

# Interfacial stabilization of tannic acid-modified polyvinylidene fluoride membranes via iron(III) coordination for enhanced antifouling and long-term stability

Ulfa<sup>1</sup>, Miftahul Arzaq<sup>1</sup>, Anisa Luthfiana<sup>2</sup>, Syawaliah Muchtar<sup>3</sup>,  
Umi Fathanah<sup>3</sup>, Muhammad Roil Bilad<sup>4</sup>, Sri Mulyati<sup>3\*</sup>

<sup>1</sup> Graduate School of Chemical Engineering, Universitas Syiah Kuala, Banda Aceh, Indonesia

<sup>2</sup> School of Engineering, Post Graduate Program, Universitas Syiah Kuala, Banda Aceh, 23111, Indonesia

<sup>3</sup> Department of Chemical Engineering, Universitas Syiah Kuala, Jalan Syech Abdur Rauf, Banda Aceh 23111, Indonesia

<sup>4</sup> Faculty of Integrated Technologies, Universiti Brunei Darussalam, Jalan Tungku Link, Bandar Seri Begawan BE1410, Brunei

\* Corresponding author's e-mail: [sri.mulyati@usk.ac.id](mailto:sri.mulyati@usk.ac.id)

## ABSTRACT

Polyvinylidene fluoride (PVDF) membranes are commonly used in ultrafiltration because of their good chemical resistance and mechanical strength. However, the hydrophobic nature of PVDF often leads to fouling, which gradually lowers membrane performance during operation. In this study, PVDF membranes were modified using tannic acid (TA) and Fe<sup>3+</sup> to improve antifouling behaviour and membrane stability. Commercial tannic acid and gambir-derived tannins were used as modifiers, followed by Fe<sup>3+</sup> treatment to strengthen the surface-modification layer via metal–phenolic coordination. The results showed that tannic acid incorporation increased membrane hydrophilicity and permeability. However, during repeated filtration cycles, a gradual decline in flux was still observed, indicating that improved hydrophilicity alone could not fully maintain stable membrane performance. The membranes treated with Fe<sup>3+</sup> exhibited slightly lower initial flux values, but their filtration performance remained more stable, with flux retention above 85% after five cycles. In addition, all modified membranes maintained humic acid rejection values above 90%, indicating that membrane selectivity remained stable. The improved flux retention observed in Fe<sup>3+</sup>-modified membranes indicates that interfacial stabilisation plays a critical role in sustaining long-term filtration performance. The combination of tannic acid and Fe<sup>3+</sup> offers a simple way to balance permeability and membrane stability in PVDF membranes. Furthermore, gambir-derived tannins performed comparably to commercial tannic acid, indicating that they could serve as a more sustainable alternative for membrane modification.

**Keywords:** PVDF membrane modification, tannic acid, Fe<sup>3+</sup> coordination, antifouling ultrafiltration, hydrophilic membranes, sustainable membrane technology.

## INTRODUCTION

Ultrafiltration (UF) membranes are widely used in water and wastewater treatment because they can effectively remove suspended solids, macromolecules, and natural organic matter with relatively low energy consumption (Zhang et al., 2023). Among various polymeric membrane materials, polyvinylidene fluoride (PVDF)

is commonly used due to its excellent chemical resistance, thermal stability, and mechanical strength, allowing stable operation under harsh conditions (Dallaev et al., 2022). However, the hydrophobic nature of PVDF remains a major limitation in membrane applications. Hydrophobic membrane surfaces tend to interact strongly with organic foulants such as proteins and humic substances, leading to severe fouling, rapid flux

decline, and increased cleaning requirements (Chatterjee et al., 2022; Chen et al., 2021).

Improving membrane surface hydrophilicity is widely considered an effective approach for reducing fouling and improving filtration efficiency (Mulyati et al., 2020). Hydrophilic functional groups can reduce the interaction between foulants and the membrane surface, thereby limiting foulant accumulation and improving water permeability (Shen et al., 2017). Various modification methods, including blending, surface coating, grafting, and the incorporation of functional additives, have been investigated to introduce polar groups such as hydroxyl, carboxyl, and amine functionalities into the membrane matrix (Dmitrieva et al., 2022; Yan et al., 2020). Although these approaches often improve the initial filtration properties, their effectiveness may decrease during prolonged operation.

During membrane filtration, fouling may occur through several mechanisms, including pore blockage, surface adsorption, and cake layer formation, depending on feed composition and operating conditions (Mulyati et al., 2023). Biofouling can further accelerate membrane deterioration by causing irreversible surface contamination and structural damage. Chemical cleaning is commonly used to restore membrane permeability (Mulyati et al., 2023). However, repeated or aggressive cleaning may adversely affect membrane integrity and operational lifetime (Yu et al., 2023). These conditions indicate that improving hydrophilicity alone is insufficient to maintain stable membrane operation during continuous filtration.

Polyphenolic compounds, particularly tannic acid (TA), have recently attracted considerable interest as membrane modifiers. The hydroxyl groups present in tannic acid improve membrane wettability and promote the formation of a hydration layer, which helps reduce foulant adhesion (Li et al., 2023). Previous studies have shown that tannic acid can increase membrane porosity, enhance water permeability, and improve antifouling properties (Mulyati et al., 2025). In addition, its antioxidant and metal-chelating properties provide additional opportunities for membrane functionalisation (Sahiner et al., 2025). However, the interaction between tannic acid and the polymer matrix is often relatively weak, which may reduce the stability of the modified layer during long-term filtration.

To improve modification layer stability, several studies have explored the use of metal–phenolic

coordination systems involving  $\text{Fe}^{3+}$  ions. The coordination interaction between tannic acid and  $\text{Fe}^{3+}$  can form metal–phenolic networks (MPNs), which strengthen the interfacial layer and improve its stability during filtration. MPNs have also been reported to improve antifouling resistance and membrane mechanical stability. However, the formation of coordinated TA– $\text{Fe}^{3+}$  structures may alter the accessible pore structure and increase transport resistance, resulting in reduced permeability (Kinfu et al., 2023; Yang et al., 2020). Although promising results have been reported, the long-term behaviour of these coordinated membrane systems under repeated filtration conditions is still not fully understood.

Sustainable and bio-based materials have also gained attention for membrane fabrication. Natural tannins derived from *Uncaria gambir* are considered a potential alternative to commercial tannic acid because of their high phenolic compound content and wide availability. The phenolic groups present in gambir-derived tannins may provide modification behaviour similar to commercial tannic acid. However, their application in membrane systems is still limited, and their interaction with metal ions, as well as their long-term stability, have not been thoroughly investigated (Munggar et al., 2022; Saad et al., 2020).

Several aspects of polyphenol-based membrane modification are still not fully understood. Most previous studies mainly focused on improving initial permeability and antifouling performance, while the stability of the modification layer during prolonged filtration received less attention. In particular, the relationship between membrane hydrophilicity and interfacial layer stability remains unclear, especially for the systems involving natural polyphenolic compounds. The long-term reliability of these modification strategies under continuous water treatment conditions, therefore, still requires further investigation.

In this study, PVDF membranes were modified using tannic acid and TA– $\text{Fe}^{3+}$  coordination systems derived from both commercial tannic acid and gambir extracts. The membrane performance was evaluated under short-term and repeated filtration conditions. This work focused on the influence of interfacial stabilisation on membrane wettability, antifouling behaviour, and long-term filtration stability. The incorporation of tannic acid was expected to improve membrane wettability and permeability, while  $\text{Fe}^{3+}$  coordination was expected to enhance the stability of

the modification layer through the formation of metal–phenolic networks. Therefore, this study investigates how  $\text{Fe}^{3+}$  coordination influences membrane structure, fouling resistance, and long-term filtration behaviour.

## MATERIAL AND METHODS

### Materials

Poly(vinylidene fluoride) (PVDF; Sigma-Aldrich, product no. 182702; powder), with a supplier-reported weight-average molecular weight (Mw) of approximately  $534,000 \text{ g mol}^{-1}$  as determined by gel permeation chromatography (GPC) (Sigma-Aldrich, n.d.), was used as the base polymer because of its high chemical resistance and mechanical strength. *N,N*-Dimethylacetamide (DMAc; 99.8%, Sigma-Aldrich) was employed as the solvent, whereas distilled water was used as the nonsolvent during membrane formation.

Commercial tannic acid (Merck) and commercial gambir-derived tannin were used as membrane modifiers. The gambir-derived tannin was purchased through the Shopee Indonesia e-commerce platform, where it was marketed as “tannin/tannic acid extract from *Uncaria gambir*.” The material was used as received without further extraction, purification, or chemical treatment. The product information did not specify the manufacturer, extraction procedure, purity grade, or detailed chemical composition, and the seller did not provide a certificate of analysis. Moreover, its composition and purity were not independently determined in this study. Therefore, to avoid identifying the material as chemically pure tannic acid, it is consistently referred to as commercial gambir-derived tannin throughout this manuscript.

Iron (III) chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ; Merck) was used as a source of  $\text{Fe}^{3+}$  ions to promote coordination with the phenolic groups of tannic acid and gambir-derived tannin, thereby facilitating the formation of a metal–phenolic modification layer. Humic acid (technical grade, 50–60%; Sigma-Aldrich) was employed as a model organic foulant to evaluate the fouling behaviour of the prepared membranes during filtration. Unless otherwise stated, all chemicals were used as received without further purification.

### Membrane preparation

Membranes were prepared using the non-solvent induced phase separation (NIPS) method to produce asymmetric PVDF membranes. In this process, phase separation occurs when the polymer solution is immersed in a non-solvent bath, leading to the formation of a porous membrane structure. The exchange rate between solvent and non-solvent influences the final membrane morphology.

The casting solution was prepared by dissolving 3 wt% tannic acid, either commercial or gambir-derived, in DMAc under continuous stirring for approximately 20 min. PVDF was then gradually added and stirred for 24 h until a homogeneous solution was obtained. Before casting, the solution was degassed to remove trapped air bubbles. Membrane casting was carried out on a clean glass plate using a casting knife with controlled thickness, followed by immersion in a coagulation bath. Distilled water was used as the coagulation medium for membranes without  $\text{Fe}^{3+}$  coordination, while a 0.01 M  $\text{FeCl}_3$  solution was used for  $\text{Fe}^{3+}$ -modified membranes. The immersion process allowed in situ formation of metal–phenolic networks through coordination between

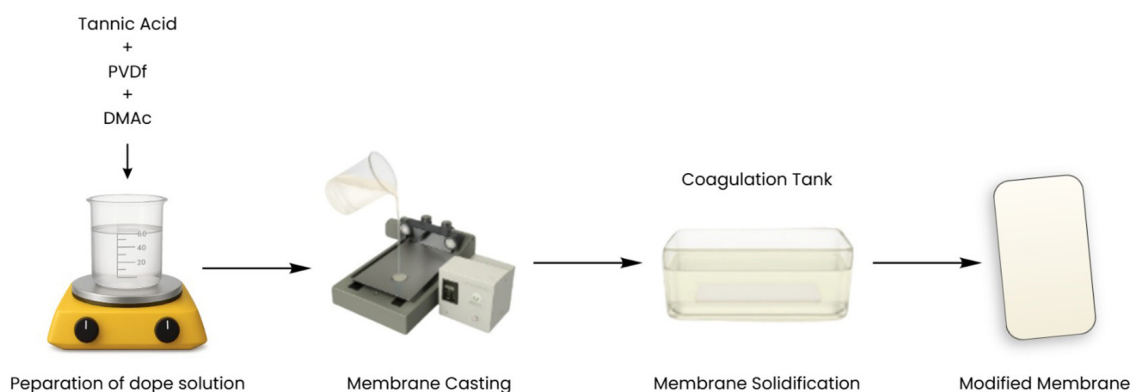


**Figure 1.** Membrane preparation process

tannic acid and  $\text{Fe}^{3+}$  ions. All membranes were prepared at room temperature and stored in distilled water before characterisation and filtration tests. The overall membrane fabrication procedure is shown in Figure 1. Five types of membranes were prepared: pristine PVDF (M-O), tannic acid-modified membranes using gambir (M-TG) and commercial tannic acid (M-TA), and their corresponding  $\text{Fe}^{3+}$ -coordinated membranes (M-TA/Fe and M-TG/Fe). The compositions of these membranes are summarised in Table 1.

## Membrane characterisation

### *Fourier transform infrared spectroscopy (FTIR)*

FTIR analysis was conducted to identify the functional groups present on the membrane surface and to confirm the incorporation of tannic acid and  $\text{Fe}^{3+}$  coordination. The analysis focused on characteristic absorption bands related to hydroxyl groups, aromatic structures, and metal–oxygen interactions.

### *Scanning electron microscopy (SEM)*

SEM analysis was conducted to characterise the surface and cross-sectional morphologies of the membranes. For cross-sectional observation, the membrane samples were cryofractured in liquid nitrogen. Both the membrane surface and cryofractured cross-section were subsequently sputter-coated with a thin gold layer to enhance electrical conductivity. Imaging was performed at an accelerating voltage of 15 kV using a back-scattered-electron detector. Surface micrographs were acquired at 5000 $\times$  magnification for M-O, M-TA/Fe, M-TG, and M-TG/Fe and at 7000 $\times$  for M-TA, whereas all cross-sectional micrographs were acquired at 4000 $\times$  magnification. For each membrane sample, one specific field was selected from the surface and one from the cryofractured

cross-section. Thus, the displayed micrographs represent individual selected locations rather than multiple independently examined areas. Scale bars are provided in each panel, while the assembled Figure 4 has a resolution of 1847  $\times$  517 pixels. The resulting micrographs were used to evaluate the pore distribution, surface texture, and internal membrane structure and to relate these morphological characteristics to the membrane permeability and separation performance.

### *Water contact angle (WCA) measurement*

Surface wettability was evaluated by measuring the water contact angle using a contact angle goniometer. A distilled water droplet ( $\sim 5 \mu\text{L}$ ) was placed on the membrane surface, and the contact angle was recorded. Measurements were taken at three different positions on each membrane sample, and the reported value represents the average result.

### *Porosity and pore size analysis*

Membrane porosity was determined using a gravimetric method based on the difference between wet and dry membrane weights. Pore size distribution was analysed using the bubble point method. All measurements were performed in triplicate, and the results are reported as mean  $\pm$  standard deviation (SD).

## Filtration performance evaluation

### *Pure water flux*

Pure water flux (PWF) was measured using a cross-flow filtration system to evaluate membrane permeability. The same effective membrane area of 9.075  $\text{cm}^2$  was used for both PWF and humic acid filtration measurements. Before testing, the membranes were compacted at 1 bar for 30 min to obtain stable operating conditions. Flux measurements were recorded after steady permeation had been reached. All experiments were conducted

**Table 1.** Membrane composition

| Membrane code | PVDF (%) | Commercial tannic acid (TA) (%) | Gambir-derived tannic (TG) (%) | DMAc (%) | Concentration $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in coagulation bath (M) |
|---------------|----------|---------------------------------|--------------------------------|----------|---------------------------------------------------------------------------------|
| M-O           | 15       | 0                               | 0                              | 85       | 0                                                                               |
| M-TA          | 15       | 3                               | 0                              | 82       | 0                                                                               |
| M-TA/Fe       | 15       | 3                               | 0                              | 82       | 0.01                                                                            |
| M-TG          | 15       | 0                               | 3                              | 82       | 0                                                                               |
| M-TG/Fe       | 15       | 0                               | 3                              | 82       | 0.01                                                                            |

at room temperature and repeated at least three times, with the reported values representing the average results.

### Humic acid filtration and rejection

Membrane separation performance was evaluated using humic acid as a model organic foulant. Filtration experiments were conducted using a cross-flow filtration system operated at 1 bar with an effective membrane area of 9.075 cm<sup>2</sup>. The cross-flow velocity was maintained at approximately 0.15 m/s to minimise concentration polarisation. A 20 mg/L humic acid solution prepared in distilled water was used as the feed solution under neutral pH conditions (pH ≈ 7). The filtration test consisted of three stages: initial pure water filtration (Jw1), humic acid filtration (Jha), and pure water filtration after membrane cleaning (Jw2). Membrane rejection was determined from the humic acid concentrations in the feed and permeate solutions. All experiments were carried out at room temperature and repeated at least three times, with the reported values representing the average results. The cross-flow filtration setup is shown in Figure 2.

### Antifouling performance assessment

Antifouling performance was evaluated using the flux recovery ratio (FRR), calculated from the ratio of pure water flux after cleaning to the initial pure water flux. After each fouling test, the membranes were rinsed with distilled water for 10–15 min under the same cross-flow conditions to remove loosely attached foulants. Chemical cleaning agents were not used so that the intrinsic antifouling properties of the membranes could be assessed more clearly.

### Long-term stability and durability testing

The long-term stability of the membranes was evaluated through repeated filtration cycles using a cross-flow filtration system operated at 1 bar. Each cycle included pure water filtration, humic acid filtration, and membrane cleaning. After each fouling test, the membrane was rinsed with distilled water for 10–15 min under cross-flow conditions to restore permeability. Pressure and flow rate were maintained constant throughout the experiments.

Membrane durability was assessed from the normalised flux ( $J/J_0$ ) over five consecutive filtration cycles, where  $J$  represents the permeate flux at a given cycle and  $J_0$  is the initial pure water flux. Flux measurements were recorded after stable operating conditions were reached. All experiments were conducted under identical conditions and repeated at least three times, with the reported values representing the average results.

## RESULTS

### Membrane characterisation

#### FTIR analysis

The FTIR spectra of the pristine and modified PVDF membranes confirmed the incorporation of tannic acid and its coordination with Fe<sup>3+</sup> ions. The pristine PVDF membrane showed characteristic absorption bands associated with the PVDF structure, including C–F stretching vibrations at 1175–1400 cm<sup>-1</sup>, CH<sub>2</sub> vibrations at 840–880 cm<sup>-1</sup>, and C–H stretching near 2980 cm<sup>-1</sup> (Mulyati et al., 2022). After tannic acid incorporation, a broad absorption

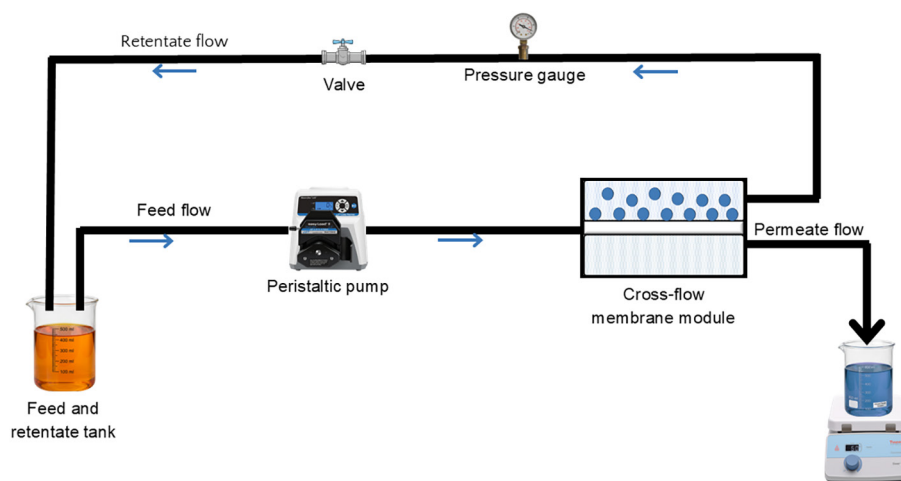


Figure 2. Cross-flow membrane filtration setup

band appeared at 3200–3400  $\text{cm}^{-1}$ , corresponding to O–H stretching vibrations, along with an additional peak near 1600  $\text{cm}^{-1}$  related to aromatic C=C groups (Ricci et al., 2015; Yan et al., 2020). These peaks confirm the presence of polyphenolic functional groups on the membrane surface.

After  $\text{Fe}^{3+}$  treatment, the O–H absorption band became broader, while the intensity of the aromatic peaks decreased. These spectral changes indicate coordination interactions between tannic acid and  $\text{Fe}^{3+}$  ions, leading to the formation of metal–phenolic networks. Similar spectral changes have been reported for metal–phenolic coordination systems (Ejima et al., 2017; Razavi et al., 2020), supporting the formation of coordination interactions between phenolic groups and  $\text{Fe}^{3+}$  ions (Figure 3).

### SEM analysis

SEM analysis showed clear morphological changes after tannic acid incorporation and  $\text{Fe}^{3+}$  coordination. The pristine PVDF membrane (M-O) exhibited a relatively dense surface with only a few visible pores, consistent with its relatively low permeability. In contrast, the membranes modified with tannic acid (M-TA and M-TG) showed higher surface porosity and more uniform pore distribution, particularly for the M-TA membrane. This result suggests that tannic acid influenced the phase inversion process and promoted the formation of a more porous membrane structure (Li et al., 2019; Mulyati et al., 2022) (Figure 4). After  $\text{Fe}^{3+}$  coordination, the M-TA/Fe and

M-TG/Fe membranes exhibited a denser surface morphology with fewer visible pores. This observation is consistent with the deposition of TA–Fe complexes on porous polymeric membrane surfaces, which can modify the accessible pore structure (Yang et al., 2020; Kinfu et al., 2023). This change indicates partial membrane densification caused by the formation of metal–phenolic networks. The transition from a more porous structure to a denser morphology suggests improved structural stability, which may influence membrane behaviour during prolonged filtration.

### Water contact angle

Water contact angle (WCA) measurements were used to examine membrane surface wettability. Lower contact angle values generally indicate greater surface hydrophilicity, which can reduce foulant–surface interactions (Mulyati et al., 2022). The results are shown in Figure 5. The pristine PVDF membrane exhibited a contact angle of approximately  $86^\circ$ , indicating the hydrophobic nature of the membrane surface (Moradi et al., 2015). After tannic acid incorporation, the contact angle decreased to around  $75\text{--}78^\circ$ , reflecting improved wettability due to the presence of hydroxyl groups (Mulyati et al., 2022). A further decrease to approximately  $66\text{--}70^\circ$  was observed after  $\text{Fe}^{3+}$  coordination. This reduction indicates stronger interaction between the membrane surface and water, which is likely associated with the formation of metal–phenolic interactions (Yang et al., 2020).

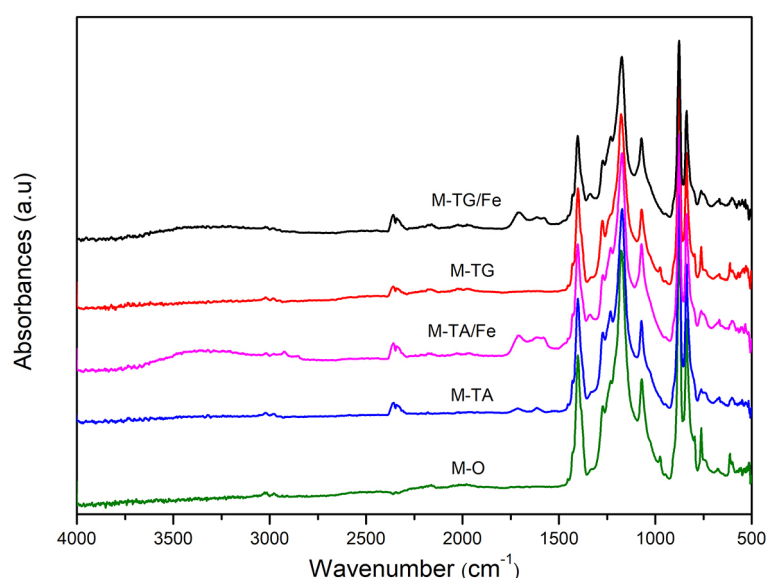


**Figure 3.** FTIR spectra of pristine PVDF and the PVDF membranes modified with tannic acid and  $\text{Fe}^{3+}$  complexes

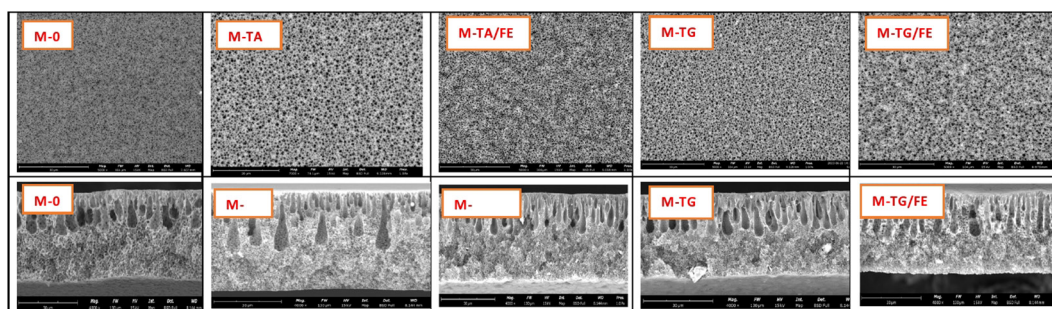


**Figure 4.** SEM images of pristine PVDF and PVDF membranes modified with tannic acid and  $\text{Fe}^{3+}$  complexes: surface views (top row) and cross-sectional views (bottom row)

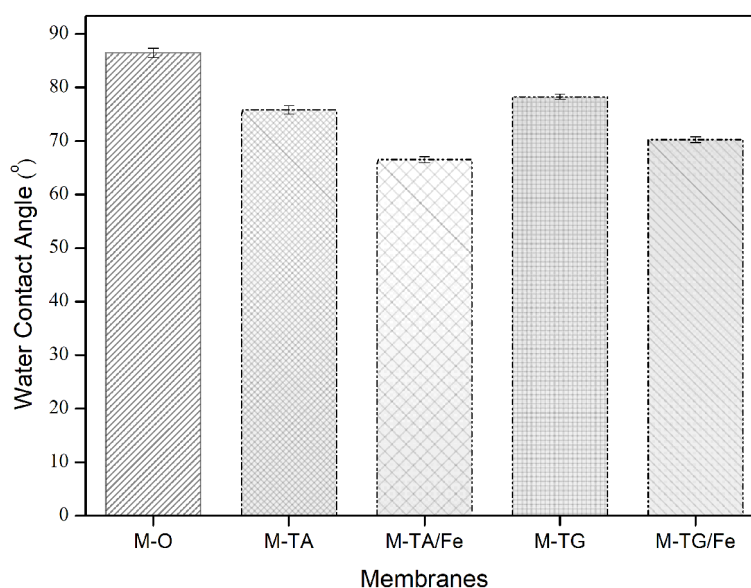


**Figure 5.** Water contact angle (WCA) of pristine PVDF and the PVDF membranes modified with tannic acid and  $\text{Fe}^{3+}$  complexes

### Porosity and pore size

Porosity and pore size strongly affect membrane permeability, selectivity, and fouling behaviour during filtration. In general, the membranes with higher porosity and appropriate pore size distribution tend to exhibit higher water flux while maintaining good separation performance (Guo et al., 2012). The porosity and pore size results are presented in Figure 6.

The incorporation of tannic acid and  $\text{Fe}^{3+}$  coordination caused noticeable changes in membrane structure, consistent with the SEM observations. The pristine membrane showed a porosity of approximately 60.6% with an average pore size of 7.5 nm. After tannic acid addition, the porosity increased to around 71.6–71.7%, while the average pore size increased to approximately 8.9–9.3 nm, indicating the formation of a more porous membrane structure. A similar pore-forming effect of

tannic acid in PVDF membranes has been previously reported (Mulyati et al., 2022). After  $\text{Fe}^{3+}$  coordination, the membrane porosity decreased to around 67%, indicating partial membrane densification. This result suggests that the formation of metal–phenolic networks partially restricted the accessible pore structure, resulting in a denser membrane structure (Kinfu et al., 2023; Li et al., 2023).

### Membrane performance

#### Pure water flux

Pure water flux (PWF) is commonly used to evaluate membrane permeability (Mahmoudian et al., 2022). Higher flux values are generally associated with improved membrane hydrophilicity and porosity, while lower flux values may indicate greater transport resistance within the membrane structure (Mahmoudian et al., 2022).

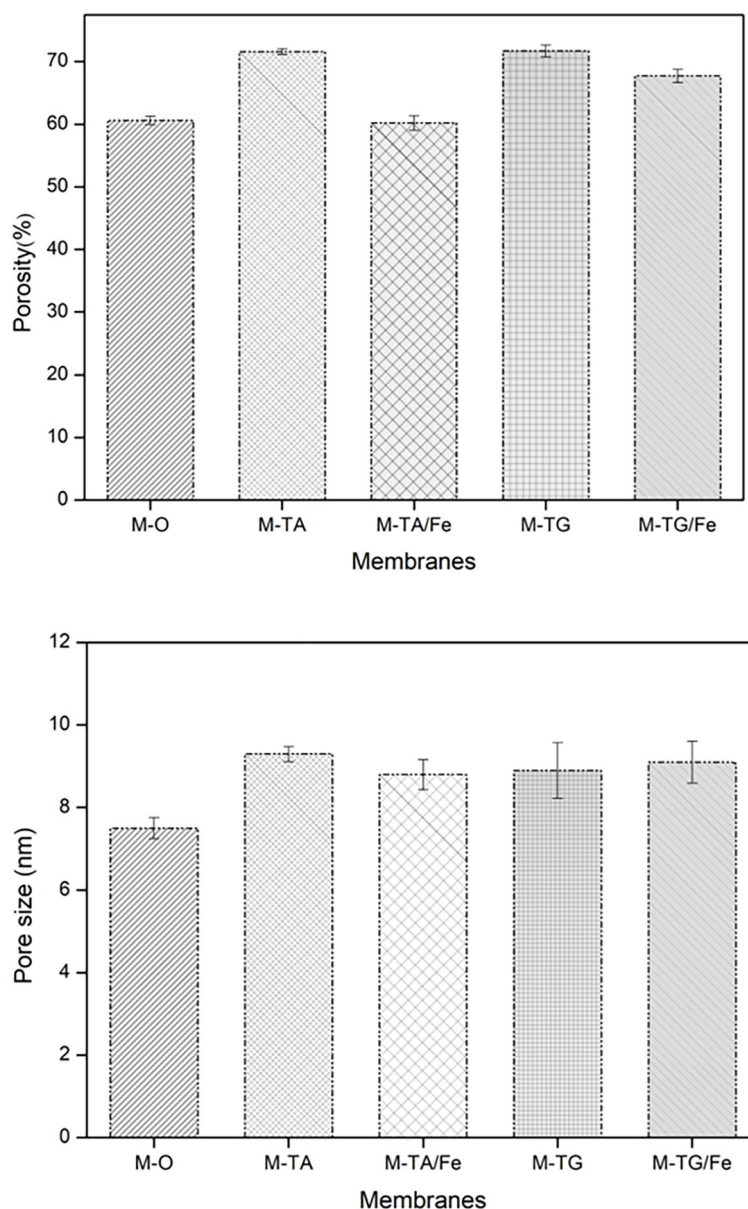


**Figure 6.** Porosity (top) and pore size (bottom) of pristine PVDF and PVDF membranes modified with tannic acid and  $\text{Fe}^{3+}$  complexes

The PWF results are presented in Figure 7. The pristine PVDF membrane showed the lowest flux value ( $\sim 27 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ ), which was related to its relatively dense and hydrophobic structure. After tannic acid incorporation, the flux increased to approximately  $42\text{--}46 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ , corresponding to an improvement of around 30–50%. This increase was likely caused by improved membrane wettability and the formation of a more porous structure, as supported by the contact angle and porosity results (Mulyati et al., 2022; Tang et al., 2026). The membranes modified with  $\text{Fe}^{3+}$  showed slightly lower flux values ( $\sim 37\text{--}39 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ ) compared with the membranes modified only

with tannic acid. This reduction suggests that  $\text{Fe}^{3+}$  coordination caused partial membrane densification, which limited water transport through the membrane. However, the flux values remained higher than those of the pristine membrane, indicating that the improved surface hydrophilicity was still maintained despite the denser membrane structure (Ejima et al., 2017; Kinfu et al., 2024).

#### Humic acid flux and rejection

Membrane performance toward natural organic compounds was evaluated using humic acid filtration and rejection tests. These parameters were used to examine the ability of the membrane to

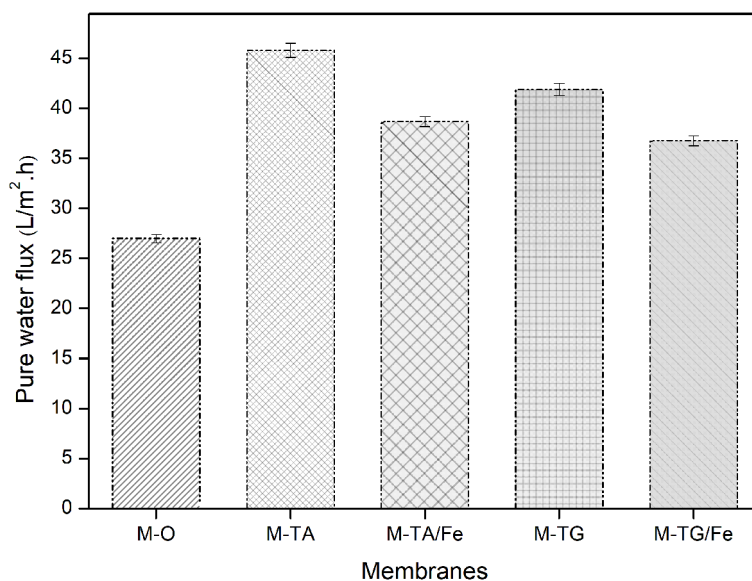


**Figure 7.** Pure water flux of pristine PVDF membranes and membranes modified with tannic acid and  $\text{Fe}^{3+}$  complexes

maintain water permeability while retaining organic contaminants. The results are presented in Figure 8. All membranes showed relatively high humic acid rejection. The pristine membrane exhibited a rejection value of approximately 92%, although the flux remained relatively low ( $\sim 23 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ ). After tannic acid incorporation, the flux increased to around  $36\text{--}37 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$  while the rejection values remained within 90–92%. This result indicates that the increase in permeability did not significantly affect membrane selectivity. The membranes modified with  $\text{Fe}^{3+}$  coordination showed slightly lower

flux values ( $\sim 29\text{--}32 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ ), but the rejection performance remained stable or slightly increased ( $\sim 91\text{--}93\%$ ). The relatively stable rejection behaviour of  $\text{Fe}^{3+}$ -modified membranes indicates that the coordinated layer helped maintain membrane stability during filtration.

#### Long-term stability and durability performance

The normalised flux ( $J/J_0$ ) profiles showed clear differences in membrane stability during repeated

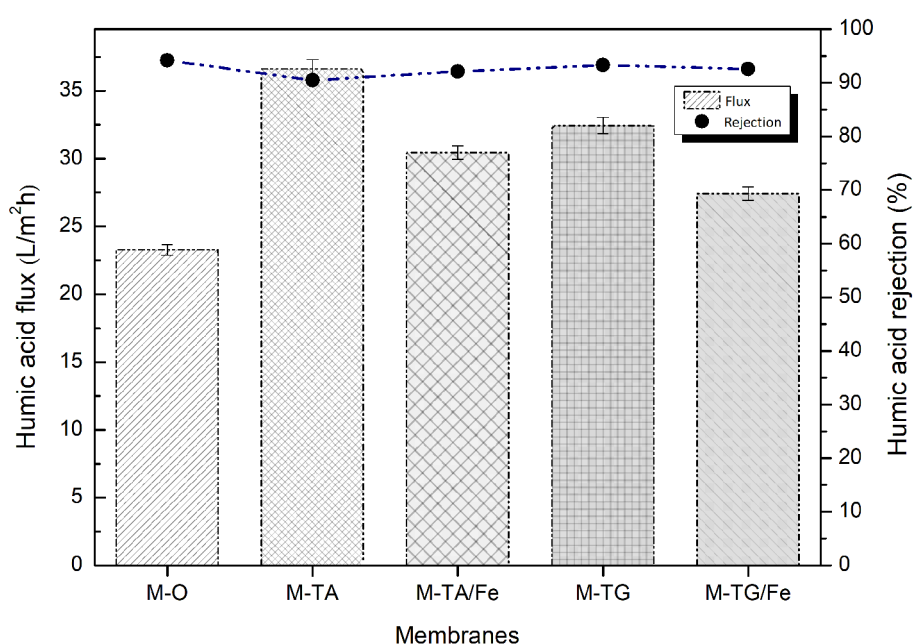


**Figure 8.** Humic acid flux and rejection performance of PVDF membranes

filtration cycles. The pristine PVDF membrane (M-O) exhibited the largest flux decline, reaching a normalised flux value of approximately 0.70 after five cycles, indicating a higher tendency toward fouling. The membranes modified with tannic acid (M-TA and M-TG) showed better flux retention, with normalised flux values of around 0.75–0.76. However, the gradual decrease in flux during repeated cycles indicates that improved surface hydrophilicity alone was insufficient to maintain stable filtration behaviour over prolonged operation.

In contrast, the  $\text{Fe}^{3+}$ -modified membranes (M-TA/Fe and M-TG/Fe) maintained normalised flux values above 0.85 after five filtration cycles, indicating better operational stability. This result suggests that  $\text{Fe}^{3+}$  coordination helped stabilise the modification layer during filtration. The normalised flux profiles during repeated filtration cycles are presented in Figure 9. A similar trend was observed in the flux stability results shown in Figure 10. The pristine membrane exhibited the lowest flux stability, while tannic acid-modified membranes showed moderate improvement. The highest stability was observed for the  $\text{Fe}^{3+}$ -modified membranes, which retained more than 85% of their initial flux after five cycles. These results indicate that  $\text{Fe}^{3+}$  coordination improved resistance to flux decline compared with pristine PVDF membranes and the membranes modified only with tannic acid.

## DISCUSSION

The filtration behaviour observed in this study was affected by the combined influence of membrane wettability, pore characteristics, and the stability of the modification layer. These factors are closely related, and changes in one property may influence other membrane characteristics, particularly permeability and fouling resistance during prolonged filtration.

The incorporation of tannic acid improved membrane hydrophilicity and water permeability. The hydroxyl groups present in tannic acid promoted the formation of a hydration layer on the membrane surface, which reduced direct interaction between organic foulants and the membrane. This condition contributed to the higher initial flux and improved antifouling properties observed during the early stage of filtration (Kammakakam et al., 2025; Yun et al., 2026). In addition, tannic acid affected the phase inversion

process by accelerating solvent–non-solvent exchange, leading to a more porous membrane structure, as confirmed by the SEM and porosity results (Li et al., 2019). Similar improvements in permeability and antifouling behaviour have also been reported for tannic acid-modified PVDF membranes (Dewi et al., 2023).

Despite the improved initial filtration properties, membranes modified only with tannic acid gradually lost flux during repeated filtration cycles. The continuous decrease in normalised flux indicates that enhanced surface hydrophilicity alone was insufficient to suppress fouling during prolonged operation. Although the hydration layer may delay foulant attachment, the gradual decline in normalised flux suggests progressive foulant accumulation and/or changes at the modified interface during repeated operation. Since modifier leaching was not directly evaluated in this study, its contribution to the observed flux decline cannot be confirmed. As a result, the beneficial effect of tannic acid on membrane permeability and antifouling behaviour became less pronounced during long-term operation.

A different trend was observed after  $\text{Fe}^{3+}$  coordination was introduced into the membrane system. The interaction between tannic acid and  $\text{Fe}^{3+}$  formed metal–phenolic networks (MPNs), which improved the stability of the modification layer. Compared with physical adsorption, the coordination interaction provided stronger interfacial bonding and reduced the possibility of modifier detachment during filtration. Consequently,  $\text{Fe}^{3+}$ -modified membranes showed slower flux decline and better operational stability throughout repeated filtration cycles. Similar improvements in membrane durability and antifouling resistance have also been reported for PVDF membranes modified through metal–phenolic coordination systems (Choi et al., 2024; Dewi et al., 2023). In this study, the flux retention of  $\text{Fe}^{3+}$ -modified membranes remained above 85% after five filtration cycles, indicating improved operational stability. This result indicates that the combination of phase inversion and in situ coordination contributed to improved filtration stability.

The introduction of  $\text{Fe}^{3+}$  also affected membrane morphology. Compared with the membranes modified only with tannic acid,  $\text{Fe}^{3+}$ -modified membranes showed lower porosity, smaller pore size, and slightly reduced initial flux. This densification likely increased transport resistance, but it also limited foulant penetration

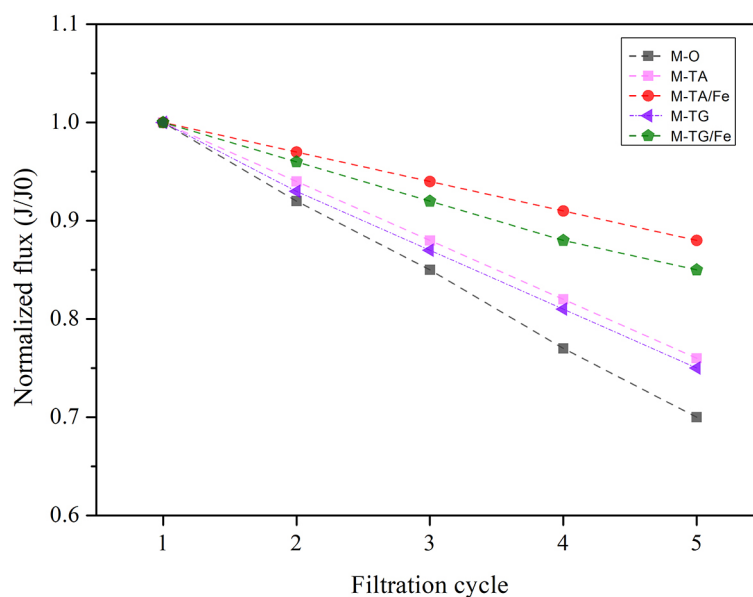


**Figure 9.** Normalised flux ( $J/J_0$ ) of PVDF membranes over five filtration cycles

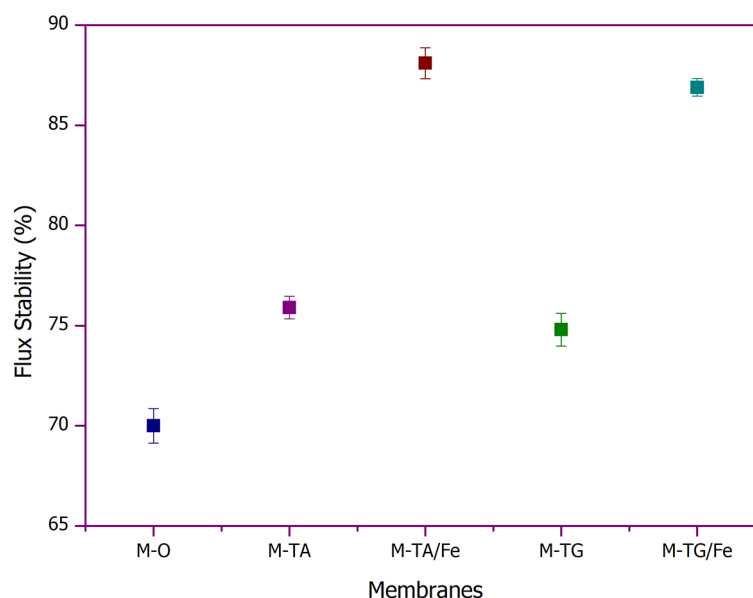


**Figure 10.** Flux stability of PVDF membranes after five filtration cycles

into the membrane pores. Achieving high permeability without sacrificing membrane stability remains challenging in membrane fabrication (Li et al., 2019; Razavi et al., 2020). Although the initial water flux slightly decreased after  $\text{Fe}^{3+}$  coordination, the membranes maintained better flux stability during repeated filtration. The denser membrane morphology likely reduced irreversible fouling and contributed to more stable filtration behaviour over time.

The rejection results further support this observation. All membranes maintained rejection values above 90%, indicating that the modification

process did not significantly affect membrane selectivity.  $\text{Fe}^{3+}$ -modified membranes also showed more stable rejection behaviour during repeated filtration cycles, suggesting that the coordinated layer helped preserve membrane stability during operation. This behaviour contrasts with highly porous membranes, where pore enlargement or structural deformation may lead to fluctuations in selectivity. The results, therefore, indicate that metal–phenolic networks contributed not only to antifouling properties but also to maintaining membrane pore stability during filtration (Kinfu et al., 2023; Razavi et al., 2020).

The comparison between commercial tannic acid and gambir-derived tannins showed relatively similar membrane behaviour. Both modifiers improved membrane wettability, permeability, and antifouling properties, indicating that gambir-derived tannins may serve as an alternative to commercial tannic acid. The phenolic-rich composition of *Uncaria gambir* has been well documented (Munggari et al., 2022; Saad et al., 2020). However, gambir-based membranes showed slightly lower stability during prolonged filtration. This difference may be associated with the heterogeneous phytochemical composition of gambir-derived tannins, which could affect the uniformity of metal–phenolic coordination. Since the composition of the commercial gambir-derived tannin was not independently characterised in this study, this mechanism requires further investigation.

The results obtained in this study demonstrate that membrane durability was strongly influenced by the stability of the interfacial modification layer. Improved hydrophilicity alone was insufficient to maintain stable membrane operation during prolonged filtration. Instead, stronger interfacial interactions provided by  $\text{Fe}^{3+}$  coordination played a major role in reducing flux decline and maintaining filtration stability. The combination of tannic acid and  $\text{Fe}^{3+}$ , therefore, offers an effective approach for improving both membrane wettability and operational durability in ultrafiltration applications.

## CONCLUSIONS

The modification of PVDF membranes using tannic acid and  $\text{Fe}^{3+}$  successfully improved membrane wettability, permeability, and filtration stability. Tannic acid increased membrane hydrophilicity and promoted the formation of a more porous structure, resulting in higher water flux. However, the membranes modified only with tannic acid still experienced a gradual flux decline during repeated filtration. The introduction of  $\text{Fe}^{3+}$  improved the stability of the modification layer through metal–phenolic coordination, which reduced flux deterioration and enhanced fouling resistance despite a slight decrease in the initial permeability.  $\text{Fe}^{3+}$ -modified membranes maintained better flux stability during prolonged filtration, indicating the importance of interfacial stability in sustaining membrane operation. The Gambir-derived tannins also showed performance comparable to commercial tannic acid,

demonstrating their potential as a sustainable membrane modifier. Overall, the results show that stable membrane operation depends not only on hydrophilicity but also on the stability of the interfacial layer. The combination of tannic acid and  $\text{Fe}^{3+}$  therefore provides a promising approach for developing durable ultrafiltration membranes for water treatment applications.

## Acknowledgments

This research was funded by the Ministry of Higher Education, Science, and Technology of the Republic of Indonesia, under the Penelitian Tesis Magister (PTM) scheme for the 2025 funding year, Contract No. 203/UN11.L1/PG.01.03/DPPM/2025.

## REFERENCES

1. Chatterjee, P., Ali, U., Kumar, P. (2022). Role of membrane filtration in modular drinking water treatment system. In S. K. Brar, P. Kumar, A. Cuprys (Eds.), *Modular treatment approach for drinking water and wastewater* (pp. 267–279). Elsevier. <https://doi.org/10.1016/B978-0-323-85421-4.00004-8>
2. Chen, M., Ding, W., Zhou, M., Zhang, H., Ge, C., Cui, Z., Xing, W. (2021). Fouling mechanism of PVDF ultrafiltration membrane for secondary effluent treatment from paper mills. *Chemical Engineering Research and Design*, 167, 37–45. <https://doi.org/10.1016/j.cherd.2020.12.021>
3. Choi, Y., Lee, M., Nam, C. (2024). Catechol-Fe(III) complexes modified PVDF membrane for hazardous pollutants separation and antifouling properties. *Chemosphere*, 364, Article 143094. <https://doi.org/10.1016/j.chemosphere.2024.143094>
4. Dallaev, R., Pisarenko, T., Sobola, D., Orudzhev, F., Ramazanov, S., Trčka, T. (2022). Brief review of PVDF properties and applications potential. *Polymers*, 14(22), Article 4793. <https://doi.org/10.3390/polym14224793>
5. Dewi, R., Shamsuddin, N., Abu Bakar, M. S., Thongratkaew, S., Faungnawakij, K., Bilad, M. R. (2023). Development of tannic acid coated polyvinylidene fluoride membrane for filtration of river water containing high natural organic matter. *Sci*, 5(4), Article 42. <https://doi.org/10.3390/sci5040042>
6. Dmitrieva, E. S., Anokhina, T. S., Novitsky, E. G., Volkov, V. V., Borisov, I. L., Volkov, A. V. (2022). Polymeric membranes for oil-water separation: A review. *Polymers*, 14(5), Article 980. <https://doi.org/10.3390/polym14050980>
7. Ejima, H., Richardson, J. J., Caruso, F. (2017).

- Metal-phenolic networks as a versatile platform to engineer nanomaterials and biointerfaces. *Nano Today*, 12, 136–148. <https://doi.org/10.1016/j.nantod.2016.12.012>
8. Guo, W., Ngo, H.-H., Li, J. (2012). A mini-review on membrane fouling. *Bioresource Technology*, 122, 27–34. <https://doi.org/10.1016/j.biortech.2012.04.089>
  9. Kammakakam, I., Mir, I. S., Baig, N., Riaz, A., Messaddeq, Y. (2025). Dual-functional tannic acid-infused AgNPs-PVDF membranes via coagulation methods: An integrated study on antibacterial and antifouling performances for oil-in-water separation. *Materials Advances*, 6(16), 5588–5604. <https://doi.org/10.1039/D5MA00355E>
  10. Kinfu, H. H., Rahman, M. M., Cevallos-Cueva, N., Abetz, V. (2024). Nanofiltration membranes containing a metal–polyphenol network layer: Using casting solution pH as a tool to tailor the separation performance. *ACS Omega*, 9(46), 45870–45883. <https://doi.org/10.1021/acsomega.4c04804>
  11. Kinfu, H. H., Rahman, M. M., Schneider, E. S., Cevallos-Cueva, N., Abetz, V. (2023). Charge and size selective thin film composite membranes having tannic acid–ferric ion network as selective layer. *Journal of Membrane Science*, 679, Article 121709. <https://doi.org/10.1016/j.memsci.2023.121709>
  12. Li, H., Li, X., Ouyang, G., Li, L., Zhong, Z., Cai, M., Li, W., Huang, W. (2023). Tannic acid/Fe<sup>3+</sup> interlayer for preparation of high-permeability polyetherimide organic solvent nanofiltration membranes for organic solvent separation. *Chinese Journal of Chemical Engineering*, 57, 17–29. <https://doi.org/10.1016/j.cjche.2022.09.014>
  13. Li, M., Wu, L., Zhang, C., Chen, W., Liu, C. (2019). Hydrophilic and antifouling modification of PVDF membranes by one-step assembly of tannic acid and polyvinylpyrrolidone. *Applied Surface Science*, 483, 967–978. <https://doi.org/10.1016/j.apsusc.2019.04.057>
  14. Mahmoudian, M., Gharabaghlo, M. A., Shadjou, N. (2022). Utilization of a mixed matrix membrane modified by novel dendritic fibrous nanosilica (KCC-1-NH-CS<sub>2</sub>) toward water purification. *RSC Advances*, 12(27), 17514–17526. <https://doi.org/10.1039/D2RA02963D>
  15. Moradi, R., Karimi-Sabet, J., Shariaty-Niassar, M., Koochaki, M. A. (2015). Preparation and characterization of polyvinylidene fluoride/graphene superhydrophobic fibrous films. *Polymers*, 7(8), 1444–1463. <https://doi.org/10.3390/polym7081444>
  16. Mulyati, S., Aprilia, S., Muchtar, S., Syamsuddin, Y., Rosnelly, C. M., Bilad, M. R., Samsuri, S., Ismail, N. M. (2022). Fabrication of polyvinylidene difluoride membrane with enhanced pore and filtration properties by using tannic acid as an additive. *Polymers*, 14(1), Article 186. <https://doi.org/10.3390/polym14010186>
  17. Mulyati, S., Muchtar, S., Arahman, N., Meirisa, F., Syamsuddin, Y., Zuhra, Z., Rosnelly, C. M., Shamsuddin, N., Mat Nawi, N. I., 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(8), Article 1807. <https://doi.org/10.3390/polym12081807>
  18. Mulyati, S., Rosnelly, C. M., Riza, M., Muchtar, S., Ambarita, A. C., Luthfiana, A., Aulia, M. P., Bilad, M. R. (2025). Tailoring PVDF membrane antifouling properties via tannic acid blending and chitosan surface coating. *Results in Chemistry*, 18, Article 102709. <https://doi.org/10.1016/j.rechem.2025.102709>
  19. Mulyati, S., Rosnelly, C. M., Syamsuddin, Y., Ambarita, A. C., Muchtar, S. (2023). Household bleach products as high-performance and cost-effective cleaning agents for membrane fouling. *South African Journal of Chemical Engineering*, 46, 35–41. <https://doi.org/10.1016/j.sajce.2023.07.005>
  20. Munggari, I. P., Kurnia, D., Deawati, Y., Julaeah, E. (2022). Current research of phytochemical, medicinal and non-medicinal uses of *Uncaria gambir* Roxb.: A review. *Molecules*, 27(19), Article 6551. <https://doi.org/10.3390/molecules27196551>
  21. Razavi, S. R., Shakeri, A., Mirahmadi Babaheydari, S. M., Salehi, H., Lammertink, R. G. H. (2020). High-performance thin film composite forward osmosis membrane on tannic acid/Fe<sup>3+</sup> coated microfiltration substrate. *Chemical Engineering Research and Design*, 161, 232–239. <https://doi.org/10.1016/j.cherd.2020.06.032>
  22. Ricci, A., Olejar, K. J., Parpinello, G. P., Kilmartin, P. A., Versari, A. (2015). Application of Fourier transform infrared (FTIR) spectroscopy in the characterization of tannins. *Applied Spectroscopy Reviews*, 50(5), 407–442. <https://doi.org/10.1080/05704928.2014.1000461>
  23. Saad, M. F. M., Goh, H.-H., Rajikan, R., Yusof, T. R. T., Baharum, S. N., Bunawan, H. (2020). *Uncaria gambir* (W. Hunter) Roxb: From phytochemical composition to pharmacological importance. *Tropical Journal of Pharmaceutical Research*, 19(8), 1767–1773. <https://doi.org/10.4314/tjpr.v19i8.28>
  24. Sahiner, N., Guven, O., Demirci, S., Suner, S. S., Sahiner, M., Ari, B., Can, M. (2025). Tannic acid-based bio-MOFs with antibacterial and antioxidant properties acquiring non-hemolytic and non-cytotoxic characteristics. *Colloids and Surfaces B: Biointerfaces*, 252, Article 114669. <https://doi.org/10.1016/j.colsurfb.2025.114669>
  25. Shen, L., Feng, S., Li, J., Chen, J., Li, F., Lin, H., Yu, G. (2017). Surface modification of polyvinylidene fluoride (PVDF) membrane via radiation grafting: Novel mechanisms underlying the interesting enhanced membrane performance. *Scientific Reports*, 7, Article 2721. <https://doi.org/10.1038/s41598-017-02605-3>
  26. Sigma-Aldrich. (n.d.). *Poly(vinylidene fluoride)*, product no. 182702, CAS no. 24937-79-9. Retrieved

- August 18, 2026, from <https://www.sigmaaldrich.com/US/en/product/aldrich/182702>
27. Tang, Y., Zhou, D., Sun, X., Sheng, Z., Huang, D. (2026). Functionalized tannic acid/poly(vinylidene fluoride) (PVDF) selective ultrafiltration membranes: Excellent hydrophilicity and antifouling potential. *Iranian Polymer Journal*, 35(9), 1953–1968. <https://doi.org/10.1007/s13726-026-01627-x>
28. Yan, W., Shi, M., Dong, C., Liu, L., Gao, C. (2020). Applications of tannic acid in membrane technologies: A review. *Advances in Colloid and Interface Science*, 284, Article 102267. <https://doi.org/10.1016/j.cis.2020.102267>
29. Yang, J., Wang, L., Xie, A., Dai, X., Yan, Y., Dai, J. (2020). Facile surface coating of metal-tannin complex onto PVDF membrane with underwater superoleophobicity for oil-water emulsion separation. *Surface and Coatings Technology*, 389, Article 125630. <https://doi.org/10.1016/j.surfcoat.2020.125630>
30. Yu, H., Shangguan, S., Yang, H., Rong, H., Qu, F. (2023). Chemical cleaning and membrane aging of poly(vinylidene fluoride) (PVDF) membranes fabricated via non-solvent induced phase separation (NIPS) and thermally induced phase separation (TIPS). *Separation and Purification Technology*, 313, Article 123488. <https://doi.org/10.1016/j.seppur.2023.123488>
31. Yun, K. H., Sim, S., Jeong, C., Jeong, K. J., Bae, T.-H. (2026). Hydrophilic modification of PES microfiltration membranes via tannic acid/silica coating for enhanced sterile filtration. *Journal of Membrane Science*, 740, Article 124969. <https://doi.org/10.1016/j.memsci.2025.124969>
32. Zhang, J., Li, G., Yuan, X., Li, P., Yu, Y., Yang, W., Zhao, S. (2023). Reduction of ultrafiltration membrane fouling by the pretreatment removal of emerging pollutants: A review. *Membranes*, 13(1), Article 77. <https://doi.org/10.3390/membranes13010077>