*Desalination and Water Treatment*
www.deswater.com

18 (2010) 292–296
June


doi: 10.5004/dwt.2010.1795

# Membrane fouling in nanofiltration/reverse osmosis membranes coupled with a membrane bioreactor used for municipal wastewater treatment

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Received 3 June 2009; Accepted 15 January 2010

**ABSTRACT**

Securing a new water resource is becoming an important issue as severe shortage of water is seen throughout the world. Reuse of highly treated wastewater can be a viable option to address this issue. In this study, an advanced wastewater treatment system comprised of a membrane bioreactor followed by nanofiltration (NF) and reverse osmosis (RO) membranes was examined at pilot-scale with real wastewater. Treatment performance of the system was evaluated on the basis of 40 days continuous operation. At the end of the operation, membrane fouling in NF/RO membranes was investigated by disassembling the membrane modules. Although there was no significant difference in water qualities of the permeates between the NF and the RO membranes, membrane fouling was more significant in the NF membrane than in the RO membrane. After disassembling the membrane modules, a portion of the fouled membranes was cleaned stepwise and pure water permeabilities of the membrane specimen at each cleaning step were determined with a bench-scale cross-flow filtration unit. It was revealed that contribution of the cake/gel layers to the total filtration resistance was limited in both NF and RO membranes. It was found that inorganic matter, particularly silica, was main foulant in the NF membrane whereas organic matter mainly caused fouling in the RO membrane.

***Keywords:*** Wastewater treatment; Nanofiltration membrane; Reverse osmosis membrane; Membrane fouling

## 1. Introduction

Water resource is becoming scarce in many regions of the world and wastewater therefore is considered as a quantitatively stable resource in urbanized areas [1]. Nanofiltration (NF)/reverse osmosis (RO) membranes process can produce high grade water from wastewater and is therefore expected to be widely used in water reuse systems in the future. Similar to other types of membrane processes, however, membrane fouling is a big obstacle for widespread use of NF/RO membranes at present. In the application of NF/RO membranes to wastewater treatment, pre-treatment is indispensable to prevent membrane fouling. Conventional activated sludge process followed by media filtration or microfiltration/ultrafiltration membrane filtration has been commonly used for this purpose [2]. Membrane bioreactor (MBR) seems to be more suitable as a pre-treatment step for NF/RO membranes since quality of water treated by a MBR is much better than those by conventional

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methods. [3–7]. It was reported that organic macromolecules produced in MBRs would have different natures from those produced in conventional processes [8]. This would certainly have an impact on the evolution of membrane fouling in following NF/RO membranes. Nevertheless, there is still limited information regarding fouling in NF/RO membranes used for municipal wastewater treatment and previous studies mostly used conventional methods as pre-treatments [9,10]. In this study, a pilot-scale experiment using municipal wastewater was carried out with an MBR followed by NF/RO membranes to investigate the performance of the system. After 40 days of continuous operation, autopsy of the membrane module was carried out and characteristics of membrane fouling in NF/RO membranes were analyzed.

## 2. Materials and methods

### *2.1. Membrane bioreactor-nanofiltration/reverse osmosis system*

Continuous operation of the MBR-NF/RO system was carried out at an existing municipal wastewater treatment plant (Souseigawa municipal wastewater treatment plant, Sapporo, Japan). The characteristics of the feed wastewater are shown in Table 1. The MBR was equipped with 0.1 μm polyvinylidenfluoride membranes and operated with mixed liquor-suspended solids concentration of 14.9 g/L. Average concentration of total organic carbon (TOC) in MBR effluent was 5.6 mg/L. Effluent from the MBR was used as the feed water for the NF/RO membranes. Two 2-inch spiral-wound NF/RO membrane modules were examined in parallel in this study: NF membrane (LES90, Nitto Denko, Tokyo, Japan) and RO membrane (ES10, Nitto Denko, Tokyo, Japan). Membrane characteristics of the NF/RO membranes are given in Table 2. Membrane flux and recovery in the continuous operation were fixed at 460 $Lm^{-2}day^{-1}$ and 70%, respectively, for both membranes. Operation was continued with regular monitoring of water qualities and transmembrane pressure (TMP). At the end of the 40 days operation, the membrane modules were disassembled and divided into three sections (Fig. 1), and various analyses were carried out to investigate membrane fouling.

Table 1
Characteristics of the feed wastewater.

| TOC (mg/L) | UV absorbance at 260 (nm/cm) | Calcium (mg/L) | Silica (mg/L) | Sodium (mg/L) |
|---|---|---|---|---|
| 57.9 | 0.10 | 20 | 10 | 56 |

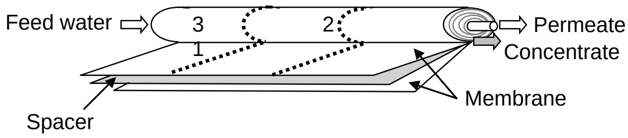


Fig. 1. Division of the membranes for analysis.

### *2.2. Assessment of membrane fouling in nanofiltration/reverse osmosis membranes*

After disassembling the membrane modules, a portion of the fouled membranes was cleaned stepwise and pure water permeabilities of the membrane specimen at each cleaning step were determined with a bench-scale cross-flow filtration unit (C70-F, Nitto Denko, Tokyo, Japan). Fouled membranes were firstly wiped with a sponge. Differences in water permeabilities observed before and after sponge wiping could be attributed to fouling caused by deposited cake/gel layers. Amounts of foulants on the fouled membranes were assessed as total suspended solids (TSS) and volatile suspended solid (VSS). Cake/gel layers scraped from the fouled membranes were dried at 110°C and weighted. Subsequently, the dried sample was burned at 600°C to volatile organic fraction. Membranes from which cake/gel layers had been removed were soaked in acid solution (HCl, pH2) for 24 hours to estimate the degree of fouling caused by inorganic constituents that strongly bound with the membranes. Finally, cleaning with alkaline solution (NaOH, pH11) was carried out for 24 hours to estimate the degree of fouling caused by adsorption of organic matter. Surfaces of the fouled membranes were analyzed by using a scanning electron microscopy (SEM) and infrared spectroscopy.

Table 2
Membrane characteristics.

| Membrane | Material | Water permeability ($Lm^{-2}day^{-1}kPa^{-1}$) | Zeta potential (mV) | Nominal salt rejection(%) |
|---|---|---|---|---|
| NF(LES90) | Polyamide | 1.6 | –8.6 | 90.0 |
| RO(ES10) | Polyamide | 1.2 | –15.3 | 95.5 |

*2.3. Analytical methods*

Concentration of TOC and total nitrogen (T-N) were determined by a TOC analyzer (TOC-VGSH, Shimadzu, Kyoto, Japan). Measurement of total phosphorus (T-P) was carried out by the method reported by Menzel and Corwin (1965). Samples for SEM analysis were fixed with glutaraldehyde and coated with platinum palladium. Fourier transform infrared (FTIR) spectra of the surfaces of physically cleaned membranes (i.e., after sponge cleaning) were obtained by using an attenuated total reflection (ATR)-FTIR spectrophotometer (FTIR-8400S, Shimadzu, Kyoto, Japan). Concentrations of inorganic elements were determined by inductive coupled plasma-atomic emission spectrometry (ICP-AES) (ICPS-7500, Shimadzu, Kyoto, Japan).

## 3. Results and discussion

*3.1. Water quality*

Table 3 summarizes quality of the treated water. It was expected the RO membrane would produce water with better qualities than the NF membrane. However, in this study, there was no significant difference in water qualities of the permeates from the two membranes in terms of TOC, T-N, T-P, electric conductivity (EC), and selected pharmaceuticals (data not shown). This might be attributed to the fact that operation of the RO membrane was carried out with considerably lower TMP than the value recommended by the manufacturer as shown below.

*3.2. Membrane fouling in NF/RO membranes*

*3.2.1. Changes in transmembrane pressure*

Fig. 2 shows the increases of TMP in the NF and RO membranes. Interestingly, membrane fouling was more significant in the NF membrane than in the RO membrane. The value of TMP in the NF membrane continuously increased throughout the operation whereas increase in TMP was limited in the RO membrane.

Table 3
Water characteristics.

| | Permeate of MBR | Permeate of NF | Permeate of RO |
|---|---|---|---|
| TOC (mg/L) | 4.8±0.4 | 0.18±0.04 | 0.14±0.03 |
| T-N (mg/L) | 4.4±2.3 | 0.58±0.31 | 0.53±0.42 |
| T-P (mg/L) | 0.1±0.1 | <0.01 | <0.01 |
| EC (μs/cm) | 341±34 | 27.1±12.7 | 23.3±7.1 |

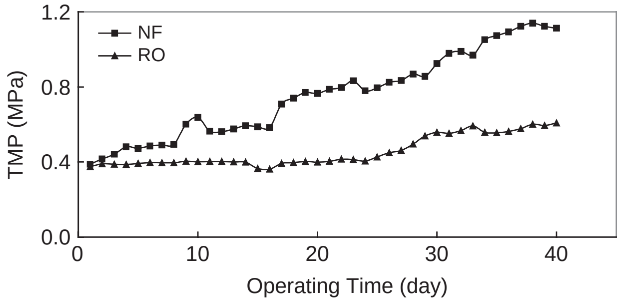


Fig. 2. Time-course changes in TMP.

*3.2.2. Amounts of foulants deposited on the membranes*

Fig. 3 shows amounts of TSS/VSS deposited at the end of the operation. It was found that cake/gel accumulation was most significant at the feed water inlet section and gradually decreased in the direction of the feed water flow. There was no significant difference in quantity and quality of cake/gel between the NF and the RO membranes. This implies that the difference in membrane fouling shown in Fig. 2 was not attributed to cake/gel layer deposition.

*3.2.3. Division of total filtration resistances*

Fig. 4 shows decreases of filtration resistances achieved by physical/chemical cleanings. Physical cleaning

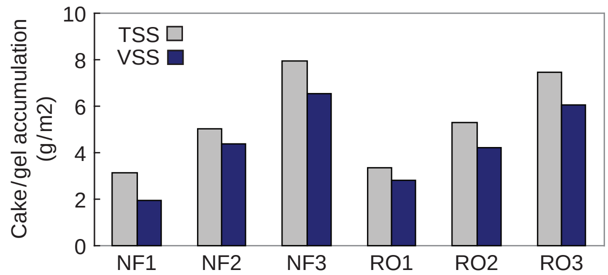


Fig. 3. Amounts of TSS/VSS deposited on the membranes.

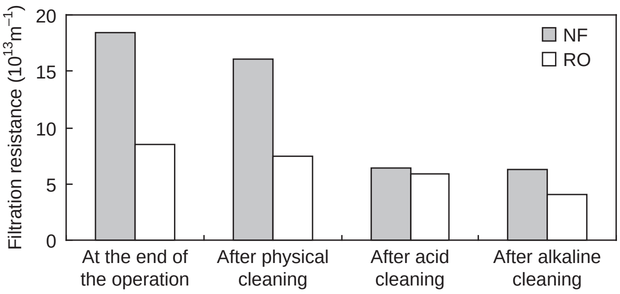


Fig. 4. Filtration resistances of the fouled membranes determined after physical/chemical cleanings.

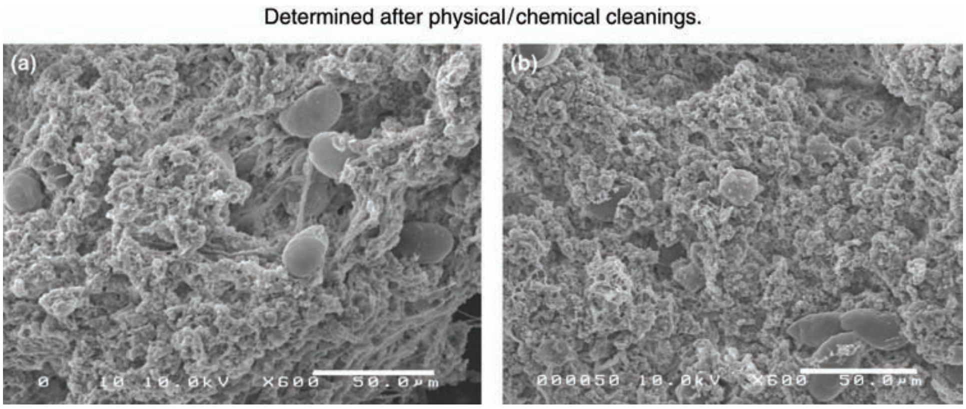


Fig. 5. SEM images of (a) NF3 and (b) RO3.

(sponge cleaning) was assumed to remove cake/gel layer resistance. In contrast, acid and alkaline cleanings were assumed to eliminate the resistance caused by inorganic and organic matter that strongly bound to the membrane, respectively. It is apparent that contribution of the cake/gel layers to the total filtration resistance was minimal in both NF and RO membranes. Fig. 5 shows the SEM images taken for NF3 and RO3 without sponge cleaning. Developments of biofilms on the membrane surface could be recognized on the basis of SEM observations. However, according to Fig. 4, it seemed that filtration resistance caused by so-called biofouling was limited in this study. Acid cleaning was very effective for restoring the water permeability of the NF membrane. This indicates that contribution of inorganic constituents to membrane fouling was significant in the case of the NF membrane. Alkaline cleaning was the most effective for the RO membrane, implying that some organic matter was the major foulant in the case of the RO membrane.

### *3.2.4. Inorganic elements extracted from the fouled membranes*

Fig. 6 shows the amounts of selected inorganic elements that strongly bound to the membrane at the end of the operation, which was estimated by ICP analysis of the acid cleaning solutions. More amounts of inorganic elements were extracted from the NF membrane than from the RO membrane. A significant difference in the compositions of extracted inorganic elements was seen between the NF and the RO membranes: Considerable amount of silica was extracted from the NF membrane. Rejection of silica by the NF membrane was limited (20%), whereas almost complete removal of silica was seen with the RO membrane. This means that a portion of silica penetrated the NF membrane and formation of silica scale on/in the NF membrane was more likely to occur.

### *3.2.5. Attenuated total reflection-Fourier transform infrared analysis*

Fig. 7 shows ATR-FTIR spectra of the NF/RO membranes measured after removing accumulated cake/gel with a sponge. Many peaks that could be assigned to a

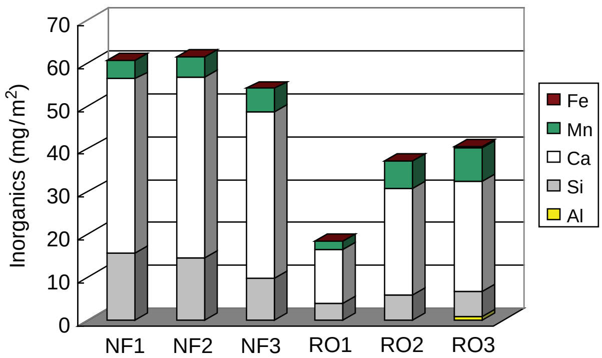


Fig. 6. Composition of inorganic elements accumulating in the fouled membranes.

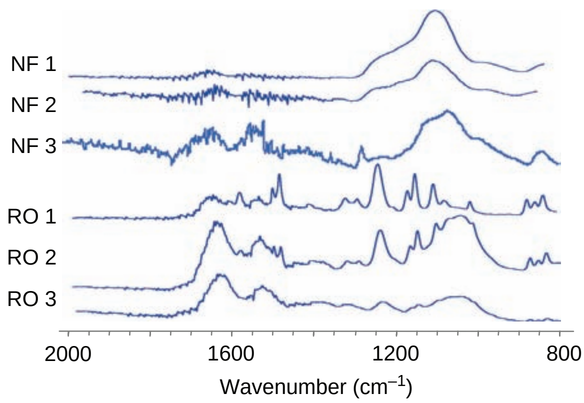


Fig. 7. FTIR spectra of the NF and the RO membranes measured after physical cleaning.

variety of organic compounds are seen in the spectrum measured for the RO membrane, whereas one broad peak is dominant in the spectrum measured for the NF membrane. The broad peak around 1050 $cm^{-1}$ found in the NF membrane spectrum might be attributed to silica [11], which coincides with the hypothesis stated above.

## 4. Conclusions

In this study treatment performance and membrane fouling of NF/RO membranes used for municipal wastewater treatment were investigated. There was no significant difference in water qualities of the permeates from the NF and the RO membranes. However, membrane fouling was more significant in the NF membrane than in the RO membrane. There was no significant difference in quantity and quality of cake/gel layers accumulating on the two membranes. It was revealed that contribution of the cake/gel layers to the total filtration resistance was limited in both NF and RO membranes. Inorganic matter was main foulants in the NF membrane whereas organic matter mainly caused fouling in the RO membrane. ICP analysis of the acid cleaning solutions and ATR-FTIR spectra of membrane surface after physical cleaning suggested that a major foulant in the NF membrane was silica. These differences in membrane fouling between NF and RO membranes should be investigated in the future work.

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