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Iron and manganese fouling in microfiltration as a pretreatment of seawater reverse osmosis processes

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ABSTRACT

Two sets of pilot test were carried out to investigate the fouling behaviours of microfiltration (MF) system as a pretreatment for seawater reverse osmosis (SWRO) processes for about two years. One set used clean seawater as feed water while the other adopted surface water with lower quality than the seawater. Both systems introduced commercial hollow fiber MF modules from the same manufacturer. During the operation period, raw water quality parameters related to reverse osmosis (RO) performance were collected and analyzed. Regardless of raw water quality, the product water of both MF systems without coagulation exhibited high water quality as RO feed water. The MF system for SWRO pretreatment underwent more severe fouling than the MF system for surface water treatment although the tested seawater quality is much better than the tested surface water quality in terms of fouling potentials. Iron and manganese turned out to be main foulants through water analysis for discharged water from the chemical cleaning procedure. The sources of these ions were stainless steel corroded by seawater. As a conclusion, the metal corrosion by seawater does not only affect leakage in water treatment systems but also induces iron and manganese fouling.

Keywords: Seawater reverse osmosis (SWRO); Pretreatment; Fouling; iron; Manganese; Corrosion

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1. Introduction

Seawater reverse osmosis (SWRO) processes are widely used for desalination to solve the water shortage problem. SWRO processes need pretreatment to decrease the effect of reverse osmosis (RO) membrane fouling. Fouling types are dependent upon water quality parameters [1]. Turbidity and silt density index (SDI) can be related to colloidal or particulate fouling. Hydrogen ion concentration (pH) and sparingly soluble ions concentration affect scaling. Dissolved organic carbon (DOC) and microbial counts are main reasons for organic and biofouling.

Iron and manganese are also potent sources of membrane fouling. If these metallic ions are present in membrane feed water, they can be precipitated to membrane surface and pores as metallic oxide or hydroxide forms in oxidation condition [2]. Seawater, in general, contains very small amounts (parts per billion (ppb) level) of iron and manganese ions [3], however the metallic components of MF/UF system such as feed pump, backwash pump, valves, and pipes can be good sources of iron

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and manganese with a high risk of metal corrosion by seawater.

Generally duel media filtration (DMF) followed by coagulation is most popular option for the pretreatment. This process is economical and effective to control colloidal fouling. Recently microfiltration (MF) or ultrafiltration (UF) is applied as a pretreatment in SWRO processes frequently because of high reliability in treated water quality and less sludge occurrence [4]. Although the construction and operation costs of MF/UF pretreatment system are higher than those of DMF system, it makes it possible to operate SWRO process with higher permeate flux, which decreases its construction and operation cost [5–7].

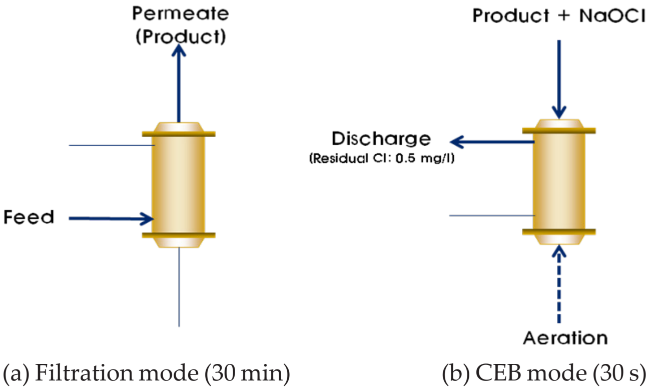
In this study two MF pretreatment systems using the same types of hollow fiber modules were tested for seawater and surface water, respectively. The main purpose of comparing two MF systems was to investigate the effect of metal corrosion on membrane fouling because the MF system using seawater will be affected by corrosion more than that with surface water. These two MF systems were operated with constant flux mode. Changes in trans-membrane pressure with time and water analysis results of cleaning solutions were monitored to elucidate the mechanism and source of MF membrane fouling.

2. Methods

2.1. The MF system for SWRO pretreatment

A commercial hollow fiber MF module manufactured by Toray Industries, Inc. is used for the SWRO pretreatment system. The system details are listed in Table 1.

As listed in Table 1, the system was operated with dead-end filtration mode. Accumulated foulants during filtration were removed by periodic backwash. During backwash, sodium hypochlorite (NaOCl) was introduced to inhibit microbial growth and decrease biofouling potential. The amount of sodium hypochlorite was controlled to maintain 0.5 mg/l of residual chlorine concentration of backwash discharge water. This kind of backwash method is called chemical enhanced backwash (CEB). Aeration was also included to CEB to help attached foulants on the membrane surface to be removed more easily. Fig. 1 shows schematics of filtration and CEB modes used in this system.



(a) Filtration mode (30 min) (b) CEB mode (30 s)

Fig. 1. Schematics of filtration and CEB operation modes. Solid and dashed arrows represent water and air flow directions, respectively while thin solid lines represent the closed pipelines.

Since the system was operated with constant flux mode, transmembrane pressure (TMP) increases when fouling occurs and TMP represents the amount of fouling. When TMP reaches a preset limiting value (i.e. 1.5–2.5 kgf/cm^2 for MF/UF system), membrane should be cleaned using chemicals. The terminology, cleaning in place (CIP), is used when the chemical cleaning procedure is performed without detaching fouled membrane modules. Acid-oriented CIP was carried out by oxalic acid ($(COOH)_2$) with hydrochloric acid (HCl) to remove inorganic foulants such as scaling and heavy metals. Base-oriented CIP was performed by sodium hypochlorite (NaOCl) with sodium hydroxide (NaOH) to remove organic and bio-foulants.

Table 1
The system details for the MF system for SWRO pretreatment

Raw water		Seawater	Membrane type	MF
Operation type		Pressurized	Module type	Hollow fiber
Filtration type		Dead-end	Fiber diameter (mm)	1.5 (outer)/0.9 (inner)
Control type		Constant flux	Pore size (μm)	0.05
Cleaning method	Backwash	Period: 30 min, Duration: 30 s, Chemical enhanced backwash with aeration	Membrane material	PVDF[1]
	CIP[2]	Acid: $(COOH)_2$+HCl Base: NaOCl+NaOH	Membrane area(m^2)	7

[1] PVDF: polyvinylidene fluoride
[2] CIP: cleaning in place

2.2. The MF system for surface water treatment

As discussed earlier, we tested two MF systems to compare the performance in terms of fouling behaviour. One is for SWRO pretreatment as explained above. The other is used for surface water treatment. These two systems are very similar except three following features. First, they were tested with different water sources, seawater and surface water. Second, the MF system for SWRO pretreatment included hollow fiber MF module with 29 m^2 of membrane area while the MF system for surface water treatment adopted the same type of MF module with 7 m^2 of membrane area. Third, sodium hypochlorite (NaOCl) was not used at backwash in case of MF system for surface water treatment.

2.3. Water quality analysis

In a fundamental point of view, fouling behaviour is combination of interfacial interaction between foulant and membrane surface [8–10] and concentrations of the foulants in feed water. Water quality parameters analyzed in this study are listed in Table 2 with analysis method and effect on SWRO processes. Micobial or algae counts were not obtained during the research period. Instead, DOC was regarded as an indirect index for biofouling since organic matter can be a good nutrient source for microbes which induces biofouling. In addition, residual chlorine can be used as another index of biofouling potential. An MF system without residual chlorine should be regarded as being threatened by biofouling. Because sodium hypochlorite was not introduced to the MF system for surface water treatment, it can be said to be exposed by biofouling threatening more than the MF system for SWRO pretreatment.

3. Results and discussion

3.1. Water quality analysis

Results of raw water quality and recommend concentration as RO feed water were listed in Table 3. Water quality of seawater used in this study was almost good enough not to introduce any pretreatment systems while surface water should be treated to be flowed into RO system. As discussed earlier, two similar types of MF

Table 2
Water quality parameters: Analysis method and effect on SWRO processes

Parameter	Turbidity (NTU)	SDI	DOC (mg/l)	Fe (mg/l)	Mn (mg/l)	pH	Ca (mg/l)	Mg (mg/l)	TDS (mg/l)
Method	2100N Turbidimeter, Hach	D 4189-95 ASTM [11]	TOC-V CPH, Shimadzu	AAs[1], AAnalyst 700, Perkin Elmer		pH electrode, Thermo Orion	ICP/MS[2], ELAN DRC-e mode, Perkin Elmer		Conductivity electrode, Thermo Orion
Effect on SWRO	Colloidal fouling		Organic and bio-fouling	Oxidation–precipitation		Scaling			Osmotic pressure

[1] Atomic absorption spectroscopy
[2] Inductively coupled plasma/mass spectroscopy

Table 3
Raw water quality data in case of seawater and surface water

Parameter	Seawater		Surface water		Recommended concentration
	Min	Max	Min	Max	
Turbidity (NTU)	0.10	0.35	0.42	1.02	Turbidity < 1 NTU
SDI	0.1	4.9	>6.67		SDI <3–5
DOC (mg/l)	0.79	1.08	2.02	4.98	DOC <3 mg/l
Fe (mg/l)	<0.01		<0.01		Fe <0.05 mg/l
Mn (mg/l)	<0.01		<0.01		Mn <0.05 mg/l
pH	7.2	8.2	6.4	7.5	Dependent upon recovery rate of SWRO
Ca (mg/l)	373	470	14.6	53.4	
Mg (mg/l)	1,170	1,340	3.4	13.9	
TDS (mg/l)	32,926	34,626	86	472	

[1] Reference: Dow Technical Manual [12]

systems were introduced to make these raw waters into qualified RO feed water. For both cases, product water qualities were highly qualified as RO feed water with regards to colloidal fouling. In the case of seawater, SDI and turbidity were in the range of 0.1 and 1.8 and less than 0.1 NTU, respectively. In the case of surface water, SDI and turbidity were in the range of 1.2 and 2.7 and less than 0.1 NTU, respectively.

It is expected that water quality parameters related to colloidal, organic and bio- fouling should affect not only RO fouling but also MF fouling. According to Table 3, surface water had higher values in turbidity, SDI, DOC, iron, and manganese concentrations, which means surface water was supposed to have higher potential of MF fouling compared to seawater.

3.2. Operation data analysis

The MF system for SWRO pretreatment was operated during about two years. Fig. 2 shows the operation data including TMP and permeate flux with operation time. TMP, an index of MF fouling, was sharply increased with time, which was an abnormal result when we considered a good raw water quality as listed in Table 3. There were less potentials of colloidal fouling (SDI <5 and turbidity <0.4 NTU), organic and bio-fouling (DOC <1 mg/l), and oxidation-precipitation (Fe, Mn <0.01 mg/l). So it was very difficult to elucidate the mechanism of fouling during the operation period. This system underwent three CIP for two years. The time periods from the start-up to each CIP was gradually decreased from 9 months to 7 months. TMP came back its original value at tge start-up (i.e. ~0.05 kgf/cm^2) after CIP, which possibly means there was no irreversible biofouling thanks to CEB.

Since the steep increase of TMP was observed in the MF system for SWRO pretreatment, it can be expected that the TMP increase will be sharper in the MF system for surface water treatment, which had three disadvantages compared to the MF system for SWRO pretreatment in terms of fouling. First, it dealt with feed water of lower quality. Second, the permeate flux was higher (it was increased stepwise from 1 m/d to 1.5 m/d as shown in Fig. 3). Third, there was no residual chlorine in the system because it was operated without CEB, which means it was exposed to the threatening of biofouling.

However, the increase of TMP in this system was slower as shown in Fig. 3 compared to Fig. 2 and there was no need for CIP during the operation period, one and a half year because TMP did not reach the preset limiting value of 1.5 kgf/cm^2. Rather, the decrease of TMP was observed during the period from February of 2007 to October of 2007, which does not mean the foulants on the membrane surface or inside the membrane pores were removed. As the temperature of MF feed water increased during this period, its viscosity decreased to finally increase the permeability of the MF membrane. During this period, TMP decreased because the increase of permeability overcame the hydraulic resistance by MF fouling.

3.3. Fouling analysis

If colloidal, organic and bio- fouling occurred in the MF system for SWRO pretreatment, the increase of TMP would be higher in the MF system for surface water treatment. But the results were different from the prediction as shown in Figs. 2 and 3. So the reason of fouling behaviour observed in Fig. 2 should be searched using a different way from expecting from raw water analysis results as

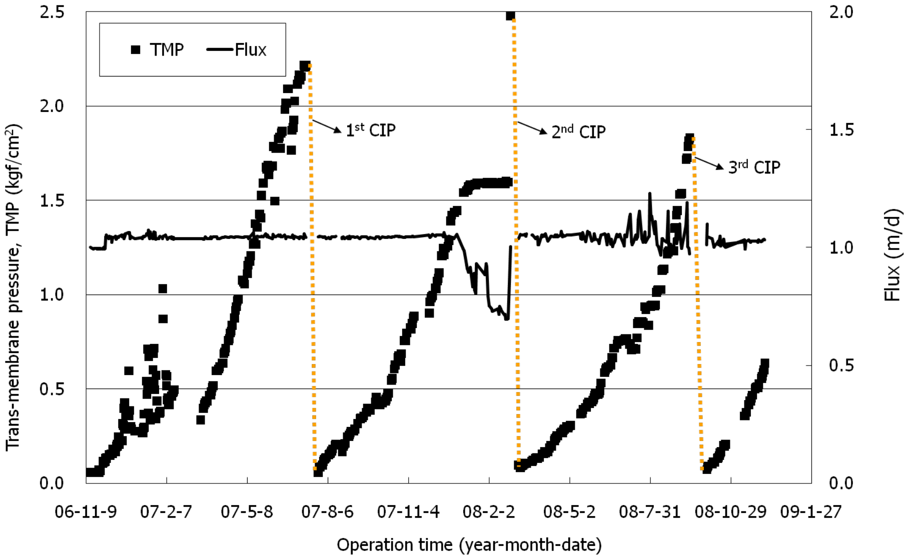


Fig. 2. Operation data of MF system for SWRO pretreatment.

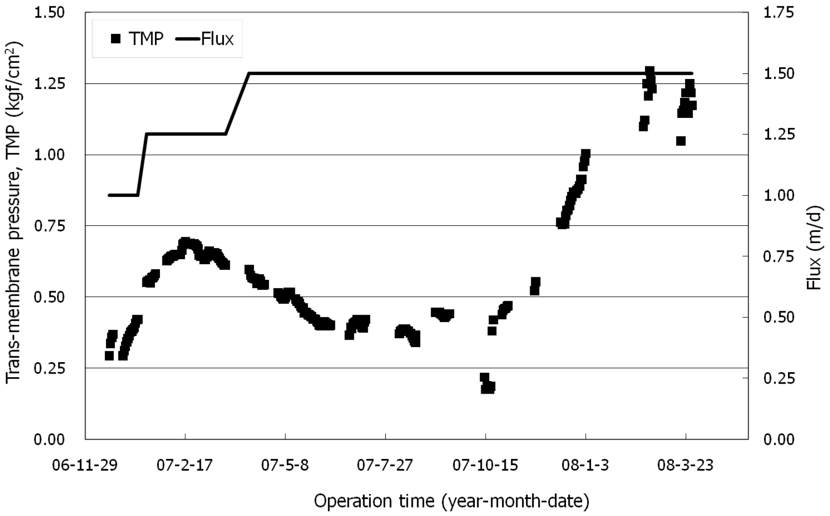


Fig. 3. Operation data of the MF system for surface water treatment.

Table 4
Water analysis data for CIP discharge water quality

	Cleaning chemicals	Ca (mg/l)	Mg (mg/l)	Turbidity (NTU)	Fe (mg/l)	Mn (mg/l)	DOC (mg/l)
1st CIP	HCl (35%) + $(COOH)_2$ (100%)	43.76	88.07	N.A.	72.69	5.62	N.A.
	NaOCl (3,000 mg/L) + NaOH (pH 12)	11.44	9.54	N.A.	0.82	0.053	N.A.
	HCl (35%) + $(COOH)_2$ (100%)	19.54	4.47	N.A.	31.48	0.86	N.A.
2nd CIP	HCl (35%) + $(COOH)_2$ (100%)	22.79	5.37	0.15	16.57	1.18	14.85
	NaOCl (3,000 mg/L) + NaOH (pH 12)	4.83	1.12	0.26	<0.01	<0.01	1.243
	HCl (35%) + $(COOH)_2$ (100%)	25.74	4.75	0.15	0.88	0.03	11.62
3rd CIP	HCl (35%) + $(COOH)_2$ (100%)	17.4	9.13	0.19	3.62	9.13	N.A.
	NaOCl (3,000 mg/L) + NaOH (pH 12)	15.9	1.98	0.25	10.87	1.98	19.97
	HCl (35%) + $(COOH)_2$ (100%)	18.7	5.08	0.08	3.51	5.08	N.A.

listed in Table 3. As the different way, discharged water samples for each CIP were collected and analyzed to find out what kinds of foulants were attached to the membrane as listed in Table 4.

Each CIP consisted of acid-, base-, and acid- oriented cleaning in order as shown in Table 4. Interestingly, iron and manganese were detected in the discharged water samples after acid-oriented cleaning. The concentrations of iron and manganese were greatly larger than those in raw seawater. Concentrations of calcium, magnesium, and turbidity were not negligible but smaller than those in raw seawater, which means these materials were not attached on the membrane surface or inside the membrane pores but they came from residual seawater in the system. Therefore iron and manganese turned out to be the main reasons of fouling behaviour observed in Fig. 2.

By the way, there were no sources of iron and manganese in raw seawater as shown in Table 3. Iron and manganese must have come from a different source. The stainless steel consists of iron, carbon, chrome, nickel, manganese, and so forth. Therefore iron and manganese ions could be extracted from the stainless steel used in the pumps and the valves in the MF system for SWRO pretreatment. Since seawater is highly corrosive, this kind of ions extraction can occur. The most definite proof for this hypothesis was iron concentration data of product water of the MF system, which were in the range of 0.6–1.2 mg/l. Manganese was not detected in the same water, which may be related to the fact that the concentrations of manganese in the CIP discharged water were smaller than those of iron as shown in Table 4. Another strong evidence of iron and manganese extraction from the stainless steel can be observed in the pictures of the rusted automatic valves and pump as shown in Fig. 4.

(a) valves (b) pump

Fig. 4. Rusted valves and pump in the MF system for SWRO pretreatment.

The full scenario for iron and manganese fouling occurred in the MF system for SWRO pretreatment can be explained as follows:

(1) Iron and manganese ions are extracted from the stainless steel used in valves and pumps.
(2) Introduction of CEB and aeration makes these ions oxidized.
(3) Oxidized manganese and iron form precipitates such as iron(III) oxide (Fe_2O_3), iron(III) hydroxide ($Fe(OH)_3$), and manganese dioxide (MnO_2).
(4) These precipitates are attached on the membrane surface or inside the membrane pores, which finally results in a large amount of hydraulic resistance as shown in Fig. 2.

4. Conclusions

It is well known that seawater is highly corrosive. Stainless steel used in seawater treatment systems could be damaged to make leakage in the systems. This study concludes that the metal corrosion by seawater does not only affect this kind of leakage but also makes severe fouling by iron and manganese in oxidation state such as aeration and residual chlorine.

Although aeration and residual chlorine are necessary to physically clean the membrane and inhibit biofouling, but we should consider iron and manganese concentration of feed water when we introduce aeration and residual chlorine to the system. In addition, selection of high-level stainless steel is essentially required to inhibit the intrusion of iron and manganese to membrane-based water treatment system, not only the high pressure systems such as NF and RO but also the low pressure systems such as MF and UF.

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