Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.912161

54 (2015) 923–928
April

Taylor & Francis
Taylor & Francis Group

Changes in characteristics of polyamide reverse osmosis membrane due to chlorine attack

Minseok Kim, Minjae Kim, Beomseok Park, Suhan Kim*

Department of Civil Engineering, Pukyong National University, 365 Sinseonro, Nam-gu, Busan 608-739, Republic of Korea, Tel. +82 51 629 7721; Fax: +82 51 629 6063; email: suhankim@pknu.ac.kr

Received 15 January 2014; Accepted 18 March 2014

ABSTRACT

In reverse osmosis (RO) process, chlorine is used in a pretreatment process to inhibit biofouling, however, its residual should be eliminated by using sodium bisulfite (SBS) before the RO process because polyamide (PA) RO membrane is damaged by free chlorine contact. In a field application, there always exists a risk that SBS injection pump is out of order so that PA membrane may be damaged by the residual chlorine. The objective of this work is to quantitatively investigate the effect of residual chlorine attack on the water flux and salt rejection of PA membrane. Lab-scale RO tests were performed to see changes in water flux and salt rejection by adding sodium hypochlorite and SBS. With a small concentration of residual chlorine and pH of 6–7, chlorination of aromatic rings in PA membrane induced a sharp flux decline at the beginning of the chlorination followed by a gradual decline. The additional exposure of chlorinated PA membrane to a high concentration (300 ppm) of residual chlorine induces the increase of flux and decrease of salt rejection. Dechlorination makes it possible to recover the declined flux although the complete recovery of flux is not possible.

Keywords: Reverse osmosis process; Chlorine; Polyamide; Chlorination of aromatic rings; Dechlorination

1. Introduction

Reverse osmosis (RO) process occupies the largest portion of desalination methods in the world these days. It is well known that membrane fouling is always a concern when RO process is applied. So far, the adequate pretreatment and membrane cleaning are common solutions for the fouling problem [1–5]. Disinfectant should be added to the pretreatment for RO process in order to prevent microbial growth in pipelines and on RO membrane surface.

Chlorination is a conventional disinfection method used widely for water treatment and desalination [6]. However, polyamide (PA) that is the most preferred material for RO membrane is degraded by chlorination. The impacts of residual chlorine contact (i.e. chlorination) with PA membrane surface have been reported in the literature [7–17], where it is concluded that chlorine causes irreversible damage to PA

---

*Corresponding author.

Presented at the 6th International Conference on the "Challenges in Environmental Science and Engineering (CESE-2013)", 29 October–2 November 2013, Daegu, Korea

membranes. So-called "chlorine attack on PA membranes" means the chlorination of the aromatic ring in PA membrane [11,16,17], which can occur by two possible ways: (1) direct aromatic substitution [16], and (2) initial chlorination of the amide nitrogen followed by an attack on the aromatic ring [7,16,17] as shown in Fig. 1. The initial chlorination of the amide nitrogen (i.e. N-chlorination through chlorine attack on the amide nitrogen) is reversible chemical reaction and an attack on the aromatic ring (i.e. ring chlorination through intermolecular rearrangement) is irreversible one [7,17].

The effect of PA membrane degradation by chlorination on water flux is known to be pH dependent. At a low pH such as 4, water flux through PA membrane drops in a huge amount (up to 50%) after the contact with residual chlorine while it increases a little (up to 12%) after the contact at a high pH such as 9 [14]. Regardless of pH, salt rejection decreases over time after chlorination of PA membrane [14].

Dechlorination is needed to prevent the PA membrane damage caused by residual chlorine. Sodium bisulfite (SBS; $NaHSO_3$) is often used to remove residual chlorine by the chemical equation as follows:

$$NaHSO_3 + 2HOCl \rightarrow H_2SO_4 + 2HCl + Na_2SO_4 \quad (1)$$

where HOCl, H_2SO_4, HCl, and Na_2SO_4 are hypochlorous acid as residual chlorine, sulfuric acid, hydrochloric acid, and sodium sulfate, respectively. SBS forms from dissolved sodium metabisulfite ($Na_2S_2O_5$). In field applications, there always exists a risk that SBS injection pumps are out of order so that polyamide RO membrane may be damaged by the residual chlorine. The objective of this work is to quantitatively investigate the effect of residual chlorine attack on polyamide RO membrane. In order to simulate a situation that SBS injection pumps are not working unexpectedly in RO plant, the concentration of residual chlorine is 3 mg/l as Cl_2, because the residual chlorine is several mg/l (e.g. 0.5–1.5 mg/l or higher) just before dechlorination by SBS in a typical RO plant [18], while previous researches used several thousand mg/l as Cl_2 [9,14]. This study focuses on: (1) the effect of chlorine attack on PA membrane on water flux and salt rejection in RO plant; and (2) the effect of SBS dechlorination on water flux and salt rejection after the chlorine attack.

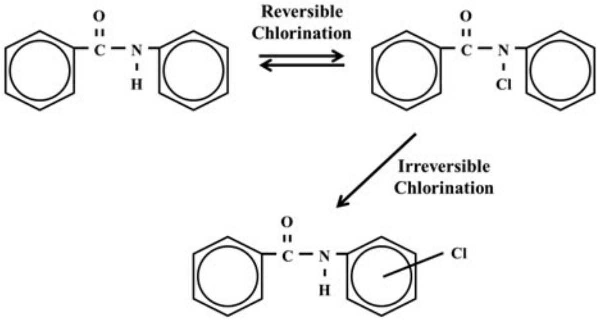

Fig. 1. Mechanism of the chlorination of aromatic ring in PA membrane.

2. Methods

2.1. Membrane and reagents

The RO membrane used in this study was provided by Woongjin Chemical, Korea. Feed water solutions are prepared using pure grade sodium chloride (NaCl) with the concentration of 35 g/l in deionized water. Residual chlorine is made by adding sodium hypochlorite (NaOCl) to the solution. Hypochlorous acid (HOCl) as residual chlorine is formed by the following chemical reaction:

$$NaOCl + H_2O \rightarrow HOCl + NaOH \quad (2)$$

where H_2O and NaOH are water and sodium hydroxide, respectively. SBS was used as an agent for dechlorination.

2.2. Lab-scale RO test and analyses

Lab-scale RO tests are performed using a cross-flow RO system described in Fig. 2. Feed water enters into the feed channel in the RO cell and are separated into permeate (through RO membrane) and concentrate (out of the feed channel). Then, both permeate and concentrate out of the RO cell return to the feed tank to maintain the feed salinity at a constant value. The feed channel dimensions in the RO cell are 11 cm in length, 6 cm in width, and 1 mm in height. Membrane surface and cross-sectional flow areas are then $6.6 \times 10^{-3}\,m^2$ and, $6.0 \times 10^{-5}\,m^2$, respectively. A recirculating chiller is used to maintain a constant temperature in the feed tank.

At the start of each RO test, deionized water is filtered through RO membrane for 16–24 h at constant pressure and temperature of 50 bars and 20℃, respectively, to allow for membrane compaction and other unknown causes of flux decline inherent to lab-scale recirculation systems. After stable flux was achieved, pure water permeability (A) is determined by measuring flux over a range of applied pressures

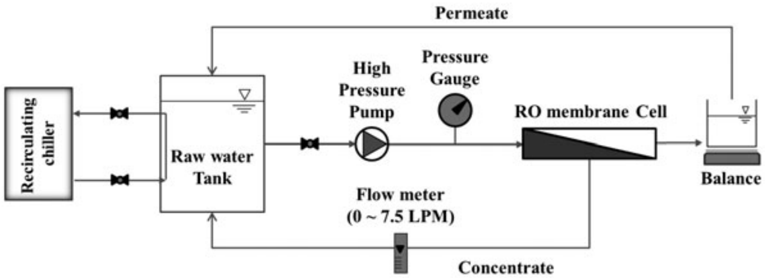

Fig. 2. Lab-scale RO test system.

(e.g. 10–50 bars). Water flux (J_w, m/s) is measured by weighing the permeate for one minute using a balance. The relationship governing the pure water flux is:

$$J_w = A\Delta p \quad (3)$$

where A (m/s Pa) is determined from a linear regression of the measured pure water flux and applied pressure data (Δp, Pa).

After water permeability of RO membrane is determined, the deionized water in the feed tank is replaced by the salt solution prepared with sodium chloride of 35 g/l. The applied pressure and cross-flow velocity are set at 50 bars and 0.42 m/s, respectively. During the experiment, pH of feed water is unadjusted by adding acid or base and temperature is maintained at 20°C. The salt rejection (r) of RO membrane is determined by

$$r = 1 - c_p/c_f \quad (4)$$

where c_p and c_f are permeate and feed conductivity (μS/cm) measured using YSI63 (YSI, USA). The RO system is allowed to equilibrate up to several hours to ensure the stable salt rejection.

After the equilibrium is reached, sodium hypochlorite is spiked with a desired concentration of residual chlorine (e.g. 3 mg/l as Cl_2). After the injection, water flux, salt rejection, and residual chlorine concentration, and pH in feed water are monitored in every 30 min periodically. The residual chlorine concentration and pH in feed water is measured using DR3900 (Hach, Germany) and YSI63, respectively. SBS is added with a required concentration to remove residual chlorine in the RO system (3 mg of sodium metabisulfite is normally used to remove 1 mg/l of residual chlorine [18]) when it is necessary.

At the end of each experiment, the RO system is cleaned by deionized water and the pure water permeability of the used RO membrane is determined using Eq. (2). Then, it was removed from the system and the scanning electron microscope (SEM) image of the used RO membrane was taken using S2700 (Hitach, Japan) at an accelerating voltage of 10 kV. In order to get a reliable experimental result, the RO test was repeated with the same chlorination condition.

3. Results and discussion

3.1. Residual chlorine contact with RO membrane at a low concentration

Fig. 3 shows the effect of chlorination and dechlorination on water flux and salt rejection at a low concentration of 3 mg/l as Cl_2, which is called Test 1. After the residual chlorine was spiked in the RO feed tank, water flux dropped suddenly (decreased by 13.9% in only 10 min of residual chlorine attack on the RO membrane). Even in the very short concentration-time (CT) of 0.5 ppm h (equivalent to 10 min with 3 mg/l

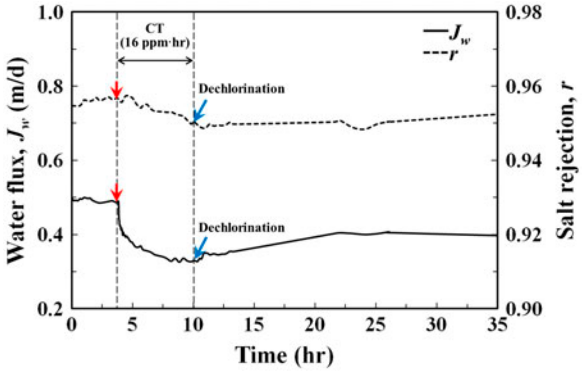

Fig. 3. Effect of chlorination and dechlorination on water flux and salt rejection (Test 1). Residual chlorine of 3 mg/l is spiked after the equilibrium of the RO system (the arrow indicates the time when the residual chlorine is added), and SBS is added for dechlorination after the CT value of 16 ppm h.

as Cl_2), the permeability of PA membrane decreased by a considerable rate. Total 32.5% loss of the initial flux was observed in the CT value of 16 ppm h and salt rejection decreased by 0.6% during the same CT value. The change in salt rejection due to chlorination was not significant compared to that in water flux. During the chlorination, the pH and residual chlorine concentration in feed are 6.15–6.50 and 1.6–3.5 mg/l as Cl_2, respectively.

When residual chlorine contacts with PA membrane, the replacement of hydrogen with chlorine on the amide group (N–H) of the membrane caused the loss of most of the hydrogen bonding sites (Fig. 1). According to literatures [9,14], the breakage of most hydrogen bonds supporting the structure of the polyamide layer could provide a large increase of rotational freedom and flexibility of the polymer chains. By the high pressure (50 bars) during the experiment, the polymer chains having large rotational freedom and flexibility could collapse or compact [14], which could block the passage of water molecules through the polymeric membrane, resulting in the decline of flux after chlorination.

After the CT value of 16 ppm h, SBS of 9 mg/l was added to remove residual chlorine. Although the flux and salt rejection were not recovered to their initial values, both water flux and salt rejection increased by 23.3 and 0.2% in maximum since the time when the residual chlorine was removed by SBS. This might be caused by the replacement of chlorine with hydrogen back on the functional group (N–Cl) of the membrane which is a reversible reaction as shown in Fig. 1 [7,17].

Fig. 4 shows the effect of chlorination and dechlorination on water flux and salt rejection when residual chlorine of 3 mg/l was added to the RO tank three times, which is called Test 2. During the chlorination, the pH and residual chlorine concentration in feed are 6.57–7.30 and 1.5–9.3 mg/l as Cl_2, respectively. After the first injection of the residual chlorine, water flux dropped suddenly (decreased by 9.6% in only 10 min of residual chlorine attack on the RO membrane). However, no significant flux decline was observed at the second and third injections of the residual chlorine, which means additional injections for chlorination does not impact on the flux and salt rejection significantly. During the total CT value of 118 ppm h, the total loss of the initial flux was 41.6% and total 26.7% loss of the initial flux was observed at the CT value of 14.5 ppm h. This flux decline (26.7%) at the CT value of 14.5 ppm h is smaller than that (32.5%) at the CT value of 16 ppm h in Test 1, which is because pH of Test 2 is in a higher range (6.57–7.30) than that of Test 1 (6.15–6.50). As reported in a literature [14], the chlorination of aromatic ring in PA membrane occurs more significantly at lower pH.

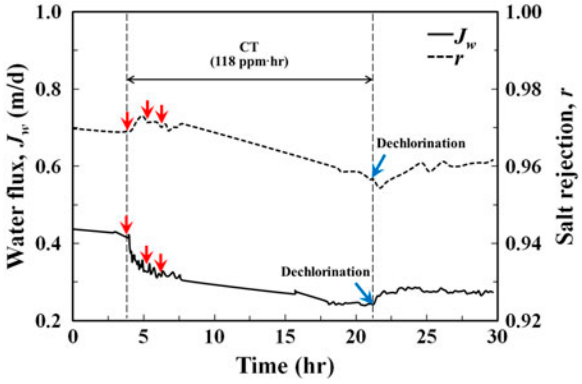

Fig. 4. Effect of chlorination and dechlorination on water flux and salt rejection (Test 2). Residual chlorine of 3 mg/l is spiked three times after the equilibrium of the RO system (each arrow indicates the time when residual chlorine is added each time), and SBS is added for dechlorination after the CT value of 118 ppm h.

In Test 2, salt rejection decreased by 1.2% in the CT value of 118 ppm h. As in the case of Test 1, the change in salt rejection was not significant compared to the change in water flux. After the CT value of 118 ppm h, SBS of 27 mg/l was added to remove residual chlorine. Both water flux and salt rejection increased by 18.2 and 0.5% in maximum since the time when the residual chlorine was removed by SBS. This recovery of water flux (18.2%) is smaller than that (23.3%) in Test 1, because a considerable part of the reversible chlorination of aromatic rings might move to the irreversible one (Fig. 1) due to longer CT value in Test 2.

3.2. *Residual chlorine contact with RO membrane at a high concentration*

Fig. 5 shows the effect of chlorination and dechlorination on water flux and salt rejection when residual chlorine of 3 mg/l is spiked after the equilibrium of the RO system and residual chlorine of 300 mg/l is spiked after CT value of 13 ppm h, which is called Test 3. During the first chlorination (the CT value of 13 ppm h), the pH and residual chlorine concentration in feed are 6.10–6.15 and 2.4–3.0 mg/l as Cl_2, respectively. After the first injection of the residual chlorine, water flux dropped suddenly (decreased by 21.8% in only 10 min of residual chlorine attack on the RO membrane). This is the largest flux decline in an early stage of chlorination (10 min from the addition of residual chlorine) for all the tests in this study. This may be caused by the lowest pH range in Test 3 (As reported in literatures [6,7,9,14,17], the effect of chlorination on PA membrane increases at lower pH.) or

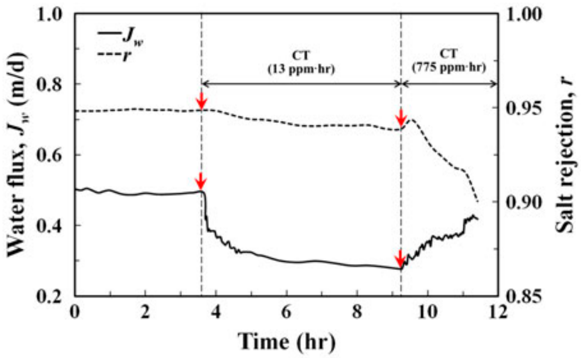

Fig. 5. Effect of chlorination with a high concentration of residual chlorine on water flux and salt rejection (Test 3). Residual chlorine of 3 mg/l is spiked after the equilibrium of the RO system and that of 300 mg/l is spiked after CT value of 13 ppm h (each arrow indicates the time when the residual chlorine is added each time).

the non-homogeneity of RO membrane coupons tested in this work. The total CT value of 13 ppm h for the first chlorination, the total loss of the initial flux was 43.7%, and the change in salt rejection was not significant (decreased by 1.1%) compared to that in water flux.

After the first chlorination, residual chlorine of 300 mg/l was spiked, which is called the second chlorination. The feed pH is 11.39–11.62 due to sodium hydroxide formed from the chemical equation (Eq. (2)). On the contrary to Test 1, Test 2, and the first chlorination in Test 3, flux increased and salt rejection decreased sharply. This might be because collapsed or compacted polymer chains are re-arranged by recovered hydrogen bond at a high pH and the re-arranged structure is loose compared to that of the virgin membrane. But this hypothesis should be verified carefully with a further study. Fig. 6 shows the SEM images under the magnification of 1,000 times of virgin and chlorinated PA membrane after the end of Test 3. The darker parts in the image of chlorinated PA membrane (Fig. 6(b)) which is not observed in that of the virgin membrane (Fig. 6(a)) may be the damaged parts.

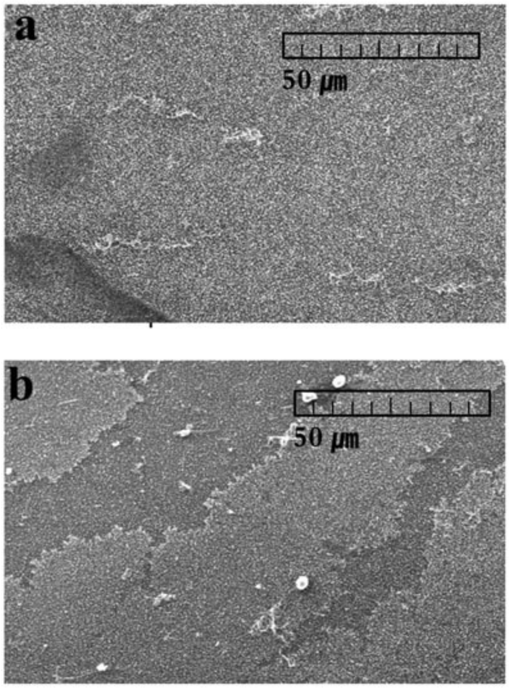

Fig. 6. The SEM images under the magnification of 1,000 times of (a) virgin and (b) chlorinated PA membranes.

4. Conclusions

This study focuses on the effects of chlorination and dechlorination on PA membrane. It is already known that the chlorination of PA membrane is a pH dependent chemical reaction and causes a considerable decline at lower pH and a small increase in flux at higher pH, respectively. The new findings in this work are as follows:

(1) Even in a small CT value like 0.5 ppm h, chlorination of aromatic rings in PA membrane occurs and induces a sharp flux decline at the beginning of the chlorination followed by a gradual decline. The chlorination of PA might cause collapsed or compacted polymer chains, which results in the flux decline as suggested by literatures.
(2) The additional exposure of chlorinated PA membrane to a high concentration (300 ppm in this study) of residual chlorine induces the increase of flux and decrease of salt rejection possibly due to loosening the polymer chains.
(3) Dechlorination makes it possible to recover the declined flux because chlorine may be replaced by hydrogen back in the functional group (N–Cl) of the chlorinated membrane.

Acknowledgments

This research was supported by Basic Science Research Program through the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology (Grant No. 2011-0014006) and the project titled "Development of key technology in seawater desalination using gas hydrate process" funded by Ministry of Oceans and Fishery, Korea.

References

[1] D. Cha, H. Park, S. Kim, J.-L. Lim, S. Kang, C.-H. Kim, A statistical approach to analyze factors affecting silt density index, Desalin. Water Treat. 45 (2012) 276–283.

[2] Y.-H. Hwang, C.-M. Moon, Y.-T. Ahn, S. Kim, J.-L. Lim, H.-S. Shin, Selection of pretreatment process and reverse osmosis membrane for a wastewater reclamation system for the industrial water use, Desalin. Water Treat. 51 (2013) 5466–5474.

[3] S. Kim, I.S. Lee, K.J. Kim, D.M. Shon, L.S. Kang, Dual media filtration and ultrafiltration as pretreatment options of low-turbidity seawater reverse osmosis processes, Desalin. Water Treat. 33 (2011) 329–336.

[4] S. Kim, Osmotic pressure-driven backwash in a pilot-scale reverse osmosis plant, Desalin. Water Treat. 52 (2014) 580–588.

[5] J.-L. Lim, N.-S. Park, S. Kang, C.-H. Kim, S. Lee, S. Kim, Iron and manganese fouling in microfiltration as a pretreatment of seawater reverse osmosis processes, Desalin. Water Treat. 33 (2011) 323–328.

[6] M.J. Cran, S.W. Bigger, S.R. Gray, Degradation of polyamide reverse osmosis membranes in the presence of chloramine, Desalination 283 (2011) 58–63.

[7] N.P. Soice, A.C. Maladono, D.Y. Takigawa, A.D. Norman, W.B. Krantz, A.R. Greenberg, Oxidative degradation of polyamide reverse osmosis membranes: Studies of molecular model compounds and selected membranes, J. Appl. Polym. Sci. 90 (2003) 1173–1184.

[8] M.K. da Silva, I.C. Tessaro, K. Wada, Investigation of oxidative degradation of polyamide reverse osmosis membranes by monochloramine solutions, J. Membr. Sci. 282 (2006) 375–382.

[9] Y.-N. Kwon, J.O. Leckie, Hypochlorite degradation of crosslinked polyamide membranes: I. Changes in chemical/morphological properties, J. Membr. Sci. 283 (2006) 21–26.

[10] S. Wu, J. Xing, G. Zheng, H. Lian, L. Shen, Chlorination and oxidation of aromatic polyamides. II. Chlorination of some aromatic polyamides, J. Appl. Polym. Sci. 61 (1996) 1305–1314.

[11] N.P. Soice, A.R. Greenberg, W.B. Krantz, A.D. Norman, Studies of oxidative degradation in polyamide RO membrane barrier layers using pendant drop mechanical analysis, J. Membr. Sci. 243 (2004) 345–355.

[12] C.J. Gabelich, J.C. Frankin, F.W. Gerringer, K.P. Ishida, I.H. Suffet, Enhanced oxidation of polyamide membranes using monochloramine and ferrous iron, J. Membr. Sci. 258 (2005) 64–70.

[13] I.C. Tessaro, J.B.A. da Silva, K. Wada, Investigation of some aspects related to the degradation of polyamide membranes: Aqueous chlorine oxidation catalyzed by aluminum and sodium laurel sulfate oxidation during cleaning, Desalination 181 (2005) 275–282.

[14] Y.-N. Kwon, J.O. Leckie, Hypochlorite degradation of crosslinked polyamide membranes: II. Changes in hydrogen bonding behavior and performance, J. Membr. Sci. 282 (2006) 456–464.

[15] G.-D. Kang, C.-J. Gao, W.-D. Chen, X.-M. Jie, Y.-M. Cao, Q. Yuan, Study on hypochlorite degradation of aromatic polyamide reverse osmosis membrane, J. Membr. Sci. 300 (2007) 165–171.

[16] J. Glater, S.-K. Hong, M. Elimelech, The search for a chlorine-resistant reverse osmosis membrane, Desalination 95 (1994) 325–345.

[17] T. Kawaguchi, H. Tamura, Chlorine-resistant membrane for reverse osmosis. I. Correlation between chemical structures and chlorine resistance of polyamides, J. Appl. Polym. Sci. 29 (1984) 3359–3367.

[18] Dow liquid separations, Filmtec reverse osmosis membranes technical manual, The Dow Chemical Company Form No. 609-00071-0705, 2005.