AN INSIGHT OF TIO_2 AND SPENT BLEACHING EARTH (SBE) EFFECT OF PHASE CRYSTALLINE STRUCTURES FOR PVDF HOLLOW FIBER MEMBRANE

Rhafiq Abdul Ghani[*], Muthia Elma[**], Aulia Rahma[***], Wahyu[****]

[*]*Materials and Membranes Research Group (M^2ReG), Banjarbaru, Indonesia, rhafiqjockam@gmail.com*

[**]*Chemical Engineering Department, Faculty of Engineering, Lambung Mangkurat University, Banjarbaru, Indonesia, melma@ulm.ac.id*

[***]*Environmental Science Doctoral and Postgraduate Program, Lambung Mangkurat University, Banjarbaru, Indonesia, arahma@mhs.ulm.ac.id*

[****]*Social Studied Education Department, Lambung Mangkurat University, Kayutangi, Banjarmasin, South Kalimantan, Indonesia, wahyu@ulm.ac.id*

Email Correspondence : melma@ulm.ac.id

Received : December 19, 2023 Accepted : April 23, 2024 Published : June 30, 2024

Abstract: Polyvinylidene fluoride (PVDF) hollow fiber membranes have excellent mechanical properties and chemical stability. However, their hydrophobicity can lead to fouling and hinder permeability. Modifying this hydrophobicity is challenging due to PVDF's complex polymorphous structures, with the β-phase offering superior fouling resistance. One approach to improve PVDF hollow fiber membranes is the addition of inorganic additive materials to reduce hydrophobicity. The objective of this study is to offer new insights into the preparation of PVDF hollow fiber membranes using wet spinning with various additives, such as TiO_2 and SBE. The investigation focused on the functional groups of PVDF in both the α and β phases. The membrane was fabricated using regenerated SBE and TiO_2, which were incorporated through dope solution preparation and phase inversion through a wet spinning technique. The study used the Fourier Transform Infrared (FTIR) technique to characterize the PVDF hollow fiber membranes. The study found that the PVDF hollow fiber membranes exhibit differences in α and β phase crystalline structures when combined with various additives. The addition of SBE to PVDF hollow fiber membranes results in a dominant β-phase crystalline structure, as indicated by the relative fraction of 0.70 and the largest peak area of 2.27. This has successfully improved the hydrophilic properties of the PVDF-SBE hollow fiber membrane.

Keywords: PVDF; hollow fiber membrane; α phase; β phase; TiO_2; SBE

Abstrak: Membran hollow fiber polyvinylidene fluoride (PVDF) memiliki sifat mekanik dan stabilitas kimia yang sangat baik. Namun, sifat hidrofobiknya dapat menyebabkan fouling dan menurunkan permeabilitas membran. Oleh karena itu memodifikasi sifat hidrofobisitas ini cukup menantang karena struktur polimorf PVDF yang kompleks, terutama dengan keberadaan fase β yang memberikan ketahanan terhadap fouling. Salah satu pendekatan yang dapat dilakukan untuk meningkatkan membran hollow fiber PVDF adalah dengan penambahan bahan aditif anorganik untuk mengurangi hidrofobisitas. Tujuan dari penelitian ini adalah untuk menguak wawasan baru dalam pembuatan membran serat berongga PVDF menggunakan wet spinning dengan berbagai aditif, seperti TiO_2 dan SBE. Investigasi difokuskan pada gugus

fungsional PVDF berupa fase α dan β. Membran dibuat dengan menggunakan TiO_2 dan SBE regenerasi, yang dibuat melalui pembuatan larutan dope dan inversi fasa melalui metode wet spinning. Penelitian ini menggunakan teknik Fourier Transform Infrared (FTIR) untuk mengkarakterisasi membran serat berongga PVDF. Penelitian ini menemukan bahwa membran serat berongga PVDF menunjukkan perbedaan struktur kristal fase α dan β ketika dikombinasikan dengan berbagai aditif. Penambahan SBE pada membran serat berongga PVDF menghasilkan struktur kristal fase β yang dominan, seperti yang ditunjukkan oleh fraksi relatif 0,70 dan area puncak terbesar 2,27. Hal ini telah berhasil meningkatkan sifat hidrofilik membran serat berongga PVDF-SBE.
Kata kunci: PVDF; membran hollow fiber; fase α; fase β ; TiO_2; SBE

Recommended APA Citation :

Ghani, R. A., Elma, M., Rahma, A., & Wahyu. (2024). An insight of TiO_2 and Spent Bleaching Earth (SBE) Addition Effect of β Phase Crystalline Structures for PVDF Hollow Fiber Membrane. *Elkawnie*, *10*(1), 143-157. https://doi.org/10.22373/ekw.v10i1.21455

Introduction

Nowadays, membrane technology is favorable for water treatment among researchers and industries, due to high selectivity, environmentally friendly and offering good performance (Darmawan et al., 2024; Elma et al., 2024; G. Ji et al., 2024; Zahratunnisa et al., 2024). Commonly, membranes are fabricated from several materials i.e., inorganic, polymer or composite materials. Polyvinylidene fluoride (PVDF) has gained significant attention in the field of polymer-based hollow fiber membranes due to its excellent mechanical properties and favorable temperature and chemical stability (D. Ji et al., 2022; Suhendra et al., 2023). Nevertheless, the hydrophobic characteristic of PVDF may lead to membrane fouling (Elma, Pradana, et al., 2022; Wang & Sun, 2020) and hinder its permeability (Febriyanti, Elma, Nata, Saraswati, & Simatupang, 2023a; Razmgar, Saljoughi, & Mousavi, 2019). Therefore, enhancing the performance of the resultant membrane proves challenging as modifying the hydrophobicity of the hollow fiber polyvinylidene fluoride membrane constitutes a difficulty (Elma, Lamandau, Fatimah, Suhendra, & Rahma, 2023; Pradhana et al., 2021).

PVDF is a semi-crystalline polymer that exhibits complex polymorphous structures. The most common crystalline structures for PVDF membranes synthesized by the NIPS method are the α and β phases (Elma, Pradana, et al., 2022; Zhang et al., 2019). Among these crystalline structures, PVDF membranes with predominantly β phases showed superior fouling resistance compared to PVDF membranes with predominantly α phase (Elma, Rahma, Mustalifah, Wahid, Lamandau, Fatimah, Huda, Alsiren, Nasruddin, et al., 2023). Therefore, a lot of research work has been devoted to the study of the formation of the b-phase of PVDF by different approaches (Su, Sim, Li, Coster, & Chong, 2021).

One approach to improve PVDF hollow fiber membranes is the addition of inorganic particulate materials to reduce the hydrophobicity of the membrane

surface, which can significantly improve membrane performance (Salahshoori et al., 2023; Wei et al., 2019). Numerous prior studies have documented the utilization of particles in the modification of polymer-based membranes, incorporating inorganic materials like SiO_2, TiO_2, Al_2O_3, zeolite, Ag, GO, ZnO, ZrO_2, and others (Muthia, Rhafiq Abdul, Aulia, Alya Dita, & Novrian, 2022; Pratiwi et al., 2023; Razmgar et al., 2019). One of the outcomes of the incorporation of TiO_2 in hollow fiber PVDF membranes are enhancing their antifouling capabilities since it enhances the hydrophilic properties of the membrane surface (Elma, Pradana, et al., 2022; Elma, Saraswati, et al., 2023). However, the particle material used is synthetic and a large amount of chemical addition is required, making it less efficient. Therefore, similar materials that are renewable and practical in use are needed (Maulida, Fitriah, Aliah, Rampun, & Elma, 2023; Sari et al., 2023).

Spent bleaching earth (SBE) is an inorganic material with enough Al_2O_3 and SiO_2 to be a renewable substitute for synthetic materials in membrane manufacturing (Eliche-Quesada & Corpas-Iglesias, 2014; Elma, Lestari, Harivram, Mustalifah, & Rahma, 2023; Rahma et al., 2023). SBE originates from the crude palm oil (CPO) refining process and is being recycled to become a potential membrane component material. Sodium bentonite extract (SBE) is commonly used in the refining process of 2.5-3% per ton of CPO (Rahma et al., 2024). In addition, South Kalimantan has many SBE resources from the CPO refinery mills, which connect the supply chain from 20 CPO mills with a 797.89 tons/hour capacity in this region. (Muhamad, Mokhtar, Lau, Ismail, & Naim, 2022; Triwibowo, Elma, Suhartono, & Riduan, 2023). This study enhanced the PVDF hollow fiber membrane by integrating TiO_2 and regenerating local SBE. Additionally, it will investigate the crystallinity phase characteristics of the resulting hollow fiber PVDF membrane through its functional group spectra.

This work aims to provide new insights into the preparation of PVDF hollow fiber membranes with various additives such as TiO2 and SBE through wet spinning. The functional groups of PVDF in both the α and β phases were investigated. Deconvolution was performed using Origin software to determine the material's surface area during vibration and stretching (Elma, Septyaningrum, Rahmawati, & Rahma, 2023; Ghani, Elma, Lestari, Alsiren, & Rahma, 2023).

Experimental

Materials

Polyvinylidene fluoride (PVDF) (Solef 6012), N, N-Difmethylacetamide (DMAC) (Sigma-Aldrich), Titanium oxide (TiO_2) (Merck), regenerated spent bleaching earth (SBE), aquadest, and tap water were used in this work. All of the chemicals were of the analytical reagent grade and were employed exactly as directed.

Membrane Preparation and Characterization

The solution was prepared initially by dissolving TiO_2 and regenerating SBE in DMAC, following the guidelines in Table 1. The mixture was agitated at 70°C for a duration of 24 hours. Thereafter, 18% of PVDF was incorporated into the dope solution and thoroughly mixed at 70°C until it reached a homogeneous state. Once cooled, the dope solution was poured into the dope tank for the spinning process of the hollow fiber membrane. The spinning setup of the hollow fiber membrane was illustrated in Figure 1, where the dope solution was extruded. Details of the spinning conditions can be found in Table 2. The resultant hollow fiber membrane underwent immersion in tap water for 24 hours, followed by immersion in 50% ethanol for 1 hour and immersion in 98% ethanol for another hour. Subsequently, the hollow fiber membrane was left to dry at room temperature for 24 hours.

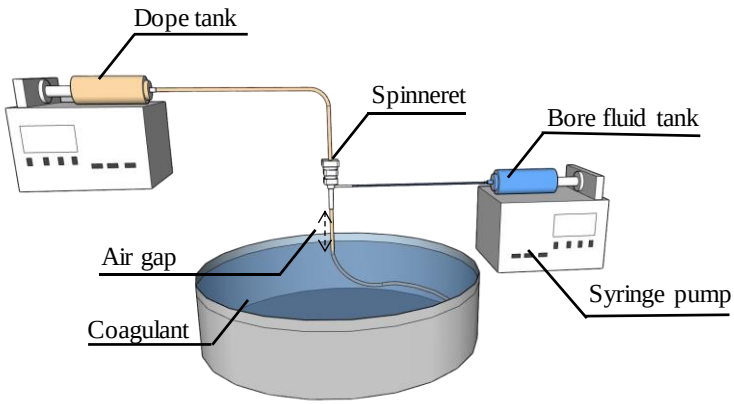

Figure 1. Schematic of spinning hollow fiber membrane

The Fourier Transform Infrared (FTIR) technique was used to characterize the hollow fiber membranes utilizing the Attenuated Total Reflectance (ATR) method with Bruker Diamond instrument at a wavenumber of 4,000-500 cm^{-1}. The results are displayed as a graph of FTIR spectra, and the peaks identified as functional groups. The relative fraction of β phase was calculated using FTIR result through Lambert-Beer Law in equation (1) (Pramono, Sejati, Wahyuningsih, & Purnawan, 2023). F(β) represents the proportion of the β phase, while Aα corresponds to the absorbances at 769 cm^{-1} and Aβ corresponds to the absorbances at 840 cm^{-1} peaks. The value of 1.26 is obtained from the ratio ratio of K_β to K_α. The K_α has a value of 6.1104 $cm^2.mol^{-1}$ and K_β has a value of 7.7104 $cm^2.mol^{-1}$ (Chen et al., 2019). Fourier self-deconvolution was carried out on the 850 cm^{-1} and 650 cm^{-1} bands, utilizing Gaussian band shapes, after background substruction with Origin software.

$$F(\beta)=\left(\frac{A\beta}{A\beta+1.26A\alpha}\right) \quad \ldots\ldots\ldots\ldots\ldots (1)$$

Table 1. Dope Solution compositions of hollow fiber membranes

Membrane Code	PVDF (% mass)	DMAC (% mass)	TiO2 (% mass)	SBE (% mass)
3:0			3	0
2:1			2	1
1.5:1.5	18	79	1.5	1.5
1:2			1	2
0:3			0	3

Table 2. Spinning conditions of hollow fiber membranes

Spinning Conditions	Unit	Value
Dope extrusion rate	mL/min	4
Bore fluid flow rate	mL/min	2
Bore fluid composition	-	Demineralize water
Coagulation medium	-	Tap Water
Spinneret OD/ID	mm	2.4/1.9
Air gap	mm	0
Dope solution's temperature	°C	25
External coagulation's temperature	°C	25

Results

Fourier transform infrared spectroscopy (FTIR) is a method for determining the functional groups of substances (Elma, Mawaddah, et al., 2023; Elma, Septyaningrum, et al., 2023; Febriyanti, Elma, Nata, Saraswati, & Simatupang, 2023b). This work also used FTIR analysis to identify the crystal structure of the manufactured PVDF hollow fiber membrane (Mohammadpourfazeli et al., 2023; Muthia, Aulia, Uun, Reza Satria Kelik, & Alya Dita, 2022). Figure. 2 depicts the FTIR spectra of a hollow fiber membrane in the wavenumber range 860 - 690 cm^{-1}, which corresponds to the vibration of C-C, C-H and C-F in various conformations. The 769 cm^{-1} peak relates to C-C, C-H and C-F as α phase, whereas the 840 cm^{-1} peak refers to C-F vibration as β phase (Pramono et al., 2023). The α phase, in particular, adopts the non-polar trans-gauche (TGTG) conformation, whereas the β phase is extremely polar, adopting the all-trans (TTTT) conformation (Pradhana et al., 2021). These crystal phases can be obtained through a different processing method like the addition of additives (Su et al., 2021). In the specific case of this work, the addition of an additive substance such as TiO_2 and SBE to the PVDF material indicates a different content of the α and β crystalline phases (Chen et al., 2019).

The polarity of the C-F functional group is mainly responsible for the surface hydrophobicity of PVDF hollow fiber membranes (Ghani et al., 2023; Wu et al., 2020). The more polar this group is, the more it marks the crystallinity of PVDF formed into the β phase. Therefore, altering the PVDF material to be more hydrophilic aligns with its polar nature, as water and polar materials are attracted

to each other due to Van der Waals forces. Hollow fiber membranes with hydrophilic properties have significant potential for various applications due to their resistance to fouling and ability to improve the separation process. (Elma, Bilad, et al., 2022; Elma, Ghani, Rahma, Alyanti, & Dony, 2022; Elma, Nata, et al., 2022; Elma, Pratiwi, et al., 2022; Elma, Rahma, Kusumawati, Pratama, & Alyanti, 2022). Their hydrophilic nature provides better antifouling properties, making them suitable for applications such as ultrafiltration, membrane distillation, water treatment, and oil-water separation (Elma, Rahma, Mustalifah, Wahid, Lamandau, Fatimah, Huda, Alsiren, Saraswati, et al., 2023); Mahmud et al. (2023); (Rahma, Elma, Kusumawati, & Dony, 2022; Rahma, Elma, Rampun, Sintungkir, & Hidayat, 2022).

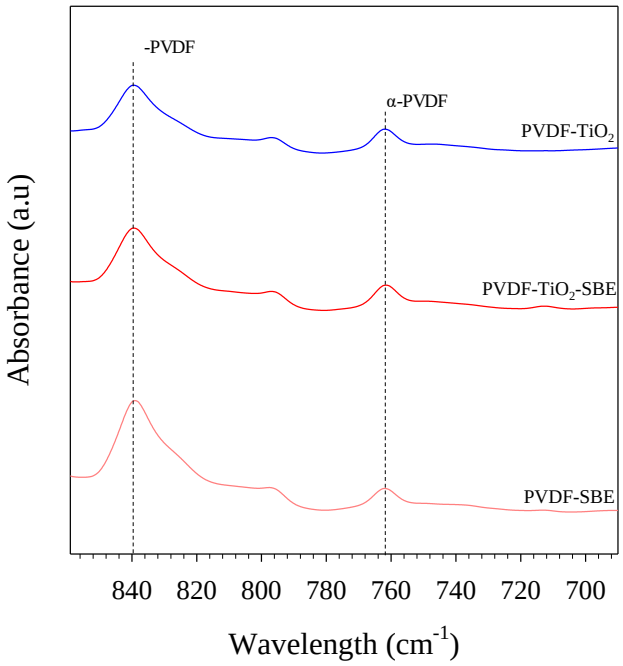

Figure 2. FTIR spectra of hollow fiber membrane PVDF

To quantify the proportion of β phase in each hollow fiber membrane, F(β) was calculated using equation (1). The relative fraction of the β phase in the PVDF hollow fiber membrane is shown in figure 3. The PVDF-SBE hollow fiber membrane displays the highest β phase fraction, reaching 0.70. Due to its intense vibrational band at about 840 cm^{-1}, PVDF-SBE hollow fiber membrane demonstrates the highest degree of hydrophilicity among the produced PVDF hollow fiber membranes (Dhatarwal & Sengwa, 2020). The presence of the β phase also indicates the polar nature of the PVDF hollow fiber membrane (Pramono et al., 2023). In contrast, the addition of TiO_2 to the PVDF hollow fiber membrane resulted in the lowest β phase fraction among other membranes, which was 0.63. A slight increase in the β fraction of 0.64 is observed when an additive mixture of TiO_2 and SBE is applied to PVDF compared to the PVDF-SBE membrane. This is

caused by the fact that TiO_2 can reduce the formation of the β phase in PVDF. (Erusappan et al., 2021).

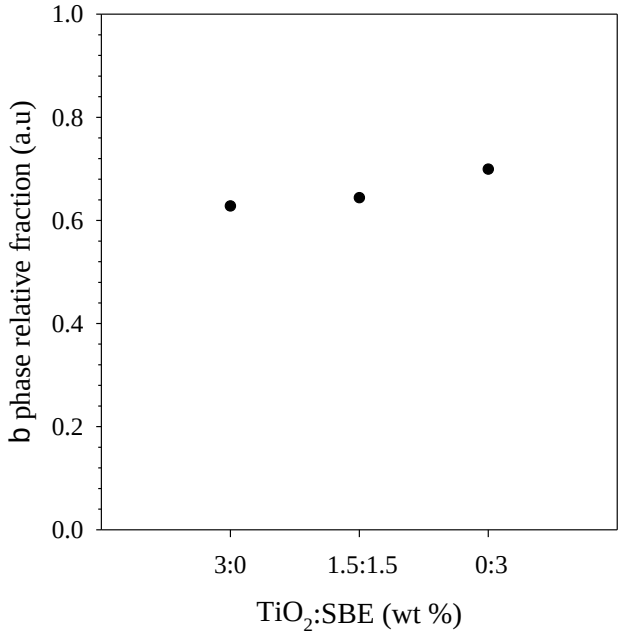

Figure 3. β phase fraction of hollow fiber membrane PVDF

The results of the FTIR graph can be further analyzed using the deconvolution method to better illustrate the graphical changes of the PVDF hollow fiber membranes (Morali, Mandal, Skorobogatiy, & Bodkhe, 2023; Zahratunnisa et al., 2024). Deconvolution of the FTIR spectra was performed by the Gaussian function after baseline correction, after that overlapping the peaks until the deconvoluted spectra matched the experimental data spectra (He, Mohsenzadeh, Zhang, Rault, & Salaün, 2023). The utilization of the Gaussian model has already proven to be an efficient method for distinguishing the overlaps and revealing "hidden" peaks during spectroscopic analysis (Song et al., 2019). Figure 4 illustrates the Gaussian bands of FTIR spectra of a PVDF hollow fiber membrane. The graph indicates that even after deconvolution, the three membranes still exhibit regions of β phase and α phase, plotted as purple and green curves, respectively. There is a difference in the area under the curve for the three membranes, particularly in the peak area of the β phase (purple curve). The PVDF-SBE hollow fiber membrane displays a higher peak area in the β phase compared to the other membranes.

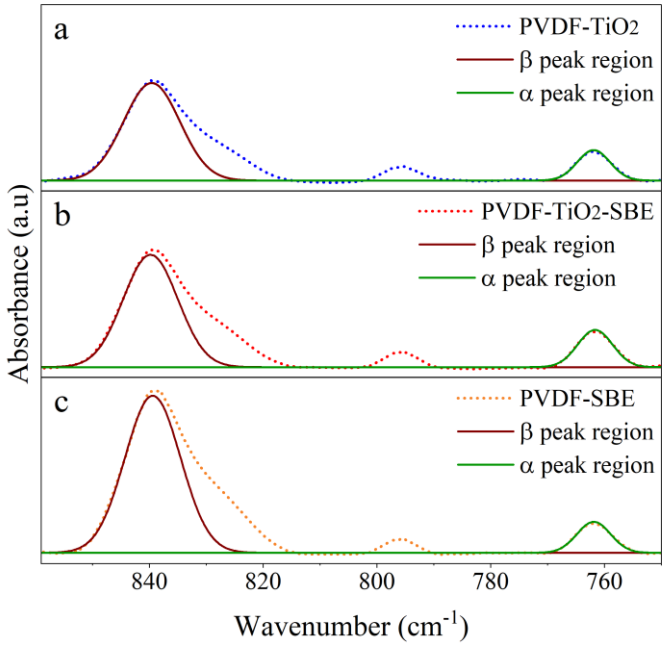

Figure 4. Deconvolution of FTIR spectra of hollow fiber membrane

From the deconvolution of the FTIR graph of the hollow fiber membrane, the peak area value of each peak can be ascertained. The peak areas of the FTIR graph were measured for the normalized spectra using a local baseline (Aliah et al., 2022; Aulia, Muthia, Aliah, Uun, & Novrian, 2022; Elma, Septyaningrum, et al., 2023). The peak area values of α phase and β phase are indicated in figure. 5. The results show that the yield of the β phase of the PVDF-SBE hollow fiber membrane is 2.27, which corresponds to the widest peak area. The peak area of the β phase is also linear with the relative fraction of the β phase. On the other side, the largest peak area of α phase is shown by the PVDF-TiO_2-SBE hollow fiber membrane reaching 0.34. However, the relative fraction of the β phase in the PVDF-TiO_2-SBE hollow fiber membrane is still relatively larger than in the PVDF-TiO_2 hollow fiber membrane. Therefore, the PVDF-TiO_2-SBE hollow fiber membrane is still more hydrophilic than the PVDF-TiO_2 membrane (Pradhana et al., 2021).

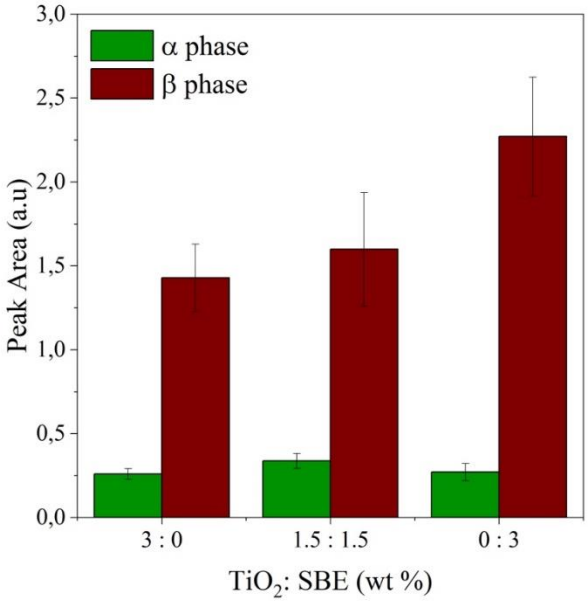

Figure 5. Represents peak area of α and β phase in hollow fiber membrane PVDF.

Conclusion

The study compared the effects of adding TiO_2, SBE, and both particles to the PVDF hollow fiber membrane. PVDF hollow fiber membranes exhibit differences in α and β phase crystalline structures when combined with various additives. The addition of SBE to PVDF hollow fiber membranes produces a dominant β-phase crystalline structure, as indicated by the relative fractions is 0.70 and the largest peak area reaching 2.27. So the crystalline structure of the PVDF-SBE hollow fiber membrane has successfully improved its hydrophilicity properties.

Acknowledgements

This work is supported by the Materials and Membranes Research Group (M^2ReG) and Kurita Overseas Research Grant Program 2023. Special acknowledgement to the oil palm research grant [PRJ-371/DPKS/2022] for the financial support. Muthia Elma also thanks to Applied Research Universities Grant 2023 [026/E5/PG.02.00.PL/2023] Thesis Grant [130/E5/PG.02.00.PL/2023] the Ministry of Research and Technology/National Research and Innovation Agency, the Ministry of Education and Culture of the Republic of Indonesia.

References

Aliah, A., Elma, M., Nata, I. F., Maulida, N. A., Fitriah, S. H., Rampun, E. L. A., & Rahma, A. (2022). *Organosilica Multichannel Membranes Prepared by*

Inner Coating Method Applied for Brackish Water Desalination. Paper presented at the Materials Science Forum.

Aulia, R., Muthia, E., Aliah, Uun, K., & Novrian, D. (2022). Novel Multi-Channel Coated Silica Based Membranes Applied for Peat Water Ultrafiltration. *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences, 100*(3), 133-145. doi:10.37934/arfmts.100.3.133145

Chen, Y., Feng, R., Li, Y., Dan, N., Yang, C., Yu, G., . . . Dan, W. (2019). Development and analysis of a novel PVDF membrane with higher content of β phase. *International Journal of Polymer Analysis and Characterization, 24*(8), 684-695.

Darmawan, A., Muhtar, H., Pratiwi, D. N., Elma, M., Astuti, Y., & Azmiyawati, C. (2024). Robust Construction of Polyvinyl Alcohol Intercalated Graphene Oxide Nanofiltration Membrane for Desalination Via Pervaporation. *Chemosphere*, 142437.

Dhatarwal, P., & Sengwa, R. (2020). Tunable β-phase crystals, degree of crystallinity, and dielectric properties of three-phase PVDF/PEO/SiO2 hybrid polymer nanocomposites. *Materials Research Bulletin, 129*, 110901.

Eliche-Quesada, D., & Corpas-Iglesias, F. (2014). Utilisation of spent filtration earth or spent bleaching earth from the oil refinery industry in clay products. *Ceramics International, 40*(10), 16677-16687. doi:10.1016/j.ceramint.2014.08.030

Elma, M., Bilad, M. R., Pratiwi, A. E., Rahma, A., Asyyaifi, Z. L., Hairullah, H., . . . Lestari, R. A. (2022). Long-Term Performance and Stability of Interlayer-Free Mesoporous Silica Membranes for Wetland Saline Water Pervaporation. *Polymers, 14*(5), 895. doi:https://doi.org/10.3390/polym14050895

Elma, M., Ghani, R. A., Rahma, A., Alyanti, A. D., & Dony, N. (2022). Banana Peels Pectin Templated Silica Ultrafiltration Membrane in Disk Plate Configuration Applied for Wetland Water Treatment. *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences, 100*(1), 77-88. doi:10.37934/arfmts.100.1.7788

Elma, M., Lamandau, D. R., Fatimah, S., Suhendra, S. A., & Rahma, A. (2023). *Reverse electrodialysis membrane for harvesting salinity gradient energy with and without spacer under natural wetland water.* Paper presented at the AIP Conference Proceedings.

Elma, M., Lestari, R. A., Harivram, A. S., Mustalifah, F. R., & Rahma, A. (2023). *Alat Filtrasi-Membran untuk Penyediaan Air Bersih Mandiri di Desa Tinggiran II Luar Kecamatan Tamban Kabupaten Barito Kuala Provinsi Kalimantan Selatan.* Paper presented at the PRO SEJAHTERA (Prosiding Seminar Nasional Pengabdian kepada Masyarakat).

Elma, M., Mawaddah, Y., Wati, L., Sumardi, A., Rampun, E., & Rahma, A. (2023). *TEOS/TEVS membrane by dual acid-base catalyzed in seawater*

desalination with different temperature feeds. Paper presented at the AIP Conference Proceedings.

Elma, M., Nata, I. F., Maulida, N. A., Fitriah, S. H., Rampun, E. L. A., & Rahma, A. (2022). *Organosilica Multichannel Membranes Prepared by Inner Coating Method Applied for Brackish Water Desalination.* Paper presented at the Materials Science Forum.

Elma, M., Pradana, E. A., Ul-haq, M. D., Rampun, E. L., Rahma, A., Harivram, A. S., . . . Kamelia, Y. (2022). Hollow fiber membrane applied for Sasirangan wastewater desalination integrated with photocatalysis and pervaporation set-up. *Materials Today: Proceedings, 51*, 1298-1302.

Elma, M., Pratiwi, A. E., Rahma, A., Rampun, E. L. A., Mahmud, M., Abdi, C., . . . Bilad, M. R. (2022). Combination of Coagulation, Adsorption, and Ultrafiltration Processes for Organic Matter Removal from Peat Water. *Sustainability, 14*(1), 370. doi:https://doi.org/10.3390/su14010370

Elma, M., Rahma, A., Kusumawati, U., Pratama, R. S. K., & Alyanti, A. D. (2022). Single Vs Multichannel Silica-Pectin Ultrafiltration Membranes for Treatment of Natural Peat Water. *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences, 100*(2), 33-46.

Elma, M., Rahma, A., Mustalifah, F., Wahid, A. R., Lamandau, D., Fatimah, S., . . . Saraswati, N. (2023). Nanofiltration Technology Applied for Peat and Wetland Saline Water. In *Nanofiltration Membrane for Water Purification* (pp. 217-245): Springer.

Elma, M., Rahma, A., Mustalifah, F., Wahid, A. R., Lamandau, D., Fatimah, S., . . . Simatupang, P. (2023). Nanofiltration Technology Applied for Peat and Wetland Saline Water. In *Nanofiltration Membrane for Water Purification* (pp. 217-245): Springer.

Elma, M., Saraswati, N. K. D. A., Simatupang, P. F. A., Febriyanti, R., Rahma, A., & Mustalifah, F. R. (2023). Hydrogel derived from water hyacinth and pectin from banana peel as a membrane layer. *Materials Today: Proceedings*. doi:10.1016/j.matpr.2023.01.368

Elma, M., Septyaningrum, L., Rahmawati, R., & Rahma, A. (2023). *Vacuum versus air calcination of modified TEOS-MTES based membrane for seawater desalination.* Paper presented at the AIP Conference Proceedings.

Elma, M., Syauqiah, I., Oktaviana, E. N., Fatimah, S., Rahma, A., Harivram, A. S. K., & Rampun, E. L. (2024). *Fabrication of silica-nypa membrane applied for water desalination.* Paper presented at the AIP Conference Proceedings.

Erusappan, E., Thiripuranthagan, S., Radhakrishnan, R., Durai, M., Kumaravel, S., Vembuli, T., & Kaleekkal, N. J. (2021). Fabrication of mesoporous TiO2/PVDF photocatalytic membranes for efficient photocatalytic degradation of synthetic dyes. *Journal of Environmental Chemical Engineering, 9*(4), 105776.

Febriyanti, R., Elma, M., Nata, I. F., Saraswati, N. K. D. A., & Simatupang, P. F. A. (2023a). Hydrogel Films Derived Water Hyacinth Stems And Banana Peels Pectin: Tensile Performance And Swelling Ability. *Elkawnie: Journal of Islamic Science and Technology, 9*(1), 81-98.

Febriyanti, R., Elma, M., Nata, I. F., Saraswati, N. K. D. A., & Simatupang, P. F. A. (2023b). Hydrogel Films Derived Water Hyacinth Stems And Banana Peels Pectin: Tensile Performance And Swelling Ability. *Elkawnie, 9*(1). doi:10.22373/ekw.v9i1.16419

Ghani, R., Elma, M., Lestari, R., Alsiren, A., & Rahma, A. (2023). *Characterization of sprayable mulch film from yam nagara starch for agricultural application.* Paper presented at the IOP Conference Series: Earth and Environmental Science.

He, Z., Mohsenzadeh, E., Zhang, S., Rault, F., & Salaün, F. (2023). Development of high-sensitive piezoelectric nanogenerators of all-organic PVDF multilayer nanofibrous membrane with innovative 3D structure via electrohydrodynamic processes. *Journal of Polymer Research, 30*(10), 385.

Ji, D., Gao, Y., Wang, W., Feng, H., Chen, K., & Xiao, C. (2022). Green preparation of PVDF hollow fiber membranes with multiple pore structure via melt spinning method for oil/water separation. *Journal of Environmental Chemical Engineering, 10*(5), 108337.

Ji, G., Kou, X., Anjum, T., Khan, A. L., Yin, X., Elma, M., & Olguin, G. (2024). The interpretation of diverging hydrogen and carbon dioxide permeations with temperature across silica-based membranes. *Journal of Membrane Science, 695*, 122472.

Mahmud, M., Elma, M., Rahma, A., Huda, N., Lestari, R. A., Harivram, A. S., . . . Bilad, M. R. (2023). Step-by-Step Fabrication of PVDF-TiO2 Hollow Fiber Membrane and Its Application Desalination of Wetland Saline Water via Pervaporation. *Indonesian Journal of Science and Technology, 8*(3), 499-516.

Maulida, N. A., Fitriah, S. H., Aliah, A., Rampun, E. L. A., & Elma, M. (2023). *Preparation and performance of interlayer-free organosilica membranes on zirconia support.* Paper presented at the AIP Conference Proceedings.

Mohammadpourfazeli, S., Arash, S., Ansari, A., Yang, S., Mallick, K., & Bagherzadeh, R. (2023). Future prospects and recent developments of polyvinylidene fluoride (PVDF) piezoelectric polymer; fabrication methods, structure, and electro-mechanical properties. *RSC advances, 13*(1), 370-387.

Morali, A., Mandal, A., Skorobogatiy, M., & Bodkhe, S. (2023). Unleashing the piezoelectric potential of PVDF: a study on phase transformation from gamma (γ) to beta (β) phase through thermal contact poling. *RSC advances, 13*(44), 31234-31242.

Muhamad, N., Mokhtar, N., Lau, W., Ismail, A., & Naim, R. (2022). Fouling studies on hydrophobic PVDF-bentonite hollow fiber membrane during membrane distillation of palm oil mill effluent. *Journal of Water Process Engineering, 49*, 102969. doi:10.1016/j.jwpe.2022.102969

Muthia, E., Aulia, R., Uun, K., Reza Satria Kelik, P., & Alya Dita, A. (2022). Single Vs Multichannel Silica-Pectin Ultrafiltration Membranes for Treatment of Natural Peat Water. *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences, 100*(2), 33-46. doi:10.37934/arfmts.100.2.3346

Muthia, E., Rhafiq Abdul, G., Aulia, R., Alya Dita, A., & Novrian, D. (2022). Banana Peels Pectin Templated Silica Ultrafiltration Membrane in Disk Plate Configuration Applied for Wetland Water Treatment. *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences, 100*(1), 77-88. doi:10.37934/arfmts.100.1.7788

Pradhana, E., Elma, M., Othman, M., Huda, N., Ul-haq, M., Rampun, E. L., & Rahma, A. (2021). *The Functionalization Study of PVDF/TiO2 Hollow Fibre Membranes Under Vacuum Calcination Exposure.* Paper presented at the Journal of Physics: Conference Series.

Pramono, E., Sejati, G. P. W., Wahyuningsih, S., & Purnawan, C. (2023). Polyvinylidene Fluoride (PVDF)/Modified Clay Hybrid Membrane for Humic Acid and Methylene Blue Filtration. *Indonesian Journal of Chemistry, 23*(2). doi:10.22146/ijc.78979

Pratiwi, E. N., Elma, M., Mahmud, M., Basir, B., Rezki, M. R., Oktaviana, E. N. R., . . . Rahma, A. (2023). *Novel carbon templated silica membrane prepared from Nypa fruticans leaf for seawater desalination.* Paper presented at the AIP Conference Proceedings.

Rahma, A., Elma, M., Bilad, M. R., Wahid, A. R., Huda, M. S., & Lamandau, D. R. (2023). Novel spent bleaching earth industrial waste as low-cost ceramic membranes material: elaboration and characterization. *Materials Today: Proceedings*. doi:10.1016/j.matpr.2023.02.387

Rahma, A., Elma, M., Kusumawati, U., & Dony, N. (2022). Novel Multi-Channel Coated Silica Based Membranes Applied for Peat Water Ultrafiltration. *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences, 100*(3), 133-145.

Rahma, A., Elma, M., Rampun, E. L., Sintungkir, S. L., & Hidayat, M. F. (2022). Effect of backwashing process on the performance of an interlayer-free silica–pectin membrane applied to wetland saline water pervaporation. *Membrane Technology, 2022*(3).

Rahma, A., Elma, M., Roil Bilad, M., Syauqiah, I., Patria, R. A., Ziqri, M., & Kartikawati, D. (2024). Functionalization and Deconvolution of Tubular Ceramic Support Membrane Prepare from High Silica Spent Bleaching Earth by Centrifugal Casting. *Key Engineering Materials, 975*, 87-94.

Razmgar, K., Saljoughi, E., & Mousavi, S. M. (2019). Preparation and characterization of a novel hydrophilic PVDF/PVA/Al2O3 nanocomposite membrane for removal of As (V) from aqueous solutions. *Polymer Composites, 40*(6), 2452-2461.

Salahshoori, I., Mohseni, A., Jorabchi, M. N., Ghasemi, S., Afshar, M., & Wohlrab, S. (2023). Study of modified PVDF membranes with high-capacity adsorption features using Quantum mechanics, Monte Carlo, and Molecular Dynamics Simulations. *Journal of Molecular Liquids*, 121286.

Sari, D. P., Elma, M., Mahmud, M., Basir, B., Rezki, M. R., Rahmawati, R., . . . Rahma, A. (2023). *Fabrication of organo-silica thin film for water desalination from dual silicate precursor (tetraethylorthosilicate & methyltriethoxysilane).* Paper presented at the AIP Conference Proceedings.

Song, F., Li, T., Zhang, J., Wang, X., Bai, Y., Giesy, J. P., . . . Wu, F. (2019). Novel insights into the kinetics, evolved gases, and mechanisms for biomass (sugar cane residue) pyrolysis. *Environmental Science & Technology, 53*(22), 13495-13505.

Su, Y. P., Sim, L. N., Li, X., Coster, H. G., & Chong, T. H. (2021). Anti-fouling piezoelectric PVDF membrane: Effect of morphology on dielectric and piezoelectric properties. *Journal of Membrane Science, 620*, 118818.

Suhendra, S. A., Elma, M., Syauqiyah, I., Lamandau, D. R., Fatimah, S., & Rahma, A. (2023). Energy from Salinity Gradient of Wetland Saline Water Using Reverse Electrodialysis Membrane. *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences, 101*(2), 46-59. doi:10.37934/arfmts.101.2.4659

Triwibowo, D., Elma, M., Suhartono, E., & Riduan, R. (2023). Comprehensive evaluation of coal mine pit lake hydrological connectivity in South Kalimantan, Indonesia.

Wang, W., & Sun, H. (2020). Effect of different forms of nano-ZnO on the properties of PVDF/ZnO hybrid membranes. *Journal of Applied Polymer Science, 137*(36), 49070.

Wei, D., Zhou, S., Li, M., Xue, A., Zhang, Y., Zhao, Y., . . . Yang, D. (2019). PVDF/palygorskite composite ultrafiltration membranes: Effects of nano-clay particles on membrane structure and properties. *Applied Clay Science, 181*, 105171. doi:10.1016/j.clay.2019.105171

Wu, Q., Tiraferri, A., Li, T., Xie, W., Chang, H., Bai, Y., & Liu, B. (2020). Superwettable PVDF/PVDF-g-PEGMA ultrafiltration membranes. *ACS omega, 5*(36), 23450-23459.

Zahratunnisa, Elma, M., Aisyah, E. R., Hastati, Subkhan, R., Widiawardani, S., . . . Syauqiah, I. (2024). Polyamide 66 hybrid TiO2–pectin flat-sheet membrane applied to wetland water ultrafiltration. *Membrane Technology, 2024*(1).

Zhang, Y., Ye, L., Zhang, B., Chen, Y., Zhao, W., Yang, G., . . . Zhang, H. (2019). Characteristics and performance of PVDF membrane prepared by using NaCl coagulation bath: Relationship between membrane polymorphous structure and organic fouling. *Journal of Membrane Science*, *579*, 22-32.