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Modification of Hydrophobic Polymer-Based Membranes with Gambir Tannin as a Natural Additive to Reduce Humic Acid in Water

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ABSTRACT
Membrane technology is widely used in water treatment processes. This study aims to evaluate the effect of gambir tannin, a natural additive, on the performance of hydrophobic polymer membranes made from polyvinylidene fluoride (PVDF) and polyethersulfone (PES). Membranes were fabricated using the casting–phase inversion method with 0% and 1% tannin concentrations. Membrane characterization included functional group analysis, permeability tests with pure water and humic acid, antifouling performance, and chemical stability. Addition of tannin introduced hydrophilic functional groups into the polymer matrix, resulting in improved membrane porosity, flux recovery ratio (FRR), and fouling resistance. The most significant finding of this study is that the incorporation of 1% gambir tannin increased the pure water flux up to 20.67 L/m²·h for PVDF membranes and 102.46 L/m²·h for PES membranes, while maintaining high antifouling properties and stable performance in acidic and alkaline environments. These results demonstrate the potential of gambir tannin as a sustainable additive for enhancing membrane performance in water purification applications.

Keyword: Antifouling, Organic Fouling, Gambir (*Uncaria Gambier roxb*), Membrane, Natural Additives

ABSTRAK
Teknologi membran banyak digunakan dalam proses pengolahan air. Penelitian ini bertujuan untuk mengevaluasi pengaruh tanin gambir sebagai aditif alami terhadap kinerja membran berbahan dasar polimer hidrofobik, yaitu polivinilidena fluorida (PVDF) dan polietersulfon (PES). Membran difabrikasi menggunakan metode pencetakan–inversi fasa dengan variasi konsentrasi tanin sebesar 0% dan 1%. Karakterisasi dilakukan melalui analisis gugus fungsi, uji permeabilitas terhadap air murni dan asam humat, pengujian antifouling, serta stabilitas kimia membran. Penambahan tanin memperkenalkan gugus fungsional hidrofilik ke dalam matriks polimer, yang meningkatkan porositas, rasio pemulihan fluks (FRR), dan ketahanan terhadap fouling. Temuan paling signifikan dari penelitian ini adalah bahwa penambahan 1% tanin gambir meningkatkan fluks air murni hingga 20,67 L/m²·jam untuk membran PVDF dan 102,46 L/m²·jam untuk membran PES, dengan sifat antifouling yang tinggi dan kinerja yang stabil dalam lingkungan asam dan basa. Hasil ini menunjukkan potensi tanin gambir sebagai aditif berkelanjutan untuk meningkatkan kinerja membran dalam aplikasi pemurnian air.

Kata Kunci: Aditif Alami, Anti-*fouling*, *Fouling* Organik, Gambir (*Uncaria Gambier roxb*.), Membran

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1. Introduction

Demanding for water resources is increasing globally due to population growth and industrialization. Membranes contribute to nearly 50% of the total volume of water treatment processes worldwide. A membrane can be defined as a physical material that acts selectively as a barrier to retain unwanted substances on its surface while allowing certain compounds to pass through, depending on their physical and chemical properties, when a force is applied across the membrane [1]. However, most membranes are made from hydrophobic materials, making them more prone to blockage by organic molecules on the surface or within their pores—a phenomenon known as fouling.

Membrane fouling results in low flux and reduced permeate flow due to pore blockage by organic compounds in water, which shortens the membrane's operational time and reduces its effective lifespan. Costly cleaning procedures and periodic regeneration are required to prevent performance degradation and minimize the need for higher pressure and energy consumption to maintain constant flux. Organic compounds are generally hydrophobic, and during filtration, they interact with the membrane and may deposit on its surface.

Humic acid is a type of natural organic acid formed from humic substances, which result from the decomposition of accumulated organic matter in the environment[2]. Polyethersulfone (PES) and polyvinylidene fluoride (PVDF) are two of the most commonly used hydrophobic polymers for membrane fabrication. However, their main drawback lies in their hydrophobicity, which causes surface and pore clogging [3]. This fouling phenomenon can be mitigated by modifying the membrane to exhibit antifouling properties.

Membrane modification using hydrophilic additives can be achieved through grafting, coating, or blending methods, with the aim of improving the antifouling characteristics of the membrane [3]. Blending involves mixing two or more compounds into a casting solution using the same solvent. Several additives have been used, including polysulfone oxide amide[4], polyvinylpyrrolidone (PVP) [5], polydopamine [6], and polyethylene glycol (PEG) [7]. Natural additives such as nanocarbon from palm shell[8], activated carbon from castor seeds [9], and nanosilica from rice husk and bagasse [10] have also been explored. One promising natural additive is tannin.

Tannin can be extracted from gambir plants, which are reddish-brown to black in color. Gambir is a tropical plant with high economic value. Gambir extract contains natural polyphenol compounds such as tannin, catechin, fluorescein, quercetin, and wax. These polyphenolic compounds can enhance membrane hydrophilicity by substituting hydroxyl (-OH) groups into the polymer structure. Gambir extract possesses antioxidant and antifouling properties. Tannin can prevent humic acid from adhering to the membrane surface, thereby reducing the attachment of organic particles in water.

Previous studies include research by Fahrina et al.[11], who modified hydrophobic PVDF membranes with bio-based ginger extract; Mulyati et al.[12], who modified PES membranes using extracted silica additives; and Liu et al.[13], who modified PVDF membranes with commercial tannin additives via co-deposition to improve hydrophilicity and oil fouling resistance. However, membrane performance remains suboptimal. This study utilizes tannin derived from natural gambir as an additive for ultrafiltration membranes. Traditionally, gambir has been used as a betel quid component and medicine, while in modern applications, it serves as a raw material in the pharmaceutical and food industries. Tannin helps prevent heavy metals like lead from adhering to the membrane surface, thus inhibiting the attachment of metal particles in wastewater. Therefore, this research is essential to enhance the hydrophilic properties of hydrophobic polymer-based membranes using natural gambir tannin as an additive.

While commercial tannins have been studied as hydrophilic modifiers, no previous research has systematically evaluated the performance of membranes modified with gambir tannin extracted from Uncaria gambier Roxb, particularly in terms of humic acid removal and antifouling capability under acidic and alkaline conditions. This study fills this research gap by investigating the fabrication, characterization, and performance of PVDF and PES membranes modified with gambir tannin using a straightforward and scalable casting–phase inversion method.

2. Materials and Methods

2.1. Materials

The materials and equipment used in this study include Polyvinylidene Fluoride (PVDF) with a molecular weight of 534,000 Da (Sigma Aldrich, USA) and Polyethersulfone (PES, Ultrason E6020P). Dimethylacetamide (DMAc) (Wako Pure Chemical Industries, Japan) and N-Methyl-2-pyrrolidone (NMP, 99.5%) were used as solvents. Distilled water was used as a non-solvent. The membrane additives included gambir tannin (Uncaria gambier Roxb) and commercial tannin (Sigma Aldrich, USA). Humic acid was used as a model solution to analyze the removal of organic compounds in water.

2.2. Fabrication and Modification Membrane

Membranes were fabricated using the casting–phase inversion method. Two types of hydrophobic base polymers—polyvinylidene fluoride (PVDF) and polyethersulfone (PES)—were used, each combined with either 1% (w/w) natural gambir tannin or 1% (w/w) commercial tannin, relative to the polymer weight. For PVDF membranes, a dope solution was prepared by dissolving 15% (w/v) PVDF in dimethylacetamide (DMAc) as solvent, along with the tannin additive. The solution was stirred at 55°C for 24 hours until homogeneous, followed by degassing for 6 hours to remove air bubbles. For PES membranes, a solution of 15% (w/v) PES in N-methyl-2-pyrrolidone (NMP) was prepared at room temperature, and the same concentration of tannin (1% w/w) was added based on polymer mass. This solution was stirred for 24 hours and also degassed for 6 hours. Each casting solution was then poured onto a clean glass plate and spread using a casting knife with a gap thickness of 200 µm. The cast film was immediately immersed in a coagulation bath containing distilled water to induce phase inversion. Membranes were left in water for at least 24 hours to ensure complete solvent removal before further testing.

2.3. Membrane Performance

Membrane performance testing was conducted using a crossflow test module with a batch system and horizontal pressure direction. The membrane was cut to fit the module's cross-sectional area. The module was then filled with distilled water and subjected to a transmembrane pressure of 1 bar from the top. Quantitatively, permeability is expressed in terms of flux. Humic acid rejection testing aimed to determine the membrane's ability to retain the targeted compounds. The procedure was the same as for pure water permeability testing. The permeate concentration was analyzed using a UV-VIS spectrophotometer. Antifouling testing was conducted to assess membrane resistance to fouling. In this stage, the membrane was filtered using the model solution with the same procedure as before. Afterward, the membrane was cleaned and re-filtered using pure water until the original pure water flux was recovered. The final stage of membrane performance testing was the membrane stability test. The goal was to determine membrane stability when used in strong acid and strong base feed solutions. This test involved soaking the membrane in 0.1 N HCl and 0.1 N NaOH solutions for one week.

3. Result and Discussion

3.1 Membrane Performance

3.1.1 Pure Water Flux

After modification, pure water flux of PVDF-tannin and PES-tannin membranes increased with addition of gambir tannin and commercial tannin compared to unmodified PVDF and PES membranes. As shown in Figure 1(a), pure water flux of PVDF membranes increased from 15.04 $L/m^2 \cdot h$ to 19.44 $L/m^2 \cdot h$ and 20.67 $L/m^2 \cdot h$ for gambir and commercial tannin at 1% concentration, respectively. In Figure 1(b), pure PES membrane had a flux of 52.71 $L/m^2 \cdot h$, which increased to 57.72 $L/m^2 \cdot h$ and 102.36 $L/m^2 \cdot h$ after addition of 1% gambir and commercial tannin. Results indicate that membranes modified with commercial tannin showed higher flux compared to natural tannin, possibly due to the higher purity and concentration of commercial tannin compared to lab-scale extracted gambir tannin [14].

Table 1. Comparison of pure water flux ($L/m^2 \cdot h$) of PVDF membranes with different additives in this and previous studies.

Researcher	Additive	Pure Water Flux ($L/m^2 \cdot h$)
Fahrina et al. (2020)	Ginger extract	5.07
This study (gambir tannin)	-	15.04
This study (commercial tannin)	-	20.67

Table 2. Comparison of pure water flux ($L/m^2 \cdot h$) of PES membranes with different additives in this and previous studies.

Researcher	Additive	Pure Water Flux ($L/m^2 \cdot h$)
Mulyati et al. (2020)	Bio-silica	10.35
This study (gambir tannin)	-	52.71
This study (commercial tannin)	-	102.36

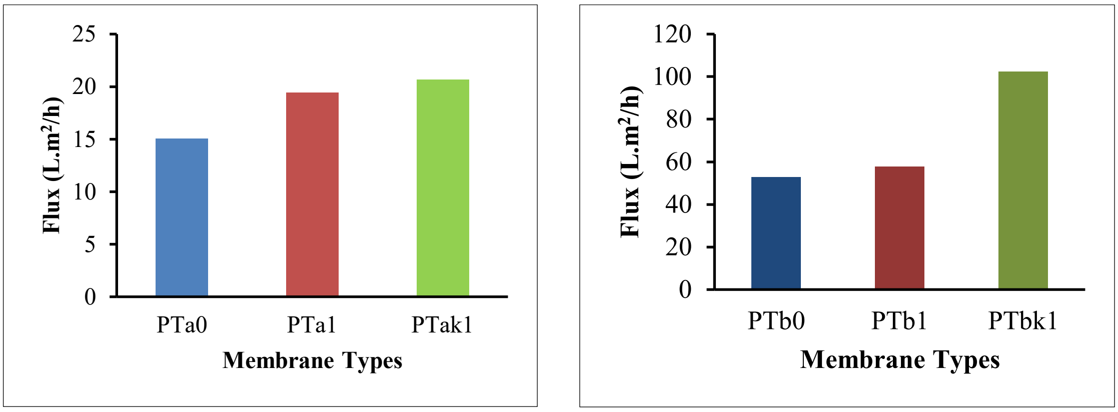

Figure 1. Pure water flux (L/m²·h) of PVDF (a) and PES (b) membranes modified with 1% gambir and commercial tannin additives.

Pure water flux is an important parameter in assessing membrane filtration capability. Results show that both PVDF and PES membranes with tannin (natural or commercial) exhibited good performance.

3.2 Selectivity / Humic Acid Rejection

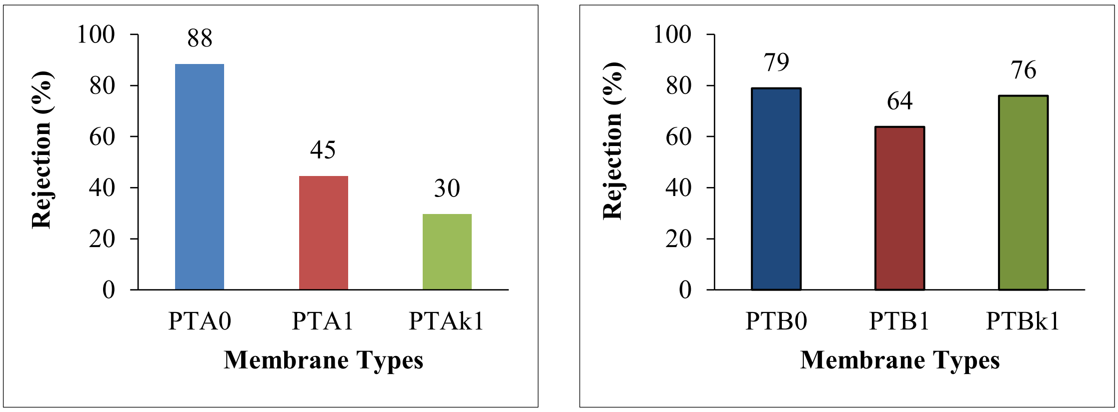

Figure 2. Humic acid rejection efficiency (%) of PVDF (a) and PES (b) membranes before and after tannin modification.

Percentage of humic acid rejection by PVDF and PES membranes varied depending on type and concentration of tannin. In Figure 2(a), unmodified PVDF membrane showed the highest rejection at 89%, but after adding 1% tannin, rejection decreased to 45% (natural tannin) and 30% (commercial tannin). On other hand, PES membranes showed better results, as shown in Figure 2(b), where the unmodified PES membrane had 79% rejection, increasing to 64% (natural tannin) and 76% (commercial tannin). This suggests that tannin addition was more effective in enhancing humic acid rejection in PES membranes than in PVDF membranes. In case of PVDF membranes, the addition of both gambir and commercial tannin at 1% concentration resulted in a decrease in humic acid rejection from 89% (unmodified) to 45% and 30%, respectively. This may be attributed to the formation of larger or more numerous pores due to increased hydrophilicity and porosity upon tannin incorporation. Although this enhances water flux, it could reduce the size-exclusion capability of the membrane, allowing more humic acid molecules to pass through. Furthermore, tannin may alter surface charge interactions, potentially reducing electrostatic repulsion between the membrane surface and negatively charged humic acid molecules. These changes suggest a trade-off between permeability and selectivity when modifying PVDF with hydrophilic additives like tannin.

3.3 Antifouling Test

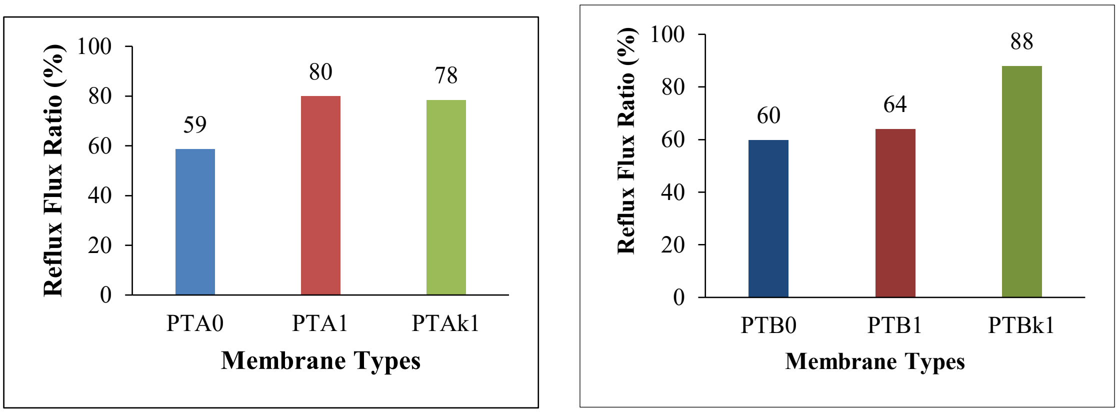

Figure 3. Flux recovery ratio (FRR, %) of PVDF (a) and PES (b) membranes after fouling and cleaning cycles, comparing natural and commercial tannin additives.

Antifouling tests were conducted during pure water filtration. In Figure 3(a), PVDF membrane with 1% natural tannin had a flux recovery ratio (FRR) of 79%, while that with commercial tannin reached 78.34%, indicating excellent fouling resistance. For PES membranes (Figure 3(b)), the FRR was 64% for 1% natural tannin and 88% for commercial tannin. The PES membrane without tannin had the lowest FRR, indicating that the hydrophobic nature of pure PES makes it more prone to fouling.

3.3 Membrane Stability

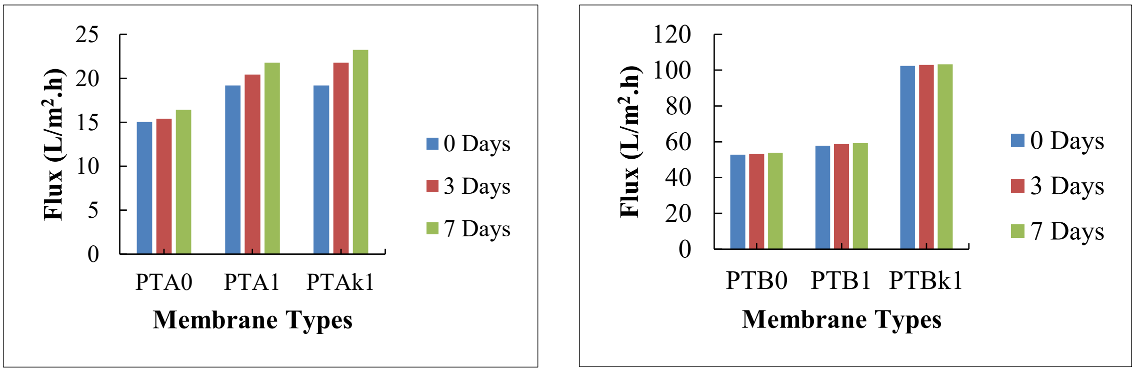

Figure 4. Stability in solution (a) 0.1 N Acid (HCl) and (b) 0.1 N Alkaline (NaOH) 0.1 N PVDF Membrane

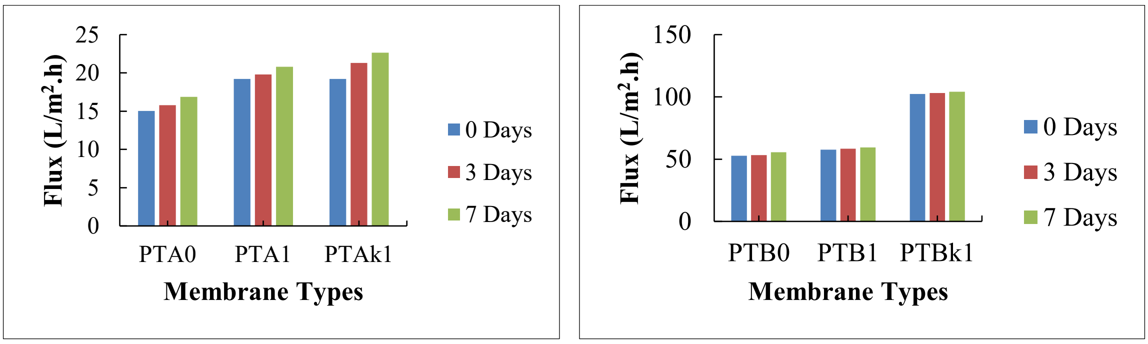

Figure 5. Stability in solution (a) 0.1 N Acid (HCl) and (b) 0.1 N Alkaline (NaOH) 0.1 N PVDF Membrane

Membrane stability was evaluated by immersing PVDF and PES membranes in 0.1 N HCl and 0.1 N NaOH for one week. After immersion, a slight increase in pure water flux was observed for both membrane types. For example, PVDF-tannin membranes exhibited an increase from 19.44 to 21.05 $L/m^2 \cdot h$ (HCl) and 22.18 $L/m^2 \cdot h$ (NaOH), while PES-tannin membranes increased from 57.72 to 60.93 $L/m^2 \cdot h$ (HCl) and 63.84 $L/m^2 \cdot h$ (NaOH). This increase may be attributed to partial leaching of tannin molecules, particularly in alkaline medium, which could slightly alter membrane surface properties or pore structures. Improved hydrophilicity of membranes modified with tannin is likely due to the introduction of polar functional groups such as hydroxyl (-OH) and carboxyl (-COOH) from polyphenolic compounds in tannin. These groups can form hydrogen bonds with water molecules, enhancing water affinity and reducing surface tension. The presence of these functional groups was confirmed by FTIR analysis, where broader O–H stretching peaks were observed in tannin-modified membranes compared to controls. However, tannin leaching under alkaline conditions suggests that some of these hydrophilic functional groups may detach from the polymer matrix over time, potentially affecting the membrane's long-term antifouling performance. Although the increase in flux post-soaking was not drastic, the long-term retention of hydrophilic character requires further evaluation—possibly via long-duration filtration cycles and total organic carbon (TOC) analysis of the soak solution. These findings indicate that while gambir tannin imparts hydrophilic and antifouling properties, its interaction with the polymer matrix might be physically blended rather than chemically grafted, thus more susceptible to desorption. Future work could focus on crosslinking strategies or co-polymerization to improve additive retention and membrane durability.

4. Conclusion

This study demonstrates successful modification of hydrophobic PVDF and PES membranes using gambir tannin as a natural additive through the casting–phase inversion method. The incorporation of 1% tannin significantly enhanced membrane hydrophilicity, as reflected in increased pure water flux, improved porosity, and higher flux recovery ratios (FRR). PES-tannin membranes showed the highest pure water flux (102.46 $L/m^2 \cdot h$) and antifouling performance (FRR up to 88%), while PVDF-tannin membranes exhibited moderate improvements. These results confirm that gambir tannin is a promising, sustainable additive for improving membrane performance in water filtration applications, particularly in reducing organic fouling caused by humic acid. Findings have practical implications for developing environmentally friendly and cost-effective membrane materials for wastewater treatment, especially in regions with abundant gambir resources. However, this study has limitations. The experiments were conducted under controlled conditions using model humic acid solutions. The performance of tannin-modified membranes in real wastewater with complex organic and inorganic contaminants remains to be evaluated. Furthermore, the optimal concentration of tannin and its long-term stability under continuous operation were not fully explored. Future research should focus on testing membrane performance using actual wastewater samples, optimizing tannin concentration to balance permeability and selectivity, investigating tannin retention and potential leaching under prolonged operation, and exploring chemical grafting methods to enhance additive stability.

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References

[1] B. Díez and R. Rosal, *Nanotechnology for Environmental Engineering*. Springer, 2020.
[2] O. A. A. Al-Timimi, L. K. Hassan, and I. S. Salman, "Proceedings," 2020, pp. 4138–4141.
[3] G. R. Guillen, Y. Pan, M. Li, and E. M. V Hoek, "Preparation and characterization of membranes formed by nonsolvent induced phase separation: A review," *Ind Eng Chem Res*, vol. **50**, no. 7, pp. 3798–3817, 2011.
[4] R. Kumar and A. F. Ismail, "Fouling control on microfiltration/ultrafiltration membranes: Effects of morphology, hydrophilicity, and charge," *J Appl Polym Sci*, vol. **132**, no. 21, 2015.
[5] A. Rahimpour, S. S. Madaeni, A. Shockravi, and S. Ghorbani, "The effect of polyvinylpyrrolidone (PVP) addition on properties and performance of polyethersulfone ultrafiltration membranes," *J Memb Sci*, vol. **334**, no. 1–2, pp. 64–73, 2009.
[6] Y. Kourde-Hanafi *et al.*, "Hydrophilic surface modification of polyethersulfone membranes using polydopamine: Effects on morphology, mechanical, and fouling properties," *J Memb Sci*, vol. **533**, pp. 261–269, 2017.
[7] S. Muchtar *et al.*, "Fabrication of PES-based blend membranes incorporated with polyaniline nanoparticles," *J Appl Polym Sci*, vol. **136**, no. 10, 2018.
[8] S. Mulyati *et al.*, "Development of activated carbon composite membrane from palm shell for organic removal," *Membranes (Basel)*, vol. **10**, no. 1, p. 17, 2020.

[9] N. Arahman, M. Yusuf, S. Muchtar, T. Maimun, and M. Bilad, "Adsorption study of phenol onto activated carbon from castor seeds," *International Journal of GEOMATE*, vol. **15**, no. 48, pp. 51–57, 2018.

[10] S. Aprilia *et al.*, "Sintesis dan karakterisasi membran nanokomposit menggunakan nanosilika dari abu sekam padi dan ampas tebu," *Jurnal Rekayasa Kimia dan Lingkungan*, vol. **13**, no. 1, pp. 82–97, 2018.

[11] A. Fahrina *et al.*, "Modification of hydrophobic PVDF membrane using bio-based additives for enhanced filtration performance," *Polymers (Basel)*, vol. **12**, no. 9, pp. 1–11, 2020.

[12] S. Mulyati *et al.*, "The performance of silica-extracted membranes for water treatment," in *IOP Conference Series: Materials Science and Engineering*, 2018, p. 12034.

[13] C. Liu, L. Wu, C. Zhang, W. Chen, and S. Luo, "Fabrication of superhydrophilic and underwater superoleophobic membranes via tannin-inspired co-deposition for oil/water separation," *Appl Surf Sci*, vol. **434**, pp. 1328–1337, 2018.

[14] N. Arahman, A. Fahrina, S. Amalia, R. Sunarya, and S. Mulyati, "Characteristics and performance of hybrid membrane modified with nanomaterials: A preliminary study," *F1000Res*, vol. **6**, p. 668, 2017.