Evaluation of a long-term operation of a submerged nanofiltration membrane bioreactor (NF MBR) for advanced wastewater treatment

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Abstract Nanofiltration (NF) is considered as one of the most promising separation technologies to obtain a very good-quality permeate in water and wastewater treatment. A submerged NF membrane bioreactor (NF MBR) using polyamide membranes was tested for a long-term operation and the performance of the NF MBR was compared with that of a microfiltration MBR (MF MBR). Total organic carbon (TOC) concentration in the permeate of the NF MBR ranged from 0.5 to 2.0 mg/L, whereas that of the MF MBR showed an average of 5 mg/L. This could be explained by the tightness of the NF membrane. Although the concentration of organic matter in the supernatant of the NF MBR was higher than that in the permeate due to high rejection by the NF membrane, the NF MBR showed excellent treatment efficiency and satisfactory operational stability for a long-term operation.

Keywords Advanced wastewater treatment; hollow fiber membrane; microfiltration (MF) membrane; nanofiltration (NF) membrane; nanofiltration membrane bioreactor (NF MBR)

Introduction

The membrane bioreactor (MBR) system is a combination of biological wastewater treatment and membrane separation process. It has several advantages over the conventional activated sludge process such as a small footprint, complete solid-liquid separation, no bulking sludge problem and retrofitting potential. The submerged MBR system using a microfiltration (MF) membrane has demonstrated good treatment performance in terms of permeate quality and quantity. The MBR system, therefore, has been increasingly applied in small-scale wastewater treatment plants for last two decades (Stephenson *et al.*, 2000).

A variety of chemicals with known or unknown health risks are being synthesized every year, and these compounds are found eventually in the aquatic environment through discharges of municipal, agricultural, and industrial treated wastewater. To ensure a safe and adequate water supply in the present and future, it is of paramount importance to minimize and prevent the discharge of micro-contaminants such as endocrine disrupting chemicals into receiving water bodies. The nanofiltration (NF) process is a potential wastewater treatment technology that controls the discharge of micro-contaminants into the water environment, allowing protection of existing water sources from pollution. Until recently, NF membranes have been limited to treating the secondary effluent from conventional activated sludge process or MF MBR system for advanced wastewater

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treatment. However, some recent findings demonstrated that the combination of bioreactor and NF membrane, i.e., a submerged NF MBR, could provide extra-clean permeate and reasonable operational performance (Dockko and Yamamoto, 2001; Choi *et al.*, 2002). In addition, a submerged NF MBR using cellulose triacetate (CA) NF membranes has been tested recently in order to investigate whether the NF MBR system is available for a long-term operation in the treatment of real municipal wastewater (Choi *et al.*, 2005). The results showed that CA membrane has considerably good performance in terms of water productivity and water quality. However, as the permeate quality from the CA membrane deteriorated with operation time, the performance of the NF MBR was unsatisfactory for practical use. Hence, polyamide (PA) membranes, which offer better rejection of dissolved organic matter consistently, were used in this study.

The objective of this study was to assess the performance of a submerged NF MBR by comparing it with that of a conventional MF MBR for municipal wastewater treatment, and to evaluate the viability of a submerged NF MBR for long-term operation.

Methods and materials

Membrane characteristics

A hollow fiber module of the NF membrane (Toyobo, Japan) made of PA materials was used in this study. The original membrane modules were modified for adaptation in the submerged MBR system. As the NF membrane has low water productivity, the hollow NF fiber membrane module was constructed with a significantly large number of membrane fibers in order to provide a large effective membrane surface for achieving better water productivity. To compare the performance between the NF and MF MBRs, an MBR using MF membranes (Mitsubishi Rayon, Japan) was operated simultaneously. Table 1 presents the specifications of the NF and MF membrane used in this study.

Experimental setup

Three NF membrane modules (NF#1, #2 and #3) and a MF membrane module were immersed in the NF MBR and the MF MBR, respectively. Municipal wastewater obtained from a wastewater treatment plant located in Tokyo, Japan, was used as the influent for each MBR. The average concentration in the influent wastewater for total organic carbon (TOC) was 62.6 ± 15.4 mg/L, for total nitrogen (T-N) was 24.9 ± 7.5 mg/L, and for total phosphorus (T-P) was 6.5 ± 6.1 mg/L.

Each MBR was seeded with activated sludge from a wastewater treatment plant at mixed liquor suspended solid (MLSS) concentration of approximately 3,600 mg/L. The hydraulic retention time (HRT) for each MBR was set at two days by which initial flux as low as 0.0005 m/d was attained in order to minimize membrane fouling. Daily withdrawal of mixed liquor (ML) was carried out from each MBR to maintain a sludge retention time (SRT) of

Table 1 Characteristics of NF and MF membrane module

Items	NF membrane	MF membrane
Membrane module	U-shaped hollow fiber	Parallel-shaped hollow fiber
Membrane material	Polyamide	Hydrophilic polyethylene
Nominal pore size	n.a.[a]	0.1 μm
Number of fiber/module	60,000	1,210
Surface area	10.4 m^2	0.2 m^2
Salt rejection[b]	94%	n.a.
Pure water permeability[c]	0.080 $L/m^2 \cdot kPa \cdot d$	n.a.

[a]Not available
[b]The information on the salt rejection was obtained from the membrane manufacturer
[c]Mean value of three NF membranes (operating temperature: 25 °C)

40 days from reactor startup to Day 38, and 80 days thereafter. For the NF MBR, the NF membrane modules were wrapped with nylon fabric in order to control cake development on the membrane fibers. The operating conditions of each MBR are summarized in Table 2.

Analytic methods

Water samples for all analysis, except the TOC and T-P of influent, were prefiltered using 0.45 μm membrane filters prior to measurement. Supernatant was obtained by centrifuging each ML from the bioreactors for five minutes at 3,000 × *g* using a centrifuge (H-3R, Kokusan, Japan) followed by filtering with a 0.45 μm cellulose acetate membrane filter. TOC and dissolved organic carbon (DOC) of the influent and supernatant were measured using a Shimadzu TOC 500 analyzer with an auto-sampler. TOC of the permeate was analyzed using a Shimadzu TOC 5000A analyzer.

To fractionate the dissolved organic matter (DOM) in the supernatant and permeate, XAD-8 and XAD-4 resins were used in this study. The detailed measurement protocol is given elsewhere (Imai *et al.*, 2002). Gel permeation chromatography (GPC) was used to determine the molecular weight (MW) distribution of DOM in water samples. GPC analysis was carried out by high-performance liquid chromatography (LC 10A, Shimadzu, Japan) using the Protein KW 802.5 column (Shodex, Japan). To calibrate the equipment, a variety of polystyrene sulfonates (PSS; MW 208, 1800, 4600, 8000 and 18000 Daltons) were used as the standards. Other water quality indices were analyzed in accordance with the *Standard Methods* specified by Japan Sewage Works Association (1997).

Results and discussion

Removal and fractionation of organic matter

Figure 1 illustrates the profile of TOC concentrations in the permeate produced from the NF and MF MBRs during the operation. These results showed that the NF MBR outperformed the MF MBR in terms of permeate quality. The TOC concentrations in the permeate of the NF MBR ranged from 0.5 to 2.0 mg/L, with NF#2 and #3 consistently below 1.0 mg/L after Day150. Hence, PA membranes could produce consistently high quality permeate, suggesting that a NF MBR is better in the removal of organic matter compared to a MF MBR.

The molecular weight (MW) distribution of the DOC in the supernatant and TOC of the permeate of the NF MBR was analyzed using a GPC and expressed in terms of UV absorbance at a wavelength of 260 nm over the elution time (Figure 2). The UVA peak of supernatant responded from approximately 23,684 Daltons with the largest fraction of 2,096 Daltons, whereas the response peak of permeates appeared from 9,358 Daltons with the highest peaks of 1,317 Daltons and 607 Daltons. These results suggest that the NF membranes employed in this study did not reject completely organic matter with molecular weight higher than 607 Daltons. This unexpected finding indicates that the NF membranes are not as tight as expected. To obtain a permeate with better quality from the NF MBR, tighter NF membranes would be required.

To fractionate the DOM in the supernatant and permeate of the NF MBR, water samples were taken at five different time intervals during the operation, fractionated using XAD-8 and XAD-4 resins, and analyzed for DOC concentrations (Table 3).

Table 2 Operating conditions in each reactor

	Volume (L)	Initial flux (m/d)	HRT (days)	SRT (days)	Filtration mode
NF MBR	31.2	0.0005	2.0	40 → 80	Intermittent (5-min run and 5-min pause)
MF MBR	10	0.025			

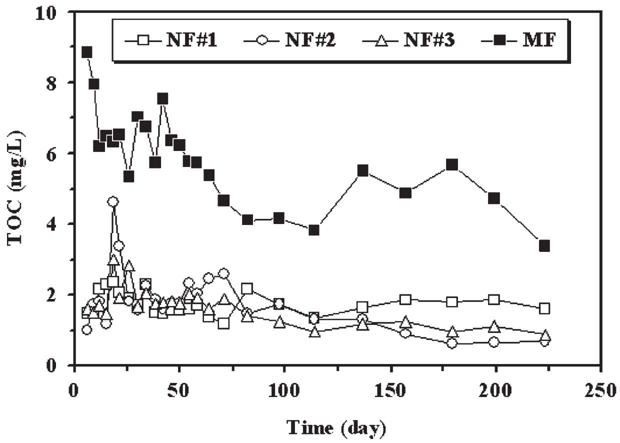

Figure 1 Profile of TOC concentrations in the permeates of the NF and MF MBRs

The DOC of the supernatant consisted of 45% of hydrophobic (HPO; XAD-8 adsorbable) fraction, 30% of transphilic (TPI; XAD-4 adsorbable) fraction, and 25% of hydrophilic (HPI; neither XAD-8 nor XAD-4 adsorbable) fraction, whereas the HPO, TPI, and HPI fractions in the permeates were approximately 20%, 30% and 50%, respectively. This indicates that electrical property and size exclusion of the NF membranes was functioning properly throughout the operation. Since the HPO and TPI fractions possess MW higher than HPI fraction and negative charge due to deprotonated carboxylic groups, size exclusion and electrostatic repulsion may decrease permeation of the fractions in NF process.

Organic matter and sludge concentration in the bioreactors

NF membranes have generally high rejection in terms of salts, color and organic carbon. Thus, periodic withdrawal of ML from the NF MBR is required to prevent their accumulation for a sustainable long-term operation. Figure 3 shows the changes of DOC in the supernatants of the NF and MF MBRs. Due to high rejection of NF membranes, the DOC concentration of supernatant in the NF MBR increased rapidly from about 18 mg/L to a maximum of approximately 30.0 mg/L within the first 60 days of reactor operation. In contrast, the supernatant of the MF MBR showed a low concentration of DOC with minimal fluctuations. Although such increase influenced the performance of NF MBR negatively, particularly in terms of its flux and transmembrane pressure (TMP), which is

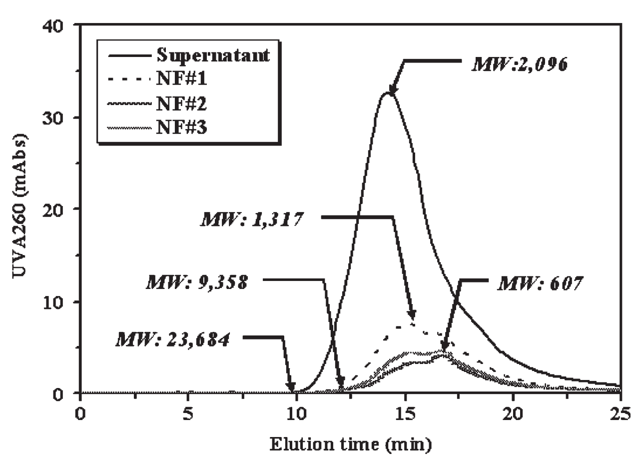

Figure 2 MW distribution of the supernatant and permeates of the NF MBR

Table 3 Fractionation of DOC in the supernatant and TOC in the permeates of the NF MBR

Items	HPO fraction		TPI fraction		HPI fraction	
	DOC* (mg/L)	Percent (%)	DOC* (mg/L)	Percent (%)	DOC* (mg/L)	Percent (%)
Supernatant	11.0 ± 2.12	45.4 ± 4.09	7.29 ± 1.02	30.4 ± 2.21	5.74 ± 1.04	24.2 ± 4.86
NF#1	0.32 ± 0.23	17.0 ± 11.1	0.69 ± 0.19	41.4 ± 8.78	0.69 ± 0.14	41.6 ± 8.46
NF#2	0.31 ± 0.24	17.6 ± 9.78	0.51 ± 0.39	32.2 ± 10.8	0.77 ± 0.50	50.2 ± 11.1
NF#3	0.24 ± 0.17	15.7 ± 5.84	0.32 ± 0.18	21.7 ± 9.90	0.90 ± 0.30	62.6 ± 14.0

*For permeate, TOC is equal to DOC
The data represent mean value ± standard deviation

being discussed in the next section, the submerged NF MBR showed satisfactory treatment efficiency and stability over 200 days of operation (see Figure 1).

MLSS and mixed liquor volatile suspended solid (MLVSS) concentrations in the NF MBR dropped rapidly during the first 20 days due to the attachment of biomass on the nylon fabric and membrane surface. Thereafter, the values varied between 510 and 940 mg/L and between 320 and 680 mg/L, respectively (data not shown). Interestingly, there were no significant increases in MLSS and MLVSS in the NF MBR after Day 20. This could be attributed to a low volumetric load (approximately 0.03 g TOC/L day), a large surface area of the NF membrane and periodic withdrawal of ML to achieve the target SRT.

Salt rejection and change of permeate flux and TMP

Since salt rejection is an important parameter for assessing the performance of NF membranes, the rejection in the submerged NF MBR was monitored throughout the operation in terms of monovalent (Cl^-) and multivalent (SO_4^{2-} and PO_4^{3-}) anions rejection (data not shown). The rejection of chloride ion was found to be relatively low (20% more or less), while the rejection of sulfate and phosphate ion was almost higher than 80%. In addition, the stable salt rejections observed in the NF MBR suggest that the electrostatic property of the NF membrane surfaces remained consistent throughout the operation.

Figure 4 shows the averaged values of relative flux (water productivity) and TMP of the three NF membranes in the NF MBR, since their differences between the NF membranes employed in this study were effectively negligible. Both the relative flux and the TMP in the NF MBR did not show significant changes throughout the operation because the initial fluxes of PA membranes were very low (0.0005 m/d) and the wrapping of the NF membranes using nylon fabric had prevented biomass from attaching to the

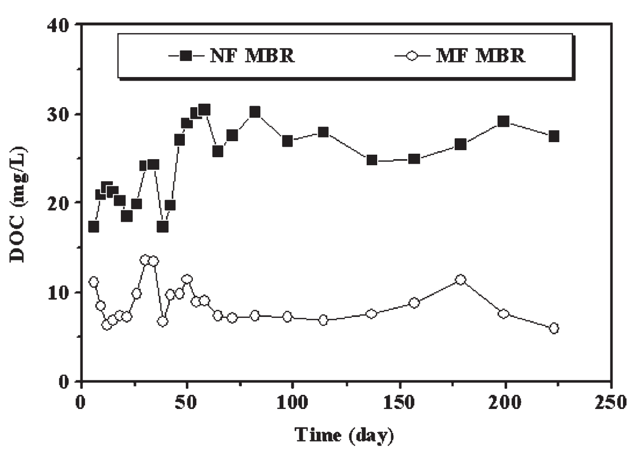

Figure 3 DOC change in the supernatant of each MBR

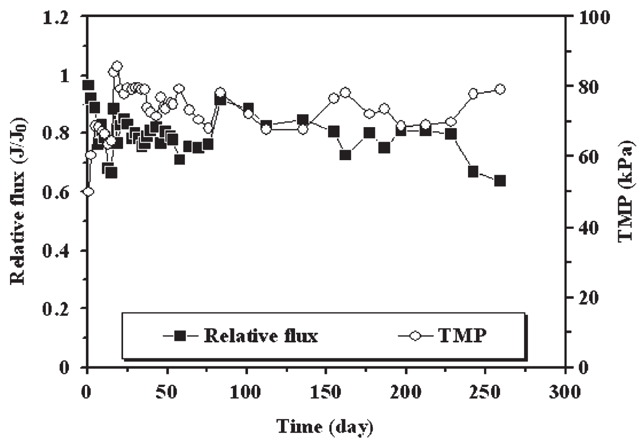

Figure 4 Changes of relative flux and TMP in the NF MBR. Each value was expressed as the average of tyhe results of the NF membranes

membrane surface significantly. Averaged TMP of the NF membranes increased from an initial value of approximately 45 kPa to between 65 to 80 kPa subsequently. The increase in TMP from the initial value could be attributed to the buildup of osmotic pressure due to high salt rejection by the NF membrane.

Conclusions

To evaluate the feasibility of a submerged NF MBR for advanced municipal wastewater treatment, the performance of a submerged NF MBR was investigated for a long-term operation. The submerged NF MBR using PA membranes consistently produced excellent-quality permeates, with TOC concentration ranging from 0.5 to 2.0 mg/L. The result of the GPC analysis showed that the UVA peak of permeates from the NF MBR appeared from 9,358 Daltons with the highest peaks of 1,317 Daltons and 607 Daltons. MW distribution data of permeate indicates that permeate quality in the NF MBR can be improved further if tighter NF membranes are used. The rejections of monovalent ion, Cl^-, and multivalent ions, such as SO_4^{2-} and PO_4^{3-}, were about 20% and almost above 80%, respectively. Due to consistent high salt rejection, the averaged TMP was maintained around 80 kPa after increasing from an initial value of about 45 kPa. It was concluded that a submerged NF MBR could be a sustainable process for advanced municipal wastewater treatment.

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