Comparison of treatment efficiency of submerged nanofiltration membrane bioreactors using cellulose triacetate and polyamide membrane

Water Science & Technology **Vol 51 No 6–7 pp 305–312** © IWA Publishing 2005

J.-H. Choi*, K. Fukushi and K. Yamamoto*****

*Department of Urban Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan (E-mail: *cjh@env.t.u-tokyo.ac.jp*)

**Environmental Science Center, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan (E-mail: *fukushi@esc.u-tokyo.ac.jp*)

***Environmental Science Center, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan (E-mail: *yamamoto@esc.u-tokyo.ac.jp*)

Abstract This study evaluates the performance of nanofiltration membrane bioreactor (NF MBR) systems using cellulose triacetate (CA) and polyamide (PA) membranes. The results indicated that both NF membranes could produce high quality permeate in the submerged NF MBR system. In addition, hollow fiber CA membranes exhibited the capability of higher permeate productivity than PA membranes. However, to obtain high quality permeate for a long-term operation, CA membranes should be maintained using an appropriate method, such as chlorine disinfection, in order to control the membrane biodegradation. The results demonstrated that PA membranes were capable of producing higher quality permeate for a long period than CA membranes. In order to enhance the practicability of PA membranes in submerged NF MBR systems, it is required that the membranes should have the lowest possible intrinsic salt rejection.

Keywords Cellulose triacetate; membrane performance; nanofiltration; polyamide; submerged system; treatment efficiency

Introduction

Membrane separation technology, mainly microfiltration (MF) and ultrafiltration (UF) membranes, has been widely used in membrane bioreactor (MBR) systems. The MBR systems are biological wastewater treatment processes that employ membrane as a liquid-solid separator. These systems have demonstrated their potential and superiority as an advanced wastewater treatment process for the improvement of wastewater effluent quality in the last two decades.

Nanofiltration (NF) membranes, positioned between reverse osmosis (RO) and UF membranes, are the same as RO membranes except that their network structure is more open. NF membranes can reject uncharged organic molecules and ionic matter. Uncharged materials are dominantly rejected by size exclusion, and ionic substances are removed by electrostatic interaction between ions and the functional groups of membrane surface (Childress and Elimelech, 1996). It has been demonstrated that organic compounds with low molecular weight such as pesticides can be effectively removed using NF membranes (Agbekodo *et al.*, 1996). Additionally, applications of NF membranes have been increasingly broadened in advanced water and wastewater treatment due to the development of high-performance membranes including low-pressure membranes.

Meanwhile, the introduction of tighter or denser membranes such as NF membranes into the submerged MBR technology has been tested to obtain better wastewater effluent, and consequently meet increasingly stringent wastewater discharge standards (Dockko and Yamamoto, 2001; Choi *et al.*, 2002). Although NF membranes are rarely applied to the MBR systems due to their high hydraulic resistance, the NF MBR system has the potential for rejecting micro-contaminants such as endocrine disrupting chemicals (EDCs) and pesticides that adversely affect human health and safety. The MBR system using MF and UF membranes cannot remove the micro-contaminants to a satisfactory level, whereas the submerged NF MBR system can minimize their release into the water environment.

This study aims to compare the treatment efficiency of submerged NF MBR using cellulose triacetate (CA) and polyamide (PA) membranes, and to evaluate the performance of both NF MBR systems in order to develop an adequate NF MBR system for advanced wastewater treatment.

Methods

Representative NF membrane modules

Commercial hollow fiber NF membrane modules (Toyobo Co., Ltd.) were used in this study. These modules were modified to the submerged type for the suction mode, since they were originally designed for the pressure-driven mode. The membranes are classified into two types, CA and PA membranes. Specifications of the NF membranes are listed in Table 1. These membranes are tighter or denser than the cellulose diacetate (CDA) membrane used in the previous study (Choi *et al.*, 2002).

Experimental set-up

Experimental work was conducted in two series, that is, three modules of each NF (CA and PA) membrane were directly immersed in the bioreactors, respectively. During all experimental stages, peristaltic pumps were used for suction from the membrane modules. Although the bioreactors were operated at room temperature, there were some deviations of water temperature in the reactors. A schematic diagram of the experimental set-up is illustrated in Figure 1.

Feed was obtained from a municipal wastewater treatment plant in Tokyo, Japan. The average water qualities of raw wastewater are listed in Table 2.

Activated sludge at MLSS concentration of approximately 3,600 mg/L was initially added to each bioreactor as seed. The hydraulic retention time (HRT) was set at approximately two days by which initial flux could be got as low as 5×10^{-4} m/d. The CA and PA membrane modules were wrapped with nylon fabric in order to control activated sludge's attachment to the membrane fibers.

For the CA membrane bioreactor, the membrane material is susceptible to hydrolysis between pH 6 to 8 and also biodegradation using microorganisms. CA#2 and CA#3 membranes were, therefore, periodically flushed with tap water containing residual free chlorine (below 0.4 mg/L) as a preventive measure against microorganism' attack. This equipment is expected to control severe concentration polarization at the surface of NF membranes as well. The operating conditions of each bioreactor are listed in Table 3.

Table 1 Properties of the NF membrane modules

Items	CA membranes	PA membranes
Membrane configuration	U-shaped hollow fiber	U-shaped hollow fiber
Membrane material	Cellulose triacetate	Polyamide
Outer diameter	177 μm	205 μm
Inner diameter	86 μm	86 μm
Number of hollow fiber per module	81,000	60,000
Surface area per module	12.1 m^2	10.4 m^2
Membrane length	270 mm	270 mm
Salt rejection*	94%	94%
Manufacturer	Toyobo Co., Ltd.	Toyobo Co., Ltd.

*Test conditions: (1) target solution: 500 mg/L NaCl solution, (2) operating pressure: 0.98 MPa, (3) temperature: 25 °C, (4) recovery ratio: 30%

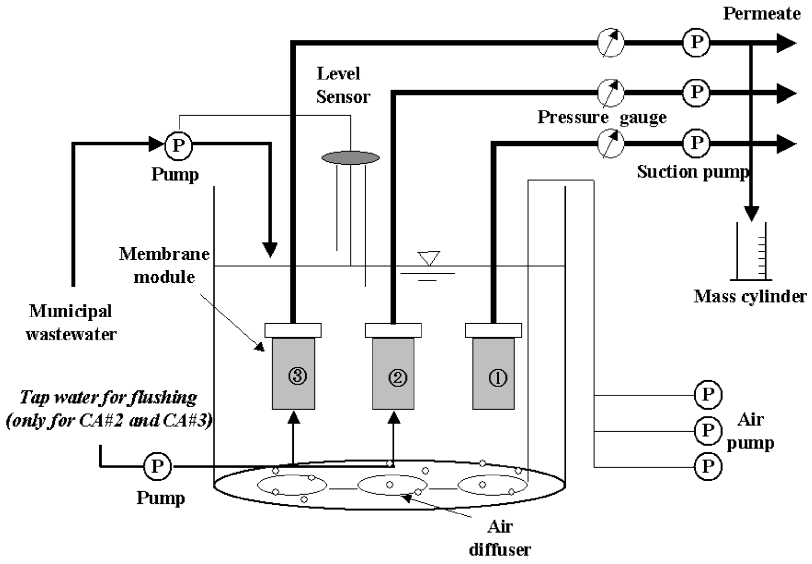

Figure 1 Schematic diagram of the experimental set-up of NF MBRs; there was set with the flushing equipment for membrane in CA MBR and excluding it in PA MBR

Analytical methods

In order to measure water qualities except for total COD and total phosphorus, all samples were filtered using 0.45 μm cellulose acetate membrane filters (DISMIC, Toyobo). Organic compounds such as total organic carbon (TOC) and dissolved organic carbon (DOC) were measured using TOC analyzers (TOC 500 and 5000A, Shimadzu), and anions (NO_3-N, Cl^-, SO_4^{2-}) were determined using an Ion Chromatographic Analyzer (IC7000, Yokogawa). Other water qualities including phosphorus compounds were measured according to the Standard Methods edited by Japan Sewage Works Association (1997).

Results and discussion

Changes in relative flux and transmembrane pressure

The time profile of relative flux and transmembrane pressure (TMP) in each reactor were monitored for approximately 250 days (see Figure 2). Relative flux has increased and TMP inversely decreased for the CA membrane bioreactor, while there was no significant change in terms of relative flux and TMP for the PA membrane bioreactor during both the operations.

For the CA membranes, the trend of water flux and TMP was almost comparable to the result of the CDA membrane used in the previous study (Choi *et al.*, 2002). The result would be caused by the increase in pore size and the disappearance of electrical property of the membrane surface, which allowed the decrease in salts rejection. The decrease in osmotic pressure at the membrane surface and the increase in net driving pressure are largely caused by the change in salts rejection. This phenomenon can be explained by hydrolysis (desalting of a polymer matrix) and biological degradation of cellulose acetate material (Cantor and Mechalas, 1969; Murphy *et al.*, 2001). The result also suggests that

Table 2 Average water qualities of raw wastewater for all the operation days

T-COD, mg/L	TOC, mg/L	DOC, mg/L	T-N, mg/L	T-P, mg/L	pH	Conductivity, mS/m	Temperature, °C
210	61.8	29.6	26.0	6.53	7.61	125	16.1–22.3

Table 3 Operating parameters for both the NF MBRs

Parameters	CA MBR	PA MBR
Filtration mode	Suction	Suction
Working volume	36.3 L	31.2 L
Membrane flux	5×10^{-4} m/day	5×10^{-4} m/day
Hydraulic retention time (HRT)	2.0 → 1.5 days (since the 162nd day)	2.0 days
Sludge retention time (SRT)	40 → 80 days (since the 38th day)	40 → 80 days (since the 38th day)
Filtration mode	Intermittent (suction for five min and pause for five min)	Intermittent (suction for five min and pause for five min)
Air-flow rate	36 L/min (three air pumps × 12 L/min)	36 L/min (three air pumps × 12 L/min)
Flushing using tap water	CA#2 and CA#3	–
Flushing water volume/day	(1,500 ± 150) mL/day for CA#2 (2,000 ± 150) mL/day for CA#3	–

measures introduced for controlling membrane biodegradation, intermittent flushing with tap water, and nylon fabric, do not function effectively.

Unlike the CA membranes, there was no significant change with regard to the relative flux and TMP for the PA membranes. This result indicates that the intrinsic quality of PA membranes is not deteriorated by hydrolysis and biodegradation. It is reported that PA membranes have a higher fouling rate than the CA membranes in terms of colloidal fouling (Elimelech *et al.*, 1997). Nevertheless, there was no occurrence of membrane fouling and significant flux decline during all the operation days. This is clear because the initial fluxes of the PA membranes were set very low and the wrapping using nylon fabric could prevent microbial flocs and particles from attaching themselves to the membrane surface to a large extent.

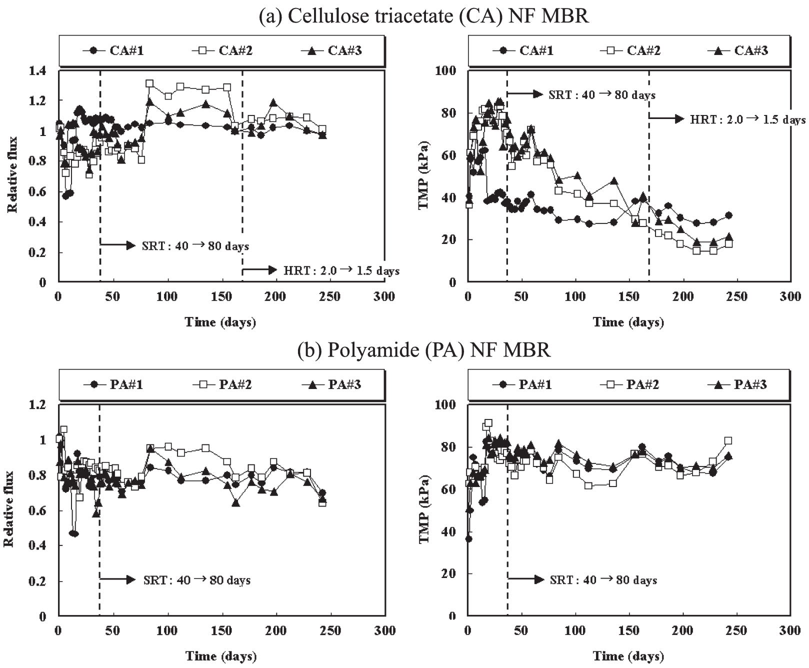

Figure 2 Changes in relative flux and TMP in each NF MBR

Rejection of DOC

Figure 3 illustrates the change in DOC concentration of permeates of CA and PA NF MBR. For CA membranes, the DOC concentration of permeates, except CA#1, ranged from 0.5 to 2.0 mg/L for the initial 120 days. For CA#1 membrane, an unexpected performance appeared in DOC rejection and TMP change. This result may be related to the configuration change of membrane module, that is, the membrane module was not wrapped with nylon fabric until the 17th day. This suggests that the surface of the CA#1 membrane is attached with massive activated sludge. Thereafter, the membrane was set with the fabric after physical washing. Unexpected performance of CA#1 may be related to organic matter accumulation caused by this configuration change.

For the PA MBR, DOC concentrations of all permeates were between 0.5 and 2.0 mg/L throughout the operation period, and the concentrations became lower as the operation reached the second half of the days. Compared with CA membranes, the PA membranes can produce a very good-quality permeate and also obtain water steadily for a long-term operation period.

Change in salts rejection

The rejection of monovalent and divalent anions, such as chloride (Cl^-) and sulfate (SO_4^{2-}) ions, in each NF MBR was measured in order to observe the property change of membrane surface for all the operation days (see Figures 4 and 5).

Similar to the trend of TMP change, the salts rejection by CA membranes was relatively high for the initial 80 days, and then gradually decreased according to the time. This result indicates that the electrical property and heavy concentration polarization of the CA membranes disappear with the deterioration of membrane quality. The salts rejection of PA membranes was maintained at a constant level (Cl^- rejection: 0.2 and

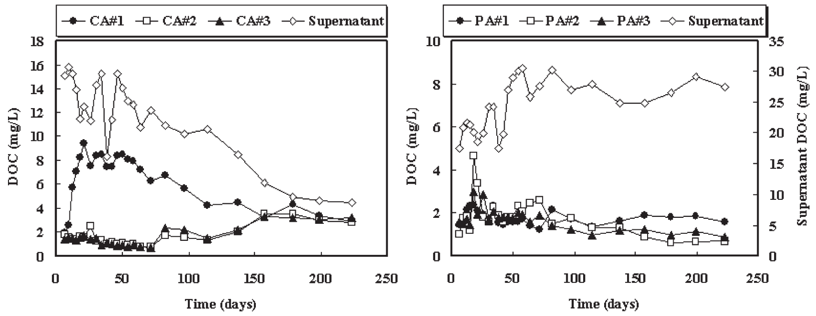

Figure 3 Evolution of DOC concentrations in CA and PA NF MBRs

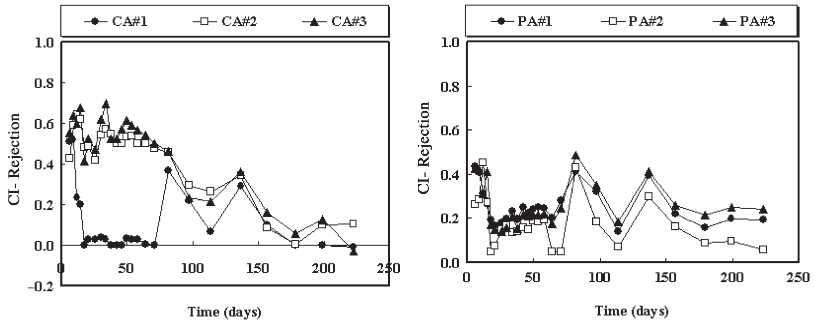

Figure 4 Change in monovalent anion (Cl^-) rejection in each NF MBR

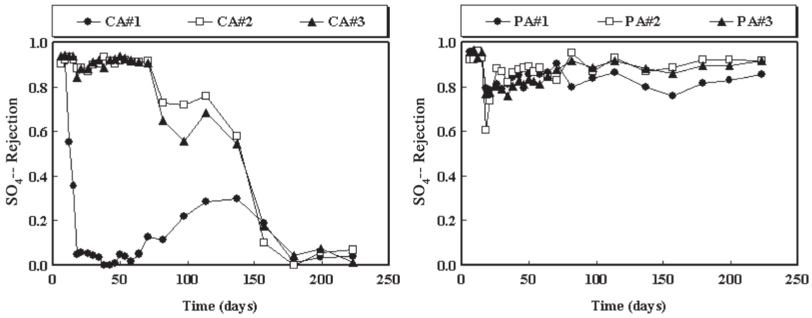

Figure 5 Trend of divalent anion (SO_4^{2-}) rejection in each NF MBR

SO_4^{2-} rejection: 0.8). This implies that the treatment efficiency of PA membranes is considerably reliable and predictable for a long period because the PA membrane' quality is almost unchanged. However, these could not obtain higher permeate flux than CA membranes on account of high salts rejection.

Contrary to other membrane modules, CA#1 exhibited a unique trend of salts rejection as well as DOC rejection, i.e., the function of the NF membrane did not work properly from an early stage of the operation. There may be difficulties in the connection of fibers and suction port and module configuration with the nylon fabric, judging from the low rejection of charged and non-charged materials simultaneously.

Rejection of nitrate and phosphate ions

In general, nitrogen compounds are almost transformed into nitrate ion (NO_3^-) through dynamic nitrification caused by sufficient aeration and long SRT in the membrane bioreactor. Thus, the rejection of nitrate ion was observed in order to investigate the performance of nitrogen compounds removed by NF membranes for the entire operation (see Figure 6).

The rejection of nitrate ion by CA membranes consistently decreased with time, but the rejection steadily increased since the 180th day. It is reported that the rejection of nitrate ion by NF membranes is generally lower than that of other monovalent anions such as chloride ion. In addition, the increase at the late stage of the operation can be explained by denitrification within the membrane modules similar to the result of the CDA membrane (Choi *et al.*, 2002). Namely, microorganisms intruded and attached to the membrane surface despite the wrapping; consequently, the anoxic condition for denitrification was built up inside the modules.

For the PA membranes, the rejection of nitrate ions was also rather decreased, compared with the result of CA membranes. NO_3-N rejection was preferably lowered to

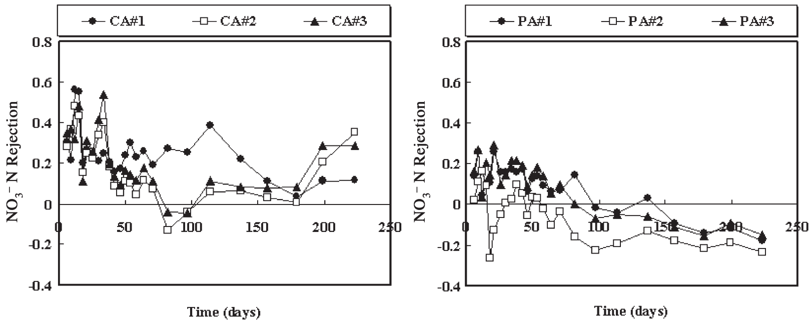

Figure 6 Rejection of nitrate ion (NO_3^-) in CA and PA NF MBRs

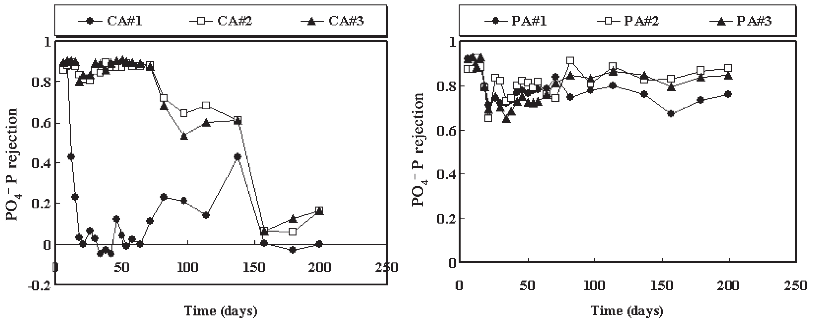

Figure 7 Rejection of phosphate ion (PO_4^{3-} in CA and PA NF MBRs

Table 4 Average water qualities of permeates in each NF MBR throughout the operation

Items	DOC, mg/L	Cl^-, mg/L	SO_4^{2-}, mg/L	T-N, mg/L	NO_3-N, mg/L	T-P, mg/L	PO_4-P, mg/L
CA#1 permeate	6.23	294	41.7	22.1	17.8	13.0	11.8
CA#2 permeate	1.66	176	17.5	20.9	19.1	3.22	2.75
CA#3 permeate	1.62	162	17.0	20.2	18.2	2.94	2.53
PA#1 permeate	1.75	244	25.8	24.6	22.6	6.83	5.93
PA#2 permeate	1.78	265	27.1	27.2	25.6	6.57	5.22
PA#3 permeate	1.64	243	24.8	24.2	22.3	6.86	5.85

negative value from the middle phase of the operation. This might result from membrane materials and ion affinity to the membrane surface (Ratanatamskul *et al.*, 1997).

To monitor the removal of phosphorus compounds, rejection of phosphate ion (PO_4^{3-}) by NF membranes was also observed during the entire operation (see Figure 7). The result demonstrated that the rejection by CA membranes was similar to SO_4^{2-} rejection, that is, the rejection was decreased with time. For PA membranes, the rejection of PO_4^{3-} was approximately 80% on an average, and this was caused by the charge effect of the membrane surface.

Comparison of water qualities of permeates in cellulose triacetate and polyamide NF MBRs

To compare the treatment efficiency of NF membrane bioreactors, the permeate qualities of CA and PA membrane bioreactor are summarized in Table 4. The results indicate that all permeates apart from CA#1 are very comparable in terms of water qualities.

Conclusions

Based on the study, both CA and PA NF MBRs were stable systemically, and obtained very good-quality permeates. The results demonstrated that PA membranes have better treatment efficiency than CA membranes, and CA membranes obtained higher water productivity than PA membranes. The submerged NF MBR has, therefore, promising competitiveness in advanced wastewater treatment. To improve the practicability of NF MBR systems, the membranes require characteristics such as high organic matter rejection and low salts rejection. In addition, hollow fiber membrane modules are preferable and more competent in NF MBR systems, since they are self-protective and can have enough water productivity.

Acknowledgements

The authors acknowledge Toyobo Co. Ltd., Japan, especially Mr. Hideki Yamada, for providing some NF membrane modules for this study.

References

Agbekodo, K.M., Legube, B. and Dard, S. (1996). Atrazine and simazine removal mechanisms by nanofiltration: influence of natural organic matter concentration. *Wat. Res.*, **30**(11), 2535–2542.

Cantor, P.A. and Mechalas, B.J. (1969). Biological degradation of cellulose acetate reverse osmosis membranes. *J. Polym. Sci.: C*, **28**, 225–241.

Childress, A.E. and Elimelech, M. (1996). Effect of solution chemistry on the surface charge of polymeric reverse osmosis and nanofiltration membranes. *J. Membrane Sci.*, **119**, 253–268.

Choi, J.H., Dockko, S., Fukushi, K. and Yamamoto, K. (2002). A novel application of a submerged nanofiltration membrane bioreactor (NF MBR) for wastewater treatment. *Desalination*, **146**, 413–420.

Dockko, S. and Yamamoto, K. (2001). Wastewater treatment using directly submerged nanofiltration membrane bio-reactor (NF MBR). In: *Proceedings of the International Conference on Membrane Technology for Wastewater Reclamation and Reuse*, Tel-Aviv, Israel, 21–28.

Elimelech, M., Zhu, X., Childress, A.E. and Hong, S. (1997). Role of membrane surface morphology in colloidal fouling of cellulose acetate and composite aromatic polyamide reverse osmosis membranes. *J. Membrane Sci.*, **127**, 101–109.

Murphy, A.P., Moody, C.D., Riley, R.L., Lin, S.W., Murugaverl, B. and Rusin, P. (2001). Microbiological damage of cellulose acetate RO membranes. *J. Membrane Sci.*, **193**, 111–121.

Ratanatamskul, C., Urase, T. and Yamamoto, K. (1997). Description of behavior in rejection of pollutants in ultra low pressure nanofiltration. *Wat. Sci. Tech.*, **38**(4–5), 453–462.

Standard Methods for the Examination of Wastewater (1997). Japan Sewage Works Association (In Japanese).