

Article

Development of Tannic Acid Coated Polyvinylidene Fluoride Membrane for Filtration of River Water Containing High Natural Organic Matter

Rosmaya Dewi ^{1,2}, Norazanita Shamsuddin ^{1,*} , Muhammad Saifullah Abu Bakar ¹ , Sutarat Thongratkaew ³,
Kajornsak Faungnawakij ³  and Muhammad Roil Bilad ^{1,*} 

¹ Faculty of Integrated Technologies, Universiti Brunei Darussalam, Jalan Tungku Link, Bandar Seri Begawan BE1410, Brunei

² Department of Pharmacy, Universitas Bakti Tunas Husada, Kota Tasikmalaya 46115, Indonesia

³ National Nanotechnology Center (NANOTEC), National Science and Technology Development Agency (NSTDA), 111 Thailand Science Park, Pathum Thani 12120, Thailand

* Correspondence: norazanita.shamsudin@ubd.edu.bn (N.S.); roil.bilad@ubd.edu.bn (M.R.B.)

Abstract: River water can be used as a source of drinking water. However, it is vital to consider the existence of natural organic matter (NOM) and its possible influence on water quality (low turbidity, high color). The level of NOM in river water significantly impacts the ecosystem's health and the water's quality, and needs to be removed. A membrane-based approach is attractive for treating NOM successfully, but is still hindered by the membrane fouling problem. This study aims to develop polyvinylidene fluoride (PVDF)-based membranes customized for NOM removal from river water. The anti-fouling property was imposed by a coating of tannic acid (TA) and Fe³⁺ on the pre-prepared PVDF membrane. The results show that the TA-Fe coatings were effective, as demonstrated by the FTIR spectra, SEM, and EDS data. The coatings made the membrane more hydrophilic, with smaller pore size and lower clean water permeability. Such properties offer enhanced NOM rejections (up to 100%) and remarkably higher fouling recovery (up to 23%), desirable for maintaining a long-term filtration performance.

Keywords: membrane filtration; polyvinylidene fluoride; tannic acid; antifouling; natural organic matter



Citation: Dewi, R.; Shamsuddin, N.; Abu Bakar, M.S.; Thongratkaew, S.; Faungnawakij, K.; Bilad, M.R.

Development of Tannic Acid Coated Polyvinylidene Fluoride Membrane for Filtration of River Water Containing High Natural Organic Matter. *Sci* **2023**, *5*, 42. <https://doi.org/10.3390/sci5040042>

Academic Editor: Beat Knechtle

Received: 12 September 2023

Revised: 7 November 2023

Accepted: 15 November 2023

Published: 20 November 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

River water can serve as a source of drinking water. However, it is crucial to consider the presence of natural organic matter (NOM) in river water and its potential impact on the treated water's quality. NOM is an intricate mix of organic substances naturally occurring in the environment, including rivers. NOM consists of various organic compounds such as humic acids, fulvic acids, and other organic compounds derived from plants, animals, soil, and microbial activity [1].

The amount of NOM in river water significantly impacts the water's quality and the ecosystem's health. The water's physical, chemical, and biological characteristics are impacted by the presence of NOM. NOM, for instance, can affect water's appearance, flavor, and odor. It may also impact the movement and eventual fate of other elements in the water, such as pollutants and nutrients [2]. The presence of NOM in water can also have implications for disinfection processes. Chlorine, commonly used as a disinfectant, can react with NOM to form disinfection by-products such as trihalomethanes. Trihalomethanes are of concern due to their potential carcinogenicity and health risks [3].

Membrane technology has been widely used in the treatment of river water to produce potable water and other applications. The use of membranes in river water treatment largely depends on the specific water quality challenges faced and the desired level of treatment. They can be used at various stages, but commonly after physical treatment as

the main treatment unit or as the post-treatment to polish the water from the conventional treatment unit. One of the membrane materials is polyvinylidene fluoride (PVDF). Due to its durability, biocompatibility, chemical resistance, and insolubility in most organic solvents, PVDF is a well-liked polymer [4]. The concentration of PVDF used during the membrane fabrication is one of many variables that can affect its filtration performance [5,6]. PVDF can be blended with other polymers, which can be dissolved in a variety of solvents, such as N-Methyl-2 Pyrrolidone, Tetrahydrofuran, and Dimethylformamide [5]. However, the application of water as a green and cost-effective non-solvent in the phase inversion process for PVDF membrane fabrication requires a hydrophobic polymer that later imposes an issue of membrane fouling [7].

Due to the hydrophobic nature of neat PVDF membranes, their application for water-based filtration—including river water filtration—is highly restricted. Fouling is the buildup of undesirable compounds on the surface of a membrane, which can negatively impact its effectiveness and performance [8]. Researchers have devised strategies to alter the hydrophobic PVDF membrane's surface and make it hydrophilic to overcome its drawbacks. The authors of references [4,9,10] use chemical grafting, electrospinning, blending PVDF with other polymers, and coating as their methods.

Coating methods are frequently employed in membrane development to change the surface characteristics of membranes and enhance their functionality. These methods entail covering the membrane surface with a thin material layer, improving the membrane's hydrophilicity, anti-fouling abilities, and water permeability [10]. Several factors throughout the coating process of membrane formation heavily influence the qualities and performance of the coated membranes. These factors include layer thickness and density, coating techniques, interfacial crosslinking, ionic strength, pH, and the choice of coating materials [11].

One of the more well-known coating materials is tannic acid [12]. It has been shown to create super hydrophilic and anti-fouling surfaces, high-compatibility polymer/nanoparticle interfaces, and thin film composite membranes with high permselectivity. Tannic acid can react with metal ions like Fe^{3+} . Tannic acid/metal complexes are created by the coordination of phenolic hydroxyl groups with metal ions. Phenolic hydroxyl groups and metal ions form powerful coordination connections [12].

Tannic acid has been extensively studied for its potential to enhance the anti-fouling properties of PVDF membranes. Several studies have investigated using tannic acid to modify PVDF membranes and improve their anti-fouling properties. One study focused on grafting a zwitterionic polymer brush onto the PVDF membrane surface using UV treatment [13]. The modified PVDF membrane exhibited enhanced ultrafiltration performance and improved anti-fouling properties. Another study reported the efficient preparation of a super anti-fouling PVDF ultrafiltration membrane through the one-step sulfonation of PVDF and polyaniline blend membrane in situ [14]. The addition of self-doped sulfonated polyaniline as a zwitterionic polymer improved the anti-fouling property of the PVDF membrane.

The mechanisms by which tannic acid enhances the anti-fouling properties of PVDF membranes are not fully understood. However, it is believed that tannic acid can change the chemical properties of the membrane surface by adsorbing onto the membrane surface and reducing the water contact angle. This leads to increased hydrophilicity and reduced fouling propensity. Tannic acid can also form a crosslinking network with other polymers, such as polyethyleneimine, to strengthen the coating on the membrane surface and improve its stability [15]. In previous work, tannic acid was assembled directly into the membrane matrix by blending it with polymer in the dope solution [14,16], and the complex of tannic acid- Fe^{3+} was formed in one-step assembly during the phase inversion process. The Fe^{3+} was dissolved in water as the non-solvent. This one-step assembly was reported effective in imposing anti-fouling properties, but alters the overall membrane morphologies as well as imposing swelling vulnerabilities, which lower the permeabilities [16]. To avoid such

limitations, a multi-step process involving phase inversion for membrane fabrication and coatings for surface modification was proposed in this study.

The objective of this study is to develop a fouling-resistant PVDF-based membrane by coating it with tannic acid and Fe^{3+} at various coating durations. The tannic acid was expected to act as a hydrophilic agent by incorporating polar groups into the membrane matrix. At the same time, complexation with Fe^{3+} would limit the leaching of tannic acid from the membrane matrix. Such a fabrication method was expected to enhance the membrane's hydrophilicity and anti-fouling capabilities in treating river water containing high NOM concentration. This study presents several notable advantages in comparison to others. Foremost, it utilized real river water contaminated with a high concentration of NOM, which provided more realistic data, instead of using model feeds. The approach of tannic acid coating was also relatively simple and straightforward, and allows rapid optimization when required in the future.

2. Materials and Methods

2.1. Membrane Preparation and Development

Four membranes were prepared using the phase inversion method, followed by tannic acid and Fe^{3+} coatings. Tannic acid (Sigma Aldrich, St. Louis, MI, USA) and iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, Sigma Aldrich, St. Louis, MI, USA) were used as the coating agents. At the same time, PVDF (average M_w 534,000 by GPC, Sigma Aldrich, St. Louis, MI, USA) served as the polymer. Distilled water was used as the non-solvent in the phase inversion process.

The polymer solution was made by mixing PVDF (12 wt. %) and DMF (88 wt. %) at 60°C in a Schott bottle and agitated until homogeneous. In order to prevent membrane defects, air bubbles were removed from the homogenous solution by letting the solution idle in a 60°C oven for at least 2 h. The solution was then cast using a casting knife with a wet thickness of $200\ \mu\text{m}$ on a glass plate, as depicted in Figure 1. The cast film was immediately placed in a coagulation bath and left for 15 min to complete the phase inversion. Before being coated, the membrane sheet was trimmed to the dimensions needed for the filtration cell. The coating solutions included 1 g/L of tannic acid and 0.25 g/L of Fe^{3+} . The coating procedure involved submersion in the tannic acid solution for a specified time and then exposure to Fe^{3+} for a given duration.

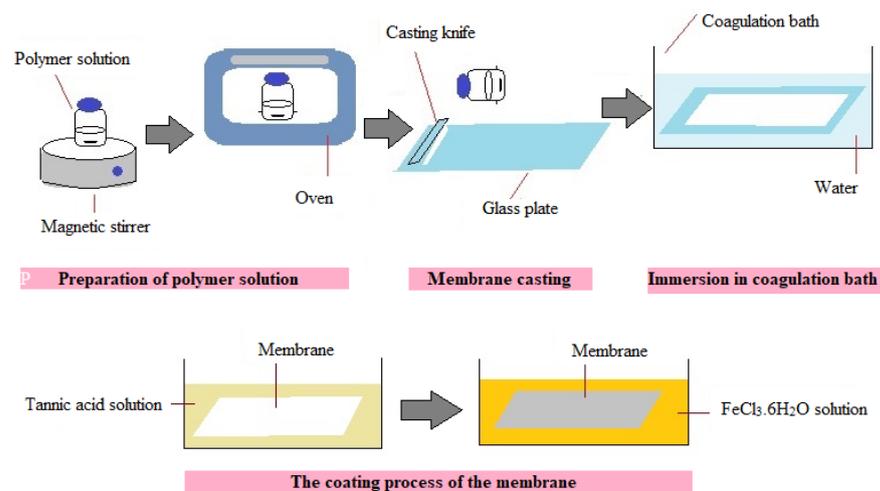


Figure 1. An illustration of the phase inversion technique used to prepare the membrane samples.

The four membrane samples were a PVDF membrane without coating, PVDF-C2.5 with 2.5 min of coating, PVDF-C5 with 5 min of coating, and PVDF-7.5 with 7.5 min of coating. Up until use, the membrane was kept moist. Due to its low clean water flux, PVDF-C7.5 was held back for additional testing and characterization. In order to prevent a considerable difference in the samples' intrinsic permeabilities ($<10\%$), the clean water

permeability (CWP) of the pristine sheet was first assessed for the coated samples, and the clean water permeabilities were ensured to deviate by less than 10% of the pristine PVDF.

2.2. Membrane Properties

2.2.1. Morphology and Elemental Mapping

The membranes' surface and cross-section pictures were captured using scanning electron microscopy (SEM, FEI Quanta-250, Thermo Fisher Scientific, Waltham, MA, USA) for the membrane morphology analysis. Liquid nitrogen was used to freeze-fracture the samples before testing, and a tiny film of gold was subsequently applied to them. Energy-dispersive X-ray (EDX) mapping was carried out on the membranes' surface to glean insights into the chemical surface distribution. The primary detector was NCTC, with a serial number of UVA11361. This method made it easier to see and analyze how different chemical elements were distributed throughout the membrane's surface.

2.2.2. Surface Chemistry

The membranes' chemical functional groups and spectrum shifts were analyzed using Fourier transform infrared spectroscopy (FTIR; PerkinELmer Inc., Waltham, MA, USA), encompassing a spectral range from 500 to 4000 cm^{-1} .

2.2.3. Surface Hydrophilicity

The hydrophilicity of the membrane surface was assessed by measuring the water contact angle. Membrane samples were dried in an oven at 50 °C prior to measurement. Distilled water was dropped onto the membrane surface for each measurement. A contact angle meter (LR-sdc-10, Lonroy Equipment Co., Ltd., Dongguan, China) was used to measure the contact angles between the membrane surface and the water microdroplet. Dynamic contact angle measurements were made at ten points every 30 s for 5 min, and this was done using multiple samples with the results presented as average \pm standard deviation.

2.3. Filtration Test

The crossflow microfiltration setup used to assess the hydraulic performance of the created membranes is shown in Figure 2. The filtration was run at a fixed trans-membrane pressure of 8 kPa driven by a peristaltic pump (Type KCP600, Kamoer, Shanghai, China) using a membrane sheet with an effective membrane area of 12 cm^2 . The filtering process was carried out continuously, beginning with a 60 min membrane compaction at 8 kPa, followed by a 60 min filtration test for clean water permeability (CWP) measurement. Then, the feed was replaced with river water, followed by river water filtration (RWF) for 60 min, with 10 min of water flushing (WF) and 20 min of subsequent RWF. The incorporation of WF allowed the assessment of membrane fouling recovery.

The volume of the feed tank was 1 L, and the collected permeate volume in 10 min was around 0.25–2.5 mL. The permeate volume was measured and collected every 10 min. After volume measurement, the permeate was returned to the feed tank to allow full recirculation and maintain the feed condition. A portion of the collected permeate was set aside for analysis to determine the rejection of NOM. The membrane permeability (L , L/m^2 h bar) and NOM rejection (R , %) were calculated using Equations (1) and (2), respectively. The NOM concentration was indirectly inferred using platinum–cobalt standards and a photometer (Multiparameter photometer, HI83399, HANNA Instrument, Smithfield, RI, USA), according to earlier work [17].

$$L = \frac{\Delta V}{\Delta t A \Delta P} \quad (1)$$

$$R = \frac{C_{\text{feed}} - C_{\text{permeate}}}{C_{\text{feed}}} \times 100 \quad (2)$$

where ΔV is the collected permeate volume (L), Δt is the filtration time (h), A is the membrane effective area (m^2), ΔP is the transmembrane pressure (bar), and C (PCU) is the NOM value. The river water sample was obtained from Tutong River, Brunei, as shown in Figure 2 (bottom). The sampling was taken near to Jetty Sungai Tutong with the GPS coordinate of 4.80445,114.6571638 on 14 January 2023. The river water had the color of 204 PCU corresponding to UV_{254} and a humic acid concentration of 5.3 ppm obtained from the color calibration of humic acid solutions. The river water used as the feed for the filtration had turbidity of 18 NTU, pH of 5.9, aluminium content of 0.1 mg/L and manganese of 0.74 mg/L. A river’s water composition can vary significantly depending on its location, surrounding geology, human activities in the area, and other factors. However, the typical composition of river water consists of water, dissolved gas, ions, suspended solids, organic matter, nutrients, microorganisms, pollutants, and trace elements. The specific composition of a river can change over time due to natural processes and human activities. Water from River Tutong has been used as the resource for up to 85% of the household water supply in Brunei Darussalam.

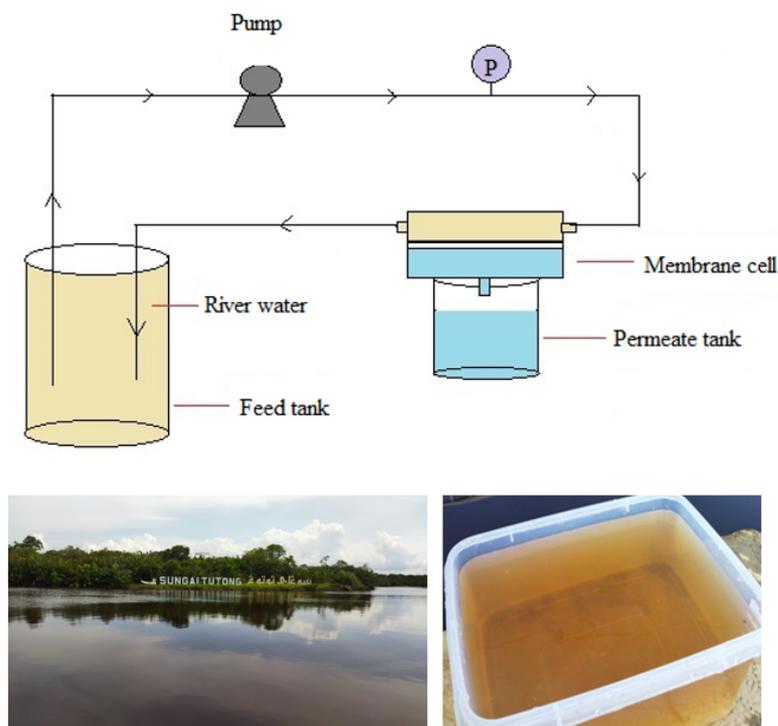


Figure 2. Illustration of the cross-flow filtration setup (top), and the river water sampling and appearance of the river water sample in a container (bottom).

2.4. Membrane Fouling Analysis

The progression of permeability over the RWF was examined to assess the fouling characteristics of the produced membranes. The percentage of flow recovery following water flushing, as demonstrated in Equation (3), was used as the parameter of fouling reversibility (FR , %).

$$FR = \frac{L_F - L_I}{L_F} 100\% \tag{3}$$

where L_F ($L/(m^2 \text{ h bar})$) is the final permeability of the water filtration before flushing, and L_I ($L/(m^2 \text{ h bar})$) is the initial water permeability after flushing.

3. Results and Discussion

3.1. Membrane Properties

3.1.1. Membrane Morphology

In this study, the pristine PVDF and modified PVDF membranes are microfiltration membranes with pore size ranges between 0.2 and 0.3 μm . Figure 3 shows the microstructure of the developed membranes. The pristine PVDF membrane (PVDF) possessed a smooth surface with a uniform spatial distribution of surface pores. Compared to PVDF, the surface pore size of PVDF-C2.5 and PVDF-C5 experienced a slight decrease, as shown in Figure 3. The finding clearly demonstrates that introducing TA-Fe additives altered the quantity and size of the surface pores on the membrane surface. This observation aligns with the findings of the authors of references [4,16], where the pristine PVDF membrane displayed a uniform pore size. The modified membranes exhibited a reduction in pore size due to the formation of an additional TA-Fe coating layer onto the membrane's surface or on the pore wall of the membrane, constricting the pore mouth. The surface SEM image also shows that the coated membrane surfaces were rougher than the pristine one, indicating the presence of the TA-Fe complex on the membrane surface.

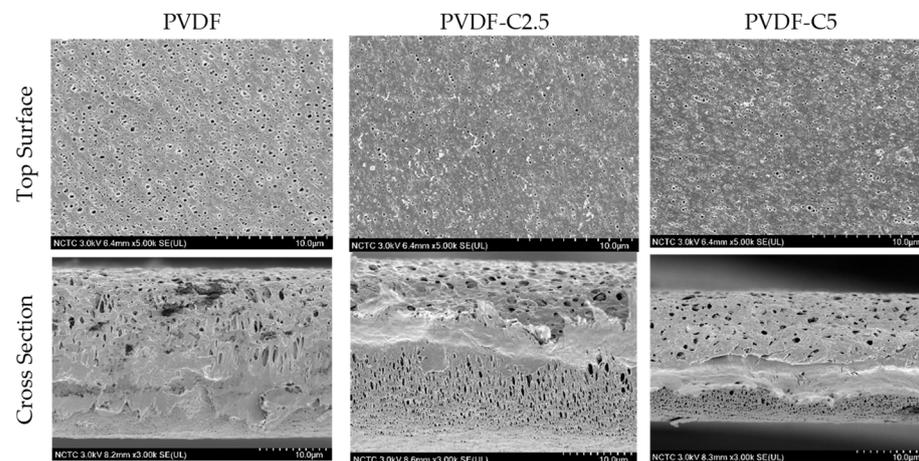


Figure 3. The top surface and cross-sectional morphologies of PVDF, PVDF-C2.5, and PVDF-C5.

The formation of TA-Fe complexes on the membrane surface did not alter the PVDF membrane's fibre structure, as seen by the cross-sectional SEM image (cross-section pictures of PVDF, PVDF-C2.5, PVDF-C5). The coating layer atop the membrane was expected to improve its hydrophilicity and anti-fouling capabilities. The authors of reference [4] mentioned that the effective assembly of TA-Fe³⁺ complexes on the surface of a membrane enhances its hydrophilicity, leading to improved anti-fouling performance.

The coating of tannic acid on the microfiltration membrane's surface has been found to have several effects on the membrane's morphology and pore size, as also demonstrated by the results in Figure 3. Chheang et al. (2022) [18] found that a tannic acid coating on PVDF membranes reduced the membrane's water contact angle, indicating increased hydrophilicity. Wu et al. (2019) [15] observed that the tannic acid/polyethyleneimine coating layer on the membrane was denser and more stable after the addition of metal ions, potentially due to the coordination bond formed between the coating and metal ions. Additionally, tannic acid has been shown to increase the number of nucleation centers and render the morphology more uniform in other coating applications [19]. These findings suggest that a tannic acid coating can modify the surface morphology of microfiltration membranes and potentially affect the pore size, in line with the findings obtained in the present study.

3.1.2. FTIR Spectra

The spectrum analysis of the PVDF membrane revealed unique peaks at wavenumbers 1403, 1174, and 875 cm^{-1} , as shown in Figure 4, which, in turn, correspond to the skeleton vibration of C–C bonds, the stretching vibration of $-\text{CF}_2$ groups, and the planar mixing vibration of $-\text{CH}_2$ groups, respectively [4,7,20]. The FTIR spectrum of tannic acid reveals absorption bands for its functional groups, which include C=C aromatic, C–OH aromatic, C=C skeletal, C=O phenolic ester and O–H stretching [21]. When tannic acid forms a complex with PVDF and Fe^{3+} , there might be changes or shifts in the FTIR spectrum. Shifts or variations in peak intensity in the characteristic peaks of the tannic acid or PVDF can be formed when the tannic acid and PVDF interact or produce a complex. Peaks in complex mixes may overlap. Strong changes are also brought about in the 1300–1000 cm^{-1} region by complexation with iron. The strong bands at this range in the tannic acid spectrum become less prominent. Since these bands receive a large contribution from the $\nu(\text{C}-\text{O})$, $\delta(\text{C}-\text{OH})$, and $\nu(\text{C}-\text{C})$ vibrations, an interaction of iron with the $-\text{OH}$ groups of the phenolic group is deduced [22].

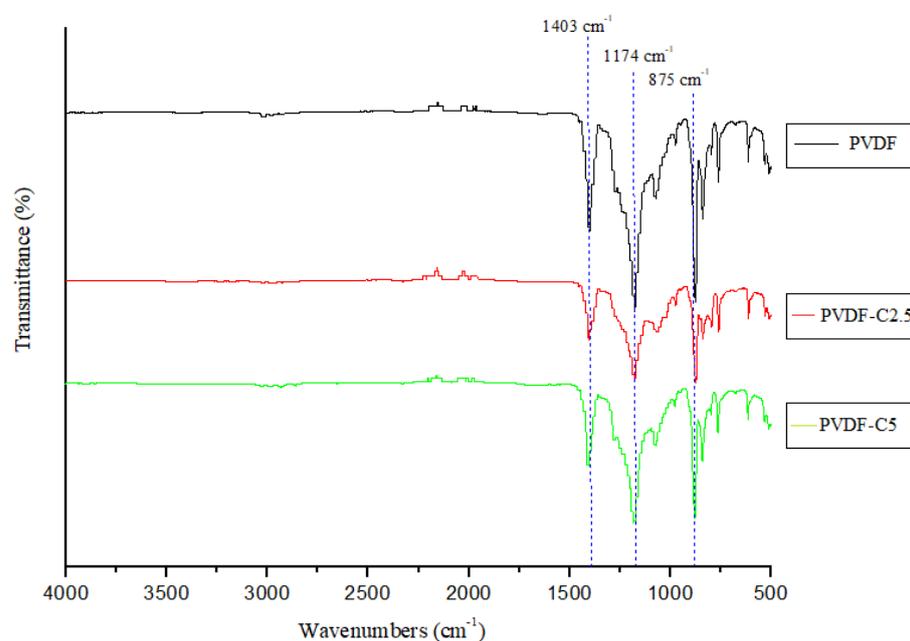


Figure 4. FTIR spectra of PVDF, PVDF-C2.5 and PVDF-C5.

The proportion of components inside the membrane matrix can be determined by comparing the relative intensities of the peaks within one sample to those of another. The decreased intensities seen at 875, 1403, and 1174 cm^{-1} in the cases of PVDF-C2.5 and PVDF-C5 compared to PVDF indicate a diminished presence of functional groups from the PVDF polymer. The intensity of additional peaks connected to the existence of additives within PVDF-C2.5 and PVDF-C5 was responsible for this decline, as suggested elsewhere [20]. This finding further confirms the presence of the TA–Fe complex on the coated membrane.

The effects of a tannic acid coating on PVDF microfiltration membranes on surface chemical composition were observed through changes in functional groups and peaks in the FTIR spectra, as also reported elsewhere [23]. The introduction of tannic acid onto the surface of PVDF membranes can lead to the appearance of O–H and N–H peaks in the FTIR spectra [23]. These changes in functional groups suggest the presence of tannic acid on the membrane's surface. Furthermore, the near-surface compositions of PVDF membranes containing tannic acid can be determined using X-ray photoelectron spectroscopy spectra analysis [20,24]. Overall, tannic acid coating alters the surface chemical composition of PVDF membranes, resulting in increased hydrophilicity and the presence of tannic acid functional groups.

3.1.3. Surface Elemental Composition

The elements on the membrane surface were mapped using energy-dispersive X-ray spectroscopy (EDS) to demonstrate further the preservation of the TA–Fe in the modified membranes (Figure 5). The findings show that carbon (C) and oxygen (O) are present in each membrane in varying proportions (Table 1). Increasing percentages of oxygen elements are seen on the modified membranes compared to the pristine membrane, which supports the successful integration of tannic acid additives into the membrane matrix. This result is comparable to the one reported earlier [20].

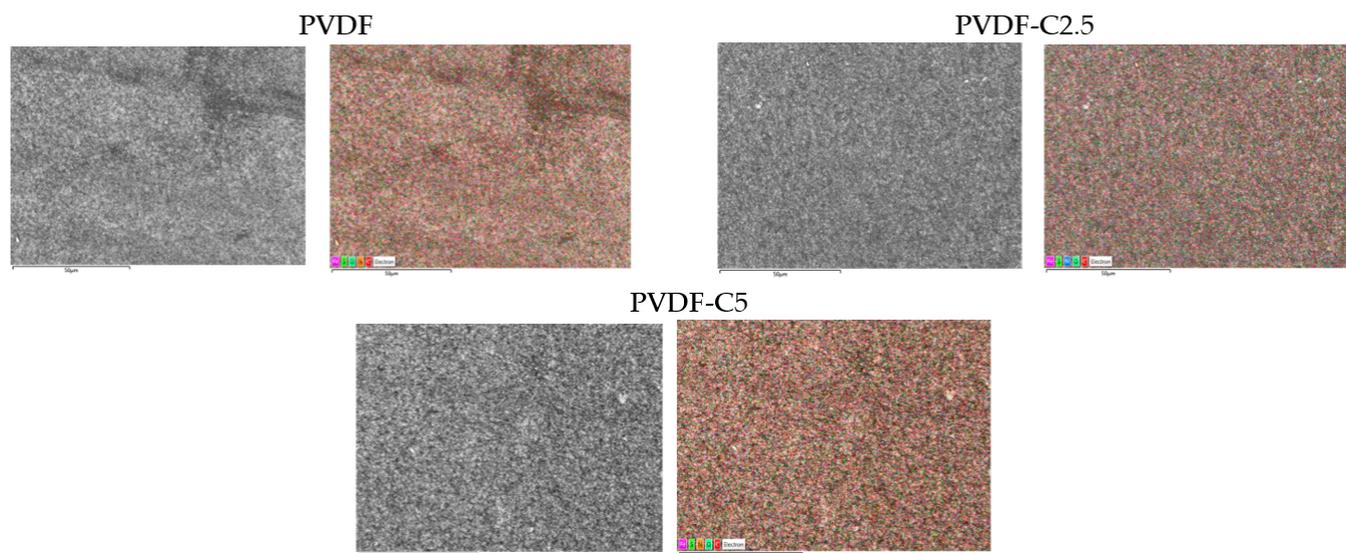


Figure 5. EDS mapping of each membrane.

Table 1. The elemental composition of each membrane was obtained by EDS spectroscopy on the surface of the SEM sample.

Membrane	Relative Composition (%)		
	C	O	O/C
PVDF	79.95	19.54	0.244
PVDF-C2.5	77.11	22.51	0.292
PVDF-C5	77.82	21.80	0.280

Figure 5 demonstrates that the relative amount of C decreases while the amount of O elements rises, as the O/C ratio for PVDF, PVDF-C2.5 and PVDF-C5 were 0.244, 0.292 and 0.280, respectively. The earlier hypothesis of a greater retention of TA–Fe in the modified membrane matrix is supported by the rising relative amount of O components. A good distribution of the elements indicates a homogeneous membrane structure.

The presence of tannic acid on the surface of PVDF membranes has been found to have significant effects on the surface elemental composition, as confirmed in earlier reports. Tannic acid coatings on PVDF membranes have been shown to reduce the membrane's water contact angle, indicating changes in the surface chemistry [18]. X-ray photoelectron spectroscopy spectra analyses of modified PVDF membranes with tannic acid have revealed alterations in the surface elemental composition [25]. Additionally, the addition of metal ions to tannic acid/polyethyleneimine coatings on PVDF membranes has been found to result in a denser and more stable coating layer, potentially due to the coordination bonds formed between the coating and metal ions [15]. These findings highlight the impact of tannic acid on the surface elemental composition of PVDF membranes.

3.1.4. Surface Hydrophilicity

Figure 6 depicts the effects of TA–Fe coating on the PVDF membrane’s wettability, as represented by the water contact angle (WCA). The membrane surface composition was significantly altered by the coating TA–Fe, as clearly shown by the membrane’s hydrophilicity properties. Xue et al. (2021) reported that the increase in surface wettability was a result of the decrease in the WCA [26]. The pristine PVDF membrane had a greater WCA than both PVDF-C2.5 and PVDF-C5. A longer coating duration in the tannic acid and Fe solution resulted in a lower WCA, as seen from the WCA data of PVDF-5 and PVDF-C2.5. The drop in WCA demonstrates that the modified membranes’ hydrophilicity improved categorically. The TA–Fe complex network endowed the membrane with surface-rich oxygen groups, which aid in forming a hydrated layer by forming hydrogen bonds with water molecules. This hydration layer reduced direct contact between the NOM and the membrane surface, which improved the fouling resistance of the membrane. This hydration layer is the primary cause of the membrane’s significantly changed hydrophilicity before and after the modification, as discussed elsewhere [4].

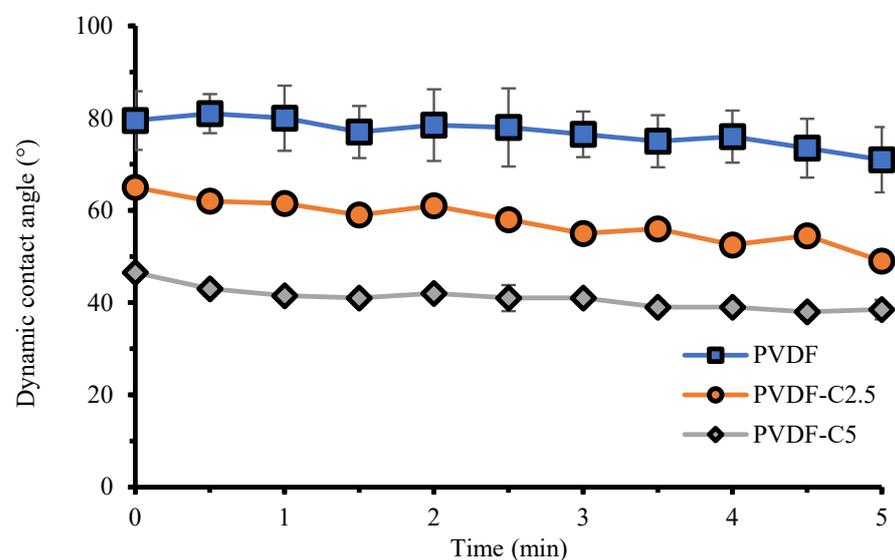


Figure 6. Dynamic water contact angle formed on the membrane surface as measured by the sessile-drop method.

The effect of tannic acid coating on the hydrophilicity of PVDF membranes has been extensively studied in earlier works, with the overall results agreeing with those of the present study. The polyphenolic compound in tannic acid has been shown to enhance the hydrophilicity of PVDF membranes, leading to improved water contact angles. Chheang et al. (2022) [18] found that tannic acid coating on PVDF membranes reduced the water contact angle by 17–27%, depending on the concentration of tannic acid. This indicates that tannic acid treatment can significantly increase the hydrophilicity of PVDF membranes. Furthermore, Wu et al. (2019) [15] developed a stable and anti-fouling PVDF membrane by surface coating tannic acid, polyethyleneimine (PEI), and metal ions. The resulting membrane exhibited improved hydrophilicity and anti-fouling properties, making it suitable for various filtration applications. In addition, Kan et al. (2023) successfully prepared a tannic acid–Fe@PVDF nanocomposite membrane by coating Fe^{3+} and tannic acid on the surface of PVDF membranes [27]. This nanocomposite membrane showed the positive effect of tannic acid on the hydrophilicity and separation efficiency of PVDF membranes. Overall, the research suggests that a tannic acid coating can significantly enhance the hydrophilicity of PVDF membranes. This improvement in hydrophilicity can lead to reduced fouling, as also proven in this work.

3.2. Membrane Filtration Performance

3.2.1. Clean Water Permeability

Figure 7 shows that the CWP of the modified membranes (PVDF-C2.5 and PVDF-C5) were lower than those of the pristine membrane. The decrease in the CWP could be attributed to the swelling of the hydrophilic segment on the pore wall, arising from a significant quantity of TA-Fe remaining in the membrane matrix, constricting the flow path of water permeation across the membrane pores. When water permeates, it moistens the hydrophilic segments in the membrane matrix, causing them to expand and reducing their flow paths, lowering the CWP, as reported elsewhere [20].

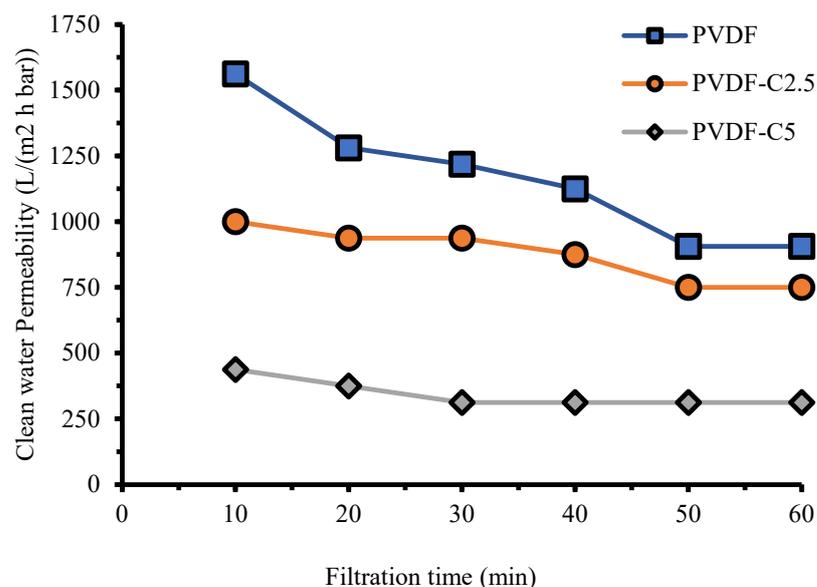


Figure 7. Clean water permeability of each membrane.

As shown in Figure 7, the CWP loss due to compaction was less for the coated membranes. The coated layer on top of the membrane surface and the pore walls seemed to enhance the PVDF matrix stiffness, resulting in lower compaction [28]. The tannic acid could fill in the PVDF matrix voids and prevent it from being compressed due to the applied trans-membrane pressure. The swollen hydrophilic segment could also form elastic hydrophilic segments that could absorb the force of the applied trans-membrane pressure.

Tannic acid coating has been found to have a significant effect on the clean water permeability of PVDF membranes. Mulyati et al. (2022) [7] focused on the fabrication of PVDF membranes with enhanced pore and filtration properties, using tannic acid as an additive. The study found that the addition of tannic acid increased the bulk porosity, water uptake, and hydrophilicity of the membranes. This resulted in an improved clean water flux of the tannic acid-modified membranes, which was 3.3 times higher than that of the pristine PVDF membrane. Another study by Nawi et al. (2021) [29] investigated the development of PVDF membranes via vapor-induced phase separation (VIPS), by incorporating a hydrophilic additive. The study found that the best performing membrane showed an elevation of 84% in clean water permeability compared to the pristine PVDF membrane. The increased clean water permeability was attributed to the incorporation of tannic acid in the membrane. Furthermore, Chheang et al. (2022) [18] found that tannic acid coating on PVDF membranes enhanced the clean water permeability. These reports suggest that the tannic acid coating on PVDF membranes can improve clean water permeability by increasing membrane hydrophilicity and pore properties. The addition of tannic acid enhances the bulk porosity, water uptake, and hydrophilicity of the membranes, leading to improved clean water flux.

3.2.2. River Water Permeability

Figure 8 displays the RWP of each membrane, showing the ability of the coated membrane to recover from membrane fouling. The CWP is considered steady after one hour of compaction, followed by one hour of CWP filtration. The drop from the final reading of CWP in Figure 7 could then be used as a benchmark to assess the permeability loss brought on by the membrane fouling. Compared to PVDF-C2.5 and PVDF-C5, PVDF exhibited the highest ultimate permeability out of the river water filtrations. The high RWP was caused by the larger pore diameter and the absence of swelling. As discussed earlier, a significant drop in permeability was found for all membranes, which may have been caused by the formation of membrane fouling, preventing water from penetrating [4]. Moreover, due to the reduction in pore size, as seen in the SEM image, the flux of river water was reduced for the modified PVDF membranes.

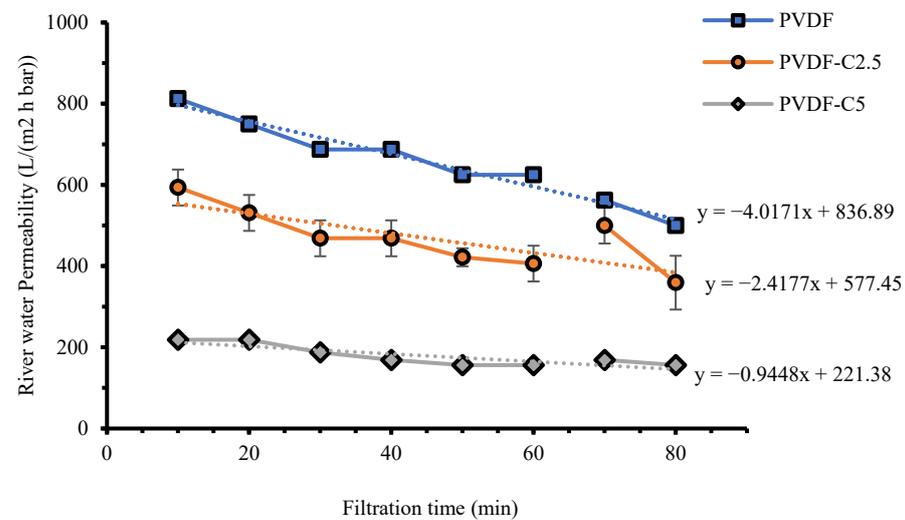


Figure 8. River water permeability.

The positive effect of tannic acid coating on increasing the filtration performance of PVDF membranes has been well documented in the literature, confirming the findings of the present study. Singhal et al. (2020) [30] focused specifically on the development of tannic acid-crosslinked graphene oxide membranes for the treatment of oil-contaminated water. The researchers found that the tannic acid coating improved the stability and efficiency of the membranes in removing oil and turbidity from water. Chheang et al. (2022) [18] reported that hydrophilic surface modification via tannic acid coating enhanced the filtration performance of membranes by reducing fouling and improving permeability. Overall, the literature supports the positive effect of tannic acid coating on increasing the filtration performance of PVDF membranes. The coating improves the hydrophilicity of the membrane surface, reduces fouling, and enhances stability. These findings have important implications for various membrane technologies, including water treatment, oil–water separation, and the filtration of feed containing NOM, as confirmed by the results of the present study.

3.2.3. NOM Rejection

Figure 9 shows the separation efficiency of the pristine and developed membranes. The relationship between water flux and solute rejection is frequently inversely correlated with the characteristics of the membrane pore: large pores lead to low rejection but high flux, and vice versa [7]. The NOM rejection of pristine PVDF, PVDF-C2.5, and PVDF-C5 had respective separation efficiencies of 82.2%, 95.6%, and 100%. The developed membranes have a high separation efficiency and only require low operating pressure. It is noteworthy that the membrane preparation process uses raw materials very effectively. As a result, the membrane developed here has great potential for usage in real applications.

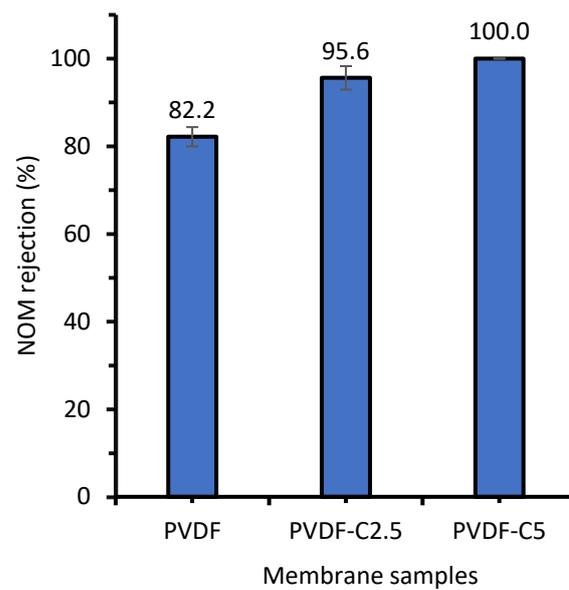


Figure 9. Rejection of natural organic matter.

The PVDF-C5 membrane displayed the highest NOM rejection, fully rejecting the NOM, followed by PVDF-C2.5 and the pristine PVDF membrane. This high rejection can be attributed to the smaller pore size, as shown in the surface SEM images and the high hydrophilicity. Small pores restrict the permeation of solutes (i.e., NOM) with larger sizes and retain them in the feed side. The hydrophilic nature of the membrane limits the interaction of the NOM materials with the membrane surface. The internal hydrophilicity of PVDF-C5 could limit NOM transport across the membrane matrix and contribute to significant rejection. Unfortunately, the high hydrophilicity also led to a swelling impact, reducing permeability, as discussed elsewhere [20]. The high rejection of NOM for the TA-Fe coated membrane suggests the potential of this approach to developing a membrane targeted for NOM removal. However, the decrease in RWP indicates the need for further optimization.

3.2.4. Fouling Resistance Analysis

Figure 10 shows the fouling reversibility (FR) results for all membranes, highlighting the benefit of modified membranes with higher FR values. FR is frequently employed to measure a membrane's ability to recover flux performance following membrane flushing. By looking at how easily a fouled membrane can be removed via simple flushing, the FR also reveals the cleanability of a membrane [7]. Negative FR means that simply flushing with the feed could not restore permeabilities, but could further consolidate the fouling and increase the filtration resistance. The positive FR values indicate the effectiveness of the water flushing in partially removing the foulant, in which an FR of 100% represents the full recovery performance.

Figure 10 shows that PVDF-C2.5 had the highest FR. A simple flushing could remove almost a quarter of the fouling resistance for the PVDF-2.5 membrane. The PVDF-C5 membrane showed a lower FR, and the pristine PVDF showed a negative FR. The findings clearly show the advantages of the fouled membrane in handling the fouling. As can be seen from FR after flushing with water, NOM particles on the pristine PVDF membrane surface caused the initial water permeability after flushing to be lower than the final permeability of the water filtering before flushing. The FR became negative, indicating that the pristine PVDF membrane lacked anti-fouling properties. Instead of removing the foulant, flushing the water helped the foulant to consolidate, forming a denser layer and higher resistance. Conversely, the TA-Fe-coated membranes (PVDF-C2.5 and PVDF-C5) showed positive FR values of 23.1% and 8%, respectively, exhibiting anti-fouling capabilities.

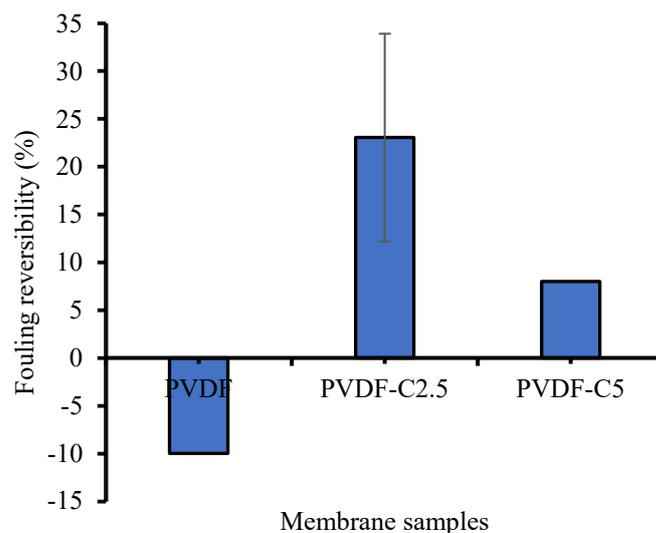


Figure 10. Permeance recovery after flushing with water.

It is worth noting that a long-term filtration involving multiple filtration and cleaning cycles could not be done in this study because of the limited volume of the river water samples. A limited sample volume might not represent the entire river water system, especially if the river shows temporal changes in water quality. NOM characteristics can vary over time due to seasonal changes, rainfall events, human activities, and other factors. A limited sample might not capture this variability. With a limited volume of river water, studying the longevity and saturation point of the tannic acid-coated PVDF membrane might be challenging. Over time, as the membrane gets used, the efficiency of NOM removal could decrease. However, by evaluating the RWF and FR values, the PVDF-C2.5 is expected to show better long-term performance by maintaining a high RWF when combined with an intermittent RWF recovery via regular membrane cleanings (i.e., flushing, backwashing, chemical aids cleanings, etc.).

Recycling PVDF membranes is a crucial step towards sustainable membrane technology, considering the environmental concerns related to the disposal of used membranes. The recycling process for PVDF membranes typically involves steps such as collection and pre-treatment, depolymerization, separation, repolymerization, membrane fabrication and quality checks. Researchers continuously improve the recycling processes to make them more efficient and eco-friendly. Practically, a membrane can be used over 3–12 years, depending on the nature of the operation. Enhancing the sustainability of membrane materials is a research topic that has attracted great interest recently.

4. Conclusions

This study has revealed that coating a PVDF membrane using TA–Fe altered the material properties and filtration performance when evaluated for the filtration of river water containing high NOM concentrations. TA–Fe assembly could be developed via consecutive coatings, as proven by the SEM images, the FTIR spectra, and elemental mapping via EDS. The TA–Fe coating introduced a hydrophilic segment (i.e., non-polar groups) into a hydrophobic PVDF matrix. This made it more hydrophilic, as shown by a decrease in water contact angle, and at the same time, lowered the surface pore size and CWP. When evaluated for the filtration of NOM containing river water, the NOM rejection rates of the pristine PVDF, PVDF-C2.5 and PVDF-C5 were 82.2%, 95.6%, and 100%, respectively. Unlike the pristine PVDF membrane with a negative FR, the TA–Fe-coated membranes (PVDF-C2.5 and PVDF-C5) featured anti-fouling characteristics (with positive FR being the highest for PVDF-C2.5) of the scale desired to maintain long-term filtration performance. The overall findings suggest the effectiveness of a simple consecutive coating of tannic acid and Fe^{3+} to alter a PVDF membrane's properties and enhance its anti-fouling properties

for the filtration of real river water containing high concentrations of NOM. Developing PVDF membranes using tannic acid holds promise from economic and environmental perspectives. Economically, as a natural and sustainable material, tannic acid offers cost advantages. Environmentally, the utilization of tannic acid aligns with sustainability objectives. It diminishes chemical waste and energy consumption during production, reducing the carbon footprint. Furthermore, these membranes effectively remove contaminants from water, supporting cleaner water resources. Regarding the commercialization of these membranes, the prospects are highly promising. As environmental concerns and regulations continue to tighten, there is a growing demand for sustainable and eco-friendly technologies.

Author Contributions: Conceptualization, M.R.B. and N.S.; methodology, R.D., S.T. and K.F.; validation, M.S.A.B., M.R.B. and N.S.; formal analysis, R.D., N.S., S.T., M.S.A.B. and M.R.B.; investigation, R.D. and M.R.B.; data curation, R.D. and M.R.B.; writing—original draft preparation, R.D.; writing—review and editing, M.S.A.B., M.R.B. and N.S.; visualization, R.D. and M.R.B.; supervision, M.S.A.B.; funding acquisition, N.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data available after request.

Acknowledgments: The authors would like to thank the Universiti Brunei Darussalam Graduate Scholarship (UGS) for the financial support.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Ramirez, L.; Gentile, R.S.; Zimmerman, S.; Stoll, S. Behavior of TiO₂ and CeO₂ Nanoparticles and Polystyrene Nanoplastics in Bottled Mineral, Drinking and Lake Geneva Waters. Impact of Water Hardness and Natural Organic Matter on Nanoparticle Surface Properties and Aggregation. *Water* **2019**, *11*, 2–14. [CrossRef]
2. Health Canada, Guidance on Natural Organic Matter in Drinking Water, July 2020. Available online: <https://www.canada.ca/en/health-canada/services/publications/healthy-living/guidance-natural-organic-matter-drinking-water.html> (accessed on 14 November 2023).
3. Moustafa, I.H.; Bream, A.S.; Awaad, A.M.E.-S.; Nader, A.M.Y. Assessment of Disinfection By-Products Levels in Aga Surfacewater Plant and Its Distribution System, Dakhliya, Egypt. *Int. J. Adv. Res. Biol. Sci.* **2017**, *4*, 37–43. [CrossRef]
4. Xu, J.; Xie, A.; Sun, H.; Wu, Y.; Li, C.; Xue, C.; Cui, J.; Pan, J. Construction of Tannic Acid-Fe Complex Coated PVDF Membrane via Simple Spraying Method for Oil/Water Emulsion Separation. *Colloids Surf. A Physicochem. Eng. Asp.* **2023**, *671*, 131621. [CrossRef]
5. Ali, I.; Bamaga, O.A.; Gzara, L.; Bassyouni, M.; Abdel-Aziz, M.H.; Soliman, M.F.; Drioli, E.; Albeirutty, M. Assessment of Blend PVDF Membranes, and the Effect of Polymer Concentration and Blend Composition. *Membranes* **2018**, *8*, 13. [CrossRef] [PubMed]
6. Yardimci, A.I.; Kayhan, M.; Durmus, A.; Ai, Y.; Kayhan, M.; Durmus, A.; Aksoy, M.; Synthesis, T.O.; Yardimci, A.I.; Kayhan, M.; et al. Synthesis and Air Permeability of Electrospun PAN / PVDF Nanofibrous Membranes To Cite This Article Synthesis and Air Permeability of Electrospun PAN/PVDF Nanofibrous Membranes. *Res. Eng. Struct. Mater.* **2022**, *8*, 223–231.
7. Mulyati, S.; Aprilia, S.; Muchtar, S.; Syamsuddin, Y.; Rosnelly, C.M.; Bilad, M.R.; Samsuri, S.; Ismail, N.M. Fabrication of Polyvinylidene Difluoride Membrane with Enhanced Pore and Filtration Properties by Using Tannic Acid as an Additive. *Polymers* **2022**, *14*, 186. [CrossRef]
8. Yalcinkaya, F.; Siekierka, A.; Bryjak, M. Preparation of Fouling-Resistant Nanofibrous Composite Membranes for Separation of Oily Wastewater. *Polymers* **2017**, *9*, 679. [CrossRef]
9. Chen, F.; Ding, X.; Jiang, Y.; Guan, Y.; Wei, D.; Zheng, A.; Xu, X. Permanent Antimicrobial Poly(Vinylidene Fluoride) Prepared by Chemical Bonding with Poly(Hexamethylene Guanidine). *ACS Omega* **2020**, *5*, 10481–10488. [CrossRef]
10. Xing, J.; Zhang, G.; Jia, X.; Liu, D.; Wyman, I. Preparation of Multipurpose Polyvinylidene Fluoride Membranes via a Spray-Coating Strategy Using Waterborne Polymers. *ACS Appl. Mater. Interfaces* **2021**, *13*, 4485–4498. [CrossRef]
11. Brinke, T.E.; Achterhuis, I.; Reurink, D.M.; De Groot, J.; De Vos, W.M. Multiple Approaches to the Buildup of Asymmetric Polyelectrolyte Multilayer Membranes for Efficient Water Purification. *ACS Appl. Polym. Mater.* **2020**, *2*, 715–724. [CrossRef]
12. Yan, W.; Shi, M.; Dong, C.; Liu, L.; Gao, C. Applications of Tannic Acid in Membrane Technologies: A Review. *Adv. Colloid Interface Sci.* **2020**, *284*, 102267. [CrossRef]

13. Chiao, Y.H.; Chen, S.T.; Sivakumar, M.; Ang, M.B.M.Y.; Patra, T.; Almodovar, J.; Wickramasinghe, S.R.; Hung, W.S.; Lai, J.Y. Zwitterionic Polymer Brush Grafted on Polyvinylidene Difluoride Membrane Promoting Enhanced Ultrafiltration Performance with Augmented Antifouling Property. *Polymers* **2020**, *12*, 1303. [[CrossRef](#)] [[PubMed](#)]
14. Zhao, X.; He, C. Efficient Preparation of Super Antifouling PVDF Ultrafiltration Membrane with One Step Fabricated Zwitterionic Surface. *ACS Appl. Mater. Interfaces* **2015**, *7*, 17947–17953. [[CrossRef](#)]
15. Wu, L.; Lin, Q.; Liu, C.; Chen, W. A Stable Anti-Fouling Coating on PVDF Membrane Constructed of Polyphenol Tannic Acid, Polyethyleneimine and Metal Ion. *Polymers* **2019**, *11*, 1975. [[CrossRef](#)]
16. Li, M.; Wu, L.; Zhang, C.; Chen, W.; Liu, C. Hydrophilic and Antifouling Modification of PVDF Membranes by One-Step Assembly of Tannic Acid and Polyvinylpyrrolidone. *Appl. Surf. Sci.* **2019**, *483*, 967–978. [[CrossRef](#)]
17. Ghernaout, D. Natural Organic Matter Removal in the Context of the Performance of Drinking Water Treatment Processes—Technical Notes. *OALib* **2020**, *7*, 1–40. [[CrossRef](#)]
18. Chheang, M.; Hongprasith, N.; Ratanatawanate, C.; Lohwacharin, J. Effects of Chemical Cleaning on the Ageing of Polyvinylidene Fluoride Microfiltration and Ultrafiltration Membranes Fouled with Organic and Inorganic Matter. *Membranes* **2022**, *12*, 280. [[CrossRef](#)] [[PubMed](#)]
19. Zhu, B.; Wang, S.; Wang, L.; Yang, Y.; Liang, J.; Cao, B. Preparation of Hydroxyapatite/Tannic Acid Coating to Enhance the Corrosion Resistance and Cytocompatibility of AZ31 Magnesium Alloys. *Coatings* **2017**, *7*, 105. [[CrossRef](#)]
20. Naw, N.I.M.; Amat, S.O.; Bilad, M.R.; Nordin, N.A.H.M.; Shamsuddin, N.; Prayogi, S.; Narkkun, T.; Faungnawakij, K. Development of Polyvinylidene Fluoride Membrane via Assembly of Tannic Acid and Polyvinylpyrrolidone for Filtration of Oil/Water Emulsion. *Polymers* **2021**, *13*, 976. [[CrossRef](#)]
21. Tangarfa, M.; Semlali Aouragh Hassani, N.; Alaoui, A. Behavior and Mechanism of Tannic Acid Adsorption on the Calcite Surface: Isothermal, Kinetic, and Thermodynamic Studies. *ACS Omega* **2019**, *4*, 19647–19654. [[CrossRef](#)] [[PubMed](#)]
22. Espina, A.; Cañamares, M.V.; Jurašková, Z.; Sanchez-Cortes, S. Analysis of Iron Complexes of Tannic Acid and Other Related Polyphenols as Revealed by Spectroscopic Techniques: Implications in the Identification and Characterization of Iron Gall Inks in Historical Manuscripts. *ACS Omega* **2022**, *7*, 27937–27949. [[CrossRef](#)] [[PubMed](#)]
23. Syawaliah, S.; Arahman, N.; Riza, M.; Mulyati, S. The Influences of Polydopamine Immersion Time on Characteristics and Performance of Polyvinylidene Fluoride Ultrafiltration Membrane. In Proceedings of the 3rd Annual Applied Science and Engineering Conference (AASEC 2018), Banda Aceh, Indonesia, 12 September 2018; Volume 197. [[CrossRef](#)]
24. Hester, J.F.; Banerjee, P.; Won, Y.Y.; Akthakul, A.; Acar, M.H.; Mayes, A.M. ATRP of Amphiphilic Graft Copolymers Based on PVDF and Their Use as Membrane Additives. *Macromolecules* **2002**, *35*, 7652–7661. [[CrossRef](#)]
25. Zhao, X.; Xuan, H.; He, C. Enhanced Separation and Antifouling Properties of PVDF Ultrafiltration Membranes with Surface Covalent Self-Assembly of Polyethylene Glycol. *RSC Adv.* **2015**, *5*, 81115–81122. [[CrossRef](#)]
26. Xue, X.; Tan, G.; Zhu, Z. All-Polymer and Self-Roughened Superhydrophobic PvdF Fibrous Membranes for Stably Concentrating Seawater by Membrane Distillation. *ACS Appl. Mater. Interfaces* **2021**, *13*, 45977–45986. [[CrossRef](#)]
27. Kan, J.; Zhang, Z.; Ren, L.; Han, J.; Zhang, H.; Li, J.; Wu, H.; Chen, J. Hydrophilic Modification of PVDF Membranes for Oily Water Separation with Enhanced Anti-Fouling Performance. *J. Appl. Polym. Sci.* **2023**, *140*, e53538. [[CrossRef](#)]
28. Bilad, M.R.; Junaeda, S.R.; Khery, Y.; Nufida, B.A.; Shamsuddin, N.; Usman, A.; Violet, V. Compaction of a Polymeric Membrane in Ultra-Low-Pressure Water Filtration. *Polymers* **2022**, *14*, 3254. [[CrossRef](#)]
29. Naw, N.I.M.; Sait, N.R.; Bilad, M.R.; Shamsuddin, N.; Jaafar, J.; Nordin, N.A.H.; Narkkun, T.; Faungnawakij, K.; Mohshim, D.F. Polyvinylidene Fluoride Membrane via Vapour Induced Phase Separation for Oil/Water Emulsion Filtration. *Polymers* **2021**, *13*, 427. [[CrossRef](#)]
30. Singhal, A.V.; George, R.; Sharma, A.K.; Malwal, D.; Lahiri, I. Development of Superhydrophilic Tannic Acid-Crosslinked Graphene Oxide Membranes for Efficient Treatment of Oil Contaminated Water with Enhanced Stability. *Heliyon* **2020**, *6*, e05127. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.