Impact of Oxidative Chemicals on Hydrophobic Porous Membranes Used in Membrane Distillation

Submitted to
ACS Applied Engineering Materials

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ABSTRACT

Direct treatment of water purification membranes with strong oxidative chemicals, such as ozone and chlorine, is a promising avenue to prevent fouling and improve water treatment performance. In this work, we investigate the oxidation resistance of hydrophobic polymers commonly used in membrane distillation by probing the impact of ozone and chlorine exposure on membrane structure, chemistry, and desalination performance. To probe oxidative behavior, polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), and polypropylene (PP) membranes were exposed to sodium hypochlorite (10 000 ppm, pH 4) and ozone (15 ppm, pH 7) solutions for up to 72 hours and 3 hours, respectively. We then characterized the membrane samples using Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), water contact angle measurements, and desalination performance testing. Our results indicate that PTFE membranes show no chemical, structural, or desalination performance changes after exposure to the highest doses of chlorine and ozone, with only minor decreases in water contact angle (less than 15%) after exposure to oxidants. PVDF also showed no observable changes in structure and performance, although XPS analysis indicated possible defluorination of the surface after oxidant exposure. PP membranes showed the most severe degradation, with surface cracking, chemical changes, and complete failure in desalination testing after exposure to 10 000 ppm chlorine for 1 h or 15 ppm ozone for 30 min. Measurements of salt rejection and water flux of the pristine and oxidized membranes showed greater than 99.9% rejection and minimal changes in water flux regardless of oxidant or exposure length, except in the case of PP which showed failure during testing. Our results provide insights on the degradation behavior of hydrophobic polymer membranes and demonstrate the promise of using PTFE and PVDF membranes combined with strong oxidants in water treatment.

Keywords: Membrane distillation, chlorine, ozone, desalination, hydrophobic membrane.

Synopsis: The impact of ozone and chlorine exposure on the chemistry, structure, and performance of hydrophobic porous membranes is examined.

1. INTRODUCTION

Anthropogenic climate change has contributed to worsening drought conditions and decreased the reliability of water supplies.[1] Water reuse and desalination offer secure and consistent water supplies outside the natural hydrological cycle that can supplement existing water resources.[2] Membrane-based technologies have been increasingly implemented for advanced water treatment due to their high energy efficiency and ease-of-implementation.[3,4] However, fouling from contaminants in feedwater is a persistent challenge that limits the performance of membrane-based systems, increasing the cost of water treatment by necessitating intensive pre-treatment processes and reducing membrane lifetime.

The use of oxidative disinfectants upstream of a membrane process is an effective technique to reduce fouling and enhance water treatment performance.[5] Chlorination or ozonation of feedwater inactivates microbes before they reach the membrane surface, preventing biofilm formation and the associated performance decline due to biofouling.[6] Strong oxidants can also transform organic matter into more hydrophilic materials that have a lower fouling propensity.[7] Furthermore, strong oxidation combined with membrane processes may enhance removal of contaminants in the feed water.[8] Therefore, implementing strong oxidation upstream of, or directly in contact with, membranes used in advanced water treatment is highly desirable.

Although strong oxidants have the potential to enhance membrane performance, materials commonly used in salt-rejecting membranes, such as polyamide and cellulose acetate, degrade when exposed to strong oxidizing agents such as chlorine and ozone.[9–12] Disinfection pretreatment strategies upstream of these membranes are therefore limited to the use of chloramines, weaker disinfectants that reduce the effectiveness of downstream ultraviolet treatment processes and are associated with the formation of highly toxic disinfection byproducts, including *N*-nitrosodimethylamine.[13,14] Alternatively, chlorine is sometimes used upstream of membrane systems, but a costly dechlorination step must be implemented prior to reverse osmosis (RO) to protect the membranes. The development of membrane materials that withstand exposure to strong oxidants is therefore a well-acknowledged need in the field of membrane separations.

Hydrophobic porous membranes used in membrane distillation (MD), osmotic distillation, and pressure-driven distillation have material properties that hold potential to be placed in direct contact with strong oxidants.[15–18] Unlike conventional membranes, distillation membranes require hydrophobic materials that can trap air within sub-micron scale pores. Water vapor can then travel through the membrane driven by a partial vapor pressure gradient resulting from a temperature or concentration difference. A variety of hydrophobic materials have been used in membrane-based distillation systems. Among these, polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), and polypropylene (PP) have been the most widely studied.[19] All these polymers have chemical structures that are stable and, in theory, have stronger tolerance towards chemical oxidation than hydrophilic polyamide and cellulose acetate polymers used in conventional salt-rejecting membranes.

Despite the potential of combining membrane-based distillation systems with strong oxidants, the oxidation resistance and long-term stability of hydrophobic porous membranes has not been well-characterized for ozone and chlorine, the two strong oxidizing agents that are most commonly used in water treatment. The perfluorinated C-F bonds in PTFE are not known to react with even very strong oxidants such as hydroxyl radical since no lone pairs for electron transfer or hydrogens available for abstraction exist in the chemical structure of PTFE.[20] Experimentally, PTFE membranes have been used in studies involving ozone without noticeable changes in performance, but the chemical properties of PTFE membranes after exposure were not characterized.[21,22] PVDF membranes have been suspected to swell when exposed to ozone, though materials characterization has been inconclusive regarding any chemical changes to the polymer.[23–25] PP and PVDF membranes also have been observed to react with chlorine, but implications for membrane performance are unclear.[26,27] Prior literature thus indicates that some polymers used in distillation systems have the potential to operate with prolonged exposure to strong oxidants such as chlorine and ozone. However, the impact of such exposure on membrane chemical stability and physical structure has not been well-studied. Studying the chemical resilience of hydrophobic polymer membranes used in distillation systems is particularly relevant because small changes in surface chemistry may result in membrane wetting and compromise membrane performance.

In this work, we investigate the effects of oxidant exposure on hydrophobic membranes commonly used in membrane-based distillation processes. We first examine changes in the chemistry and hydrophobicity of PTFE, PVDF, PP membranes after exposure to varying doses of chlorine and ozone, allowing us to gain insights into degradation mechanisms. We then examine changes in membrane polymer structure and characteristics after exposure to oxidants. Finally, we show changes in water flux and salt rejection that occur after membranes have been exposed to varied doses of oxidants. Overall, this work provides important insights on the limits of different MD membrane materials in resisting damage from strong chemical oxidants.

2. MATERIALS AND METHODS

2.1. Membranes and chemicals

Three hydrophobic, porous polymer membranes commonly used in distillation processes, PTFE (Sterlitech Corporation, USA), PVDF (Durapore, Millipore, Ireland), and PP (Sterlitech Corporation, USA), were tested. All membranes had a nominal pore diameter of 0.2 µm. Characteristics of membranes are summarized in Table S1. Each type arrived as flat sheet membranes in a dry state. Samples were cut from flat sheets prior to oxidation and testing. Deionized (DI) water was obtained using a Millipore Synergy UV Remote Water Purification System. Solutions for chlorine degradation experiments were prepared using a sodium hypochlorite solution (NaOCl 5% w/v, LabChem) and DI water with pH adjusted using hydrochloric acid (HCl 1N, Fisher Chemical). Gaseous ozone was produced by a TG-40 ozone generator (Ozone Solutions, USA) for ozone degradation experiments. Sodium chloride (NaCl, Fisher Chemical) dissolved in DI water was used as the feed solution in desalination testing.

2.2. Oxidation of membrane materials

Oxidant exposure occurred in the form of passive treatment in which the membrane samples were submerged in prepared solutions for a specified amount of time. Aqueous ozone was generated by feeding pure oxygen into an ozone generator which was then diffused as gaseous ozone into a beaker containing DI water. Due to the rapid degradation of ozone, a constant flow of gaseous ozone was supplied during membrane exposure. Ozone concentration within the beaker was monitored using a spectrophotometer (HACH DR6000, Colorado, USA). The ozone solution was maintained at a concentration of 15 ppm and a pH of 7 for oxidation experiments. PVDF and PTFE membranes were exposed to ozone for up to 3 h. PP membranes were exposed to ozone for less time since severe degradation was observed; PP membranes used in desalination performance testing were exposed to ozone for a maximum for 0.5 h, and PP membranes used for material characterization were exposed to the ozone solution for 1 h. A summary of oxidant exposure conditions for each membrane based on characterization method is provided in Table S2.

NaOCl solutions were prepared by diluting a 5% w/v NaOCl solution with DI water to a concentration of 10,000 ppm for all experiments. The solution was adjusted to a pH of 4 using hydrochloric acid to promote the dissociation of NaClO into hypochlorous acid, which has been found to have a higher oxidative strength than the species present at a different pH.[28] The solution was covered and reprepared every 24 hours to maintain a constant concentration and pH. PVDF and PTFE membranes were exposed to the chlorine solution for up to 72 h. PP membranes were exposed for up to 60 min in desalination performance testing. Additional PP membranes were exposed for up to 24 h for material characterization. Following oxidant exposure, membrane samples were thoroughly rinsed with DI water and left in DI water for 24 h. Membranes were rinsed with methanol to remove any surface contamination, dried, and stored in a desiccator prior to surface characterization.

2.3. Membrane characterization

Contact angle was measured with a Biolin Scientific tensiometer using the sessile drop technique. For all measurements, a droplet of DI water (less than 10 uL) was deposited onto the active side of the membrane surface using a pipette. Contact angle was measured on different areas of each sample and reported values represent an average of at least three measurements.

Membrane morphology and surface topography was viewed with scanning electron microscopy (SEM) on a Hitachi SU8010 microscope. Prior to SEM imaging, platinum was sputtered onto the PTFE, PVDF, and PP surfaces until a thickness of 3 nm was achieved on the surface. SEM images were taken of pristine PTFE, PVDF, and PP and the membranes exposed to the highest doses of chlorine and ozone.

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were acquired from 400–4000 cm^{-1} using a ThermoScientific Nicolet iS50 FTIR with a Smart iTX attachment with ATR capacities and an ATR diamond crystal. Measurements were taken of PTFE, PVDF, and PP prior to submersion into the oxidant solution and after subsequent exposures.

X-ray photoelectron survey spectra were acquired from 0–1200 eV using a Kratos Supra X-ray photoelectron spectrometer. Polymer samples were isolated on the sample plate to ensure consistent charging through the samples. The Al K alpha X-ray source was operated at 1486.7 kV and 15 mA current emission. Charge neutralization parameters were determined through use of continuous scans of the carbon 1s peak. Survey spectra were used to calculate the atomic percent of elements on the surface while the high-resolution C 1s spectra were peak fitted to determine the changes in the carbon binding after exposure. High resolution scans of O 1s, F 1s, and C 1s were taken to obtain the chemical state of the polymers after oxidant exposure. A Shirley background was used and a Gaussian-Lorentzian sum function with an added asymmetric parameter were used to fit component peaks for the polymers. All spectra were calibrated using a C-C/C-H peak position of 284.8 eV.

2.4. Desalination performance testing

A bench-scale crossflow direct contact MD system was used for performance testing on pristine and oxidized membrane samples. Membranes were placed within a flat sheet membrane module with an active surface area of 20.02 cm². PP membranes required the use of mesh spacers on either side of the membrane for support. A 0.05 M NaCl feed solution was circulated at 60 ºC in contact with the active side of the membrane. DI water was simultaneously circulated on the permeate side at 20 ºC. Feed and permeate temperatures were continuously monitored prior to entering and upon exiting the membrane module and regulated using a heater and chiller, respectively. Flow rate was measured upon exiting the membrane module and regulated using pumps. Water velocity through the channels was maintained at 0.14 m s^{-1} across the membrane surface. Water flux across the membrane during operation was determined by measuring the mass change of the permeate reservoir using an analytical balance. Salt rejection across the membrane was measured using a conductivity probe in the permeate reservoir. Measurements were collected in one-minute intervals after the system reached steady state conditions. Steady state was determined to be the point at which a constant water flux was maintained (less than 2 L $m^{-2}h^{-1}$ deviation over 30 min) after the desired operating temperatures and crossflow velocities were achieved. Water flux and salt rejection across the membrane, presented as the average value over a 2-hour test period, were then evaluated as a function of oxidant exposure.

3. RESULTS AND DISCUSSION

3.1. Oxidation impacts on membrane structure and hydrophobicity

To examine the impact of oxidation on hydrophobic porous membranes, 0.2 µm nominal pore size hydrophobic membranes made from PTFE, PVDF, and PP were acquired and exposed to chlorine at pH 4 and ozone at pH 7. Membranes were then thoroughly characterized for chemical, structural, and performance changes in direct contact MD (Figure 1A). Exposure to chemical oxidants may lead to loss of surface hydrophobicity and pore wetting (Figure 1B) or damage to the bulk polymer membrane structure (Figure 1C) In this Section, we will discuss changes in membrane structure and hydrophobicity that were observed after oxidant exposure. Subsequent sections will further analyze chemical changes and MD performance of the oxidant-exposed membranes.

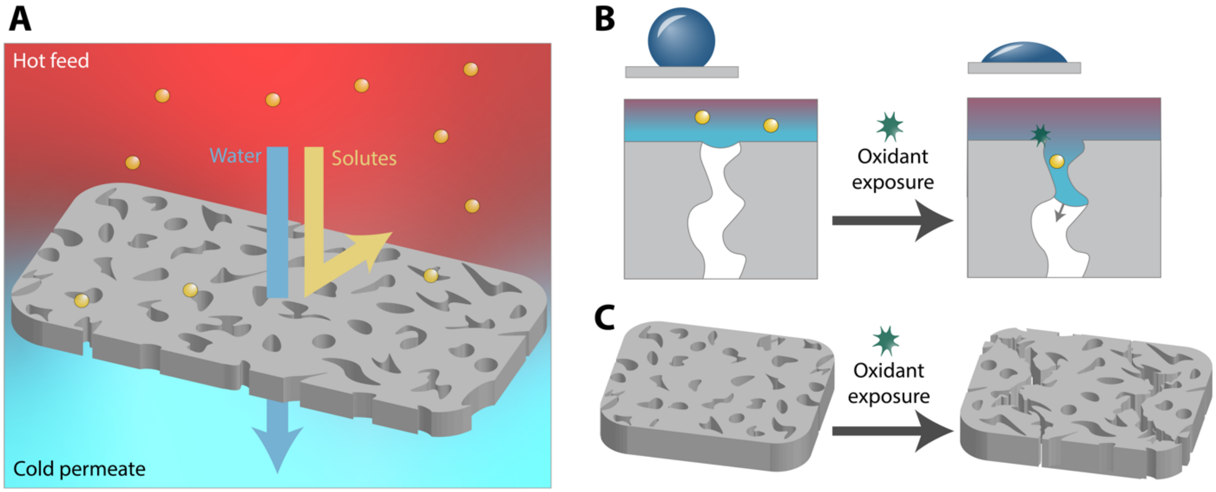

Figure 1. (A) Schematic diagram of membrane distillation. (B) Loss of membrane hydrophobicity as a result of oxidant exposure may lead to pore wetting. (C) Damage to the membrane morphology may also result from exposure to oxidants.

Following oxidant exposure, physical inspection and SEM imaging were used to examine possible structural degradation in the membranes. After the highest exposures for chlorine (72 h at 10000 ppm) and ozone (3 h at 15 ppm), both PTFE and PVDF showed no changes in their overall morphology in SEM images (Figure 2) and upon physical inspection. Polypropylene, on the other hand, showed significant changes in its macroscale morphology after exposure to lower doses of chlorine (10000 ppm for 24 h), with cracking and tearing occurring on the membrane surface (Figure S1). SEM imaging further revealed that larger than 10 µm cracks were present on

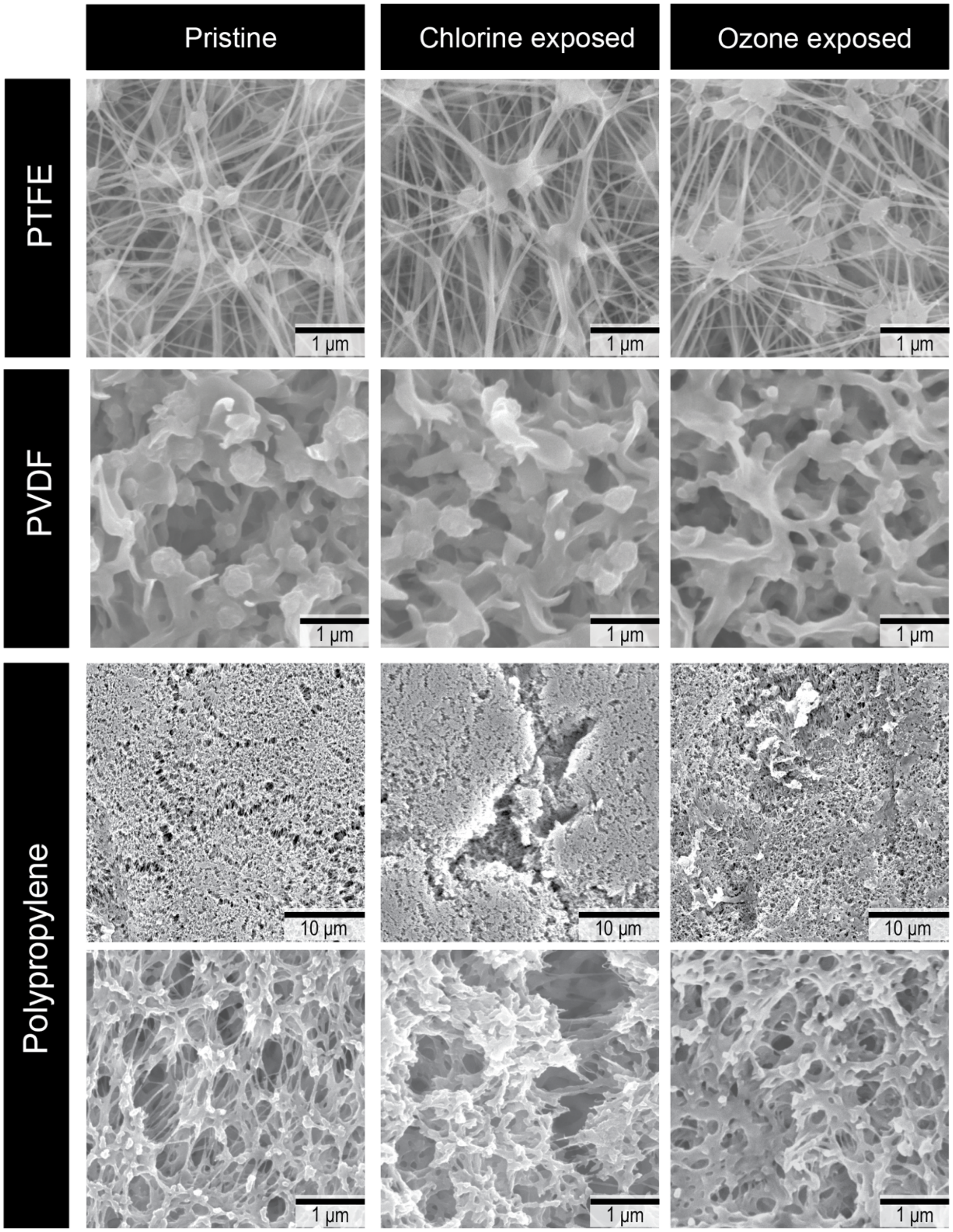

Figure 2. Scanning electron micrographs of polytetrafluorethylene (PTFE), (b) polyvinylidene fluoride (PVDF), and polypropylene membranes before and after exposure to chlorine and ozone oxidants. Polytetrafluoroethylene and polyvinylidene fluoride membranes were exposed to 10000 ppm chlorine for 72 h or 15 ppm ozone for 3 h. Polypropylene membranes were exposed to 10000 ppm chlorine for 24 h or 15 ppm ozone for 1 h.

the membrane surface and apparent pore sizes at the membrane surface increased from approximately 0.2 µm to 2 µm. For ozone (1 h at 15 ppm), we observed macroscale cracking and debris on the surface of the membrane. Overall, inspection of the membrane samples indicated significant damage to the PP membrane structure after ozone and chlorine exposures.

Measurements of the water contact angles after oxidant exposure showed small changes in the overall hydrophobicity in all cases (Figure 3). After the maximum exposure to chlorine (720000 ppm·h), the contact angle of water on PTFE and PVDF changed from 132° to 117° and 120° to 108°, respectively. After the maximum exposure to ozone (45 ppm· h), the contact angle on PTFE and PVDF decreased from 132° to 111° and 120° to 112°, respectively. PP membranes were exposed to lower doses of chlorine (up to 10000 ppm·h) and ozone (up to 7.5 ppm·h) since they suffered from severe cracking. PP membranes showed more rapid changes in water contact angle during oxidant exposure, experiencing a decrease in contact angle of 140° to 120° and 140° to 117° for chlorine and ozone, respectively. Generally, contact angle measurements showed modest changes in the surface properties across all membranes, with a less than 15% change in contact angle in all cases. Even the PP membranes that showed macroscale membrane cracking showed relatively small changes in contact angle prior to failure.

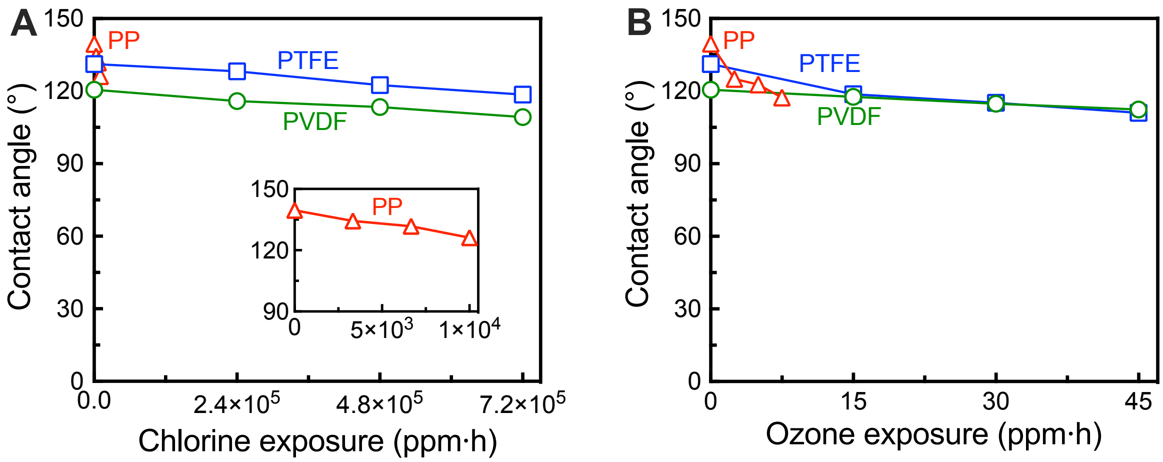

Figure 3. Static water contact angle of polytetrafluroethylene (PTFE), polyvinylidene fluoride (PVDF), and polypropylene (PP) membranes following exposure to (A) 10000 ppm chlorine solution and (B) 15 ppm ozone solution.

3.2. Understanding chemical changes in polymers after exposures

The changes in structure and hydrophobicity of membranes after exposure to chlorine and ozone motivated further investigations into membrane surface chemistry. Attenuated total reflectance

Fourier transform infrared spectroscopy (ATR-FTIR) was used to gain information on changes in the overall bond structure of membranes before and after oxidation. The PTFE and PVDF membrane showed no changes in ATR-FTIR spectra after exposure to chlorine and ozone (Figure S2). In contrast, PP membranes, which showed significant structural changes after exposure to both chlorine and ozone, also had observable changes in their ATR-FTIR spectra (Figure 4). Following ozonation, we noted the development of a small peak at 1700 cm^{-1} which corresponds to the presence of a carbonyl group. We saw more significant changes in the chlorinated PP in the region between 4000 cm^{-1} and 3000 cm^{-1} where there is a broad peak characteristic of an alcohol group. We also observed the evolution of a broad carbonyl peak between 1800 cm^{-1} and 1500 cm^{-1}. The formation of similar peaks characteristic of alcohol and carbonyl functional groups is typical in oxidized polyproypylene.[29] Additionally, we see the formation of an alkyl halide group in the chlorinated PP at 800–600 cm^{-1}.[30] The chemical changes in PP are consistent with our understanding that the tertiary carbon makes it susceptible to oxidation.[31] The attached hydrogen is more likely to be abstracted and an alkoxy radical is formed which stabilizes itself through a rearrangement into an alkyl radical and forms a ketone.[32,33]

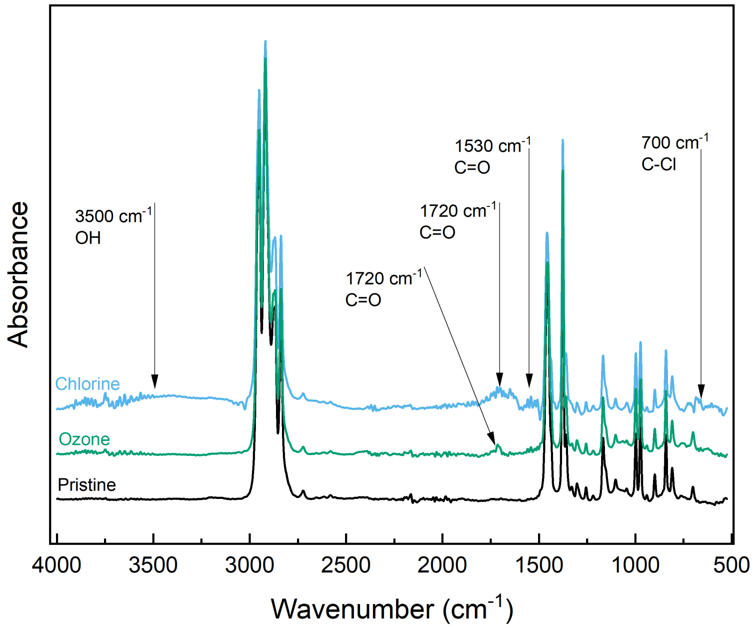

Figure 4. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy scans of polypropylene membranes after before and after exposure to ozone and chlorine. Polypropylene membranes were exposed to 10000 ppm chlorine for 24 h or 15 ppm ozone for 1 h.

XPS was used to gain more information on the atomic compositions of the top surface (approximately 10 nm) of the membrane polymer, where we expected to observe the most chemical changes due to oxidation (Figure 5). For PTFE samples, XPS analysis indicated minor changes in surface chemistry between samples that were likely due to carbon contamination. Pristine PTFE shows the characteristic C-F peak at 291.8 eV, and following exposures to chlorine and ozone, there are no changes to this peak (Figure 5C). There is an additional weak peak at 284.8 eV which corresponds to C-H bonds; this peak is commonly attributed to carbon contamination.[34] Overall, PTFE membranes showed XPS peaks characteristic of its highly fluorinated carbon chain that were not affected by chlorine or ozone exposure.

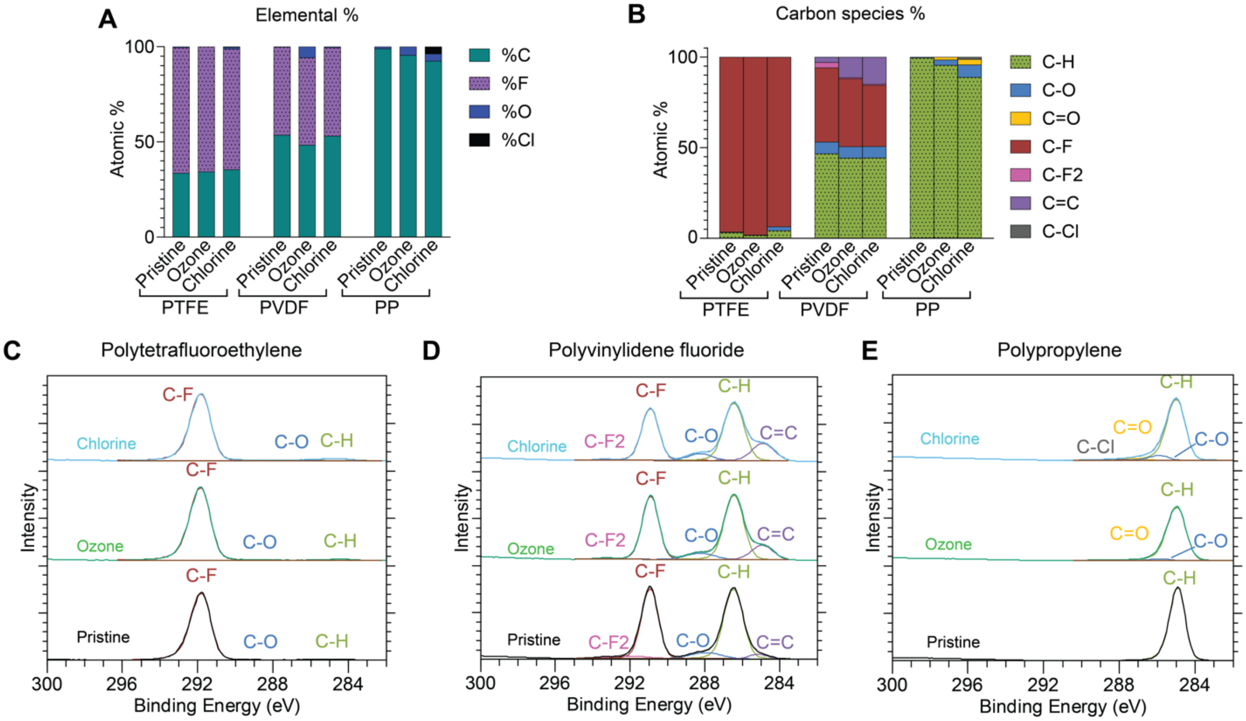

Figure 5. (A) Atomic percent of different elements observed in the XPS survey spectra for PTFE, PVDF, and PP membranes exposed to chlorine and ozone. (B) Summary of results from carbon core scans indicating the binding environment of the carbon atoms on the surface of membrane. (C,D,E) Spectra from carbon core scans of PTFE, PVDF, and PP membranes. PTFE and PVDF membranes were exposed to 10,000 ppm chlorine for 72 h or 15 ppm ozone for 3 h. PP membranes were exposed to 10,000 ppm chlorine for 24 h or 15 ppm ozone for 1 h.

XPS analysis of the PVDF and PP membranes observed more obvious changes to the membrane surface chemistry following oxidation than those seen with PTFE. In pristine PVDF, there are two characteristic peaks: the C-F peak at 291.0 eV and the C-H peak at 286.4 eV (Figure 5D). Following oxidation with ozone and chlorine we see decreases of 8.1% and 17.3%, respectively, in the C-F peak which indicates possible surface defluorination. Additionally, we see an evolution of a peak at 284.8 eV. Since there is indication of defluorination on the PVDF, we believe that the peak at 284.8 eV corresponds to the formation of C=C on the surface which has been suggested to form following defluorination in PVDF.[35,36]

For PP membranes, there is only a peak for C-H at 284.8 eV in the pristine membrane (Figure 5E). This structure corresponds to the repeating units of carbon and hydrogen atoms, where the carbon atoms are connected by single bonds. This differs from the C-H peak observed in the PVDF spectra since the electronegative nature of the C-F bond in PVDF will shift the C-H peak to a slightly higher binding energy.[37,38] Following oxidation, we observe widening of the carbon peak due to an evolution of carbon oxygen groups on the PP surface. Chlorination of the polypropylene led to a 5.3% and 3.0% increase of C-O and C=O respectively, while ozone led to a 2.5% and 1.5% increase of C-O and C=O respectively on the surface. An important difference between the chlorinated and ozonated polypropylene is the incorporation of Cl into the polypropylene. Following chlorine treatment, we see a 3.7% increase of Cl on the surface as observed in the XPS survey scans (Figure 5A). Further examination of the core scans of the PP (Figure 5B and 5E) shows that there is a small peak evolving at around 288.3 eV which is indicative of a C-Cl bond .[37,38] Thus, oxidation of the PP membranes led to changes in the membranes overall surface chemistry as evidenced by the presence of C-O, C=O, and C-Cl following oxidation.

3.3. Desalination performance testing

Direct contact membrane distillation (MD) testing was used to investigate the impact of chlorine and ozone exposure on the desalination performance of membranes (Figure 6). With a hot temperature of 60 ºC and a cold temperature of 20 ºC, the pristine PTFE, PVDF, and PP membranes showed water fluxes of 35.3 L $m^{-2}h^{-1}$, 24.5 L $m^{-2}h^{-1}$, and 47.1 L $m^{-2}h^{-1}$, respectively. All pristine membranes had salt rejections higher than 99.9%.

After exposure to chlorine and ozone, PTFE and PVDF membranes showed minor changes in water flux and maintained greater than 99.9% salt rejection. The measured water fluxes for PTFE membranes exposed to chlorine or ozone varied from 38.4 L m^{-2}h^{-1} to 44.7 L m^{-2}h^{-1}. For PVDF membranes, the measured water fluxes of oxidant exposed membranes varied from 26.8 L m^{-2}h^{-1} to 31.6 L m^{-2}h^{-1}. Although the water fluxes of membranes after oxidant exposure were generally higher than those of the pristine membranes, no clear dependence of water flux on oxidant exposure was observed. These results are consistent with previous data that indicate minor changes in membrane structure and minor differences in hydrophobicity following oxidant exposure.

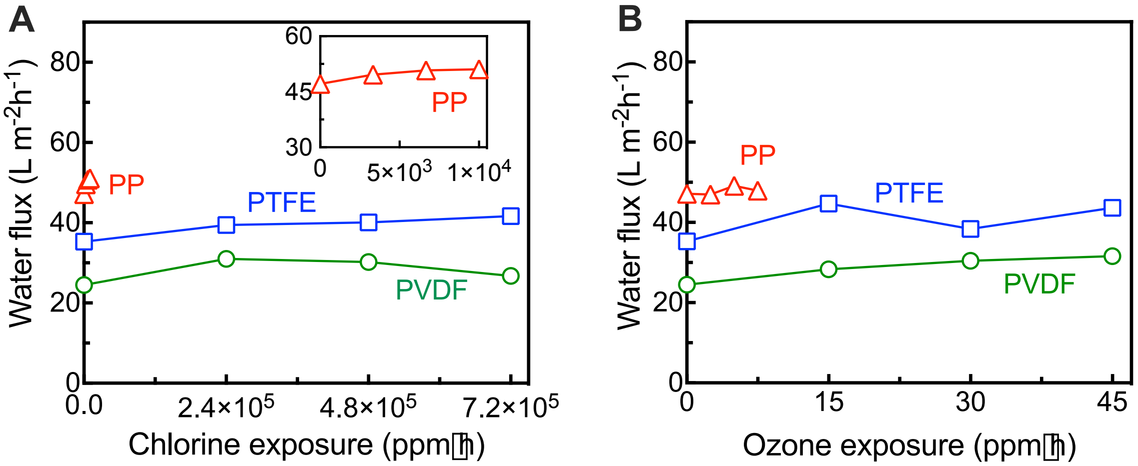

Figure 6. Water flux as a function of oxidant exposure for polytetrafluroethylene (PTFE), polyvinylidene fluoride (PVDF), and polypropylene (PP) membranes after exposure to a 10000 ppm chlorine solution (A) and a 15 ppm ozone solution (B) through a direct contact membrane distillation cell. Temperatures were 60 °C and 20 °C through the feed and permeate channels, respectively.

Unlike PTFE and PVDF, PP membranes demonstrated observable cracking which prevented them from being tested in desalination systems at doses higher than 240000 ppm·h chlorine or 15 ppm·h ozone. Within the allowable exposure for PP membranes without reaching catastrophic failure, changes in water flux and salt rejection were minor. The water flux of the pristine PP membrane was measured to be 47.1 L m^{-2}h^{-1}. Following exposure to chlorine, an 8.3% increase in water flux was observed. Ozone exposure resulted in a 1.7% increase in water flux. Similar to the PVDF and PTFE membranes, changes in salt rejection between pristine membranes and oxidized membranes were minor during the observed exposures (Figure S3). It should be emphasized that following the exposures used for PP membranes in desalination performance testing, damage to the membrane caused by oxidation resulted in complete failure within the system. This included visible breakage to the membrane with near-zero salt rejection and significantly increased water flux through the cell channels.

4. CONCLUSIONS

The impact of exposure to chlorine and ozone oxidants on three commercial hydrophobic membranes (PTFE, PVDF, and PP) was evaluated by examining changes to structure, surface chemistry, and desalination performance. PTFE and PVDF membranes appeared to be minimally impacted by strong oxidants at exposures up to the limit of this study: 720000 ppm·h chlorine and 45 ppm·h ozone. After oxidant exposure, both membranes experienced minor changes in water flux in direct contact MD without compromising selectivity and saw a less than 10% decrease in contact angle. Further characterization revealed no noticeable changes in the structure and chemistry of PTFE membranes, though changes in the chemistry of the PVDF membranes were observed through XPS. PP experienced severe degradation following maximum oxidant exposure of 240000 ppm·h chlorine or 15 ppm·h ozone which was confirmed through surface and structural characterization methods.

Given their high observed oxidation resistance, PTFE and PVDF may be promising options for water treatment applications that involve contact with oxidants or for applications that might benefit from pretreatment using ozone and chlorine. Based on the observed oxidation resistance, pretreatment of water using a typical dose of 4 ppm chlorine would be possible for at least 20 years. With an average continuous ozone dose of 0.1 ppm, both PVDF and PTFE could resist oxidation damage for at least 18 days under these experimental conditions. Past this point, the surface characterization results imply that PVDF could be at risk of failure earlier than the PTFE membranes when in direct contact with ozone.

Polypropylene demonstrates limited oxidation resistance for both chlorine and ozone compared to PTFE and PVDF. Our work indicates that with a typical chlorine dose of 4 ppm, failure of PP membranes may occur within 100 days. Similarly, the use of PP in direct contact with 0.1 ppm ozone would be limited to 9 days. Prior to membrane failure, no noticeable changes in permeability, selectivity, or hydrophobicity were observed. The rapid and unexpected failure of the PP membrane indicate that failure of the membrane may occur without warning in a water treatment system.

Further work is needed investigate the effects of direct oxidation with additional parameters not considered in this study. For example, future testing should explore the impact of additional organics, salts, and other contaminants that could contribute to membrane fouling or alter membrane surface properties. This work found that membranes made from fluorinated polymers (PTFE and PVDF) showed higher oxidation resistance than non-fluorinated membranes (PP). An additional emerging concern in the practical application of fluorinated membranes is the release of per- and polyfluoroalkyl substances (PFAS). Additional analyses are necessary to compare the advantages of membrane oxidation resistance with their potential for PFAS release.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge online.

Digital photographs of PP membranes before and after oxidant exposure (Figure S1), ATR-FTIR spectra of PTFE and PVDF membrane before and after oxidant exposure (Figure S2), salt rejection data for membrane distillation performance testing (Figure S3), and summary of membrane properties (Table S1).

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

ACKNOWLEDGEMENTS

We acknowledge financial support from the Bureau of Reclamation, Department of Interior, via DWPR agreement R22AC00425 and the National Science Foundation (NSF) under award number CBET 2227273. We also acknowledge support from the NSF Industry/University Cooperative Research Center for Membrane Science, Engineering and Technology (MAST) at the University of Colorado Boulder (UCB, award number, IIP 1624602). E.A.H. acknowledges support from the NSF Graduate Research Fellowship Program under grant number DGE 204043.

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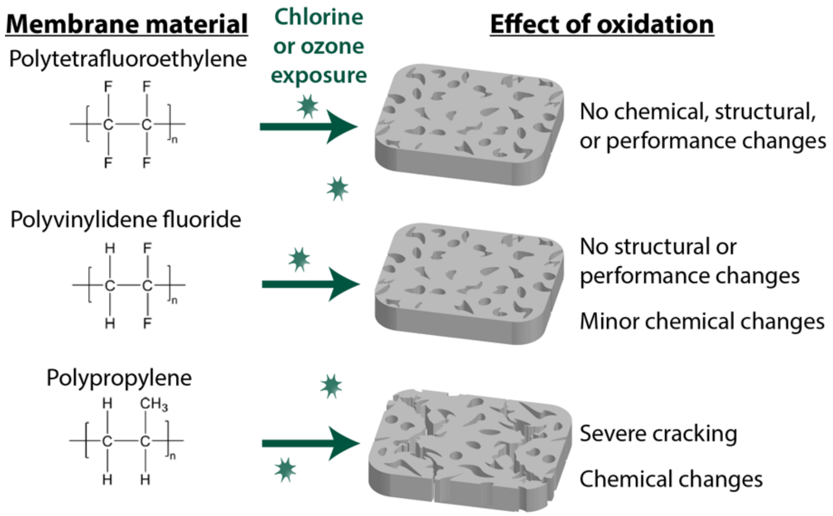
TOC Art


Membrane material
Chlorine or ozone exposure
Effect of oxidation
Polytetrafluoroethylene
F F C C F F n
No chemical, structural, or performance changes
Polyvinylidene fluoride
H F C C H F n
No structural or performance changes
Minor chemical changes
Polypropylene
H CH3 C C H H n
Severe cracking
Chemical changes