Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.21644

99 (2017) 162–166
December

Comparative evaluation of membrane characteristics between long-term operation and accelerated test

Yong-Soo Lee[a], Wooha Kim[a], Hayoung Kang[a], Jiyoung Moon[b], Jong-Oh Kim[b,*]

[a]*Department of Civil & Environmental Engineering, Hanyang University, Seoul, 04763, Korea*
[b]*Engineering Department, Water Supply Engineering Team, Korea Water Resources Corporation, 34350, Korea, Tel. +82 2 2220 0325; Fax: +82 2 2220 1945; email: jk120@hanyang.ac.kr (J.-O. Kim)*

Received 27 August 2017; Accepted 28 October 2017

ABSTRACT

In view of the maintenance and management, currently, there are insufficient diagnosis methods and guidelines of membrane filtration process applied in various water treatment facilities, which may judge the performance decrease due to the membrane property change. Despite the above situation, membrane has been continuously developed. Especially, since PVDF-material membrane, which is mostly applied nowadays, is hydrophobic, it tends to be conditioned by various additives. In this study, accelerated test was conducted for confirming the loss of C=O peak that affects the hydrophilicity, among the chemical structures of various additives, and filtration performance decrease. This study compares and evaluates the membrane property and performance between membrane of accelerated test and the membrane which is operated for long term of 3 years. In order to increase the reliability of accelerated test, attributable factors are enumerated.

Keywords: Membrane; Membrane properties; Accelerated test; Long-term operation

1. Introduction

For the past several decades, membrane process has been increasingly used in and out of the country due to its advantages compared with the previous filtration process such as an intensive design, reduced operation cost, high energy efficiency, absolute water quality stability, etc. [1,2]. During the 1980s–1990s, for the membrane performance improvement applied in numerous water treatment facilities and evaluation of maintenance and management thereof, researches on Clean In Place (CIP) have been conducted, which is performed for performance recovery from membrane fouling. In addition, from the mid-2000s, researches on the optimized condition of CIP, including deterioration research, have been increasingly conducted for the extended life [14].

In the preceding researches, CIP and deterioration researches have not been theoretically established and such researches depend on the empirical method such as field evaluation per facilities. As a result, the inherent characteristics of membrane were not considered and the method of measuring the flux recovery degree was merely used. However, as long-term operation continues, cleaning frequencies have been increased because of the irreversible membrane fouling, and performance factors such as flux have been decreased. Many researches have been reported that change of membrane inherent characteristic, that is, integrity lost, affects the performance such as stable filtrate quality and flux [5,10,12–19]. Therefore, in order to establish a systematic manual based on theory, a deterioration research which considers the membrane inherent characteristic is on the rise [19,20].

In this study, membrane properties of accelerated operation applying the same cleaning frequencies are evaluated compared with membrane properties of the long-term operation based on the initial state membrane properties. By this comparison, the performance of the long-term operated

* Corresponding author.

membrane is grasped and the different characteristic of the accelerated test membrane is evaluated. The experimental result thereof may suggest the matters to be attended during the accelerated test applying chemicals and factors to be reflected in the field.

2. Materials and methods

2.1. Membrane specification and experimental procedure

2.1.1. Membrane

The test was carried out by selecting membranes, which have advantages such as superior chemical resistance, high thermal stability and mechanical strength, etc., and which are widely used in and out of the country. The accelerated test was conducted using membrane with the same material as the long-term operated membrane used in plant A for its comparative evaluation. The specification of the applied membranes is shown in Table 1.

2.1.2. Membrane accelerated testing

In this accelerated test, HCl, which is an inorganic acid applied in chemical cleaning of A facility, was utilized. The concentration of HCl cleaning for one time CIP of A facility was 35,500 mg/L and HCl cleaning was performed in 6 h in total. In addition, since the long-term operated membrane of A facility has a history of four times of CIP, the accelerated test was applied with the same exposure intensity during 24 h as the same concentration of the long-term operated membrane, as shown in Table 2 and then the membrane properties are compared and evaluated.

2.1.3. Membrane performance evaluation

For the filtration performance comparison of Membrane_LTO and Membrane_AT vs. Membrane_I applied by the same exposure intensity, fluxes of the above three membranes were measured for three times for 5 min under the pressure of 30 ± 1 kPa, the pressure and water temperature were adjusted into 100 kPa and 25°C, and then the calculated membrane resistance (R_m) thereof are compared and evaluated.

Table 1
Membrane specification

Item	Specification
Membrane	MF (microfiltration)
Material	PVDF (polyvinylidene fluoride)
Pore size	0.05 μm
Membrane type	Hollow fiber
Outer diameter (OD)	1.4 μm
Inner diameter (ID)	0.9 μm

2.2. Membrane properties

2.2.1. Membrane surface properties

The chemical structural change of membrane surface was confirmed by the analysis of Fourier transform infrared spectroscopy (FT-IR) and energy dispersive X-ray spectroscopy (EDS). In FT-IR, Nicolet iS50 model was used and diffuse reflectance spectrum was scanned in the range of 400–4,000 cm^{-1} and the change of chemical structures and functional groups of additives was confirmed. In EDS analysis, Nova NanoSEM 450 model was used and the change of the constitutional components was measured in 5 × 5 μm area with 25,000 magnification.

2.2.2. Membrane surface morphology

The change of membrane surface structure and roughness was confirmed through scanning electron microscope (SEM) and atomic force microscopy (AFM) analysis. In SEM analysis, Nova NanoSEM 450 model was used and the surface structure of 5 × 5 μm area with 25,000 magnification was measured. In AFM analysis, how the changed surface structure affects the membrane roughness was confirmed, and XE-100 model was used for measuring average roughness (R_q) of 10 × 10 μm area.

2.2.3. Component analysis

In order to clearly confirm the membrane property differences of Membrane_LTO and Membrane_AT, thermogravimetric analysis (TGA) and X-ray photoelectron spectroscopy (XPS) analysis were conducted for Membrane_I, which is a control group. In TGA analysis, SDT Q600, Auto-DSCQ20 System models were used and N_2 gas was increased by 10°C/min, and the weight reduction change was checked up to temperature range of 20°C–800°C. In XPS analysis, XPS-Theta Probe model was used and quantitative analysis was carried out.

3. Results and discussions

3.1. Evaluation of PVDF membrane property

3.1.1. Chemical structure

FT-IR analysis result of Fig. 1 shows that three membranes were all confirmed to show 'C–F', 'C–C',

Table 2
Comparative assessment of HCl exposure intensity

Membrane condition	Chemical agent	Concentration (mg/L)	Contact time (h)	CIP times	Exposure intensity (mg/L·h)
Initial state (Membrane_I)	HCl	–	–	–	–
Long-term operating (Membrane_LTO)		35,500	6	4	852,000
Accelerated testing (Membrane_AT)		35,500	24	–	852,000

'H–C–H', which are PVDF material inherent functional groups, in the vicinity of 873, 1,180 and 1,402 cm^{-1}, respectively. It was confirmed that carbonyl group (C=O), which was produced by the additives for the hydrophilicity of hydrophobic PVDF membrane, was generated in the vicinity of 1,720–1,740 cm^{-1} [1,7].

Even though the three membranes did not show a huge change in the functional groups which constitute PVDF, it was confirmed that C–F peaks of Membrane_LTO and Membrane_AT were all decreased compared with Membrane_I. This result was assumed to be made because of the defluorination reaction [8,9]. Further, compared with Membrane_I, Membrane_AT is considered to show the increased 'C=O' peak due to the oxidation reaction [18].

As shown in EDS analysis result of Table 3, Membrane_LTO and Membrane_AT tend to show decreased 'F' and increased 'O' compared with Membrane_I in the chemical constitution of the membrane surface. Further, since Membrane_AT shows decreased 'C–F' and increased 'C=O' due to the oxidation reaction and defluorination reaction, it is predicted to generate a chemical constitutional change.

Further, as shown in the TGA analysis result of Fig. 2, weight was lost by about 27% between 150°C and 200°C in the initial state, which is considered to be caused due to the evaporation of volatile materials and moisture within the membrane. In addition, Si weight was lost by about 1.4% between 350°C and 400°C [2], which is considered to be caused due to the combustion of Si. In the XPS analysis, a small amount of Si was detected and it was confirmed that Si, which was present on the inside and surface of the membrane, was eluted on the surface due to the oxidation reaction.

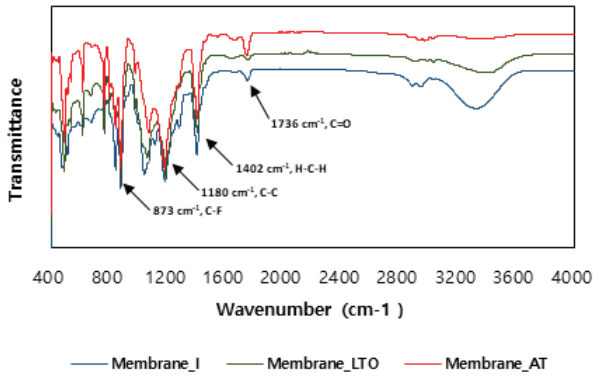

Fig. 1. FT-IR spectra of Membrane_I, Membrane_LTO and Membrane_AT.

Table 3
Result of the chemical constitutional change through EDS analysis

Elements (At %)	Membrane condition of three type		
	Membrane_I	Membrane_LTO	Membrane_AT
C	54.83	69.84	66.74
F	37.52	23.90	17.63
O	7.65	9.39	14.80
Si	–	–	0.83

In addition, it was confirmed that the highest Si weight lost between 420°C and 470°C was made because of the combustion of polymer bonded to the aromatic materials used as the additives of PVDF membrane.

In the FT-IR result of Membrane_LTO, 'C=O' functional group was all decreased but 'O' was increased in the surface chemical constitutional result.

3.1.2. Evaluation of membrane surface analysis

In the SEM analysis result of Fig. 3, it was confirmed that Membrane_LTO shows a twisted and uneven membrane surface and Membrane_AT generates an elusive material on the surface. In the AFM analysis result of Fig. 4 the initial gradual morphology of Membrane_LTO and Membrane_AT was all confirmed to be changed into rough morphology. In the EDS analysis result, it was confirmed that the component of the elusive material is Si, which is crystallized by the oxidation reaction of HCl.

Elusive materials were not detected on the surface of Membrane_LTO because Si is presumed to be removed by backwashing, air scrubbing, etc., which are performed during the filtrating operation of chemicals such as alkali, oxidizing agent, etc. Further, due to the property change caused by defluorination reaction, etc., chemical properties such as 'C=O' were damaged and the surface form is considered to be changed [18].

3.2. PVDF membrane performance evaluation

Compared with Membrane_I, Membrane LTO and Membrane_AT showed an increased filtration resistance

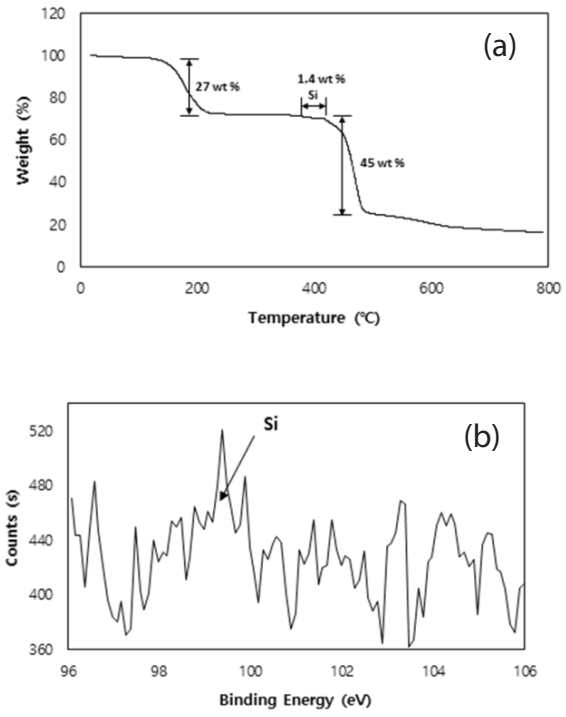

Fig. 2. (a) TGA analysis of Membrane_I, (b) XPS analysis of Membrane_I.

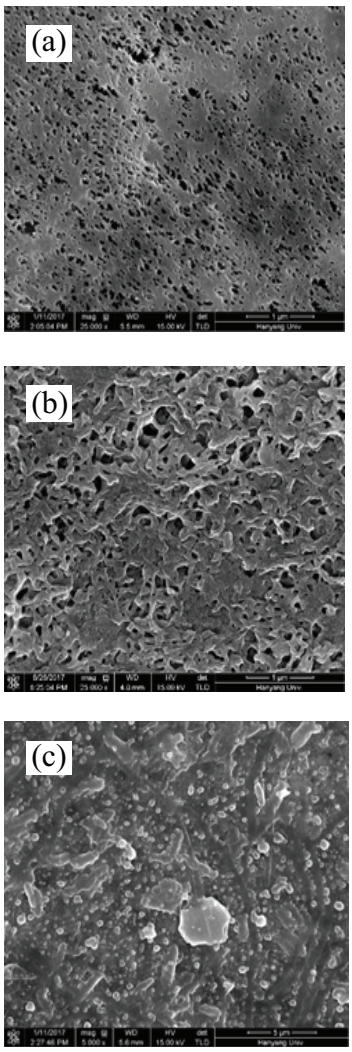

Fig. 3. SEM morphologies of (a) Membrane_I, (b) Membrane_LTO and (c) Membrane_AT.

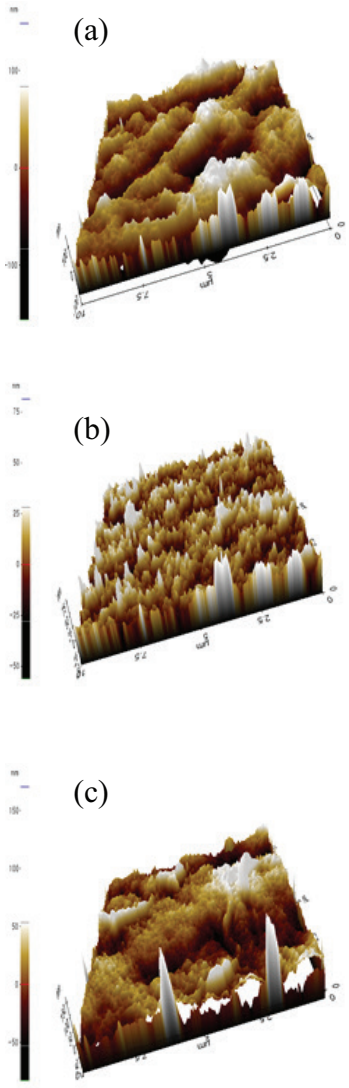

Fig. 4. AFM surface roughness of (a) Membrane_I, (b) Membrane_LTO and (c) Membrane_AT.

(Table 4), which was confirmed by the peak of 'C=O' that hugely affects the hydrophilicity, and component analysis change of FT-IR and EDS analysis [11]. Further, in the SEM and AFM analysis result, the twisted and rough surface shape is considered to be caused because of the decreased filtration performance.

Consequently, it was confirmed that Membrane_LTO and Membrane_AT were confirmed to have changed membrane surface property, and only a small damage of hydrophilic additives is considered to cause the decrease in membrane filtration performance [6].

Table 4
Measurement result of membrane filtration performance

Membrane resistance (1/m)		
Membrane_I	Membrane_LTO	Membrane_AT
5.28×10^8	13.8×10^8	6.87×10^8

4. Conclusions

In this study, the membrane filtration performance of accelerated test is to be interpreted compared with the long-term operated membrane under the same HCl intensity.

Membrane_AT is considered to lose the hydrophilic functional groups because of defluorination reaction as well as the other aged factors, which causes the chemical structure deformation of membrane surface. Further, such a surface chemical property change is predicted to affect the additives lost.

Compared with Membrane_AT, Membrane_LTO has a high filtration resistance, which is predicted to be caused by the chemical reaction of various chemicals during CIP and aging inducing factors such as fouling, etc.

The study on the membrane of accelerated test is required which may predict the performance of membrane filtration facility considering the aging inducing factors including elusive materials.

Acknowledgement

This subject is supported by Korea Ministry of Environment as 'Global Top Project (2016002100004)'.

References

[1] F.A. Sheikh, M.A. Zargar, A.H. Tamboli, H. Kim, A super hydrophilic modification of poly(vinylidene fluoride) (PVDF) nanofibers: by in situ hydrothermal approach, Appl. Surf. Sci., 385 (2016) 417–425.
[2] H.P. Ngang, A.L. Ahmad, S.C. Low, B.S. Ooi, Preparation of thermoresponsive PVDF/SiO_2-PNIPAM mixed matrix membrane for saline oil emulsion separation and its cleaning efficiency, Desalination, 408 (2017) 1–12.
[3] X. Lü, X. Wang, L. Guo, Q. Zhang, X. Guo, L. Li, Preparation of PU modified PVDF antifouling membrane and its hydrophilic performance, J. Membr. Sci., 520 (2016) 933–940.
[4] D. Liu, D. Li, D. Du, X. Zhao, A. Qin, X. Li, C. He, Antifouling PVDF membrane with hydrophilic surface of terry pile-like structure, J. Membr. Sci., 493 (2015) 243–251.
[5] C. Regula, E. Carretier, Y. Wyart, G. Ge´san-Guiziou, A. Vincent, D. Boudot, P. Moulin, Chemical cleaning/disinfection and ageing of organic UF membranes: a review, Water Res., 56 (2014) 325–365.
[6] Z. Ma, X. Lu, C. Wu, Q. Gao, L. Zhao, Functional surface modification of PVDF membrane for chemical pulse cleaning, J. Membr. Sci., 524 (2017) 389–399.
[7] V. Puspitasari, A. Granville, P. Le-Clech, V. Chen, Cleaning and ageing effect of sodium hypochlorite on polyvinylidene fluoride (PVDF) membrane, Sep. Purif. Technol., 72 (2010) 301–308.
[8] M. Momtaz, J.-L. Dewez, J. Marchand-Brynaert, Chemical reactivity assay and surface characterization of a poly(vinylidene fluoride) microfiltration membrane, J. Membr. Sci., 250 (2005) 29–37.
[9] E. Zondervan, A. Zwijnenburg, B. Roffel, Surface modification of poly(vinylidene fluoride) by alkaline treatment 1. The degradation mechanism, Polymer, 41 (2000) 1685–1696.
[10] S. Hajibabania, A. Antony, G. Leslie, P. Le-Clech, Relative impact of fouling and cleaning on PVDF membrane hydraulic performances, Sep. Purif. Technol., 90 (2012) 204–212.
[11] Y. Zhang, J. Wang, F. Gao, Y. Chen, H. Zhang, A comparison study: the different impacts of sodium hypochlorite on PVDF and PSF ultrafiltration (UF) membranes, Water Res., 109 (2017) 227–236.
[12] S. Rouaix, C. Causserand, P. Aimar, Experimental study of the effects of hypochlorite on polysulfone membrane properties, J. Membr. Sci., 277 (2006) 137–147.
[13] P.J. Evans, M.R. Bird, A. Pihlajamaki, M. Nystrom, The influence of hydrophobicity, roughness and charge upon ultrafiltration membranes for black tea liquor clarification, J. Membr. Sci., 313 (2008) 250–262.
[14] J.-y. Tian, Z.-l. Chen, Y.-l. Yang, H. Liang, J. Nan, G.-b. Li, Consecutive chemical cleaning of fouled PVC membrane using NaOH and ethanol during ultrafiltration of river water, Water Res., 44 (2010) 59–68.
[15] S.Z. Abdullah, P.R. Bérubé, S. Jankhah, Model development to access the ageing of polymeric membrane due to chemical, Procedia Eng., 44 (2012) 871–873.
[16] S.Z. Abdullah, P.R. Bérubé, Assessing the effects of sodium hypochlorite exposure on the characteristics of PVDF based membranes, Water Res., 47 (2013) 5392–5399.
[17] S. Robinson, S.Z. Abdullah, P. Bérubé, P. Le-Clech, Ageing of membranes for water treatment: linking changes to performance, J. Membr. Sci., 503 (2016) 177–187.
[18] F. Gao, J. Wang, H. Zhang, Y. Zhang, M.A. Hang, Effects of sodium hypochlorite on structural/surface characteristics, filtration performance and fouling behaviors of PVDF membranes, J. Membr. Sci., 519 (2016) 22–31.
[19] E. Arkhangelsky, D. Kuzmenko, V. Gitis, Impact of chemical cleaning on properties and functioning of polyethersulfone membranes, J. Membr. Sci., 305 (2007) 176–184.
[20] A.J. Gijsbertsen-Abrahamse, E.R. Cornelissen, J.A.M.H. Hofman, Fiber failure frequency and causes of hollow fiber integrity loss, Desalination, 194 (2006) 251–258.
[21] F. Liu, N. Awanis Hashim, Y. Liu, M.R. Moghareh Abed, K. Li, Review: progress in the production and modification of PVDF membranes, J. Membr. Sci., 375 (2011) 1–27.
[22] N. Awanis Hashim, Yutie Liu, K. Li, Stability of PVDF hollow fibre membranes in sodium hydroxide aqueous solution, Chem. Eng. Sci., 66 (2011) 1565–1575.