Change of Membrane Performance Due to Chlorination of Crosslinked Polyamide Membranes

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ABSTRACT: A systematic investigation of the relationship between chlorine exposure of a thin film composite crosslinked polyamide membrane (LE membrane, FilmTec©) and changes in membrane performance (water flux and salt rejection) is discussed here. Performance change of crosslinked polyamide membranes due to chlorination depended on pH and concentration of chlorine in the soaking bath. Membranes chlorinated at low pH and high chlorine concentration showed flux decreases at an early stage of filtration and then increases with filtration time. On the other hand, membranes chlorinated at high pH and low chlorine concentration showed flux increases at an early stage and then decreases with filtration time. Performance of chlorinated polyamide membranes was determined by the balance between rearrangement of polymer chains and the distortion of the chains due to chlorination. A conceptual model of performance change was proposed consistent with the chlorination of polyamide membranes. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 5895–5902, 2006

Key words: degradation; chlorine; crosslinked polyamide; performance; RO membrane

INTRODUCTION

Since development of the first interfacial composite reverse osmosis (RO) membrane by Loeb and Sourirajan,[1] water/wastewater treatment by membrane systems has proliferated. More than 16 million m^3/day is now treated by membrane processes, including RO and electrodialysis.[2] Reported costs of desalinating brackish water and seawater using RO membranes presently fall within the range of \$ 0.6–1.5/m^3,[2] comparable to the costs by conventional desalinating methods. Asymmetric cellulose acetate and thin film composite polyamide membranes have been the two major types of commercial RO membranes. Currently, thin film composite polyamide membranes are displacing cellulose type membranes due to their outstanding mechanical, thermal, and hydrolytic stabilities. However, the polyamide membranes are sensitive to chlorine, which is widely used as a disinfecting agent in water/wastewater treatment plants. Therefore, understanding the effects of chlorine contact with polyamide membranes is important to make membrane technology more economically feasible and competitive.

Previous studies on membrane chlorination have focused primarily on investigation of linear polyamide membranes due to the difficulties of isolating the crosslinked polyamide layer for instrumental analysis. Glater and Zachariah[4] proposed hydrogen bonding shifts from inter to intramolecular within linear polymer chains resulting in performance decline after chlorination. Avlonitis et al.[5] proposed the structural transition from crystalline to amorphous state due to the hydrogen bonding shift causes loss of structural integrity of linear polyamide membranes. However, the cause and mechanism of performance change caused by chlorination of crosslinked polyamide membranes has not been systematically investigated.

The goal of this work was to systematically investigate the change of performance behavior of thin film composite crosslinked FilmTec© LE polyamide membranes after being chlorinated at various chlorine concentration and pH conditions, and present a conceptual model of performance changes due to the chlorination.

EXPERIMENTAL

Polyamide membrane

We have used a commercially available FilmTec© LE membrane as representative of polyamides membranes. The membranes are thin film composite crosslinked aromatic polyamide membranes, which are produced by interfacial polymerization of 1,3-phenylenediamine and 1,3,5-benzentricarbonyl chloride,

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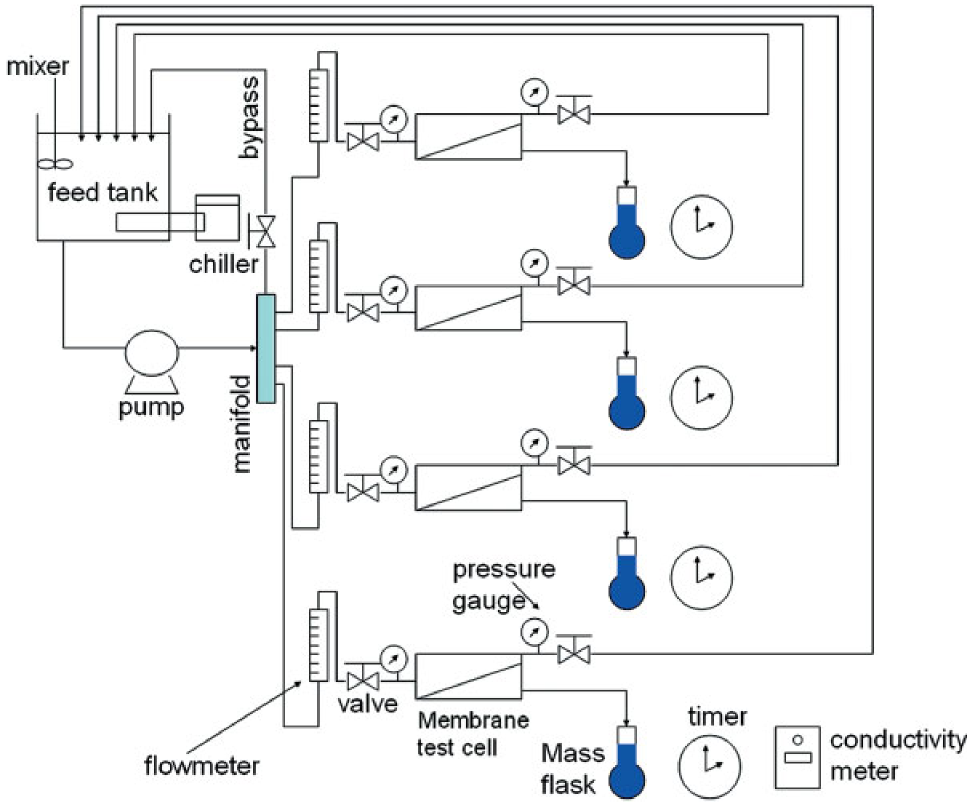

Figure 1 Schematic of a reverse osmosis filtration system. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

having amide bonds (—CONH—) and crosslinked/noncrosslinked portions in its structure. According to the X-ray photoelectron spectroscopy (XPS) investigation in our preceding work,[6] the LE membrane was composed of carbon, nitrogen, oxygen, and their percentage of atomic concentration were 72.1%, 11.8%, and 16.2%, respectively, (hydrogen atom is not included since hydrogen cannot be measured by XPS). Crosslinking density (the ratio of crosslinked amide form to total amide form in the polymer) of the membrane was about 34%. Each sample was thoroughly rinsed with flowing deionized (DI) water for 6 h, sonicated in a Milli-Q water bath for 30 min, and then dried at room temperature.

Filtration system

The system in Figure 1 was set up to provide the same operating conditions for four identical, stainless steel RO test cells (Sepa CF II, GE Osmonics©) arranged in parallel. This system contained four independent sets of pressure channels with a recirculation mode. Each pressure vessel houses 140 cm^2 of effective surface area of RO membrane with nominal dimensions of 19.1 cm × 14.0 cm. The feed solution for these cells was contained in a 100-L stainless steel cylindrical tank, and was mechanically stirred by a mixer. The temperature of the feed solution was held constant (25°C) during the experiment using a circulating water bath (RTE-111, Neslab). The solution was pumped out

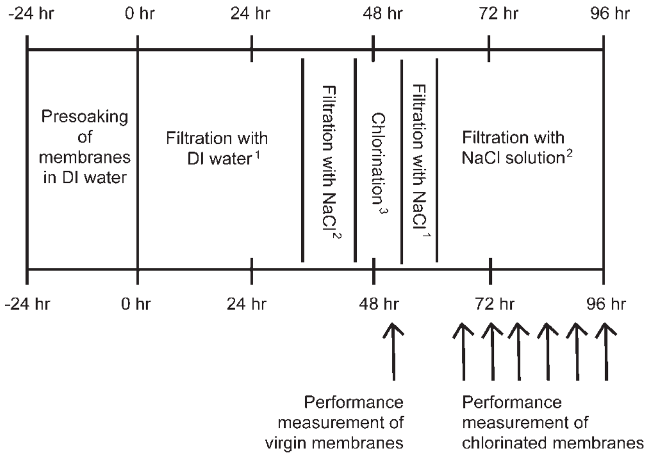

Figure 2 Protocol for the performance measurements. [1]Operating conditions: pressure = ~ 220 ± 10 psi, temperature = 25 ± 1°C, flow rate = 1 ± 0.2 LPM; [2]Operating conditions (specifically at the point of performance measurement): pressure = 225 ± 1 psi, temperature = 25 ± 1°C, flow rate = 1 ± 0.02 LPM, salt = 2000 ppm NaCl solution; [3]Chlorination conditions: chlorine concentration = 100, 500, 1000, and 2000 ppm, exposure time = 1 h, pH = 4 and 9.

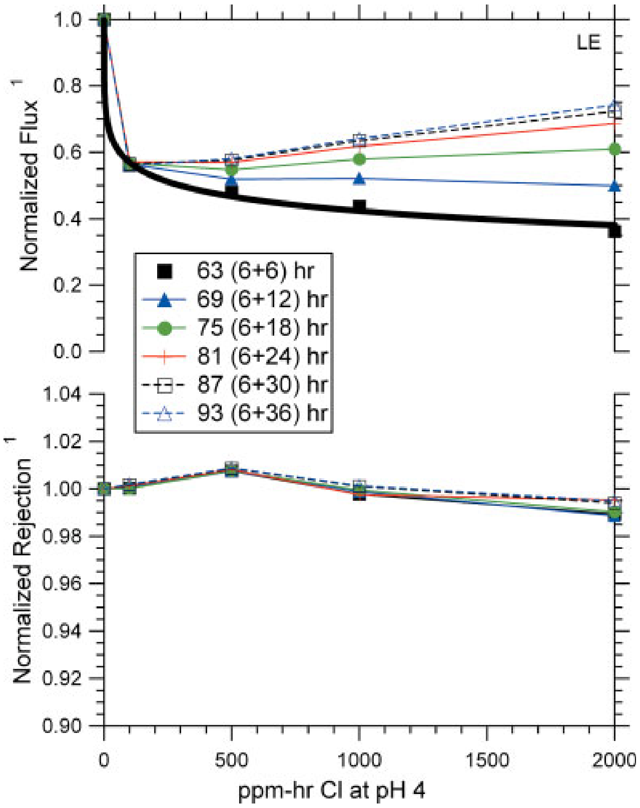

Figure 3 Normalized flux[1] and rejection[1] of LE membranes degraded at 100, 500, 1000, and 2000 ppm h Cl and pH 4. The performances were measured at 63, 69, 75, 81, 87, and 93 h total filtration time (6, 12, 18, 24, 30, and 36 h filtration with 2000 ppm NaCl solution following 6 h DI water filtration after chlorination). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of the reservoir and pressurized by a Hydracell pump (Wanner Engineering), capable of delivering 11.3 L/min (LPM) at a maximum pressure of 1000 psi. Through careful adjustment of the valves and a back pressure regulator on a by-pass line, the crossflow velocity and feed pressure were finely controlled.

Protocols for the performance measurements

The filtration test protocol is divided into six steps: presoaking, compaction, conditioning, chlorination, compaction, and conditioning.

The protocol developed for performance measurements of chlorinated membranes is summarized in Figure 2. The membranes were first presoaked in deionized water for 24 h. The membranes were then compacted near 220 psi until the permeate flux stabilized. Concentrated NaCl solution was added to the feed tank to maintain a 2000 ppm concentration. The feed solution was then fed to the RO test cells from the feed tank to condition the membranes at the same operating condition as the compaction stage. After compacting and conditioning the virgin membranes, the performance of the membranes was characterized in terms of permeate flux and salt rejection. Permeate flux was measured volumetrically (100 mL vol. flasks and stopwatch), and salt rejection was determined by measurement of feed and permeate conductivity (Ultrameter 4P, Myron L Company). After performance measurements, the membranes were taken out of the test cells, and thoroughly rinsed with DI water. The membranes were then exposed to 100, 500, 1000, and 2000 ppm chlorine solutions for 1 h at pH 4 and pH 9. The total exposure of polyamide membrane samples to chlorine was expressed as parts per million hours. The chlorine exposure was performed in Pyrex glass bottles covered with polytetrafluoroethylene caps, and the contents were mixed on a shaker. The chlorinated membranes were thoroughly rinsed with DI water and re-loaded in the GE Osmonics© test cells. The membranes were compacted again near 220 psi, and conditioned with 2000 ppm NaCl. Samples used to determine the permeate flux and salt rejection of the chlorinated membranes were taken at various time

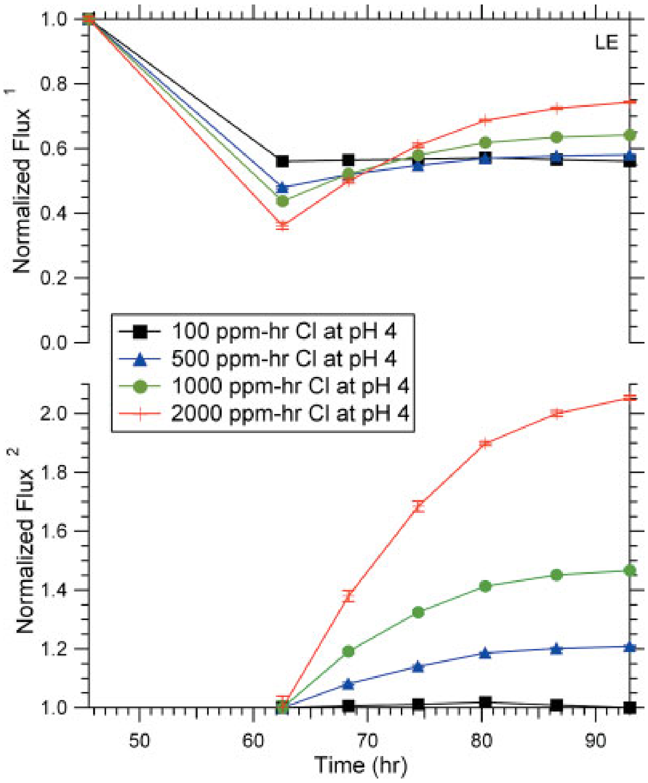

Figure 4 Normalized flux[2] of LE membranes degraded at 100, 500, 1000, and 2000 ppm h Cl and pH 4. The performances were measured at 63, 69, 75, 81, 87, and 93 h total filtration time (6, 12, 18, 24, 30, and 36 h filtration with 2000 ppm NaCl solution following 6 h DI water filtration after chlorination). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

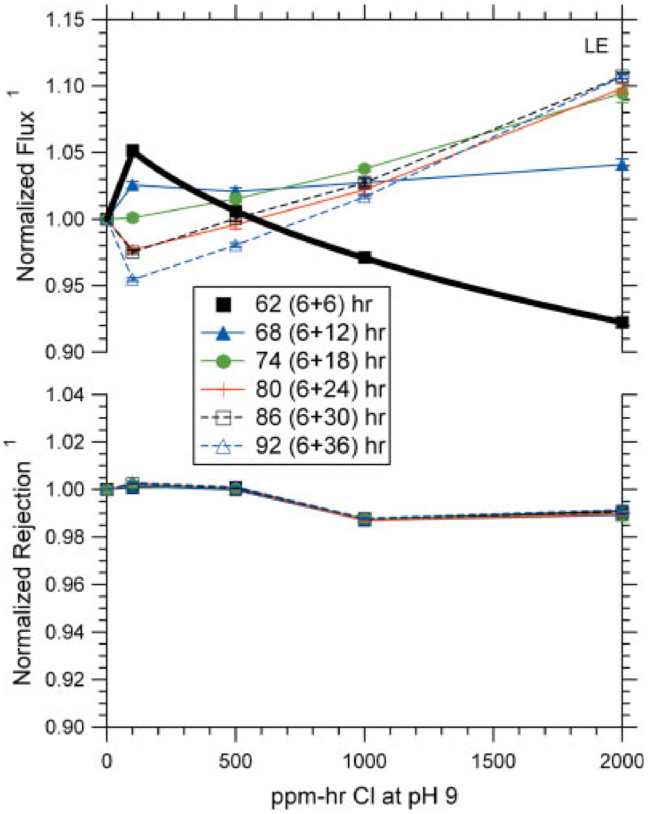

Figure 5 Normalized flux^1 and rejection^1 of LE membranes degraded at 100, 500, 1000, and 2000 ppm h Cl and pH 9. The performances were measured at 62, 68, 74, 80, 86, and 92 h total filtration time (6, 12, 18, 24, 30, and 36 h filtration with 2000 ppm NaCl solution following 6 h DI water filtration after chlorination). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

intervals. Whenever performance was measured, the operating conditions were finely readjusted to the desired values (225 psi and 1 L/min). Three measurements of flux and six measurements of rejection were averaged for each representative data point for performance measurements.

RESULTS AND DISCUSSION

Experimental observations of chlorine substitution (and resultant loss of H-bonding) with changes in performance (flux) of the membranes are presented along with a conceptual model proposed based on the systematic changes in crosslinked polymer flexibility and rotational freedom consistent with changes in hydrogen bonding. The following discussion is predicated on our understanding of the chemical changes in the polymer system correlated with the attendant systematic flux changes observed in Figures 3–8. The conceptual model is summarized in Figures 9–11.

Figure 3 shows the normalized flux and salt rejection of LE membranes, which were chlorinated under conditions of 100, 500, 1000, and 2000 ppm h chlorine and pH 4. Normalized flux^1 (or rejection^1) was defined as the flux (or rejection) of chlorinated membranes divided by the flux (or rejection) of their virgin membranes under comparable conditions. The normalized flux^1 showed an initial flux change (flux decrease at an early stage of filtration time (12 h filtration after chlorination)), and then following systematic flux change with increasing filtration time. In this work, the first measurement of performance after chlorination was designated as the initial flux, which was measured at 63 h total filtration time (equivalent to 6 h DI water filtration followed by 6 h filtration with 2000 ppm NaCl solution after chlorination. Refer Fig. 2).

Flux drop of 44, 52, 56, and 64% occurred at 100, 500, 1000, and 2000 ppm h chlorinated membranes at the initial flux measurements. On the other hand, the change of rejection due to chlorination was almost

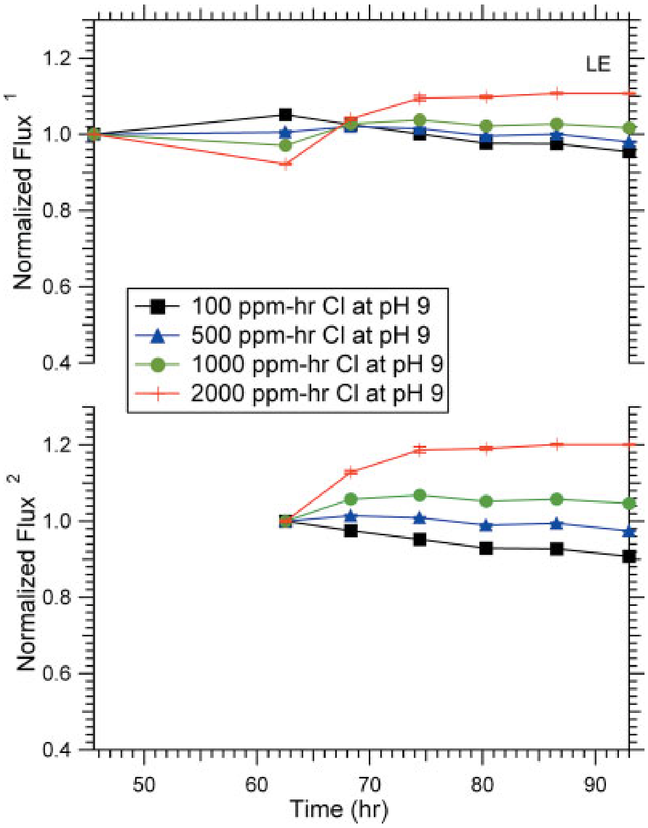

Figure 6 Normalized flux^2 of LE membranes degraded at 100, 500, 1000, and 2000 ppm h Cl and pH 9. The performances were measured at 62, 68, 74, 80, 86, and 92 h total filtration time (6, 12, 18, 24, 30, and 36 h filtration with 2000 ppm NaCl solution following 6 h DI water filtration after chlorination). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

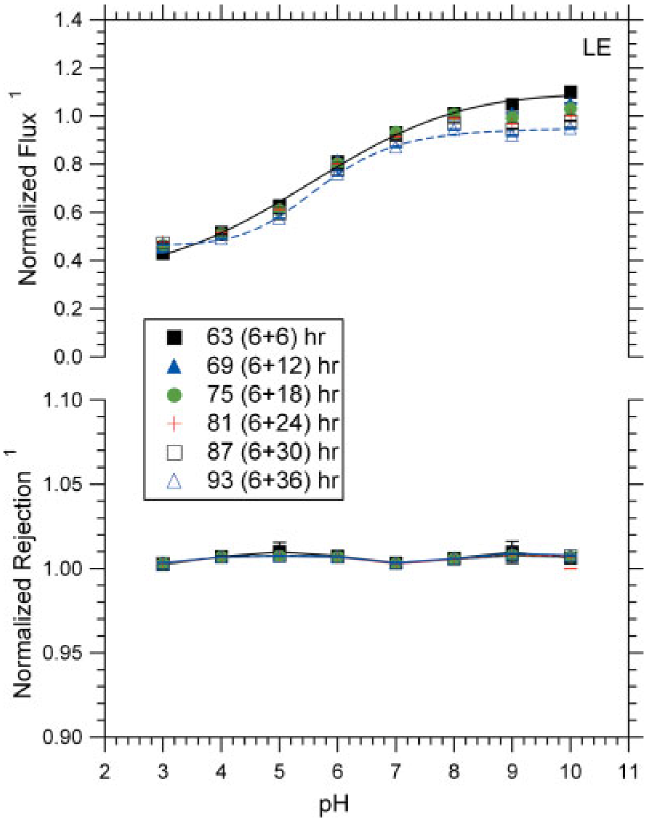

Figure 7 Normalized flux[1] and rejection[1] of LE membranes degraded at 100 ppm h Cl and pH 3, 4, 5, 6, 7, 8, 9, and 10. The performances were measured at 63, 69, 75, 81, 87, and 93 h total filtration time (6, 12, 18, 24, 30, and 36 h filtration with 2000 ppm NaCl solution following 6 h DI water filtration after chlorination). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

negligible. As shown in our previous studies,[7,8] the number of chlorines incorporated in the membrane increased and hydrogen bonding in the membranes were weakened and broken with increasing hypochlorite concentration and decreasing pH. The loss of most hydrogen bonds at low pH provided a large increase in rotational freedom and flexibility of the polymer chains due to (i) the loss of H-bonds holding a polymer chain to another chain and (ii) a lowered rotational energy barrier of the chlorinated amide bond.[8] By application of high pressure (225 psi) during the filtration test, the polymer chains having a large degree of rotational freedom and flexibility could be collapsed or compacted. The collapse or compaction of the polymer chains would block the passage of water molecules through the polymeric membrane, resulting in a decline of initial flux after chlorination at pH 4.

To investigate the flux change with filtration time, the normalized flux[1] was normalized again based on the first normalized flux measurement (63 h total filtration time in Fig. 4), and the twice normalized flux was designated as normalized flux[2]. More highly chlorinated membranes showed more flux increase with filtration time than slightly chlorinated membranes. This might also be due to the increased rotational movement and flexibility of chlorinated polymer chains. Highly chlorinated membranes could be rapidly collapsed by the initial pressure, but may also easily find more stable position for the polymer chains by means of easy rotational movement and increased flexibility.

Figures 5 and 6 show the permeate flux data for the LE membrane chlorinated at pH 9, expressed as a function of the degree of chlorine exposure and the total filtration time, respectively. The initial flux increased at low chlorine concentration and then decreased with increasing concentration of chlorine. The flux of slightly chlorinated membranes at pH 9 monotonically decreased, and the flux of highly chlorinated membranes systematically increased, and then stabilized with filtration time. The change of

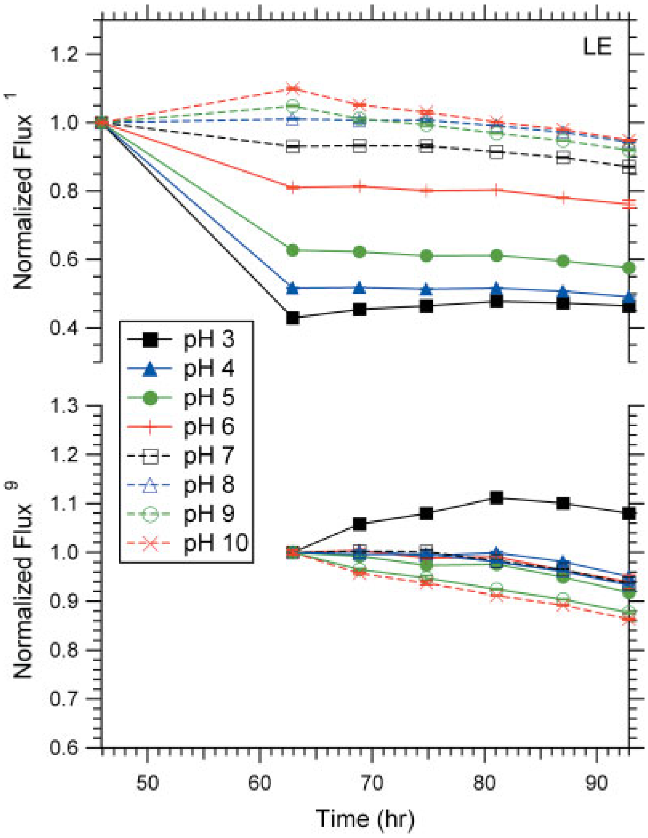

Figure 8 Normalized flux[2] of LE membranes degraded at 100 ppm h Cl and pH 3, 4, 5, 6, 7, 8, 9, and 10. The performances were measured at 63, 69, 75, 81, 87, and 93 h total filtration time (6, 12, 18, 24, 30, and 36 h filtration with 2000 ppm NaCl solution following 6 h DI water filtration after chlorination). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

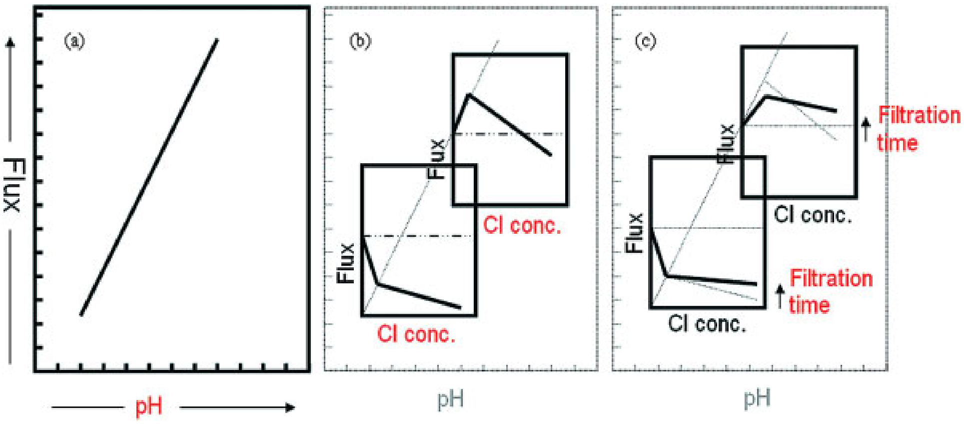

Figure 9 Steps for the performance change due to chlorination: (a) pH of the soaking bath containing chlorine determines the initial flux; (b) the flux decreases with increasing concentration of chlorine; (c) the flux changes with filtration time (low concentration of chlorine at higher pH causes the decrease of flux, and high concentration of chlorine at lower pH causes the increase of flux with filtration time). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

rejection due to chlorination was not significant when compared with the change of flux like at pH 4. As shown in our previous XPS and FTIR works,[7,8] chlorination at high pH broke small amounts of hydrogen bonds within intact polymer structure. The increased rotational flexibility of the chains without a change of polymer structure might release the restriction of water passage through the polymeric frame. This could explain the increase of initial flux for slightly chlorinated membranes (100 ppm h). Initial flux decline with increasing chlorine exposure is likely due to the local compaction of the polymer chains resulting from more chlorine bound to the membrane. The flux change with filtration time was determined by the balance between distortion of the polymer chains and rearrangement of flexible polymer chains. The systematic flux decline with filtration time for slightly chlorinated membranes (100 ppm h) is ascribed to the mechanical distortion of polymer chains due to the local collapse of polymer structures neighboring the chlorinated amide bonds, and the systematic flux increase of highly chlorinated membranes (2000 ppm h) is attributed to the rearrangement of flexible polymer chains inducing systematic flux increase.

To ascertain whether the pH of the chlorinating soaking bath is the major parameter determining the initial flux of the chlorinated membranes, the performance test was done with LE membranes chlorinated with 100 ppm h chlorine at the pH 3, 4, 5, 6, 7, 8, 9, and 10. Figure 7 shows the effect of pH on the performance change caused by the chlorination of LE membranes with 100 ppm h chlorine. Increasing pH has the same effect of decreasing the concentration of chlorine due to the hypochlorous acid speciation and ζ potential of polyamide membranes. At higher pH, the dominant species is hypochlorite, OCl^-, and has a repulsive interaction with the more negatively charged polyamide membrane, where the repulsive interaction may prevent the OCl^- species from accessing the surface of the membrane. As discussed in our previous analytical works,[7,8] chlorination at high pH broke small amounts of hydrogen bonds within the intact polymer structure, which might release the restriction of water molecules through the membrane. Chlorination at low pH broke most hydrogen bonds and caused compaction or collapse of the polymer chains, blocking the passage of water molecules through the membrane. Despite the change of flux with pH, salt rejection did not noticeably change.

The flux of membranes degraded at pH 3 with 100 ppm h chlorine systematically increased with increasing filtration time. On the other hand, the flux of the membranes chlorinated at more than pH 4 was gradually reduced (Fig. 7). At constant chlorine concentration (100 ppm h), the membranes were more highly chlorinated at low pH, resulting in a large increase in rotational freedom and flexibility among the polymer chains. The rearrangement of the flexible polymer chains due to the continuous passage of water molecules caused a systematic increase in flux with filtration time for highly chlorinated membranes (the membranes treated at low pH). On the other hand, slightly chlorinated membranes (reacted at increased pH) broke fewer hydrogen bonds within the intact polymer structures. The mechanical distortion of the polymer chains due to the application of high pressure (225 psi) increased the restriction of water molecules through the membrane, and systematically decreased flux with increasing filtration time for slightly chlorinated membranes (membrane reacted at high pH). Data in Figure 7 show a crossover at about pH 4 for 100 ppm h chlorinated LE membranes, where

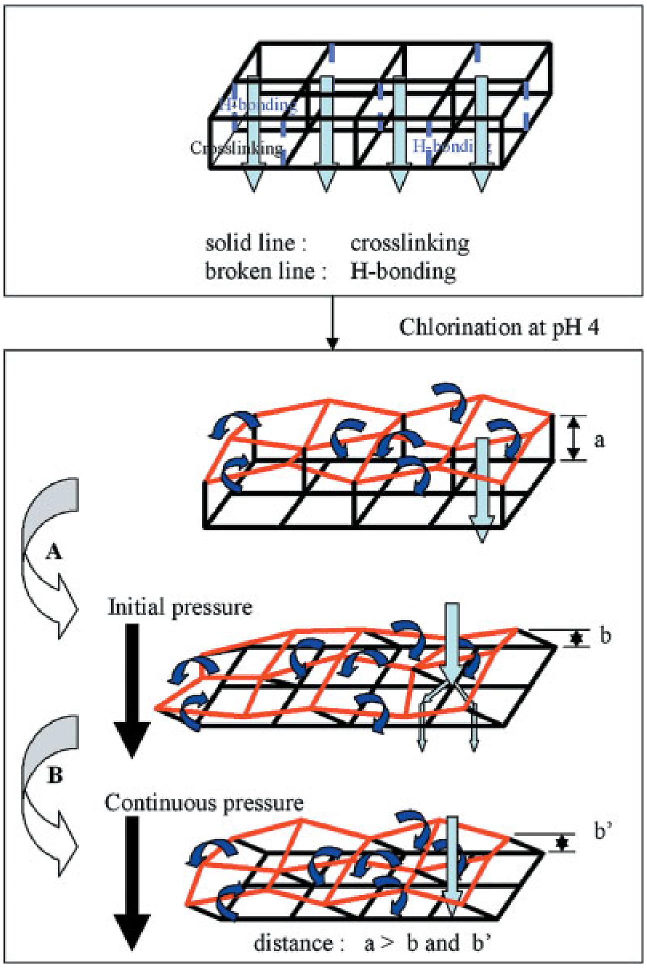

Figure 10 Mechanisms of performance change due to chlorination at pH 4. (A) Initial flux drop: Most of H-bonding among the polymer chains are broken due to chlorination, which results in the collapse or compaction of the polymer chains. The collapse and compaction blocks the passage of water molecules. (B) Flux increase of highly chlorinated membranes with filtration time: Rearrangement of flexible polymer chains induces systematic flux increase of highly chlorinated polyamide membranes. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the flux increase resulting from the rearrangement of flexible polymer chains is balanced by flux decrease resulting from the distortion of the polymer chains.

CONCLUSIONS

The performance studies revealed that chlorination of polyamide membranes showed initial flux changes, followed by systematic flux shift with filtration time. The initial flux change and flux change with filtration time depended on pH and concentration of chlorine in the soaking bath. The initial flux decreased for highly chlorinated membranes (equivalent to degradation at high concentration of chlorine and low pH), and increased for slightly chlorinated membranes (equivalent to degradation at low concentration of chlorine and high pH), and then flux changes with filtration time were determined by the balance between

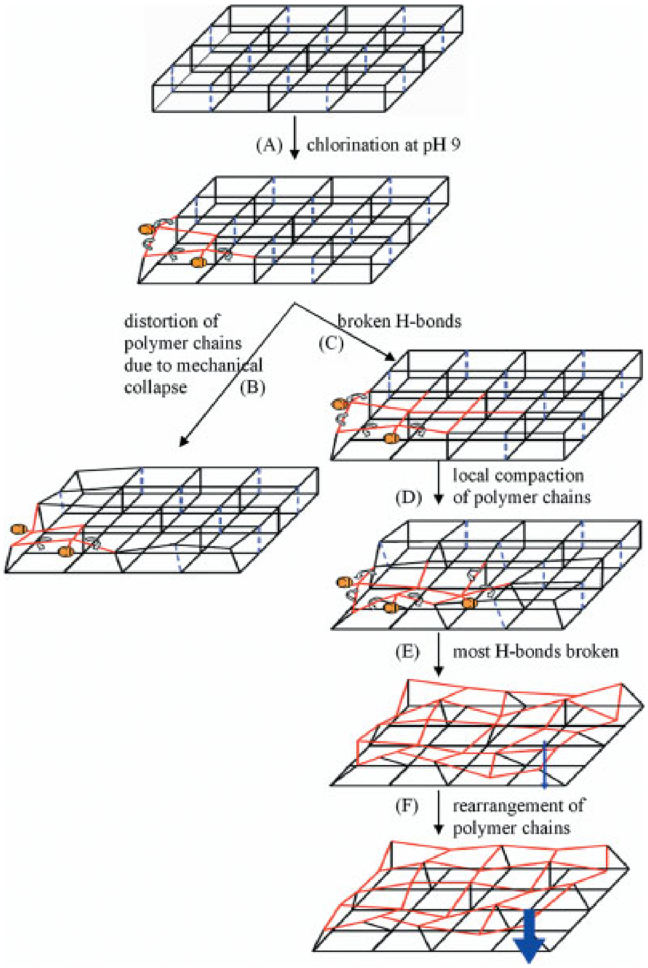

Figure 11 Mechanisms of performance change due to chlorination at pH 9. (A) Initial flux increase at low concentration of chlorine: Chlorination at high pH breaks small amounts of hydrogen bonds with intact polymer frames. The increased rotational flexibility of the chains without change of polymer structure might release the restriction of water passage through the polymeric membrane. (B) Flux decrease of slightly chlorinated membranes with filtration time: Mechanical distortion of polymer chains due to the local collapse of polymer structures neighboring the chlorinated amide bond by continuous application of high pressure (225 psi) increased the restriction of water molecules through the membrane. (C and D) Flux decreases with the increasing concentration of chlorine at initial flux measurement: More chlorine bound to the membrane due to the exposure to high concentration of chlorine causes local compaction of the polymer chains. (E) Most flux drop at most highly chlorinated membranes. (F) Systematic flux increase of highly chlorinated membranes: Rearrangement of flexible polymer chains induces systematic flux increase of highly chlorinated polyamide membranes. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

rearrangement of flexible polymer chains and distortion of the polymer chains. These flux changes caused by chlorination were attributed to the change of increased rotational freedom or the flexibility of polymer chains due to the change in hydrogen bonding behavior caused by chlorine attack. On the basis of these results, the sequence of steps of performance change by chlorination as well as the chlorination mechanisms involved are depicted and summarized in Figures 9–11.

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