Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Performance Evaluation of Alkaline Treated Poly(vinylidene fluoride) Membranes

Qi-Feng Liu[a][b]; Chang-Hee Lee[b]; Hern Kim[b]
[a] College of Environment & Resources, Inner Mongolia University, Hohhot, Inner Mongolia, China [b] Department of Environmental Engineering and Biotechnology, Energy and Environment Fusion Technology Center, Myongji University, Yongin, Kyonggi-do, Korea

To cite this Article Liu, Qi-Feng , Lee, Chang-Hee and Kim, Hern(2010) 'Performance Evaluation of Alkaline Treated Poly(vinylidene fluoride) Membranes', Separation Science and Technology, 45: 9, 1209 — 1215

To link to this Article: DOI: 10.1080/01496391003775808

URL: http://dx.doi.org/10.1080/01496391003775808

Separation Science and Technology, 45: 1209–1215, 2010
Copyright © Taylor & Francis Group, LLC
ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496391003775808

Performance Evaluation of Alkaline Treated Poly(vinylidene fluoride) Membranes

Qi-Feng Liu,[1,2] Chang-Hee Lee,[2] and Hern Kim[2]
[1]*College of Environment & Resources, Inner Mongolia University, Hohhot, Inner Mongolia, China*
[2]*Department of Environmental Engineering and Biotechnology, Energy and Environment Fusion Technology Center, Myongji University, Yongin, Kyonggi-do, Korea*

A poly(vinylidene fluoride) (PVDF) hollow fiber membrane surface was modified by alkaline treatment in this study. This subject was selected with the aim to confirm the mechanisms of alkaline degradation of PVDF membranes, characterize the variations of membrane surface morphology (e.g., average pore size, pore size distribution, porosity, etc.), and estimate the membrane fouling potential by a bench-scale test with synthetic surface water. The conditions of the alkaline treatment covered various concentrations, temperature, and processing time. The results of this study indicate that the hydrophilic PVDF membranes can be obtained after appropriate treatment without loss of integrity of the membrane surface. All factors, including the concentration of NaOH, temperature, and processing time affect membrane properties. The surface images and air flow rate of unmodified and modified membranes showed difference in their average pore size and pore size distribution. In general, the increase of the processing time decreases the average pore size at constant concentration and temperature; the increase of the NaOH concentration in solution and temperature fastens the degradation process. Membrane pure water flux decreased after alkaline treatment. This can be attributed to the decrease of pore size. However, the membrane anti-fouling potential increased after alkaline treatment due to the enhancement of hydrophilic property of membrane surface.

Keywords alkaline; hydrophilicity; membrane; PVDF

INTRODUCTION

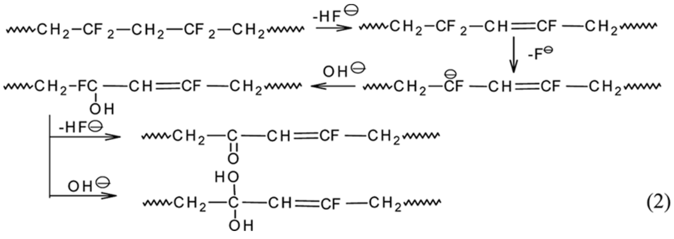
PVDF membranes have been widely used in recent years. This membrane shows a high flow rate and a high degree of strength, and excellent resistance to harsh chemical, thermal, and oxidizing conditions. As a result, it can be applicable to many fields. Especially, it is getting popular in water treatment system recently. However, the hydrophobic property of PVDF is more inclined to cause membrane fouling due to the affinity of hydrophobic organics for the membrane in a feed solution.

To solve this problem, numerous attempts (1–12) are therefore employed in order to modify the membrane surface and change membrane hydrophobicity. Examples are the plasma treatment, chemical oxidation, organic chemical functionalization, and radiation induced surface grafting. Among them, the alkaline treatment as a simple method has been investigated targeting the formation of expected properties based on the changes of its functional groups and structure of the chains.

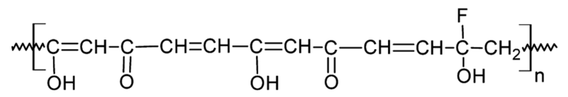
There has been a general consensus of the alkaline degradation mechanisms of PVDF as following the reaction depicted (8):

$$\sim\!(CH_2-CF_2)_n\!\sim + XOH \rightarrow \sim\!(CH=CF)_n\!\sim + XF + H_2O \quad (1)$$

Brewis et al. (1) expanded this mechanism to include the formation of the hydroxide and carbonyl groups on the polyene chain.


(2)

However, Ross et al. (8) found that the CF groups are present as an intermediate group only for the alkaline degradation of the PVDF on the basis of the XPS, ToF-SIMS, FT-IR, and Raman analysis. The oxygen present in the near surface region is mainly in the form of the hydroxyl and carbonyl groups but also to a lesser extent in the form of the COF groups according to the XPS results. A possible product in the near surface region is of the form shown below.



$$\sim\!\left[\underset{OH}{\underset{|}{C}}=CH-\underset{O}{\underset{\|}{C}}-CH=CH-\underset{OH}{\underset{|}{C}}=CH-\underset{O}{\underset{\|}{C}}-CH=CH-\overset{F}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-CH_2\right]_n\!\sim \quad (3)$$

Received 14 April 2009; accepted 16 February 2010.

Address correspondence to Hern Kim, Department of Environmental Engineering and Biotechnology, Myongji University, San 38-2 Nam-dong Cheoin-gu, Yongin, Kyonggi-do 449-728, Korea. Tel.: 82 313306688; Fax: 82 313366336. E-mail: hernkim@mju.ac.kr

Obviously, with regard to the defluorination mechanisms, the divarications still remain. Hence, one of the targets of this paper is to further confirm the degradation mechanisms of the PVDF membranes treated by alkaline solution.

On the other hand, it is well known that the alkaline treatment is very difficult to control due to its strong oxidizability. It could cause destruction of membrane integrity with improper treatment conditions. So, to estimate the impacts of experimental parameters on the membrane and find out proper and feasible treatment conditions is our other target.

What is more, instead of using the membrane cell, the bench-scale system consisted of hollow fiber membrane modules and a peristaltic pump were used to estimate the permeability and the antifouling potential in the synthetic surface water filtrating process. This new exploration can better reflect the real operating condition i.e., identify causing fouling factors than a simple buffer filtration test and the membrane fouling potential can be depicted more visually and credibly.

In summary, to confirm the degradation mechanisms of the PVDF membranes treated by alkaline solution, we estimate the impacts of experimental parameters on membrane and find out the proper and feasible treatment conditions, and evaluate the performance of alkaline treated PVDF membrane, which are the objects of this study.

EXPERIMENTAL

Materials

The hollow fiber braid membranes (Kolon Co., Korea) with an average 2 mm diameter were used in this study. The braided support layer is made of fiberglass material and was coated with PVDF via spin coating and the immersion precipitation technique. Aqueous sodium hydroxide (NaOH) solutions were made up from Extra Pure grade pellets, supplied by Duksan Co., Ltd.

Alkaline Treatments

The PVDF membranes were immersed in 1 M and 12 M NaOH bath at 20°C and 80°C for 1 minute to 120 minutes. After treatment the samples were rinsed with De-ionized (DI) water for 2 minutes, then immersed in DI water for 2 hours more, then rinsed again to thoroughly remove the residual NaOH. The samples were dried in an oven at 60°C.

Analysis

Surface infrared spectra were recorded on a Varian 2000 FTIR spectrometer. All spectra were acquired by signal averaging 32 scans at a resolution of 8 cm^{-1} in ATR mode. The membrane surface morphology and diameter of the support fiber and active layer were observed using a Hitachi S-3500 N scanning electron microscopy (SEM). The membrane mean pore size distribution was measured using a Capillary Flow Porometer (Porous Materials Inc., model CFP-1200AE). This analysis is based on a two-curve graph: dry up curve and wet up curve. DI water was used as the wetting fluid for the construction of the wet curve.

Permeation and Antifouling Properties

A single hollow fiber housed in a plastic tube with 6 mm inner diameter with the upper part sealed with epoxy resin, formed a dead-end module. This membrane module equipped with a peristaltic pump to be used to estimate the permeation properties of the untreated and treated PVDF in terms of transmembrane pressure (TMP) at constant flux condition. DI water was used to estimate the pure water flux. Subsequently, synthetic surface water (Table 1) was used to identify the antifouling characteristics by the same procedure. The synthetic water contained 2.5 mg/L of Georgia kaolinite, 2.5 mg/L of alumina, 5.0 mg/L of Aldrich humic acid (AHA), 0.5 mM of $NaHCO_3$, and 0.2 mM of $CaCl_2$. Kaolinite and alumina particles were dispersed in DI water and the suspension was placed in an ultrasound bath for 20 min, then NOM, $NaHCO_3$, and $CaCl_2$ were added and the suspension was mixed for an hour. The pressure data and the weight of the permeate were recorded via a digital pressure sensor and a digital balance at a fixed time interval. All the membranes were wetted with DI water for 30 min before flux measurements.

RESULTS AND DISCUSSION

Infrared Spectra

The PVDF braid membranes were treated with 1 M and 12 M NaOH solution for specified time period (1, 2, 5, 10, 15, 30, and 120 min) at 20°C and 80°C, respectively. The FT-IR spectra are given in Figs. 1–3 for samples before and after all of the above treatments. Fig. 1 shows several new weak absorbance peaks between 1500 cm^{-1} to 1600 cm^{-1}, which indicates the existence of conjugated carbon double bonds. According to Ross et al. (8), this absorbance is weak as a result of the fact that the C=C bond is inactive in infrared (normally conjugated structures are not active in the infrared but are Raman active). The absorbance intensity increased with processing time. This would lead to the conclusion that more thorough defluorination with increase in processing time. The absorbance intensity

TABLE 1
The characteristics of synthetic raw water

pH	Turbidity (NTU)	UV-254 (cm$^{-1)}$	TOC (mg/L)	Temperature (°C)
7.14	11.8	0.114	2.85	25

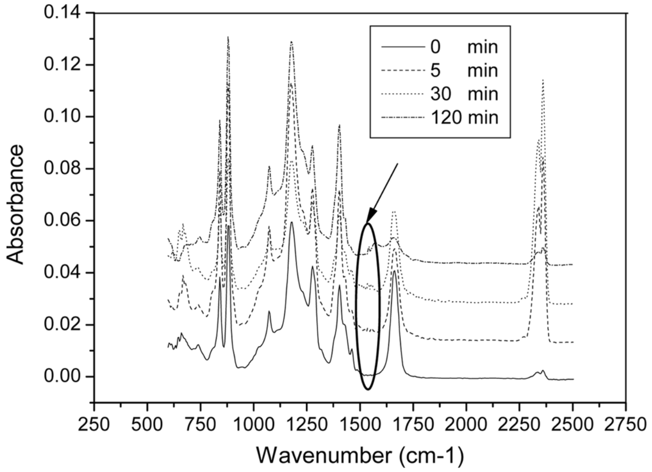


FIG. 1. FT-IR spectra of PVDF braid membranes treated with 12 M NaOH solutions at 80°C.

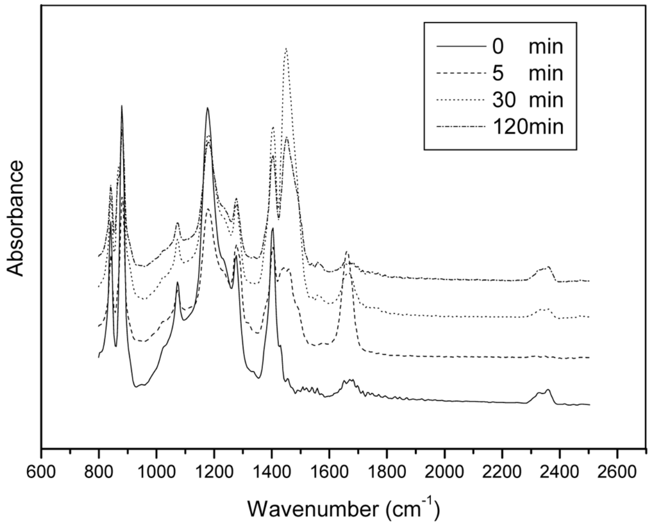


FIG. 3. FT-IR spectra of PVDF braid membranes treated with 1 M NaOH solutions at 80°C.

significantly increased at 2350 cm^{-1} after 5 min and 30 min treatment may attribute to the strength vibration of the triple carbon bond. However, the absorbance at this wave changed back to its original profile when the membranes were further treated for 120 minutes, which means that triple carbon bonds are not present in the final product, i.e., it is an intermediate species present during the reaction. There is similar absorbance phenomenon presented between 1700 cm^{-1} to 1800 cm^{-1}, which can be assigned to C=O bond. Because it appeared in the short-term process (5 and 30 min), and disappeared after long-term process (120 min), so the C=O bond also is an intermediate species. The characteristic band of the PVDF almost unchanged after treatment with 1 M NaOH at 20°C for the entire specified time period (Fig. 2). This implies that such conditions are insufficient for defluorination. With further increase of temperature to 80°C, an absorbance intensity is seen to grow in between 1400 cm^{-1} to 1600 cm^{-1} (Fig. 3). This reflects the presence of conjugated carbon double bonds. The intensity of this band increases with increasing treatment times too. However, we did not see the impact of triple carbon bonds on the intensity of adsorption at 2350 cm^{-1}.

Pore Size Distribution

The pore size distribution for PVDF braid membrane treated with 1 M and 12 M NaOH solution at 80°C for

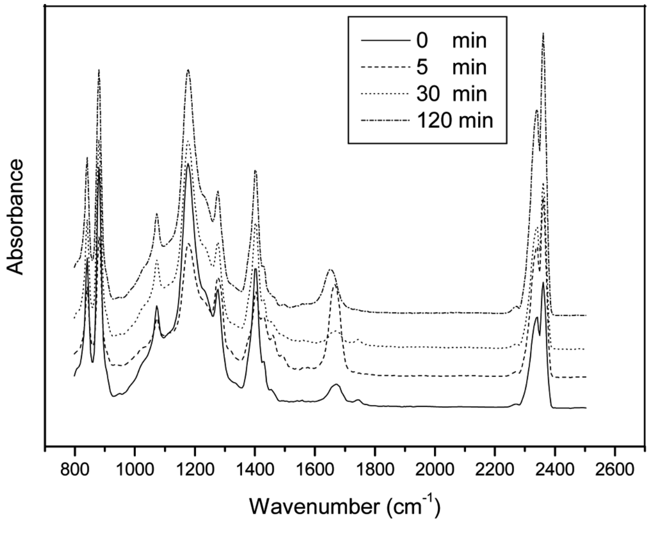


FIG. 2. 2 FT-IR spectra of PVDF braid membranes treated with 1 M NaOH solutions at 20°C.

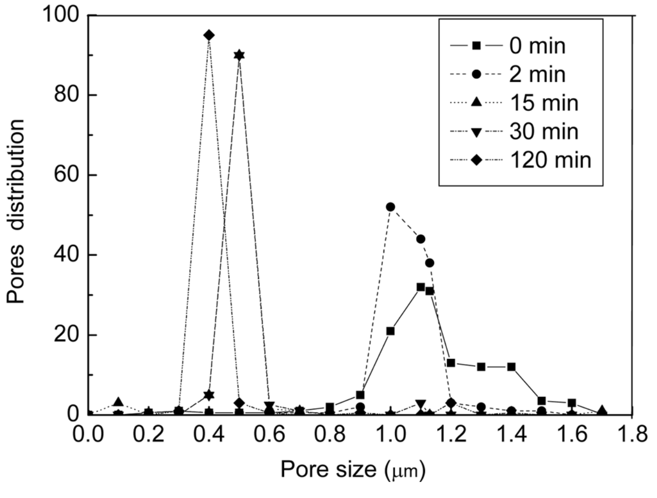


FIG. 4. Pore-size distributions for un-treated and treated PVDF braid membrane with 1 M, 80°C NaOH solution for specified time periods (0 min, 2 min, 15 min, 30 min, and 120 min).

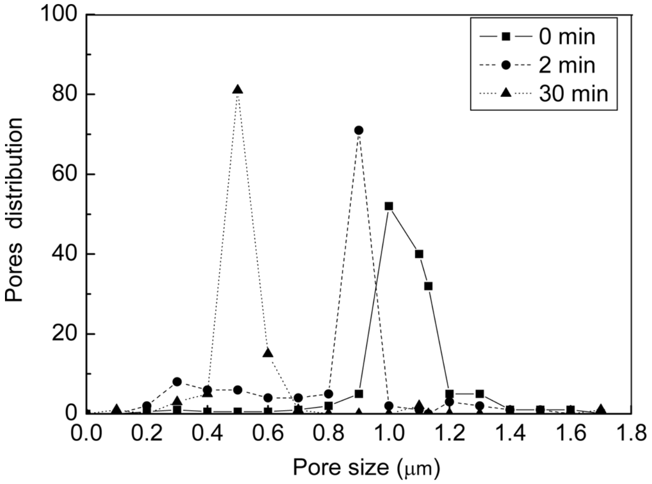


FIG. 5. Pore-size distributions for un-treated and treated PVDF braid membrane with 12 M, 80°C NaOH solution for specified time periods (0 min, 2 min and 30 min).

specified time periods were presented in Figs. 4 and 5, respectively. Overall, it can be seen that the pore size distribution is closely related to the processing time. The maximum number of pores shifted to lower values with increasing the alkaline treatment time. In detail, the pore size distribution peak of the untreated PVDF braid membrane located at 1 μm. For the treatment with 1 M NaOH at 80°C (Fig. 4), the distribution peak slightly shifted to a smaller size after 2 min treatment. The distribution peaked at about 0.5 μm after 15 and 30 min treatment. It further decreased to 0.4 μm with 120 min treatment. For the treatment with 12 M NaOH at 80°C (Fig. 5), the distribution peak moved to about 0.8 μm after 2 min treatment and 0.5 μm after 30 min treatment. It is noted that the pore size reduction may occur due to the microstructural shrinkage of the membrane by alkaline treatment. Further increasing in treatment time could lead to the destruction of the membrane integrity under this condition. The mechanical properties of the membrane, including the tensile elongation and tensile strength, need to be precisely examined in order to get optimal performance of alkaline treated membranes. So, this phenomenon leads us to the following conclusions that alkaline treatment can lead to smaller pore size distribution; this trend further enhanced with the extension of the treatment time; higher alkali concentrations can much accelerate the membrane surface degradation. However, it also can easily cause damage to the integrity of membrane surface.

Morphology of Membrane Surface

The SEM images of the cross-section and top surface of the samples are shown in Fig. 6. Figs. 6(a) and 6(b) represent the PVDF membranes before and after 120 min treatment at 12 M NaOH solution. By comparing these figures it can be seen that the treated membranes show a smaller pore size distribution and less porosity than untreated membrane. This result is consistent with the results observed by a capillary flow porometer. So, it suggests that alkaline treatment not only can change the membrane hydrophilicity but also can alter the membrane pore structure. Similar phenomena have also been found under other alkaline treatment conditions. Figs. 6(c) and 6(d) represent the treated and untreated PVDF membranes, which had been used in synthetic surface water filtration. Cake layers formed on the membrane surface after a certain time operation, which are composed mainly of the humic acid and kaolin in feed water. The cake layer formed on the untreated membrane shows a higher density in appearance than the cake formed on the surface of the treated membrane. The cake layer formed on the treated membrane obviously has higher porosity. The reason for this belief is due to the hydrophilicity improvement of the treated membrane.

Membrane Performances

Hydraulic Permeability

Pure water fluxes before and after alkaline treatment were measured and the typical results are shown in Fig. 7.

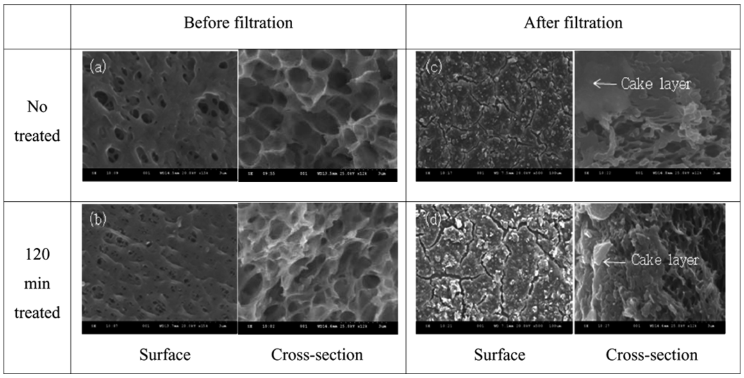


FIG. 6. SEM micrographs of the outer surface and cross section of braid membrane before and after alkaline treatment.

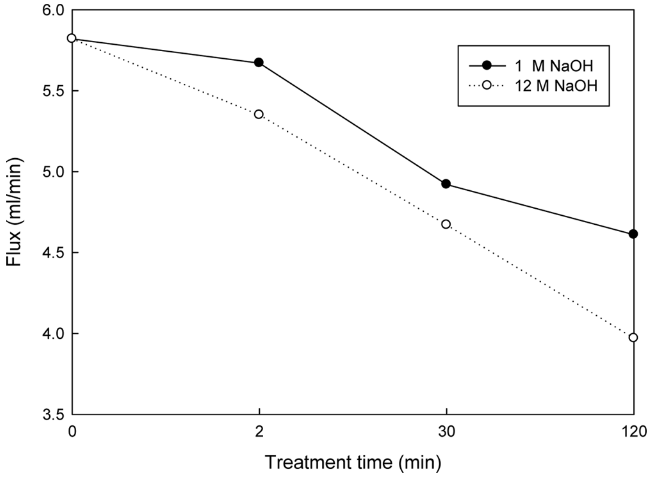


FIG. 7. Pure water flux as a function of treatment time for membrane treated with 1 M and 12 M alkaline.

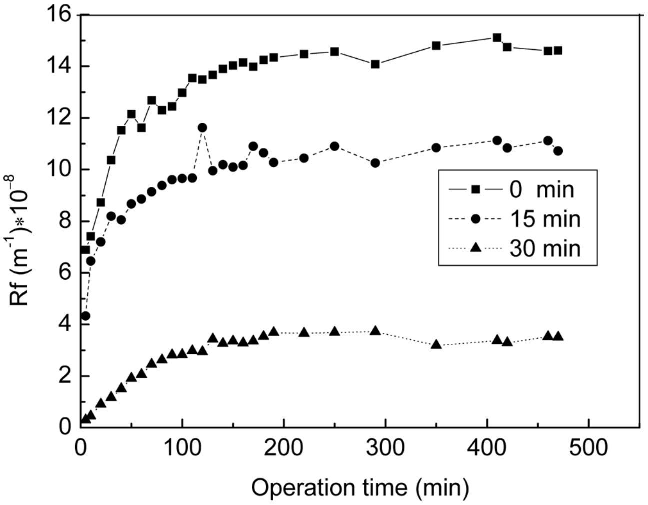


FIG. 8. Cake resistance as a function of operating time for membrane treated at specified time with 12 M NaOH solution.

It is found that the pure water fluxes slightly decreased after the alkaline treatment at both alkali concentrations of 1 M and 12 M. This trend was further enhanced with treatment time. There is a general recognition that two parameters affect the pure water flux mostly: the pore size/porosity and surface hydrophilicity/hydrophobicity. The membrane permeability increases with the increase of surface hydrophilicity and decreases with decrease of the pore size and porosity. In our cases, the pore size acts as the dominant factor and the pure water flux accordingly decreased even though the hydrophilicity has been improving after the alkaline treatment.

Antifouling Performance

Membrane fouling is a complex phenomenon, which involves many chemical and physical factors. In this study, the membrane fouling potential was estimated based on the resistance-in-series model:

$$J = \frac{\Delta p}{\mu(R_m + R_{cp} + R_c)} \tag{4}$$

where J is the filtrate flux; Δp is the pressure drop across the membrane; μ is the absolute water viscosity; R_m is the hydraulic resistance of a clean membrane, which can be estimated from pure water flux through fresh membranes; R_{cp} is the concentration polarization resistance; R_c is the cake resistance. We define R_f as the total resistance caused by cake layer and concentration polarization. It can be obtained after rearranging Eq. (4) as follows:

$$R_f = \frac{\Delta p}{\mu J} - R_m \tag{5}$$

The total resistances of membranes, which were treated with 1 M and 12 M NaOH solution for a specified time period are illustrated in Figs. 8 and 9, respectively. It is apparent from these figures that the resistance caused by fouling decreased after alkaline treatment. In other words, the alkaline modified membranes performed better fouling resistant when filtrated with synthetic surface water.

Water Quality

Residual turbidity, UV_{254}, and TOC were analyzed as the representation of water quality for the filtrate. The synthetic feed water turbidity is around 11.8 NTU (Table 1). From Fig. 10, it can be seen that the turbidity removal rate is 98.77% for the untreated membrane and it is further

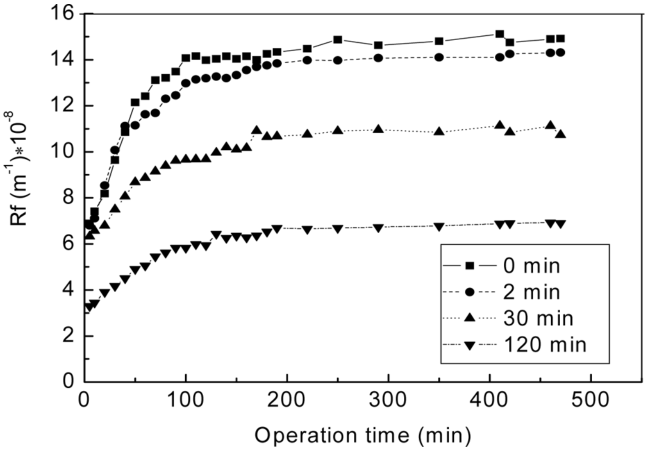


FIG. 9. Cake resistance as a function of operating time for membrane treated at specified time with 1 M NaOH solution.

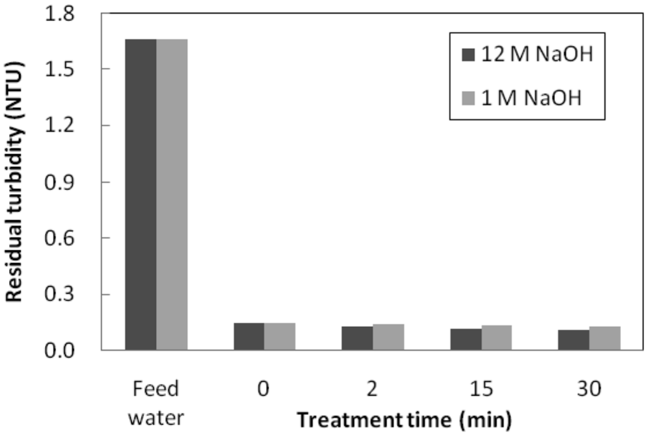


FIG. 10. Residual turbidity as a function of treatment time for membrane treated with 1 M and 12 M alkaline.

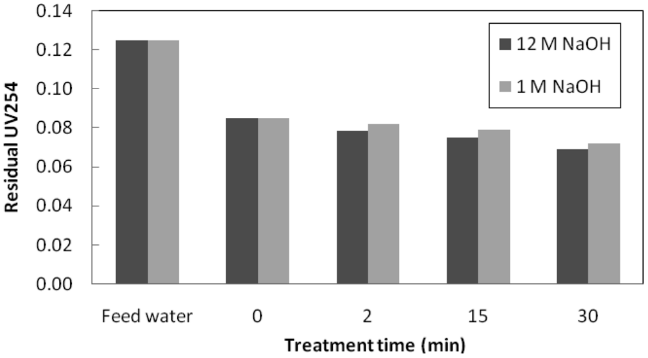


FIG. 11. Residual UV254 as a function of treatment time for membrane treated with 1 M and 12 M alkaline.

exceeded by 99% for the membrane treated with alkaline for 2, 15, and 30 minutes. Undoubtedly, the excellent capability of the turbidity control of membrane was confirmed. Moreover, this capability was further enhanced after alkaline treatment as a result of the smaller pore size distribution and improved hydrophilicity. In the same way, the UV_{254} and TOC removal rate (Figs. 11 and 12) were improved after alkaline treatment.

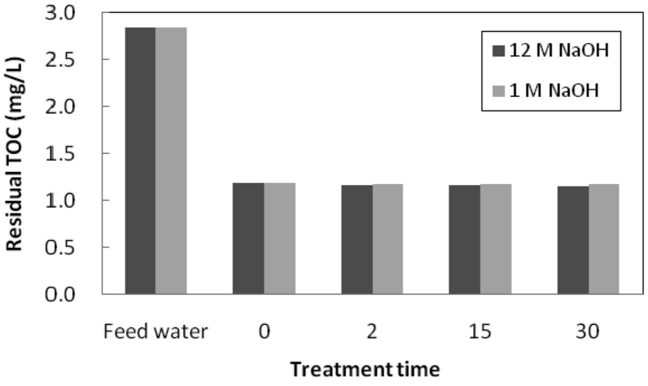


FIG. 12. Residual TOC as a function of treatment time for membrane treated with 1 M and 12 M alkaline.

CONCLUSIONS

The hydrophilic PVDF membrane can be obtained after appropriate alkaline treatment. However, extreme high alkali concentration may result in damage of membrane integrity. By comparing the various treatment conditions, the low concentration with high temperature are recommended in this case study. Besides, the alkaline treatment changed the membrane surface structure based on the results of pore size distribution. The membrane pore size decreased after alkaline treatment. This result was further confirmed by the decrease of pure water flux with the treated membrane. However, according to the cake resistance data, it can be seen that the anti-fouling potential of the treated membrane slightly increased. The reason for this result may be due to the hydrophilic property of the membrane surface after treatment.

ACKNOWLEDGEMENTS

This work was supported by the Priority Research Centers Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science, and Technology (2009-0093816).

REFERENCES

1. Brewis, D.M.; Mathieson, I.; Sutherland, I.; Cayless, R.A.; Dahm, R.H. (1996) Pretreatment of poly(vinyl fluoride) and poly(vinylidene fluoride) with potassium hydroxide. *Int. J. Adhes. Adhes.*, 16: 87.
2. Cho, J.W.; Song, H.Y. (1995) Dehydrofluorination of a copolymer of vinylidene fluoride and tetrafluoroethylene by phase transfer catalysis reaction. *J. Polym. Sci.: Part A: Polym. Chem.*, 33: 2109.
3. Crowe, R.; Badyal, J.P.S. (1991) Surface modification of poly(vinylidene difluoride) (PVdF) by Li OH. *J. Chem. Soc., Chem. Commun.*, 14: 958.
4. Dias, A.J.; McCarthy, T.J. (1985) Dehydrofluorination of poly(vinylidene fluoride) in dimethylformamide solution: Synthesis of an operationally soluble semiconducting polymer. *J. Polym. Sci.: Polym. Chem.*, 23: 1057.
5. Bhut, B.V.; Wickramasinghe, S.R.; Husson, S.M. (2008) Preparation of high-capacity, weak anion-exchange membranes for protein separations using surface-initiated atom transfer radical polymerization. *J. Membr. Sci.*, 325: 176.
6. Hahn, B.; Percec, V. (1987) Functional polymers and sequential copolymers by phase transfer catalysis. Vinylidene fluoride–trifluoroethylene copolymers by surface modification of polyvinylidene fluoride. *J. Polym. Sci. Part A: Polym. Chem.*, 25: 783.
7. Kise, H.; Ogata, H. (1983) Phase transfer catalysis in dehydrofluorination of poly(vinylidene fluoride) by aqueous sodium hydroxide solutions. *J. Polym. Sci.: Polym. Chem.*, 21: 3443.
8. Rossa, G.J.; Wattsa, J.F.; Hilla, M.P.; Morrisseyb, P. (2000) Surface modification of poly(vinylidene fluoride) by alkaline treatment 1. The degradation mechanism. *Polymer*, 41: 1685.

9. Owen, E.D.; Shah, M.; Twigg, M.V. (1996) Phase transfer catalysed degradation of poly(vinyl chloride). Product characterisation and handling. *Polym. Degrad. Stab.*, 51: 151.
10. Rossa, G.J.; Wattsa, J.F.; Hilla, M.P.; Morrisseyb, P. (2000) Surface modification of poly(vinylidene fluoride) by alkaline treatment Part 2. Process modification by the use of phase transfer catalysis. *Polymer*, 42: 403.
11. Zhang, S.C.; Shen, J.; Qiu, X.P.; Weng, D.S.; Zhu, W.T. (2006) ESR and vibrational spectroscopy study on poly(vinylidene fluoride) membranes with alkaline treatment. *J. Power Sourc.*, 153: 234.
12. Wang, W.Y.; Chen, L.; Yu, X. (2005) Preparation of temperature sensitive poly(vinylidene fluoride) hollow fiber membranes grafted with N-isopropylacrylamide by a noval approach. *J. Appl. Polym. Sci.*, 101: 833.