 nm and 200 nm Pall tubular ceramic membranes are given in Figure 6.1.

![SEM cross sections of 100 nm (left) and 200 nm (right) tubular ceramic membranes.](image)

The scanning electron microscope (SEM) was used to determine the thickness of rate determining filtration layer of the membranes (method described in Section 3.3.4). The SEM cross section of the 100 nm membrane (Figure 6.1 left) clearly shows a coating of approximately 11 μm which is likely to be the functional membrane filtration layer.
which consists of $\alpha$-$\text{Al}_2\text{O}_3$ according to the manufacturer. Below that is a 50 $\mu$m layer consisting of a coarser material which presumably is an intermediate layer that supports the thinner top layer. The 200 nm membrane on the other hand (Figure 6.1 right) has no clear additional coating and appears to be made of a single material that is of the same overall thickness of the two layers of the 100 nm membrane (62 $\mu$m). The filtration layer and the intermediate layer of the 100 nm membrane and the filtration layer of the 200 nm membrane are supported by porous support material of alumina. This large pore sized support materials provide mechanical strength to the thinner functional separation layer. This practical design ensures highest fluxes of membranes for commercial application.

### 6.4 Membrane pore size measurement

#### 6.4.1 Gas permeation method

The pore sizes were measured using gas permeation method explained in Section 3.3.1 provided in [5]. The pore sizes of the 100 nm and 200 nm Pall ceramic membranes were found to be 810 nm and 700 nm respectively (Table 6.2). These values are much larger than those from the specification of the manufacturer while at the same time shows a less significant difference in pore size between the two membranes (the larger specified pore size showed the smaller pore size by this analysis). As these membranes are supplied according to their defined pore sizes and therefore have a low probability of defects, it is likely that the difference is attributable to the measurement technique, where the supplier will use molecular weight cut-off to determine the pore size of the filtration layer and hence the pore size of the membrane in application. The pore sizes calculated by gas permeation rely on different assumptions to molecular weight cut-off.

#### 6.4.2 Porometry method

Figure 6.2 shows the flow vs. pressure graphs for the 100 nm and 200 nm Pall ceramic membrane using the porometry method (Section 3.3.2). The dry curve represents the gas flow against the applied pressure on the dry membrane sample. The half-dry curve is obtained by dividing the flow values of the dry curve by two. The wet curve represents the gas flow against applied pressure on the wet membrane sample (the sample is impregnated with wetting liquid). From the representation of the three curves of the membrane sample the first bubble point (FBP, the maximum pore size) is recorded when gas flow through the sample is detected. The mean flow pore (MFP) size
corresponds to the pore size calculated at the pressure where the wet curve and the half dry curve meet. It corresponds at the pore size at which 50% of the total gas flow can be accounted. The minimum pore size which is defined by smallest pore (SP) as well, results from the pressure at which the wet and the dry curve meet. From this point onwards the flow will be the same because all the pores have been emptied [6].

**Figure 6.2:** Flow (L/min) vs. pressure (bar) graphs for the 100 nm (left) and 200 nm (right) Pall ceramic membranes (POROLUX porometers).

The gas flow through the sample is used to calculate the pore size distribution by increasing the flow rate per unit increase in pore diameter. The pore size distribution for the 100 nm and 200 nm Pall ceramic membranes are shown in the Figure 6.3.

**Figure 6.3:** Percent flow vs. pore diameter graphs for the 100 nm and 200 nm Pall ceramic membranes (POROLUX porometer).

The calculated average first bubble point, mean flow pore and smallest pore of the 100 nm and 200 nm Pall ceramic membranes are given in Figure 6.4. It is clear from Figure 6.4 that, using the porometry method pore sizes were found to be 145 nm and 153 nm for the 100 nm and 200 nm Pall tubular ceramic membranes respectively. Using porometry the measured pore sizes of the 100 nm and 200 nm Pall ceramic membranes
are almost similar, which like gas permeation method doesn’t appear appropriate considering the supplier’s pore size value. It was shown in Section 6.3 that the thicknesses of the filtration layer of the 100 nm Pall ceramic membrane contains a coating of approximately 11 μm and below that a 50μm layer consisting of a coarser material. The 200 nm Pall ceramic membrane contains a coating of 62 μm but no additional coating. Therefore the resistance of the filtration and intermediate layers in the 100 nm membrane and the filtration layer in the 200 nm membrane controlled the results of porometry method. Where, in gas permeation method (Section 6.3.1) the 200 nm membrane showed the smaller pore size. The porometry was clearly more sensitive to the top layers where the smaller specified pore size membrane showed a slightly smaller size by this measurement, but still yielded a pore size that does not match the manufacturer’s values as the intermediate and support layers are both contributing to the measurement. The original manufacturers specified pore size, likely determined by molecular weight cut off, is more appropriate for measurement of the pore size of the critical separation layer, regardless of its thickness.

![Figure 6.4: Comparison of FBP, MFP and SP of the 100 nm and 200 nm Pall ceramic membranes (POROLUX porometer).](image)

### 6.5 Membrane porosity

The porosity of the 100 nm and 200 nm Pall ceramic membranes were measured using method explained in Section 3.3.3. The porosity of both the membranes was found to be 33% (Table 6.1). In this method, the porosity of the 100 nm and 200 nm Pall ceramic membranes were measured by the ratio of the volume of voids ($V_v$) over the total volume ($V_T$). Total volume ($V_T$) was measured by mathematical calculation using the
physical parameters. Volume of voids ($V_v$) was calculated by measuring the volume of water trapped by the membrane pores.

The porosity measured here represents the porosity of both the active layer and support layer of the Pall ceramic membranes. Porosity of the 100 nm and 200 nm Pall ceramic membranes were found similar (33%). This implies that, the physical structures of the support layers of both the membranes are almost similar. The filtration layers must be different for different pore sized membranes. Since the thicknesses of the filtration layers are very small compared to the support layers, the difference in the physical composition in the filtration layer did not significantly influence the measured porosity values.

### 6.6 Summary of the measured properties of Pall membrane

Summary of the measured properties of the 100 nm and 200 nm membranes are given in Table 6.1. The pore sizes obtained by the porometry did not match with pore sizes provided by the manufacturer of the membranes. These imply that, the ceramic membranes are comprised of thicker support layer with larger pore sizes. An intermediate layer is placed on the support layer of the 100 nm membrane. The 11 μm filtration layer was coated on the intermediate layer of the 100 nm membrane. For the 200 nm membrane, the 62 μm filtration layer was coated directly on the support layer and the porometer value provided a close estimation of this top layer pore size. However if we assume there was larger pore size intermediate layer for the 100 nm membrane, even if smaller pores are blocked as part of the pore filling technique of the measurement (measures size only of ‘through pores’), the gas flow resistance is still significant in the intermediate layer such that the restriction provided by the top layer pore blockage is not as strongly observed. Pore sizes obtained by gas permeation on the other hand gave a much larger size, representing the average of the entire membrane thickness and therefore appear to have been more sensitive to the larger pore support layer. The techniques used here therefore give values representing the pore structure of the membranes, but not always the functional separation layer. These differences will be analysed more closely in the discussion. However by understanding their underlying measurement theories, they are still useful to measure the properties of ceramic
membrane to understand the characteristics of commercial membranes without damaging them (i.e., probing them non-destructively with gases and vapours). The characteristics of the ceramic membranes will be helpful while investigating the influence of water quality parameters on basic membrane performance.

Table 6.1: Characterization of 100 nm and 200 nm tubular ceramic membranes, pure water permeability tested at 18 - 24 kPa pressure drops.

<table>
<thead>
<tr>
<th>Properties</th>
<th>100 nm membrane</th>
<th>200 nm membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure water permeability at 20°C (L/m²·h·kPa)</td>
<td>13.3±0.9</td>
<td>9.5±1.05</td>
</tr>
<tr>
<td>Average pore size (nm) measured by porometry</td>
<td>145</td>
<td>153</td>
</tr>
<tr>
<td>Average pore size (nm) by gas permeation</td>
<td>810</td>
<td>700</td>
</tr>
<tr>
<td>Thickness of the membrane material, L (µm)</td>
<td>$1.72 \times 10^3$</td>
<td>$1.68 \times 10^3$</td>
</tr>
<tr>
<td>Thickness of the filtration material, L (µm)</td>
<td>11</td>
<td>62</td>
</tr>
<tr>
<td>Porosity, ε (%)</td>
<td>33</td>
<td>33</td>
</tr>
</tbody>
</table>

6.7 Determination of porous properties

The Porosity ($\varepsilon$) of the 100 nm and 200 nm membranes were measured as 0.33 (Section 6.4). The pore sizes ($d_m$) are those provided by the manufacturer which are likely measured by molecular weight cut-off [7]. The filtration layer thicknesses ($L$) of the 100 nm and 200 nm membranes were 11 µm and 62 µm respectively, measured using SEM following method described in Section 6.3. From Equation 6.1, we can find the tortuosity ($\tau$) as,

$$\tau = \frac{d_m^2 \varepsilon \Delta P}{32 \mu L J} \quad (6.2)$$

In the right hand side of Equation 6.2, all the parameters are obtained by experimental measurements except the flux, $J$ (L/m²-h). Using the experimental values of $J$ during water flow in Equation 6.2, the tortuosity of the 100 nm and 200 nm membranes were found to be 2.2 during both the different salinity condition tests and different temperature condition tests. However estimating tortuosity by this means should not be considered as a flux fitting parameter, as it’s a real property of the material. To observe the relevance of the estimated value, generally for a random packed ceramic membrane structure (contains a wide range of particle and pore sizes), the tortuosity $\tau \approx 3$, where for straight pores the tortuosity $\tau = 1$ [8]. The value of 2.2 fits within this realistic
material values and therefore appears reasonably. Table 6.2 shows the obtained parameters considered to compare the theoretical permeability with the experimental one. Determination of these parameters can now enable the exploration of the effects of basic water properties relevant to water treatment (salinity, temperature and pH) on the flow resistance through ceramic membranes.

**Table 6.2:** Parameters considered while comparing the theoretical permeability of the 100 nm and 200 nm Pall ceramic membranes with experimental one.

<table>
<thead>
<tr>
<th>Properties</th>
<th>100 nm</th>
<th>200 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity, $\varepsilon$</td>
<td>33</td>
<td>33</td>
</tr>
<tr>
<td>Tortuosity, $\tau$</td>
<td>2.2</td>
<td>2.2</td>
</tr>
<tr>
<td>Pore size, $d_m$ (nm)</td>
<td>100</td>
<td>200</td>
</tr>
<tr>
<td>Thickness, $L$ (µm)</td>
<td>11</td>
<td>62</td>
</tr>
</tbody>
</table>

### 6.8 Effect of salinity

Figure 6.5 shows the comparison of experimental and theoretical permeability under different NaCl concentrations but similar flux (240 L/m²·h) for the 100 nm and 200 nm ceramic membranes. Using the values of different filtration parameters from Table 6.2, the theoretical permeability are calculated to fit with experimental values. The experimental permeability is observed to be consistent with theory for both membranes (100 nm and 200 nm) for salinities of 500 mg/L and above. However, the experimental permeability for DI (0 g/L salinity) water was less (on the order of 15% and 12% for the 100 nm 200 nm membranes respectively) than that of the theoretical one. This can be explained by the electro-viscous effect [9] which is further discussed in Section 6.11. For both the 100 nm and 200 nm membranes, permeability decreased slightly with increasing NaCl concentration. From 3 g/L salinity (brackish water) to 35 g/L salinity (sea water) the permeability reduced 8% and 6% for the 100 nm and 200 nm Pall ceramic membranes respectively.
Figure 6.6: Comparison of experimental and theoretical permeability for 100 nm and 200 nm Pall ceramic membranes under different NaCl concentration (Flux: 240 L·m⁻²·h⁻¹; Temperature: 22±1°C).

6.9 Effect of temperature

Figure 6.6 shows the comparison of experimental and theoretical permeability under different temperature conditions for the 100 nm and 200 nm Pall ceramic membranes. Using the values of different filtration parameters from Table 6.2, the theoretical permeability are calculated to fit with experimental values. In Figure 6.6, the experimental permeability was found to be increased with increasing temperature, consistent with the expected changes in solution viscosity for both the 100 nm and 200 nm membranes. Similar effect of temperature was found by Moosemiler et al. (1989) where the permeability of a pure water feed was investigated using 100 nm titania and 200 nm alumina membranes in the temperature range of 7°C to 40°C [10]. Although, the theoretical permeability has shown a similar trend, at higher temperatures the experimental permeability was less than the theoretical one for both the 100 nm and 200 nm membranes under different temperature conditions. This will be further discussed in Section 6.11. Based on these results, if the water in a treatment plant is changed from 15°C to 35°C, the permeability will be increased by 57% for both 100 nm and 200 nm membranes.
6.10 Effect of pH

Figure 6.7 shows the effect of pH on permeability through the 100 nm and 200 nm Pall ceramic membranes for DI water, 0.5 g/L, 5 g/L and 15 g/L NaCl solutions. The effect of various pH values in different salinity would give fundamental flux behaviour of the membranes in different operating conditions. The straight lines joining permeability at different pH conditions are a guide to the eye. The permeability of DI water at different pH values were always lower than the other salinity solutions, consistent with the salt effect shown in Figure 6.5. However, for both membranes, there is no obvious trend in permeability with pH except that in some instances, the lowest permeability was observed at highest pH (above the IEP). The variation of permeability at different pH was also inconsistent. For any salinity condition, changing pH from 6 to 7 did not change permeability more than 6%. The hollow symbols in Figure 6.7 represent the theoretical permeability calculated using Hagen-Poiseuille equation (Equation 6.1). Since there is no direct relation of permeability with pH in Equation 6.1, the variation of permeability at different pH may be due to the pore size alterations by some other effects (e.g., temperature, electro-viscous effect). Overall the effect of pH was insignificant.
Figure 6.7: Effect of pH on a 100 nm (top) and 200 nm (bottom) Pall ceramic membrane under different NaCl concentrations (Flux: 240 L·m\(^{-2}\)·h\(^{-1}\), Temperature: 20±1°C). Hollow symbols represent theoretical permeability; the expected IEP of the membrane is shown as a vertical dotted line.

6.11 Discussion

In the case of gas permeation, there is a resistance caused by the porous support layer of the ceramic membranes. It has been shown in previous studies on gas permeation through coated ceramic membranes that gas permeability is affected by the thickness of the support layer [11], which is significantly greater than the separation layer (1.72 mm vs. 11 μm for 100 nm Pall ceramic membrane). In order to analyse the contribution of support layer and filtration layer of the membrane into the resistance, partial pressure drops across the support layer and filtration layer can be calculated using Equation 6.1.
Rearranging Equation 6.1 for the filtration layer of the membrane, the following is found:

\[
\Delta P_{f(gas)} = \frac{32\mu_N L_f \tau j_N}{d_m^2 \varepsilon}
\]  

(6.3)

Where, \(\Delta P_{f(gas)}\) is the pressure drop (Pa) across the filtration layer of the membrane during gas flow, \(d_m\) is the average pore size (m) of the filtration layer, \(L_f\) is the thickness of the filtration layer obtained by SEM (Section 6.3), \(\mu_N\) is the dynamic viscosity of nitrogen gas used in the gas permeability test (N·s/m²), \(j_N\) is the gas permeate flux (m/s).

The parameters considered to calculate the pressure drop across the filtration layer using Equation 6.3 are given in Table 6.3.

### Table 6.3: Parameters considered while calculating the partial pressure drop during nitrogen gas flow across the 100 nm and 200 nm Pall ceramic membranes.

<table>
<thead>
<tr>
<th>Properties</th>
<th>100 nm</th>
<th>200 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity, (\varepsilon)</td>
<td>33</td>
<td>33</td>
</tr>
<tr>
<td>Tortuosity, (\tau)</td>
<td>2.2</td>
<td>2.2</td>
</tr>
<tr>
<td>Pore size, (d_m) (nm)</td>
<td>100</td>
<td>200</td>
</tr>
<tr>
<td>Thickness, (L_f) ((\mu)m)</td>
<td>11</td>
<td>62</td>
</tr>
</tbody>
</table>

The pressure drop across the support layer can be calculated using Equation 6.4:

\[
\Delta P_{s(gas)} = \Delta P_{t(gas)} - \Delta P_{f(gas)}
\]  

(6.4)

Where, \(\Delta P_{t(gas)}\) is the total pressure drop (Pa) and \(\Delta P_{s(gas)}\) is the pressure drop (Pa) across the support layer of the membrane during nitrogen gas flow across the membrane. Since total pressure drop across the membrane was kept always constant at 1.00±0.01 kPa, the pressure drop across the support layer can be calculated using Equation 6.4. Table 6.4 shows the pressure drop across the support layer and filtration layer for the 100 nm and 200 nm Pall ceramic membranes. It is clear from Table 6.4 that, the pressure drops across the support layers of both membranes are higher than that of the filtration layers. This indicates that the support layers contribute significantly to the overall flow resistance during gas permeation through a porous ceramic membrane.
Table 6.4: Pressure drop across the support layer and filtration layer of the 100 nm and 200 nm Pall ceramic membranes.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Support layer (kPa)</th>
<th>Filtration layer (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 nm Pall ceramic membrane</td>
<td>0.71</td>
<td>0.29</td>
</tr>
<tr>
<td>200 nm Pall ceramic membrane</td>
<td>0.58</td>
<td>0.42</td>
</tr>
</tbody>
</table>

Zhang et al. (2007) studied hydrogen permeance through palladium composite membranes prepared by modified α-alumina supports and a dense Pd/α-Al₂O₃. It was observed that, the main resistance of the composite membrane to hydrogen permeation lies in the aluminium ceramic support rather than the thin Pd layer [12]. Therefore gas permeation technique is more sensitive to the relative thickness differences between the support and the top layer, where the thicker support layer offers the most resistance to diffusion and thus dominates in the calculation of pore size, where the support layer is expected to have a much larger pore size of around 1000 nm [13]. All these indicate that, the physical properties like pore structure and thickness of the membrane play significant role during permeation of gas through ceramic membranes.

The pore sizes using the porometry method were found to be 145 nm and 153 nm for the 100 nm and 200 nm Pall tubular ceramic membranes respectively (Section 6.4.2). The method consists of increasing the pressure and keeping it constant for a certain time to allow all pores of the same diameter (but different length and tortuosity) to be empty before accepting a data point. The pressure required to empty pores of a certain diameter is used to calculate the pore size accordingly to the Young–Laplace formula (Equation 3.9). Interestingly, the filtration layer in the ceramic membranes may contain complex pore structures where two or more different sized pores are bulked in to a bigger pore. Therefore, while filtering liquids, through microfiltration ceramic membranes, pore sizes should be measured using some meaningful techniques like size-exclusion method.

During the different salinity tests, the experimental permeability is observed to be consistent with the theoretical one, obtained from Hagen-Poiseuille equation (Equation 6.1). A slight decrease in permeability was observed with increase in salinity for both 100 nm and 200 nm Pall ceramic membranes. As observed in Figure 6.5, higher salinity (0.5 g/L – 30 g/L) led to reduced permeability in the range of 15.3 to 14.3 L/m²·h·kPa (7%) and 10.6 to 10.1 L/m²·h·kPa (5%) for the 100 nm and 200 nm membranes
respectively, which was well fitted to simple bulk viscosity changes in the Hagen-Poiseuille equation. However below 0.5 g/L a decrease in permeability (on the order of 20% for the 100 nm membrane) was observed for DI water (Figure 6.5) relative to a 1 g/L salt solution. This trend was also reported by Henniker (1952), while measuring the retardation of flow in narrow capillaries [14]. This permeability reducing effect cannot be directly explained by the Hagen-Poiseuille model, where all the parameters on the right hand side of Equation 6.1 are assumed to be constant for a particular membrane with changing salinity and/or temperature. Pore size can be considered constant, but can vary in effective size depending on the chemistry of the surface, for example due to surface hydration and/or formation of electrostatic double layer from charged solutes. This instead indirectly influences the Hagen-Poiseuille model.

It is well known that, if a ceramic oxide surface is exposed to water, it becomes hydrated. When the surface is in contact with polar liquids, the amphoteric MOH groups (M = metal cation, e.g., Al$^{3+}$, Zr$^{4+}$ or Ti$^{4+}$) will dissociate. This causes the amphoteric groups to become either negatively or positively charged above or below the iso-electric point (IEP) respectively [15, 16].

\[ MOH + H^+ \rightarrow MOH_2^+ \leftrightarrow M^+ + H_2O \]  \hspace{1cm} (6.5)

\[ MOH + OH^- \rightarrow M(OH)_2^- \leftrightarrow MO^- + H_2O \]  \hspace{1cm} (6.6)

The surface of the membrane develops a potential that is moderated away from the surface through an electrical double layer. When an electrolyte solution is passed through the pores with charged surfaces, ions are moved away from their preferred position in the double layer. This costs additional energy and can be described as an increase in the apparent viscosity. This phenomenon is called the electro-viscous effect [17]. Levine et al. [18] showed the apparent viscosity $\mu_a$ in a cylindrical pore is related to the zeta potential $\zeta$ of the pore wall by,

\[ \frac{\mu_a}{\mu} = \left( 1 - \frac{8\beta (e \zeta)^2 (1 - G)F}{(kr)^2} \right)^{-1} \]  \hspace{1cm} (6.7)
Where, $\mu$ is the bulk viscosity of the electrolyte solution (Pa·s), $r$ is the capillary radius (m), $G$ is the ratio of mean electrostatic potential across the capillary to the $\zeta$ potential, $F$ is the electric field strength and $\beta$ is the dimensionless parameter describing the properties of the electrolyte. For an aqueous monovalent salt solution at 20°C, $\beta=35.8/\Lambda$ (where $\Lambda$ denotes the conductivity in $\Omega^{-1}$ cm$^2$ mol$^{-1}$). $\kappa$ is the Debye constant (m$^{-1}$), $1/\kappa$ is the Debye length which is a measure of the double layer thickness (nm), whereby:

$$
\kappa^{-1} = \sqrt{\frac{\varepsilon_r\varepsilon_0 k_B T}{2 N_A e^2 I}}
$$

(6.8)

Where $I$ is the ionic strength of the solution (mole/m$^3$), $\varepsilon_\infty$ is the permittivity of free space (F/m), $\varepsilon_r$ is the dielectric constant, $k_B$ is Boltzmann’s constant ($1.381 \times 10^{-23}$ JK$^{-1}$), $T$ is absolute temperature (K), $N_A$ is Avogadro’s number ($6.022 \times 10^{23}$ mol$^{-1}$), $e$ is the elementary charge (Q) [19]. In water for a 1:1 electrolyte solution, such as NaCl, at room temperature (25°C) the Debye length, $\kappa^{-1}$ (nm) is simplified to [9]:

$$
\kappa^{-1} = \frac{0.304}{\sqrt{I(M)}}
$$

(6.9)

Where, $I(M)$ is the ionic strength (mol/L). From Equation 6.9, the Debye length is inversely proportional to the ionic strength. Assuming the thickness of the double layer affects resistance, then as the ionic strength (i.e., salinity) decreases, the Debye length increases and may become equal to the absolute pore size [17].

Calculation of the Debye length for a 1:1 electrolyte solution, which is relevant to the NaCl solution used in this study, is shown in Table 6.5. From Table 6.5, the concentration of Debye length decreases with increasing salinity, resulting in less effect in the membrane resistance. On the other hand, Debye length is very high when the concentration is less than or equal to 0.0005 g/L (0.5 mg/L), which may significantly reduce the effective pore size of a microfiltration membrane. In this study, the permeability increased for a NaCl concentration of 0.005 g/L. As per Table 6.5, the Debye length becomes significant for concentrations of 0.005 g/L or less, relative to the size of the membrane pores (100 ~ 200 nm). Thus Debye length decreases quickly and for 0.5 g/L or above, this effect diminishes. Thus, the observed decrease in permeability
is consistent with a smaller effective pore size than the actual size of the membrane pores at very low concentrations of salt.

Table 6.5: Calculation of Debye lengths for a 1:1 electrolyte solution at 25°C and $\kappa r$ values for the 100 nm and 200 nm Pall ceramic membranes.

<table>
<thead>
<tr>
<th>Salinity (g/L)</th>
<th>Debye Length, $\kappa^l$ (nm)</th>
<th>$\kappa r$</th>
<th>$\kappa r$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100 nm membrane</td>
<td>200 nm membrane</td>
<td></td>
</tr>
<tr>
<td>0.0005</td>
<td>104</td>
<td>0.48</td>
<td>0.96</td>
</tr>
<tr>
<td>0.005</td>
<td>33</td>
<td>1.52</td>
<td>3.04</td>
</tr>
<tr>
<td>0.5</td>
<td>3.3</td>
<td>15.2</td>
<td>30.4</td>
</tr>
<tr>
<td>5</td>
<td>1.0</td>
<td>48.1</td>
<td>96.2</td>
</tr>
<tr>
<td>15</td>
<td>0.6</td>
<td>83.3</td>
<td>166.6</td>
</tr>
<tr>
<td>30</td>
<td>0.4</td>
<td>117.8</td>
<td>235.6</td>
</tr>
<tr>
<td>50</td>
<td>0.3</td>
<td>152.1</td>
<td>304.1</td>
</tr>
<tr>
<td>100</td>
<td>0.2</td>
<td>215.0</td>
<td>430.1</td>
</tr>
</tbody>
</table>

The Debye length has significant impact on the electro-viscous effect. The electro-viscous effect is greatest when $\mu_a/\mu$ in Equation 6.7 is greatest. In Equation 6.7, $\mu_a/\mu$ increases with $\kappa r$ and reaches a maximum at $\kappa r = 2.5$ and then decreases for larger $\kappa r$ values [18, 20]. The $\kappa r$ values for the 100 nm and 200 nm Pall ceramic membranes used in this study with corresponding NaCl concentrations are calculated in Table 6.5. It can be seen that, the 100 nm and the 200 nm Pall ceramic membranes have $\kappa r$ values of 1.52 and 3.04 respectively at 0.005 g/L NaCl concentration. These indicate that, the electro-viscous effect is greatest for salinity below about 0.005 g/L (5 mg/L) for the 100 nm Pall membrane. Similarly, for less than about 0.005 g/L NaCl concentration, the 200 nm Pall membrane will show the greatest electro-viscous effect.

An ion interaction model was proposed by Pitzer [21] to predict the activity coefficient of each solute and osmotic coefficient of aqueous systems. Though this is a very simple model which can predict the ion interactions in more detail, the Pitzer parameters are difficult to determine experimentally. The model can be used in solutions for which the Debye-Huckel theory is inadequate. To confirm the effect of NaCl concentration at these low concentrations, ICP analysis of DI water has been conducted in the National Measurement Institute (NMI), Australia. The ICP analysis was unable to confirm the presence of Na and Cl at a detection limit of 0.05 mg/L (Method No. NT2_47) and 0.1 mg/L (Method No. NW_D3_B14) for Na and Cl respectively. Therefore, the cause
being considered here is the overlap of the electrical double layer into the pore space
due to the electro-viscous effect resulting in a decrease in the effective pore size, or an
increase in the fluid viscosity. However change to effective pore size appears more
significant because of the stronger sensitivity to pore size in Equation 6.1 discussed
earlier.

In Figure 6.6 the experimental permeability was reduced than the theoretical one. The
percentage reductions in experimental permeability are shown in Table 6.6. This
reduction of experimental permeability can be explained by the influence of temperature
on electro-viscous effect as the electro-viscous effect is nearly proportional to the
environmental temperature [22]. The solution in this case was prepared by 0.5 g/L NaCl
salt. According to Table 6.5, the $\kappa r$ values for 0.5 g/L NaCl solution are 15.2 and 30.4
respectively for the 100 nm and 200 nm Pall ceramic membranes. Levine et al. (1975)
has shown that, a measurable electro-viscous effect is obtained for $\kappa r$ roughly in the
interval $30 \pm 0.3$ [18]. Therefore the reason being considered here is the increase of
electro-viscous effect by the influence of temperature which further resulted in decrease
in permeability. It can be seen that the experimental permeability differed greatest at
highest temperature conditions (50°C) for both the 100 nm and 200 nm ceramic
membrane. This implies that, for higher operating temperature, the effect of electro-
viscous effect is greatest. These results are consistent with others studies [17, 23].

Table 6.6: Reduction (%) of experimental permeability compared to HP
model using fixed parameters for the 100 nm and 200 nm Pall ceramic
membranes under different temperature conditions (Salinity: 0.5 g/L
NaCl).

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>100 nm membrane</th>
<th>200 nm membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1%</td>
<td>1%</td>
</tr>
<tr>
<td>20</td>
<td>7%</td>
<td>7%</td>
</tr>
<tr>
<td>30</td>
<td>5%</td>
<td>9%</td>
</tr>
<tr>
<td>50</td>
<td>9%</td>
<td>10%</td>
</tr>
</tbody>
</table>

As noted from Figure 6.7, the permeability of DI water at different pH values was
always lower than the other salinity solutions, consistent with the salt effect shown in
Figure 6.5. However, for both membranes, there is no obvious trend in permeability
with pH except that in some instances, the lowest permeabilities were observed at
highest pH (above the IEP). As per Equation 6.5 and 6.6, ionization of surface hydroxyl
groups on the membrane surface, once in contact with water, will lead to a positive
surface below and negative surface above the IEP [16, 24]. An increase in surface charge is likely to cause an increase in the electro-viscous effect with a consequential decrease in permeability. Despite this expectation, the penetration of the electrical double layer into the pore space is small for all but the lowest salt solutions. As such, the observation that there was only a weak effect of pH on permeability is consistent with expectations. However, the effect of pH on the permeation of NaClO$_4$ through ceramic TiO$_2$ and γ-Al$_2$O$_3$ membranes was investigated by Moosmiler et al. (1989) where the permeability of the alumina membrane showed a maximum value at the pH value of the iso-electric point (IEP) of the membrane [10].

Considering that the Debye length can extend significantly into the membrane pore, especially at low salinity, it is possible that salt rejection can occur in these membranes. To investigate the rejection effect, samples were collected from the feed, permeate and the backwash for runs fed with DI water, 0.5 g/L NaCl and 5 g/L NaCl solutions at pH 8 and pH 5–6. Rejection of Na was observed for the DI water runs. No effect was observed for the salt solutions (purposely added NaCl) although it has already been observed that these solutions did not reduce membrane permeability through electro-viscous effects and the differences would be hard to detect in any case. In order to explore more closely if increasing NaCl concentration produced a salt rejection effect, salinity within the operational range of the ICP was chosen (namely 0.005 g/L). This concentration is also in a range where double layer extension into the pore space is minor. No rejection of Na was observed at any pH (Table 6.7) for the addition of salt.

**Table 6.7:** Na rejection by the 100 nm Pall ceramic membrane under different NaCl concentration and pH conditions (Flux: 234 L/m$^2$·h, temperature: 20°C).

<table>
<thead>
<tr>
<th>NaCl concentration (mg/L)</th>
<th>pH</th>
<th>Feed Na (mg/L)</th>
<th>Permeate Na (mg/L)</th>
<th>Reject Na (mg/L)</th>
<th>Rejection (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8</td>
<td>0.192</td>
<td>0.191</td>
<td>0.394</td>
<td>52%</td>
</tr>
<tr>
<td>0</td>
<td>9</td>
<td>0.39</td>
<td>0.416</td>
<td>1.04</td>
<td>60%</td>
</tr>
<tr>
<td>0</td>
<td>10</td>
<td>2.39</td>
<td>2.32</td>
<td>2.38</td>
<td>3%</td>
</tr>
<tr>
<td>5</td>
<td>8.3</td>
<td>1.9</td>
<td>1.94</td>
<td>1.98</td>
<td>2%</td>
</tr>
<tr>
<td>5</td>
<td>6.6</td>
<td>1.37</td>
<td>1.4</td>
<td>1.42</td>
<td>1%</td>
</tr>
<tr>
<td>5</td>
<td>3.8</td>
<td>1.75</td>
<td>1.72</td>
<td>1.74</td>
<td>1%</td>
</tr>
</tbody>
</table>

As noted, rejection was observed for the DI water case. This confirms that the membrane only rejects salt at very low salinities, where Debye lengths are significant.
The osmotic pressure developed due to the rejection of Na inside the membrane was also calculated but the pressure was found to be insignificant (< 0.5 %) compared to the total pressure developed during filtration. Overall, the effect of pH in the permeability of secondary effluent is adequately insignificant compared to the effect of other physical and chemical parameters of the secondary effluent.

In order to assess the reduction in permeability at DI water, pore size and viscosity were adjusted to fit the experimental permeability with the theoretical one. Table 6.8 shows the percentage change of pore size and viscosity for the 100 nm and 200 nm membranes. It can be seen that, pore size is required to be reduced by 7% (93 nm and 186 nm for the 100 nm and 200 nm membranes respectively) for both the 100 nm and 200 nm membrane to obtain a similar reduced permeability. This is physically impractical because the DI water did not contain any constituents which could create any fouling in the pores of ceramic membrane. However, the viscosity is required to be increased 15% to yield the same permeability reduction. Apparent viscosity can be increased by increasing the salt concentration. As we have seen in Table 6.5, increasing the salt concentration can increase the electric double layer which consequently can reduce the effective pore size of the membrane. However as shown here, the size reduction needed to drop permeability appears too large, where instead the reduction in permeability caused by the electro-viscous effect of the NaCl solution is likely due to the altered viscosity of the fluid. The change of actual viscosity by the double layer only needs to be by 15%. In the left hand side of Equation 6.6 the ratio of apparent viscosity to actual viscosity is found to be 1.15.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Adjusting pore size</th>
<th>Adjusting viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 nm</td>
<td>7%</td>
<td>15%</td>
</tr>
<tr>
<td>200 nm</td>
<td>7%</td>
<td>15%</td>
</tr>
</tbody>
</table>

**Table 6.8:** Reductions (%) of pore size and viscosity to fit the experimental permeability with the theoretical one, for the 100 nm and 200 nm ceramic membrane.

### 6.12 Summary

The study provided us some useful understandings on the influence of different physical parameters into liquid and gas filtration through micro-porous ceramic membrane. Thickness of the membrane filtration layer was found to contribute significantly in the filtration resistance. On the contrary, support layer contributed more during gas
permeation through ceramic membrane. Pore diameters measured using gas permeation method and porometry did not match with the value provided by the manufacturer. Techniques like size exclusion can provide a more direct measure of the filtration function of the thin selective layer coated on top of intermediate and support layers. Further work is required to explore the pore size measuring techniques by size exclusion method.

The permeability of ceramic membranes under different NaCl concentration and temperature fitted the Hagen-Poiseuille model. For both the 100 nm and 200 nm membranes, permeability decreased slightly with increasing NaCl concentration. From 3 g/L salinity (brackish water) to 35 g/L salinity (sea water) the permeability reduced 8% and 6% for the 100 nm and 200 nm Pall ceramic membranes respectively. However, the experimental permeability for DI water was less (on the order of 15% and 12% for the 100 nm 200 nm membranes respectively) than that of the theoretical one, which was explained by the Debye-Huckel theory. At salinity of 0.5 g/L or above, the effect of the electrical double layer on permeability was insignificant. The permeability of the membranes also increased with increasing temperature in the range of 0°C – 50°C in accordance with viscosity decreases across this temperature range. If temperature is increased from 15°C to 35°C, the permeability in a treatment plant will be increased by 52%. The effect of pH on permeability was observed to be insignificant.

These basic parameters have some effects on permeability, but not as significant in comparison to those testing real systems. Therefore the measured changes in flux due to these parameters are more closely associated with impacts on the fouling (membrane adhesion and percolation). The effect of these parameters on the permeability of microporous ceramic membranes would give us some basic information while investigating the treatment of secondary effluent through ceramic microfiltration membranes with ozone pre-treatment.

6.13 References


Ceramic Membrane Filters SCHUMASIV™ & SCHUMASIV™ H Technical Information, P. Corporation, Editor.


Chapter 7

Effect of ozone on ceramic membrane materials
7.1 Introduction
In this chapter, the decomposition of ozone amongst the individual and combined components (organics and minerals) of synthetic secondary effluent (SSE) will be investigated. This leads to the study of how this decomposition is affected by the presence of common ceramic membrane materials Al₂O₃, TiO₂ and SiC. The catalytic degradation of O₃ by Al₂O₃ and TiO₂, to hydroxyl radicals (•OH) was studied using pCBA as a probe for •OH formation. The •OH formation is significant as it is considered widely in the literature as playing a role in the beneficial features of ceramic membranes in contact with ozone. The aim of this chapter is to provide supporting knowledge of the role of ozone in wastewater treatment specifically in the presence of ceramic membrane materials.

7.2 Effect of minerals and organics on ozone decomposition
The organic and mineral components used to prepare the SSE are shown in Table 7.1 [1]. Ozone decomposition experiments were conducted with the SSE organics and minerals separately and then combined (method described in Section 3.4.5). Figure 7.1 shows the comparison of ozone decomposition after 10 minutes of ozonation in de-ionized (DI) water, then in the presence of organics of SSE, minerals of SSE and complete SSE.

<table>
<thead>
<tr>
<th>Organics</th>
<th>Composition (mg/L)</th>
<th>Minerals</th>
<th>Composition (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arabic gum powder</td>
<td>4.695</td>
<td>NaNO₃</td>
<td>30.0</td>
</tr>
<tr>
<td>Nitro humic acid</td>
<td>4.246</td>
<td>CaCl₂</td>
<td>30.0</td>
</tr>
<tr>
<td>Tannic acid</td>
<td>4.175</td>
<td>NH₄HCO₃</td>
<td>19.8</td>
</tr>
<tr>
<td>Peptone</td>
<td>2.703</td>
<td>(NH₄)₂SO₄</td>
<td>7.1</td>
</tr>
<tr>
<td>Sodium lignin sulfonate</td>
<td>2.427</td>
<td>K₂HPO₄</td>
<td>7.0</td>
</tr>
<tr>
<td>Beef extract</td>
<td>1.802</td>
<td>MgSO₄</td>
<td>0.71</td>
</tr>
<tr>
<td>Sodium laureth sulphate</td>
<td>0.942</td>
<td>Total</td>
<td>94.6</td>
</tr>
<tr>
<td>Total</td>
<td>20.99</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The DI water decay curve indicates that the decomposition of ozone was very slow and apparently stable over the 30 minute experiment duration. This is in agreement with previous work, where tests on high purity water showed ozone decomposes to
approximately 50% of the initial concentration within 6 to 17 hours [2]. Applying the same rate, only 2% of the initial ozone concentration is estimated to decompose in the first 30 minute period, which aligns with our finding where 3% of the initial ozone decomposed in the same period.

The decay of ozone in the presence of organics showed a similar stability to DI water. Meanwhile, the decay observed in minerals and in complete SSE was much more rapid over the test period. However, the initial concentration of ozone in the SSE was much lower (1.4 mg/L) than the other tests (> 5 mg/L). The likely reason is explained in the last paragraph of this section. The varying ozone decay rates can be better analysed with a reaction rate study. According to the literature, the ozone oxidation reaction follows first order kinetics when ozone is reacted with biologically treated wastewater of aniline dye production [3]. The first order reaction rate constant, \( k \) (s\(^{-1}\)), was calculated according to:

\[
  k = -\frac{1}{t} \times \ln \left( \frac{C}{C_0} \right)
\]

(7.1)

Where, \( C \) is the concentration of ozone remaining in the reactor (mol/L) at a given time \( t \). The observation that ozone decomposition in the presence of organics alone was similar to that of the DI water is interesting as it would be expected to see at least some ozone decay being evidence of a reaction [4].

![Figure 7.1: Comparison of residual ozone concentration in DI water, and SSE organics and minerals, and SSE (Temperature: 22±1°C).](image)
The slow decay of ozone with organics may relate to the way the experiment was conducted. The collected data, shown in Figure 7.1, were taken after 10 minutes of ozonation. Therefore, ozone reactions with the organics might be completed during this preliminary 10 minutes reaction. Such a case represents the way in which a real ozone system works, where some ozone reaction would occur (from several minutes, to up to 20 minutes) in a contact vessel (including piping) prior to contact with the ceramic membrane. No ozone concentration data was recorded prior to the preliminary reaction time and any ozone demand before this time was not measured.

In Figure 7.2 and Table 7.2, it is shown that the data (Equation 7.1) for ozone decay in the presence of minerals and SSE are fitting reasonably to a first order kinetic model according to the $R^2$ values shown in Table 7.2 (0.92 or greater). Due to the very low dependence of time to ozone concentration in the case of DI water and organics, lower $R^2$ values were found. Values recorded over a longer time period would be needed to increase the strength of the linear fit. However, it does show the reaction rates are very low relative to the minerals and SSE.

![Figure 7.2: First order linear plot for the decomposition of ozone in the presence of DI water, organics of SSE, minerals of SSE and SSE (S and F represent the faster and slower ozone decay in the SSE respectively, Temperature: 22±1°C).](image)

From Table 7.2, it is noted that ozone decomposition continues to occur in the presence of minerals, giving a $k$ value of $2.3 \times 10^{-3}$ s$^{-1}$ which is two orders of magnitude higher
than the decomposition rate of DI water. It has been demonstrated [5] that the solubility of ozone in water decreases as the salt concentration increases. Generally, a lower solubility results in a higher decomposition rate of ozone. Ershov et al. (2008) also found that ozone decomposition rate increases with the concentration of dissolved salt [6]. Therefore the ozone decomposition rate found in this study suggests that the ongoing reactivity of ozone after 10 minutes of prior ozonation is due to the presence of mineral components in the solution. The initial rate of ozone decomposition (SSE(F)) further increased in the full SSE complex, which contains the same quantity of minerals.

Table 7.2: Reaction rate constants $k$, with corresponding $R^2$ values for the DI water, SSE organics, SSE minerals, SSE (F) and SSE (S).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$k$ (s$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DI water</td>
<td>$0.001 \times 10^{-3}$</td>
<td>0.73</td>
</tr>
<tr>
<td>Organics</td>
<td>$0.0005 \times 10^{-3}$</td>
<td>0.13</td>
</tr>
<tr>
<td>Minerals</td>
<td>$2.3 \times 10^{-3}$</td>
<td>0.99</td>
</tr>
<tr>
<td>SSE (F)</td>
<td>$13.8 \times 10^{-3}$</td>
<td>0.92</td>
</tr>
<tr>
<td>SSE (S)</td>
<td>$0.58 \times 10^{-3}$</td>
<td>0.98</td>
</tr>
</tbody>
</table>

The initial ozone concentration at time 0 min, for the SSE was 1.4 mg/L only (Figure 7.1) whereas it was always above 5 mg/L for the DI water, SSE minerals and SSE organics. Moreover, the decay of ozone demonstrated two phases for the SSE, a faster phase for the first 1 minute and then a comparatively slower phase for the remaining test period. In Figure 7.2 and Table 7.2, the comparatively faster and slower ozone decay phases in the SSE are denoted by SSE(F) and SSE(S) respectively. The first order decay rate constant, $k$, in the faster phase of SSE was found to be $13.8 \times 10^{-3}$ s$^{-1}$ which is more than 1000-fold faster than the decomposition rate in DI water, and six-fold fast than with just minerals. The higher rate of the complete SSE in the first phase, and lower rate in the second phase compared to just the minerals cannot be determined with the present data, but may relate to effects of initially catalysed effects when minerals and organics are present. Afterwards, the remaining organic material reacts slowly [7]. The decomposition of ozone in SSE organics was too low ($k < 0.001 \times 10^{-3}$ s$^{-1}$) to be used as reference. However, the significance of the ongoing ozone decay rates after 10 minutes lies in representing the reactions that occur when the ozone approaches the membrane in an ozone-ceramic membrane filtration rig.
7.3 Effect of ceramic membrane materials on ozone decomposition

7.3.1 Effect of ceramic material types

Figure 7.3 shows the ozone decomposition in 0.5 g/L NaCl solution and in 0.5 g/L NaCl solution with 20 g/L of Al₂O₃, TiO₂ or SiC powders (method described in Section 3.4.6). As it has been observed in a study on the photo-catalysis of organic matter using titania that organics can be reduced as a result of adsorption [8], no organics were added in the solution to observe the decomposition of ozone only. Figure 7.4 shows the corresponding first order linear plot based on Equation 7.1. The values of residual ozone concentration below the limit of detection (0.2 mg/L) were not included in the calculation of the first order decay rate.

It was found that the kinetics of ozone decomposition in water and in aqueous solutions of NaCl is well described by the first-order equation as the linear correlations were always greater than 0.95, similar to the decay of ozone in the presence of SSE minerals (Figure 7.1). Moreover, Ershov et al. (2007) also found that the kinetics of ozone decomposition in solutions of Na₂SO₄, NaCl, and NaNO₃ can be described by a first-order equation [6]. First order reaction rate constants, k, for all solutions including the ceramic powders were calculated with corresponding R² values and are shown in Table 7.3. The activity of the three metal oxide powders was observed to occur in the order: SiC < Al₂O₃ < TiO₂.
Figure 7.4: First order linear plot for the decomposition of ozone in aqueous NaCl solution with the presence of SiC, Al₂O₃ and TiO₂ (initial pH of NaCl solution = 7, Temperature: 22±1°C).

The ozone decay for the TiO₂ experiment was very rapid (30 seconds), indicating that TiO₂ acts as a catalyst. The TiO₂ used in the study was P25 (Degussa). The high catalytic activity of P25 has been reported in many studies [9, 10]. It is used for destruction of organic matter. Beltran et al. (2002) showed that TiO₂ can be used as an active catalyst in the ozonation of organic molecules such as oxalic acid [11]. Yang et al. (2007) studied ozonation of nitrobenzene on nano-TiO₂ and observed that nano-TiO₂ in the form of rutile is catalytically active [12]. In the results presented in Figure 7.3, no organic matter was present; however, the results so far highlight the ozone decay in simple saline solution.

Table 7.3: Reaction rate constants k with corresponding R² values for the decomposition of ozone in aqueous NaCl solution with the presence of SiC, Al₂O₃ and TiO₂ powders.

<table>
<thead>
<tr>
<th>Sample</th>
<th>k (s⁻¹)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>1.70 × 10⁻³</td>
<td>0.99</td>
</tr>
<tr>
<td>SiC + NaCl</td>
<td>4.74 × 10⁻³</td>
<td>0.98</td>
</tr>
<tr>
<td>Al₂O₃ + NaCl</td>
<td>20.80 × 10⁻³</td>
<td>0.97</td>
</tr>
<tr>
<td>TiO₂ + NaCl</td>
<td>111.00 × 10⁻³</td>
<td>0.95</td>
</tr>
</tbody>
</table>

In order to observe any connection between the catalytic effect of the powders and their physical properties, the BET surface area and pore sizes were measured using N₂ porosimetry. The method is described in Section 3.5.11. The first order reaction rate constants of SiC, Al₂O₃ and TiO₂ and powders in NaCl solution with their
corresponding BET surface area and pore sizes are presented in Figure 7.5. It is clear from Figure 7.5, that there were no clear correlations, suggesting that the decomposition of ozone in the presence of different powders was not exclusively tied to the BET surface area or the pore sizes of the powders. While there are only three points on each figure, it is clear that TiO$_2$’s significantly higher reaction rate separates it from the other materials. This implies that, the stronger catalytic property of TiO$_2$ works more significantly than the measured porous properties. Meanwhile, the material with the lowest surface area and largest pore size (SiC) showed the lowest reaction rates. Therefore, while the decomposition of ozone in the presence of different metal oxide powders is mainly attributed to the catalytic properties of the powders, materials with lower catalytic effects such as SiC and Al$_2$O$_3$ exhibit some dependence on the pore size and surface area. Surface chemistry, such as hydrophobicity/hydrophilicity and surface charge are also potential influencing properties that haven’t been considered here.

![Figure 7.5: Comparison of first order reaction rate constants, $k$ (s$^{-1}$) with BET area (m$^2$/g) and pore size (nm) for the decomposition of ozone in the presence NaCl solution, SiC, Al$_2$O$_3$ and TiO$_2$ (initial pH of NaCl solution = 7, Temperature: 22±1°C).](image-url)

In the work presented so far, ozone decay was accelerated in the presence of Al$_2$O$_3$, and because it is a major component of the ceramic membrane (supporting material and in some cases is the coating material), it will be important to also evaluate the catalytic activity of Al$_2$O$_3$ powders using a $^\cdot$OH probe compound. As a reference, TiO$_2$ will also be used in the analysis due to its strong catalytic effect. Even though SiC is a well-known membrane material [13] it will not be studied further, since it does not exhibit any significant catalytic properties with ozone.
7.3.2 Catalytic decomposition of ozone by Al₂O₃ and TiO₂ and formation of •OH radical

The effect of Al₂O₃ and TiO₂ catalytic activity was studied by carrying out non-catalytic and catalytic ozonation experiments under similar experimental conditions (method described in Section 3.4.7). In these experiments, para-chlorobenzoic acid (pCBA) was used as the •OH-probe compound because it has a very low reactivity with molecular ozone [14] but reacts readily with •OH [15-17]. 10 μM pCBA, 1 mM phosphate buffer, 25 μM tert-BuOH in MQ water was used as a model solution. This small amount of tert-BuOH in the model solution was added because ozone decomposition in the MQ model solution was not consistent in the repeated tests. To avoid any alterations in the experimental results by even trace concentrations of organics, 25 μM tert-BuOH was added in the model solution [18]. Figure 7.6 shows the residual ozone concentration with time in the model solution only and in the model solution with Al₂O₃ and TiO₂ powders. The key difference in this experiment compared to the previous experiments, is the presence of the organic probe pCBA, phosphate buffer and tert-BuOH, and that ozone concentrations were measured immediately after introduction of ozone by spiking cold solution of ozone from stock. Therefore, the ozone decay includes the initial reactions, occurring this time in the presence of pCBA and tert-BuOH.

Interestingly, the decomposition of ozone in these tests occurred in two stages. First, an instantaneous ozone consumption phase occurred in the first few seconds (Figure 7.6).

This has been reported previously [4] where, the typical ozone decomposition trend in natural water has shown to consist of a practically instantaneous ozone consumption...
phase followed by a slower ozone decay phase. Since the experimental setup was not able to measure the instantaneous ozone decay phase, only the slower phase was measured here. Figure 7.7 shows the first order linear plot for decomposition of ozone during the slower phase in the model solution only and in the model solution with Al₂O₃ and TiO₂ powders, including linear fits and corresponding R² values. From the linear fits for each solution, the first order reaction rate constants of the slower decay stages were derived and are shown in Table 7.4.

In Figure 7.7, first order rate constants of ozone decomposition during the slower decay phase for the model solution only, model solution with Al₂O₃ and TiO₂ powders were $3.5 \times 10^{-3}$ s⁻¹, $3.9 \times 10^{-3}$ s⁻¹ and $8.5 \times 10^{-3}$ s⁻¹ respectively. The residual ozone concentration in the model solution decreases much faster in the presence of TiO₂ compared to model solution only or even in the presence of Al₂O₃ sample, which is in agreement with our previous results in Section 7.3.1. Al₂O₃ has minor but some catalytic effect on ozone decomposition. This is an interesting finding compared to the study using just NaCl solution and ceramic materials (Figure 7.3), where Al₂O₃ dispersed in solution led to a much greater increase of the ozone decay rate. Similar to the reaction of minerals and organics with ozone (in Figure 7.1), the model solution reacted in Figure 7.6 on their own facilitated ozone decay. Therefore, it appears that ozone decay in solutions of minerals with organics is already occurring at a significant rate in comparison to the increased rate due to the presence of Al₂O₃. This implies little additional effect of the Al₂O₃ present as the mm thick ceramic membrane support material. However, membrane coatings can be made from other metal oxides. In the case of TiO₂, an additional decay effect could be harnessed if a similar material was included within the support, or as a surface coating, but would need specific investigation as the TiO₂ powder is a purpose designed catalyst containing a high proportion (70%) of the catalytically active anatase phase, while commercial ceramic membranes with TiO₂ coatings are more likely to consist of the more chemically stable, but poorer catalytic, rutile phase. Therefore it appears from the results so far, that conventional ceramic membranes may offer little catalytic effect on top of the existing reactions between minerals and organics present in wastewaters, where typical ozone treatment is usually limited to no more than 20 minutes of contact time in practice.
Figure 7.7: Rate constants for the decomposition of ozone in model solution* only, model solution with Al₂O₃ powder and TiO₂ powder (* MQ water with 10 μM pCBA, 1 mM phosphate buffer, 25 μM tert-BuOH, Temperature: 22±1°C).

To explore the breakdown more closely, •OH radical formation can be analysed via measurement of pCBA. The rate of pCBA decomposition in an ozonation process can be expressed as [19]:

$$\frac{d[pCBA]}{dt} = -k_{OH,pCBA}[pCBA] \cdot [\cdot OH] \quad (7.2)$$

Equation 7.2 can be rearranged and integrated as:

$$\ln([pCBA]/[pCBA]_0) = -k_{OH,pCBA} \int [\cdot OH]dt \quad (7.3)$$

Elovitz and von Gunten [20] proposed the term $R_{ct}$ as the ratio of •OH radical exposure vs. ozone exposure. As $R_{ct}$ represents the ratio of •OH radical formed and ozone therefore, higher $R_{ct}$ is the indication of greater formation of •OH radical. Since, the more •OH radical represents the better catalyst, therefore, $R_{ct}$ might be used to explain the catalytic properties of the ceramic materials. $R_{ct}$ can be expressed as:

$$R_{ct} = \frac{\int [\cdot OH]dt}{\int [O_3]dt} \quad (7.4)$$

•OH radical exposure can be obtained from Equation 7.3:
\[ \int [\cdot OH]dt = -\ln([pCBA]/[pCBA]_0)/k_{OH,pCBA} \quad (7.5) \]

The ozone exposure can be calculated by the integration of the ozone concentration over the reaction time. Substituting Equation 7.5 into 7.4 gives:

\[ \ln([pCBA]/[pCBA]_0) = -R_{ct} \times k_{OH,pCBA} \int [O_3]dt \quad (7.6) \]

When the \( pCBA \) concentration is plotted with respect to \( O_3 \) exposure (product of ozone concentration and time) as shown in Figure 7.8, the slope represents the \( R_{ct} \times k_{OH,pCBA} \) value. Since \( k_{OH,pCBA} \) is well known to be \( 5 \times 10^9 \text{ M}^{-1}\text{s}^{-1} \) [20], the \( R_{ct} \) value can be obtained from this slope.

\[ R^2 = 0.9911 \quad \triangle \text{ Model solution} \]
\[ R^2 = 0.9975 \quad \times \text{ Model solution} + \text{Al}_2\text{O}_3 \]
\[ R^2 = 0.991 \quad \square \text{ Model solution} + \text{TiO}_2 \]

\[ -1.5 \quad 0.0000 \quad 0.0020 \quad 0.0040 \quad 0.0060 \quad 0.0080 \quad 0.0100 \]
\[ 0.000 \quad 0.002 \quad 0.004 \quad 0.006 \quad 0.008 \quad 0.010 \]
\[ \ln \frac{pCBA}{[C/C_0]} \]

\[ \text{O}_3 \quad [\text{Mol} \cdot \text{sec}] \]

\text{Figure 7.8: } pCBA \text{ concentrations with respect to ozone exposure for the decomposition of ozone in model solution* only, model solution with Al}_2\text{O}_3 \text{ powder and TiO}_2 \text{ powder ( * MQ water with } 10 \mu\text{M } pCBA, 1 \text{ mM phosphate buffer, } 25 \mu\text{M tert-BuOH, Temperature: } 22\pm1\degree \text{C).} \]

According to the results of the experiments, the \( R_{ct} \) values for ozonation without any catalyst (MQ) and with \( \text{Al}_2\text{O}_3 \) and \( \text{TiO}_2 \) powders were \( 5.8 \times 10^{-8}, 6.8 \times 10^{-8} \) and \( 8.4 \times 10^{-8} \) respectively (Table 7.4). Ozonation in the presence of ceramic materials thus has a higher \( R_{ct} \) value than that of ozonation alone, which means that these metal oxides (\( \text{Al}_2\text{O}_3 \) and \( \text{TiO}_2 \) powders) act as catalysts to promote the formation of \( \cdot \text{OH} \) radicals in the ozonated solution. However, as observed, the increase in ozone decay with the common ceramic material \( \text{Al}_2\text{O}_3 \) is slightly higher than without it, but catalytic \( \text{TiO}_2 \)
shows a significant increase (more than double) in the ability to decay ozone and produce ·OH radicals.

Table 7.4: Reaction rate constants $k$ and $R_{ct}$ calculated over the second stage of decay in the model solution, model solution with Al$_2$O$_3$ and model solution with TiO$_2$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$k$</th>
<th>$R_{ct}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model solution</td>
<td>$3.5 \times 10^{-3}$</td>
<td>$5.8 \times 10^{-8}$</td>
</tr>
<tr>
<td>Model solution + Al$_2$O$_3$</td>
<td>$3.9 \times 10^{-3}$</td>
<td>$6.8 \times 10^{-8}$</td>
</tr>
<tr>
<td>Model solution + TiO$_2$</td>
<td>$8.5 \times 10^{-3}$</td>
<td>$8.4 \times 10^{-8}$</td>
</tr>
</tbody>
</table>

7.4 Discussion

Generally organic compounds with diverse structures can either accelerate or inhibit ozone decomposition via their direct reactions with ozone and participation in ·OH chain reactions [21-24]. The organic profile shown in Table 7.1 consists of a diverse range of organics, such as peptides, proteins, organic acids, biopolymers, surfactants and polysaccharides. Park et al. (2001) found that water with a significant amount of organic matter can enhance ozone decomposition via formation of ·OH radicals [4]. Westerhoff et al. (2007) directly measured the rate constants for reactions between ·OH radicals and organic matter from different sources [25]. The observed second order rate constant for reaction between the ·OH radical and organic matter ranged from $1 \times 10^8$ M$^{-1}$s$^{-1}$ to $5 \times 10^8$ M$^{-1}$s$^{-1}$. These observations cast light on the probable mechanism for the reaction between ozone and organics. In this process, the reaction probably begins with the decomposition of ozone, or its reaction with water, to form ·OH radicals. Ozone might also react with some organics very promptly. However, since the radicals are highly reactive they will disappear rapidly through reaction with organics. Therefore, after 10 continuous minutes of ozonation there is no component remaining in the solution to react with ozone and the ·OH radical. Consequently, residual ozonation then follows a profile similar to the DI water case.

The initial ozone concentration during the ozonation of SSE was very low (1.5 mg/L) compared to the case for DI water, SSE minerals and SSE organics. In the SSE case, ozone decayed simultaneously with minerals and organics. Therefore, more ozone was decomposed during the initial 10 minutes of ozonation and resulted in a lower residual ozone concentration (1.4 mg/L) after 10 minutes. In the second ozone decay phase of SSE, the residual ozone concentration was lower than for the case with minerals alone.
This is probably because the reaction of ozone with combined organics and minerals generated excess ’OH radicals, resulting in complete reaction of the minerals and majority of the organics. Some organics had a lower reactivity with ozone. Therefore, the second phase of the SSE showed a lower decay of ozone than the minerals case as the organics with lower reactivity with ozone reacted in this phase.

These tests all involved measuring ozone decay after 10 minutes of ozonation. The dose was significant in terms of representing the reactions that occur in an industrial ozone-ceramic membrane filtration plant. In ozone treatment plants, ozone can be injected (directly or by side stream) into the wastewater and reacts while flowing through a contact volume (including a specifically designed pipe channel) ahead of the membrane unit. Ozone can also be injected into a mixed contact tank with residence time of (for example) 20 minutes and fed to the ceramic membrane unit. This latter case represents the equivalent process to the tests herein. Therefore, the first order reaction rate constants measured here reflect one of the typical applications of ozone to wastewater in industry. Regardless, subsequent testing using the probe pCBA involved measurement of ozone decay upon the first contact with the organics and minerals in solution to observe the fastest reaction rate.

The complex nature of the decomposition of ozone in the model solution and in the model solution with the presence of ceramic powders can be explained by a simple method proposed by Hoigné et al. (1994). In this method, the instantaneous ozone demand and the second half-life of ozone are used to analyse the water quality during ozonation [26, 27]. Generally, when ozone is added to natural water, it is consumed in two steps: the rapid ozone consumption step and the relatively slower decay step. The quantity of ozone consumed during the first stage can be represented by an instantaneous ozone demand parameter, which corresponds to the difference between the applied ozone and the quantity of ozone measured after a few seconds. The rapid reaction step is followed by a moderate or slower ozone decay stage. Hoigné (1994) introduced a convenient parameter called the second half-life, which is defined as the ozone decomposition rate, the time within which the residual concentration decreases from 50% to 25% of its initial value [26, 27]. In this research the instantaneous ozone demand for the model solution only, model solution with Al₂O₃ and model solution with TiO₂ (Figure 7.6) were 1.18 mg/L, 2.05 mg/L and 2.18 mg/L respectively, which are 33%, 49% and 58% of the initial ozone doses respectively. The higher instantaneous
ozone demand for the Al₂O₃ and TiO₂ powders compared to the solution with our inorganic materials indicate some catalytic activity of the powders in ozone decomposition.

Based on the above mentioned discussion, the common ceramic membrane substrate material Al₂O₃ was the second most active material in increasing the ozone decay rate, being 20% of the rate of TiO₂ during the slower decay phase. Al₂O₃ is also one of the most often used catalyst or catalyst supports in research articles, as its catalytic activity was shown in one of the first papers on catalytic ozonation [28]. However, the results of many of the studies are debatable. In some studies, catalytic activity was observed [29-32], while in some studies Al₂O₃ did not cause decomposition of ozone [33-35].

In trying to resolve the inconsistency of the findings, Nawrocki et al. (2013) reported that the properties of Al₂O₃ are modified by mineral contaminants. The main contaminant of alumina is sodium, which causes a pH increase after the introduction of the oxide to water [36]. They purified the oxides by rinsing them first with 0.1 M HCl and then with water to neutrality. Another portion of the oxides were extracted with high purity water (Millipore) in a Soxhlet apparatus [37]. They found that, purification with dissolved acid was not sufficient and the process of ozone decomposition still occurred in the case of HCl purified oxides. However, extraction with water in a Soxhlet apparatus causes the oxides to practically lose their “catalytic” properties [36].

On the other hand, Ikhlaq et al. (2013) reported that ozone decomposition on alumina occurs via radical chain reactions involving the formation of active oxygen species such as •OH and •O₂⁻ [38]. They showed that alumina promotes much higher formation of reactive oxygen species (H₂O₂ and •O₂⁻) in aqueous solutions when compared to ozonation alone, and found similar results in the presence of ZSM-5 zeolites, being micro-porous alumina silicates. However, the Al₂O₃ in their study was used as supplied, without any purification. Moreover, the solution pH was adjusted with HCl or NaOH. In the study presented in this thesis, the powders were rinsed continuously with water until a stable pH value was achieved as a result of understanding the problems encountered in the literature from original synthesis impurities. The pH values were adjusted to 7 with NaOH in the NaCl solution prior to ozone application. However, there was no change in pH for the Al₂O₃ and TiO₂ powders. The pH values before and after ozonation on the powders are presented in Table 7.5. It is unknown from the present data why the pH of
less reactive solutions (NaCl only and with SiC) declines other than the possibility of the carbonate equilibrium buffering the system towards a pH of 5.8, but when more reactive ceramic materials are present, the pH is maintained. The more reactive Al$_2$O$_3$ and TiO$_2$ may have facilitated removal of residual ozone prior to pH measurement (assuming that ozone in solution reduces the measured pH), but this cannot be proven from the results presented here.

**Table 7.5: pH values before and after ozonation of aqueous NaCl solution with the presence of SiC, Al$_2$O$_3$ and TiO$_2$ powders.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH before ozonation</th>
<th>pH after ozonation</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>6.96</td>
<td>5.45</td>
</tr>
<tr>
<td>SiC + NaCl</td>
<td>7.0</td>
<td>5.52</td>
</tr>
<tr>
<td>Al$_2$O$_3$ + NaCl</td>
<td>7.0</td>
<td>6.93</td>
</tr>
<tr>
<td>TiO$_2$ + NaCl</td>
<td>7.0</td>
<td>6.9</td>
</tr>
</tbody>
</table>

While investigating the decomposition of the pCBA probe in the MQ model solution in the presence of Al$_2$O$_3$ and TiO$_2$ powders, a much higher $R_{ct}$ value was observed for the model solution containing TiO$_2$ (Table 7.5). A higher $R_{ct}$ value corresponds to a higher $\cdot$OH production [20]. The Al$_2$O$_3$ powders showed only a small catalytic enhancement on ozone decomposition with the presence of pCBA. However, the TiO$_2$ powders showed very high catalytic effect compared to the MQ model solution and model solution with Al$_2$O$_3$ powders. The properties of the surface of metal oxides strongly depend on pH. At higher pH (pH > pH$_{PZC}$, (PZC = point of zero charge, the pH value at which the net surface charge is zero)) the surface of a material is negatively charged, at acidic pH (pH <pH$_{PZC}$) its surface is positively charged, while at pH = pH$_{PZC}$ the surface is neutral (surface hydroxyl groups with no charge) [29, 39, 40]. The increase in the $R_{ct}$ value in catalytic runs supports the common assumption that $\cdot$OH radicals are generated from the interaction of OH$^-$ ions in water with surface catalyst sites together with ozone [41-43]. Since, the pH$_{PZC}$ of TiO$_2$ is 3.8 [44], at the experimental pH value of 7.5 the surface is negative, which would have increased the exposure to $\cdot$OH radicals to a considerably larger extent than activated alumina, whose pH$_{PZC}$ is 8.2 [30] and was mildly positively charged at the experimental pH. Therefore, the Al$_2$O$_3$ powders which showed reduced catalytic effect may be related to the charge of the material.
7.5 Conclusions

The residual ozone concentration after 10 minutes of ozonation in DI water, SSE, and different components of SSE were measured to investigate the ozone reaction before reaching the membrane unit in a real ozone-ceramic membrane treatment plant. The SSE had a rapid ozone decay phase and a comparatively slower ozone decay phase during ozone decomposition once ozone supply was stopped after 10 minutes of dosing. Although the organics did not show any effect in the decomposition of ozone after 10 minutes of ozonation, it was proposed that any ozone demand from the organics was exhausted by very fast initial reactions between organics and ozone.

The results of the catalytic runs showed that there is a significantly stronger catalytic effect of the TiO$_2$ powders, while the common Al$_2$O$_3$ membrane substrate material shows a very slight effect to accelerate ozone decay compared to what happens already between minerals and organics. The higher $R_{ct}$ value, which indicates the rate of $\cdot$OH radical generation, was observed on the most active catalyst (TiO$_2$) for the decomposition of dissolved ozone. This fact is consistent with the assumption that the ceramic membrane materials act as catalysts in promoting the generation of $\cdot$OH radicals, being significant for TiO$_2$ but very slight (potentially insignificant) for Al$_2$O$_3$. These metal oxide powders served to represent the widely used materials to manufacture ceramic microfiltration and ultrafiltration membranes. Investigating the ozone decomposition across the ceramic micro/ultrafiltration membranes will be shown in the next chapter to extend the exploration of the interesting mechanisms into real membrane flow conditions.

7.6 References


Chapter 8

Decomposition of ozone through ceramic membranes
8.1 Introduction

In this chapter, the decomposition of ozone will be explored when in the presence of separate components (organics and minerals) of synthetic secondary effluent (SSE) and the full composition of SSE running through a Pall tubular ceramic membrane and a multi-channel Metawater ceramic membrane. The effect of different experimental conditions during ozonation (like stirring, contact of air with ozonized samples) will be considered. Decomposition of ozone in filtered tap water with para-chlorobenzoic acid (pCBA) and bromide was conducted to investigate the beneficial role of ceramic membrane in the generation of hydroxyl (\(^{•}\)OH) radicals and the potential reduced formation of bromate. pCBA was replaced by tert-BuOH to avoid the effect of \(^{•}\)OH in the reaction pathway. The work in this chapter aimed to understand more fundamentally the ozone interaction effects that could occur in real applications involving complex fouling layers which occurred in Chapter 5.

8.2 Ozone decomposition through Pall ceramic membrane

Figure 8.1 shows the concentrations in samples taken immediately prior to entering the membrane (feed), just after passing over the membrane (concentrate) and just after passing through the membrane (permeate), described according to Section 3.4.8. The feed solutions included DI water, 500 mg/L NaCl solution at pH 7 and 9, SSE minerals separately, and full SSE through a 200 nm Pall ceramic membrane (composition of SSE in Table 7.1). Also, in order to establish any background effect associated with the module, decomposition of ozone through the membrane inside the stainless steel module was also investigated. Each concentration bar is calculated to a single value by averaging the last five measured values of concentration after the experiments reached a steady state (approximately 35 minutes). Error bars are calculated using standard errors of the mean. The concentrations are presented in the order following the experimental sequence.

All tests showed a decrease in ozone in permeate samples, while concentrations in the concentrate samples were either equal or less than the feed. In 500 mg/L NaCl solution at pH 7, the residual ozone concentration was less in the concentrate than the feed. In Chapter 7, the result of the decomposition of ozone in 500 mg/L NaCl solution at pH 7
is given (Section 7.3.1). The first order rate constant of ozone decomposition was very slow, at $1.70 \times 10^{-3}\text{ s}^{-1}$.

Moreover, it has been shown previously that the ozone decomposition rate increases with the concentration of dissolved salt [1, 2]. However, as the residual ozone concentration in the permeate was much less than the concentrate (2 mg/L approximately), this appears to be an effect by which the ozone is removed as a result of permeating through the membrane. According to the manufacturer (Pall Corporation), both the membrane coating and support material are made of Al$_2$O$_3$. It has been shown in Chapter 7 that Al$_2$O$_3$ powder has only a very slight effect to accelerate ozone decay. Therefore, while the observed reduction in the residual ozone concentration in the membrane may be due to some slight catalytic effect of the membrane material, the large decrease could be due to other mechanisms. These will be discussed later in this chapter.

The residual ozone concentrations of 500 mg/L NaCl solution at pH 7 was measured in the concentrate and permeate by placing the membrane inside a stainless steel module. Residual ozone concentrations were almost similar to the test without the module, indicating the air exposure of the permeate when not confined by the module made little difference. In the case of increased pH to 9, the residual ozone concentration behaviour was again similar (although initial ozone concentrations in this case were higher). This finding contradicts the higher decomposition rate of ozone in higher pH values. Early observations of the lifetime of aqueous ozone indicated that the decomposition of the ozone is accelerated by increasing the pH [3]. The reason is the catalytic action of hydroxyl ions OH\textsuperscript{-}. The mechanism of interaction is complex and includes a successive chain of reactions that yield H$_2$O$_2$, O$_3^-$, 'OH and HO$_2$\textsuperscript{*} radicals [4-7]. These molecular and radical products also interact with ozone and thereby initiate its chain decomposition [8]. The behaviour of the unchanged residual ozone concentration at pH 9 is not clearly understood. However, the observed lower concentration of ozone in the permeate is again consistent with the other samples indicating again that ozone is consumed when passing through the ceramic membrane.

While filtering SSE minerals, expected differences were observed for the residual ozone concentrations between the feed and the concentrate of the membrane due to decay of ozone in the presence of inorganic dissolved solids, as found in Chapter 7 (Section 7.2). However, the concentration of residual ozone in the concentrate of SSE was similar to
the feed. This can also be explained by the observations in Chapter 7 (Section 7.2). In Chapter 7, ozonation was stopped at 10 minutes and the residual ozone concentration at this time was 1.4 mg/L. In the current test, residual ozone concentrations were measured by taking average of the samples collected after 35 to 40 minutes of ozonation. 35 minutes of continuous ozonation probably minimized the efficacy of SSE to decompose ozone, resulted in similar ozone concentration in the feed and concentrate of the SSE run.

Figure 8.1: Average residual ozone concentration in the feed, concentrate and permeate of a Pall ceramic membrane while filtering different solutions of SSE (Flux: 240 L·m⁻²·h⁻¹; Temperature: 22±1°C.)

The permeate ozone was again lower than in the feed of SSE. The effect is compared to the case of permeating DI water through the membrane, which showed no rapid natural decline in ozone over the 30 minutes test (Section 7.2). Consistent with the results of Chapter 7, the concentrations of residual ozone while filtering DI water were very stable in the feed and concentrate of the membrane. Westerhoff et al. (2007) also found that tests on high purity water showed ozone decomposes to approximately 50% of the initial concentration within 6 to 17 hours [9]. Like in all other cases, ozone was depleted in the permeate of DI water. This reduction in ozone in the permeate cannot be explained by the natural ozone decay in solution in the time the water spends between the samples collected in the feed and permeate (~minutes). As the catalytic effect of Al₂O₃ was only slight (Section 7.3.2), other physical property differences may explain the consistent ozone decrease to the permeate, such as the pressure drop.
Another finding from this experimental study was the effect on pH due to ozonation of the samples. The initial pH value for all the solutions were 7.5 ~ 9, except for the DI water case. Surprisingly, the pH value after ozonation was found to be 4 ~ 4.3. In Chapter 7 the pH values of the NaCl solution and NaCl with SiC powders declined, becoming more acidic, after ozonation, where pH values were consistent before and after ozonation for the NaCl solutions with Al₂O₃ and TiO₂ powders (Table 7.5).

The pressure drops across the membrane for different solutions are given on top of the residual ozone concentration bars of each solution shown in Figure 8.1. The lowest pressure drop (24.8 kPa) was observed for the DI water run which also has shown lowest reduction (1.3 mg/L) on residual ozone concentration. However, the highest pressure drop (38.5 kPa) was observed for the SSE solution, but it did not show the highest reduction (2.5 mg/L) on residual ozone concentration. The pressure drop for the DI water was high relative to SSE because, the experiments were conducted in a way that (Section 3.4.8), ozone was continuously bubbled into the feed beaker using a bubble diffuser. After 10 minutes of ozonation, the feed pump of the membrane was turned on though the ozonation was continuing. As the reaction of ozone with the components of the SSE might have been completed within the preliminary 10 minutes of reaction, the pressure drop with the SSE was not much higher compared to that of the DI water. The residual ozone concentration in the permeate declined by 1.7 mg/L for the SSE solution. Henry's law states that the amount of a dissolved gas in a liquid is proportional to its partial pressure [10]. Therefore, the solubility of ozone is higher at higher pressure and placing the ozonized solution under reduced pressure makes the dissolved ozone less soluble. Thus, when the ozonized solution permeates through the membrane structure, depressurizing the solutions might have some effect to reduce the residual ozone concentrations in the permeate. Moreover, under reduced pressure conditions, dissolved ozone can expand and form large bubbles which may leave as gas from the solution. These further imply that the reductions in residual ozone concentrations are caused by combination of the depressurizing effect and some properties of the membrane materials. Although the physical structure of the Pall membrane is better understood, it is not as widely used in water treatment applications as a Metawater monolith. Therefore, to explore the behaviour in a more familiar water industry membrane; similar experiments were conducted using a multichannel Metawater ceramic membrane.
8.3 Ozone decomposition through Metawater ceramic membrane

Figure 8.2 shows the average residual ozone concentration through a multichannel Metawater ceramic membrane (method described in Section 3.4.9). Samples were taken for measuring the ozone concentration in the feed, concentrate and the permeate of the membrane. Each concentration bar in Figure 8.2 is calculated to a single value by averaging the last three measured values of concentration after the experiments reached a steady state (approximately 25 minutes). The error bars shown were determined from the standard error of the mean of these values. The concentration bars in Figure 8.2 are presented in the order following the experimental sequence.

![Figure 8.2: Average residual ozone concentration in the feed, concentrate and permeate of a Metawater ceramic membrane while filtering different solutions (Flux: 72 L·m⁻²·h⁻¹; Temperature: 22±1°C).](image)

Residual ozone concentrations for the 500 mg/L NaCl solution were slightly reduced in the concentrate and permeate of the Metawater ceramic membrane, relative to the feed. This is different to the Pall membrane, where the residual ozone concentration was reduced by 2.3 mg/L of ozone in the permeate (Section 8.2), which may be due to the lower pressure drop in the case of the Metawater membrane, as discussed earlier (i.e., 6-8 kPa vs. 26-39 kPa). Unlike the NaCl solution, the residual ozone concentration in the minerals of SSE were reduced in the concentrate and in the permeate of the Metawater ceramic membrane. This result is similar to the result of SSE minerals through the Pall ceramic membrane presented in Section 8.2. The residual ozone concentration in the
SSE was reduced as well in the concentrate and in the permeate of the Metawater ceramic membrane. The reduction in the concentrate can be due to the natural decomposition of ozone in the SSE minerals and SSE which differs to simple NaCl solutions as the SSE minerals contains a more complex mixture of salts.

Similar to the SSE, DI water showed decay of ozone in the concentrate and in the permeate of the Metawater ceramic membrane. This is contrary to earlier work, where the decomposition of ozone in DI water was very slow and apparently stable over the 30 minute experiment duration (Section 7.2). However, a repeated test with DI water through the Metawater ceramic membrane showed similar results. Therefore, there is an effect that cannot be explained by the pressure drop (indicated by the negligible ozone removal seen for the NaCl solution) or the decay expected from the components in solution (SSE minerals). The unique DI water decay may instead be explained by the order of experiments conducted with the Metawater ceramic membrane. The DI water run through the Metawater membrane was conducted after the SSE run. The membrane was chemically cleaned between each run using method described in Section 3.6.2. The organics and/or minerals of SSE may still be attached to the pore surfaces of the Metawater membrane, which possibly can cause ozone decomposition in the narrower channels. The repeated DI water test through the Metawater ceramic membrane was conducted after the SSE organics test. Since, the SSE organics and/or minerals may still be attached to the surface of the Metawater ceramic membrane, similar results were obtained by the repeated DI water test.

Residual ozone concentration in the SSE organics did not reduce at all in the concentrate and in the permeate of the Metawater ceramic membrane. In Chapter 7 (Section 7.2), it was observed that, after 10 minutes of continuous ozonation on the SSE organics ozone, decomposition was very slow (comparable to DI water). In this test with SSE organics through the Metawater ceramic membrane, the residual concentrations of ozone are calculated from the samples taken after 25 minutes. Therefore, no decay of ozone can be expected from that sampling time.

Similar to the results of the Pall ceramic membrane presented in Section 8.2, there was no relationship between the reductions of residual ozone concentrations with pressure drop. However, as mentioned earlier, the pressure drop was very low (6.3 ~ 7.7 kPa) during the Metawater membrane tests. The solubility of ozone in water depends on the
pressure of the water [11]. Therefore, depressurizing the ozonized solutions across the Metawater membrane may have a minor effect on reducing the residual ozone concentration. As per the advice of the manufacturer, the Metawater ceramic membrane used in this study contains a thicker $\alpha$-Al$_2$O$_3$ support layer and very thin Titania based filtration layer. The high catalytic activity of TiO$_2$ has already been reported in many previous studies [12, 13]. However, ozone decay only occurred consistently when SSE minerals were present (or for DI water, which was considered to be due to contamination from previous use with SSE). However, if the membrane played a role in catalytic decay of ozone when organics and/or minerals are present in solution or on the membrane surface, it cannot be concluded from the current data. Later in this chapter, analysis of possibly catalytic activity using a 'OH radical probe will be considered.

Similar to the Pall membranes and the results of Chapter 7, the pH values of the solutions after ozonation decreased to a value of 5 from 7.3 for the SSE minerals and SSE. Also, the pH value of the 0.5 g/L NaCl solution was reduced to 4.2 from 5.5. pH is a major influence on the ozone decomposition and catalytic behaviour [14, 15], so in order to avoid this effect, further experiments were conducted by direct liquid ozone dosing in the experimental solution. The decomposition of ozone through the Pall and Metawater ceramic membranes appears to vary according to a catalytic behaviour and changes in the environmental conditions. The formation of 'OH radical in the ceramic membranes in contact will now be explored using a 'OH radical sensitive probe, para-chlorobenzoic acid (pCBA). A fixed dosage of ozone was applied into the feed solution from a pre-prepared stock solution to avoid effects associated with changes of pH.

### 8.4 Hydroxyl radical formation through Pall ceramic membrane

To investigate the formation of 'OH radicals during combined ozonation and ceramic membrane filtration, experiments were conducted by recirculating ozonized samples through a stainless steel Pall membrane empty module, Al$_2$O$_3$ membrane, TiO$_2$ membrane and ZrO$_2$ membrane (method described in Section 3.4.10). The recirculated samples were collected from a beaker placed on a stirrer to analyse the decomposition of ozone. Samples were prepared using tap water (0.29 mg/L DOC; 220 $\mu$S/cm conductivity; 0.34 NTU turbidity) with 0.5 $\mu$M para-chlorobenzoic acid (pCBA) and
500 μg/L bromide. pCBA was selected as an ’OH-probe compound because it has a very low reactivity with molecular ozone [16] but reacts readily with ’OH [17-19]. Bromide was added to explore bromate formation, which will be discussed later in the chapter.

Figure 8.3 shows the average ozone decay rate constants of duplicate tests for the tap water solution (including pCBA and bromide) placed on a magnetic stirrer (moderate stirring) passing through an empty module, Al₂O₃ membrane, TiO₂ membrane and ZrO₂ membrane. Figure 8.4 shows the corresponding $R_{ct}$ (ratio of ’OH exposure to O₃ exposure) values calculated for the tap water solution passing through an empty module, Al₂O₃ membrane, TiO₂ membrane and ZrO₂ membrane. The calculation of $R_{ct}$ was described in Section 7.3.2.

As per Figure 8.3, the average first order decay rate constants for the tap water solution passing through an empty module and different ceramic material membranes were observed to have values in the following order: Empty module < TiO₂ membrane < Al₂O₃ membrane < ZrO₂ membrane. However, there were not significant differences between the decay rate constants of the empty module and those of the membranes. Any slight increase in ozone decay may be due to the degassing effect through the membrane. The increase in first order rate constants for the 3 membranes tested was too similar to conclude if the membrane material had any influence. The $R_{ct}$ values
presented in Figure 8.4 for the formation of \(^{1}OH\) radicals during the ozonized tap water experiment. The values with Al\(_2\)O\(_3\) membrane, TiO\(_2\) membrane and ZrO\(_2\) experiment are very close to the empty module. However, like the increased ozone decay rate of the ZrO\(_2\) membrane, it appeared that the \(R_{ct}\) for this membrane was similarly higher than all other cases. The results of ozone decay and \(^{1}OH\) radical formation from this test suggest an effect of the membrane in addition to the water components, although this is difficult to isolate. Further analysis on the commercial water treatment membrane, the multichannel Metawater ceramic membrane with a filtration area of 0.04 m\(^2\) (8 fold higher than that of Pall membranes) was also performed.

8.5 Hydroxyl radical formation through Metawater ceramic membrane

8.5.1 Hydroxyl radical formation with recirculating solution

Experiments were conducted using the same solution (tap water with 0.5 \(\mu\)M pCBA and 500 \(\mu\)g/L Bromide) through a Metawater membrane and its stainless steel empty module (method described in Section 3.4.11). An ozone decomposition test in the stirred (moderate stirring) feed beaker was conducted as a baseline to produce data for the ozone decomposition. Figure 8.5 shows the residual ozone concentration in tap water solution recirculated through the Metawater membrane and empty module and in the
stirred feed beaker. The residual ozone concentration was similar for the first two minutes of testing. However, from three minutes, the residual ozone concentration in the empty module and the Metawater membrane experiments suddenly decline at a faster rate. The sudden change in rate is because the feed beaker started to receive recirculated permeate after two minutes and 10 seconds. The first order linear reaction rate constants calculated using the samples from three minutes and onwards for the beaker, empty module and Metawater membrane were $0.47 \times 10^{-3}$ s$^{-1}$, $2.28 \times 10^{-3}$ s$^{-1}$ and $2.24 \times 10^{-3}$ s$^{-1}$ respectively (Table 8.1).

Looking at the decay rates shown in Table 8.1, the difference between ozone decomposition in the membrane and empty module is insignificant, which is visible in the samples taken starting at three minutes where the feed solution started to receive returned permeate. Between 2 and 8 minutes however, the residual ozone concentration through the Metawater membrane is lower than in the empty module. Like tests conducted in Section 8.3, there appeared to be some effect of ozone removal by the ceramic membrane but much smaller in this case where ozone was dosed instantly to the water instead of bubbling over longer time periods as conducted in the earlier tests. However, a change in pH was not occurring in this system.
Table 8.1: First order reaction rate constants $k$ and $R_{ct}$ in tap water solution in a beaker, passing through a Metawater membrane and empty module (0.5 μM pCBA: 500 μg/L bromide; applied ozone: 10 mg/L; pump flow rate: 48 mL/min, Temperature: 22±1°C).

<table>
<thead>
<tr>
<th>Test</th>
<th>$k$ (s$^{-1}$)</th>
<th>$R_{ct}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stirred feed beaker</td>
<td>$0.47 \times 10^{-3}$</td>
<td>$1.13 \times 10^{-9}$</td>
</tr>
<tr>
<td>Empty module</td>
<td>$2.28 \times 10^{-3}$</td>
<td>$1.93 \times 10^{-9}$</td>
</tr>
<tr>
<td>Metawater membrane</td>
<td>$2.24 \times 10^{-3}$</td>
<td>$2.13 \times 10^{-9}$</td>
</tr>
</tbody>
</table>

After 13 minutes (Figure 8.5), the residual ozone concentration for the membrane and empty module were much lower than for the stirred feed beaker. This indicates that, there was more significant decay of ozone occurring while sample water is passing through the membrane and/or empty module. During the experiments, the sample water was recirculating through the membrane and the module. The water was passed through the pump and piping to the membrane and/or module and then discharged from the permeate side of module. While leaving via the permeate, the tap water was exposed to air before returning to the feed beaker. These observations imply that, flowing water through a pump and piping can assist with the ozone degassing from solution, so the air exposure accelerated its removal.

The $R_{ct}$ values (ratio of $^\cdot$OH radical exposure vs. ozone exposure) calculated using the samples from three minutes and onwards for the beaker, empty module and Metawater membrane were $1.13 \times 10^{-9}$, $1.93 \times 10^{-9}$ and $2.13 \times 10^{-9}$ respectively (Table 8.1). Samples collected from the stirred feed beaker have a lower $R_{ct}$ value than that of the empty module and Metawater membrane. The lower rate of ozone decomposition in the stirred feed beaker compared to the empty module and Metawater membrane resulted in a lower $R_{ct}$ value in the stirred feed beaker samples. However, the $R_{ct}$ value for the Metawater membrane was slightly higher than that of the empty module though they have a similar rate of ozone decomposition. This is may be due to the effect of $^\cdot$OH radical formation by the ceramic membrane, being slightly higher than without the membrane in place.

However, the calculated decay rates of ozone for the Metawater membrane and empty module in Table 8.1 are not representative of the decomposition of ozone across the Metawater membrane/module alone. Since the ozonized tap water solution is recirculated to the feed beaker, the decay rates in Table 8.1 are representative of the combination of natural decomposition of ozone in the stirred feed beaker along with the
decomposition of ozone across the Metawater membrane/module. Repeated contact with air is a likely factor in the loss of ozone. Therefore, to avoid this excessive air contact and to isolate the effect of the Metawater membrane/module on the decomposition of ozone, single pass experiments were conducted with tap water solution through the Metawater ceramic membrane and empty module.

8.5.2 Hydroxyl radical formation with single-pass solution

In filtering water through the ceramic membrane, it passes through the thin selective coating and through a thicker substrate material with larger pore size. This accounts for the time the water is in contact with a ceramic membrane. To explore the contact time between the membrane material and ozonized samples, experiments were conducted using tap water solution with 0.5 μM pCBA and 500 μg/L bromide passing through the Metawater membrane and stainless steel empty module in such a way that, the ozonized tap water sample was pumped into the module for a period of time to ensure a complete fill of fresh feed. After a sufficient time, the pump was stopped and the sample was held inside the membrane rig. This was done for four different contact times (1 min, 3 min, 5 min and 7 min) over the course over a single ozonated water feed run. The feed beaker was covered with parafilm to minimise air contact with the ozone. In duplicate tests, the pCBA was replaced by 50 mM tert-BuOH. Tert-BuOH was used in order to quench •OH, as it is an effective scavenger with strong radical capturing ability. The reaction rate constants between tert-BuOH and either •OH or ozone has been reported as $k_{OH} = 5.9 \times 10^8 \text{M}^{-1} \text{s}^{-1}$ and $k_{O_3} = 3.0 \times 10^3 \text{M}^{-1} \text{s}^{-1}$ respectively [3, 20-22], highlighting the substantial ability for tert-BuOH to rapidly consume •OH radicals and remove their function from the investigation into the reaction (method described in Section 3.4.12).

Figure 8.6(a-d) shows the residual ozone concentration in tap water solution while passing through the Metawater ceramic membrane and empty module. The dashed lines in Figure 8.6(a-d) correspond to the concentration of residual ozone in the feed beaker whereas the isolated solid lines consisting of two points each correspond to the feed solution at the time it entered the module (first point) and the sample taken at the end of the hold period (second point). Therefore, any drop below the dashed line represents a concentration lower than what would be expected to occur in the original feed. The results show that running the feed solution through the membrane led to a decrease in ozone more than what would be expected if the feed where decaying in the beaker. The
amount of decline slowed as the original feed concentration declined as the run progressed, but still showed an appreciable loss from being held in the module as the hold times increased. While the differences were not large, the decrease in ozone concentration while being held with the membrane for 1 minute was larger compared to the run with tert-BuOH, giving some evidence that decay occurred via a 'OH radical pathway. The decay over 1 minute showed a smaller ozone decay with the empty module (membrane not present) when pCBA was present. However, with tert-BuOH in the module without membrane, ozone decay was similar to when the membrane was present. Therefore it appears that the entire system without the membrane will lead to ozone decay via 'OH radical formation, but the membrane uniquely facilitated the breakdown of the organic molecule. However, a more quantitative analysis is needed to confirm this very slight effect. The data in Figure 8.6 are analysed further in Section 8.7.
Figure 8.6: Comparison of residual ozone concentration in tap water with 500 μg/L bromide and a. 0.5 μM pCBA through Metawater membrane; b. 50 mM tert-BuOH through Metawater membrane c. 0.5 μM pCBA through
Metawater empty module; d. 50 mM tert-BuOH through Metawater empty module (dotted lines correspond to the ozone in feed beaker, straight line drawn as a guide between measured ozone concentrations at the start and end of the hold period; pump flow rate: 48 mL/min; Flux: 72 L·m⁻²·h⁻¹; Temperature: 22±1°C).

Figure 8.7a and 8.7b show the corresponding pCBA concentrations in tap water while passing through the Metawater ceramic membrane and empty module respectively. The dashed lines in the Figure 8.7a and 8.7b correspond to the concentration of pCBA in the feed beaker where the isolated solid lines consisting of two points each correspond to the feed solution at the time it entered the module (first point) and the sample taken at the end of the hold period (second point). Therefore, any decrease below the dashed line represents a concentration lower than what would be expected to occur in the original feed. The decrease below the dashed lines for each contact time were not large enough to confirm the ability of the membrane to generate 'OH radicals. Based on Figure 8.6 and Figure 8.7, it is possible to conclude here that the presence of pCBA (indicates the presence of 'OH radical) showed possible increased ozone decay rate. However, the measured pCBA decay at different contact times was not significant over the pCBA decay measured in the beaker (Figure 8.7).
Figure 8.7: pCBA concentration in tap water with 500 μg/L bromide and a. 0.5 μM pCBA through Metawater membrane; b. 0.5 μM pCBA through Metawater empty module; (dotted lines correspond to the pCBA in feed beaker, straight line drawn as a guide between measured pCBA concentrations at the start and end of the hold period; Flux: 72 L·m⁻²·h⁻¹; pump flow rate: 48 mL/min; Temperature: 22±1°C).

8.6 Bromate formation through Metawater ceramic membrane

8.6.1 Bromate formation with recirculating solution

In order to explore the mechanism of bromate formation during ozonation on a ceramic membrane, bromide was added to the feed solution of the experiments. The data are presented in Section 8.4 and onwards. Since bromate is a potential human carcinogen [23] and is well known to form as a result of ozone treatment of water containing bromide [22, 24-29], observing behaviour of the formation of bromate in the unique ozone-ceramic membrane process is highly significant. Figure 8.8 shows the corresponding bromide and bromate concentrations for the experimental results.
discussed in Section 8.5.1. Bromides and bromates were analysed using the same sample, taken at the 15 minute point of the experiments.

![Figure 8.8: Bromide and bromate concentration during ozonation of tap water sample passing through Metawater ceramic membrane (0.5 μM pCBA; 500 μg/L bromide; applied ozone: 10 mg/L; pump flow rate: 48 mL/min; Flux: 72 L·m⁻²·h⁻¹; Temperature: 22±1°C).](image)

As per Figure 8.8, the bromate concentrations measured in the samples taken at 15 minutes for the stirred beaker test, empty module and membrane were 560 μg/L, 203 μg/L and 101 μg/L respectively. Based on the results in Figure 8.8, the amount of bromate formed in the stirred beaker test was much higher compared to either the membrane and module tests. Further, the formation of bromate in the membrane test was found to be less than that of the empty module. The results therefore suggested bromate formation can be minimized using ceramic membranes. In previous work, it was found that the addition of a heterogeneous catalyst (TiO₂) to ozone minimized the formation of bromate from brominated surface waters [30]. The results in this chapter have identified possible effects including a slight ozone reduction by degassing and catalysis, but these were very small relative to reactions with ozone in bulk. The reduced bromate formation observed here may be due to these ozone reduction mechanisms by the membrane, resulting in limiting the oxidation of bromide to form bromate. Further study has been done on the bromate formation with samples collected in the single-pass tests (Section 8.5.2).

### 8.6.2 Bromate formation with single-pass solution

Figure 8.9 shows the corresponding bromate concentration results for the experiments discussed in Section 8.5.2. As mentioned in this section, the experiment was performed for four different contact times (1 min, 3 min, 5 min and 7 min) over the course of a single ozonated water feed run. Samples were taken from the feed beaker and the membrane permeate during each contact time for the measurement of bromate. In
Figure 8.9 (left), the concentrations of bromate in the permeate of the membrane are between 10 µg/L and 50 µg/L lower than that of the feed for all four different contact times. Whereas in Figure 8.9 (right), the concentrations of bromate in the discharge point of the empty module are essentially equal to that of the feed for all four different contact times. The average reduction of bromate formation in the membrane permeate and the empty module were 30 µg/L and 4 µg/L less than the feed, respectively. The membrane, therefore, appeared to reduce the formation of bromate, which will be discussed further in Section 8.7.2.

![Figure 8.9: Bromate formation during ozonation of tap water sample passing through the ceramic membrane (left) and the empty module (right) (0.5 μM pCBA; 500 µg/L bromide; applied ozone: 10 mg/L, pump flow rate: 48 mL/min; Flux: 72 L·m⁻²·h⁻¹; Temperature: 22±1°C).](image_url)

**8.7 Discussion**

**8.7.1 Ozone decomposition and hydroxyl radical formation**

Residual ozone concentration was reduced in the permeate of the Pall ceramic membrane compared to the feed and concentrate with almost all kinds of feed solutions (Figure 8.1). Despite some inconsistencies, the residual ozone concentration reduction to the permeate of Metawater ceramic membrane (Figure 8.2) was also observed. The removal of ozone in the permeate can be attributed to the depressurizing effect of the ozonized solution. As the solubility of ozone in water is proportional to the pressure of the water [11], solubility of ozone reduces at lower pressure. Thus, depressurizing the ozonized solution while passing across the porous membrane wall might have reduced the residual ozone concentration in the permeate. However, the pressure drop across the Metawater membrane was very low (6.3 ~ 7.7 kPa) compared to the Pall ceramic
membrane (24 ~ 27 kPa). Therefore, the permeate across the Metawater membrane was not significantly affected by the depressurizing of ozonized solution.

During the investigation of \( ^\cdot \text{OH} \) radical formation in Section 8.4, three Pall membranes with filtration layers with different materials (\( \text{Al}_2\text{O}_3 \), \( \text{TiO}_2 \) and \( \text{ZrO}_2 \)) were used. Each membrane has 1.7 mm of \( \text{Al}_2\text{O}_3 \) support layer (Chapter 6, Section 6.3). The first order rates for the decomposition of ozone were similar in the membranes with the filtration layers of different metal oxides. This is probably because the very thin filtration layers (10 µm to 60 µm (Section 6.3)) of the Pall membranes did not show any significant catalytic effect. Moreover, the substrate material (\( \text{Al}_2\text{O}_3 \) powders) did not show strong enough catalytic effect, as observed in Chapter 7.

During the investigation of \( ^\cdot \text{OH} \) radical generation through the Metawater membrane (Section 8.5), it was noticed that, air exposure of the sample enhanced the decomposition of ozone. McClurkin et al. (2013) determined the half-life of ozone in air as a function of air flow [31]. It was observed that, the half-life decreased exponentially as the air flow was increased by increasing fan speed. Moreover, the experiments were conducted in such a way, where the membranes permeate was recirculated back to the feed beaker. The observed ozone decomposition in the feed was representative of the combination of natural decomposition of ozone along with the decomposition across the membrane (if any). Considering all the factors affecting the decomposition of ozone and formation of \( ^\cdot \text{OH} \) radicals during the ozonized sample passing through ceramic membranes, the experiments were improved by avoiding air losses and by ensuring adequate reaction time between the samples and the membrane filtration material.

The results of the improved experimental conditions shown in Figure 8.6 have been simplified in Figure 8.10, which shows the schematic residual ozone concentration (mg/L) versus time (min) plot. The dotted line represents the natural decomposition of ozone in the beaker. The solid line \( C_0C \) represents the decomposition of ozone inside the membrane, where \( C_0 \) and \( C \) are the concentrations of residual ozone before and after the membrane respectively. \( t \) is the contact time (1 minute, 3 minutes, 5 minutes or 7 minutes) with an additional 40 seconds. These 40 seconds are added because 40 seconds after turning the pump on, the sample was collected in the indigo tube to measure residual ozone concentration.
Therefore, first order linear reaction rate constant $k$ can be given as,

$$k = -\frac{1}{t} \times \ln \left( \frac{C}{C_0} \right)$$  \hspace{1cm} (8.1)

The total ozone decomposition rate during each contact time can also be expressed by,

$$k_{Tot} = k_B + k_{Mem}$$  \hspace{1cm} (8.2)

Or,

$$k_{Mem} = k_{Tot} - k_B$$  \hspace{1cm} (8.3)

Where, $k_B$ and $k_{Mem}$ are the first order reaction rate constants (s$^{-1}$) of ozone inside the beaker and membrane respectively. $k_B$ was obtained from the experiments (dashed line in Figure 8.6a). $k_{Tot}$ can be calculated using Equation 8.1 for the measured $C$ and $C_0$ from the membrane decay. Therefore, ozone decomposition across the membrane, $k_{Mem}$ can be determined using Equation 8.3. Calculation of ozone decomposition in the empty module of the Metawater ceramic membrane, $k_{Mod}$ is similar to the $k_{Mem}$ but should be determined from the test when the empty module of the Metawater was used to investigate ozone decay. Therefore $k_{Mod}$ can be calculated using Equation 8.3 and Figure 8.6c.
The calculated \( k_{\text{Mem}} \) and \( k_{\text{Mod}} \) can be defined as the effective rate constants of the Metawater ceramic membrane and the empty module respectively. Figure 8.11 shows the calculated effective rate constants (\( k_{\text{Mem}} \)) of ozone decomposition for the pCBA and tert-Butanol sample solutions across the Metawater ceramic membrane for different contact times. Based on the results shown in Figure 8.11, the rate constant of ozone decomposition in the tert-Butanol solution (in the absence of \(^{\cdot}\)OH radical) through the Metawater membrane decreased noticeably for 1 min, 3 min and 5 min contact times compared to the pCBA solution (in the presence of \(^{\cdot}\)OH radical). Results indicate that, ozone decomposition was catalytically enhanced by a \(^{\cdot}\)OH radical chain reaction in the pCBA solution [3]. The reduced rate constants of ozone decomposition in the tert-Butanol solutions are caused by the absence of \(^{\cdot}\)OH radical in solution [32]. Moreover, the rate constants (\( k_{\text{Mem}} \)) in both pCBA and tert-Butanol samples were reduced upon increasing the membrane contact time. At 5 minutes and 7 minutes contact times, the residual ozone concentration became less (7 mg/L) compared to that of the 1 minute contact time (9 mg/L). This implies that the role of the membrane to the decay of ozone occurs either within the first minute of exposure, or when the concentrations of applied ozone are suitably high.

![Figure 8.11: Effective rate constants of ozone decomposition in the pCBA (0.5 \( \mu \)M) and tert-Butanol (50 mM) samples for 1 minute, 3 minutes, 5 minutes and 7 minutes contact time across the Metawater ceramic membrane (500 \( \mu \)g/L bromide; Flux: 72 L\( \cdot \)m\(^{-2}\)\( \cdot \)h\(^{-1}\); applied ozone: 10 mg/L; pump flow rate: 48 mL/min; Temperature: 22±1°C).](image)

Figure 8.12 shows the rate constants of ozone decomposition in the pCBA (in the presence of \(^{\cdot}\)OH radical) and tert-Butanol (in the absence of \(^{\cdot}\)OH radicals) solutions
across the Metawater empty module ($k_{\text{Mod}}$). The rate constants in the presence of $\cdot$OH radicals for different contact times were lower at shorter contact times than when the membrane was installed, and remained similar at longer contact times coming close to those with the membrane. This suggests the membrane had a role in accelerating ozone decay in the presence of $\cdot$OH radical. On the other hand, the ozone decay rate in the absence of $\cdot$OH radical was similar when the membrane wasn’t installed. The role of tert-Butanol to scavenge $\cdot$OH radicals appears to have accelerated ozone removal as significantly as the membrane. So while the overall system (with or without membrane) was able to facilitate ozone decay when $\cdot$OH radicals could be scavenged, the membrane uniquely directed ozone consumption by reaction with pCBA (a representative organic that reacts with $\cdot$OH radicals), albeit only slightly reducing pCBA concentrations as shown in Figure 8.7. Therefore it appears conclusive that the ceramic membrane facilitates a catalysed reaction between ozone and organic molecules. However, under the test conditions and concentrations here, which could be representative of practical water treatment, it appears that the overall impact of this reaction to the overall water chemistry will not be very significant.

**Figure 8.12:** Effective rate constants of ozone decomposition in the pCBA (0.5 μM) and tert-Butanol (50 mM) samples for 1 minute, 3 minutes, 5 minutes and 7 minutes contact time across the Metawater empty module (500 μg/L bromide; applied ozone: 10 mg/L; Flux: 72 L·m$^{-2}$·h$^{-1}$; pump flow rate: 48 mL/min; Temperature: 22±1°C).

### 8.7.2 Bromate formation

The formation of bromate during ozonation was reduced using the Metawater ceramic membrane while filtering a brominated solution (Figure 8.9). Generally, the bromide
ion reacts with molecular ozone to form hypobromous acid (HOBr), which is in equilibrium with hypobromite ion (OBr\textsuperscript{−}). Subsequently, hypobromite ion reacts with ozone to form the bromite ion (BrO\textsubscript{2}−), which further reacts with molecular ozone to form bromate (BrO\textsubscript{3}−). Bromide can also react with \textsuperscript{\dot{\text{O}}}H radicals to form the bromine radical (\textsuperscript{\dot{\text{Br}}}), which then reacts with molecular ozone in a complex set of reactions to form bromate. As such, both direct and indirect pathways play a role in bromate formation (Figure 8.13). Equations 8.4-8.6 show the direct reaction pathways to generate bromate during ozonation of bromide bearing water [28]:

\begin{align*}
Br^- + O_3 & \rightarrow OBr^- + O_2 \quad k = 160 \text{ M}^{-1}\text{s}^{-1} \\
O_3 + OBr^- & \rightarrow BrO_2^- + O_2 \quad k = 200 \pm 20 \text{ M}^{-1}\text{s}^{-1} \\
O_3 + BrO_2^- & \rightarrow BrO_3^- + O_2 \quad k \geq 10^5 \text{ M}^{-1}\text{s}^{-1}
\end{align*}

Equations 8.7-8.11 show the indirect reaction pathways [28].

\begin{align*}
Br^- + HO^- & \rightarrow Br^- + OH^- \quad k = 1.1 \times 10^9 \text{ M}^{-1}\text{s}^{-1} \\
OBr^- + HO^- & \rightarrow BrO^- + OH^- \quad k = 4.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1} \\
BrO_2^- + HO^- & \rightarrow BrO_2^- + OH^- \quad k = 2 \times 10^9 \text{ M}^{-1}\text{s}^{-1} \\
BrO_2^- + BrO_2^- & \rightarrow Br_2O_4^- \quad k = 1.4 \times 10^9 \text{ M}^{-1}\text{s}^{-1} \\
Br_2O_4^- + OH^- & \rightarrow BrO_5^- + BrO_2^- + H^+ \quad k = 7 \times 10^8 \text{ M}^{-1}\text{s}^{-1}
\end{align*}

**Figure 8.13:** Molecular ozone and \textsuperscript{\dot{\text{O}}}H radical pathways during bromate formation (Figure taken from Urs von Gunten (2003) [22]).

Since, both ozone and \textsuperscript{\dot{\text{O}}}H radicals competitively oxidize bromine, namely bromide (Br\textsuperscript{−}) and hypobromous acid/hypobromite (HOBr/OBr\textsuperscript{−}), calculating the fraction of the oxidation by \textsuperscript{\dot{\text{O}}}H radicals and ozone for both compounds would allow estimation of the relative importance of the reaction pathways towards bromate formation. Using the \(R_{e1}\),
Pinkernell et al. (2001) formulated the fraction of the oxidation by 'OH radicals and ozone in an analogous way using two different types of natural raw waters [28]. Water from Lake Zürich (Zürich, Switzerland) has a DOC of 1.3 mg/L and alkalinity of 2.4 mM. Water from River Seine (Maisons-Laffitte, France) has a DOC of 2.4 mg/L and 3.9 mM. Table 8.2 shows the calculated fractions of bromide and hypobromous acid for reactions with 'OH radicals or ozone, respectively. From Table 8.2 it is possible to predict the bromate formation pathway for the results shown in Figure 8.8. The calculated $R_{ct}$ value in the stirred beaker condition test described in Section 8.5.1 was found to be $1.13 \times 10^{-9}$ (Table 8.1). The pH of the sample tap water was 7.5. Therefore, using these $R_{ct}$ and pH values we can predict from Table 8.2 that, in the stirred beaker condition, bromide was oxidized by ozone molecules mostly (99.3%) and generated HOBr/OBr\(^{-}\). However, further oxidation of HOBr/OBr\(^{-}\) was conducted by both ozone and 'OH radicals. From Table 8.2, the fraction of oxidation by 'OH radicals and ozone can be predicted as 65% and 35% respectively.

**Table 8.2:** Fraction of ozone \((f_{O_3})\) and 'OH radicals \((f_{OH})\) pathway for the oxidation of bromide and HOBr/OBr\(^{-}\) (towards bromate) [28, 33].

<table>
<thead>
<tr>
<th>$R_{ct}$</th>
<th>f$_{O_3}$ (%)</th>
<th>f$_{OH}$ (%)</th>
<th>f$_{O_3}$ (%)</th>
<th>f$_{OH}$ (%)</th>
<th>f$_{O_3}$ (%)</th>
<th>f$_{OH}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-7}$</td>
<td>60</td>
<td>40</td>
<td>0.08</td>
<td>99.92</td>
<td>0.8</td>
<td>99.2</td>
</tr>
<tr>
<td>$10^{-8}$</td>
<td>94</td>
<td>6</td>
<td>0.8</td>
<td>99.2</td>
<td>7</td>
<td>93</td>
</tr>
<tr>
<td>$10^{-9}$</td>
<td>99.3</td>
<td>0.7</td>
<td>8</td>
<td>92</td>
<td>44</td>
<td>56</td>
</tr>
</tbody>
</table>

However, in the empty module (membrane was absent inside the module) condition, bromate formation was reduced compared to that of the stirred feed beaker. This is because; in the empty module condition the residual ozone concentration was much less than the stirred beaker condition (Figure 8.5). The reduction of residual ozone in the empty module run appeared to be more related to the contact of pumps and pipes with the ozonized sample. Therefore, less ozone was available to oxidize bromide to HOBr/OBr\(^{-}\). In the Metawater membrane run, formation of bromate was further reduced. The final residual ozone concentration in the Metawater membrane was similar to the Metawater empty module (Figure 8.5) but the $R_{ct}$ value was higher in the Membrane (Table 8.1). This indicates formation of 'OH radicals in the Metawater membrane run. The reduction in bromate formation in the Metawater membrane run can be attributed to the generated 'OH radicals. Since the 'OH radicals are less efficient to
oxidize bromide [30] the oxidation of \( \text{Br}^- \) and \( \text{HOB}r/\text{BrO}^\cdot \) to \( \text{BrO}_3^- \) by ozone is suppressed. Further, it was found that the ozone decay is also accelerated by the membrane in the presence of \( \cdot\text{OH} \) radical, which is also evidence of increased \( \cdot\text{OH} \) radical formation. So the membrane's role to decrease ozone and increase formation of \( \cdot\text{OH} \) radicals assisted with the observed effect of bromate reduction.

The reduction in bromate formation for the membrane test (Figure 8.9) described in Section 8.6.1 is further evidence to support the theory that \( \cdot\text{OH} \) radicals are being catalytically formed by the membrane. However, the rejection of bromate by the Metawater ceramic membrane can also be explained by the property of the charged surface of a metal oxide to attract and repel ions. The surface of ceramic membranes is typically charged, as the surface of metal oxides from which they are made are usually charged, due to the amphoteric nature of the surface hydroxyl groups on the metal oxide surface [34]. Previous studies have shown that due to their surface charge, ceramic ultrafiltration UF/NF membranes can reject ions, even though the pore size of the membrane is much larger than the size of the ions [35-38]. Charge effects are largely responsible for the rejection of the ions. Although pore size was not reported, Moslemi et al. (2012) has shown that, 68% of bromate was rejected by a tubular ceramic ultrafiltration membrane (TAMI North America). The membranes have a titania support and a filtration layer with three channels and a total filtering surface area of 41.2 cm\(^2\) [39]. If a charged membrane is in contact with an electrolyte solution, electrostatic repulsion will result in a lower concentration of ions with the same charge as the membrane (referred to as co-ions) near the membrane surface and within the membrane pores. On the other hand, counter-ions, which have an opposite charge to that of the membrane surface, are attracted to the membrane, and the concentration of these ions within the membrane and at its surface is higher than that in bulk solution [39]. However, in our study the experiments were conducted in the dead-end configuration. Therefore, recycling the ozonized solution continuously through the membrane reduces the possibility of any charged ion rejection. Moreover, the reduction in bromate formation was consistent in the repeated tests, which further proves that the Metawater ceramic membrane reduced the bromate formation.
8.8 Conclusion

From the above discussion we may conclude that a very slight catalytic effect is observed for the Metawater ceramic membrane because of the very thin catalytically active filtration layer thickness. However, the catalytic effect to generate $'\text{OH}$ radicals was observed either during the first minutes of ozone exposure or higher applied ozone dosage conditions. The contact of pipes and pump of the membrane rig and the air exposure also reduce the residual ozone concentration. An effective reduction of bromate formation by using ozonation followed by the Metawater ceramic membrane filtration was also demonstrated. Under the conditions that $\text{O}_3$ dose of 10 mg/L, initial $\text{Br}^-$ concentration of 500 μg/L, $p\text{CBA}$ of 0.5 μM, Metawater membrane reduced 30 μg/L bromate formation where the empty module reduced only 4 μg/L. The mechanisms responsible for the diminished bromate formation were the suppression of the oxidation of $\text{Br}^-$ and $\text{HOBr/BrO}^-$ to $\text{BrO}_3^-$ due to the decomposition of ozone. The ozone was hypothesised to be decomposed by the $'\text{OH}$ radicals generated by the catalytic effect of the Metawater membrane materials. Degassing of the solution due to pressure drop across the membrane is also a likely contributor to reduced ozone and in turn reduced bromate formation. From a practical point of view for application to water treatment, it was concluded that although these effects on the overall organic concentration will be minor, subtle effects such as reduction of bromate, could be useful features of the unique catalytic effect of ceramic membranes which work simultaneously with ozone.

8.9 References

Chapter 9

Conclusions and recommendations for future work
9.1 Conclusions

The goal of this thesis was to explore the role of ozone in contributing towards the well documented effect of high flux when combined with ceramic membranes. The investigation uncovered some interesting findings towards this goal but also found some additional findings that would benefit both the water industry and sciences. The approach taken was to present the performance of ceramic membrane under real water treatment scenarios, determine the water flow resistance in the fouling layer, investigate the material properties of a commercial membrane type then its water filtration performance under basic environmental conditions, explore the ozone decay and formation of hydroxyl (‘OH) radicals on membrane materials and membranes themselves in wastewater solution matrices, and finally observe bromate (disinfection by-product) formation potential.

The finding from the first step of the approach identified the higher molecular weight (MW) biopolymers and the low MW humic substances (HS) as the major fouling contributor in the treatment of secondary effluent (SE) by microfiltration (MF) ceramic membrane. This was concluded because of the rejection of these components by the membrane during filtration of real secondary treated effluent. It was also observed that, ozone pre-treatment allows ceramic membrane to be operated with a more stable permeability condition compared to the no pre-treatment option, biological activated carbon (BAC) filtration and combined ozone-BAC pre-treatment option. This was concluded as the permeability of the ozone pre-treated membrane flux reduced from 11.5 L/m²·h·kPa to 7.8 L/m²·h·kPa after one complete filtration cycle and ended at 5.7 L/m²·h·kPa after completing seven successive cycles of filtration. Where, the permeability in all other cases showed a much steeper flux decline. For example the raw feed flux reduced from 10.4 L/m²·h·kPa to 2.7 L/m²·h·kPa while BAC treated feed flux reduced from 11.4 L/m²·h·kPa to 2.7 L/m²·h·kPa and combined ozone-BAC flux reduced from 13.0 L/m²·h·kPa to 4.1 L/m²·h·kPa after completing a single filtration cycle. The thesis set out to answer a series of questions in Chapter 2. The first question was, is there any beneficial effect of combined ozonation and BAC filtration prior to MF ceramic membrane system for the treatment of SE wastewater? This was answered by the above mentioned results which conclude that the combined ozonation and BAC pre-treatment has lesser effect in terms of permeability
compared to the ozone pre-treatment alone prior to MF ceramic membrane system for the treatment of SE. The result further implies that, if BAC was to be applied with ozone in this case, it should follow ceramic membrane filtration (CMF).

The second question was, how the fouling layer formed on the membrane appears physically and how does its resistance contribute to the ability for ceramic membranes to operate at higher fluxes when ozone is used prior to the membrane? As fouling is generally the major performance limiting issue in membrane filtration, the effect of ozone on fouling layers was observed in the second step of the approach to assess the physical changes in fouling layer property on altering filtration resistance. The permeability of the filtered real secondary effluent (RSE) solution and an ozonized + filtered RSE solution have shown an increasing tendency but both were similar until a pressure of 80 kPa. This was because; the cake layers for both samples have been compressed to a similar extent of 80 kPa. However, above 80 kPa, the ozonized + filtered RSE indicated higher permeability across the pre-fouled membrane compared to the filtered RSE. This was attributed to the breaking down of higher MW compounds to smaller components by the ozonation. Which further results in the penetration of smaller MW compounds across the pore openings and channels of the cake fouling layer at a higher applied pressure (300 kPa). The assumption was further strengthened by observing the SEM images of the fouling layer with and without ozone pre-treated sample RSE. The gel like structured fouling layer of the raw RSE observed in the SEM had a grainy appearance after ozonation, indicating the removal of specific components (high MW aromatic compounds) of the RSE by ozonation. Moreover, the cracked openings showed in the ozonized RSE filtered membrane, indicating a weaker structure of the fouling layer.

The physical characteristics (e.g., pore size, porosity and thickness of the filtration layer) of the commercial ceramic membrane were then explored to understand the properties of the ceramic membrane. It was also identified that, during gas permeation through MF ceramic membrane, the support layer contributes significantly (65% on average as calculated in this study) in the resistance of gas flow. This led to the conclusion that gas permeation approaches to measure pore size of the top selective layer can give incorrect interpretations of the pore size value. The results infer that, measurement of the pore size of MF ceramic
membranes requires more practical technique that aligns with their application in the industry. Therefore, size exclusion method could be a useful technique to measure the pore size of the MF ceramic membrane.

The third question was, how do basic water properties of salinity, temperature and pH affect the permeability of MF ceramic membrane? In order to answer this question, performance of the commercial ceramic membrane under simple water conditions was explored to establish a standard for the membrane performance. As observed in the findings, the permeability of MF ceramic membrane can be fitted with Hagen-Poiseuille model. The permeability of the MF ceramic membrane can be affected by the electro-viscous effect at salinity below 0.5 g/L, but does not become significant until below 0.05 mg/L (50 mg/L).

In uncovering the key goal of this study, the decomposition of ozone in the presence of different components (minerals and organics) of synthetic secondary effluent (SSE) was then studied in the next approach step. The decomposition of ozone in the presence of different ceramic materials and their potential to generate 'OH radicals has also been studied. The fourth question was, how the presence of minerals and organics of synthetic SE affect the decomposition of ozone? As per the observed results, the SSE has a high initial ozone demand which causes rapid ozone decay. In the presence of minerals, ozone decomposition continues to occur, giving a $k$ value of $2.3 \times 10^{-3}$ s$^{-1}$ however, the presence of organics did not show any effect in the decomposition of ozone after stopping the continuous bubbling of ozonation at 10 minutes. This was attributed to the very fast initial reactions between organics and ozone. The next question was, how the presences of different ceramic materials affect the decomposition of ozone? Among the different ceramic materials, TiO$_2$ was found to act as a catalyst to promote formation of 'OH radicals where Al$_2$O$_3$ (a key material used in ceramic membrane manufacture) did not show a major catalytic effect.

The next question was, what is the mechanism of 'OH radical formation during filtering ozonized solution through ceramic membrane? In order to answer this question, the investigation then turned to explore the mechanism of ozone decomposition across the commercial ceramic membranes and their influence on the 'OH radical formation. Results
showed that the Metawater ceramic membrane (a commercial ceramic membrane well known for application to water treatment) can offer very slight catalytic effect which was evident by measuring the ozone decay rate of an ozonized solution across the membrane and its empty module in the presence of pCBA ('OH radical probe compound) and tert-BuOH ('OH radical scavenger). The Metawater ceramic membrane showed that ozone decayed at a higher rate ($1.35 \times 10^{-3} \text{ s}^{-1}$) in the presence of pCBA for the ozonized solution than the empty module ($0.5 \times 10^{-3} \text{ s}^{-1}$), indicating ceramic membrane facilitated catalytic reaction between ozone and organic molecule by generating 'OH radical. However, the catalytic effect was found to be more prominent during the first minutes of ozone exposure or at higher applied ozone dosage condition.

The last question was, what is the potential for bromate formation during ozonation of bromide containing water, a major issue in ozone treatment of water, in the context of ozone use in conjunction with CMF? In order to answer this question, the ozone decomposition study was then followed by investigating the influence of ozone and ceramic membrane interactions on the formation of bromate which is a well-known by-product formed when ozone is applied to treat water containing bromide. The findings showed that bromate formation can be reduced when ozone and ceramic membranes are used in combination. The main reason for this was related to both the ozone drop across the ceramic membrane, which acted to degas the ozone from solution, as well as the effect to convert ozone to 'OH radicals which can also reduce the formation of bromate.

The findings from this study provided useful knowledge for both industry (i.e., the water industry) while also contributing to science. The industry contributions included providing evidence of superior performance when locating the ceramic membrane immediately after ozone, and not placing a BAC filter in between (may instead be located after the ceramic membrane). The results obtained from the effect of different water conditions (salinity, temperature and pH) on ceramic membrane permeability showed influence to performance which can be extended to practical operations. For example, the permeability of the ceramic membrane reduces only slightly from changing salinity, i.e., 7% from 3 g/L salinity (brackish water) to 35 g/L salinity (sea water). However, increasing temperature strongly influence the permeability by increasing 57% for a rise in the temperature from 15°C to
35°C in the water treatment plants. pH had no significant effect to flux within the range of pH 2 to pH 10. These results show performance of basic environmental conditions, however their influence on fouling must also be considered for practical adoption of these findings.

In addition to these industrial benefits, the research has also provided contributions to water treatment and membrane sciences. The study identified the high MW biopolymers and the low MW HS as the major cause of fouling in MF ceramic membranes. The effect of ozone on the properties of the cake fouling layer revealed that, ozone can breakdown the high MW organic matter in the fouling layer into smaller MW compounds. The smaller compounds can then easily penetrate through the MF membrane pores, resulting in higher membrane flux. The pores of the ceramic MF membrane can also be affected by the electro-viscous effect at low salinities. When exposed to water, the surface of the ceramic membrane pores can be charged with positive or negative ions. If an electrolyte solution is passed through these pores with charged surface, ions are moved away from the surface, resulting in an increase in the electric double layer thickness. The thickness of the electric double layer is known as the Debye length, which is inversely proportional to the ionic strength of the solution. Thus at a very low salt concentration (< 0.0005 g/L (0.5 mg/L)), the double layer penetrates in the pore space resulting in reduced pore size in the MF ceramic membrane.

Further contribution to membrane science includes the very slight potential of Metawater ceramic membrane to catalytically effect the reaction of ozone with organic molecules. According to the manufacturer, the Metawater ceramic membrane has a titania based filtration layer, which would be more catalytically active than the alumina substrate. Moreover, titania is known to promote ozone decomposition and the formation of \( \cdot \text{OH} \) radicals. The catalytic activity of the Metawater membrane is stronger with higher initial ozone concentration during the first minute of ozone exposure. However, concentration of residual ozone across the ceramic membrane can also be reduced by the degassing effect, due to the pressure drop across the membrane. The formation of bromate can be reduced when ozone and ceramic membrane are used in combination. Generally, the bromide ion reacts with molecular ozone to form hypobromous acid (HOBr), which is in equilibrium
with hypobromite ion (OBr\(^-\)). Consequently, hypobromite ion reacts with ozone to form the bromite ion (BrO\(_2\)^-), which further reacts with molecular ozone to form bromate. Bromide ion can also react with ‘OH radicals to form the bromine radical (’Br), which then reacts with molecular ozone in a complex set of reactions to form bromate. Due to the degassing effect, when the residual ozone concentration is dropped across the membrane, the oxidation of Br\(^-\) and HOBr/BrO\(^-\) to BrO\(_3\)\(^-\) is suppressed. Thus bromate formation is reduced during the ozonation of bromide containing water across the ceramic membrane.

### 9.2 Recommendations for future work

A key limit in the study was the scale of testing for the ozone-BAC-CMF test, which was conducted by a lab scale experimental setup. Pilot scale testing with optimized operating conditions would give more useful information as it can be provide scalable and repeatable data with longer operating duration. The results can further be compared with chlorination, which is one of the most commonly used disinfectants for water disinfection. The organic matter present in the RSE was characterized by HPLC, where the analysis revealed that the biopolymers and HS are significantly contributing in to the MF ceramic membrane fouling. As the HPLC is not sufficient to characterize the chemical and physical properties of the particular MW components of the DOM, more detailed analysis of the organic matters of RSE could be obtained by liquid chromatography-organic carbon detection (LC-OCD) technique. LC-OCD can provide quantitative information regarding the organic carbon content (e.g., polysaccharides and proteins) in the RSE. The fate of dissolved organic carbon (DOC) of the RSE by distinct treatment process would be detected more precisely by the LC-OCD, as it can separate and quantify the DOC in to biopolymers, HS, building blocks, low MW acids and low MW neutrals.

The pore sizes measured by the gas permeation and porometry did not match with the pore size value provided by the manufacturer. The size exclusion method which includes separation of large molecules from the smaller one can be applied to quantify the pore size of the membranes more accurately, measured in terms of molecular weight (molecular weight cut-off). The technique is well known by industry and scientists, but is usually more difficult to operate compared to gas permeation techniques. Whether this technique or an improved more rapid approach could be developed, it shows future work is needed as the
conventional gas permeation or porometry techniques are not suitable for measuring the functional separation layer pore size of ceramic membranes.

The investigation of the catalytic activity of ceramic membrane has shown slight catalytic effect of the membrane material when in contact with ozone. However, the full high flux effect from ozone is well known to occur in conjunction with coagulation, which has been dosed just after the injection of ozone in site trials by others. Further, the study was limited to overall measures of fouling. Therefore further work could consider a model describing the fouling interaction forces between the particles in solution and the membrane surface. The electro-interaction relationship of the fouling particles and membrane surface obtained from the surface tensions and zeta-potential data can be used to model fouling of the ceramic membrane. This could also be undertaken using computational methods to look at specific interactions, particularly in the full system which includes coagulation.