Vol. 12 No. 1 (2021) 1-6

Jurnal Riset
Teknologi Pencegahan Pencemaran Industri

Journal homepage : http://www.jrtppi.id

Kementerian Perindustrian
REPUBLIK INDONESIA

PVDF-TiO2 Hollow Fibre Membrane For Water Desalination

Muthia Elma [1,3]*, Mahmud[2], Nurul Huda[1,3], Zaini L. Assyaifi[1,3], Elsa Nadia Pratiwi[4], Mita Riani Rezki[4], Dewi Puspita Sari[4], Erdina L. A. Rampun[3], Aulia Rahma[3]

[1]Chemical Engineering, Faculty of Engineering, Lambung Mangkurat University, JL.A. Yani KM 36, Banjarbaru, South Kalimantan, 70714, Indonesia

[2]Environmental Engineering, Faculty of Engineering, Lambung Mangkurat University, Jl. A. Yani KM 36, Banjarbaru, South Kalimantan, 70714, Indonesia

[3]Materials and Membranes Research Group (M2ReG), Lambung Mangkurat University, JL.A.Yani KM 36, Banjarbaru, South Kalimantan, 70714, Indonesia

[4]Natural Resources and Environmental Management, Postgraduate Program, Lambung Mangkurat University, JL.A.Yani KM 36, Banjarbaru, South Kalimantan, 70714, Indonesia

ARTICLE INFO

Article history:
Received 08 October 2020
Received in revised form 16 February 2021
Accepted 23 March 2021
Available online 27 May 2021

Keywords :
Hollow fibre membrane
PVDF-TiO_2
Desalination
Pervaporation

ABSTRACT

The clean water crisis is increasing along with the increasing human population. Seawater is one of the largest water sources that can be utilized on the earth. However, the high salt concentration dissolved in seawater must be treated before it can be used. Desalination is the directly technology for treating seawater with PVDF-TiO2 hollow fibre membrane via pervaporation process. This research aimed to determine the performance of PVDF-TiO_2 hollow fibre membrane against variations of feed temperature in the artificial seawater pervaporation process. Method for fabrication membrane is using dry-wet spinning method. The membrane was fabricated with TiO_2 3 wt%, PVDF 21 wt% and DMAC 75 wt%. The result showed that the highest flux permeate of 8.96 kg.m^{-2}.h^{-1}occurred at feed temperature of 60°C, with salt rejection > 92.86%. The SEM result showed that of the membrane surface morphology, there is a white spot on the membrane surface is TiO_2 because the dope solution is too thick. The PVDF-TiO_2 hollow fibre membrane in this research is can be applied for seawater pervaporation.

1. INTRODUCTION

The clean water crisis is increasing along with the increased human population. Water is a very important material for all organism. Seawater is one of the most abundant sources of its existence on the earth. However, seawater consist of various kinds of solids and gases dissolved in it. Organic salts that come from living organisms are substances dissolved in seawater (Sefentry 2020). One of the water treatment technologies has a fairly high performance by using membrane technology (Husnah 2018).

Membrane technology is becoming more popular and widely used in separation processes, especially in water treatment (Rahman et al. 2020). Membrane technology has inherent characteristics, namely membrane technology has high efficiency, simple operation, stability and flexibility and high selectivity (Elma et al. 2020b). Another advantage,

*Correspondence author.
E-mail : melma@ulm.ac.id (Muthia Elma)

doi : https://10.21771/jrtppi.2021.v12.no.1.p1-6

Accreditation number : (LIPI) 756/Akred/P2MI-LIPI/08/2016

there is no need to add chemicals and is more efficient in production costs (Rahman et al. 2020).

The desalination process for seawater treatment can be carried out with pervaporation membranes. Pervaporation is a promising desalination technology to treat clean water with relatively low energy consumption compared to reverse osmosis membranes. Pervaporation can be operated at high temperatures and produces a relatively high flux permeate (Rahma et al. 2019). It also does not require a heavy piping system and pumping, so it does not produce too much fouling like the reverse osmosis membrane and can be operated using a variety of renewable energies such as the sun and geothermal (Halakoo and Feng 2020). Pervaporation operates in a phase of change to separate water molecules and hydrated ions under vacuum using a membrane (Lestari et al. 2020b).

Pervaporation can be carried out using a hollow fibre membrane. The advantages of hollow fibre membranes are easy membrane maintenance and high separation efficiency (Wang et al. 2016a). In addition, hollow fibre membranes have a higher packing density compared to flat sheets and tubular membranes (Koonaphapdeelert and Li 2007). Generally, the fabrication of hollow fibre membrane uses the dry-wet spinning method to produce an asymmetric cross-sectional structure. When it is compared with other methods such as dry spinning, polymer pyrolysis and phase inversion, the dry-wet spinning method is superior because it is more simple and faster (Othman et al. 2017).

Effectiveness of the pervaporation process requires a membrane that has the most optimum performance (Kujawska et al. 2020). Temperature is an important parameter in the pervaporation process. In their research, Wang et al. (2016b) mentioned that heating feed with a certain temperature can cause diffusivity and can reduce the viscosity of the solution. Previously, Fang et al. (2012) has conducted a research on seawater desalination process using hydrophobic alumina hollow fibre membranes and obtained the best operating conditions with an operating pressure of 0.4 bar, flux permeate is 42.9 L/h.m^2 and salt rejection of 99.5%. Therefore, this research was carried out using PVDF-TiO_2 hollow fibre membranes to determine the quality of PVDF-TiO_2 hollow fibre membranes in determining optimum temperature in the pervaporation process.

2. METHOD

Material used in this research consists of Polyvinylidene fluoride (PVDF, Kynar 760 powder series), TiO_2 (commercial), dimethylacetamide (DMAc, QReC), ethanol, aquadest, epoxy resin (E30CL Loctite Corporation, USA), liquid nitrogen and seawater artificial (3.5% NaCl).

The manufacture of PVDF-TiO_2 hollow fibre membrane in this research is divided into 3 stages, based on research conducted by Othman et al. (2017), namely: (1) preparation of the dope solution, by drying 21 wt% PVDF and 3 wt% commercial TiO_2 in an oven at 50°C for 24 h to remove moisture, (2) making a dope solution by mixing PVDF and commercial TiO2 with DMAC as a solvent and stirring until the dope solution is homogeneous and (3) membrane spinning using the dry-wet spinning method. The membranes were characterized using Scanning Electron Microscope (SEM) analysis.

The performance of PVDF-TiO_2 hollow fibre membrane pervaporation process is determined by passing the various types of feeds through the PVDF-TiO_2 hollow fibre membrane at various feed temperatures, at 25°C, 40°C and 60°C. Feeds used in this research were aquadest and 3.5% NaCl. The feed was mixed using magnetic stirrer for homogenous purpose. The set up of pervaporation process was shown in Figure 1. The membrane was put into a beaker glass which filled with the feed. During pervaporation, the feed selectively transported across the membrane. The feed phase was changed from liquid to gaseous by using a vacuum. A clean permeate cooled by liquid nitrogen and collected in a cold trap. The salt rejection was determined based on Equation 1 and water flux was determined based on Equation 2.

$$\%\,Salt\ Rejection = \frac{C_i - C_o}{C_i} \quad \ldots. (1)$$

Explanation:

R= Rejection value (%), C_i = The feed concentration of salt (% wt), C_o= The feed concentration of permeate (% wt)

$$F = \frac{W}{A\,x\,t} \quad \dots (2)$$

Explanation:

F= Water flux (kg.m^{-2}.h^{-1}), W= the mass of permeate (kg), A= The surface active area (m^2), Δt = The time measurement (h)

Desalination pervaporation set up can be seen in Figure 1:

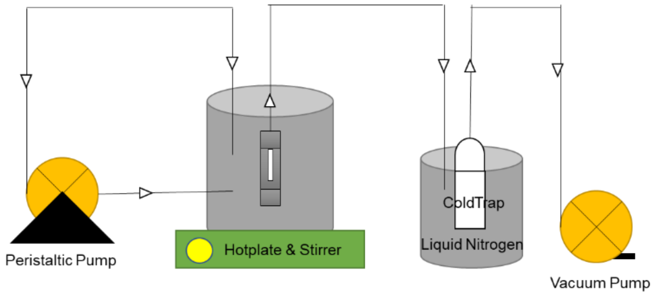

Figure 1. Desalination pervaporation set up

3. RESULT AND DISCUSSION

3.1. The analysis of morphological structure of PVDF-TiO_2 hollow fibre membrane

The morphological structure of the PVDF-TiO_2 hollow fibre membrane was analyzed by SEM analysis. The PVDF-TiO_2 hollow fibre membrane pore structure on the membrane surface was analyzed by using SEM analysis. SEM analysis was carried out to determine the surface morphological structure of the membrane.

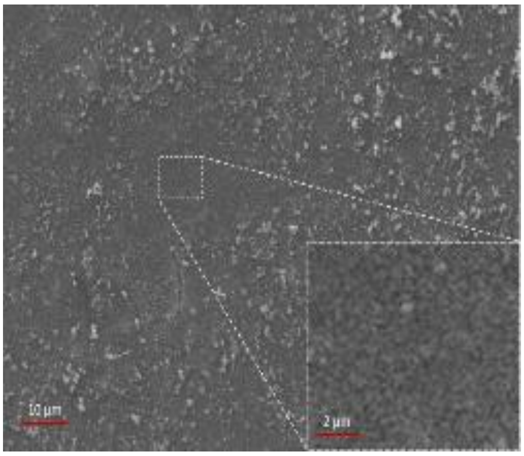

Figure 2. Surface of SEM Image of PVDF-TiO_2 Hollow Fibre Membrane

Figure 2 depicted the surface of PVDF-TiO_2 hollow fibre membrane. On the surface of the membrane, there were visible white dots. These white dots were TiO_2. The TiO_2 seen on the membrane surface was caused by the dope solution being too thick. The addition of TiO_2 to the polymer solution can increase the viscosity thus affecting the phase inversion and aggregation of TiO_2 particles in the dope solution. TiO_2 also caused the membrane surface to be rugged, compared to membranes without using TiO_2 (Sakarkar et al. 2020). Bore fluid functions to form the diameter of the membrane. Bore fluid velocity depends on the dope solution flow rate. While the air gap is the distance between the spinnerets and the water surface in the coagulation tank. The bigger the air gap, then the membrane thickness will be smaller (Humairo 2015).

3.2. The performance of PVDF-TiO_2 hollow fibre membranes under variations in feed temperature

The performance of PVDF-TiO_2 hollow fibre membranes which have been fabricated with TiO_2 3 wt%, PVDF 21 wt% and DMAC 75 wt% for seawater artificial desalination was then tested using a pervaporation process with variations in feed temperature (NaCl 3.5%). Water flux and salt rejection pf the membrane can be seen in Figure 4, as follow:

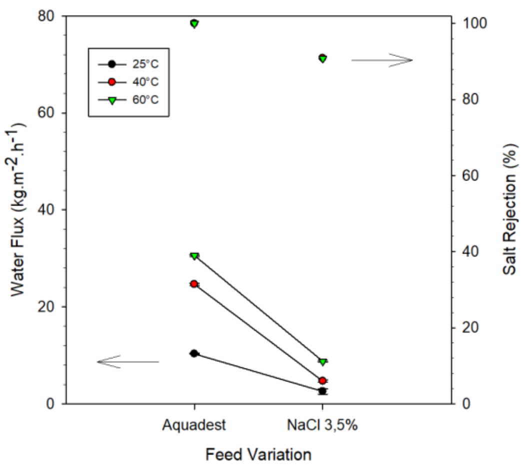

Figure 3. Effect of Variations in Feed Temperature (~25°C, 40°C and 60°C) Against Water Flux and Salt Rejection on PVDF-TiO_2 Hollow Fiber Membrane

Figure 3 illustrates the relationship between the value of water flux and salt rejection to temperature variations in feed, during 20 minutes pervaporation time The highest NaCl water flux value was 8.96 kg.m^{-2}.h^{-1} at 60ºC. Figure 3 showed that when feed temperature increased, the rejection of salt in the permeate decreased. At room temperature (25ºC), the salt rejection value was 90.87%. When the feed temperature increased to 40ºC, there was deflation in the rejection value of salt. When the feed temperature increased to 60°C, there was a slight drop in salt rejection by 0.01%.

Due to the variation in salt concentration in each bait, this research was using NaCl (0.3% to 7.5% NaCl) variation as already conducted by Elma et al. (2015) as feed. The high concentration of salt in water caused polarization in concentration, which had a negative impact on reducing membrane performance (Elma et al. 2012). The decline of salt rejection when feed temperature increased was caused by the random thermal movement of the polymer chains, which resulted in free volume, causing permeate molecules to diffuse through the membrane (Jyoti Ghoshna 2015). Based on the results of this research, it can be concluded that the pervaporation process using PVDF-TiO_2 hollow fibre membrane has a good performance because it produced a higher permeate flux of 8.96 gm^{-2}.h^{-1} and the salt removal produced in this study was 90.86%.

Table 1 showed the performance of various types of membranes for seawater artificial desalination (NaCl 3.5%). This study showed a permeate flux value of 8.96 kg.m^{-2}.hr^{-1} and salt rejection of 90.86% at 60°C. **Table 1** showed a higher permeate flux value compared to the research conducted by Elma et al. (2020a). Whereas, the research using a 0.1% silica pectin membrane with a calcination temperature of 300°C which was applied to 0.3% NaCl produced a water flux of 5.45 kg/m^{-2}.h^{-1} with a percentage of salt rejection of 91.94%. In addition, in research conducted by Lestari et al. (2020a) using 3.5% NaCl produced a water flux of 0.2290 kg/m^{-2}.h^{-1} with a salt rejection percentage of 99%. Unlike the research produced by Elma et al. (2013) using 0.3% NaCl feed which resulted in a water flux of 9.5 kg/m^{-2}.h^{-1} with a salt rejection percentage of 99.6%.

This may be due to the type of membrane and the temperature used for the feed. Hollow fibre membranes are good for the desalination process of seawater using the pervaporation process because the hollow fibre membrane has a good density due to its very small diameter and thin wall thickness. (Fang et al. 2012).

Table 1. Performance of Various Types of Membranes for Seawater Desalination

Membrane Variation	Feed Temperature (ºC)	Feed Variation	Water Flux (kg.m^{-2}.h^{-1})	Salt Rejection (%)	Reference
PVDF-TiO_2 Hollow Fibre Membrane	60ºC	NaCl 3.5%	8.96	90.86	This work
Silica Membrane	22°C	NaCl 0.3%	9.5	99.6	(Elma et al. 2013)
Silica Pectin Membrane 0.1% With Calcination 300ºC and 400ºC	25°C	NaCl 0.3%	5.45-13.70	91.94-92.08	(Elma et al. 2020a)
Organo Silica Membrane	50ºC	NaCl 3.5%	0.2290	99	(Lestari et al. 2020a)

4. CONCLUSION

PVDF-TiO_2 hollow fibre membranes have been successfully fabricated and characterized by SEM analysis. Membrane characterization through SEM analysis showed that the outer diameter of the membrane was 1800 µm and the inner diameter was 1100 µm so that the membrane had a thickness of 700 µm. The membrane in this research can be categorized as hollow fibre because the outer diameter of the membrane is >500 µm. The performance of the PVDF-TiO_2 hollow fibre membrane had a good effect on the increase in feed temperature from 25°C to 60°C as measured by the water flux value and salt rejection. The optimum water flux and salt rejection resulted at a temperature of 60°C, namely 8.96 $kg.m^{-2}.h^{-1}$ and >90.6%. Thus, it can be said that the PVDF-TiO_2 hollow fibre membrane is good for the seawater desalination process.

ACKNOWLEDGMENT

The authors would like to thank for facilities at AMTEC – UTM Malaysia and M2ReG ULM, Muthia Elma thanks to Basic Research Grant 2021-2022, Applied Research Universities Grant 2021-2023, Thesis Magister Grant 2019-2020, World Class Research Grant 2021-2023 Deputy of Research and Development National Research and Innovation Agency, The Ministry of Education and Culture, Research and Technology Republic of Indonesia.

REFERENCE

Elma, M., M. Mahmud, A. Akhbar, L. Suryani, F. R. Mustalifah, A. Rahma, D. Rahmah, and N. Baity. 2020a. "Aplikasi Membran Silika-Pektin Untuk Desalinasi Air Payau" *Jukung (Jurnal Teknik Lingkungan)* 6 (1)

Elma, M., E. L. Rampun, A. Rahma, Z. L. Assyaifi, A. Sumardi, A. E. Lestari, G. S. Saputro, M. R. Bilad, and A. Darmawan. 2020b. "Carbon templated strategies of mesoporous silica applied for water desalination: A review" *Journal of Water Process Engineering* 38:101520

Elma, M., D. K. Wang, C. Yacou, and J. C. D. da Costa. 2015. "Interlayer-free P123 carbonised template silica membranes for desalination with reduced salt concentration polarisation" *Journal of Membrane Science* 475:376-383

Elma, M., C. Yacou, J. C. Diniz da Costa, and D. K. Wang. 2013. "Performance and long term stability of mesoporous silica membranes for desalination" *Membranes* 3 (3):136-150

Elma, M., C. Yacou, D. K. Wang, S. Smart, and J. C. Diniz da Costa. 2012. "Microporous silica based membranes for desalination" *Water* 4 (3):629-649

Fang, H., J. Gao, H. Wang, and C. Chen. 2012. "Hydrophobic porous alumina hollow fiber for water desalination via membrane distillation process" *Journal of membrane science* 403:41-46

Halakoo, E., and X. Feng. 2020. "Layer-by-layer assembly of polyethyleneimine/graphene oxide membranes for desalination of high-salinity water via pervaporation" *Separation and Purification Technology* 234:116077

Humairo, F. Y. 2015. Preparasi Dan Karakterisasi Membran Serat Berongga Pvdf/Peg400-Tio2 Untuk Pemisahan Limbah Sintetik Air-Minyak, Institut Teknologi Sepuluh Nopember.

Husnah, H. 2018. "Aplikasi Membran Keramik Buatan Dengan Pretreatment Pada Penjernihan Air Sungai Musi" *Jurnal Redoks* 3 (1):1-8

Jyoti Ghoshna, A. K., J. Anandkumar. 2015. "Review on Pervaporation: Theory, Membrane Performance, and Aplication to Intensification of Esterification Reaction" *Journal of Engieering*:1-24.http://dx.doi.org/10.1155/2015/927068.

Koonaphapdeelert, S., and K. Li. 2007. "Preparation and characterization of hydrophobic ceramic hollow fibre membrane" *Journal of Membrane Science* 291 (1-2):70-76

Kujawska, A., K. Knozowska, J. Kujawa, G. Li, and W. Kujawski. 2020. "Fabrication of PDMS based membranes with improved separation efficiency in hydrophobic pervaporation" *Separation and Purification Technology* 234:116092

Lestari, A. E., M. Elma, S. Rabiah, E. L. A. Rampun, A. Rahma, and A. E. Pratiwi. 2020a. Performance of Mesoporous Organo Silica Membrane for Desalination. Paper read at Materials Science Forum.

Lestari, R. A., M. Elma, A. Rahma, D. Suparsih, S. Anadhliyah, N. L. Sari, D. A. Pratomo, A. Sumardi, A. Lestari, and Z. L. Assyaifi. 2020b. Organo Silica Membranes for Wetland Saline Water Desalination: Effect of membranes calcination temperatures. Paper read at E3S Web of Conferences.

Othman, M. H. D., S. K. Hubadillah, M. R. Adam, A. F. Ismail, M. A. Rahman, and J. Jaafar. 2017. Silica-based hollow fiber membrane for water treatment. In *Current Trends and Future Developments on (Bio-) Membranes*: Elsevier, 157-180.

Rahma, A., M. Elma, M. Mahmud, I. Chairul, E. Amalia, Pratiwi, and L. Erdina, A, Rampun. 2019. "Penyisihan Bahan Organik Alami pada Desalinasi Air Rawa Asin Menggunakan Proses Koagulasi-Pervaporasi" *Jurnal Kimia Sains dan Aplikasi*

Rahman, S. K., E. L. A. Rampun, A. Rahma, and M. Elma. 2020. "Deconvolution of carbon silica templated thin film using ES40 and P123 via rapid thermal processing method" *Materials Today: Proceedings*

Sakarkar, S., S. Muthukumaran, and V. Jegatheesan. 2020. "Polyvinylidene Fluoride and Titanium Dioxide Ultrafiltration Photocatalytic Membrane: Fabrication, Morphology, and Its Application in Textile Wastewater Treatment" *Journal of Environmental Engineering* 146 (7):04020053

Sefentry, A. 2020. "Pemanfaatan Teknologi Membran Reverse Osmosis (RO) Pada Proses Pengolahan Air Laut menjadi Air Bersih" *Jurnal Redoks* 5 (1):58-64

Wang, D. K., M. Elma, J. Motuzas, W.-C. Hou, D. R. Schmeda-Lopez, T. Zhang, and X. Zhang. 2016a. "Physicochemical and photocatalytic properties of carbonaceous char and titania composite hollow fibers for wastewater treatment" *Carbon* 109:182-191

Wang, Q., N. Li, B. Bolto, M. Hoang, and Z. Xie. 2016b. "Desalination by pervaporation: A review" *Desalination* 387:46-60. https://doi.org/10.1016/j.desal.2016.02.036.