JTE HCMUTE
ISSN: 2615-9740

JOURNAL OF TECHNICAL EDUCATION SCIENCE
Ho Chi Minh City University of Technology and Education
Website: https://jte.edu.vn
Email: jte@hcmute.edu.vn

Water Reclamation from Primary Municipal Wastewater Treatment Plant Effluent by Membrane Distillation

Quynh-Mai Nguyen
Faculty of Chemical and Food Technology, Ho Chi Minh City University of Technology and Education, Vietnam
Corresponding author. *Email:* mainq@hcmute.edu.vn

ARTICLE INFO

Received:	02/05/2023
Revised:	21/05/2023
Accepted:	29/05/2023
Published:	28/06/2023

KEYWORDS

Membrane distillation (MD);
Water reclamation;
Primary MWWTP effluent;
Pretreatment;
Membrane cleaning.

ABSTRACT

In this work, Direct Contact Membrane Distillation (DCMD) was applied for the treatment of municipal wastewater collected from the primary clarifier of a municipal wastewater treatment plant (MWWTP). The water flux at 60°C and 20°C for the feed and permeate side, respectively was 51 kg/m^2h in treating the primary effluent. Meanwhile, the electrical conductivity of distillate was in the good range at 1.5 – 1.8 μS/cm. Most of the representative parameters for water reuse (SS, nitrate, nitrite, phosphate, total coliform, and turbidity) in the primary effluent were completely removed in MD module operation with PTFE (polytetrafluoroethylene)/ PP (polypropylene) bi-composite membrane. However, limited rejection rate was observed only in ammonia removal due to the volatility of ammonia. Pretreatment of the primary MWWTP effluent by NaOCl showed only 15% decline in water flux for 28 hours of continuous operation. Periodic membrane cleaning with 3% HCl applied for non-pretreated feed recovered initial permeate flux up to 80 - 95% and yielded highly purified distillate in long-term operation of MD system.

Doi: https://doi.org/10.54644/jte.77.2023.1389

1. Introduction

Water scarcity caused several issues such as water supply and water pollution control as well as the development of new water resources with the least environmental impact became one of the most important demands in many countries. Reclamation of wastewater effluent is one of the emerging alternatives for the water supply resource.

Recently, membrane distillation (MD), a thermal-driven membrane process, has gained intensive attention. Driving forces of the MD process are heat and partial pressure gradient across the hydrophobic porous membrane and only vaporized molecules can transport through the membrane pores [1]-[3]. Due to the separation mechanism based on vapor/liquid equilibrium, non-volatile compounds could be removed completely through the membrane in theory and the hydrophobic membrane with micro pore size in MD process also shows less fouling problem against contaminants compared to hydrophilic membrane with a much smaller pore size (several nanometer or lesser) used in conventional pressure-driven processes such as reverse osmosis (RO), microfiltration (MF), and nanofiltration (NF) [4]-[6]. Based on the selectivity for contaminants and the fouling resistance, MD process could have great advantages for wastewater treatment.

For the practical application of the MD process, very limited numbers of pilot plants were applied in treatments of petrochemical, oil production and gas refinery wastewater, seawater desalination and fruit juices concentration [7]-[11] despite the great potential advantages for wastewater treatment. As many previous researches pointed out, one of the major obstacles in practical application of MD system is low energy efficiency than current membrane process (i.e. RO) because relatively high energy is needed to maintain the temperatures in feed and permeate reactors, so MD systems based on the reusable or waste heat such as solar and geo-thermal energy that can enhance the capability of the MD technology were investigated predominantly [12]-[15].

Lately, numerous researches on the application of MD to purify water from feed contaminated by various spiked individual organic and inorganic substances such as humic acids, carbohydrates, proteins, NaCl, and $CaCO_3$ have been reported. The extent of humic acid fouling in membrane distillation for water treatment was examined by Srisurichanet et al. [16]. M. Gryta [17] found significant amounts of Aspergillus and S. faecalis on the polypropylene membrane surface used in the examined MD module for treating saline wastewater. Additionally, the used membranes did not reject S. faecalis bacteria that were detected in the distillate. Using MD, M. Gryta et al. concentrated a NaCl solution containing natural organic materials [18].

However, no report about water reclamation from actual complex composition sources like MWWTP effluent was available. Therefore, the practical investigations on the MD performances in terms of water flux, produced water quality and the application of countermeasures for mitigating the fouling in the MD treatment of MWWTP effluent using the high flux PTFE/PP bi-composite membrane would provide us meaningful information on the MD application for the reclamation of MWWTP effluent.

In this study, to fulfill the aforementioned objectives, MD treatments of actual primary MWWTP effluents were carried out. The effects of some pretreatments such as glass microfiber filtration and feed chlorination on the permeate flux and generated water quality were investigated. Additionally, the influence of hydrochloric acid solution as a chemical cleaning agent on the membrane flux and permeate conductivity in long-term operation of the MD process was also examined.

2. Materials and Methods

2.1. Feed water

Actual primary effluents from a local municipal wastewater treatment plant (MWWTP) in Seoul were used as feed solutions. Obtained primary MWWTP effluent samples were immediately used for physicochemical parameter analysis and stored less than a week at 4℃ for MD experiments. Table 1 lists the composition of feed solution.

2.2. Membrane

The membrane used for all experiments is a flat-sheet type bi-composite membrane made of a polytetrafluoroethylene (PTFE) active layer and a polypropylene (PP) support layer purchased from Pall Corp. (USA). The membrane has a mean active layer pore size of 0.45 μm, active layer/support layer porosity of 72.6/67.2%, and active layer/support layer thickness of 36/53 μm

2.3. Direct contact membrane distillation (DCMD) system and operation

PTFE/PP membrane was placed between two chambers (hot feed and cold permeate) in a plate-and-frame configuration designed for the DCMD module. The DCMD module was made of transparent acryl to observe the membrane condition during operation. The module has an active membrane surface area of 0.0023 m^2 (0.029 × 0.079 m) and thickness of flow channel was 0.003 m.

Figure 1 displays a schematic of the DCMD configuration. By using a gear pump (75211-15, Cole-Parmer Instrument Company, USA), feed solution in an acrylic cylinder tank was transferred through silicon tubing. The water bath was used to adjust the temperature of the feed and permeate streams. Before entering the DCMD module, the pressure and flow rate were checked using flow meters and pressure gauges. The permeate solution and DCMD module outflow were cycled to the feed and permeate tank, respectively. An analytical balance (CUX6200H, CAS corporation, Korea) was used to balance the permeate tank and quantify the continuously rising water weight. Water flux was calculated using permeate mass information. The produced water mass (kg), operation time (h), and the membrane area (m^2) were used to compute water flux (J) in kg/ m^2h

An electronic conductivity meter (HQ40d, Hach, USA) and probe (CDC40101, Hach, USA) were used to continuously monitor the electrical conductivity of the feed and permeate streams. For each experiment, the flow rates at the feed and permeate sides were kept at 1.6 and 1.2 L/min, respectively. For each experiment, the temperature at the feed and permeate sides was fixed at 60 and 20 degrees Celsius, respectively.

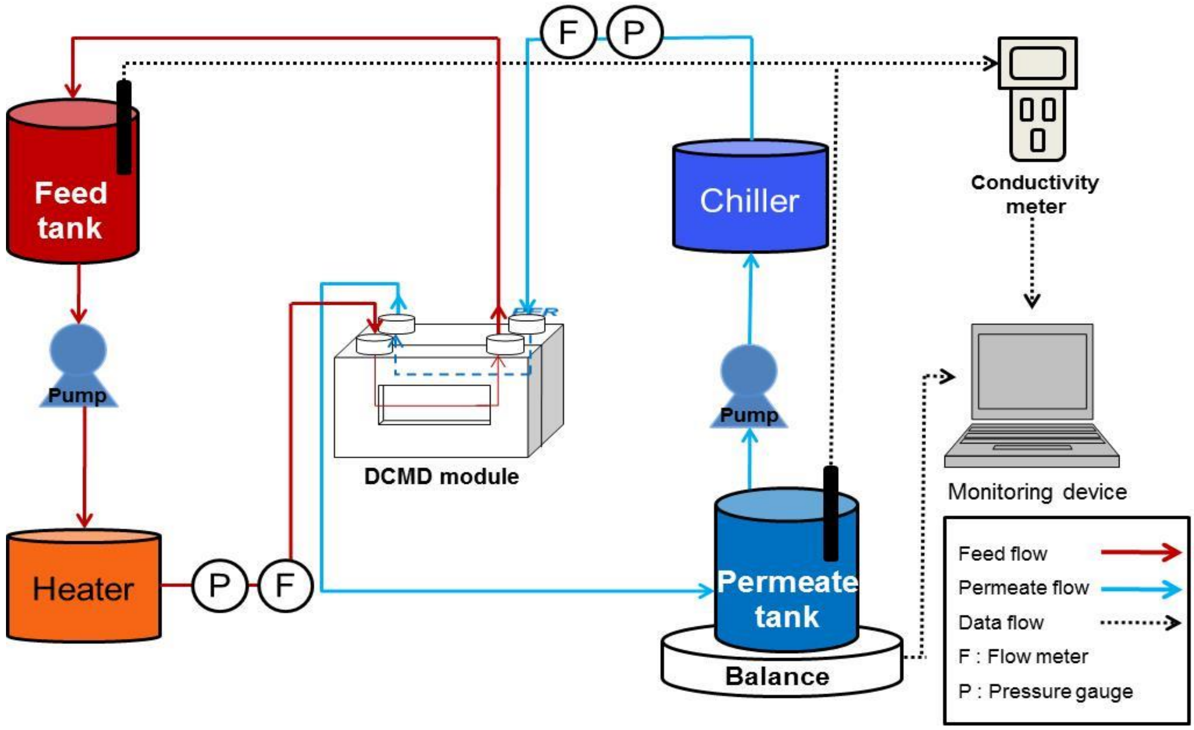


Figure 1. *The diagram of DCMD setup*

For all batch experiments of MD treatment, 5 L of feed solution (primary MWWTP effluents) and 1 L of permeate solution (deionized water) were placed in 6 L tank, respectively. The system operated for 24h for each batch then collected water in the permeate tank (the distillate) was taken for water quality analysis. Glass microfiber filters with pore size of 1.2 μm (GF/C, Whatman, UK), 1.0 μm (GF/B, Whatman, UK), and 0.7 μm (GF/F, Whatman, UK) were used for pretreatment of the samples. When using sodium hypochlorite solution (6-14% active chlorine, Emplura, Germany) as a chemical pretreatment, the feed solution was chlorinated and stirred in the dark until the chlorine residual concentration reached 0.5 mg Cl_2/L. 20 L of feed solution in a 22 L tank was employed for the long-term experiment, and the distillate was obtained for water quality examination at the termination of the MD process run (after 120h).

Membrane cleaning was accomplished using solutions of hydrochloric acid (ACS reagent 37%, Merck, Germany). The fouled membrane was placed in a 50 mL polystyrene tube filled with 3% HCl solution and after capped, the tube was rotated by an end-over-end rotator at 30 rpm for 6 hours. The membrane was then cleaned with deionized water 3 times before being reused.

2.4. Analytical techniques

Water samples underwent several analyses to determine physicochemical parameters such as pH, electrical conductivity, nitrate, nitrite, ammonia, phosphate, SS (suspended solid), COD, total coliform, and turbidity. A pH meter (AB15 Plus, Fisher Scientific) and a conductivity meter (HQ40d, Hach, USA) fitted with a probe (CDC40101, Hach, USA) were used to test the pH and conductivity, respectively. Nitrate and nitrite were analyzed by using IC (Ion chromatography). Hach Test Kits (Hach, USA) were used for ammonia, phosphate, and COD (21259-15) measurements. Turbidity was measured by a turbidity meter (Orion AQUAfast AQ45, Thermo Scientific Orion). Suspended solid (SS) and total coliform were measured following the Korean Standard Methods for the Examination of Water and Wastewater [19]. The residual chlorine content was determined by the colorimetric DPD method using a DR 5000, Hach UV-VIS spectrometer.

The morphology of the virgin, fouled and cleaned membrane was investigated by using a field emission scanning electron microscope (FE-SEM, S-4100, Hitachi, Japan).

3. Results and Discussion

3.1. MD treatment of primary MWWPT effluents

Figure 2 presents the permeate flux and electrical conductivity of the distillate during the treatment of primary MWWTP effluents by MD process. As seen in Figure 2, initial water flux was 51 kg/m^{2}h, and after 24 hours of MD operation, the water fluxes reduced by 46% (to 28 kg/m^{2}h), whereas that of DI water run was approximately 60 kg/m^{2}h. The water flux at feed temperature 60℃ was one of the highest fluxes in MD process. The optimized temperature and flowrate at both sides of feed and permeate applied for DCMD can be found in prior work [20], [21]. In each experiment with primary MWWTP effluent as feed solutions, the electrical conductivity of distillate was constant in the range 1.5 – 1.8 μS/cm, indicating that no membrane wetting occurred during the operation of MD module. The initial high flux along with good produced water quality indicated that it might be a huge benefit when using the MD process to recover MWWTP effluents.

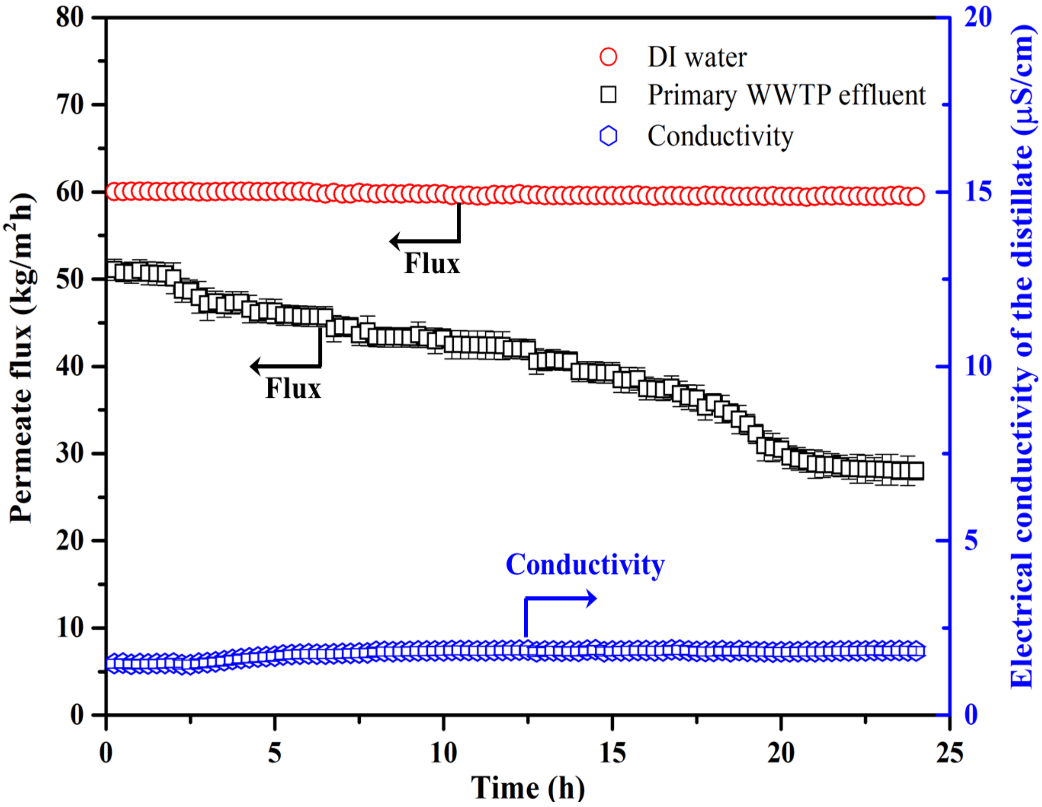


Figure 2. T*he permeate fluxes and the electrical conductivity of the distillate as a function of time*

Important water quality parameters of primary effluents before/after MD treatment were summarized in Table 1. As shown in Table 1, observed particulate and ionic contaminants in the feed stream such as SS (53.3 mg/L), nitrate (0.3 mg/L), nitrite (0.03 mg/L), phosphate (11.5 mg/L) were completely removed after 24 hours of MD treatment. The incomplete removal of the COD (removal rate: 88%) was found in MD treatment of primary effluent. Furthermore, the very limited removal rate of ammonia (removal rate: 6.4%) was observed. Penetration of ammonia through the MD membrane is commonly reported problem due to the volatility of ammonia [22], [23]. Low treatability of ammonia in this study cannot cause problem to meet the regulation for wastewater reuse (10 mg/L as T-N) as nitrate and nitrite were completely removed. For the turbidity and total coliform, concentrations of turbidity for MD treated primary effluents were 0.42 ± 0.05 mg/L, which is much lower than regulation (2.0 mg/L) for wastewater reuse and no total coliforms were detected in the permeate stream.

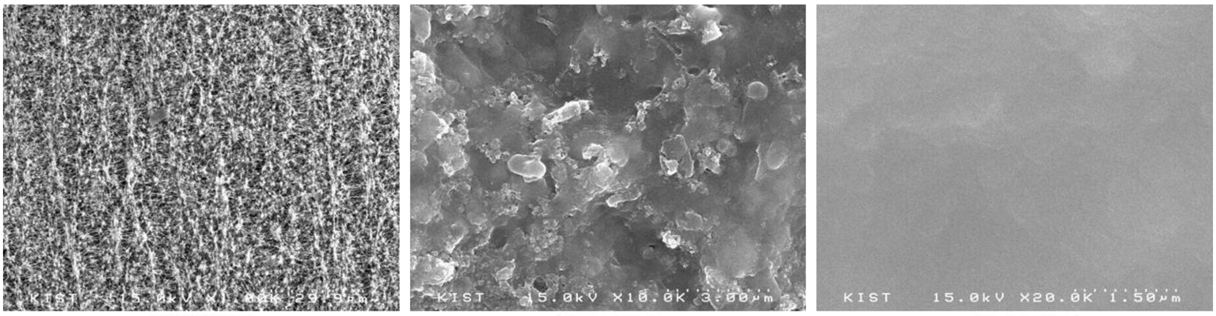
Table 1. *Water quality of MWWTP effluents before and after treated by MD process*

Parameters	**Feed** Average measurement (Std.Dev)	**Distillate (24h)** Average measurement (Std.Dev)	**Distillate (120h)** Average measurement (Std.Dev)
pH	7.4 (0.1)	7.5 (0.1)	7.1 (0.1)
COD (mg/L)	100 (5.04)	12 (1.0)	5 (0.2)
SS (mg/L)	53.3 (0.88)	ND	ND
Nitrate (mg/L)	0.3 (0.01)	ND	ND
Nitrite (mg/L)	0.03 (0.001)	ND	ND
Ammonia (mg/L)	21.84 (1.0)	20.45 (0.5)	12.85 (0.45)
T-N (mg/L)	22.17 (1.0)	20.45 (0.5)	13.64 (0.5)
Phosphate (mg/L)	11.5 (1.0)	ND	ND
Total coliforms (CFU/100ml)	3000	0	0

Detection limits for COD, SS, nitrate, nitrite, and phosphate were 0.3, 0.1, 0.01, 0.001, and 0.05 mg/L, respectively.

3.2. Pretreatment for mitigating the fouling

According to the previous results, the permeate flux decreased with time when the primary MWWTP was employed as a direct feed for the MD process. The flux of the membrane fell by 46% during the course of the 24 hour experiment, from 51 kg/m^{2}h to 28 kg/m^{2}h (Figure 2). The initial water flux decline is likely from membrane fouling as mixed stream like municipal wastewater has many different foulants and scalants over a wide range of concentrations. This suggests that considerable amounts of foulant accumulated on the membrane surface, and the SEM observation in Figure 3 supports this notion. Figure 3 demonstrates how the SEM image of the used membrane coupon (Figure 3 (b)) showed the deposition of a fouling layer on the entire membrane surface as opposed to the virgin membrane (Figure 3 (a)). It suggested that the permeate flux is decreased as a result of the fouling layer. Based on these observations, pretreatment experiments were performed to lessen the organics and scalants in the feed composition and further enhance the MD performance.



(a) (b) (c)

Figure 3. *SEM of virgin membrane (a), fouled membrane by primary MWWTP effluent (b) and cleaned membrane (c)*

Primary MWWTP effluents were filtered via glass microfiber filters with varying pore sizes (1.2, 1.0, and 0.7 μm) in the first pretreatment experiment. In the second, the sample was chlorinated using sodium hypochlorite in order to oxidize the fouling-causing compositions. According to Figure 4, no improvement in the water flux was observed after filtering the water samples through papers with different pore sizes, showing that the majority of probable foulants are typically less than 0.7 μm. However, the percentage of water flux decline in the NaOCl added sample was 15% for 28 hours. NaOCl, a strong oxidizing reagent has the ability to destruct the potential foulants in the wastewater sample [24]. In addition, the distillate's electrical conductivity was maintained between 1.5 – 1.8 μS/cm, and stable pH of around 7 was also determined. There were no variations in the quality of the distillate as compared to earlier trials. The outcomes demonstrated that effective pretreatment can reduce membrane fouling.

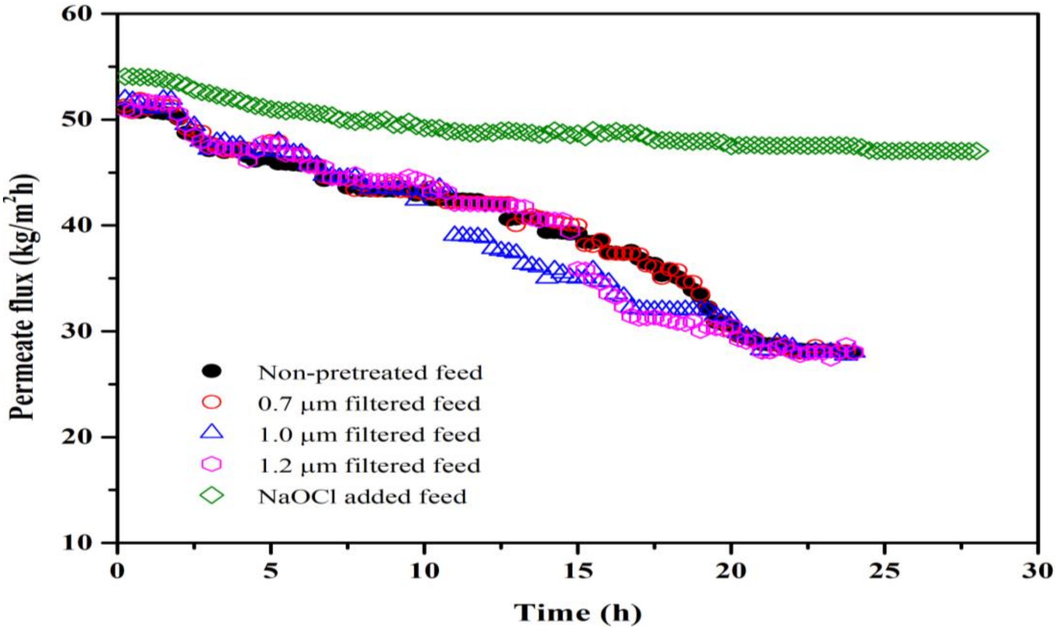


Figure 4. *Water fluxes of MD treatment of primary MWWTP effluent with various pretreatments*

3.3. Long-term MD operation with periodic membrane cleaning

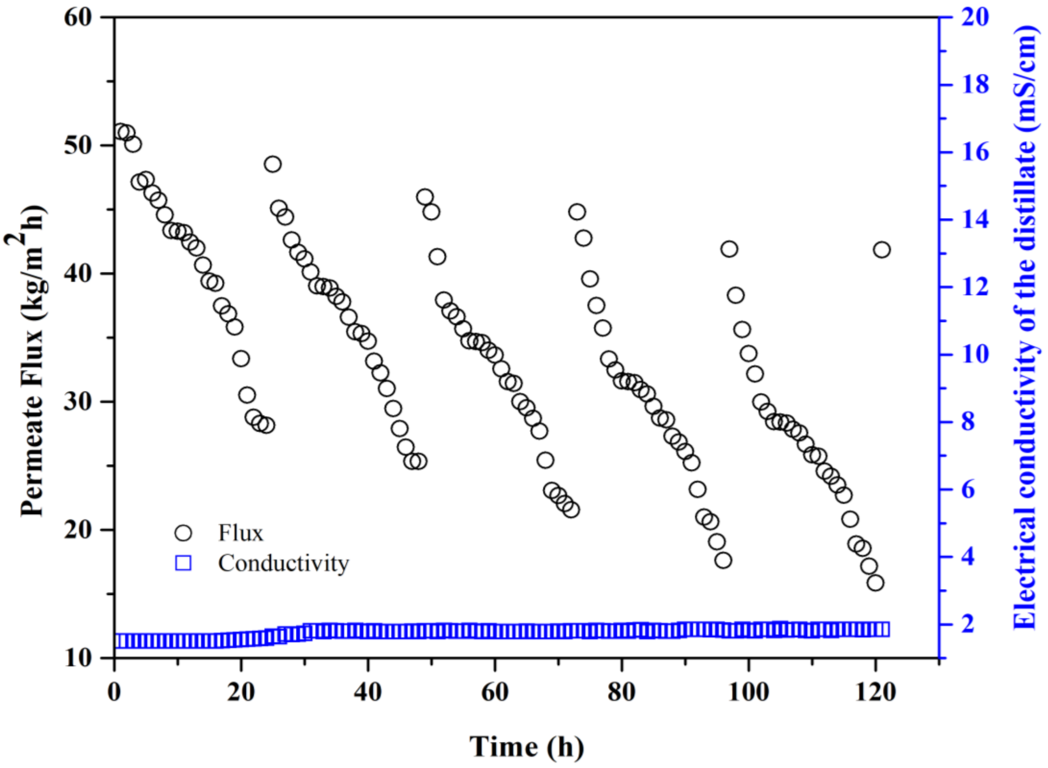


Figure 5. *Change in flux and electrical conductivity of distillate during long-term MD operation*

Long-term MD operation along with periodic membrane cleaning was conducted with 20 L of un-pretreated feed to examine the changes in water flux and the distillate quality. The membrane was cleaned with 3% HCl solution after every 24 hours during the MD run. Over the course of 120 hours of module operation, the flux and electrical conductivity of the distillate are shown in Figure 5. The MD module could recover the flux upto 80 - 95% with membrane rinsing and electrical conductivity of the distillate remained constant at 1.5 – 1.85 μS/cm during the course of the process. After acid rinsing, the membrane surface was still covered by leftover materials and the pores were not visible (Figure 3(c)). Periodic cleaning was unable to restore the flux to its original value because of those leftovers and membrane pore blockage.

Regarding to the result of the permeated water quality analyses, most of the compositions such as SS, nitrate, nitrite, and phosphate in the distillate collected after 120 hours of MD operation were not detected and the pH was kept at 7.0 (Table 1). High removal efficiencies for organic matter (95% - measured as COD) were obtained, indicating the treatment effectiveness. The concentration of ammonia in the distillate (12.85 mg/L) was relatively high; however, the content of ammonia after 120h was lower than that after 24h. This was because the increase in distillate mass was greater than that of ammonia transfer.

4. Conclusions

Reclamation of practical primary effluents from MWWTP by direct contact membrane distillation (DCMD) process with PTFE/PP bi-composite membrane was investigated. In the MD treatment of primary effluent, PTFE/PP bi-composite membrane showed fairly high initial water flux (51 L/m^{2}h) and crucial water reuse parameters as SS, nitrate, nitrite, phosphate, and total coliform were completely removed. However, a very low removal rate of ammonia was observed due to the volatility of the ammonia.

Pretreatment of the primary MWWTP effluent by filtration using glass microfiber filters (pore size of 1.2, 1.0, 0.7 μm) showed no effectiveness on flux enhancement. Chemical pretreatment using NaOCl only caused a 15% decrease in water flux for 28 hour operation.

Periodic membrane cleaning with 3% HCl during long-term operation helped recovered initial water flux up to 80-95% and provided good quality distillate. The recovery rate of the water flux after acid washing was promising, but a more rapid decrease in the water flux was observed, indicating that some irreversible foulants on the membrane promoted fouling in the re-operation, necessitating further research into the characteristics of the foulants.

The secondary effluent was deemed more appropriate in reclaiming water production than primary effluent due to the high intrinsic concentrations and relatively low rejection rates of the COD and ammonia as well as the quicker decrease of the water flux in MD treatment of the primary effluent. Further research will be conducted with the secondary effluent.

REFERENCES

[1] A. Alkhudhiri, N. Darwish, and N. Hilal, "Membrane distillation: A comprehensive review," *Desalination,* vol. 287, pp. 2-18, 2012.
[2] M. Khayet, "Membranes and theoretical modeling of membrane distillation: A review," *Advances in Colloid and Interface Science,* vol. 164, no. 1, pp. 56-88, 2011.
[3] M. S. El-Bourawi, Z. Ding, R. Ma, and M. Khayet, "A framework for better understanding membrane distillation separation process," *Journal of Membrane Science,* vol. 285, no. 1, pp. 4-29, 2006.
[4] M. Hassan, E. Summers, H. Arafat, and J. V, "Effects of membrane properties on water production cost in small scale membrane distillation systems," *Desalination,* vol. 306, pp. 60–71, 2012.
[5] M. Khayet, C. Cojocaru, and M. C. García-Payo, "Experimental design and optimization of asymmetric flat-sheet membranes prepared for direct contact membrane distillation," *Journal of Membrane Science,* vol. 351, pp. 234-245, 2010.
[6] E. Curcio and E. Drioli, "Membrane Distillation and Related Operations-A Review," *Separation & Purification Reviews,* vol. 34, no. 1, pp. 35-86, 2005.
[7] A. Alkhudhiri, N. Darwish, and N. Hilal, "Produced water treatment: Application of Air Gap Membrane Distillation," *Desalination,* vol. 309, pp. 46-51, 2013.
[8] R. Asadi *et al.*, "Solar desalination of Gas Refinery wastewater using membrane distillation process," *Desalination,* vol. 291, pp. 56–64, 2012.
[9] M. Krivorot, A. Kushmaro, Y. Oren, and J. Gilron, "Factors affecting biofilm formation and biofouling in membrane distillation of seawater," *Fuel and Energy Abstracts,* vol. 376, pp. 15-24, 2011.
[10] T. H. Khaing, J. Li, Y. Li, N. Wai, and F. Wong, "Feasibility study on petrochemical wastewater treatment and reuse using a novel submerged membrane distillation bioreactor," *Separation and Purification Technology - SEP PURIF TECHNOL,* vol. 74, pp. 138-143, 2010.
[11] F. Vaillant *et al.*, "Concentration of passion fruit juice on an industrial pilot scale using osmotic evaporation," *Journal of Food Engineering,* vol. 47, no. 3, pp. 195-202, 2001.
[12] M. Khayet, "Solar desalination by membrane distillation: Dispersion in energy consumption analysis and water production costs (a

review)," *Desalination,* vol. 308, pp. 89-101, 2013.
[13] M. R. Qtaishat and F. Banat, "Desalination by solar powered membrane distillation systems," *Desalination,* vol. 308, pp. 186-197, 2013.
[14] H. Susanto, "Towards practical implementations of membrane distillation," *Chemical Engineering and Processing: Process Intensification,* vol. 50, pp. 139-150, 2011.
[15] J. Blanco Galvez, L. García-Rodríguez, and I. Martín-Mateos, "Seawater desalination by an innovative solar-powered membrane distillation system: The MEDESOL project," *Desalination,* vol. 246, pp. 567-576, 2009.
[16] S. Srisurichan, R. Jiraratananon, and A. G. Fane, "Humic acid fouling in the membrane distillation process," *Desalination,* vol. 174, pp. 63-72, 2005.
[17] M. Gryta, "The assessment of microorganism growth in the membrane distillation system," *Desalination,* vol. 142, no. 1, pp. 79-88, 2002.
[18] M. Gryta, M. Tomaszewska, J. Grzechulska, and A. W. Morawski, "Membrane distillation of NaCl solution containing natural organic matter," *Journal of Membrane Science,* vol. 181, no. 2, pp. 279-287, 2001.
[19] Korean Ministry of Environment, "Korean standard methods for the examination of water and wastewater," 2002, doi: 10.54644/jte.77.2023.1389
[20] N. Q. Mai and S. Lee, "Fouling analysis and control in a DCMD process for SWRO brine," *Desalination,* vol. 367, pp. 21-27, 2015.
[21] N. Q. Mai, S. Jeong, and S. Lee, "Characteristics of membrane foulants at different degrees of SWRO brine concentration by membrane distillation," *Desalination,* vol. 409, pp. 7-20, 2017.
[22] Z. Ding, L. Liu, Z. Li, R. Ma, and Z. Yang, "Experimental Study of Ammonia Removal from Water by Membrane Distillation (MD): The Comparison of Three Configurations," *Journal of Membrane Science - J MEMBRANE SCI,* vol. 286, pp. 93-103, 2006.
[23] Z. Xie, T. Duong, M. Hoang, C. Nguyen, and B. Bolto, "Ammonia removal by sweep gas membrane distillation," *Water Research,* vol. 43, no. 6, pp. 1693-1699, 2009.
[24] Z. Zhou, X. He, M. Zhou, and F. Meng, "Chemically induced alterations in the characteristics of fouling-causing bio-macromolecules – Implications for the chemical cleaning of fouled membranes," *Water Research,* vol. 108, pp. 115-123, 2017.

Quynh-Mai Nguyen received the B.E. degree in Environmental Engineering from Ho Chi Minh City University of Technology, Vietnam, in 2006; the M.S. degree in Environmental Technology from Ho Chi Minh City University of Technology, Vietnam, in 2009; the Ph.D. degree in Energy and Environment Engineering from University of Science and Technology (UST), Republic of Korea, in 2015.

From 2015 to 2017, she was a Post-Doc scholar at Korea Institute of Science and Technology (KIST), Republic of Korea. From 2019 to 2020, she was a Research Professor in Dankook University, Republic of Korea. She is currently a Lecturer at the Faculty in Chemical and Food Technology, Ho Chi Minh City University of Technology and Education, Ho Chi Minh City, Vietnam.

Her research focuses on membrane technologies applied for water and wastewater treatment, environmental materials from agro-food by-products and hydrogen energy. Email: mainq@hcmute.edu.vn.