Fouling and Cleaning of Reverse Osmosis Membranes during Municipal Tap Water Treatment on a Pilot-Scale Plant

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ABSTRACT
This study in situ investigated the membrane performance of reverse osmosis (RO) elements along longitudinal direction in a pilot-scale plant with six CSM-2540 RO elements during municipal tap water treatment at the constant recovery and flux. The continuous chemical cleaning processes were carried out with hydrochloric acid cleaning, sodium hydroxide cleaning and hydrochloric acid cleaning. The membrane performance was in situ monitored by the system and element pressure drop and the rejection of organic and inorganic foulants. According to this study, the tail-elements were easily suffered more serious fouling than the other in the RO system. The pressure drop at back-end unit was larger than that at the other as a result of high osmotic pressure and concentration polarization, especially at the end of fouling operation. In the whole RO system, the rejection of cations was higher than the anions of the same valence at initial operation and close to that of anions at the later stage of fouling experiment. Further, it was found that the organic foulant mainly deposited on the lead-elements, and the inorganic salt mainly precipitated on the tail-elements. Moreover, the performance of fouled membranes was restored by using the conventional acid-base cleaning protocol.

Keywords: Reverse osmosis; Membrane fouling; Pilot-scale system; Water treatment; Acid-base cleaning

1.0 INTRODUCTION
Reverse osmosis (RO) membranes are currently being used in a wide range of applications, including brackish and seawater desalination as well as in membrane mediated waste water reclamation. However, membrane fouling is a major problem to be typically caused by inorganic and organic materials present in water that adhere to the surface and pores of the membrane and results in deterioration of performance with a consequent increase in costs of energy and early membrane replacement (Al-Amoudi 2010). So far many full-scale water reclamation plants are challenged by low production yield and frequent membrane cleaning. Accordingly, a significant amount of research has been conducted to better understand the mechanism of RO membrane fouling and cleaning so as to develop preventative methods for membrane fouling (Karabelas et al. 2010; Jung et al. 2006). In particular, most of controlled
laboratory experiments have been performed to study different pollutants contributing to membrane performance including organic fouling and inorganic fouling (Lee et al. 2005; Wang et al. 2007; Dirk et al. 2010).

Although these studies have improved our understanding of various aspects of membrane fouling during water treatment and desalination, laboratory-scale studies are limited in appropriately simulating hydrodynamic conditions of full-scale applications. The laboratory-scale with single membrane module could not provide valuable data for industrial application. Consequently, some researchers have both numerically and experimentally focused on the fouling type and mechanisms in the pilot- or full-scale system during the water treatment.

With regard to experimental study, Jacquet et al. (2006) showed that dry matter and organic concentration decrease and the extended biofilm created an important pressure drop along the tube in a RO plant during brackish water treatment. Xu et al. (2010) demonstrated that the fouling of the lead elements was mainly caused by adsorption and deposition of effluent organic matter in a 2-stage pilot-scale plant with twenty-one 4040 spiral wound NF/RO elements during filtration of the non-nitrified effluent. In addition, they found that membrane fouling was dominated by biofouling in combination with organic fouling, colloidal fouling, and inorganic scaling during treatment of the nitrified/denitrified effluent.

With regard to numerical study, Hoek et al. (2008) described the effects of fouling on the performance of a RO system treating micro-filtered secondary effluent with a semi-empirical model relying on mass and momentum balance equations and two empirical correlation coefficients. The model confirmed that cake formation predominated in lead elements causing a localized flux decline. Hence, a high flux in tail elements could enhance solute rejection and concentration polarization. Meanwhile, some effective numerical methods were used for assessing fouling characterization and indicating fouling development in RO process (Roth et al. 1999; Chen et al. 2004; Song et al. 2005). Chen et al. (2004) reported that a full-scale RO system could maintain a constant average permeate flux for a period of time even though fouling development had occurred right from the start of operation with the increase in resistance as an indicator of membrane fouling. Song et al. (2005) proposed the filtration coefficient relating to distribution of the membrane resistance as the indicators or measurements of membrane fouling in full-scale RO processes. Roth et al. (1999) proposed a method to reveal the degree of fouling and the solute permeation mechanism by comparing the sodium chloride distribution in the outlets of the RO membrane modules.

The objective of the study is in situ to investigate the performance of every element along longitudinal direction in a pilot-scale plant with six CSM-2540 RO elements during municipal tap water treatment at the constant recovery and permeate flux. The membrane performance was monitored by pressure drop and the rejection of organic and inorganic foulants for every element and RO system. Moreover, a continuous chemical cleaning process was carried out with hydrochloric acid cleaning (pH=2.5), sodium hydroxide cleaning (pH=11.5) and hydrochloric acid cleaning (pH=2.5) to clean the fouled membrane elements so as to provide insight into chemical cleaning protocols and cleaning efficiency.

2.0 MATERIALS AND METHODS

2.1 Pilot-Scale RO Plant

The design of pilot-scale membrane plant simulated a conventional RO plant including
pretreatment and RO system as shown in Figure 1. The pretreatment part constituted with the sand filter, carbon filter and fine filter. The pretreatment aims to remove silica colloids, adsorbed organic compounds, particulate matter of iron and aluminum colloids, microorganisms and metallic oxides. Therefore, these undesirable contaminants in raw water should be removed before it is fed into RO membrane. The pilot-scale membrane unit with a capacity of 10.2 L/min and employing six spiral-wound RO elements were constructed and used in this study. The six elements were configured in three pressure vessels in series with each pressure vessel holding two elements called RO1-2, RO3-4 and RO5-6 along the fluid direction, respectively.

The pilot-scale plant was equipped with a customized supervisory control and data acquisition system to online monitor and log permeate flux, pressure and water quality parameters (e.g. pH, temperature and conductivity). The inlet and outlet operation pressures of each pressure vessel were also detected by four pressure gauges, respectively as shown in Figure 1. The composite polyamide spiral-wound RO membrane elements with a membrane area of 2.5 m² (RE2540-TL, SAEHAN Korea) were used for this study.

2.2 Water Quality Analysis

Key parameters of Tianjin municipal tap water quality used in the pilot-scale study are summarized in Table 1. Total organic carbon (TOC) was quantified using the TOC-VCPH Analyzer (Shimadzu, Japan). ICS-1500 ion sub-spectrometer (Dionex, USA) was employed to determine the concentration of key inorganic ions. Silting Density Index (SDI) was determined using manual SDI tester (Millipore-ZLFI00001, USA). The conductivity was determined by online conductivity meter (KDD6-DCK-8550). The flow rate and pressure were measured by online flowmeter (WLG-8351) and pressure gauge (DGN-8310), respectively.

Figure 1 Schematic diagram of the pilot-scale RO plant for treating the municipal tap water
Table 1  Average feed water quality

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.5</td>
</tr>
<tr>
<td>Sodium(mg/L)</td>
<td>33</td>
</tr>
<tr>
<td>Magnesium(mg/L)</td>
<td>30</td>
</tr>
<tr>
<td>Calcium(mg/L)</td>
<td>54</td>
</tr>
<tr>
<td>Chlorine(mg/L)</td>
<td>65</td>
</tr>
<tr>
<td>Sulfate(mg/L)</td>
<td>85</td>
</tr>
<tr>
<td>SDI10</td>
<td>7.46</td>
</tr>
<tr>
<td>TOC(mg/L)</td>
<td>1.2</td>
</tr>
<tr>
<td>Conductivity(μs/cm)</td>
<td>650</td>
</tr>
<tr>
<td>Total hardness(mg/L)</td>
<td>260</td>
</tr>
</tbody>
</table>

2.3 Experimental Procedures

Pilot-scale testing was conducted with the municipal tap water (Tianjin, China) at a constant recovery and flux. The recovery and production flux of RO system was kept at 80% and 22.4 L/(m².h) on average during the fouling experiments, respectively. The initial operation pressure of all experiments was kept as 1.0±0.02 MPa, while the temperature was controlled at 25.0±1.0°C with a cooling system. The online operational parameters of each membrane module and the RO system including production flow, conductivity and the pressure drop etc. are measured at regular intervals of 5h. Simultaneously, the permeate water were collected for testing organic and inorganic content. Each fouling experiment stopped when the operation pressure of the RO system increased by 31%. All the experimental results were the average of triplicate laboratory samples.

After the fouling experiment, the off-line cleaning process was conducted. The cleaning process was carried at constant pressure of 0.25±0.02 MPa and temperature of 30±2°C with temperature controlling system. At first, the fouled membrane element was washed with pure water for 10 min to remove unbound substances from the membrane surface. It was followed by hydrochloric acid cleaning (pH=2.5) for 1 h and pure water washing for 5 min to remove precipitated salts. Then sodium hydroxide cleaning (pH=11.5) was carried out for 1 h and pure water washing for 5 min to clean organic contaminants. At last the hydrochloric acid cleaning (pH=2.5) was conducted for 1 h and pure water washing for 5 min to further clean fouled membrane surface. After membrane cleaning, the permeate flux and rejection were measured. The same cleaning agents and procedure (time, concentration, sequence, etc.) were used to wash each fouled spiral-wound RO membrane module in all the cleaning experiments. In order to evaluate membrane fouling degree, the components of the eluent were analyzed. At the same time, the performance of each RO membrane element was obtained before and after each cleaning phase.

3.0 RESULTS AND DISCUSSION

3.1 Membrane Operational Performance

The RO membranes were tested at pilot-scale for 160 h using Tianjin municipal tap water treatment at the constant recovery and permeate flux. Operation pressure and system rejection versus operation time were illustrated in Figure 2. Both of the operation
pressure and rejection of the system were almost kept constant at the initial 120 h of operation as shown in Figure 2, while the system pressure drop increased gradually from 0.04 MPa to 0.06 MPa at the initial 120 h of operation (Figure 3). However, the operation pressure increased rapidly from 1.05 MPa to 1.33 MPa after 120 h of operation. Simultaneously, the system pressure drop rose from 0.058 MPa to 0.135 MPa (Figure 3). At that time, the rejection of the system declined slightly from 98.15% to 97.03% (Figure 2). These results revealed that the whole system suffered from the severe fouling after 120 h of fouling operation. It also implies that the new membrane element surface might be too smooth for pollutants to adsorb the foulants at the beginning of experiments. With fouling time, the continued deposition of contaminants which made the surface roughness increase and provided the conditions for contaminants, so as to accelerate membrane fouling eventually (Subramani et al. 2009).

It can also be found in Figure 3 that similar to the system pressure drop, the pressure drop of every membrane unit increased slightly with operation time at the initial 120 h of operation, and increased rapidly after 120 h of operation. Moreover, the pressure drop of membrane unit along the feed flow direction decreased at the initial 120 h of the fouling experiments. The reason was that the feed flow velocity in RO5-6 unit was lower than the RO1-2 elements owning to hydraulic drag to the passage of the permeate in serial RO membrane modules (López-Ramírez et al. 2006). An interesting phenomenon is that the increment rate of pressure drop at RO5-6 unit was faster than that at RO1-2 unit after 120 h of fouling operation. Especially, the pressure drop of RO5-6 unit was larger than that of RO1-2 unit at 160 h of fouling operation. It suggests that RO5-6 units made the same contribution to the increment of system pressure drop after 120 h of fouling operation. This is because the high osmotic pressure and concentration polarization at RO5-6 unit led to high hydraulic resistance and the greater scaling coverage at a constant recovery of RO system (80%) (Bu-Ali et al. 2007; Rahardianto et al. 2006).

![Figure 2](image-url)  
*Figure 2* Operation pressure and system rejection vs. operation time during the fouling experiment
Equally, the decrease in the system rejection obtained is related to an increase in the conductivity of permeate during the fouling experiments. In general, the conductivity of permeate from different units and RO system increased with the operation time as shown in Figure 4. However, the linear trend was quite different. The conductivities of permeate obtained from the RO system and RO1-2 unit had a little increase, while those from RO3-4 and RO5-6 units rose rapidly with the operation time. Particularly, the conductivities of permeate from RO3-4 and RO5-6 units increased from 12.6 S/cm to 56.7 S/cm, and from 43.5 S/cm to 153.2 S/cm, respectively, with an increase in the operation time from 120 h to 160 h. It implies that the salt penetration rate at the RO units increased along fluid direction as a result of concentration polarization although the salt penetration rate kept a low level at RO1-2 unit. On the other hand, the elements in back-end of the RO system suffered more severe fouling than the other. As the increasing concentration induced by concentration polarization increases gradually along the flow channel and exceeds the salt saturation level, the precipitation and fouling occurs on the surface of back-end elements (Zhang et al. 2007). In sum, the conductivity observations are in agreement with the results obtained from the operation pressure and pressure drop in this pilot-scale RO plan.
3.2 Membrane Rejection of Organic and Key Inorganic Foulants

Based upon the conductivity results, the following studies were carried out to investigate the membrane rejection of organic and key inorganic foulants so as further to illustrate the performance of the pilot-scale plant. As shown in Figure 5(a), the transmission rate of TOC and salt in the RO system was almost kept constant at the initial 120 h of fouling operation. After 120 h of operation, the transmission rate of TOC increased slightly from 6.9% to 8.1%, and that of salt increased from 2.3% to 3.6%. Further, the transmission rate of monovalent cation such as Na\(^+\) and K\(^+\) was higher than that of bivalent cation including Mg\(^{2+}\) and Ca\(^{2+}\) (Figure 5b). Among others, the transmission rate of Na\(^+\) or K\(^+\) was higher than that of Mg\(^{2+}\) or Ca\(^{2+}\), respectively, due to their different hydrated ion radii (Tansel et al. 2006). Similar phenomenon can be observed in Figure 5c that the transmission rate of monovalent anion (NO\(_3^-\) and Cl\(^-\)) was higher than that of bivalent anion (SO\(_4^{2-}\)). Additionally, scaling anion as SO\(_4^{2-}\) is much easier to deposit on the membrane surface than non-scaling anion as NO\(_3^-\).

Furthermore, the rejection of bivalent anion SO\(_4^{2-}\) was higher than that of bivalent cation Ca\(^{2+}\) at the initial 120 h of fouling operation (Figure 5). This is correlated with the aromatic polyamide on the membrane surface with negative charge, which is easy to attract to cation and repulse to anion. However, the transmission rate of SO\(_4^{2-}\) increased fast with the operation time. At the end of operation, the transmission rate of SO\(_4^{2-}\) (5.6%) was higher than that of Ca\(^{2+}\) (2.6%). It was ascribed to negative charges on the membrane surface attracting more cations with the fouling operation time until the charge of the membrane surface was offset. Finally, the rejection of cations was close to that of anions at the later stage of fouling experiment. Oo et al. (2010) also obtained the similar results.

![Figure 5(a)](image-url)
Moreover, two typical inorganic ions including Ca\(^{2+}\) and SO\(_4^{2-}\) were selected to illustrate the ion rejection in every unit along the feed flow direction during the fouling experiment as shown in Figure 6. It can be seen in Figure 6 that the concentration of both Ca\(^{2+}\) and SO\(_4^{2-}\) in every permeate increased with the fouling time. There was a sharp rise after 80 h of fouling operation. In particular, the concentrations of both Ca\(^{2+}\) and SO\(_4^{2-}\) in the permeate from RO5-6 unit increased faster and higher than those in the permeate from RO1-2 and RO3-4 units. It further confirms that the elements in back-end of the RO system suffered more serious fouling than those in front-end. Therefore, it suggests that either using the RO membrane of high rejection rate in the back-end of the RO system or conducting high cleaning frequency to RO membrane in the back-end of the system would enhance membrane rejection and improve permeate quality (Redondo et al. 2001).
Figure 6 Changes in the ion concentration of permeate with the fouing operation (a) $\text{Ca}^{2+}$; (b) $\text{SO}_4^{2-}$.

3.3 Cleaning Experiments

As mentioned before, the off-line cleaning process was carried out after the fouling experiment. The component analyses of eluent from RO1-2 and RO5-6 units after each cleaning phase were summarized in Table 2 and Table 3. As shown in Table 2 and Table 3, the amount of TOC deposited in RO1-2 unit was 2.35 times than that in RO5-6. On the contrary, the organic foulants deposited in RO5-6 unit were much more than those in RO1-2 unit. These results reveal that the organic fouling was relatively serious in RO1-2 unit and the inorganic fouling was mainly located in RO5-6 unit. Similar results obtained by Xu et al. (2010) showed that the lead-elements suffered from adsorption and deposition of effluent organic matter during non-nitrified effluent treatment on a pilot-scale plant.

It also can be seen from Table 2 and Table 3 that the cleaning by NaOH aqueous solution is the best way to remove organic foul-
ing substances from the RO system. At the same time, the cleaning by HCl aqueous solution is an effective approach to eliminate inorganic pollutants from the surface of the membrane (Zondervan et al. 2007; Al-Amoudi et al. 2007). As shown in Table 2 and 3, the removal quality of organic and inorganic foulants after the second acid cleaning decreased to approximately fifty percent than that after the first acid cleaning, indicating that the foulants were not completely cleaned and still deposited on the membrane surface. So it was essential to investigate cleaning efficiency by the following studies on the permeate production and rejection of the elements.

Table 2 The component analysis of eluent from RO1-2 unit after each cleaning phase

<table>
<thead>
<tr>
<th>Ion</th>
<th>Removal quantity (mg/L) (%)</th>
<th>HCl (mg/L)</th>
<th>NaOH (mg/L)</th>
<th>HCl (mg/L)</th>
<th>Total (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg^{2+}</td>
<td>15.7 (59.7)</td>
<td>1.4 (5.3)</td>
<td>9.2 (35)</td>
<td>26.3</td>
<td></td>
</tr>
<tr>
<td>Ca^{2+}</td>
<td>11.7 (45.3)</td>
<td>3.7 (14.3)</td>
<td>10.4 (40.3)</td>
<td>25.8</td>
<td></td>
</tr>
<tr>
<td>SO_{4}^{2-}</td>
<td>8.6 (58.5)</td>
<td>2.3 (15.6)</td>
<td>3.8 (25.9)</td>
<td>14.7</td>
<td></td>
</tr>
<tr>
<td>TOC</td>
<td>6.7 (23.0)</td>
<td>18.0 (61.9)</td>
<td>4.4 (15.1)</td>
<td>29.1</td>
<td></td>
</tr>
</tbody>
</table>

Table 3 The component analysis of eluent from RO5-6 unit after each cleaning phase

<table>
<thead>
<tr>
<th>Ion</th>
<th>Removal quantity (mg/L) (%)</th>
<th>HCl (mg/L)</th>
<th>NaOH (mg/L)</th>
<th>HCl (mg/L)</th>
<th>Total (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg^{2+}</td>
<td>25.0 (65.4)</td>
<td>1.8 (4.7)</td>
<td>11.4 (29.8)</td>
<td>38.2</td>
<td></td>
</tr>
<tr>
<td>Ca^{2+}</td>
<td>396.0 (67.4)</td>
<td>4.9 (0.8)</td>
<td>185.5 (31.6)</td>
<td>586.4</td>
<td></td>
</tr>
<tr>
<td>SO_{4}^{2-}</td>
<td>37.8 (50.7)</td>
<td>12.1 (16.2)</td>
<td>24.7 (33.1)</td>
<td>74.6</td>
<td></td>
</tr>
<tr>
<td>TOC</td>
<td>1.30 (10.5)</td>
<td>10.6 (85.5)</td>
<td>0.5 (4.0)</td>
<td>12.4</td>
<td></td>
</tr>
</tbody>
</table>

To further investigate the cleaning efficiency at every membrane element, the permeate production and rejection before and after fouling and cleaning operation were shown in Figure 7. It can be seen from Figure 7 that the permeate production and rejection obtained from the elements deceased along longitudinal direction in a pilot-scale plant after fouling experiment. In particular, the permeate production and rejection obtained from back-end of the system declined seriously. For example, the permeate production of RO1 and RO6 reduced to 87.5% and 6.2% of initial permeate production (1.59 L/min) after the fouling operation. The rejection of RO1 and RO6 declined to 98.5% and 93% at the end of fouling operation. These results are also in agreement with those obtained from the operation pressure and pressure drop in this pilot-scale RO plant. Although the performance of the membrane after chemical cleaning was as close to that before fouling, the permeate production and rejection obtained from the elements were still a little bit lower than their initial values. Especially, the recovery of the rejection and permeate production of RO5-6 as only 98% and 95%, respectively. It might be a good way to conduct a high cleaning frequency to RO membrane in the back-end of the system to improve the membrane performance.
Figure 7  The permeate production (a) and rejection (b) of every membrane element before and after fouling and cleaning operation

4.0 CONCLUSIONS

This study provided valuable insight into the membrane fouling by monitoring the pressure drop and rejection of organic and inorganic foulants of every element and system during municipal tap water treatment on a pilot-scale plant. It was found that the tail-elements suffered more serious fouling than others in the RO system. The changes in pressure drop of membrane unit along longitudinal direction were associated with the hydraulic drag to the passage of permeate at the initial operation as well as high osmotic pressure and concentration polarization. Simultaneously, the rejection of cations was higher than the anions of the same valence at initial operation and close to that of anions at the later stage of fouling experiment. Further, the lead-elements were mainly affected by
organic fouling. The fouling of tail-elements was mainly caused by deposition of inorganic matter. Three-step cleaning procedure is reasonable and effective for recovering membrane performance in the pilot-scale experiments.

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REFERENCES

the FilmTec SW30HR-380 and SW30HR-320 elements Technical-economic review. Desalination, 134(1-3), 83-92.


