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Hypochlorite treatment of polyamide membrane for improved reverse osmosis performance

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Abstract. The pH-dependent inter-conversion of the three free chlorine species (Cl_2, HOCl, OCl-) present in the aqueous hypochlorite solution was theoretically investigated. Each species was found overwhelmingly present in a characteristic pH range. Hypochlorite treatment of the polyamide membrane was carried out over these pH ranges and various membrane responses were observed. As pH is less than 8, membrane tends to be N-chlorinated by Cl_2 and HOCl, and N-chlorinated membrane showed reduced water permeance and salt rejection. As pH rises to 10-12, OCl appears to be the dominating chlorine species. Membrane hydrolysis was found to well interpret the improved water permeance and salt rejection. When the pH is between 8-10, both N-chlorination and hydrolysis contribute to the response of the membrane, and the treated membrane showed improved salt rejection but reduced water permeation. Excessive hydrolysis occurred while the membrane was treated at pH 13 for the much stronger alkalinity.

Keywords: polyamide; hypochlorite treatment; reverse osmosis; salt rejection; water permeance; membrane chemistry; chlorinating species; hydrolysis; N-chlorination

1. Introduction

Reverse Osmosis (RO) is an important water treatment technology (Petersen (1993), Nath (2008)). To date, a daily capacity of providing 100 million tons of clean water has been made possible by RO plants. Like energy, water is also an important resource helping fuel growth of economy, which is making world's demand for clean water increase.

Over the past decades, RO industry experienced great advances in both the membrane manufacturing technique and membrane materials. The interfacial polymerization method had been invented for mass producing new generations of high flux RO membranes. And the aliphatic and aromatic polyamide (PA) had become the mainstream material for making RO membranes, which display advantages unmatched by the traditional materials such as cellulose acetate (CA). The high salt-rejection property (99%) of the PA membrane and its wide pH tolerance (Glater (1983, 1994), Silva *et al.* (2006)) greatly improved the energy-efficiency of desalination process and allowed a broader range of its application. This reliable and energy-efficient RO technology has well-established itself in treating various water from brackish and seawater to municipal and

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Better energy efficiency is always an objective pursued in the development of RO membranes. The basic strategy in this regard is to create more selective and more productive membranes. Since a more selective membrane needs a lower feed pressure to achieve the same level of water desalination, and a more productive membrane can generate more clean water with the same energy input. Various post-treatments (Nam *et al.* (2001), Gabelich *et al.* (2005), Shin *et al.* (2011), Tang *et al.* (2007, 2009a, 2009b), Elimelech *et al.* (1997)) have been found useful in improving these performances, some of which include: i) surface-coating: an external coating layer made of a cross-linked hydrophilic polymer (such as chitosan) can drastically reduce the membrane fouling in actual applications, and thus increasing the membrane productivity, ii) nosylation: a chemical process which is effective in decreasing the density of the terminal amine group in and particularly on the membrane, and thus contributing to the negative Zeta-potential of the membrane for bettered salt-rejection properties, and iii) hypochlorite treatment.

The weakness of the PA membrane lies in its lower chlorine tolerance. It has been reported that prolonged chlorine exposure can cause membrane degradation and even damage. The exposure limit is 1000 ppmh, over which the membrane is shown to fail (Tessaro *et al.* (2005), Ague *et al.* (2009), Shao *et al.* (2006)), and the failed membrane displays increased water flux and much-lowered salt rejection. It is also known that a proper selection of the membrane treatment condition can, however, simultaneously improve both the water permeance and salt rejection of the membrane.

Degradation of the polymeric materials is generally considered to be responsible for the changed membrane performance, and numerous chemical pathways have also been proposed to interpret the membrane degradation. However, the degradation chemistry of the treated membrane over different pH ranges is still an ambiguity. Attention was therefore paid to identifying the chemical changes of the treated membrane in a hope of reaching a better understanding on the different membrane responses observed in the treatment over different pH ranges.

As an important aspect of the investigation, the inter-conversion of the free chlorine species (Cl_2, HOCl, and OCl^-) in the hypochlorite solution was identified and modeled. A theoretical study on the pH-mediated inter-conversion shows that each species has a characteristic pH range, in which the presence of one species is exclusively favored. By treating the PA membrane over these characteristic pH ranges, differentiated membrane responses were observed. A right hypochlorite treatment condition (1% for achieving both improved selectivity and productivity of the PA membrane was thus obtained. A defect pore model was proposed to help interpret the various membrane responses observed in the treatment.

2. The inter-conversion of the three chlorine species in the aqueous hypochlorite solution

Suppose the nominal molar concentration of hypochlorite in its aqueous solution is [*a*]. The actual concentration of the salt is reduced to [*a*-*x*] due to the hydrolysis as shown in Eq. (1).

$$\underset{[a\text{-}x]}{\mathrm{OCl^- + H_2O}} \rightleftharpoons \underset{[x\text{-}y]}{\mathrm{HOCl + OH^-}} \qquad (1)$$

Again, because of the chemical equilibrium shown in Eq. (2), part of the resulting HOCl is spontaneously converted into Cl_2 [*y*] dissolved in the acidic solution. For the sake of convenience in correlating these important free chlorine species, the ionization equilibrium of HOCl is also presented as Eq. (3), which can be obtained from Eq. (1) by making use of the equation of water disassociation.

$$\underset{[10^{-pH}]}{\mathrm{HCl}} + \underset{[x\text{-}y]}{\mathrm{HOCl}} \rightleftharpoons \underset{[y]}{\mathrm{Cl_2}} + \mathrm{H_2O} \tag{2}$$

$$\underset{[x\text{-}y]}{\mathrm{HOCl}} \rightleftharpoons \underset{[10^{-pH}]}{\mathrm{H^+}} + \underset{[a\text{-}x]}{\mathrm{OCl^-}} \tag{3}$$

Eqs. (2) and (3) give: $K_1 = \dfrac{[OCl^-][H^+]}{[HOCl]}$, $K_2 = \dfrac{[HOCl][HCl]}{[Cl_2]}$

Inserting the molar concentration of each species into the above two equations yields

$$10^{-pK_1} = \frac{(a-x)\cdot 10^{-pH}}{(x-y)} \tag{4}$$

$$10^{-pK_2} = \frac{(x-y)\cdot 10^{-pH}}{y} \tag{5}$$

The obtained dimensionless x and y are given below

$$\left[\frac{x}{a}\right] = \frac{10^{-pH}}{10^{-pH} + 10^{-(pK_1+pK_2)}\big/(10^{-pK_2}+10^{-pH})} \tag{6}$$

$$\left[\frac{y}{a}\right] = \frac{10^{-pH}}{10^{-pK_2}+10^{-pH}} \cdot \frac{10^{-pH}}{10^{-pH} + 10^{-(pK_1+pK_2)}\big/(10^{-pK_2}+10^{-pH})} \tag{7}$$

Therefore, the fraction of the three chlorine species (Cl_2, HOCl, and OCl^-) in the hypochlorite solution can be determined by

$$X^{Cl_2} = \left[\frac{y}{a}\right] \tag{8}$$

$$X^{HOCl} = \left[\frac{x}{a}\right] - \left[\frac{y}{a}\right] \tag{9}$$

$$X^{ClO^-} = 1 - \left[\frac{x}{a}\right] \tag{10}$$

The equilibrium constants K_1 and K_2 can be estimated as follows

$$K_i = EXP\left(\frac{-\Delta G_i}{RT}\right) \tag{11}$$

where ΔG_i is the Gibbs free energy change of the Eq.(2) or Eq.(3). Eqs. (7) and (8) show that the fractions of the chlorine species in the solution are independent of the hypochlorite concentration; they are instead determined by the pH and temperature of the solution.

3. Experimental

3.1 Membrane and Chemicals

A received commercial thin-film-composite PA was used as the model membrane for conducting the hypochlorite treatment. The active PA thin film is synthesized upon a porous polysulfone support by interfacial polymerization based on 1, 3-phenylenediamine and 1, 3, 5-benezentricarbonyl chloride. Sodium hypochlorite was obtained from Aldrich, with a free chlorine content of 5.2 %. The concentration of hydrochloric acid used for pH adjustment was 37 %. All the other chemicals (such as NaCl and $NaHSO_3$) used for membrane processing and characterization were of purity no less than 99.0 %. All water used in the experiments was ultrapure, generated by a Milli-Q® water purification system.

3.2 Hypochlorite treatment of the PA membrane

The prepared dry membrane coupons (10 × 10 cm^2) were soaked in water for 12 h. The fully wetted membrane coupons were then immersed into a beaker containing 1L hypochlorite solution to perform the membrane treatment. The temperature of the solution was controlled at 15°C. The attempted hypochlorite concentration range was 2000-15000 ppm. The pH of the aqueous solution varied from 3-13. After a typical exposure time of 5 min, the membrane coupons were taken out and rinsed and soaked in water for 30 sec. To exclude continued membrane exposure of to the residual chlorine species, the treated membrane coupons were also neutralized in 0.5wt.% $NaHSO_3$ solution for 1h. The neutralized membrane coupons were fully rinsed, and then kept in water before characterized.

3.3 Characterization of RO membrane performance

Eight treated and four untreated membrane coupons were characterized in the same batch using a cross-flow system as illustrated in Fig. 1. A model brackish water containing 2000 ppm NaCl was used to test the desalination properties of the membranes. The brackish water was circulated

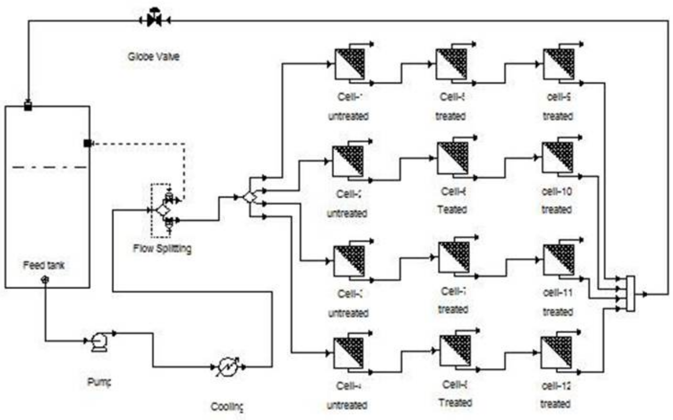


Fig. 1 The schematic representation of the cross-flow RO membrane test system

in the system by a pump. The feed flow-rate can be regulated using the by-path designed in the system. The feed pressure and temperature were controlled at 225 psig, and 25°C. Permeate water was collected and measured after one hour's permeation. The membranes were characterized in terms of water permeance (J^{Water}), and salt-rejection (R), as defined below

$$J^{Water} = \frac{V}{\Delta t}\cdot\frac{1}{A}\cdot\frac{1}{\Delta p-\Delta\pi}\left(\frac{cm^{3}}{cm^{2}.\sec.Bar}\right) \tag{9}$$

$$R = 1 - P^{salt} = \left(1-\frac{c_{permeate}}{c_{feed}}\right)\cdot 100\% \tag{10}$$

where V (ml) is the volume of water collected in a time interval Δt (sec), A (cm^2) is the effective membrane area, Δp (bar) is the trans-membrane pressure, $\Delta\pi$ (bar) is the osmotic pressure difference between the feed and permeate, c is the salt concentration, which was determined by measuring the conductivity of the water streams. P^{salt} is the salt passage of the membrane.

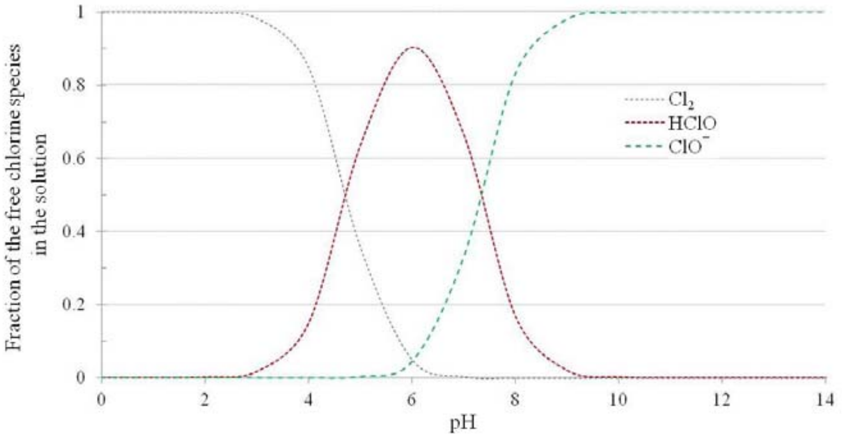


Fig. 2 The distributions of the free chlorine species in the aqueous hypochlorite solution at 15°C

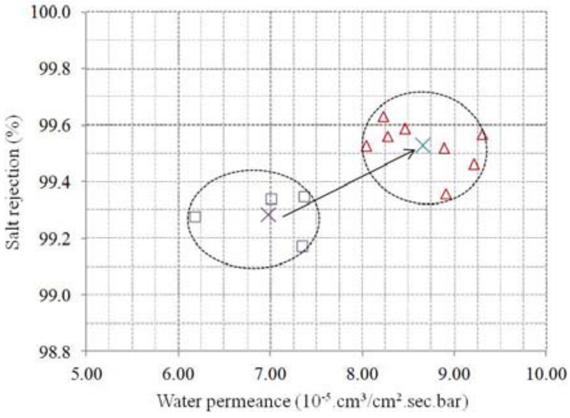


Fig. 3 The response of the membrane treated at 15°C in the aqueous 10000 ppm hypochlorite solution at pH10

4. Results and discussion

4.1 Characteristic pH ranges of the free chlorine species in the hypochlorite solution

The distributions of the 3 free chlorine species in the hypochlorite solution at 15°C are illustrated in Fig. 2. Clearly, as the pH is higher than 8, the key free chlorine species is OCl^-, accounting for over 83.4% of the total free chlorine, the reminder is essentially the molecular HOCl. The dissolved molecular chlorine in such basic solutions is unstable, and it spontaneously turns into HOCl and mostly OCl^-. It is found that pH 10 is also a critical pH, over which significant presence of both Cl_2 and HOCl is impossible. For clarity, the pH-dependent fractions of Cl_2 and HOCl are listed in Table 1.

At pH 4, the fraction of the dissolved chlorine in the solution is over 0.85, this fraction increases as pH is lowered further. At pH 2, this dissolved molecular chlorine is essentially the only free chlorine species due to the forward shift of the chemical reaction shown in Eq. (2). The solubility of chlorine in water is about 0.3-0.7 wt.% at room temperature. In case a high concentration of sodium hypochlorite is acidified to such a low pH as being 1, the excess chlorine may come out of the acidified solution. In this situation, the fraction of dissolved chlorine in the solution is more determined by its solubility in water than the by chemical equilibrium. These extreme situations were not considered herein estimating the relative presence of the chlorine species, since the concentration of sodium hypochlorite used for membrane treatment was usually controlled very low, and also the lowest pH attempted in the experiments was at 3.

The presence of HOCl in the hypochlorite solution is essentially within the pH range of 3-9. As the pH is lowered from 8, the fraction of HOCl increases to 0.5 at pH 7.3, and reaches its peak value of 0.92 at pH 6.2. At 15°C, the dominating presence of HOCl (with > .5 fraction) in the solution corresponds to the pH range 4.75-7.3. The peak fraction is determined by pK_1 (7.3 at 15°C) as well as pK_2 (4.75 at 15°C). At a higher temperature, this peak fraction value might be increased due to the bigger pK_1 (e.g., 7.53 at 25°C) implying a smaller degree of HOCl ionization and the profile of OCl^- would be shifted to the right in such a case.

4.2 The responses of membrane treatment within pH10-12

The response of the membrane treated at pH 10 is shown in Fig. 3. The four data points represented by the diamond refer to the RO performance of four virgin membrane coupons. The sign (*X*) inside the oval stands for average of the data group. The standard deviation of the untreated, and treated membrane group is found to be 0.55, 0.48, respectively. These relatively great deviations justified the statistical approach employed in this investigation. In RO membrane characterization, it usually takes the membrane coupon one-hour permeation before the water permeate is sampled. Considering the likely variation of temperature and feed pressure in this pre-sampling time period and its impacts on the membrane characterization, the treated and untreated

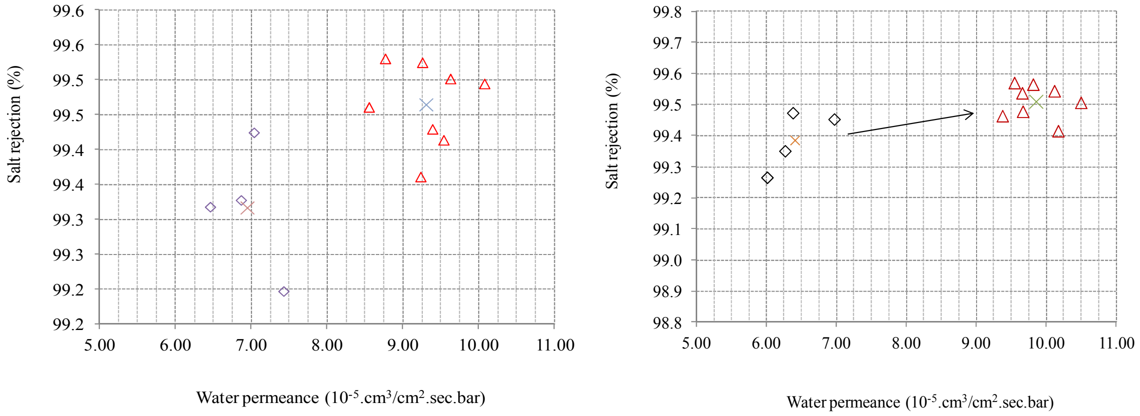
Table 1 Fractions of Cl_2 and HOCl when the pH is higher than 10

pH	Fraction of Cl_2	Fraction of HOCl
10	$1.2*10^{-8}$	$2.0*10^{-3}$
11	$1.2*10^{-10}$	$2.0*10^{-4}$
12	$1.2*10^{-12}$	$2.0*10^{-5}$

membrane coupons were therefore characterized in the same batch to minimize the effects of such controlling errors. The comparable standard deviations (0.55 and 0.48) of these two groups of membrane coupons suggests that no significant extra deviations (e.g., in treatment time, or membrane rinsing and neutralization) was introduced in the course of membrane treatment, and the observed membrane response to the treatment is statistically confident.

As indicated in Fig. 3, the salt-rejection of the treated membrane increased from 99.28 to 99.52%. The significance of this improvement can be better understood by translating the salt-rejection into salt passage. Simple calculations show the salt passage of the membrane decreases from 0.72 to 0.48%, a significant reduction of 33%. According to the industrial empiricism, to achieve this same amount of improvement, great effort is needed from optimizing the monomer recipes to providing significant better control over the whole membrane manufacturing process. Furthermore, for the RO membrane fabricated by the interfacial polymerization process, the improved salt rejection is generally obtained by sacrificing water permeance of the membrane. It is thus attractive that a simple treatment of largely performing a short time membrane immersion in the hypochlorite solution can produce a significant increase in both salt rejection and water permance. It is indicated in Fig. 3 that the water permeance of the treated membrane increased from 6.98 to 8.63 (10^{-5} cm^3/cm^2.sec.bar).

Same trend was observed as the membrane was treated at pH 11 and 12 as shown in Fig. 4. Comparing Figs. 3, 4(a) and 4(b) also shows that the membrane treatment in a higher pH solution can give a better improved water permeance (a 23.4, 33.8 and 54.8 % increase at pH 10, 11 and 12, respectively). According to Fig. 2, the free chlorine species in the hypochlorite solution is essentially OCl^- when the pH is higher than 10. This suggests that there is essentially no difference in the concentration of OCl^-. It is therefore pH or alkalinity of the hypochlorite solution that makes a difference in the membrane response. According to the literature (Glater *et al.* (1983), Silva *et al.* (2006), Shao *et al.* (2006), Soice *et al.* (2003)), N-chlorination, and polymer chain splitting are the two mechanisms accounting for chemistry of the membranes exposed to hypochlorite solutions. The improved salt rejection and water permeance in these three cases is attributed to the cleavage of the amidic linkage or membrane hydrolysis as shown in Fig. 5. This attribution is supported by the finding of Soice *et al.* (2003), who studied the chlorination of



(a) (b)

Fig. 4 The response of the membrane treated at 15°C in the aqueous 10000 ppm hypochlorite solution at pH11(a) and pH 12 (b)

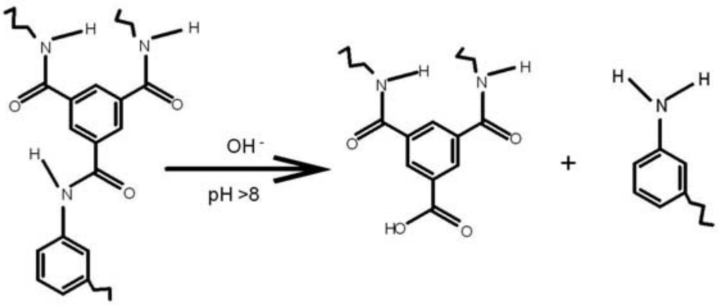


Fig. 5 The mechanism of membrane hydrolysis in the hypochlorite solution at pH 10-12, there is essentially no presence of HOCl and Cl_2, but a strong presence of alkalinity

various model amide compounds using hypochlorite solutions, no chlorinated compounds were observed in the solutions at the high pH. The absence of chlorinated compounds was attributed to the weak chlorinating strength of OCl^- relative to HOCl and Cl_2. The XPS characterization results obtained by A. Ettori *et al.* (2011) also showed that there is no N-chlorination occurring to the polyamide membrane at a higher pH (e.g., 12) treatment.

As it is shown in Fig. 2 that both HOCl and Cl_2 are not stable in the alkali hypochlorite solution with a pH higher than 10, N-chlorination can thus be excluded from the membrane chemistry in all these three treatments.

Direct proof on polymer chain splitting was reported by Rouaix *et al.* 2006 who characterized the decreased molecular weight of polysulfone after 16 days' contact of the membrane with 100 ppm hypochorite at pH 10. No noticeable chain splitting was found in membranes treated at lower pH (5-8) (Rouaix *et al.* 2006), suggesting that the membrane hydrolysis occurs easily in an alkaline environment. According to the chemistry of membrane hydrolysis shown in Fig.5, the hydrolyzed PA membrane has more hydrophilic groups (e.g., $-COO^-$, $-NH_2$) both on the membrane surface and in the membrane matrix, and the depth of the intruding hydrolysis depends upon the time of membrane exposure to the hypochlorite solution and the alkalinity/pH of the solution. These generated hydrophilic groups increase the solubility and diffusivity of water in the membrane, according to the solution-diffusion theory, the membrane demonstrates the improved water permeance and reduced salt passage.

It is also found that the improved salt rejection of the membranes depends upon their prior rejection properties. As shown in Fig. 6, the membrane with a lower prior salt rejection (98.7%) showed a greater rejection enhancement. It can be reasonably assumed that for a less salt-rejecting membrane, the contribution of salt passage through the defects is greater. And presumably, the sizes of defects in the membrane are at a level of 0.4-0.6 nm, which is large enough to allow passage of both water and the salt yet small enough to ensure the membrane has a quite good prior salt-rejection as shown in Fig. 6. As is known the hydrolysis can create more hydrophilic groups on the membrane surface. Such hydrophilic groups must have the comparable probability appearing on the wall of the defect pores. It is likely that these hydrophilic groups posse more free space within the pore than the localized terminal groups, which are originally present on the surface. The association of these hydrophilic groups with water molecules can effectively reduce the pore size and thus help hinder salt passage (Mika *et al.* 2002, Isabel *et al.* 1992, Hong *et al.* 2011, Zhou *et al.* 2005) through these narrowed/repaired defect pores. A schematic representation

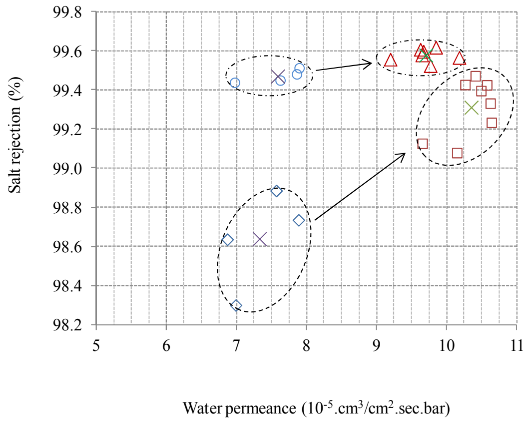


Fig. 6 The responses of the membranes treated at 15°C in the aqueous 10000 ppm hypochlorite solution at pH11 with different salt rejection before treatment

of these generated groups in interaction with water is illustrated in Fig. 7. It seems that most of defects in the membrane can be effectively repaired by the membrane hydrolysis in the treatment as shown in Fig. 6 so that an even higher salt-rejection membrane can be achieved.

To acquire a better understanding on the membrane hydrolysis, membrane treatment at an even higher pH was also attempted. The results of the treatment at pH 13 were summarized in Table 2. The treating time varied from 3 to 8 min, and the hypochlorite concentration ranged from 5000 to 10000 and 15000 ppm. Compared to the performance of untreated PA membrane listed at the bottom of the Table, it can be viewed that the treated membrane invariably exhibited a higher water permeance but a lowered salt rejection. Very likely, these membranes were over-hydrolyzed in the solution due to the too strong alkalinity at pH13. Excessive membrane swelling generally occurs in such an over-hydrolyzed membrane, which shows a higher water flux and salt passage. Clearly, membrane treatment under improper conditions lowered membrane performance. A proper selection of membrane treatment condition is critically important.

Table 2 Responses of PA membrane treated at pH 13 at 15°C

Treating conditions		Water permeance		NaCl rejection	
Conc.	Time	J	S.D.[1]	R	S.D.
(ppm)	(min.)	$(10^{-5}cm^3/cm^2.sec.bar)$		(%)	
5000	3	7.05	0.25	98.76	0.18
5000	8			98.69	0.03
12000	5	9.2	0.2	98.84	0.07
15000	3	8.3	0.2	98.70	0.28
15000	8	11.7	0.12	97.98	0.10
n/a	n/a	6.5	0.2	99.25	0.06

[1] S.D. stands for the standard deviation

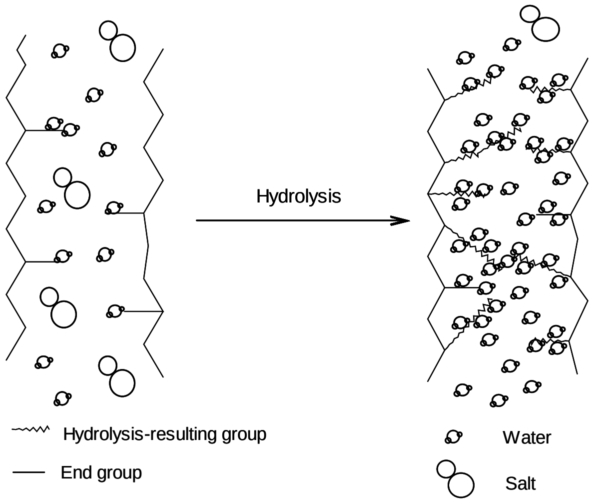


Fig. 7 A defect-pore model illustrating the hydrophilic interactions before and after the membrane hydrolysis

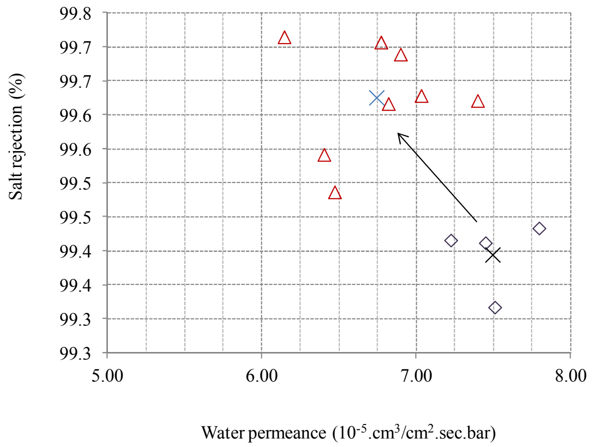


Fig. 8 The response of the membrane treated at 15°C in the aqueous 10000 ppm hypochlorite solution at pH 9.5

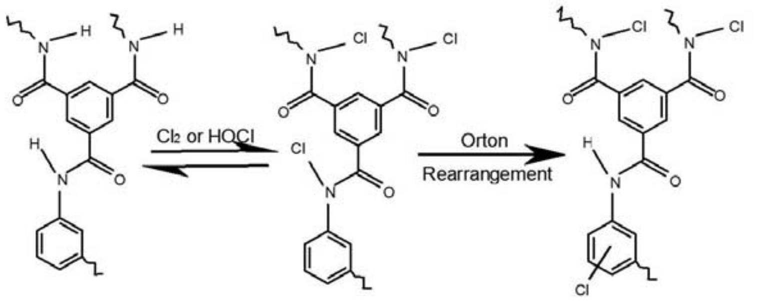


Fig. 9 N-chlorination of the membrane in the hypochlorite solution at lower pH, where there is sufficient presence of such chlorine species as HOCl and Cl_2

4.3 The responses of membrane chlorinated at pH and 9.5, 7.5 and acidic pH

The response of the membrane treated at pH 9.5 is shown in Fig. 8. The improvement of salt rejection of the treated membrane was accompanied with an obvious loss in water permeance. Because of the alkalinity of the solution at pH 9.5, it is probable that significant hydrolysis took place in the membrane, and defects in the membrane can still be repaired by the hydrolysis. However, according to Fig. 2, HOCl fraction in the solution at pH 9.5 is up to 0.02, the stronger chlorinating capability (Soice *et al.* 2003) of HOCl though at a low level starts playing a part in defining the membrane response. The hydrolyzed membrane should have displayed a higher water permeance and salt rejection. However the triggered N-chlorination as shown in Fig. 9 consumed most of the membrane's amine groups. Clearly, N-chlorination made the hydrolyzed membrane less hydrophilic, and a reduced water permeance was finally observed.

The response of the membrane treated at pH 7.5 was shown in Fig. 10. This represents the most undesired outcome of the membrane treatment: a slight decrease in membrane salt rejection is accompanied with a significant loss in water permeance from 7.05 to 3.55 (10^{-5} cm^3/cm^2.sec.bar).

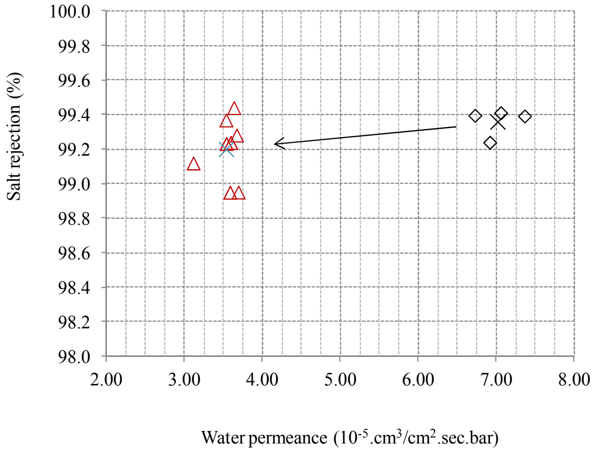


Fig. 10 The response of the membrane treated at 15°C in the aqueous 10000 ppm hypochlorite solution at pH 7.5

Table 3 Responses of the membrane treated at pH 3 and 4

Treating conditions			Water permeance		NaCl rejection	
pH	Conc. (ppm)	Time (min.)	J (10^{-5} cm^3/cm^2.sec.bar)	S.D.[1]	R (%)	S.D.
4	10000	1	2.55	0.30	98.16	0.49
4	10000	5	2.87	0.27	97.8	0.58
3	2000	5	2.56	0.05	98.61	0.33
3	2000	1	2.62	0.23	98.78	0.23
n/a	n/a	n/a	7.45	0.07	99.16	0.13

[1] S.D. stands for the standard deviation

This great loss in water permeance resulted from the significant presence of HOCl, by which the PA membrane was readily N-chlorinated, and the inability of the hypochlorite solution at pH 7.5 to cause significant membrane hydrolysis.

The response of the membrane treated in the acidic solutions at pH 3 and 4 are summarized in Table 3. It should be noted that the key chlorine species in these acidified solutions is the dissolved molecular chlorine, which possesses the highest chlorinating strength (Soice *et al.* 2003). Since membrane hydrolysis is generally not taking place in the acidic solutions, particularly within such a short time of exposure. These severely N-chlorinated membranes exhibited the lowest water permeance and salt rejection.

5. Conclusions

Three characteristic pH ranges were identified. OCl- is the dominating free chlorine species in the hypochlorite solution at pH higher than 10. HOCl is stable only between pH 3-10 at 15°C. The main presence of HOCl is within pH 4.75-7.3 with the peak fraction of 0.92 at pH 6.2. The dissolved Cl_2 is overwhelmingly present in the solution when the pH is less than 3.

At lower pH, particularly less than 8, the membrane is mainly N-chlorinated, and the N-chlorinated PA membrane shows reduced water permeance and salt rejection. Membrane hydrolysis (cleavage of amide chains) occurred to the membrane when treated at pH 8-10, and N-chlorination also took place due to the presence of HOCl, and the treated membrane showed improved salt rejection, and usually reduced water permeance, depending on the extent of membrane hydrolysis. When membrane is treated in the solution at pH 10-12, hydrolysis is the only chemistry observed of the treated membrane, and the hydrolyzed membrane showed both improved water permeance and salt rejection. It was also found that water permeance of the treated membrane increased with an increase in pH from 10 to 12. Membrane was over-hydrolyzed when treated at pH 13 for 3-8 min, and the treated membrane showed improved water permeance but lowered salt rejection.

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