



Vanillin from Food Flavoring Product as A Cheaper Alternative Hydrophilic Agent for Modifying PVDF Membranes in The Treatment of Organic Compounds in Water

Nurbayani¹, Aulia Chintia Ambarita², Sri Mulyati^{2*}

¹ Magister of Environmental Management, Syiah Kuala University, Banda Aceh, Aceh, Indonesia, 23111

²Department of Chemical Engineering, Engineering Faculty, Universitas Syiah Kuala, Banda Aceh, Indonesia, 23111

*E-mail: sri.mulyati@unsyiah.ac.id

Article History

Received: 16 July 2024; Received in Revision: 15 August 2024; Accepted: 27 August 2024

Abstract

Membrane fouling is an unavoidable challenge in ultrafiltration, resulting in reduced flux and increased operating costs. Surface modification of polyvinylidene fluoride (PVDF) membranes can improve hydrophilicity and extend membrane lifetime. This study investigates vanillin from food flavoring product (VFFP) as a hydrophilic additive for PVDF membranes to enhance antifouling properties. The immersion precipitation phase inversion method was used to prepare membranes with 0-3% (w/w) vanillin. The results of FTIR analysis of VFFP show similarity in absorption peaks with commercial vanillin. The addition of 3% w/w VFFP to PVDF membrane can improve the hydrophilicity by reducing the contact angle from 86° to 76.26°. Membrane performance showed good results with modified membranes having higher water fluxes than unmodified membranes. In addition, higher flux recovery ratio (FRR) values indicated better antifouling properties. The addition of vanillin significantly improved the performance of PVDF membranes, confirming its use as a hydrophilic additive.

Keywords: antifouling, food flavoring product, polyvinylidene fluoride, vanillin

Copyright ©2024 Published by JTK-USK

1. Introduction

The expansion of global industrialization exacerbates the risk of water resource contamination, driven by ecological pollutants and energy crises. Consequently, advancements in water treatment technologies are imperative (Mu et al., 2021). As an efficient separation technology, membrane technology has been increasingly developed in various fields, including wastewater treatment, water filtration, the food industry, and pharmaceuticals. Compared to traditional biological and chemical technologies, membrane technology is characterized by high selectivity, excellent adaptability, strong flexibility, and low pollution levels (Zheng et al., 2023). In membrane synthesis, materials used typically possess excellent chemical, physical, and thermal properties, enabling adaptation to specific environments. Polymer membranes are preferred in membrane separation due to

their cost-effectiveness, performance, formation capabilities, flexibility, and low cost. Specific component affinity is crucial in polymer membranes, with pore size easily controlled during formation (Sonawane et al., 2021).

Polyvinylidene fluoride (PVDF) is a synthetic polymer widely used as a membrane-forming material in various applications. PVDF exhibits excellent mechanical, thermal, and chemical properties, including resistance to chemicals such as salt solutions, acids, oxidizers, aliphatic and polar aprotic solvents, outstanding antioxidative properties, superior thermal and hydrolytic stability, as well as excellent mechanical and membrane-forming capabilities (Shen et al., 2022). During membrane operation, performance decline typically occurs, known as membrane fouling. Membrane fouling is defined as the accumulation of trapped particles, colloids, emulsions, suspensions, macromolecules,

salts, and other substances on the membrane surface or within the pores of the membrane walls (Gul et al., 2021). Fouling reduces membrane flux both temporarily and permanently during the separation process under constant pressure conditions. Therefore, membrane fouling impairs membrane performance, increases operational costs, and ultimately shortens membrane lifespan.

Generally, membrane fouling results from interactions between the membrane surface and foulants, which include inorganic, organic, and biological substances in various forms. Foulants not only physically interact with the membrane surface but also chemically damage the membrane material. PVDF polymer-based membranes are susceptible to fouling, especially in aquatic environments due to their relatively high surface energy and hydrophobic nature. This can increase the PVDF membrane's affinity for specific fouling agents such as humic acids, proteins, or bacteria that adhere to the membrane surface and cause fouling (Xu et al., 2020).

Fouling in membranes is considered an unavoidable situation in ultrafiltration process applications. Fouling can easily lead to decreased flux and membrane service life, significantly increasing the operational costs of the ultrafiltration process. Fouling in membrane processes is a major barrier that limits widespread applications. Therefore, the hydrophilicity and anti-fouling properties of membrane materials must be enhanced, and these efforts have been a focus in ultrafiltration processes (Sun et al., 2021).

The properties of a membrane are determined by its active layer. Foulant interaction with the membrane is significantly influenced by surface properties, including hydrophilicity, roughness, and charge density. Significant efforts have been made to adjust these factors (Zhu et al., 2019). Hydrophilicity plays a crucial role in preventing membrane fouling. More hydrophilic membranes have higher surface energy, thus showing stronger resistance to contaminants. Increasing the hydrophilicity of the membrane surface can significantly enhance the membrane's anti-fouling performance due to the formation of an effective hydration layer that prevents dirt deposits.

Surface modification of PVDF membrane is a common and effective method that enhances hydrophilicity or alters surface properties to extend the lifespan of PVDF membranes.

Several hydrophilic materials such as graphene oxide-polyethylene glycol (Ma et al., 2020), zwitterionic compounds (Ma et al., 2020), polydopamine (Liu et al., 2023), and tannic acid (Mulyati et al., 2020) have been employed as additives in membrane casting solutions to enhance fouling resistance in hydrophobic polymer membranes. Surface modification of membranes with natural additives is considered a new paradigm in enhancing membrane performance.

Vanillin is one of the potential hydrophilic additives known for its high antioxidant properties. This compound has a polar and nonpolar structure and is widely used as a flavoring agent in food products (Esmaeilil et al., 2019). Several researchers have used vanillin compounds as membrane additives (Esmaeilil et al., 2019; Yadav et al., 2020; Yadav et al., 2022). The use of high purity vanillin improves membrane performance and antifouling properties, as reported in recent studies. Furthermore, vanillin is widely available in traditional markets and supermarkets as a food flavoring agent at a very low price compared to commercial prices. High purity vanillin costs up to \$23.5, while vanillin from food flavoring products (VFFP) costs only \$0.5 per 20 grams. Therefore, in terms of economic value, using VFFP has advantages. Moreover, the use of VFFP as a PVDF membrane additive has never been reported.

This additive is expected to improve antifouling properties and increase hydrophilic properties. The modification involves blending the polymer with VFFP, followed by characterization by FTIR spectroscopy for chemical composition, SEM for morphological analysis, porosity and pore size measurements, water absorption tests, and water contact angle measurements to evaluate hydrophilicity. Membrane performance was evaluated for humic acid selectivity and anti-fouling properties using the Flux Recovery Ratio (FRR) test.

2. Methodology

2.1. Materials

Polymer PVDF (Mw ~534 kDa, Merck, Germany) is used as the main material for membrane fabrication. Dimethyl acetamide (DMAc 99.8%, Merck) serves as the solvent for PVDF polymer. VFFP (Koepoe Koepoe®, PT Gunacipta Multirasa, Tangerang, Indonesia) is used as an additive to enhance the hydrophilicity of the membrane. Humic acid

(Merck) is used as a foulant model in filtration processes. Distilled water is used as a non-solvent in membrane preparation and pure water filtration processes.

2.2. Membrane Preparation

The Phase Inversion via Immersion Precipitation method is employed as a technique for membrane fabrication. VFFP is dissolved in DMAc solvent and stirred until homogeneous, then PVDF is gradually added to the solution and stirred for 24 hours until a homogeneous mixture is obtained. This mixture, referred to as the dope solution, is then allowed to stand to remove air bubbles (debubbling). Subsequently, the dope solution is cast onto a glass plate using a casting knife and immersed in a coagulation bath containing distilled water until a thin layer forms. The process continues until the membrane detaches from the glass plate. The resulting membrane is then washed and stored in a container filled with distilled water. The composition of the dope solution is detailed in Table 1.

Table 1. Casting solution composition.

No.	Membrane	PVDF (%w/w)	VFFP (%w/w)	DMAc (% w/w)
1	M0	15	0	85
2	M1	15	1	84
3	M2	15	3	82

2.3. Membrane Characterization

The water contact angle was employed to assess the hydrophilicity of the membranes. Prior to measurement, the samples underwent overnight freezing in a freeze-dryer (FD-1000, Eyela, Japan). Subsequently, the membrane samples were affixed onto glass using double-sided tape. Following this, 1 μ L of Milli-Q water was deposited onto the membrane surface, and the contact angle was measured using a Drop Master 300 contact angle meter (Kyowa Interface Science Co., Japan). Distilled water was carefully dispensed onto the membrane samples using a micro-syringe. Contact angle measurements were performed at 10 points per membrane, with the procedure repeated three times per sample.

The membrane surface was observed using FE-SEM (JSF-7500F, Jeol Co. Ltd., Japan). Prior to measurement, the sample was dried using a freeze-dryer (FD-1000, Eyela, Japan). Subsequently, the sample was coated with osmium coater (Neoc-STB, Meiwafoysis Co.

Ltd., Japan) to form a thin and ultra-thin osmium layer on the sample surface. Fourier Transform Infrared Spectroscopy (FTIR) is used to analyze functional groups present in the membrane and identify the components of the membrane material. Prior to analysis, samples are cut into 4 x 4 cm pieces and dried with tissue to avoid moisture content that could affect the IR spectrum. Functional group analysis is conducted using FTIR Shimadzu 8400 with a wavenumber range of 400 cm^{-1} to 4000 cm^{-1} , producing transmission spectra.

2.4. Filtration performance and antifouling properties

The impact of membrane modification was evaluated through a performance test experiment, which included measurements of pure water flux, humic acid flux, and rejection of humic acid. Experimental data was collected and empirical equations were used for calculations in this study. Filtration tests were conducted using ultrafiltration cells under an input pressure of 1 bar. The feed rate through the membrane was controlled by a peristaltic pump (MasterFlex® L/S®, Cole-Parmer Instrument Company).

This study used two types of feed solutions: pure water (distilled water) and humic acid (50 mg/L). Measurements were conducted by introducing a specific volume of pure water (to measure pure water flux) and a humic acid solution (to evaluate flux and rejection). Filtration tests were carried out for several hours, with 2 hours dedicated to compaction, and data were collected every 10 minutes until the specific volume remained constant. To ensure reliable results, each membrane sample was tested with at least 5 replicates. The solution that remained on the membrane surface was termed retentate, while the solution that passed through the membrane was termed permeate. The permeate was used to assess membrane performance, including flux (J , $\text{L}/\text{m}^2\text{h}$) and rejection (R , %), as calculated using Equations (1) and (2), respectively. In the case of antifouling properties, the measurement was performed in a cycle including the initial pure water flux (J_w , $\text{L}/\text{m}^2\text{h}$), then the humic acid flux, and finally the secondary pure water flux (after backflushing at 0.1 bar) (J_{wr} , $\text{L}/\text{m}^2\text{h}$). The flux recovery ratio was then calculated using Equation (3).

$$J = \frac{\Delta V}{\Delta t \cdot A} \quad (1)$$

$$R = \frac{C_o - C_p}{C_o} \cdot 100\% \quad (2)$$

$$\text{FRR} = \frac{J_w}{J_{wr}} \cdot 100\% \quad (3)$$

where ΔV (L) represents the volume, Δt (h) indicates the filtration time, A (m^2) denotes the effective surface area of the membrane, and C_0 and C_p (mg/L) represent the humic acid concentration in the feed and permeate, respectively.

3. Results and Discussion

3.1. The impact of modification on membrane characteristics

3.1.1. Surface hydrophilicity

The wetting property of a surface is measured by the contact angle, where the surface tension between a water droplet and a membrane surface determines how well the water droplet spreads or wets on the membrane surface. The effect of concentration VFFP to hydrophilicity of membrane is shown in Figure 1. This shows that the addition of additives affects the water contact angle slightly. In comparison to the pure PVDF, the decrease was 7.2 % (M1) and 12.1 % (M2), respectively. The concentration of vanillin plays a crucial role in influencing the hydrophilicity of membranes (Yadav et al., 2020). At low concentrations, the interaction of Vanillin from food flavoring product with the membrane surface, which contains polar functional groups, can slightly increase hydrophilicity. As the concentration increases, vanillin significantly enhances surface wettability, potentially increasing water flux and resistance to deposition by hydrophobic substances (Esmailil et al., 2019).

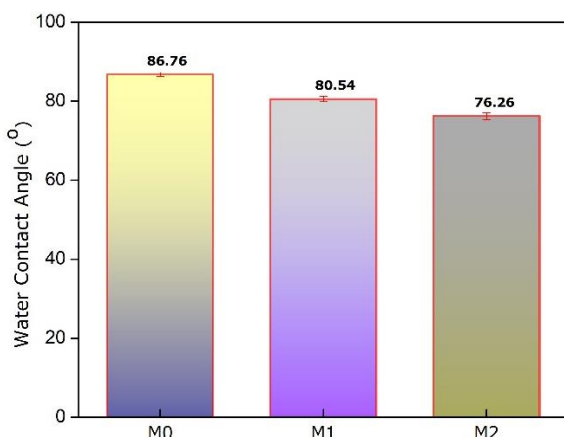


Figure 1. Water Contact Angle of Pristine PVDF membranes and after addition of VFFP

3.1.2. Chemical functional groups

Figure 2a shows the IR spectra of VFFP. The broad peak around 3200 cm^{-1} suggests the presence of O-H stretching vibrations, indicating hydroxyl groups. A sharp peak

around 1680 cm^{-1} is characteristic of C=O stretching vibrations from carbonyl groups, such as in aldehyde groups. Peaks around 1506 cm^{-1} can be attributed to C=C stretching in alkenes or aromatic compounds. The region near 1050 , 900 , and 800 cm^{-1} corresponds to C-H stretching vibrations typical of aromatic ring. The results of FTIR analysis of VFFP show similarity in absorption peaks with commercial vanillin (Mulyati et al., 2024). Therefore, this additive has the potential to be a cheaper alternative hydrophilic agent.

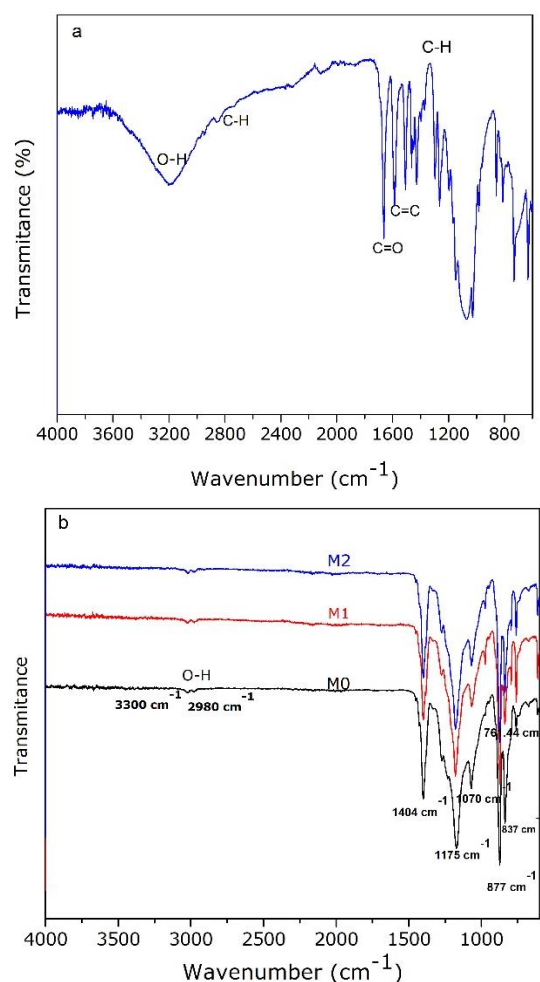


Figure 2. Ir spectra of VFFP (a), and Pristine PVDF and modified PVDF with VFFP

Figure 2b presents the IR spectra of membranes to identify the chemical compounds in both the original and modified PVDF membranes. The characteristic functional groups of CF_2 deformation, vibration shown at wavenumbers 1175 cm^{-1} . The peak at wavenumber 1404 cm^{-1} in the IR spectra of PVDF membranes is associated with the CH_2 bending vibrations. New groups due to hydrogen bonding between VFFP and PVDF were observed in the O-H and C-H region of the PVDF-vanillin membrane. Hydroxyl groups

(-OH) were identified as part of the phenolic structure and C-H bond associated with aromatic groups (Mulyati et al., 2024).

3.1.3. Membrane morphology

The effect of VFFP modification on the morphology of PVDF membranes was observed through analysis using FE-SEM. The 'A' designation represents the surface structure, whereas the 'B' designation represents the cross-sectional structure, which is essential for visualizing the macrovoid structure.

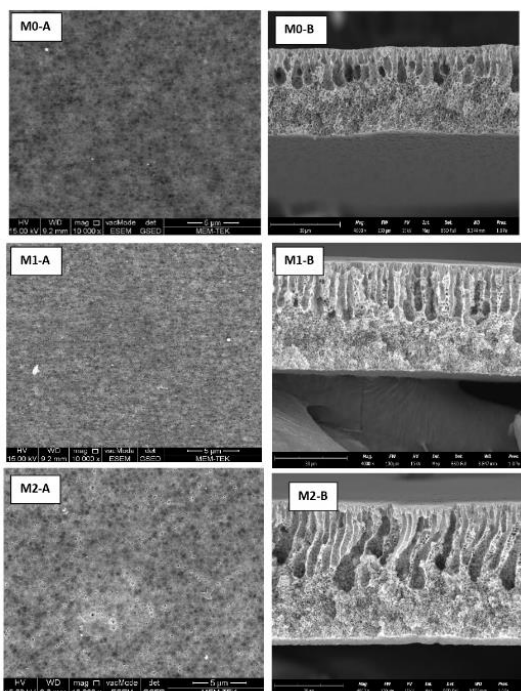


Figure 3. SEM Image of Pristine PVDF membranes and after addition of VFFP

From Figure 3, it can be seen that the addition of VFFP to the casting solution causes significant changes on the surface of the PVDF membrane. These changes are evident in the shape, size, and number of pores formed on the membrane surface. The M0 membrane (without modification) has a smaller number of pores, fewer pores overall, and an uneven distribution compared to the membrane modified with vanillin.

Increasing the concentration of vanillin results in larger pore sizes on the membrane surface. Vanillin, as a phenolic compound, can interact with the chemical structure of the membrane, form complexes with polymers, and lead to the formation of larger pores. The addition of vanillin leads to an increase in both the size and quantity of membrane pores. The pores

on the surface structure increased with the higher concentration of vanillin. Significant additive quantities may fill voids within the membrane structure or induce polymer compaction, thereby decreasing overall porosity. The membranes M1 and M2 exhibit significant differences, with an increase in macrostructure size (greater depth of the finger structure). The pure PVDF membrane produced small micropores and macropores, while the PVDF-VFFP membrane produced larger macropores.

3.2. The Filtration performance and antifouling properties

3.2.1. Pure Water Flux

Flux data provide critical insights into the internal structure of membranes, which are essential for practical applications. The size and distribution of pores within the membrane significantly impact water transport efficiency. Figure 4 presents comparative water flux values between untreated PVDF membranes (M0) and those modified with VFFP. Specifically, M0 exhibits a flux of 16.13 L/m²·h, whereas modified membranes M1 and M2 demonstrate flux values of 19.19 L/m²·h and 26.61 L/m²·h, respectively. Increased vanillin content in the casting solution enhances water flux through the membrane by promoting greater hydrophilicity and enlarging pore size, as confirmed by SEM analysis. Membranes with higher affinity for water reduce hydraulic resistance and exhibit larger pores.

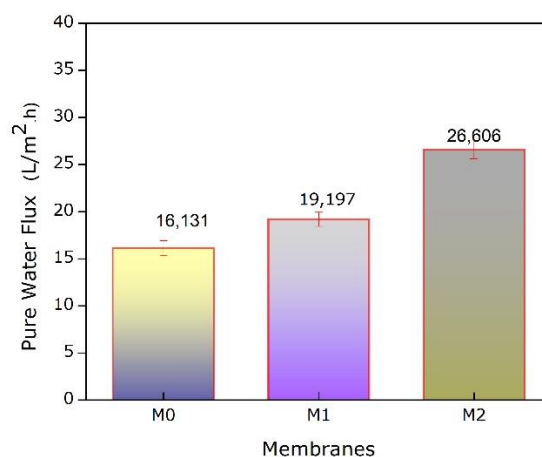


Figure 4. Pure Water Flux of Pristine PVDF membranes and after the addition of VFFP

3.2.2. Humic acid: flux and rejection

Modification of PVDF membranes using vanillin derived from VFFP has been successfully

conducted. Figure 5 shows the flux and the humic acid rejection, with an inverse trend in each membrane, for example in the M2 membrane, which is 21.25 L/m² h and 67.46%. The addition of vanillin additives resulted in an increase in flux with a decrease in humic acid rejection, especially at higher vanillin loading in the dope solution. This indirectly demonstrates the role of vanillin in increasing pore size. The results of this study indicate that vanillin from food flavors has the ability to modify the main structure of PVDF membranes, specifically hydrophilicity and flux. However, further modification is needed to improve the selectivity performance of PVDF-VFFP membranes.

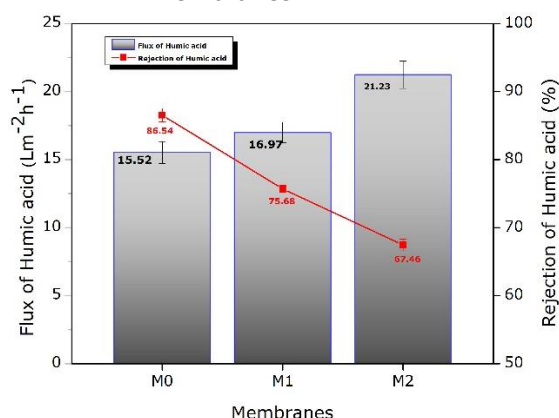


Figure 5. Flux and Rejection of Humic acid of Pristine PVDF membranes and after addition of VFFP

3.2.3. The impact of modification on antifouling properties

After filtering the Humic acid solution, the membranes were thoroughly cleaned to reassess water flux. An increase in water flux after cleaning indicated that humic acid molecules were effectively removed, improving flux recovery. The flux recovery ratio (FRR, %) was calculated from the measured flux values to evaluate the membranes' antifouling capacity. Higher FRR values indicated better antifouling performance (Asif Khan et al., 2023). M0 has the lowest FRR value, which is about 75.9%, while the FRR value increases with the increase in the percentage of VFFP in the PVDF membranes, as shown in Figure 6. The FRR values were observed to be 83.8%, 86.5%, and 90.0% for M1 and M2 respectively. A higher FRR value also indicates that a higher number of adsorbed humic acid particles were eliminated from the membrane surface during the washing process.

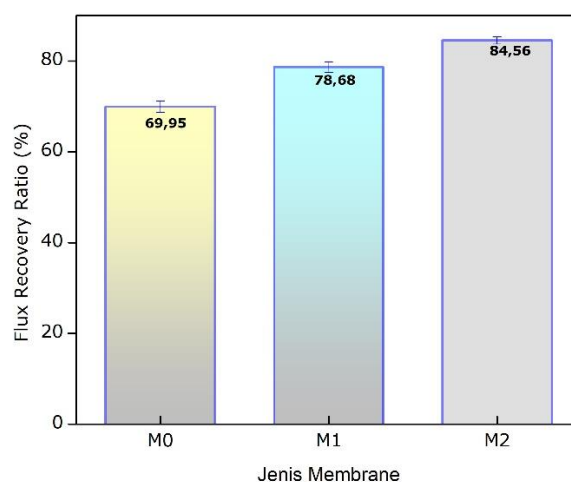


Figure 6. Flux Recovery Ratio (FRR) of Pristine PVDF membranes and after addition of VFFP

Conclusion

In this study, vanillin from food flavoring product (VFFP) was investigated as a hydrophilic additive to improve PVDF membranes. FTIR characterization identified new peaks, which are O-H and C-H groups, with significant morphological changes with increased pore distribution. Water contact angle measurements showed that VFFP improved membrane hydrophilicity, decreasing the angle from 86.76° to 76.26°. The improved hydrophilicity was confirmed by increased humic acid flux values, with modified membranes (M1 and M2) showing higher flux rates (16.97 and 21.25 L/m²-h) compared to the unmodified membrane (M0) at 15.52 L/m²-h. Improved antifouling properties were indicated by higher FRR, which was 84.56% for M2. These results confirm the potential of VFFP to improve membrane performance, making it a promising low-cost additive. Future research should evaluate the chemical stability and long-term performance of these modified membranes.

Author contribution

Conceptualization, N; Formal analysis, A.C.A; Investigation, N; Project administration, A.C.A; Supervision, S.M; Writing – original draft, A.C.A; Validation, S.M; Writing –review and editing, N.

Data availability Statement

Available on request to the corresponding author.

Declaration of Competing Interest

The author declares that there is no competing of interest regarding the publication of this manuscript.

Acknowledgement

The author expresses sincere gratitude to the Material and Polymer Laboratory of Chemical Engineering for the support and provision of facilities that greatly contributed to the successful completion of this research.

References

- Asif Khan, R.M., Ahmad, N.M., Nasir, H., Mahmood, A., Iqbal, M., Janjua, H.A. (2023) Antifouling and water flux enhancement in polyethersulfone ultrafiltration membranes by incorporating water-soluble cationic polymer of poly [2-(dimethyl amino) ethyl methacrylate], *Polymers*, 15. <https://doi.org/10.3390/polym15132868>
- Esmaeilil, M., Virtanen, T., Lahti, J., Mänttari, M., Kallioinen, M. (2019) Vanillin as an antifouling and hydrophilicity promoter agent in surface modification of polyethersulfone membrane, *Membranes*, 9. <https://doi.org/10.3390/membranes9040056>
- Gul, A., Hruza, J., Yalcinkaya, F. (2021) Fouling and chemical cleaning of microfiltration membranes: A mini-review, *Polymers*, 13. <https://doi.org/10.3390/polym13060846>
- Liu, Z., Wu, Y., Lan, F., Xie, G., Zhang, M., Ma, C., Jia, J. (2023) Improvement of permeability and antifouling performance of PVDF membranes via dopamine-assisted deposition of zwitterionic copolymer, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 656, 130505. <https://doi.org/10.1016/j.colsurfa.2022.130505>
- Ma, C., Hu, J., Sun, W., Ma, Z., Yang, W., Wang, L., Ran, Z., Zhao, B., Zhang, Z., Zhang, H. (2020) Graphene oxide-polyethylene glycol incorporated PVDF nanocomposite ultrafiltration membrane with enhanced hydrophilicity, permeability, and antifouling performance, *Chemosphere*, 253, 126649. <https://doi.org/10.1016/j.chemosphere.2020.126649>
- Mu, Y., Feng, H., Wang, S., Zhang, S., Luan, J., Zhang, M., Yu, Z., Wang, G. (2021). Combined strategy of blending and surface modification as an effective route to prepare antifouling ultrafiltration membranes, *Journal of Colloid and Interface Science*, 589, 1–12. <https://doi.org/10.1016/j.jcis.2020.12.114>
- Mulyati, S., Muchtar, S., Arahman, N., Meirisa, F., Syamsuddin, Y., Zuhra, Z., Rosnelly, C.M., Shamsuddin, N., Nawi, N.I.M., Wirzal, M.D.H., Bilad, M.R., Takagi, R., Matsuyama, H. (2020) One-Pot polymerization of dopamine as an additive to enhance permeability and antifouling properties of polyethersulfone membrane, *Polymers*, 12. <https://doi.org/10.3390/polym12081807>
- Mulyati, S., Riza, M., Muchtar, S., Ambarita, A. C., Amilia, Putri, E. F. A., Luthfiana, A. (2024) A high performance of polyvinylidene fluoride membrane modified with vanilin for humic acid removal, *Case Studies in Chemical and Environmental Engineering*, 9, 100654. <https://doi.org/10.1016/j.cscee.2024.100654>
- Shen, S., Shen, Y., Wu, Y., Li, H., Sun, C., Zhang, G., Guo, Y. (2022) Surface modification of PVDF membrane via deposition-grafting of UiO-66-NH₂ and their application in oily water separations, *Chemical Engineering Science*, 260. <https://doi.org/10.1016/j.ces.2022.117934>
- Sonawane, S., Thakur, P., Sonawane, S.H., Bhanvase, B.A. (2021) Nanomaterials for membrane synthesis: Introduction, mechanism, and challenges for wastewater treatment, *Handbook of Nanomaterials for Wastewater Treatment: Fundamentals and Scale up Issues*, Elsevier Inc. <https://doi.org/10.1016/B978-0-12-821496-1.00009-X>
- Sun, M. feng, Wang, T., Wu, L. guang, Wang, Y. xing. (2021) Enhancing the permeation and antifouling performance of PVDF hybrid membranes by incorporating Co-Fe hydroxide nanoparticles in reverse microemulsion, *Journal of Environmental Chemical Engineering*, 9, 106556.

- <https://doi.org/10.1016/j.jece.2021.106556>
- Xu H, Xiao K, Wang X, Liang S, Wei C, Wen X, Huang X. (2020) Outlining the roles of membrane-foulant and foulant-foulant interactions in organic fouling during microfiltration and ultrafiltration: a mini-review, *Frontiers in Chemistry*, 8, 417. <https://doi.org/10.3389/fchem.2020.00417>
- Yadav, S., Ibrar, I., Altaee, A., Déon, S., Zhou, J. (2020) Preparation of novel high permeability and antifouling polysulfone-vanillin membrane, *Desalination*, 496, 114759. <https://doi.org/10.1016/j.desal.2020.114759>
- Yadav, S., Ibrar, I., Samal, A.K., Altaee, A., Déon, S., Zhou, J., Ghaffour, N. (2022) Preparation of fouling resistant and highly perm-selective novel PSf/GO-vanillin nanofiltration membrane for efficient water purification, *Journal of Hazardous Materials*, 421. <https://doi.org/10.1016/j.jhazmat.2021.126744>
- Zheng, H., Zhu, M., Wang, D., Zhou, Y., Sun, X., Jiang, S., Li, M., Xiao, C., Zhang, D., Zhang, L. (2023) Surface modification of PVDF membrane by CNC/Cu-MOF-74 for enhancing antifouling property, *Separation and Purification Technology*, 306, 122599. <https://doi.org/10.1016/j.seppur.2022.122599>
- Zhu, X., Liang, H., Tang, X., Bai, L., Zhang, X., Gan, Z., Cheng, X., Luo, X., Xu, D., Li, G. (2019) Supramolecular-based regenerable coating layer of a thin-film composite nanofiltration membrane for simultaneously enhanced desalination and antifouling properties, *ACS Applied Materials & Interfaces*, 11, 21137–21149. <https://doi.org/10.1021/acsami.9b03761>