Performance and foulants characterization of the industrial integrated membrane system

Huijia Luo1,2,a, Yong Cui 2,b, Zhan Wang1,c*, Yangyang Guo1,d and Xi Wang3,e*

1Beijing Key Laboratory for Green Catalysis and Separation, Department of Chemistry and Chemical Engineering, Beijing University of Technology, Beijing, 100124, China
2Beijing Boda Water Co., Ltd, Beijing 100176, China
3Centre of Sino-Western Cultural Studies, School of Humanities and Social Sciences, Macao Polytechnic Institute, Macao, China

aemail: luohuijia123@126.com, bemail: shushang111@126.com, demail: y18831333348@163.com

c*Corresponding author’s e-mail: cemail: wangzh@bjut.edu.cn

eemail: dwhx4077@163.com

Abstract. In order to objectively elucidate the state of the membrane after long-term operation, the performance of a full-scale microfiltration-reverse osmosis (MF-RO) integrated membrane system with production capacity of 20,000 m$^3$/d for wastewater reclamation was evaluated by collecting 10 years performance data. The foulants on 1 MF membrane and 12 RO membranes along the feed channel also were analyzed by membrane autopsy. The results indicate that the water quality of the system can still meet the customer requirements while the mechanical and desalting properties of the membranes were close to the abandoned standards. In terms of foulants distribution, the MF membrane surface was covered by a thick cake layer and the leading RO membrane suffered the highest fouling load. The predominate organic foulants on the membrane surface were protein and polysaccharide, and the main inorganic foulants were Fe and Ca, and their distribution showed two different trends along the feed channel. Regarding bio-foulants, the compositions of bacterial colonies on 12 RO membranes were basically the same, but the relative abundance of the dominant bacteria was different and the microbial diversity increased gradually from the leading element to the terminal one in both the two stages.

1. Introduction

Among the numerous wastewater depth treatment technologies, the integrated membrane system consisting of the microfiltration (MF) membrane followed by the reverse osmosis (RO) membrane have occupied a large market share due to their advantages in outstanding water quality, easy operation and stability [1,2]. However, although the secondary effluent meets the discharge standard, it still contains higher concentrations of suspended particles, organics and organisms [3,4]. So, the membrane fouling is inevitable and it resulted in the decreasing permeate flux and frequent chemical cleaning [5,6].

Identifying the membrane foulants could help to understanding the fouling mechanisms and developing an optimal cleaning procedure. Membrane autopsy is undoubtedly the most direct and effective way to achieve this goal. In terms of the MF membrane, Nghiem and Schäfer [7] investigated the cause of the membrane fouling in a small water recycling system and found that the membrane
surface was fouled with a mixture of colloids and organic matters. Pontié et al. [8] found that the membrane material was more sensitive to hydrophobic organics. Gupta and Chellam [9] reported the fouling mechanisms of effluent organic matters on the PVDF MF membrane. Regarding the RO membrane, Tang et al. [10] autopsied one used membrane from a wastewater reclamation plant and elucidated the composition relationship between fouls and feed water. Yu et al. [5] compared the composition of fouls on the four RO membranes before and after cleaning and proved that some bacteria cannot be removed by chemical cleaning. Kim et al. [11] found that the major contributor to RO membrane fouling was fulvic acid. However, all of the autopsy experiments were performed only on the leading element and the terminal one or collected from different plants, there are still no reports concerning both the MF membrane and RO membrane along the feed channel. Meanwhile, most of the published researches did not show the long-term operating data before autopsy.

In this study, we analyzed the performance of a full-scale integrated membrane system based on the 10 years’ operating date. The fouls on the surface of the MF and RO membranes along the feed channel were characterized by autopsy method. The aim of the study was to evaluate the performance of the membrane after 10 years of operation and identify the major foulants on the membrane surface.

2. Materials and Methods

2.1. The MF-RO integrated membrane system description
The MF-RO integrated system studied in the present study has a capacity of 20,000 m³/d and has been operating continuously for 10 years under the set filtering and cleaning procedure. Its feed water is secondary effluent from an adjacent sewage treatment plant. The RO unit in the integrated system has two stages, and each stage contain 6 membrane elements. The 12 RO membrane elements were numbered in sequence along the feed channel (from RO 1-RO 12).

2.2. Methods of membrane property evaluation and surface observation
Before membrane autopsy, the weight of the used membrane was measured. The tensile strength and elongation at break of the MF membrane were measured with electronic tensile testing machine (JBDL-200, China). The salt rejection of each RO elements was determined using a single testing device. The microstructure of the used membrane surface was observed by a scanning electron microscope coupled with energy dispersive X-ray fluorescence spectrometer (SU8200, HITACHI, Japan).

2.3. Methods of foulants characterization
ICP-MS (ELANDCR-e, PerkinElmer, USA) and fluorescence spectrophotometer (F-7000, Hitachi, Japan) were respectively employed to identify inorganic and organic foulants. E.Z.N.A.® Water DNA Kit (Omega Bio-tek, USA), Gel Extraction Kit (QIAEX II, Qiagen, Germany) and sequencing using the Illumina MiSeq platform (PE300, Illumina, USA) were used to analyze microbial community.

3. Results & Discussion

3.1. Performance of the integrated membrane system
The water quality at different locations in the integrated membrane system were summarized in Table 1. Due to the span of 10 years, the change range of water quality was relatively large. For example, the TOC and TN in the feed water was respectively in the range of 1.43-8.2 mg/L and 9.56-25.8 mg/L. Even so, the effluent quality of the integrated membrane system was relatively stable and still could meet the water standard of downstream customers (TDS below 80 mg/L).

| Water quality index | Feed water | MF membrane permeation | RO membrane permeation |
|---------------------|------------|------------------------|-----------------------|
| Total organic carbon (TOC, mg/L) | 1.43-8.2 | 1.17-5.53 | 0.5-1.96 |
| Total nitrogen (TN, mg/L) | 9.59-25.8 | 10.4-23.2 | 0.16-3.26 |

Table 1. Summary of water quality at different locations in the integrated membrane system.
Chemical oxygen demand (COD, mg/L) | 8-53.6 | 13.1-48.6 | < 5 
Total Dissolved Solids (TDS, mg/L) | 967-1370 | 1020-1380 | 30-77 
Fe (mg/L) | 0.02-0.84 | 0.001-0.088 | < 0.001 
Ca (mg/L) | 79.1-178 | 53-169 | 0.15-6.36 
Mg (mg/L) | 13.3-33.5 | 1.47-22.7 | 0.063-1.54

Table 2. Tensile strength and elongation at break of the used MF membrane and new membrane.

| Membrane type | Tensile strength (MPa) | Elongation at break (%) |
|---------------|------------------------|------------------------|
| The used membrane | 0.93±0.09 | 43.62±2.06 |
| New membrane | 1.09±0.13 | 65.18±3.47 |

The images of the used MF membrane highlight the presence of a fouling layer over the outer and inner surfaces (figure 2(a) and figure 2(c)). The EDX spectra of cake layer indicated that the foulants on the outer surface of hollow-fiber had high levels of Si, Fe, Al, Mn, Zn and P (figure 2(b)), whereas the foulants on the inner surface had high levels of Fe, Ca, Zn and P (figure 2(d)).
3.3. RO Membrane properties analyzing and foulants characterization

In order to analyze the property of each RO membrane along the feed channel, 12 RO membranes were collected from the same pressure vessel of the first and second stages. As showed in Table 3, the weights of all the used membrane were higher than that of the new one and RO 1 was the heaviest (16.25 kg). Along the feed channel, except for RO 10, the membrane becomes lighter and lighter. Regarding for the salt rejection efficiency, the rejection value first increased and then decreased along the feed channel, and RO 5, RO 6 and RO 9 have higher salt rejection efficiency (97.55-97.86%) but still was lower than that of the new one (about 98.85%). In terms of the contact angle, all the used membranes exhibit hydrophobicity, and compare to that of the leading membrane (RO 1) and terminal membrane (RO 12), the membrane elements in the middle showed higher hydrophobicity. This mainly because that the feed water contains many hydrophilic components, which were cannot be rejected by MF membrane and more likely to deposit at both ends of the RO membrane system. However, this hydrophilic change is limited because hydrophobic substances are more likely to deposit on the RO membrane surface, even if there were more hydrophilic fractions in the feed water.

Table 3. Weights, salt rejection and contact angle of the used RO membranes and new membrane.

|       | RO 1 | RO 2 | RO 3 | RO 4 | RO 5 | RO 6 | RO 7 | RO 8 | RO 9 | RO 10 | RO 11 | RO 12 | New one |
|-------|------|------|------|------|------|------|------|------|------|-------|-------|-------|---------|
| Membrane weights (kg) | 16.2 | 15.1 | 15.1 | 14.9 | 14.8 | 14.4 | 14.7 | 14.7 | 14.5 | 15.3 | 14.4 | 14.3 | 13.2    |
| Salt rejection (%)     | 93.5 | 94.9 | 97.0 | 97.3 | 97.6 | 97.8 | 97.6 | 97.2 | 97.8 | 95.6 | 96.7 | 95.3 | 98.5    |
| Contact angle (°)      | 91.5 | 93.8 | 96.6 | 96.2 | 96.9 | 97.8 | 95.7 | 96.4 | 98.8 | 98.8 | 94.3 | 92.3 | 91.7    |

Figure 3(a) shows the relationship between the contents of major inorganic elements on the used membranes and its concentrations in the feed water. Obviously, in either membrane, the contents of Fe and Ca are higher than that of Mn, Mg and Si, and the biggest content of Fe on RO1 was 208 mg/m² even the concentration of Fe in the feed water only was 0.84 mg/L. This indicates that the previous chemical cleaning has limited removal of Fe, allowing it accumulated continuously. Along the feed channel, the Fe content basically becomes lower and lower, while the Ca content becomes higher and higher. This is closely related to their interactions with organic foulants on the membrane surface. As showed in the figure 3(b), the fluorescence intensity of organic foulants mean that R1 has the highest levels of organic foulants and the main organic foulants on the RO membranes were protein and polysaccharide which were abundant in wastewater.
Figure 3. Concentration of inorganic elements in feed water and content in cake layers (a) and Fluorescence EEM spectra of organic foulants (b) on the 12 RO membranes.

Regarding for microbial foulants, the structure of the microbial communities on the 12 membranes were showed in figure 4. At order level, the composition of microbial communities was basically the same, and the dominant bacteria all were Burkholderiales, Cytophagales and Sphingobacteriales. However, the relative abundance of each bacteria varied across 12 membranes. For example, the relative abundance of Burkholderiales on RO1, RO5 and RO12 respectively was 15.95%, 20.09% and 13.01%, while the relative abundance of Sphingobacteriales on RO1, RO5 and RO12 respectively was 5.55%, 30.01% and 23.97%. In addition, the variation trend of Shannon-Wiener diversity index indicated that both in the first and second stages, the microbial diversity were increasing from the leading membrane to the terminal one. The main reason may be that under the constant flux mode, the hydraulic pressure and cross-flux velocity on the surface of the first membrane is higher than others in the same pressure vessel. This makes it difficult for new bacteria to attach and colonize on the membrane surface.

Figure 4. Microbial communities of the foulants on the RO membranes surface at the order level

4. Conclusions

In this study, the performance of a full-scale MF-RO integrated membrane system was evaluated and the foulants on the membrane surface were identified. Results showed that although the inlet water quality has a wide range of variation and the system has been in continuous production for 10 years, its permeation can still meet the standard of customers. But the elongation at break of the MF membrane was 67% of that of the new one, and the desalting rate of 12 RO membranes along the feed channel was in the range of 93.57% to 97.86%. All these indicate that both MF membranes and RO membranes equipped in the integrated system were close to the replacement standard. Among the 12 RO membranes, the leading membrane (RO1) suffered the most serious membrane fouling, and it was 13.29% heavier than the new membrane. For all used RO membranes, the major inorganic foulants are Fe (the highest
is 208 mg/m²) and Ca (the highest is 27.8 mg/m²). The predominant organic foulants were protein and polysaccharide. About biofouling, the composition of microbial communities on the 12 membranes were basically the same. However, the relative abundance of the dominant bacteria varied in each membrane and the microbial diversity increased gradually from the leading element to the terminal one in both the first stage (from RO1 to RO6) and the second stage (from RO7 to RO12).

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