

Degradation of Polyamide Reverse Osmosis Membranes in the Presence of Chloramine

Marlene J. Cran, Stephen W. Bigger, Stephen R. Gray

Institute for Sustainability and Innovation, Victoria University,
Werribee Campus, PO Box 14428, Melbourne, 8001, Australia

Abstract

Exposure to relatively low concentrations of chlorinated chemicals such as hypochlorite can reduce the performance and ultimately result in the failure of polyamide (PA) reverse osmosis membranes. Whereas the tolerance of PA membranes to chloramine solutions is considerably higher than that of hypochlorite, the presence of some metal ions can potentially catalyze and accelerate degradation reactions. Spectroscopic techniques are commonly used to qualitatively assess the chemical degradation of membranes by observing changes in structural peaks. This paper presents a technique to quantitatively evaluate changes in PA membranes exposed to chloramine by means of a peak ratio derived from a typical amide peak and an invariant peak in the same spectrum. The effect of some common metal ions and combinations of these on the peak ratio parameter derived from a typical amide peak is also reported.

Keywords

Polyamide membranes; chloramine; hypochlorite; degradation; Fourier-transform infrared spectroscopy

Introduction

In conventional water treatment processes, chlorination using hypochlorite is traditionally the preferred method of disinfecting drinking water [1]. Other common methods of disinfection include the use of ultraviolet radiation [2], ozonation [3], chlorine dioxide [4], hydrogen peroxide [3] and chloramine [5]. The presence of natural organic matter in feed water can result in the formation of potentially harmful disinfection by-products such as trihalomethane compounds when hypochlorite is introduced [6]. To minimize the formation of such disinfection by-products, chloramine is considered to be a suitable alternative for drinking water disinfection [7]. Chlorine solutions are also used to slow the fouling of polyamide (PA) reverse osmosis (RO) membranes and to enhance their permeability by periodically cleaning these when they are partially or completely fouled [8]. However, prolonged or sometimes infrequent exposure to chlorine solutions can be detrimental resulting in PA degradation and consequently reducing the service lifetime of the membrane [9-12]. It is therefore important to understand the mechanisms of the changes that result from chemical degradation in order to minimize and potentially prevent premature membrane failure as a result of chlorine exposure.

The effects of chlorination on RO membranes that are made of PA have been widely reported in the literature [10-18]. Generally these studies conclude that chlorine causes irreversible damage to the PA membrane resulting in a loss of membrane integrity. Several researchers have also investigated the mechanism of chlorine attack on PA membranes [14, 19, 20] and have suggested that chlorination of the aromatic ring can occur by two possible reaction pathways. In the first, direct aromatic substitution by chlorine is suggested [19] whereas the second mechanism, the "Orton Rearrangement" [20] involves initial chlorination of the amide nitrogen followed by an attack on the aromatic ring. This second mechanism has been further explored to describe potential morphological changes in the PA structure with chlorine transforming the crystalline regions of the polymer to an amorphous state followed by chlorine attack on the amorphous regions [20]. Other degradation mechanisms have been reported including the formation of hydroxyl radicals [21-24] that are responsible for the chemical attack on the membrane. Some studies suggest that the radicals are formed only when both forms of hypochlorite (HClO and ClO^-) are present [23] whereas others suggest that the radicals can be formed in the presence of HClO only [24]. In addition to the damaging effects of chlorine on PA membranes, the presence of transition metal ions can effectively catalyze the degradation processes [16, 25, 26].

The mechanism of chloramine attack on PA membranes has also been reported in the literature [11, 15, 27]. In these studies, the formation of amidogen radicals ($\bullet\text{NH}_2$) has been suggested with the presence of some metal ions acting to catalyze their formation [15]. The formation of the radical species occurs by a two-step electron transfer mechanism with the $\bullet\text{NH}_2$ radical produced as an intermediate product [28-30]. The radical species attack the aromatic PA ring allowing for direct chlorination by excess chloramine. It is suggested that the mechanism of degradation is the same as that observed for chlorine and chlorine dioxide although the aggressiveness of chloramine is somewhat lower [11, 31]. The precise degradation pathways that lead to the ultimate failure of the PA membrane layer in the presence of chloramine are still relatively unexplored [15].

Fourier-transform infrared (FTIR) spectroscopy is a valuable analytical technique that is typically used qualitatively to assess the structures and changes in materials such as PA membranes [18, 32-35] [39]. The usefulness of this technique can extend to quantitative analyses that can reveal more detailed information regarding changes in polymer structures that are the result of degradation or other physical and/or chemical changes. The carbonyl index, for example, is commonly used to quantify the oxidative degradation of many polymers including polyethylene [36-40], polypropylene [41-44] and PA [45]. This index is obtained by measuring the peak height or area of the carbonyl functional group as a ratio of an invariant peak in the same infrared spectrum. This study aims to explore the use of quantitative FTIR measurements for the purpose of evaluating the effects of chloramine and metal ions on PA membranes.

Experimental

Membrane Materials and Conditioning

The RO membrane used in this study was a thin film composite PA membrane (BW30) cast on a polysulfone backing supplied by Dow FilmTec Australia. A series of pieces were cut from a large flat sheet of the membrane material prior to conditioning and performance testing (salt rejection and flux) through a GE Osmonics RO apparatus using 2000 ppm NaCl. Conditioning commenced under a pressure of 16 bar and was gradually increased by 2 bar every 10 min until reaching 36 bar. The pressure was maintained at 36 bar with permeate recirculation for up to 1 h. The permeate was collected until 40% recovery was obtained and the conductivity and flux were determined.

Chloramine and Metal Ion Solution Preparation

Chloramine was prepared using analytical (AR) grade ammonium chloride supplied by Merck Australia and hypochlorite containing 10-15% (v/v) available chlorine obtained from Sigma Aldrich Australia. Other chemicals used were reagent or AR grade obtained from various suppliers. Concentrated chloramine solutions were prepared by dissolving ammonium chloride in 0.1 M phosphate buffer solution adjusted to pH 8.3 to ensure the formation of monochloramine [46]. The concentration of hypochlorite was determined spectrophotometrically at a wavelength of 290 nm and using a molar extinction coefficient of $350.4 \text{ M}^{-1} \text{ cm}^{-1}$ [47]. The ammonium chloride and hypochlorite solutions were equilibrated in an ice bath for 1 h, shielding them from air and light. The hypochlorite solution was then added to the ammonium chloride by drop-wise addition through a burette with constant stirring whilst the pH was maintained at 8.3. Solutions were stored on ice or refrigerated until used. The concentration of the prepared chloramine was determined spectrophotometrically at a wavelength of 243 nm using a molar extinction coefficient of $458 \text{ M}^{-1} \text{ cm}^{-1}$ [48]. Stock solutions of ferrous sulfate, aluminium sulfate and copper sulfate were prepared using AR grade reagents and phosphate buffer solution to obtain final concentrations of 0.1, 0.3 and 1.0 ppm of Fe^{2+} , Al^{3+} and Cu^{2+} respectively. These are the typical maximum concentrations of these ions that would be found in drinking water [49]. To determine the loss of chloramine with time, the concentration of chloramine solutions in the presence of metal ions were determined using the same spectrophotometric method. For these experiments, samples were left uncovered and at room temperature.

Scanning Electron Microscopy

Images of the membrane surfaces before and after exposure were obtained using a JOEL NeoScope (JCM-5000) scanning electron microscope (SEM). Samples were dried overnight and coated with 2 nm of gold using a NeoCoater (MP19020NCTR) coater prior to acquiring the SEM images.

Membrane Degradation

Chloramine test solutions were prepared at pH 8.3 and experiments were conducted at room temperature. Samples of the membrane material were immersed in solutions of various chloramine concentrations for up to 36 h with or without metal ions and the vessels were covered to protect them from light for the duration of the experiments. The samples were rinsed after exposure and preserved in sodium metabisulfite solution prior to analysis and performance testing.

Membrane Performance

Performance testing of the exposed membrane samples was conducted using the same GE Osmonics RO apparatus used for conditioning with a 2000 ppm NaCl solution. A pressure of 16 bar was initially applied and was gradually increased by 2 bar every 10 min until reaching 36 bar. The pressure was maintained at 36 bar with permeate recirculation for up to 1 h. The permeate was then collected until 40% recovery was obtained and the conductivity and flux were determined.

Fourier-transform Infrared Spectroscopy

Changes in chemical composition of the membrane samples were measured regularly using spectroscopic techniques [18]. Horizontal attenuated total reflectance (HATR) infrared spectroscopy and specular reflectance spectroscopy were used to measure changes in major functional groups of the samples. A Bruker Vector 22 Fourier-transform infrared (FTIR) spectrophotometer fitted with a Pike Technologies HATR accessory or a Shimadzu IRAffinity-1 FTIR spectrophotometer fitted with a Pike Technologies 30Spec Specular Reflectance accessory was used. The spectra were recorded at a resolution of 4.0 cm^{-1} in the range $4000\text{-}400\text{ cm}^{-1}$ with an acquisition time of 1 min.

Results and Discussion

Loss of Chloramine in the Presence of Metal Ions

The effect of metal ions on the concentration of chloramine solutions was studied in order to determine the stability of chloramine in the presence of the ions. Figure 1 is a plot of the normalized chloramine concentration as a function of time with or without metal ions. This plot shows that in the absence of metal ions, the chloramine concentration decreases slowly over 8 h. When metal ions are introduced, chloramine loss is accelerated with significant losses in the presence of Cu^{2+} and the combination of $\text{Al}^{3+}/\text{Fe}^{2+}$. This suggests that the metal ions catalyse the formation of the $\bullet\text{NH}_2$ radicals that can, in turn, lead to increased membrane degradation [15, 27]. The addition of either Al^{3+} or Fe^{2+} to chloramine results in similar losses of *ca.* 10% after 3 h and up to *ca.* 15% after 8 h. This is in contrast to the losses that result in the presence of both ions, which is significantly greater. Figure 2 shows the loss of chloramine after 8 h and 24 h with or without metal ions. After 24 h, a loss of *ca.* 25% of chloramine is observed with no metal ions present. With the addition of the individual metal ions, losses of *ca.* 55-70% are observed whereas the addition of the $\text{Al}^{3+}/\text{Fe}^{2+}$ combination results in a loss of $>97\%$.

Effect of Chloramine on Membrane Surface

In Figure 3, SEM images of membranes before and after exposure to chloramine and some of the metal ions are presented. The images show that the surface before and after exposure (Figure 3(a) and 3(b)) are similar with no adverse effects observed due to the presence of chloramine. Indeed, such images are generally representative of the polysulfone support layer given that the active membrane layer is very thin [50]. The images of the membranes exposed to Cu^{2+} (Figure 3(c)) and the combination of $\text{Al}^{3+}/\text{Fe}^{2+}$ (Figure 3(d)) show evidence of ubiquitous particles on the surface that varied in size and shape. The presence of these particles could potentially block some of the membrane pores resulting in changes in permeate conductivity and flux [51].

Effect of Chloramine on Membrane Performance

To investigate the effect of a relatively high chloramine exposure on the performance of the PA membrane, samples were exposed to 100 ppm chloramine and the percentage change in permeate flux ($\text{L m}^{-2} \text{h}^{-1}$) and permeate conductivity ($\mu\text{S m}^{-1}$) was measured. Figure 4 shows the percentage change in these parameters relative to the control membrane as a function of the time of exposure to the chloramine solution. The results show that with increasing chloramine exposure, the permeate flux of the membrane increases by $>200\%$ after 18 h. Interestingly, the conductivity of the permeate decreases by up to 50% which is a similar effect that has been reported in cases of oxidant exposure [11, 31]. In these studies, it was suggested that membrane pores might undergo an initial “tightening”, resulting in higher rejection.

Structural Changes Measured by Infrared Spectroscopy

In addition to changes in performance induced by chloramine exposure, chemical changes in the PA membrane were investigated by FTIR spectroscopy. In Figure 5, the FTIR spectra of a sample of membrane that was soaked in 100 ppm chloramine solution for 4 h and an unexposed control sample are shown. The peak observed at 1487 cm^{-1} remains relatively unchanged whereas the peak at *ca.* 1540 cm^{-1} decreases in intensity and undergoes a slight hypochromic shift with exposure. The peak at 1487 cm^{-1} corresponds to a characteristic peak (CH_2 stretch) of polysulfone [52] whereas the peak at 1540 cm^{-1} corresponds to the C-N stretch of the PA (II) group [18]. It appears that the polysulfone layer of this material is not affected by the chloramine solution as evidenced by the unchanged characteristic peak however a chemical change in the PA structure has occurred as a result of chloramine exposure.

It is clear from the FTIR results that significant changes in the PA structure occur in the presence of chloramine alone. The potential for some metal ions to accelerate these structural changes is reflected in Figure 6 with an example of the FTIR absorbance of a membrane that was exposed to 25 ppm chloramine containing 0.1 ppm Al^{3+} and 0.3 ppm Fe^{2+} for 4 h and 18 h. In each case, the peak at 1540 cm^{-1} decreases in intensity upon exposure whereas the peak at 1487 cm^{-1} once again remains relatively unchanged. This is in accordance with the notion that the PA (II) bond undergoes degradation in the presence of chloramine with the metal ions whereas the characteristic methylene bonds in the polysulfone remain intact.

For the purposes of a quantitative analysis, the peaks at *ca.* 1540 cm^{-1} (C-N stretch of the PA (II)) and at 1487 cm^{-1} (CH_2 stretch of the polysulfone) were used to calculate the absorbance ratio (A_{1540}/A_{1487}). Each result was normalized such that the ratio of the control (unexposed) sample was unity. In all cases, the data were verified by plotting the normalized absorbance ratio of two invariant peaks in the polysulfone support (dashed line) to confirm the validity of using the calculated absorbance ratio and to confirm that a significant change was occurring in the PA structure. It is possible that multiple peaks could be used to assess changes in complex structures such as PA including the various amide bending and stretching vibrations [34] but in this case, the C-N stretch appears to be suitably sensitive.

In order to quantitatively assess the effects of metal ions on the degradation of the PA membranes in the presence of chloramine, a series of experiments were conducted in which the type and combination of metal ion was varied. Figure 7(a) shows a plot of the normalized absorbance ratio versus time for a sample of membrane exposed to 25 ppm chloramine solution alone. After *ca.* 18 h a 25% reduction in the PA peak is observed. This exposure approximates to the “concentration time equivalent” of *ca.* 450 ppm h and suggests that significant structural changes are occurring in the membrane during contact with the solution. Figure 7(b) shows a plot of the normalized absorbance ratio versus time for a sample of membrane exposed to 25 ppm chloramine containing 0.1 ppm Al^{3+} . The decrease in the PA peak is slightly greater than that observed without Al^{3+} , which suggests that the addition of these ions may have a catalyzing effect on the PA membrane. A reduction in the peak of *ca.* 28% is observed and after 17 h of exposure and it has been suggested that aluminium can accumulate on the surface of membranes over time resulting in reduced flux [51]. A plot of the normalized absorbance ratio versus time for a sample of the membrane exposed to 25 ppm chloramine and 0.3 ppm Fe^{2+} solution is shown in Figure 7(c). The initial decrease in the PA peak is lower than that observed with aluminium suggesting that the addition of these ions has little additional adverse effect on the PA membrane in the early hours

of exposure. An overall reduction in the peak of *ca.* 29%, however, is observed and after 18 h of exposure, which is similar to that observed in the case of aluminium ions with chloramine. Other studies have shown that the presence of ferric [??? Are you sure??? ferric = Fe³⁺, ferrous = Fe²⁺ and we have considered ferrous ions throughout this paper] ions can have a catalyzing effect on the degradation of PA membranes [27] with other studies reporting that combinations of some metals can catalyze PA degradation [16]. Figure 7(d) shows a plot of the normalized absorbance ratio versus time for the membrane exposed to 25 ppm chloramine with a combination of 0.1 ppm aluminium sulfate and 0.3 ppm Fe²⁺ solutions. Although the effect of adding these species is less than additive, a significant decrease of the absorbance ratio of *ca.* 40% is observed suggesting a detrimental effect on the PA structure due to the simultaneous introduction of two ionic species in the test solution. This is consistent with there being a complex series of reactions occurring both in solution and on the surface of the membrane as suggested by Gabelich *et al.* [27]. The normalized absorbance ratio versus time for the membrane exposed to 25 ppm chloramine and 1 ppm Cu²⁺ solutions is shown in Figure 7(e). A significant and continuous decrease of the absorbance ratio is observed demonstrating a considerable effect of this ion on the degradation process in the presence of chloramine. This finding may have practical implications as copper is sometimes added to feed water due to its biocidal properties [53] although this is not common practice.

It is evident from the preceding data that similar trends exist for each system with a significant decrease in the absorbance ratio with time. Moreover, it is possible to compare the percentage reduction in the PA (II) peak for each system after prolonged exposure. Figure 8 shows a comparison of the percentage reduction in this peak for each system after *ca.* 17 h exposure. From this plot it is clear that considerable degradation is observed in the presence of chloramine in all cases. Although the presence of Al³⁺ or Fe²⁺ individually with chloramine appears to catalyze the peak reduction, the combination of these two ions appears to induce a significant detrimental effect. The presence of Cu²⁺ also considerably catalyzes membrane degradation in the presence of chloramine. The trends observed in the percentage reduction of the PA (II) peak are in accordance with the percentage loss of chloramine in the presence of the metal ions shown in Figure 2. This is consistent with the notion that the metal ions are catalyzing the reduction of chloramine resulting in the formation of •NH₂, which in turn attacks the PA structures.

The results suggest that changes in the chemical structure of the aromatic PA occur within the first hours of exposure to chloramine. This is in accordance with the changes observed for hypochlorite exposure where initial chlorination of the amide nitrogen occurs [19, 20] resulting in a reduction of the amide (II) peak. The presence of Cu²⁺ or a combination of Al³⁺ and Fe²⁺ ions

appears to catalyze the formation of radicals from the chloramine resulting in an accelerated reduction of the amide (II) peak [22]. The changes resulting from the relatively low levels of exposure in this study suggest that membrane performance is initially enhanced with higher flux and improved salt rejection although higher concentrations in combination with longer exposures could have a more detrimental effect [11]. Indeed, most studies on accelerated degradation of PA membranes use considerably high oxidant concentrations that may not be representative of real exposures [11, 15, 27, 54].

Conclusions

The stability of chloramine solutions in the presence of metal ions decreased significantly with Cu^{2+} and a combination of $\text{Al}^{3+}/\text{Fe}^{2+}$ suggesting that these ions catalyze the reduction of chloramine, which can lead to the formation of the amidogen radical species. Membrane imaging showed that in the presence of some metal ions, particles were formed on the surface and these might potentially impact upon membrane performance. Changes in membrane performance with chloramine exposure resulted in an unfavorable increase in the permeate flux but a more favorable reduction in permeate conductivity. Structural changes in the aromatic PA structure in the presence of chloramine were observed by FTIR with the peak corresponding to the C-N stretch of the PA (II) decreasing with exposure time. Although the presence of Al^{3+} or Fe^{2+} in solution with chloramine slightly increased the reduction of the PA (II) peak, the combination of these two ions with chloramine induced a faster peak reduction. The presence of Cu^{2+} with chloramine also significantly accelerated the reduction of the PA (II) peak. The results of this study suggest that FTIR can be successfully used not only qualitatively, but quantitatively to observe and measure structural changes in PA membranes.

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Figure Captions

Figure 1. Reduction in chloramine concentration in the presence of metal ions.

Figure 2. Percentage change in chloramine concentration after 8 h and 24 h in the presence of metal ions.

Figure 3. SEM images of membranes: (a) before exposure, (b) exposed to NH_2Cl , (c) exposed to NH_2Cl in the presence of 1 ppm Cu^{2+} and (d) exposed to NH_2Cl in the presence of 0.1 ppm Al^{3+} and 0.3 ppm Fe^{2+} ions.

Figure 4. Percentage change in permeate (\circ) flux and (\bullet) conductivity as a function of the time of exposure of the membrane to 100 ppm NH_2Cl .

Figure 5. Infrared spectra of samples of membrane exposed to: (i) 0 ppm and (ii) 100 ppm NH_2Cl .

Figure 6. Infrared spectra of samples of membrane exposed for: (i) 4 h and (ii) 18 h to 25 ppm NH_2Cl in the presence of 0.1 ppm Al^{3+} and 0.3 ppm Fe^{2+} ions.

Figure 7. Normalized absorbance ratio as a function of exposure time for samples of membrane exposed to 25 ppm NH_2Cl in the presence of metal ions.

Figure 8. Change in the PA (II) peak with prolonged exposure to NH_2Cl and metal ions.