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Synthesis and Characterization of Crosslinked Polysaccharide Derivative (O-Pul/Pei) Coatings for the Development of Modified Polyvinylidene Fluoride Membranes

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Abstract

This study investigated the synthesis, characterization, and performance evaluation of crosslinked oxidized pullulan/polyethyleneimine (O-Pul/PEI) coatings for the modification of polyvinylidene fluoride (PVDF) membranes. The research was conducted under controlled laboratory conditions simulating real-world water treatment challenges typical of the Suzhou region, using model foulants such as bovine serum albumin (BSA), humic acid, oil emulsions, and bacteria. A two-step dip-coating method was employed to fabricate modified membranes with varying PEI concentrations (0.2 - 0.5 wt.%). Oxidized pullulan was synthesized via sodium periodate oxidation to introduce reactive aldehyde groups, enabling covalent crosslinking with PEI through Schiff-base and Michael-type reactions. Membrane characterization was performed using scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and water contact angle (WCA) measurements to assess morphology, chemical structure, and hydrophilicity. The results confirmed the successful formation of a stable crosslinked coating, evidenced by the appearance of characteristic functional groups (C=N, C-N) and the emergence of O1s and N1s peaks in XPS spectra. SEM analysis revealed that an optimal PEI concentration (0.4 wt.%) produced a thin, uniform, and well-adhered coating layer, effectively modifying the membrane surface without compromising its structural integrity. This optimized membrane exhibited

enhanced hydrophilicity, improved surface smoothness, and superior antifouling performance. In contrast, lower PEI concentrations resulted in insufficient coating coverage, while excessive concentrations led to poor adhesion due to bulk crosslinking in solution. The study concludes that the O-Pul/PEI crosslinking system provides an effective, reproducible, and environmentally sustainable approach for enhancing PVDF membrane performance. The incorporation of hydrophilic functional groups significantly improves wettability and fouling resistance, making the modified membranes suitable for advanced water treatment applications. It is recommended that future studies focus on long-term performance evaluation, scale-up potential, and application under real industrial wastewater conditions. Additionally, further optimization of coating parameters and exploration of other biopolymer combinations could enhance multifunctional membrane properties for sustainable water purification technologies.

Keywords

PVDF Membrane Modification, Oxidized Pullulan (O-Pul), Polyethyleneimine (PEI), Schiff-Base Reaction, Hydrophilicity Enhancement, Antifouling Performance

1. Introduction

Polymers are high-molecular-weight macromolecules composed of numerous repeating structural units (monomers) linked predominantly by covalent bonds (Gedde et al., 2025; Haque et al., 2022; Gandini & Lacerda, 2021). Their structural characteristics vary according to the number and type of repeating monomer units, molecular architecture, sequence regularity, and degree of cross-linking, where individual polymer chains are interconnected through covalent bonds to form three-dimensional networks (Zheng et al., 2021; Jia et al., 2024). Based on their physicochemical properties, including density, crystallinity, tensile strength, molecular weight, hydrophobicity, surface charge, solubility, and thermal behaviour, polymers are broadly classified into synthetic polymers and natural polymers (biopolymers) (Parida et al., 2025; Maity et al., 2026; Gieroba et al., 2023).

Synthetic polymers have been extensively developed for industrial applications and include plastics (e.g., polyethylene and polystyrene), elastomers, adhesives, coatings, and synthetic fibres such as nylon and polyester (Geyer, 2020; Desidery & Lanotte, 2022). Their widespread use is attributed to their excellent mechanical properties, durability, and ease of processing. However, growing environmental concerns associated with their non-biodegradability and dependence on fossil resources have accelerated interest in renewable and environmentally sustainable biopolymers. Natural polymers are biosynthesized by plants, animals, fungi, algae, and microorganisms, and are generally characterized by their biodegradability, biocompatibility, renewability, and low toxicity, making them attractive for bio-

medical, environmental, and membrane separation applications (Kurowiak et al., 2023; Arif et al., 2019). Natural polymers are commonly classified into three major groups: polypeptides, polynucleotides, and polysaccharides (Khan et al., 2019). Among these, polysaccharides represent one of the most abundant and structurally diverse classes of biopolymers. They consist of monosaccharide units linked through O-glycosidic bonds and are synthesized by higher plants, algae, fungi, microorganisms, and animals (Trincone, 2018; Dharani et al., 2020). Their molecular diversity arises from different saccharide isomers, branching patterns, glycosidic linkages, and chemical substitutions such as amino, acetyl, phosphate, and carboxyl groups, which impart diverse physicochemical and biological properties (Reddy et al., 2021; Nandita et al., 2021). Common naturally occurring polysaccharides include cellulose, hemicellulose, starch, pectin, chitosan, dextran, glucan, carrageenan, xanthan gum, alginates, and glycosaminoglycans (Singh et al., 2023; Benalaya et al., 2024).

Polysaccharides possess numerous hydroxyl functional groups that allow them to undergo chemical modification through reactions such as etherification and esterification, thereby improving their physicochemical properties for specific applications. Etherification introduces ether linkages by reacting hydroxyl groups with carbon-containing molecules, whereas esterification forms ester bonds between hydroxyl and carboxyl groups. These modifications can alter hydrophilicity, mechanical strength, chemical stability, and intermolecular hydrogen bonding, enabling the design of advanced functional biomaterials (Wang et al., 2020; Kim & Jung, 2022). Owing to their abundance of hydroxyl, carboxyl, and amino groups, chemically modified polysaccharides have become promising candidates for membrane surface engineering because they can enhance surface hydrophilicity, improve water permeability, and reduce membrane fouling while maintaining environmental sustainability (Vatanpour et al., 2022). Among polymeric membrane materials, polyvinylidene fluoride (PVDF) has attracted considerable attention because of its excellent chemical resistance, thermal stability, mechanical strength, film-forming ability, and compatibility with a wide range of membrane fabrication and surface modification techniques (Teng et al., 2026; Li et al., 2025; Zhang et al., 2026). These outstanding properties have made PVDF one of the most widely used membrane materials in microfiltration and ultrafiltration for water purification, wastewater reclamation, oil-water separation, and numerous environmental applications. Nevertheless, the long-term operational performance of PVDF membranes is significantly constrained by membrane fouling, which remains one of the major challenges affecting membrane efficiency, permeability, cleaning frequency, and service life (Wu et al., 2026; Lin et al., 2025). In practical water treatment systems, PVDF membranes are continuously exposed to a wide variety of foulants, including proteins, natural organic matter, humic substances, polysaccharides, oils, colloids, inorganic precipitates, and microorganisms (Sisay et al., 2023; Nie et al., 2025). These contaminants adhere to membrane surfaces through hydrophobic interactions, hydrogen bonding, electrostatic attraction,

and physical deposition. Because pristine PVDF is inherently hydrophobic and possesses relatively low surface energy, it readily adsorbs organic foulants such as bovine serum albumin (BSA), humic acid, oil droplets, and microbial cells, leading to severe membrane fouling, reduced permeate flux, increased operational costs, and shortened membrane lifespan (Nthunya et al., 2019; Chakraborty et al., 2025; Nie et al., 2025). To address these limitations, improving membrane surface hydrophilicity has become one of the most effective strategies for mitigating membrane fouling. Natural polysaccharides have emerged as particularly attractive coating materials because they are renewable, biodegradable, environmentally benign, and rich in hydrophilic functional groups capable of forming stable hydration layers on membrane surfaces (Kocira et al., 2021; Pillai et al., 2024). The hydration layer acts as both a physical and energetic barrier that minimizes direct contact between foulants and the membrane surface, thereby reducing foulant adhesion, enhancing antifouling performance, improving cleaning efficiency, and maintaining long-term membrane permeability (Lang et al., 2026; Yuan et al., 2026). Among the various polysaccharide-based surface modification strategies, cross-linked coatings prepared from oxidized pullulan (O-Pul) and polyethyleneimine (PEI) have demonstrated considerable potential because of their ability to combine the hydrophilicity of polysaccharides with the abundant amine functionality of PEI, resulting in robust, highly hydrophilic, and chemically stable membrane coatings. Previous studies have shown that polysaccharide-derived and amine-containing coatings significantly improve membrane wettability, permeability, and antifouling behaviour. However, the specific role of PEI concentration in regulating the formation, cross-linking density, surface morphology, and separation performance of O-Pul/PEI coatings on PVDF membranes remains insufficiently understood (Tassakan et al., 2026; Jiang et al., 2025). Therefore, this study focuses on the development and characterization of O-Pul/PEI-modified PVDF membranes to investigate the influence of PEI concentration on coating formation, membrane surface properties, hydrophilicity, permeability, and antifouling performance. By optimizing the cross-linked polysaccharide coating, the study aims to develop highly efficient and environmentally sustainable PVDF membranes capable of improving water flux, reducing membrane fouling, and enhancing separation efficiency for advanced water and wastewater treatment applications.

2. Research Methodology

2.1. Description of the Study Area

This study was conducted at the Membrane Materials and Water Treatment Laboratory, School of Environmental Science and Engineering, Suzhou University of Science and Technology (SUST), located in Suzhou, Jiangsu Province, China. The laboratory provides advanced facilities for membrane fabrication, surface modification, and performance evaluation under controlled conditions. Suzhou lies in the Yangtze River Delta region (30˚47' - 32˚02'N, 119˚55' - 121˚20'E), an area characterized by extensive water networks and proximity to Taihu Lake. The

region experiences a subtropical monsoon climate, with average temperatures of 15˚C - 17˚C and annual rainfall of 1000 - 1200 mm. These warm and humid conditions promote microbial growth, making membrane fouling a significant challenge in water treatment systems. The study area is highly relevant due to water quality issues such as organic pollution, oil-water emulsions, natural organic matter, and microbial contamination associated with rapid industrialization and urbanization. Although experiments were conducted in the laboratory, they simulated real-world conditions using common foulants such as BSA, humic acid, oil emulsions, and bacteria.

2.2. Chemicals, Instruments, and Experimental Context

All chemicals used in this study were of analytical grade and used as received without further purification. Pullulan was purchased from Macklin Biochemical Co., Ltd. (China), while hydrophobic polyvinylidene fluoride (PVDF) membranes (0.45 μm pore size, 47 mm diameter), sodium periodate ($NaIO_4$), sodium hydroxide (NaOH), calcium chloride ($CaCl_2$), and ethylene glycol were obtained from Tansoole. Branched polyethyleneimine (PEI) with an average molecular weight of approximately 25,000 Da was supplied by Sigma-Aldrich (USA). Deionized water was used throughout the study for solution preparation, oxidation reactions, membrane coating, and washing procedures.

The experimental work was conducted at the Membrane Materials and Water Treatment Laboratory, School of Environmental Science and Engineering, Suzhou University of Science and Technology (SUST), Suzhou, Jiangsu Province, China. The study focused on the synthesis of oxidized pullulan (O-Pul), fabrication of O-Pul/PEI-coated PVDF membranes, and evaluation of the influence of PEI concentration on membrane surface modification.

Membrane characterization was performed using several analytical techniques. Fourier Transform Infrared Spectroscopy (FTIR) was used to identify functional groups and confirm chemical modifications on the membrane surface, while X-ray Photoelectron Spectroscopy (XPS) was employed to determine surface elemental composition and chemical states. Scanning Electron Microscopy (SEM) was used to examine membrane surface morphology and coating uniformity, and a contact angle goniometer was utilized to evaluate membrane hydrophilicity by measuring water contact angles. Standard laboratory glassware, including beakers, was used for solution preparation, oxidation, and dip-coating processes, whereas Petri dishes were employed for antibacterial evaluation through zone-of-inhibition tests.

The scope of the investigation was limited to laboratory-scale membrane fabrication and physicochemical characterization. Performance evaluations focused on membrane surface properties, including wettability, coating formation, antifouling behaviour, and antibacterial activity, rather than pilot-scale or full-scale water treatment applications. This controlled laboratory approach enabled systematic investigation of the effects of PEI concentration on the structure and surface per-

formance of O-Pul/PEI-coated PVDF membranes.

2.3. Determination of the Aldehyde Content and Degree of Oxidation of Oxidized Pullulan (O-Pul)

The aldehyde content and degree of oxidation (DO) of oxidized pullulan (O-Pul) were determined using the hydroxylamine hydrochloride titration method, a widely accepted technique for quantifying aldehyde groups in dialdehyde polysaccharides (Bruneel & Schacht, 1993). In this method, aldehyde groups in O-Pul react quantitatively with hydroxylamine hydrochloride to form oximes, releasing an equimolar amount of hydrochloric acid (HCl), according to the following reaction:

$$R - CHO + NH_2OH{\cdot}HCl \rightarrow R - CH = NOH + HCl + H_2O$$

The liberated HCl was titrated with standardized sodium hydroxide (NaOH), and the volume of NaOH consumed was used to determine the aldehyde content of the oxidized polymer.

The aldehyde content (mmol·g^{-1}) was calculated using:

$$\text{Aldehyde Content} = (V_s - V_b) \times CNaOH/m$$

where (V_s) is the volume of NaOH consumed by the sample (L), (V_b) is the volume consumed by the blank (L), (CNaOH = nNaOH/VNaOH) is the NaOH concentration (mol·L^{-1}), and (m) is the mass of O-Pul (g). The results were expressed as millimoles of aldehyde per gram of O-Pul (mmol·g^{-1}).

The degree of oxidation (DO) was calculated by relating the number of aldehyde groups formed to the number of pullulan anhydroglucose units (AGU; molecular weight = 162 g·mol^{-1}), assuming a theoretical maximum of two aldehyde groups per oxidized AGU:

$$DO = VNaOH \times NNaOH/2 \times (m/162)$$

The degree of oxidation was expressed either as mol aldehyde per mol AGU or as percentage oxidation:

$$DO\ (\%) = DO \times 100$$

2.4. Membrane Filtration and Antifouling Performance

The filtration and antifouling performance of the pristine and O-Pul/PEI-modified PVDF membranes were evaluated using a laboratory-scale dead-end filtration system with an effective membrane area of 33.18 cm^2 (0.003318 m^2). Prior to testing, each membrane was compacted with deionized water at 1.5 bar for 30 min to stabilize the membrane structure and permeate flux. The operating pressure was subsequently reduced to 1.0 bar, and the pure water permeate flux was determined using:

$$J = \Delta V/A \times \Delta t$$

where J is the permeate flux (L·m^{-2}·h^{-1}), ΔV is the permeate volume (L), A is the effective membrane area (0.003318 m^2), and Δt is the filtration time (h).

The antifouling properties of the membranes were assessed using 1.0 g·L^{-1} bo-

vine serum albumin (BSA) as a model protein foulant in a cross-flow filtration system operated at 0.15 MPa. The initial pure water flux (J_{w1}) was measured after membrane compaction, followed by filtration of the BSA solution to obtain the fouling flux (J_p). Flux values were recorded at 5-minute intervals until a steady state was achieved. After fouling, the membranes were rinsed thoroughly with distilled water for 30 min, and the recovered pure water flux (J_{w2}) was measured to evaluate membrane cleaning efficiency.

Membrane fouling behaviour was assessed using the normalized flux, flux recovery ratio (FRR), total fouling ratio (R_t), reversible fouling ratio (R_r), and irreversible fouling ratio (R_{ir}), calculated using the following equations:

$$\text{Normalized Flux} = J_p/J_{w1}$$

$$F_{rr} = J_{w2}/J_{w1} \times 100\%$$

$$R_t = (J_{w1} - J_f)/J_{w1} \times 100\%$$

$$R_r = (J_{w2} - J_f)/J_{w1} \times 100\%$$

$$R_{ir} = (J_{w1} - J_{w2})/J_{w1} \times 100\%$$

where J_{w1} is the initial pure water flux before fouling, J_p is the flux during BSA filtration, and J_{w2} is the pure water flux after membrane cleaning.

The O-Pul/PEI-modified PVDF membranes were expected to exhibit enhanced filtration performance compared with pristine PVDF due to the formation of a hydrophilic coating that promotes water transport, minimizes protein adsorption, and suppresses irreversible fouling. Consequently, the modified membranes are anticipated to demonstrate higher permeate flux, greater flux recovery, and lower irreversible fouling, indicating improved long-term operational stability for water treatment applications.

2.5. Membrane Pretreatment, O-Pul Synthesis, Membrane Fabrication, and Characterization

The study focused on the fabrication and surface modification of polyvinylidene fluoride (PVDF) membranes using oxidized pullulan (O-Pul)/polyethyleneimine (PEI) coatings to improve membrane hydrophilicity, antifouling behaviour, antibacterial properties, and surface stability for potential water treatment and wastewater reuse applications. All experimental work was conducted under laboratory conditions at the Membrane Materials and Water Treatment Laboratory, Suzhou University of Science and Technology (SUST), China.

2.5.1. Membrane Pretreatment and Fabrication

Pristine hydrophobic PVDF membranes (0.45 μm pore size, 47 mm diameter) were first immersed in ethanol for 30 min to remove residual contaminants, thoroughly rinsed with deionized water, and designated as M0 (**Figure 1**). Surface modification was then carried out using a simple two-step dip-coating method. The pretreated membranes were immersed in a 2.5 wt.% O-Pul solution for 1 min at room temperature and immediately transferred into PEI solutions with concentrations of 0.2, 0.3, 0.4, and 0.5 wt.% for an additional 1 min. The coated mem-

branes were dried at 40˚C for 15 min to stabilize the crosslinked coating layer and subsequently immersed in deionized water for more than 24 h, with the washing solution replaced every 12 h to remove unreacted chemicals. The resulting membranes were designated M1, M2, M3, and M4, corresponding to increasing PEI concentrations.

Membrane Name	O-Pul (wt%)	PEI (wt%)
M0	0	0
M1	2.5	0.2
M2	2.5	0.3
M3	2.5	0.4
M4	2.5	0.5

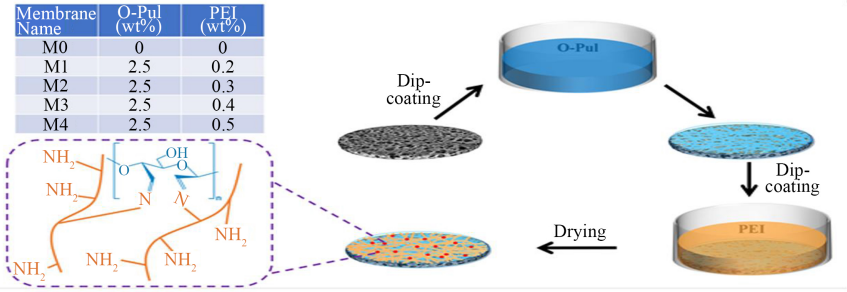

Figure 1. Membrane fabrication and characterization.

2.5.2. Synthesis of Oxidized Pullulan (O-Pul)

Oxidized pullulan was synthesized by sodium periodate oxidation. Briefly, 4 g of pullulan was dissolved in 70 mL of deionized water at 40˚C, and the solution pH was adjusted to 4.0. A sodium periodate solution (1.2 g in 30 mL deionized water) was then added, and the reaction mixture was stirred in the dark at 40˚C for 4 h. Oxidation was terminated by adding ethylene glycol, after which anhydrous $CaCl_2$ was introduced to precipitate calcium iodate. The precipitate was removed by filtration, and the product was purified by dialysis followed by freeze-drying to obtain O-Pul. Successful oxidation and aldehyde formation were confirmed using FTIR, XPS, and aldehyde titration (**Figure 2**).

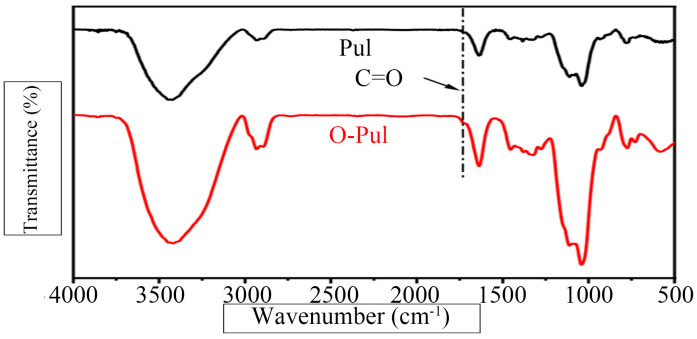

Figure 2. The FTIR spectrum of synthesized Pul, O-Pul.

2.5.3. Crosslinking and Membrane Characterization

The O-Pul coating was crosslinked with branched PEI (Mw ≈ 25,000 Da) through Schiff-base (imine) formation and Michael-type reactions between aldehyde and amine groups, producing a stable hydrophilic coating on the PVDF membrane surface (**Figure 3**). The influence of PEI concentration on coating formation and membrane performance was investigated.

The modified membranes were characterized using Scanning Electron Micros-

copy (SEM) to examine surface and cross-sectional morphology, Fourier Transform Infrared Spectroscopy (FTIR) to identify functional groups and confirm chemical bonding, and X-ray Photoelectron Spectroscopy (XPS) to determine surface elemental composition and verify successful coating formation. Membrane hydrophilicity was evaluated using a water contact angle (WCA) goniometer, while coating stability was assessed under sonication, varying pH, saline conditions, and thermal stress. These characterization techniques provided comprehensive information on coating morphology, chemical composition, wettability, and stability, enabling evaluation of the effects of PEI concentration on the physicochemical properties and surface performance of the modified PVDF membranes.

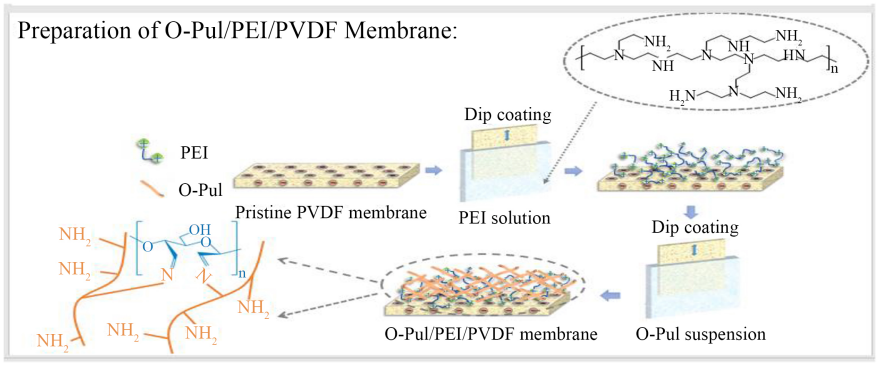

Figure 3. Dip coating of pristine PVDF into O-Pul/PEI solution.

3. Results and Discussion

3.1. Spectroscopic and Morphological Evidence of Successful O-PUL/PEI Crosslinked Coating Formation

FTIR confirmed successful pullulan oxidation (new 1733 cm^{-1} band) and formation of the crosslinked network (broad 3400 - 2800 cm^{-1} band from O-H/N-H overlap; new bands at ≈1472 and 1560 cm^{-1} linked to N-H and C-N vibrations), consistent with Schiff-base formation (Luís et al., 2020; Gaffney et al., 2012). XPS showed the emergence of O1s and N1s peaks on coated surfaces and increasing C=O/C-O contributions with coating ratio, while high-resolution N1s spectra revealed −NH/−NH_2, C-N, and C=N species (evidence of covalent crosslinking). SEM images displayed a thin, uniform coating layer for intermediate PEI concentrations (e.g., M3, 0.4 wt.%), whereas excessive PEI led to poorer adhesion and the reappearance of pores likely due to homogeneous crosslinking in solution rather than on the surface, indicating an optimal PEI window for *in-situ* coating formation (Song et al., 2020; Zhou et al., 2022.) Collectively, chemical and morphological analyses demonstrate that the controlled oxidation of pullulan yields reactive aldehyde groups and that PEI crosslinking produces a stable network on substrates (Reddy et al., 2022; Agrawal et al., 2022). The spectroscopic signatures (C=N and C-N formation) and XPS elemental changes indicate successful surface chemistry modification, rather than mere physisorption, which explains the improved durability in subsequent stability tests (Marsotto et al., 2023; Yuan et al.,

2021).

3.2. SEM Analysis of Surface Morphology of Pristine and O-Pul/PEI Modified PVDF Membranes

The surface morphology of the pristine PVDF membrane and those coated with various modifications was examined using SEM, focusing on both the top surface and cross-sectional views. As shown in **Figures 4(a1)-(a3)**, the pristine PVDF membrane displays a porous structure with a smooth framework. However, its top surface is irregular, which negatively affects its anti-fouling capabilities. In contrast, after the deposition of O-Pul and cross-linking with PEI on the membrane surface, noticeable differences among the coated membranes are apparent in **Figures 4(b1)-(e3)** as the PEI concentration varies. For M1, the low PEI concentration used as the cross-linking agent causes minimal changes in the membrane's morphology, which is also reflected in the subsequent water flux measurements. As the O-Pul concentration remains steady and the PEI concentration increases, noticeable changes in the surface pore structure of M3 can be seen. The modifier successfully adheres to the original PVDF membrane's skeleton without altering its basic structure at a PEI concentration of 0.4 wt.%. **Figure 4(d2)** shows that the surface of the modified membrane M3 no longer has visible pores. Additionally, **Figure 2(d3)** presents the SEM cross-sectional image of a thin, smooth, and uniform modified layer firmly bonded to the PVDF membrane after co-deposition of O-Pul and PEI. This confirms that the PVDF membrane surface has been effectively coated with O-Pul/PEI (Yu et al., 2023; Cao et al., 2020).

The likely reason for this is the formation of covalent bonds between the aldehyde groups of O-Pul and the amine groups of PEI through Michael addition and Schiff base reactions under the applied conditions. This strong interaction ensures the stable attachment of the O-Pul/PEI coating to the PVDF membrane, enhancing its structural integrity and anti-fouling properties. (Moreno et al., 2024). However, in **Figures 4(e1)-(e3)**, distinct pore structures reappear on the modified membrane. This phenomenon may be attributed to the high concentration of PEI. When the membrane, which had already undergone the first deposition of O-Pul, is immersed in the PEI solution, the rapid reaction rate between O-Pul and PEI causes the cross-linked material to form in the aqueous solution rather than firmly adhering to the membrane surface. As a result, the cross-linked material fails to stabilize on the membrane, leading to the reappearance of pores on the modified membrane surface. This suggests that an excessively high PEI concentration can hinder the effective formation of a stable coating, emphasizing the importance of optimizing the PEI concentration for successful membrane modification (Chen et al., 2020; Lv et al., 2018; Kim et al., 2025).

Selection of 0.4 wt.% PEI (M3) as the optimum coating concentration was based on an overall qualitative assessment of membrane surface characteristics, including coating continuity, uniformity, adhesion, and structural integrity, rather than surface morphology alone. M1 (0.2 wt.% PEI) exhibited limited surface modification

because the PEI concentration was insufficient to form a continuous crosslinked O-Pul/PEI layer. M2 (0.3 wt.% PEI) showed improved coating coverage; however, noticeable surface openings remained, indicating incomplete membrane coverage. In contrast, M3 (0.4 wt.% PEI) produced the most uniform, continuous, and well-adhered coating while preserving the underlying porous PVDF support structure, suggesting an optimal balance between crosslinking and surface deposition. At the highest concentration, M4 (0.5 wt.% PEI) exhibited partial pore reappearance and reduced coating stability, likely because excessive PEI accelerated bulk-solution crosslinking instead of controlled interfacial film formation. Consequently, 0.4 wt.% PEI (M3) was selected as the optimum formulation, as it provided the best balance between coating coverage, surface uniformity, membrane structural preservation, and expected filtration and antifouling performance.

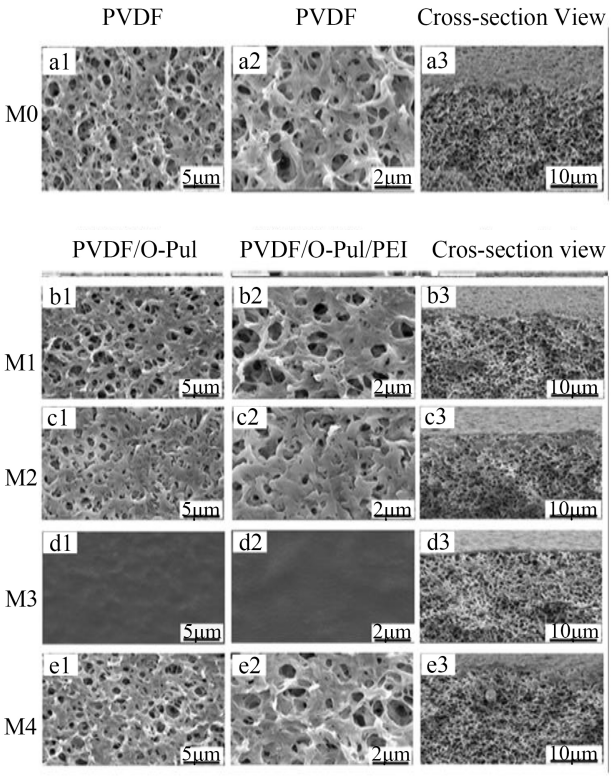

Figure 4. SEM images of the various modified and unmodified membranes.

3.3. FTIR and XPS Confirmation of Aldehyde Functionalization and Schiff-Base Crosslinking in O-Pul/PEI-Modified PVDF Membranes

In addition, the successful preparation of the coated membranes was further confirmed through surface physicochemical characterization using FTIR and XPS. The FTIR spectra of Pul and O-Pul are shown in **Figure 5**. Compared to Pul, O-Pul exhibits a characteristic peak at 1733 cm^{-1}, corresponding to the aldehyde (C=O) group. This peak confirms the successful aldehyde modification of Pul, indicating the introduction of aldehyde functional groups into the O-Pul struc-

ture. This modification is crucial for the subsequent cross-linking reactions with PEI, as the aldehyde groups enable the formation of covalent bonds with the amine groups of PEI through Schiff base reactions. The presence of this peak in the FTIR spectrum provides strong evidence for the chemical alteration of Pul and supports the effectiveness of the coating process (Luís et al., 2020; Verma, 2019; Shariatmadar et al., 2024). The test results confirm the successful introduction of aldehyde groups into pullulan. The FTIR spectra of the pristine PVDF membrane and the O-Pul cross-linked PEI-modified membrane (M3) are shown in **Figure 4**. Compared to the spectrum of the original PVDF membrane, the spectrum of M3 exhibits a broad peak in the range of 3400 - 2800 cm^{-1}, which is likely due to the overlapping stretching vibrations of hydroxyl (O-H) and amine (N-H) groups. Additionally, a new absorption peak at 1472 cm^{-1} corresponds to the N-H vibration, while a new peak at 1560 cm^{-1} is attributed to the C-N bond. These observations indicate that the amine groups in PEI and the aldehyde groups in O-Pul have formed chemical cross-links through Schiff base reactions, successfully coating the PVDF membrane (Kmetik et al., 2024; Ádám et al., 2025; Karimipour et al., 2021).

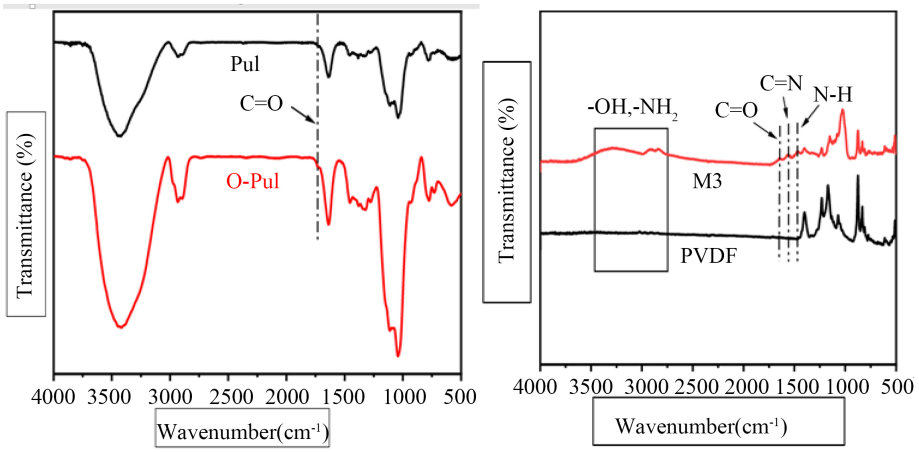

Figure 5. The FTIR spectrum of Pul, O-Pul, and M3.

3.4. Surface Chemical Characterization of O-Pul/PEI-Modified PVDF Membranes by XPS

As shown in **Figure 6**, compared to the XPS spectrum of the pristine PVDF membrane, which only shows C and F signal peaks, the XPS spectrum of the coated membrane reveals two new peaks corresponding to O 1s and N 1s. With increasing coating ratios, the high-resolution C1s spectrum shows a significant decrease in the area of the C-F bond while the areas of the C=O and C-O bonds steadily increase. Furthermore, the N1s signal peak of the coated membrane M3 was fitted using the Gaussian-Lorentzian algorithm, and the high-resolution XPS spectrum is presented in **Figure 6**. It was observed that the surface of the O-Pul and PEI-coated membrane primarily contains $-NH/-NH_2$, C-N, and C=N bonds (Zhang et al., 2017). The formation of the C=N bond is likely due to the Schiff base reac-

tion between the aldehyde groups of O-Pul and the amine groups of PEI. These findings align with the FTIR results, confirming that O-Pul and PEI were effectively coated on the membrane surface (Xie et al., 2023; Bandara et al., 2019; Teng, 2023). These observations demonstrate that the dip-coating method is effective, rapid, and compatible with mild conditions. Performance, including hydrophilicity, flux, and fouling resistance, correlates strongly with coating morphology. A continuous film (M3) exhibits the most pronounced hydrophilic effect and superior antifouling performance with coatings that are too thin (M1) or poorly adhered (M4) underperform (Xie et al., 2023; Teng, 2023).

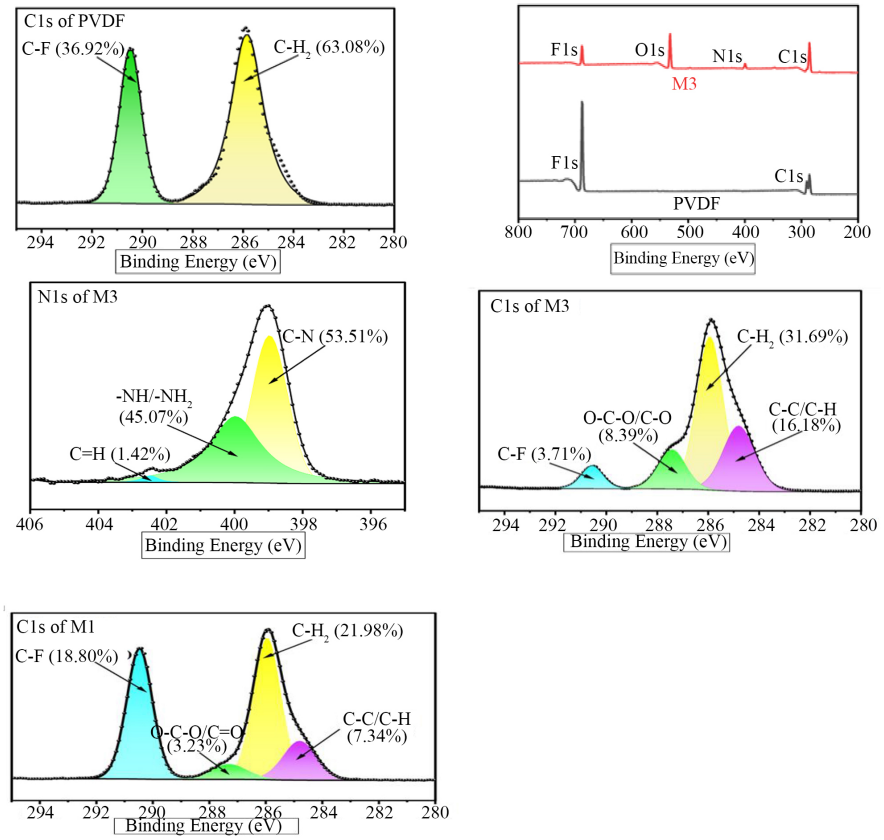

Figure 6. XPS spectrum comparing pristine PVDF with the O-Pul/PEI-coated membrane (M3).

3.5. Surface Wettability

The water contact angle (WCA) and water flux bar charts are consistent (**Figure 7**). Generally, enhanced hydrophilicity ultimately improves the anti-fouling efficiency of the membrane (Liu et al., 2025a). This is because a more hydrophilic surface tends to form a hydration layer, which repels foulants and reduces their adhesion to the membrane surface (Liu et al., 2025a). As a result, membranes with lower water contact angles (higher hydrophilicity) typically exhibit higher water flux and better anti-fouling performance, as demonstrated by the data in the bar charts. This correlation highlights the importance of surface hydrophilicity in de-

signing membranes with superior anti-fouling properties (Li et al., 2025). The wettability of the membranes was investigated by measuring their water contact angles (WCA). The figure shows the different contact angles of the various membranes. The pristine PVDF membrane maintains a water contact angle of approximately 97.5˚, indicating its strong hydrophobic nature. However, as the concentration of the cross-linking agent PEI increases, water droplets on the coated membranes rapidly spread into the membrane, causing the water contact angle to decrease quickly and reach zero within ten seconds. This phenomenon is likely due to the synergistic effect of the hydrophilic layers containing hydroxyl and amine groups from O-Pul and PEI (Liu et al., 2025b). Additionally, these results suggest that increasing the PEI concentration promotes stable Schiff base cross-linking of the copolymer on the membrane surface, enabling effective coating on the PVDF membrane. This demonstrates the successful enhancement of membrane hydrophilicity through the O-Pul/PEI modification process.

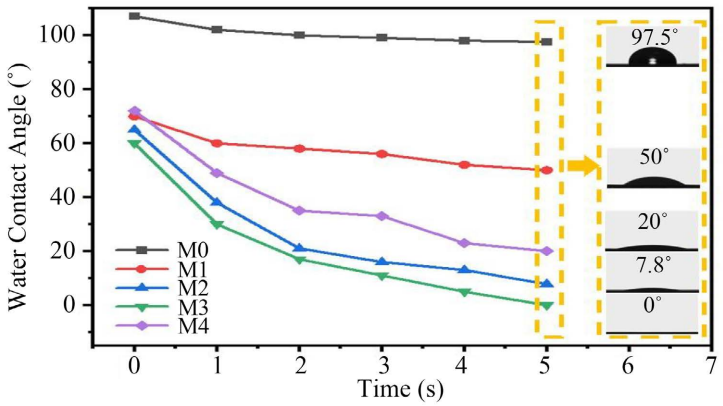

Figure 7. A Graph showing the Water contact angle (˚) result of the modified and Unmodified membranes and water flux test ($L \cdot m^{-2} \cdot h^{-1}$).

3.6. Antifouling Performance of Membranes

The antifouling performance of membranes is a critical factor in evaluating their practical applications. As shown in **Figure 8**, three different pollutants-bovine serum albumin (BSA), humic acid (HA), and sodium alginate (SA) were used as simulated wastewater to assess the antifouling performance of the membranes. Compared to the pristine PVDF membrane, all coated membranes exhibited significantly higher flux recovery ratios (FRR). This improvement is likely due to the introduction of a hydrophilic coating and the enhancement of surface smoothness. Generally, surface roughness and hydrophilicity influence the deposition of pollutants and, consequently, the antifouling performance of membranes (Wang et al., 2026; Al Sawaftah et al., 2021). The coated membrane surfaces are covered with a hydrophilic cross-linked layer of O-Pul and PEI, which readily binds with water to form a hydration layer. This hydration layer can repel BSA molecules. As observed in previous SEM images, the surface of the coated membranes becomes smoother with changes in the coating ratio, which also contributes to the repul-

sion of pollutants.

In the case of BSA as a simulated pollutant, the flux of all membranes decreased at the beginning of filtration. This is likely because BSA was separated by the membrane and deposited on the surface, thereby blocking the membrane pores (Wang et al., 2026). As BSA filtration continued, a balance was gradually reached between the deposition of BSA on the membrane surface and its detachment from the deposited layer (Wang et al., 2026), leading to a stabilization of the permeate flux. Furthermore, the flux decline was more pronounced during HA filtration, possibly because HA molecules are smaller than BSA and, thus, more prone to blocking membrane pores. However, this had little impact on the subsequent cleaning process. During SA filtration, SA tends to aggregate and precipitate, forming a gel layer that is difficult to remove through ordinary water rinsing. As a result, SA's flux recovery ratio was relatively lower than the other two pollutants.

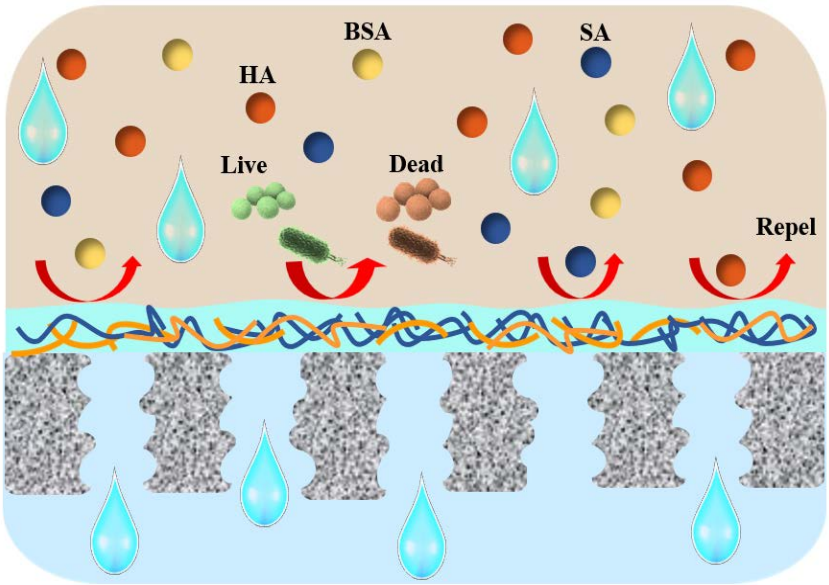

Figure 8. Graphical simulation of wastewater to assess the antifouling performance of the membranes using Bovine serum albumin (BSA), humic acid (HA), and sodium alginate (SA).

4. Conclusion and Recommendation

This study developed and characterized oxidized pullulan/polyethyleneimine (O-Pul/PEI) crosslinked coatings for the surface modification of hydrophobic polyvinylidene fluoride (PVDF) membranes using a simple and environmentally friendly two-step dip-coating technique. Pullulan was oxidized with sodium periodate to introduce reactive aldehyde groups, which subsequently reacted with polyethyleneimine through Schiff-base crosslinking to form stable hydrophilic coatings on the membrane surface. The successful synthesis and coating formation were confirmed by FTIR and XPS, which identified aldehyde, amine, and imine functional groups, while SEM analysis demonstrated that PEI concentration strongly

influenced coating morphology, surface coverage, and structural integrity. Among the formulations evaluated, the membrane coated with 0.4 wt.% PEI (M3) exhibited the most continuous, uniform, and well-adhered coating while preserving the porous structure of the PVDF support. Water contact angle measurements further demonstrated a marked improvement in membrane hydrophilicity, attributed to the introduction of hydroxyl and amino functional groups that enhance surface wettability and are expected to reduce foulant adhesion. In contrast, lower PEI concentrations resulted in incomplete surface coverage, whereas excessive PEI (0.5 wt.%) promoted rapid bulk crosslinking, poorer coating adhesion, and pore reappearance. Overall, the findings demonstrate that the O-Pul/PEI crosslinking strategy provides a reproducible, sustainable, and effective approach for improving the surface properties of PVDF membranes, with strong potential for enhancing antifouling performance and membrane efficiency in water treatment and separation applications. Controlled coating techniques, such as automated dip-coating, should be adopted to enhance coating uniformity and scalability. Additional characterization, including TGA, DSC, AFM, and mechanical stability analyses, is recommended to assess coating durability.

Conflicts of Interest

The authors declare no conflict of interest.

References

Ádám, B. Á., Spátay, S., Jávor, B., László, S., Illés, L., Fürjes, P. et al. (2025). Atmospheric Air Plasma Pre-Activation and Customizable Covalent Functionalization of PVDF-Membranes of Microtiter Filter Plates. *Scientific Reports, 15,* Article No. 3238. https://doi.org/10.1038/s41598-024-85040-5

Agrawal, S., Budhwani, D., Gurjar, P., Telange, D., & Lambole, V. (2022). Pullulan Based Derivatives: Synthesis, Enhanced Physicochemical Properties, and Applications. *Drug Delivery, 29,* 3328-3339. https://doi.org/10.1080/10717544.2022.2144544

AlSawaftah, N., Abuwatfa, W., Darwish, N., & Husseini, G. (2021). A Comprehensive Review on Membrane Fouling: Mathematical Modelling, Prediction, Diagnosis, and Mitigation. *Water, 13,* Article 1327. https://doi.org/10.3390/w13091327

Arif, U., Haider, S., Haider, A., Khan, N., Alghyamah, A. A., Jamila, N. et al. (2019). Biocompatible Polymers and Their Potential Biomedical Applications: A Review. *Current Pharmaceutical Design, 25,* 3608-3619. https://doi.org/10.2174/1381612825999191011105148

Bandara, P. C., Nadres, E. T., & Rodrigues, D. F. (2019). Use of Response Surface Methodology to Develop and Optimize the Composition of a Chitosan-Polyethyleneimine-Graphene Oxide Nanocomposite Membrane Coating to More Effectively Remove Cr(VI) and Cu(II) from Water. *ACS Applied Materials & Interfaces, 11,* 17784-17795. https://doi.org/10.1021/acsami.9b03601

Benalaya, I., Alves, G., Lopes, J., & Silva, L. R. (2024). A Review of Natural Polysaccharides: Sources, Characteristics, Properties, Food, and Pharmaceutical Applications. *International Journal of Molecular Sciences, 25,* Article 1322. https://doi.org/10.3390/ijms25021322

Bruneel, D., & Schacht, E. (1993). Chemical Modification of pullulan: 1. Periodate Oxida-

tion. *Polymer, 34,* 2628-2632.

Cao, M., Zhang, Y., Zhang, B., Liu, Z., Ma, X., & Chen, C. (2020). The Preparation of a Modified PVDF Hollow Fiber Membrane by Coating with Multiwalled Carbon Nanotubes for High Antifouling Performance. *RSC Advances, 10,* 1848-1857. https://doi.org/10.1039/c9ra07542a

Chakraborty, T., Yadav, D., Bedar, A., Joshi, R., Kumar Pandey, M., Saxena, S. et al. (2025). Modified PVDF Ultrafiltration Membrane with Host-Guest Supramolecular Trapping for Efficient Separation of Multiple Organic Contaminants. *Separation and Purification Technology, 356,* Article 129725. https://doi.org/10.1016/j.seppur.2024.129725

Chen, Z., Lv, Z., Sun, Y., Chi, Z., & Qing, G. (2020). Recent Advancements in Polyethyleneimine-Based Materials and Their Biomedical, Biotechnology, and Biomaterial Applications. *Journal of Materials Chemistry B, 8,* 2951-2973. https://doi.org/10.1039/c9tb02271f

Desidery, L., & Lanotte, M. (2022). Polymers and Plastics: Types, Properties, and Manufacturing. In F. Giustozzi, & S. Nizamuddin (Eds.), *Plastic Waste for Sustainable Asphalt Roads* (pp. 3-28). Elsevier. https://doi.org/10.1016/b978-0-323-85789-5.00001-0

Dharani, S. R., Srinivasan, R., Sarath, R., & Ramya, M. (2020). Recent Progress on Engineering Microbial Alginate Lyases towards Their Versatile Role in Biotechnological Applications. *Folia Microbiologica, 65,* 937-954. https://doi.org/10.1007/s12223-020-00802-8

Gaffney, J. S., Marley, N. A., & Blake, D. R. (2012). Baseline Measurements of Ethene in 2002: Implications for Increased Ethanol Use and Biomass Burning on Air Quality and Ecosystems. *Atmospheric Environment, 56,* 161-168.

Gandini, A., & M. Lacerda, T. (2021). Monomers and Macromolecular Materials from Renewable Resources: State of the Art and Perspectives. *Molecules, 27,* Article 159. https://doi.org/10.3390/molecules27010159

Gedde, U. W., Hedenqvist, M. S., Johansson, M., Berglund, L., & Wohlert, J. (2025). Introduction to Polymer Science. In U. W. Gedde, M. S. Hedenqvist, M. Johansson, L. Berglund, & J. Wohlert (Eds.), *Fundamental Polymer Science* (pp. 1-58). Springer. https://doi.org/10.1007/978-3-032-06562-9_1

Geyer, R. (2020). Production, Use, and Fate of Synthetic Polymers. In T. M. Letcher (Ed.), *Plastic Waste and Recycling* (pp. 13-32). Elsevier. https://doi.org/10.1016/b978-0-12-817880-5.00002-5

Gieroba, B., Kalisz, G., Krysa, M., Khalavka, M., & Przekora, A. (2023). Application of Vibrational Spectroscopic Techniques in the Study of the Natural Polysaccharides and Their Cross-Linking Process. *International Journal of Molecular Sciences, 24,* Article 2630. https://doi.org/10.3390/ijms24032630

Haque, F. M., Ishibashi, J. S. A., Lidston, C. A. L., Shao, H., Bates, F. S., Chang, A. B. et al. (2022). Defining the Macromolecules of Tomorrow through Synergistic Sustainable Polymer Research. *Chemical Reviews, 122,* 6322-6373. https://doi.org/10.1021/acs.chemrev.1c00173

Jia, Y., Xie, H., Qian, J., Zhang, Y., Zheng, H., Wei, F. et al. (2024). Recent Progress on the 3D Printing of Dynamically Cross-Linked Polymers. *Advanced Functional Materials, 34,* Article ID: 2307279. https://doi.org/10.1002/adfm.202307279

Jiang, M., Sun, Y., Zhu, J., Lin, B., & Zhang, X. (2025). Confinement Synthesis via Ph-Responsive Polyethyleneimine-Glutaraldehyde Cross-Linked Networks for Cu@Ag with Enhanced Conductivity and Oxidation Resistance for Electronic Applications. *Chemical Engineering Journal, 522,* Article 166931. https://doi.org/10.1016/j.cej.2025.166931

Karimipour, H., Shahbazi, A., & Vatanpour, V. (2021). Fouling Decline and Retention In-

crease of Polyethersulfone Membrane by Incorporating Melamine-Based Dendrimer Amine Functionalized Graphene Oxide Nanosheets (GO/MDA). *Journal of Environmental Chemical Engineering, 9,* Article 104849. https://doi.org/10.1016/j.jece.2020.104849

Khan, M. J., Svedberg, A., Singh, A. A., Ansari, M. S., & Karim, Z. (2019). Use of Nanostructured Polymer in the Delivery of Drugs for Cancer Therapy. In S. K. Swain, & M. Jawaid (Eds.), *Nanostructured Polymer Composites for Biomedical Applications* (pp. 261-276). Elsevier. https://doi.org/10.1016/b978-0-12-816771-7.00013-2

Kim, M., Lee, J. W., Nam, M. G., Ho, J., Song, H. J., Choi, Y. et al. (2025). Post-Densified Conformal Coating of a Pyrogallol/Polyethyleneimine Complex as a Durable Electrolyte-Blocking Organic Layer for High-Capacity Anode Materials. *Chemical Engineering Journal, 510,* Article 161649. https://doi.org/10.1016/j.cej.2025.161649

Kim, Y., & Jung, C. (2022). Reaction Mechanisms Applied to Starch Modification for Biodegradable Plastics: Etherification and Esterification. *International Journal of Polymer Science, 2022,* Article ID: 2941406. https://doi.org/10.1155/2022/2941406

Kmetik, M., Kopal, I., Král, M., & Dendisová, M. (2024). Characterization of Modified PVDF Membranes Using Fourier Transform Infrared and Raman Microscopy and Infrared Nanoimaging: Challenges and Advantages of Individual Methods. *ACS Omega, 9,* 24685-24694. https://doi.org/10.1021/acsomega.4c01197

Kocira, A., Kozłowicz, K., Panasiewicz, K., Staniak, M., Szpunar-Krok, E., & Hortyńska, P. (2021). Polysaccharides as Edible Films and Coatings: Characteristics and Influence on Fruit and Vegetable Quality—A Review. *Agronomy, 11,* Article 813. https://doi.org/10.3390/agronomy11050813

Kurowiak, J., Klekiel, T., & Będziński, R. (2023). Biodegradable Polymers in Biomedical Applications: A Review-Developments, Perspectives and Future Challenges. *International Journal of Molecular Sciences, 24,* Article 16952. https://doi.org/10.3390/ijms242316952

Lang, L. P., Wang, H. Y., Cheng, K., Chen, D. Y., Tian, X., Cheng, Y. Q. et al. (2026). Anti-Biofouling Hydrogels: Surface Hydration, Classification, and Biomedical Applications. *Chinese Journal of Polymer Science, 44,* 1606-1632. https://doi.org/10.1007/s10118-026-3585-x

Li, L., Pan, W., Kong, F., Xiao, A., & Duan, Y. (2025). Engineering Polyvinylidene Fluoride-Based Lithium-Ion Battery Separators via Blending Modification. *Academia Engineering, 2,* 1-25. https://doi.org/10.20935/acadeng7608

Lin, F., Lin, X., Li, J., Zeng, J., Lin, W., & Wang, J. (2025). High Efficiency and Sustainability of PVDF Membrane in Wastewater Treatment and Reuse. *Green Technologies and Sustainability, 4,* Article 100317. https://doi.org/10.1016/j.grets.2025.100317

Liu, C., Gao, R., Wang, X., Faria, A. F., Yang, L., Zhang, B. et al. (2025a). Maximizing Membrane Antifouling Potential: The Impact of Fluoride Positioning in Multifunctional Designs. *Water Research, 281,* Article 123565. https://doi.org/10.1016/j.watres.2025.123565

Liu, Y., Gong, S., Zhang, M., Zhang, X., Wang, H., Wen, H., Chang, S., Guo, W., & Hao Ngo, H. (2025b). Enhanced Anti-Fouling Performance through Integrated Coagulation and Membrane Co-Deposition Modification for Sustainable Water Treatment. *Separation and Purification Technology*, *361*, Article 131407. https://doi.org/https://doi.org/10.1016/j.seppur.2025.131407

Luís, Â., Ramos, A., & Domingues, F. (2020). Pullulan Films Containing Rockrose Essential Oil for Potential Food Packaging Applications. *Antibiotics, 9,* Article 681. https://doi.org/10.3390/antibiotics9100681

Lv, Y., Yang, S., Du, Y., Yang, H., & Xu, Z. (2018). Co-Deposition Kinetics of Polydopamine/Polyethyleneimine Coatings: Effects of Solution Composition and Substrate Surface. *Langmuir, 34,* 13123-13131. https://doi.org/10.1021/acs.langmuir.8b02454

Maity, P., Dhore, N., & Kumar, N. (2026). Structure-Property-Process Correlation of Polymers. In S. Chattopadhyay, & N. Kumar (Eds.), *Polymer Characterization* (pp. 39-66). Springer. https://doi.org/10.1007/978-981-95-2609-3_2

Marsotto, M., De Santis, S., Sotgiu, G., Battocchio, C., Iucci, G., Ceccucci, A. et al. (2023). Multifunctional Platform for Covalent Titanium Coatings: Micro-FTIR, XPS, and NEXAFS Characterizations. *Langmuir, 39,* 6837-6845. https://doi.org/10.1021/acs.langmuir.3c00424

Moreno, C. A. O., Ghaddar, N., Sehit, E., Schomäcker, R., & Altintas, Z. (2024). Surface Modification of PVDF Ultrafiltration Membranes Using Spacer Arms and Synthetic Receptors for Virus Capturing and Separation. *Talanta, 279,* Article 126558. https://doi.org/10.1016/j.talanta.2024.126558

Nandita, E., Bacalzo Jr., N. P., Ranque, C. L., Amicucci, M. J., Galermo, A., & Lebrilla, C. B. (2021). Polysaccharide Identification through Oligosaccharide Fingerprinting. *Carbohydrate Polymers, 257,* Article 117570. https://doi.org/10.1016/j.carbpol.2020.117570

Nie, L., Li, X., Li, D., Zhang, J., Long, S., Huang, Y. et al. (2025). Superhydrophilic, Multi-Level Antifouling PVDF Microfiltration Membrane with Ionically Crosslinked "Organic-Inorganic" Bridging in Oily Wastewater Treatment. *Chemical Engineering Journal, 524,* Article 169162. https://doi.org/10.1016/j.cej.2025.169162

Nthunya, L. N., Gutierrez, L., Khumalo, N., Derese, S., Mamba, B. B., Verliefde, A. R. et al. (2019). Superhydrophobic PVDF Nanofibre Membranes Coated with an Organic Fouling Resistant Hydrophilic Active Layer for Direct-Contact Membrane Distillation. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 575,* 363-372. https://doi.org/10.1016/j.colsurfa.2019.05.031

Parida, P. K., Alam, M. I., Tomy, A., Gogoi, D., Pradhan, A. K., & Pandit, M. K. (2025). Polymer Materials Properties and Characterization Study with Focus on Sustainability. In N. K. Bhoi, H. Singh, & H. S. Nanda (Eds.), *Advanced Functional and Composite Materials* (pp. 63-119). CRC Press. https://doi.org/10.1201/9781003664611-4

Pillai, A. R. S., Eapen, A. S., Zhang, W., & Roy, S. (2024). Polysaccharide-Based Edible Biopolymer-Based Coatings for Fruit Preservation: A Review. *Foods, 13,* Article 1529. https://doi.org/10.3390/foods13101529

Reddy, C. N., Mishra, B., Mandal, S. K., Agrawal, D. C., & Kruthiventi, C. (2022). An Insight into Pullulan and Its Potential Applications. In J. M. Oliveira, H. Radhouani, & R. L. Reis (Eds.), *Polysaccharides of Microbial Origin* (pp. 247-277). Springer International Publishing. https://doi.org/10.1007/978-3-030-42215-8_15

Reddy, M. S. B., Ponnamma, D., Choudhary, R., & Sadasivuni, K. K. (2021). A Comparative Review of Natural and Synthetic Biopolymer Composite Scaffolds. *Polymers, 13,* Article 1105. https://doi.org/10.3390/polym13071105

Shariatmadar, M., Gholamhosseini, P., Abdorrezaee, Z., Ghorbanzadeh, S., Feizollahi, S., Hosseini, F. S. et al. (2024). Leveraging Polyaniline Grafted Micaceous Iron Oxide as a Dual Active-Barrier Pigment for Anti-Corrosion Polymer Coatings. *Surface and Coatings Technology, 479,* Article 130501. https://doi.org/10.1016/j.surfcoat.2024.130501

Singh, S., Sharma, P. K., Malviya, R., & Gupta, A. (2023). Modified Polysaccharides and Their Biomedical Applications: Advancement and Strategies. *Current Materials Science, 16,* 316-351. https://doi.org/10.2174/2666145416666221208150926

Sisay, E. J., Al-Tayawi, A. N., László, Z., & Kertész, S. (2023). Recent Advances in Organic

Fouling Control and Mitigation Strategies in Membrane Separation Processes: A Review. *Sustainability, 15,* Article 13389. https://doi.org/10.3390/su151813389

Song, Y., Wang, F. F., Lu, G. X., Zhou, L. Y., & Yang, Q. B. (2020). Preparation of PEI Nanofiber Membrane Based on *in Situ* and Solution Crosslinking Technology and Their Adsorption Properties. *Journal of Applied Polymer Science, 137,* Article No. 48279. https://doi.org/10.1002/app.48279

Tassakan, N., Amornsakchai, T., Rungrattanachai, C., & Amornsakchai, P. (2026). Influence of Glutaraldehyde Cross-Linking on the Structure and Metal-Binding Properties of Pei-Modified Pineapple Leaf Microfiber. *ACS Omega, 11,* 24424-24435. https://doi.org/10.1021/acsomega.6c00096

Teng, J., Lu, Z., Ma, X., Zhu, W., Yang, Y., Li, P. et al. (2026). Organic-Inorganic Co-Modified PVDF Membrane for High-Flux Oil/Water Separation and Simultaneous Multi-Pollutant Removal. *Molecules, 31,* Article 1372. https://doi.org/10.3390/molecules31081372

Teng, L., Yue, C., & Zhang, G. (2023). Epoxied Sio2 Nanoparticles and Polyethyleneimine (PEI) Coated Polyvinylidene Fluoride (PVDF) Membrane for Improved Oil Water Separation, Anti-Fouling, Dye and Heavy Metal Ions Removal Capabilities. *Journal of Colloid and Interface Science, 630,* 416-429. https://doi.org/10.1016/j.jcis.2022.09.148

Trincone, A. (2018). Update on Marine Carbohydrate Hydrolyzing Enzymes: Biotechnological Applications. *Molecules, 23,* Article 901. https://doi.org/10.3390/molecules23040901

Vatanpour, V., Pasaoglu, M. E., Barzegar, H., Teber, O. O., Kaya, R., Bastug, M. et al. (2022). Cellulose Acetate in Fabrication of Polymeric Membranes: A Review. *Chemosphere*, *295*, Article 133914.

Verma, G. (2019). Weathering, Salt Spray Corrosion and Mar Resistance Mechanism of Clay (Nano-Platelet) Reinforced Polyurethane Nanocomposite Coatings. *Progress in Organic Coatings, 129,* 260-270. https://doi.org/10.1016/j.porgcoat.2019.01.028

Wang, X., Huang, L., Zhang, C., Deng, Y., Xie, P., Liu, L. et al. (2020). Research Advances in Chemical Modifications of Starch for Hydrophobicity and Its Applications: A Review. *Carbohydrate Polymers, 240,* Article 116292. https://doi.org/10.1016/j.carbpol.2020.116292

Wang, Y., Wang, R., Zhao, Q., Tian, Y. L., Li, K., Liu, L. Y. et al. (2026). Biomedical Applications of Polymer Porous Materials: Design, Properties, and Future Perspectives. *MedMat, 3,* 132-146.

Wu, J. J., Li, D., Lai, Q., Bian, J., Zhang, A. P., Yang, S. K. et al. (2026). Polyvinylidene Fluoride (PVDF)-Based Composite for Energy and Environmental Applications: A Comprehensive Review. *Polymer Composites, 47,* 8745-8775. https://doi.org/10.1002/pc.70779

Xie, T., Wang, H., Chen, K., Li, F., Zhao, S., Sun, H. et al. (2023). High-Performance Polyethyleneimine Based Reverse Osmosis Membrane Fabricated via Spin-Coating Technology. *Journal of Membrane Science, 668,* Article 121248. https://doi.org/10.1016/j.memsci.2022.121248

Yu, R., Senocrate, A., Bernasconi, F., Künniger, T., Müller, L., Pauer, R. et al. (2023). Flexible and Ultrathin Waterproof Conductive Cellular Membranes Based on Conformally Gold-Coated PVDF Nanofibers and Their Potential as Gas Diffusion Electrode. *Materials & Design, 225,* Article 111441. https://doi.org/10.1016/j.matdes.2022.111441

Yuan, B., Guo, M., Murugadoss, V., Song, G., & Guo, Z. (2021). Immobilization of Graphitic Carbon Nitride on Wood Surface via Chemical Crosslinking Method for UV Resistance and Self-Cleaning. *Advanced Composites and Hybrid Materials, 4,* 286-293.

https://doi.org/10.1007/s42114-021-00235-y

Yuan, S., Zhang, J., Tao, Z., Jin, X., & Wang, Z. (2026). Enhancing Anti-Oil Fouling Performance of Hydrophobic Membranes via Surfactant Pretreatment: Atomistic Insights into Interfacial Hydration Dynamics. *Journal of Membrane Science, 757,* Article 125872. https://doi.org/10.1016/j.memsci.2026.125872

Zhang, H., Ji, X., Wang, Z., Tang, S., Wang, Z., & Zhu, W. (2026). Advances in Intelligent Polyvinylidene Fluoride-Based Piezoelectric Composites for Self-Powered Wearable Electronics. *Small, 22,* e09387. https://doi.org/10.1002/smll.202509387

Zhang, P. B., Liu, C. J., Sun, J., Zhu, B. K., & Zhu, L. P. (2017). Fabrication of Composite NANOFILTRATION membranes by Dopamine-Assisted Poly (Ethylene Imine) Deposition and Cross-Linking. *Journal of Zhejiang University-SCIENCE A, 18,* 138-150.

Zheng, N., Xu, Y., Zhao, Q., & Xie, T. (2021). Dynamic Covalent Polymer Networks: A Molecular Platform for Designing Functions Beyond Chemical Recycling and Self-Healing. *Chemical Reviews, 121,* 1716-1745. https://doi.org/10.1021/acs.chemrev.0c00938

Zhou, Q., Liu, S., She, J., Wang, X., Lu, X., & Wu, C. (2022). *In-Situ* Aeration-Assisted Polydopamine/Polyethyleneimine Copolymerization and Deposition for Rapid and Uniform Membrane Modification. *Journal of Membrane Science, 657,* Article 120662. https://doi.org/10.1016/j.memsci.2022.120662