Evaluation of a MF membrane system composed of pre coagulation-sedimentation and chlorination for water reuse

S.H. Lee*, B.C. Lee*, S.Y. Moon*, Y.S. Choi*, N.Y. Jang and Y. Watanabe*****

*Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul, 130-650, South Korea (E-mail: *Yisanghyupwhong@kist.re.kr*)

**Chemistry & Biotechnology Examination Bureau, Korean Intellectual Property Office, South Korea

***Department of Urban and Environment Engineering, Faculty of Engineering, Hokkaido University, Japan

Water Science & Technology **Vol 54 No 10 pp 115–121** © IWA Publishing 2006

Abstract In this research, we investigated the variation of transmembrane pressure and permeate water quality in pre-coagulation and sedimentation with iron based coagulant, and chlorination of feed water for PVDF (Polyvinylidene fluoride) based MF membrane filtration. NaClO was fed to the membrane module at a dosage of 0.5 mg/L and maintained during filtration. To observe the effect of raw water, three types of raw and processed waters, including river surface water, coagulated water and coagulated-settled water, were employed. In the case of river surface water, the transmembrane pressure increased abruptly in 500 hours operation. On the contrary, no significant increase in transmembrane pressure was observed for coagulated water and coagulated-settled water for 1200 hours operation. The turbidity of permeate was lower than the detection limit for all applied waters. The removal efficiency for humic substances in coagulated water and coagulated-settled water was approximately ten times higher than that in surface river water. And, the removal efficiency for TOC and DOC was approximately two times higher than that in surface river water. From the results of the operation, it can be observed that it is possible to maintain stable operation at 0.9 m^3/m^2-day filtration flux through a combination of pre-coagulation and pre-chlorination. However, the water quality of permeate was the best when the pre-coagulation-sedimentation process was combined with pre-chlorination. With respect to fouling reduction and operation efficiency increase in membrane filtration, the pre-coagulation/sedimentation process is a promising alternative.

Keywords Fouling reduction; iron-silica based inorganic coagulant; pre-treatment; PVDF MF membrane; residual chlorination

Introduction

Membrane filtration is a prospective process for wastewater reuse and water pollution control in water shortage regions like metropolitan and rural areas. However, the fouling problem is a critical obstacle in spreading membrane filtration for water and wastewater treatment. In order to solve the fouling problem, much research has been done. Among these, it has been reported that the pre-coagulation and sedimentation process could be an effective alternative for fouling reduction. From this result, fouling could be reduced owing to fouling induced substances, especially humic substances (Jang, 2001). Additionally, fouling was reduced effectively by combination with pre-coagulation only (Wiesner *et al.*, 1989). The combination of oxidation process with membrane filtration is an effective method for the prevention of membrane fouling. However, hollow fiber membranes made of organic polymer could not be used in combination with oxidant directly, such as ozone or chlorine, because organic polymer materials generally have less resistance to oxidants. Therefore, when oxidants are used as pretreatment prior to membrane filtration, an additional removal process is necessary to remove the residual oxidants before the membrane module.

doi: 10.2166/wst.2006.876

Most of membranes are made of organic polymer material at present. The research relating to membrane material development has been highly progressed. Recently, a ceramic membrane which has an alkali and acid resisting character has been actively developed. And the performance came to high level. However, in spite of a lot of advantages of the ceramic membrane, the application to water and wastewater treatment is more limited than organic polymer material membrane because of high price and low endurance. On the other hand, some membrane manufacturing companies have succeeded in developing the membrane module with resistant characteristics against chemicals made of PVDF. In the developed membrane module, it is possible to that water containing residual oxidants can be directly filtered without an additional oxidant removal process. Through this membrane development, it is possible to apply the organic polymer membrane to the membrane filtration process in conjunction with a direct oxidation process, such as ozone. It is known that this system can consistently provide a high permeate flux, such as 5 m^3/m^2-day, for various waters, especially high turbidity raw water and secondary treated municipal wastewater (Mori *et al.*, 1998; Lee *et al.*, 2004).

Even though ozonaion is a very effective pre-treatment method, some results reported that the permeate water quality might become worse (Jang, 2001; Lee *et al.*, 2004; Lee *et al.*, 2005). Especially, the removal efficiency for TOC (Total Organic Carbon) decreased and the concentration of AOC (Assimilable Organic Carbon) which is a re-growth indicator of microbiology in the distribution system increased.

This paper describes the performance of the membrane filtration process in conjunction with pre-coagulation–sedimentation and pre-oxidation. We applied NaClO as oxidant which has lower oxidation potential than ozone. NaClO is widely used as a disinfectant in water and wastewater treatment.

Materials and methods

Three kinds of raw water, including river water, coagulation treated water and coagulation–sedimentation treated water, were used to compare the effect of raw water variation. It is known that the concentration of humic substances in river water was very high. The outline of the process used in this study is summarized in Table 1. And three operation conditions were summarized in Table 2. The flux was maintained at 0.9 m^3/m^2-day. In order to observe the effect of flux change, flux was increased from 0.9 to 1.8 m^3/m^2-day in process 2 and from 0.9 to 2.5 m^3/m^2-day in process 3. The specification of membrane used in this study is summarized in Table 3. We used the iron-based coagulant, PSI (polysilicato iron) as coagulant. The optimum dosage and pH was 10 mg/L and 6.7, respectively. Because the pH of the river water was maintained between 6.56 and 7.59, we did not control the pH of the surface water. A schematic diagram of the pilot-scale experimental apparatus and coagulation–sedimentation facility, JMS (Jet Mixed Separator) used in this study are shown in Figures 1 and 2, respectively. It is reported that JMS is very effective with respect to space and energy saving (Watanabe *et al.*, 1998). The hydraulic retention time (HRT) of the JMS process is 75 min. The pilot-scale experimental apparatus was composed of three processes: 1) surface water + chlorine + MF, 2)

Table 1 Outline of the process; comparison to ordinary water treatment process

Old	Rapid mixing (Al based coagulant)	Flocculation	sedimentation	Sand filtration	Disinfection (chlorine)
New	Rapid mixing (Fe based coagulant)	JMS process		Residual chlorine and membrane filtration	

Table 2 Operation conditions of the pilot-scale apparatus

Process	Process 1)	Process 2)	Process 3)
Raw water	Surface river water	Coagulation treated water	Coagulation – sedimentation treated water
Coagulant dosage (mg/L)	–	10	10
Flux (m^3/m^2-day)	0.9	0.9/1.8	0.9/1.8/2.5
Residual NaClO concentration in permeate (mg/L)	0.5	0.5	0.5
Operation condition	Cross flow Backwashing 1 min (200 kPa) Air-scrubbing 1 min Backwashing period 30 min		Cross flow Backwashing 1 min (200 kPa) Air-scrubbing 1 min Backwashing period 60 min

Table 3 Specification of the membrane

Material	PVDF
Pore size	0.1 μm
Effective surface area/module	6.31 m^2
Length	2160 mm
Filtration mode	Outside in flow hollow fiber, cross flow filtration

coagulated water + chlorine + MF, and 3) coagulated-settled water + chlorine + MF. NaClO was maintained at more than 0.5 mg/L in the membrane module during filtration. The residual chlorine concentration of permeate was measured to be more than 0.1 mg/L during filtration.

The following parameters were analyzed according to *Standard Methods* (20th edition, 1998): turbidity (Turbidity meter; Mitsubishi chemical SEP-PT-706D), UV_{260} absorbance (spectrophotometer; Hitachi U-2000A), Total Organic Carbon (TOC analyzer; shimadzu TOC-5000A).

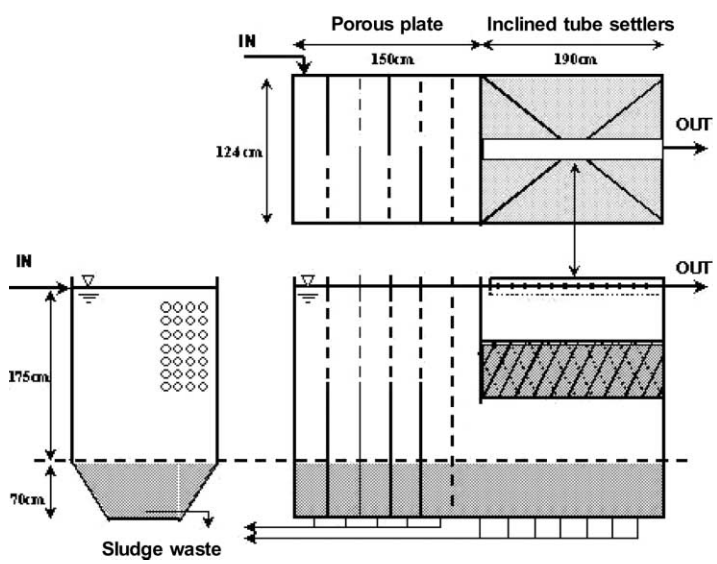

Figure 1 Schematic diagram of the Jet Mixed Separator (JMS)

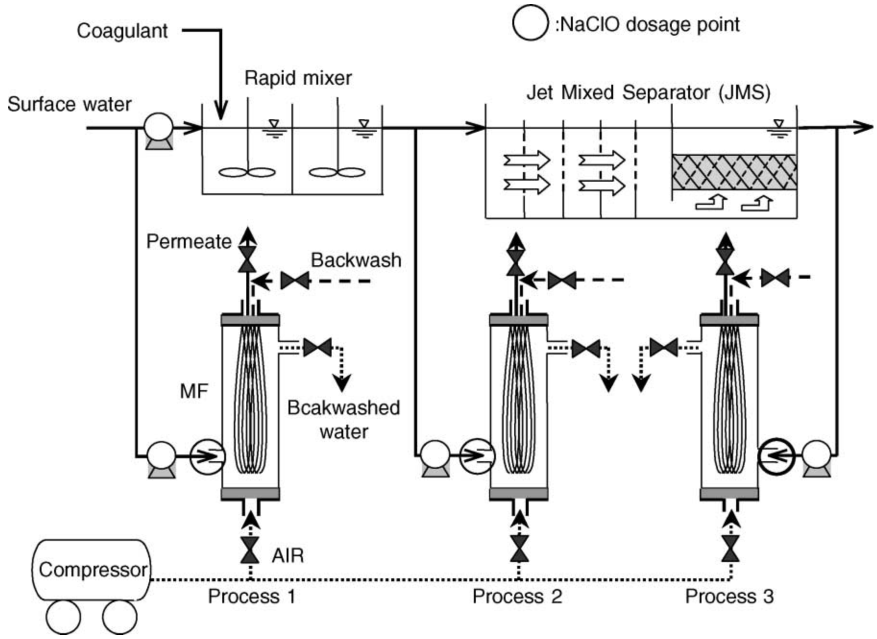

Figure 2 Schematic diagram of the pilot-scale apparatus; process 1), 2), and 3)

Results and discussion

Variation of the transmembrane pressure

The variation of transmembrane pressure is shown in Figure 3. In process 1), the transmembrane pressure (TMP) increased drastically in 500 hours operation. The time for reaching to about 100 kPa is just 70 hours. In this period, the turbidity increased to 30 NTU because of heavy rainfall. Therefore, a lot of suspended substances flew into the membrane module and effective backwashing did not occur. As a result, suspended substances are accumulated on the membrane surface. So, the oxidation effect of residual chlorine in the membrane module did not occur. On the contrary, in process 2) and 3) we observed that the transmembrane pressure did not increase and it was possible to maintain stable operation for 1200 hours despite the abrupt turbidity increase after 500 hours.

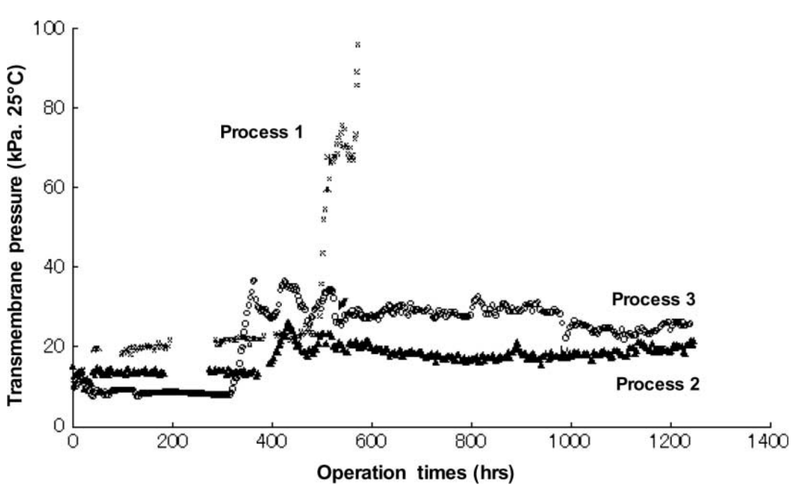

Figure 3 Variation of transmembrane pressure in process 1), 2), and 3)

From this result, it could be said that sole chlorination oxidation process was not effective for the high turbidity raw water. And the coagulation–sedimentation process is a very effective process for pre-treatment of membrane filtration. However, if the chlorination process was applied to the pre-treatment process, only the coagulation process was enough for fouling reduction and stable operation. This resulted from the 'floc re-aggregation effect' (Yonegawa *et al.*, 2003). From the floc re-aggregation effect, the floc size of coagulated floc inflow into the membrane module increased by cross flow flux on the membrane surface. Therefore, the efficiency of backwashing increased. In process 2) and 3), we increased the filtration flux from 1.8 to 2.5 m^3/m^2-day. The result is shown in Figure 4. In process 2), filtration resistance increased. However, in process 3), filtration resistance did not increase. From this result, the optimum filtration flux was 0.9 m^3/m^2-day in case of coagulation and chlorination as pre-treatment. On the other hand, the optimum filtration flux increased to 1.8 m^3/m^2-day through the sedimentation process.

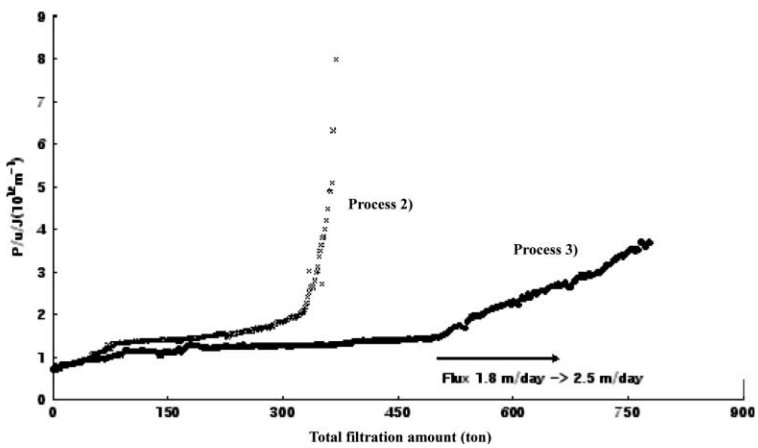

Figure 4 Variation of filtration resistance in process 2) and 3)

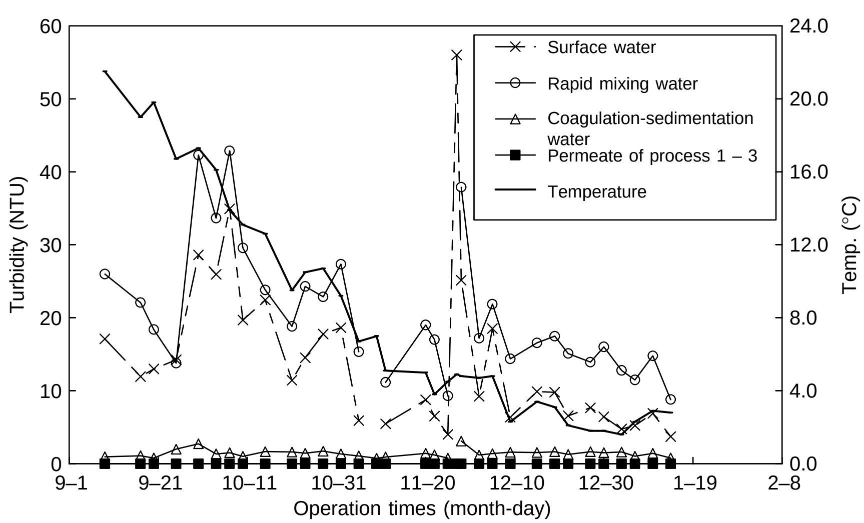

Figure 5 Variation of turbidity with time

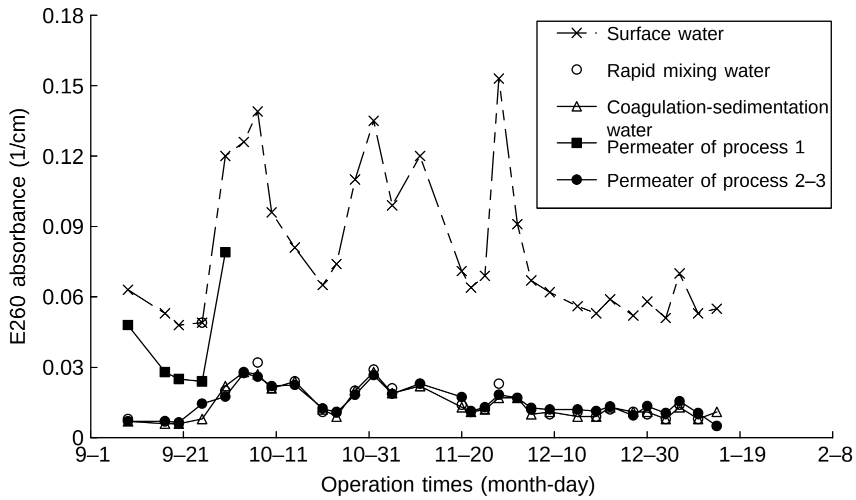

Figure 6 Variation of UV260 absorbance with time

Change of permeate water quality

Turbidity. The variation of turbidity is shown in Figure 5. The turbidity of permeate in all processes was lower than 0.1 NTU. The turbidity of coagulation treated water was about 10 NTU, which was higher than surface river water.

Humic substances (UV260 absorbance). The variation of UV_{260} absorbance is shown in Figure 6. Recently, much research suggested that the important fouling inducing substance is humic substances which result from NOM degradation. The removal efficiency in process 1) was 40%, although the membrane pore size was 0.1 μm. This resulted from the degradation of the double bond of humic substances by residual chlorine in the membrane module. On the other hand, the removal efficiencies were about 80% in both processes 2) and 3). We observed that the removal of humic substance occurred in coagulation and the coagulation–sedimentation process. From this result, the

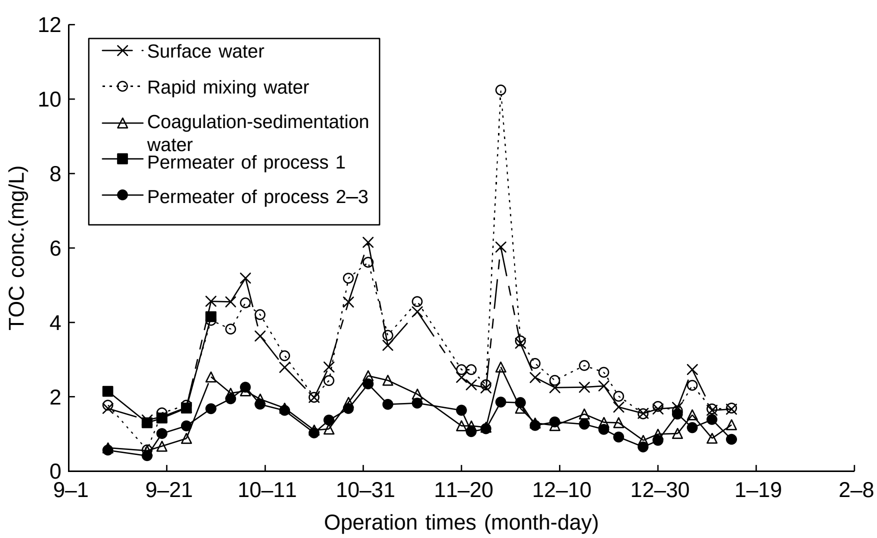

Figure 7 Variation of TOC concentration with time

combination with the coagulation or sedimentation process in the residual chlorine membrane filtration system seems to be effective for the removal of humic substances.

Total organic carbon. The variation of TOC is shown in Figure 7. In process 1), the removal efficiency was just 5%. However in process 2) and 3), it increased to 50%. In combination with the coagulation or sedimentation process in the residual chlorine membrane filtration system, it is an effective process to increase the TOC removal efficiency. However, the TOC concentration was not high compared to surface river water in all processes although application of pre-ozonation increased the TOC concentration.

Conclusions

Based on the results obtained in this study, it is possible to operate the filtration at $0.9\,m^3/m^2$-day flux in a pre-coagulation and residual chlorination hybrid membrane filtration system even for the surface river water with high turbidity. It is reported that TOC and AOC concentration was increased by the residual ozone in the membrane module. However, TOC concentration was not increased by the residual chlorine. Therefore, with respect to permeate water quality, chlorine is an effective alternative in the ozone oxidation process. However, with respect to operation, an additional process is necessary in the chlorine oxidation system.

The specific advantages are as follows:

- Increase of removal efficiency
- Easy operation
- Space and energy saving

At this time, in Korea, the topic of hybrid membrane system development for water and wastewater treatment is particularly important because of the introduction of hazardous materials in water resources and increasingly stringent discharge requirements imposed on WWTPs. This process would be the most cost-effective and energy-saving alternative owing to the advantages mentioned above.

Acknowledgement

This research was financially supported by the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

Jang, N.Y. (2001). *A Study on the Effective Pre-treatment and Physical Backwashing Method on MF and UF Membrane*, PhD thesis, Hokkaido University Hokkaido, Japan, pp. 67–87.

Lee, S., Jang, N. and Watanabe, Y. (2004). Effect of residual ozone on membrane fouling reduction in ozone resisting microfiltration (MF) membrane system. *Water Science and Technology*, **50**(12), 287–292.

Lee, S., Wan, W.M., Lee, K. and Choi, Y. (2005). Comparision of membrane permeability and a fouling mechanism by pre-ozonation followed by membrane filtration and residual ozone in membrane cell. *Desalination*, **178**, 287–294.

Mori, Y., Oota, T., Hashimoto, M., Takamura, M. and Fuji, Y. (1998). Ozone-microfiltration system. *Desalination*, **117**, 211–218.

Watanabe, Y., Kasahara, S. and Iwasaki, Y. (1998). Enhanced flocculation/sedimentation process by jet mixed separator. *Water Science and Technology*, **37**(10), 55–67.

Wiesner, M.K., Clark, M.M. and Mallevialle, J. (1989). Membrane filtration of coagulated suspensions. *Journal of Environmental Engineering*, **115**(1), 20–40.

Yonegawa, H., Tomita, Y. and Watanabe, Y. (2003). Behavior of micro-particle in monolithic ceramic membrane filtration with pre-coagulation. *Conference Proceedings of Nano and Micro Particles in Water and Wastewater Treatment*, pp. 305–313.