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Effect of pretreatment on fouling propensity of shale gas wastewater in membrane distillation process

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ABSTRACT

Membrane distillation (MD) has potential to concentrate produced water from the hydraulic fracturing process, leading to reduced disposal cost for shale gas wastewater. However, it is anticipated that MD suffers from severe membrane fouling if it is directly applied to treat such wastewater. Accordingly, this study explored the techniques for pretreatment of shale gas wastewater to mitigated fouling in MD process. Microbubble treatment and filtration were considered in lab-scale experiments. A synthetic shale gas wastewater was prepared based on the compositions of the real produced water and flowback water.Experimental results showed that the microbubble pretreatment could be successfully applied for MD treatment of the synthetic shale gas wastewater. Without pretreatment, flux decline in MD system was found to be very high (>90% decrease within 600 min). After the pretreatment using microbubbles, the flux maintained constant even after 700 min. This was attributed to the removal of colloidal particles in the feedwater by applying microbubbles. The efficiency of the pretreatment was improved by combining microbubble treatment with filtration using 1-μm filter. Based on these results, MD was applied to treat real wastewaters after pretreatment using a media filter. The flux decline was observed after 800 min of MD operation, suggesting not only particulate fouling but also scale formation should be properly controlled prior to MD treatment.

Keywords: Wastewater treatment; Fracking; Unconventional; Shale gas; Produced water; Microbubbles

1. Introduction

Shale gas is natural gas found in shale rocks, which have very low permeability, making gas production more complex and costly [1–4]. Shale gas is a so-called "unconventional gas," categorized with "tight gas" from sandstones or limestone with low permeability and "coal bed methane" [4,5]. While both conventional and unconventional deposits contain natural gas, the

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more elaborate production methods distinguish unconventional from conventional deposits [6]. Since hydraulic fracturing is required for shale gas extraction, proper treatment and management of the wastewater is important [7,8]. The wastewaters from shale gas well include produced water and flowback water, which are difficult to treat using conventional technologies due to high concentration of salts and chemicals [8–15].

Recently, membrane distillation (MD) has drawn attention as an attractive technology for the treatment of shale gas wastewater. MD is a thermal process that uses hydrophobic membranes to separate vapor from water [16,17]. Accordingly, MD possesses many advantages over other desalination technologies such as reverse osmosis, multi-stage flash distillation, and multi-effect distillation: Minimum use of electrical energy, operation under relatively low pressure conditions, capability of using low-grade heat such as waste heat and solar heat, small footprint, and low-fouling propensity [17–20]. Moreover, it is effective for treating feedwater containing high TDS [21,22] because MD is not limited by the osmotic pressure of the feedwater.

However, MD is one of the membrane-based technologies and thus is vulnerable to membrane fouling. Since the shale gas wastewater contains high concentrations of salt, chemicals, and particulate matters [7], it should have high-fouling potential. Accordingly, proper pretreatment technique is required to enable MD application for shale gas wastewater treatment.

Of particular, in this study are pretreatment methods based on filtration and microbubble prior to MD treatment of shale gas wastewater. Microbubbles are bubbles smaller than one millimeter in diameter, but larger than one micrometer. They have widespread application in industry, life science, and medicine. The composition of the bubble shell and filling material determine important design features such as buoyancy, crush strength, thermal conductivity, and acoustic properties [23]. Microbubbles were used in various fields like industry, life science, and medicine. Especially, microbubbles may be used for membrane cleaning/biofilm control and wastewater treatment purposes [23,24].

Thus, this study intended to explore the techniques for pretreatment of shale gas wastewater to mitigated fouling in MD process based on microbubble and filtration. A laboratory-scale experiment was carried out using a microbubble treatment system and MD systems. A synthetic shale gas wastewater was prepared based on the compositions of the real produced water and flowback water. The effect of pretreatment on flux decline and foulant layer on the MD membrane surface was examined. Real produced water and flowback water were also treated using MD after pretreatment using filters to confirm the feasibility of MD for shale gas wastewater treatment.

2. Materials and methods

2.1. Feed solution and reagents

Real produced water and flowback waters were collected from Bakken Williston and Eagle Ford Galvan regions in the United States. The compositions for this wastewater are listed in Table 1. Based on these compositions, synthetic produced water and flowback waters were prepared as shown in Table 2. The synthetic wastewaters were used for the laboratory-scale experiments. A set of experiments using the real wastewaters were also carried out at the end of this study.

2.2. Pretreatment

Two types of pretreatments were considered: (1) Microbubble treatment and (2) filtration. Fig. 1 shows the schematic diagram for the microbubble treatment system. This consists of a microbubble generation pump, floatation tank, and a high-pressure air source. Microbubbles are generated under 4 bar by mixing water and air through a circulation tank. The nominal

Table 1
Composition of real shale gas wastewaters

Parameter	Produced water	Flow-back water
pH	5.5	4.3
Total alkalinity (ppm as $CaCO_3$)	76	2,000.0
Total suspended solids (ppm)	3,134	1,559.1
Total dissolved solids (ppm)	357,527	1,493.1
Volatile suspended solids (ppm)	343	481.9
Total solids (ppm)	360,661	3,052.2
Turbidity (NTU)	454	2,255.0
Conductivity (μS/cm)	259,000	1,554.7

Table 2
Composition of synthetic shale gas wastewaters

	Synthetic flowback water (mg/L)	Synthetic produced water (mg/L)
NaCl	288	240,000
CaCl	258	51,300
KCl	–	13,300
$AlCl_3$	99	
NaBr	59	
$SiCl_4$	77	
$MgCl_2$	72	3.200
TDS	869	306,900
Conductivity	1,045 (μS/cm)	241,000 (μS/cm)

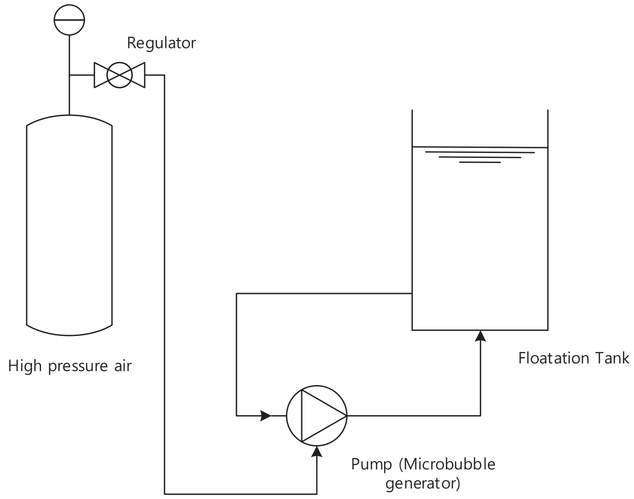


Fig. 1. Schematic diagram of laboratory-scale microbubble treatment system.

bubble size is reported by 8 μm from the manufacturer of the microbubble generator. It should be noted that this microbubble treatment is effective to decrease the turbidity of the feedwater and does not affect the TDS and conductivity. The operating conditions for the microbubble treatment are summarized in Table 3. The filtration of the synthetic wastewater was carried out using a glass filter with the pore size of 1.2 μm. On the other hand, the filtration of real wastewater was carried out using a sediment filter, which has similar pore size to the glass filter.

2.3. Membrane distillation

MD experiments were carried out using the systems shown in Fig. 2. Direct contact MD (DCMD), air gap MD (AGMD), and vacuum MD (VMD) were performed using flat-sheet membranes. DCMD and VMD were performed using hollow fiber membranes. Details are summarized in Tables 4 and 5.

3. Results and discussion

3.1. Comparison of water flux in different MD configurations under non-fouling condition

To begin, initial performances of different MD modules were compared in terms of permeate flux. Five (5) kinds of MD modules were used to measure

Table 3
Summary of microbubble treatment system

Item	Condition
Microbubble generator	Gas-water circulation-type generator
Motor	Toshiba three phase induction motor (KTM15N1D042 M-000)
Specific pressure	4 bars
Flow rate	
Water	8 L/mim
Air	0.64 L/min
Nominal bubble size	8 μm in the floatation column

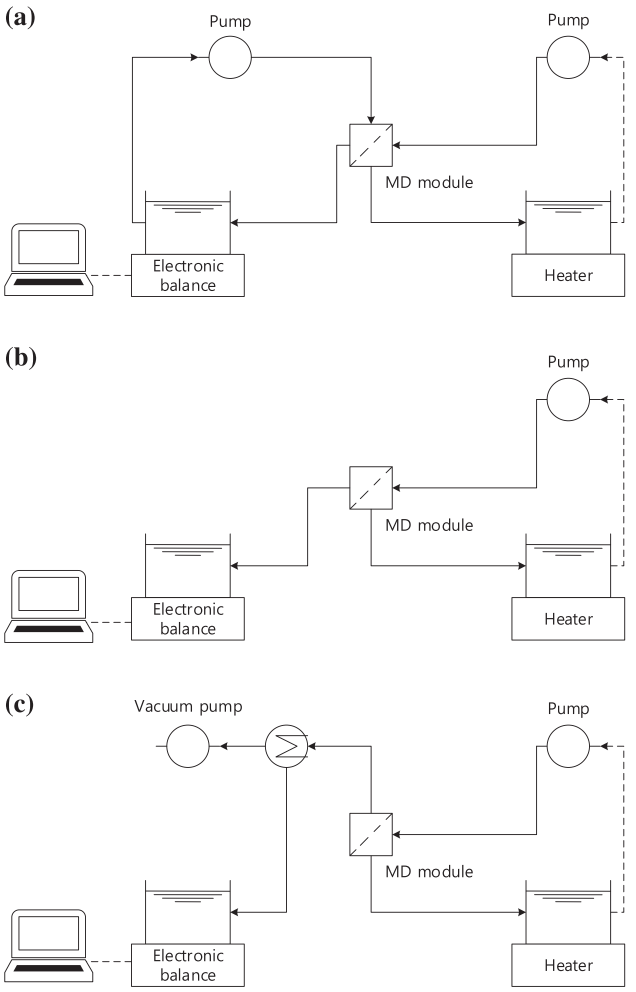


Fig. 2. Schematics of membrane distillation systems: (a) DCMD, (b) AGMD, and (c) VMD.

flux for feedwater containing NaCl of 3,000 mg/L. The results are shown in Fig. 3. Regardless of membrane types, DCMD shows the highest flux. This is because the mass transfer resistance for water vapor in DCMD is relatively small. On the other hand, VMD and AGMD show lower flux than DCMD. The flux in DCMD modes ranges from 13 to 14 kg/m^2 h after stabilization of the system. The flux in VMD mode is around 11 kg/m^2 h and that in AGMD mode is approximately 6–7 kg/m^2 h.

3.2. Fouling of MD membrane

Fig. 4 shows the flux behaviors of the MD system with time during the treatment of synthetic produced water. The black symbols show the results of MD tests without any pretreatment. Initially, the flux was maintained between 9 and 10 kg/m^2 h. After 200 min, however, the flux started to rapidly decrease. At the end of the MD test, the flux was less than 1 kg/m^2 h, which was almost 10% of the initial flux. The results clearly suggest that MD fouling is serious in the treatment of the synthetic wastewater. Since the salt concentrations are high in the wastewater, it is expected that the solution is supersaturated. Accordingly, these salts seem to precipitate on the membrane surface during the MD operation and result in membrane fouling. Moreover, the solution also contains suspended solids (turbidity ~4.5 NTU) and thus cake formation may also occur. These results clearly suggest that the pretreatment of the wastewater is required prior to MD operation.

Table 4
Operation conditions of flat sheet MD experiments

Item	Condition
Operation type	DCMD, AGMD, VMD
Membrane	PVDF 0.22 μm
Effective membrane area	12.2 cm^2
Cross-flow velocity	
Feed	0.4 L/min
Permeate	0.26 L/min (DCMD)
Solution	
Feed	Synthetic wastewater
Permeate	D.I. water (DCMD)
Temperature	
Feed side	60℃
Permeate side	20℃
Vacuum	97 mbar

Table 5
Operation conditions of hollow fiber MD experiments

Item	Condition
Operation type	DCMD, VMD
Membrane	PVDF 0.22 μm
Effective membrane area	0.125 m^2
Cross-flow velocity	
Feed	0.6 L/min
Permeate	0.4 L/min (DCMD)
Solution	
Feed	Synthetic wastewater
Permeate	D.I. water (DCMD)
Temperature	
Feed side	60℃
Permeate side	20℃
Vacuum	97 mbar (VMD)

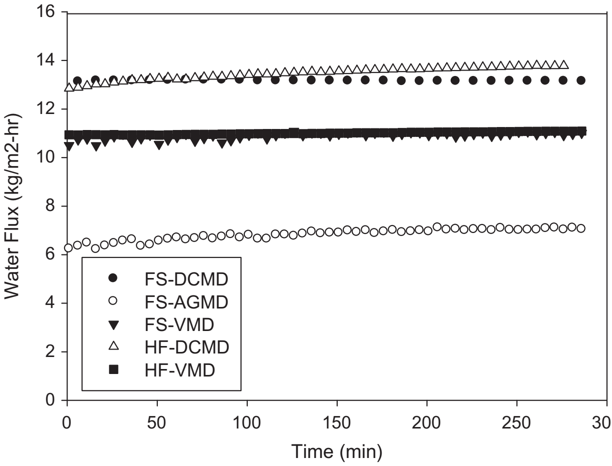


Fig. 3. Comparison of water flux in various MD configurations under non-fouling condition. Operating conditions: Feedwater: NaCl 3,000 mg/L; $T_{\text{feed}} = 60$℃; $T_{\text{distillate}} = 20$℃.

3.3. Effect of pretreatment on MD fouling control

Fig. 4 also shows the dependence of flux on time in MD using wastewater pretreated by microbubble (while symbols in the graph) and microbubble followed by filtratration (black triangle symbol). It is evident that microbubble can increase MD flux by mitigating fouling. The flux maintained high even after MD operation of 500 min. After 600 min, the flux started to gradually decrease and the fouling rate was lower than that without pretreatment.

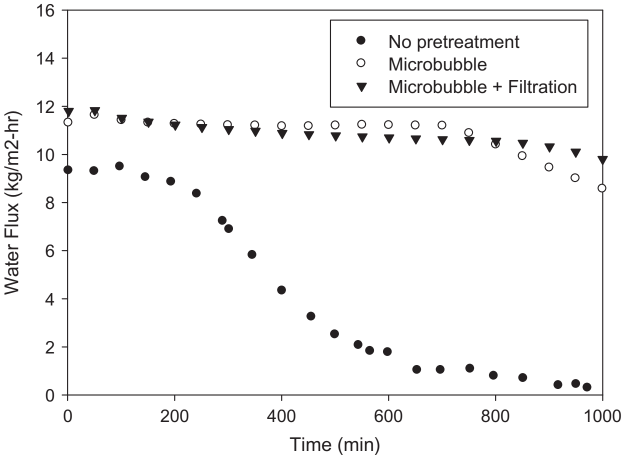


Fig. 4. Effect of pretreatment on MD flux for synthetic produced water. Operating conditions: Feedwater: Synthetic produced water; $T_{\text{feed}} = 60$℃; $T_{\text{distillate}} = 20$℃; MD configuration: DCMD.

It is interesting to note that microbubble treatment did not significantly change the water quality. As shown in Table 6, the turbidity after microbubble pretreatment was ranged from 3.1 to 3.8 NTU, while the turbidity of untreated water was 4.5 NTU. Although a small fraction of particles were removed by microbubble pretreatment, it cannot explain the significant improvement of flux shown in Fig. 5.

The effect of pretreatment becomes more significant when microbubble treatment was combined with GF/C filtration. As shown in Fig. 5, the flux was improved by the combination of microbubble and GF/C. This suggests that the particles that can be removed by microbubble and GF/C are responsible for rapid MD fouling.

3.4. Scanning electron microscopy (SEM)

Fig. 5 compares scanning electron microscopy (SEM) images of MD membrane surface under different operating conditions. As presented in Fig. 5(a), the clean membrane shows clear pore structures on its surface. After MD treatment of synthetic wastewater without pretreatment, the surface is covered by cake layers and crystal particles, which seem to be main reason for rapid flux decline. Application of pretreatment using the filter or microbubble reduced the amount of foualants on the membrane surface as illustrated in Fig. 5(c), (d), and (e). The combination of microbubble with filtration seems to result in the smallest amount of foulant on the membrane surface. These results suggest that pretreatment using either

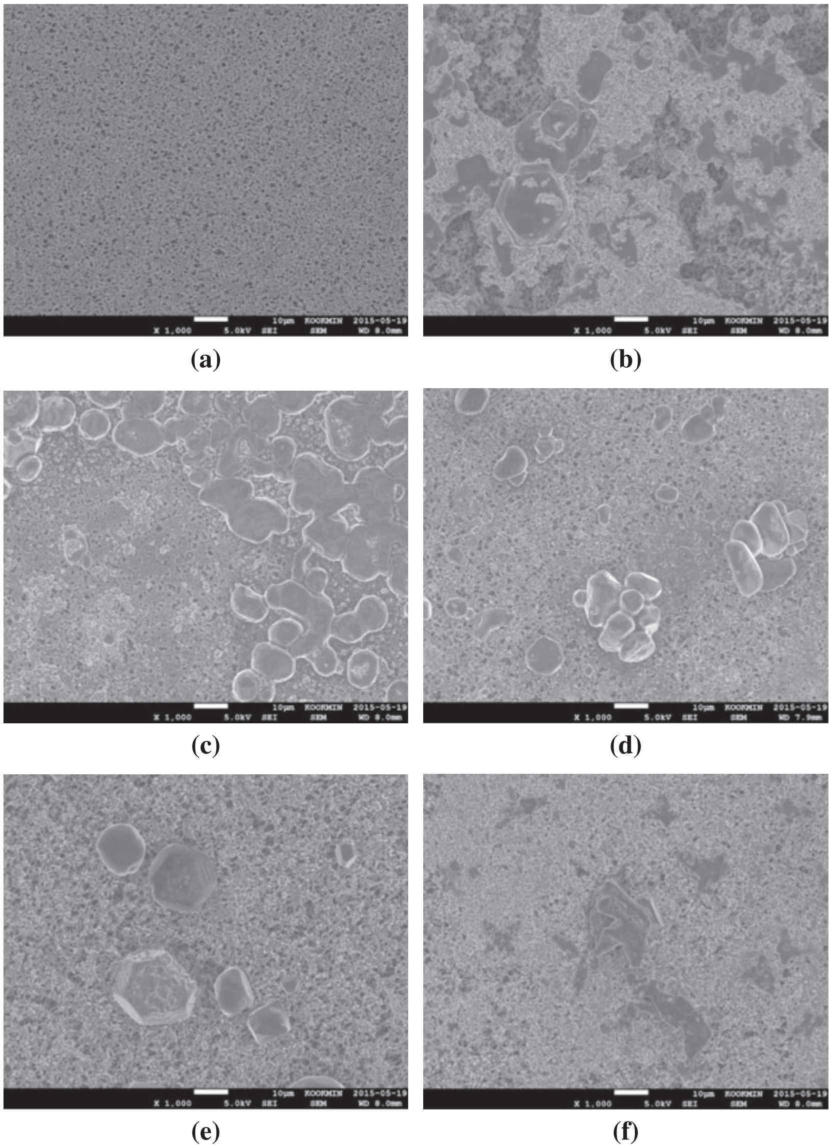
Table 6
Effect of pretreatment on water quality of synthetic produced water

	Turbidity (NTU)	Conductivity (m/S)
Synthetic produced water	4.5	241
Filtration	3.5	238
Microbubble 15 min	3.8	239
Microbubble 30 min	3.1	238

microbubble or filtration can mitigate fouling due to cake formation and crystal deposition on the MD membrane surface.

3.5. Effect of microbubble on MD fouling control in different MD configurations

As shown in Fig. 6, the dependence of water flux on time was compared in different MD configurations after the pretreatment of synthetic produced water using microbubble and filtration. The FS-DCMD process shows the highest flux of 11.6 kg/m^2 h, while the



(a) (b) (c) (d) (e) (f)

Fig. 5. SEM images: (a) original membrane, (b) without pretreatment, (c) pretreatment using filter, (d) pretreatment using microbubble (15 min), (e) pretreatment using microbubble (30 min), and (f) pretreatment using microbubble and filter.

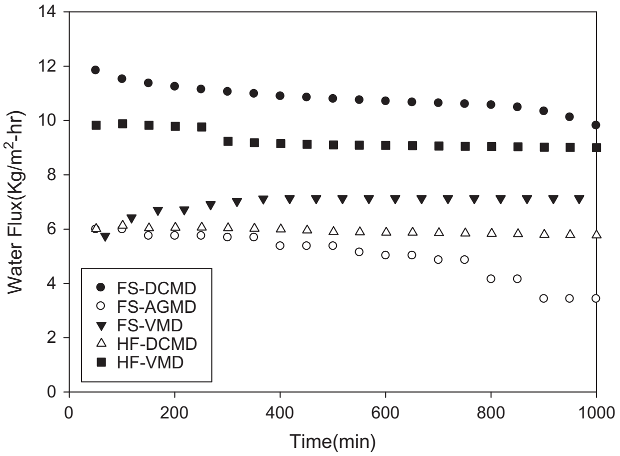


Fig. 6. Comparison of flux in various MD configurations for pretreated synthetic produced water. Operating conditions: Feedwater: Synthetic produced water after microbubble treatment and filtration; $T_{\text{feed}} = 60$°C; $T_{\text{distillate}} = 20$°C.

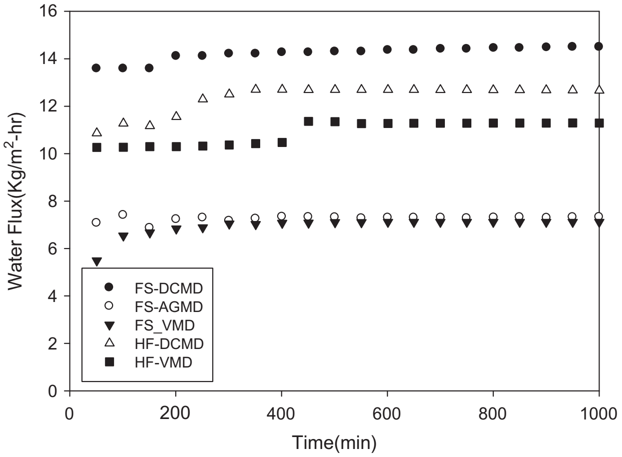


Fig. 7. Comparison of flux in various MD configurations for pretreated synthetic flowback water. Operating conditions: Feedwater: Synthetic flowback water without pretreatment; $T_{\text{feed}} = 60$°C; $T_{\text{distillate}} = 20$°C.

FS-AGMD process shows the lowest flux of 5.2 kg/m^2 h under the same conditions. The other systems show water flux values ranging from 6 to 10 kg/m^2 h. Although there were slight changes in flux with time, no significant fouling was observed in all cases.

Fig. 7 shows the flux in various MD configurations for pretreated synthetic flowback water. Since the synthetic flowback water contains lower amount of salts than the synthetic produced water, the flux values were not changed at all. This suggests that the fouling potential of the flowback water is lower than that of produced water after applying pretreatment.

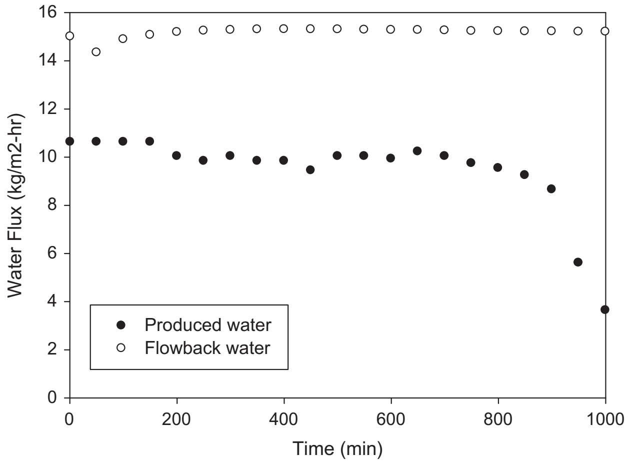


Fig. 8. Comparison of MD flux for pretreated real produced water and flowback water. Operating conditions: Feedwater: Real produced water and real flowback water after pretreatment; $T_{\text{feed}} = 60$°C; $T_{\text{distillate}} = 20$°C.

3.6. MD treatment of real shale gas wastewater after pretreatment

Fig. 8 shows the results on the MD flux for the real produced water and flowback water, which compositions are shown in Table 1. Only sediment/carbon filtration was applied for the pretreatment of the real wastewater. Nevertheless, the flux was stable during the 800 min of MD operation for both wastewaters. After 800 min, however, flux decline was observed for the real produced water. This is attributed to the scale formation of the dissolved salt in the produced water. Accordingly, it was suggested that not only the removal of particles but also the retardation of scale formation should be considered for long-term operation of MD system for produced water treatment.

4. Conclusion

This study investigated the effect of pretreatment on the fouling potential of both synthetic and real shale gas wastewaters in MD process. The following conclusions were withdrawn:

(1) Without pretreatment, MD fouling was severe: Initially, the flux was 8.7 kg/m^2 h but decreased to 1 kg/m^2 h after 600 min, suggesting that proper pretreatment is essential.
(2) Both microbubble and filtration were applied as pretreatment methods for shale gas wastew-

aters. After the pretreatment by microbubbles, the flux maintained constant even after 700 min. This was attributed to the removal of colloidal particles in the feedwater by applying microbubbles. The combination of microbubble with filtration showed better results of fouling control than microbubble alone.

(3) Application of pretreatment using filtration was also effective to control rapid fouling in the MD operation of real shale gas wastewaters. However, for long-term operation, it was anticipated that scale formation may lead to flux decline in the MD operation. Further studies are required to combine pretreatment techniques for particle removal and scale inhibition.

Acknowledgments

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References

[1] J.-L. Bessede, Eco-friendly Innovations in Electricity Transmission and Distribution Networks, Woodhead Publishing Series in Energy, Elsevier, 2014.

[2] M. Broomfield, Support to the Identification of Potential Risks for the Environment and Human Health Arising from Hydrocarbons Operations Involving Hydraulic Fracturing in Europe, European Commission DG Environment, Didcot, UK, 2012.

[3] C. Krauss, New way to tap gas may expand global supplies, The New York Times, 2009. Available from: <http://www.nytimes.com/2009/10/10/business/energy-environment/10gas.html?_r=0>.

[4] Joint Institute for Strategic Energy Analysis (JISEA). Natural Gas and the Transformation of the U.S. Energy Sector: Electricity, in: J. Logan, G. Heath, E. Paranhos, W. Boyd, K. Carlson, J. Macknick (Eds.), National Renewable Energy Laboratory, Golden, CO, 2012. Available from: <http://www.nrel.gov/docs/fy13osti/55538.pdf>.

[5] Q. Zou, B. Lin, Novel integrated techniques of drilling–slotting–separation-sealing for enhanced coal bed methane recovery in underground coal mines, J. Nat. Gas Sci. Eng. 26 (2015) 960–973.

[6] L. Torres, O.P. Tadav, E. Khan, A review on risk assessment techniques for hydraulic fracturing water and produced water management implemented in onshore unconventional oil and gas production, Sci. Total Environ. 539 (2016) 478–493.

[7] SHIP, Shale Gas Information Platform, [Online]. Available from: <http://www.shale-gas-information-platform.org/what-is-shale-gas.html>.

[8] G. Chen, Treatment of shale gas drilling flowback fluids (SGDFs) by forward osmosis: Membrane fouling and mitigation, Desalination 366 (2015) 113–120.

[9] G.P. Thiel, E.W. Tow, L.D. Banchik, H.W. Chung, J.H. Lienhard V, Energy consumption in desalinating produced water from shale oil and gas extraction, Desalination 366 (2015) 94–112.

[10] D. Wheeler, Hydraulic fracturing—Integrating public participation with an independent review of the risks and benefits, Energy Policy 85 (2015) 299–308.

[11] M.A. Sari, Mechanisms of boron removal from hydraulic fracturing wastewater by aluminum electrocoagulation, J. Colloid and Interface Sci. 458 (2015) 103–111.

[12] D. Song, Evaluation of coal seam hydraulic fracturing using the direct current method, Int. J. Rock Mechanics and Mining Sciences 78 (2015) 230–239.

[13] G.P. Thiel, Treating produced water from hydraulic fracturing: Composition effects on scale formation and desalination system selection, Desalination 346 (2014) 54–69.

[14] K.C. Wright, New fouling prevention method using a plasma gliding arc for produced water treatment, Desalination 345 (2014) 64–71.

[15] G.L. Theodori, A.E. Luloff, F.K. Willits, D.B. Burnett, Hydraulic fracturing and the management, disposal, and reuse of frac flowback waters: Views from the public in the Marcellus Shale, Energy Res. Soc. Sci. 2 (2014) 68.

[16] R.D. Vidic, S.L. Vrantley, J.M. Vandenbossche, D. Yoxtheimer, J.D. Abad, Impact of shale gas development on regional water quality, Science 340 (2013) 6134, doi: 10.1126/science.1235009.

[17] D.M. Warsinger, J. Swaminathan, E. Guillen-Burrieza, H.A. Arafat, J.H. Lienhard, Scaling and fouling in membrane distillation for desalination applications: A review, Desalination 356 (2015) 294–313.

[18] E. Drioli, Y. Wu, Membrane distillation: An experimental study, Desalination 53 (1985) 339–346.

[19] L. Devin, N.Y. Shaffer, J. Yip, M. Gilron, Elimelech, Seawater desalination for agriculture by integrated forward and reverse osmosis: Improved product water quality for potentially less energy, J. Membr. Sci. 415–416 (2012) 1–8.

[20] A. Boubakri, A. Hafiane, S.A.T. Bouguecha, Nitrate removal from aqueous solution by direct contact membrane distillation using two different commercial membranes, Desalin. Water Treat. (2014). doi: 10.1080/19443994.2014.981408.

[21] V.A. Bui, The energy challenge of direct contact membrane distillation in low temperature concentration, Asia-Pac. J. Chem. Eng. 2 (2007) 400–406.

[22] C.M. Tun, Membrane distillation crystallization of concentrated salts—Flux and crystal formation, J. Membr. Sci. 257 (2005) 144–155.

[23] A. Agarwal, W.J. Ng, Y. Liu, Principle and applications of microbubble and nanobubble technology for water treatment, Chemosphere 84 (2011) 1175–1180.

[24] M. Mukumoto, Effect of microbubbled water on the removal of a biofilm attached to orthodontic appliances—An *in vitro* study, Dent. Mater. J. 31 (2012) 821–827.