

Novel polyethersulfone membranes modified with polyvinylpyrrolidone and magnesium hydroxide: A study on performance and organic fouling mitigation

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ABSTRACT

This study explores the development and performance enhancement of polyethersulfone (PES) membranes through dual modification using polyvinylpyrrolidone (PVP) and magnesium hydroxide ($\text{Mg}(\text{OH})_2$). The objective was to investigate the impact of these additives on membrane permeability, rejection efficiency, and antifouling properties. Membranes were fabricated via non-solvent induced phase separation (NIPS) and characterized using FTIR, SEM, water contact angle (WCA) analysis, and filtration performance tests. Results showed that the PPM membrane achieved the highest pure water permeability ($90.6 \text{ L/m}^2\text{-h}$) due to improved porosity and hydrophilicity. FTIR analysis confirmed the presence of hydrophilic functional groups, while WCA measurements revealed a significant reduction in contact angle, indicating enhanced wettability. Although humic acid rejection slightly decreased to 70.5% in dual-modified membranes, the antifouling performance significantly improved, with a flux recovery ratio (FRR) of 87.2%. These findings demonstrate that the incorporation of PVP and $\text{Mg}(\text{OH})_2$ into PES membranes synergistically improves water transport and fouling resistance. The study provides valuable insights for developing next-generation membranes suitable for complex water treatment applications, particularly in improving operational efficiency and durability.

Keyword: antifouling, membrane performance, magnesium hydroxide, polyethersulfone, polyvinylpyrrolidone.

INTRODUCTION

Water pollution remains one of the most pressing global environmental challenges, with organic contaminants such as humic substances, proteins, and synthetic compounds posing serious threats to public health and aquatic ecosystems. As population growth and industrial expansion continue to strain freshwater resources, the need for efficient and sustainable water treatment technologies becomes increasingly urgent. Among the promising solutions, membrane-based filtration systems have gained widespread attention due to their high contaminant removal efficiency, operational simplicity, and scalability. Polyethersulfone (PES) membranes are frequently used in these systems owing to their

robust mechanical strength, thermal stability, and resistance to a broad range of chemical environments (Feng et al., 2021). However, the practical application of PES membranes is significantly hindered by organic fouling, a phenomenon that compromises membrane permeability, increases energy consumption, and shortens membrane lifespan (Kim et al., 2021).

Organic fouling in PES membranes is predominantly caused by the adsorption of hydrophobic organic molecules onto the membrane surface. This leads to a progressive decline in membrane performance due to the formation of a fouling layer that obstructs water flow and encourages biofilm development (Sisay et al., 2023). The hydrophobic nature of PES exacerbates fouling by promoting strong

interactions between foulants and the membrane surface (Sousa et al., 2020). This irreversible adsorption not only reduces water permeability but also increases maintenance requirements, thereby affecting the economic feasibility of PES-based filtration systems (Kadavou et al., 2024; Nia et al., 2024; Fathanah et al., 2020). To address these issues, extensive research has been devoted to modifying PES membranes with hydrophilic additives to improve their antifouling properties and operational stability (Desiriani et al., 2023).

A key strategy for enhancing the antifouling performance of PES membranes involves the introduction of hydrophilic polymers and inorganic nanoparticles into the membrane matrix. Hydrophilic modification reduces the contact angle and increases surface energy, thereby forming a hydration layer that acts as a barrier against foulant deposition (Otitoju et al., 2018). Zwitterionic polymer brushes and hydrophilic copolymers have been reported to significantly lower protein adsorption and biofouling by improving membrane wettability (Jashrapuria and Singh, 2023; Liu et al., 2017). Similarly, additives such as polyethylene glycol and its derivatives enhance membrane hydrophilicity and permeability, contributing to improved overall filtration efficiency (Jie et al., 2020). Despite these advancements, the use of single-component additives often falls short of providing long-term stability and comprehensive fouling resistance.

Among various hydrophilic agents, polyvinylpyrrolidone (PVP) has emerged as a widely used polymer for PES membrane modification due to its excellent water solubility and ability to act as a pore-forming agent. Studies have shown that PVP incorporation results in membranes with enhanced porosity and lower contact angles, which translates into higher permeability and reduced fouling (Junaidi et al., 2019; Russo et al., 2021). Nevertheless, a critical limitation of PVP is its tendency to leach out during membrane operation, leading to a gradual decline in performance and membrane durability (Mavukandy et al., 2016). On the other hand, magnesium hydroxide ($\text{Mg}(\text{OH})_2$) offers unique advantages as an inorganic additive. It introduces hydroxyl groups that contribute to hydrophilicity and also reinforces the membrane structure through hydrogen bonding (Fathanah et al., 2020; Abubakar et al., 2024). $\text{Mg}(\text{OH})_2$ -modified membranes demonstrate improved stability and fouling

resistance, yet they often lack the permeability enhancements observed with polymeric additives (Umi Fathanah et al., 2024).

Recent studies have explored the synergistic use of organic and inorganic additives to overcome the limitations of single-component modifications. For instance, the combination of PVP with graphene oxide (GO) has been shown to significantly enhance antifouling performance and separation efficiency in PES membranes (Junaidi et al., 2019; Fathurrahman et al., 2021). Similar hybrid strategies involving titanium dioxide (TiO_2) and carbon nanotubes (CNTs) alongside PVP have resulted in membranes with superior mechanical strength and water flux, as well as enhanced resistance to biofouling (Sarkar et al., 2017). These findings underscore the potential of combining organic polymers and inorganic nanoparticles to develop high-performance membranes tailored for specific water treatment applications.

Despite promising results from hybrid approaches, the combined application of PVP and $\text{Mg}(\text{OH})_2$ in PES membranes remains relatively underexplored. The few existing studies suggest that such a combination may address the drawbacks of each component when used in isolation. While PVP enhances initial hydrophilicity and permeability, $\text{Mg}(\text{OH})_2$ contributes to structural integrity and long-term stability (Fathanah et al., 2022). Furthermore, optimization of the blending ratio and dispersion technique can lead to a well-balanced membrane with superior antifouling performance. The incorporation of both components has the potential to regulate phase inversion during membrane fabrication, resulting in a uniform and interconnected pore structure with enhanced permeability and fouling resistance.

Moreover, the use of the non-solvent induced phase separation (NIPS) method enables precise control over membrane morphology and additive distribution. Characterization techniques such as Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), water contact angle (WCA) measurement, and porosity analysis provide critical insights into the structural and functional transformations induced by PVP and $\text{Mg}(\text{OH})_2$. These techniques are essential for correlating chemical composition with filtration performance, particularly in terms of permeability, humic acid rejection, and flux recovery (Yang et al., 2022). Additionally, performance tests using

model foulants like humic acid offer practical evaluations of membrane resistance to organic fouling, a critical factor in real-world water treatment scenarios (Kim et al., 2021).

This study aims to systematically investigate the combined effects of PVP and $\text{Mg}(\text{OH})_2$ on the structural, hydrophilic, and antifouling properties of PES membranes. The novelty of the research lies in its focus on optimizing the synergistic interactions between organic and inorganic additives to develop a high-performance membrane that addresses the shortcomings of conventional modification strategies. Membranes will be fabricated using the NIPS method and characterized through a suite of analytical techniques, including FTIR, SEM, WCA, porosity, permeability, humic acid rejection, and flux recovery ratio assessments. By tailoring the membrane composition and fabrication parameters, this study seeks to identify an optimal formulation that maximizes permeability while maintaining effective contaminant rejection and long-term antifouling performance.

The outcomes of this research are expected to contribute significantly to the advancement of membrane technology for water treatment applications. Specifically, the findings will provide valuable insights into the design of next-generation PES membranes with improved durability, hydrophilicity, and resistance to organic fouling. These enhancements are critical for addressing the growing demand for clean water and supporting global sustainability goals through more efficient and reliable filtration technologies.

EXPERIMENTAL

Chemicals

The fabrication of PES-based membranes in this study employed PES (E6020P, BASF) as the primary polymer due to its chemical resistance, thermal stability, and mechanical integrity, which are essential properties for water treatment applications (Hamzah et al., 2020). Polyvinylpyrrolidone (PVP) was utilized as a hydrophilic pore-forming additive to improve membrane wettability and porosity. $\text{Mg}(\text{OH})_2$ was included as an inorganic modifier to enhance hydrophilicity and antifouling characteristics. Dimethylacetamide (DMAc, 99%, Sigma Aldrich) was used as the solvent, while deionized water functioned as

the non-solvent in the coagulation bath. Humic acid was selected as the model organic foulant to evaluate membrane rejection capabilities. All chemicals were of analytical grade and used without further purification.

Membrane preparation

The membranes were fabricated using the non-solvent induced phase separation (NIPS) method, which is a widely recognized approach for producing asymmetric membranes with controlled porosity and structural integrity (Rahimpour et al., 2024). PES was dissolved in DMAc under continuous stirring to form a homogeneous base solution. Additives such as PVP, $\text{Mg}(\text{OH})_2$, and a combination of both were subsequently incorporated at designated concentrations and mixed for 24 hours to ensure uniform dispersion (Table 1). The resulting dope solutions were degassed using ultrasonication to eliminate entrapped air bubbles, which could otherwise compromise membrane structure.

Each prepared solution was cast on a glass substrate using a casting knife set at a wet thickness of 300 μm . The cast films were then immersed in a deionized water coagulation bath at room temperature to initiate phase inversion. During this process, the solvent diffused out while water infiltrated the solution, leading to membrane solidification. Membranes remained in the bath for 24 hours to ensure complete removal of residual solvents, then were rinsed and stored in deionized water until further testing.

Membrane characterization

Functional group analysis by FTIR

Thermo Scientific iD5 ATR-Nicolet iS5 (FTIR) was used to identify the chemical composition of the membranes. Membrane samples were dried at 100 $^{\circ}\text{C}$ for 1 hour before analysis. The FTIR spectra were recorded in the range of 400–4000 cm^{-1} to detect characteristic

Table 1. The polymer solution compositions

Membrane code	PES (%)	PVP (%)	$\text{Mg}(\text{OH})_2$ (%)
P0	18	0	0
PP	18	1	0
PM	18	0	1
PPM	18	1	1

functional groups in PES, PVP, and $\text{Mg}(\text{OH})_2$, particularly hydroxyl ($-\text{OH}$), carbonyl ($\text{C}=\text{O}$), and ether ($\text{C}-\text{O}$) groups, which indicate successful incorporation of additives.

Morphological structure by SEM

SEM membrane morphology was observed using a field emission scanning electron microscope (FE-SEM, JSF-7500F, Jeol Co. Ltd.). Samples were freeze-dried, fractured in liquid nitrogen, and coated with osmium to enhance conductivity. SEM imaging at various magnifications enabled detailed examination of cross-sectional structures and pore formation influenced by additive types, corroborating their effects on membrane morphology (Wu et al., 2024).

Porosity measurement

Membrane porosity was determined using the dry-wet weight method. The membranes were immersed in deionized water for 24 hours to ensure full saturation, then weighed in their wet state (W_1). The membranes were subsequently dried in an oven at 50°C until a constant weight (W_2) was achieved. The porosity (%) was calculated using Equation 1.

$$\varepsilon = \frac{(\omega_w - \omega_d)}{\rho \times A \times l} \times 100\% \quad (1)$$

where: W_1 and W_2 are the wet and dry weights of the membrane (g), ρ is the density of water (1 g/cm^3), A is the membrane surface area (cm^2), and L is the membrane thickness (cm) (Umi Fathanah et al., 2025).

Hydrophilicity by WCA

The hydrophilicity of the membranes was assessed by measuring the WCA using a Drop Master 300 contact angle meter (Kyowa Interface Science Co., Japan). Membrane samples were cut into $3 \times 1 \text{ cm}$ strips, dried in a freeze dryer, and placed on the sample holder. A $1 \mu\text{L}$ droplet of deionized water was dispensed onto the membrane surface, and the contact angle was recorded immediately after the droplet made contact. A lower contact angle indicated higher hydrophilicity. Each measurement was repeated five times at different locations on the membrane surface to ensure accuracy (Febriasari et al., 2021; Salim et al., 2022).

Membrane performance evaluation

Pure water permeability

The pure water permeability (PWP) of the membranes was evaluated using a dead-end filtration system. Membranes were compacted at 1 bar pressure for 1 hour before testing. Water flux was measured at 10-minute intervals under a constant transmembrane pressure (TMP) of 1 bar at room temperature. The pure water flux (J) was calculated using Equation 2.

$$J = \frac{\Delta V}{\Delta t A} \quad (2)$$

where: V is the volume of permeate collected (L), A is the effective membrane area (m^2), and t is the filtration time (h) (Zhang et al., 2025).

Humic acid rejection

The rejection performance of the membranes was assessed using a 50-ppm humic acid solution as the model organic pollutant. The filtration experiments were conducted in a dead-end filtration module at 2 bar pressure. The concentration of humic acid in the feed and permeate solutions was analyzed using a UV-Vis spectrophotometer at 254 nm. The rejection efficiency (R) was determined using Equation 3.

$$R = \frac{C_f - C_p}{C_f} \times 100\% \quad (3)$$

where: C_p and C_f are the concentrations of humic acid in the permeate and feed solutions, respectively.

Antifouling performance

The antifouling behavior of the membranes was evaluated using the flux recovery ratio (FRR). The experiment was conducted in three steps: (1) initial pure water flux (J_1) measurement, (2) filtration of 50 ppm humic acid solution (J_2) at 2 bar for 60 minutes, (3) backwashing the membrane with deionized water for 20 minutes, followed by measuring the final pure water flux (J_3). The flux recovery ratio (FRR) was calculated by Equation 4.

$$FRR = \frac{J_3}{J_1} \times 100\% \quad (4)$$

RESULT AND DISCUSSION

Membrane characteristic

Functional group

FTIR analysis was performed to confirm the successful incorporation of PVP and $\text{Mg}(\text{OH})_2$ into the PES membrane matrix. Figure 1 presents the FTIR spectra of the unmodified PES membrane and those modified with varying compositions of PVP, $\text{Mg}(\text{OH})_2$, and their combination. In the spectrum of the pure PES (P0 membrane), characteristic peaks were observed at 1240 cm^{-1} and 1105 cm^{-1} , corresponding to the asymmetric and symmetric stretching vibrations of sulfone (SO_2) groups, respectively. Additionally, the peak at 1485 cm^{-1} was assigned to aromatic $\text{C}=\text{C}$ stretching, which is typical for PES, confirming its intrinsic hydrophobicity.

Upon modification with PVP (PP membrane), an additional broad peak was detected around 1660 cm^{-1} , corresponding to the $\text{C}=\text{O}$ stretching of the lactam group in PVP. This confirms the successful incorporation of PVP into the membrane matrix, contributing to an increase in polar functional groups. Meanwhile, the membrane modified with $\text{Mg}(\text{OH})_2$ (PM membrane) exhibited a decrease in peak intensity within the wavenumber range of $3000\text{--}3600\text{ cm}^{-1}$ compared to the original unmodified membrane. This reduction in intensity indicates the presence of hydroxyl groups originating from the hydrophilic additive, $\text{Mg}(\text{OH})_2$.

The FTIR spectra of the PES membrane modified with PVP and $\text{Mg}(\text{OH})_2$ (PPM membrane) exhibited both the $\text{C}=\text{O}$ stretching peak from PVP and stretching vibration of hydroxyl (OH) groups from $\text{Mg}(\text{OH})_2$, confirming the successful incorporation of both additives. These findings indicate that the hydrophilic groups from PVP and $\text{Mg}(\text{OH})_2$ were effectively integrated into the PES matrix, which is expected to enhance the membrane's hydrophilicity and antifouling properties. The impact of these hydrophilic groups on water contact angle (WCA) and overall membrane performance will be discussed later.

Morphological structure

Figure 2 illustrates the cross-sectional SEM images of the fabricated membranes. P0 membrane exhibited a typical asymmetric structure with a dense skin layer and a limited number of finger-like macropores, a morphology arising from delayed demixing during phase inversion. With PVP modification, a notably more open structure was observed, characterized by elongated finger-like pores and increased pore density. This outcome affirms PVP's role as a pore-forming agent that accelerates solvent-nonsolvent exchange, thus enhancing porosity and water flux (Febriasari et al., 2021).

Conversely, membranes embedded with $\text{Mg}(\text{OH})_2$ displayed a more compact morphology with shorter, narrower pores. The interaction

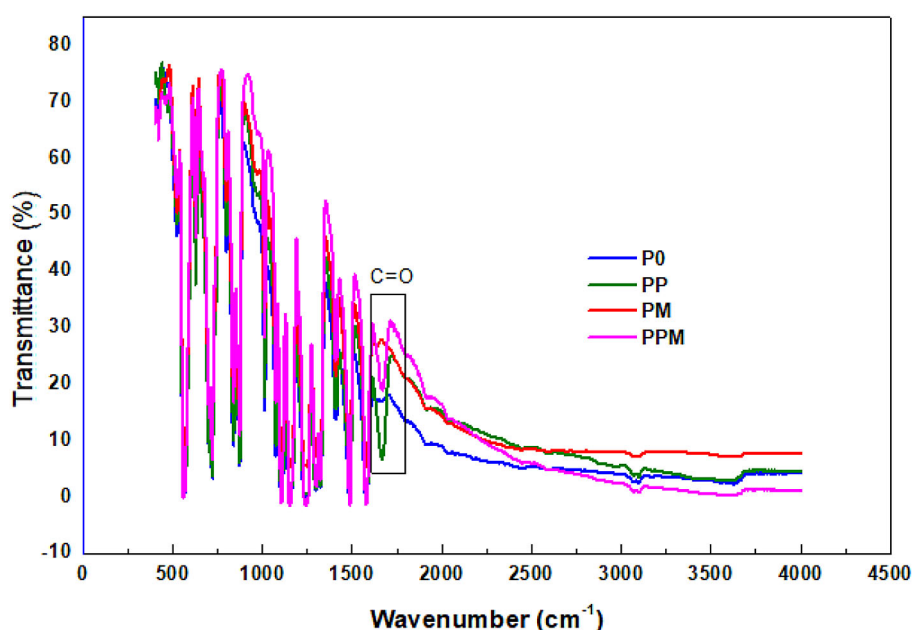


Figure 1. FTIR spectra of the prepared membranes

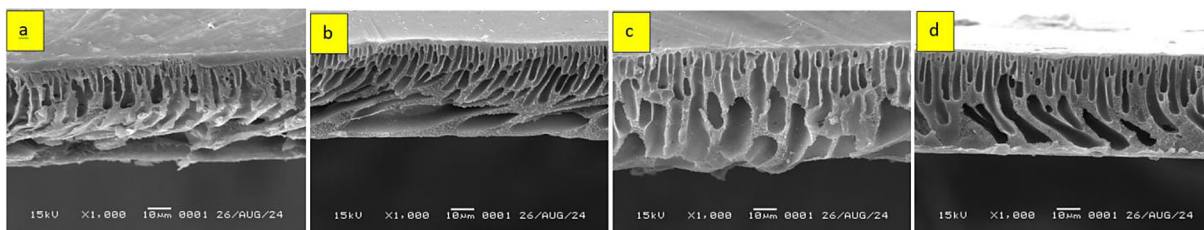


Figure 2. Cross-sectional structure of the membranes (a) P0; (b) PP; (c) PM; (d) PPM

between $\text{Mg}(\text{OH})_2$ and PES likely retarded phase separation, contributing to this dense structure. This observation aligns with earlier findings suggesting that inorganic additives can alter the kinetics of phase inversion, influencing final pore architecture (Roslan et al., 2024; Chen et al., 2023). The PPM membrane, however, presented an optimal pore morphology with well-defined finger-like structures extending from the top to bottom layers. This morphology supports the notion of a synergistic effect, where PVP promotes macrovoid formation and $\text{Mg}(\text{OH})_2$ contributes to structure regulation, producing membranes with high permeability and mechanical integrity.

Porosity

The porosity results of the prepared membranes are summarized in Figure 3. The P0 membrane exhibited the lowest porosity (25%), consistent with its dense structure observed in SEM images. The incorporation of PVP increased porosity to 31%, confirming its role as a pore-forming agent that enhances macropore formation. In contrast, the PM membrane exhibited a slightly lower porosity (27%), likely due to the denser structure induced by $\text{Mg}(\text{OH})_2$, which slowed down phase separation and reduced pore formation.

In Figure 3 it could be observed that the highest porosity (35%) was observed in the PPM membrane, suggesting that the synergistic effect of PVP and $\text{Mg}(\text{OH})_2$ enhanced phase separation dynamics, resulting in a more open and interconnected pore structure. Increased porosity is beneficial as it facilitates higher water flux and permeability. However, excessive porosity can compromise rejection efficiency, which will be further analyzed in the rejection study.

The porosity data strongly aligns with SEM observations. SEM images confirmed that PP membrane exhibited a higher density of macropores, correlating with increased porosity (Jalali et al., 2016). Similarly, the PPM membrane, which displayed the highest porosity

(35%), showed an enhanced porous network with well-distributed macropores in SEM images. Conversely, the denser morphology observed in PM membranes corresponded to slightly lower porosity values, reinforcing the role of $\text{Mg}(\text{OH})_2$ in structural regulation.

The coherence between SEM and porosity measurements highlights how different dope solution compositions influence membrane architecture. A greater pore density and openness in SEM images correlate with higher porosity values, validating that PVP enhances pore formation, $\text{Mg}(\text{OH})_2$ contributes to structural control, and their combination optimally balances porosity and mechanical stability. These findings confirm that the membrane fabrication approach effectively tailors pore architecture, optimizing permeability and antifouling performance for water treatment applications.

Surface hydrophilicity

The WCA measurements for the different membranes are presented in Figure 4. A lower contact angle indicates greater hydrophilicity, which is desirable for minimizing membrane fouling. P0 membrane exhibited the highest contact angle (78°), confirming its inherent hydrophobicity. The addition of PVP reduced the WCA to 65° , indicating improved hydrophilicity due to the presence of hydrophilic functional groups in PVP. Similarly, the PM membrane showed a further reduction in WCA (58°), which can be attributed to the hydroxyl-rich nature of $\text{Mg}(\text{OH})_2$ particles, facilitating greater water interaction. The PPM membrane exhibited the lowest WCA (55°), demonstrating the highest hydrophilicity. This enhancement is due to the synergistic effect of PVP and $\text{Mg}(\text{OH})_2$, which introduce hydrophilic functional groups ($-\text{OH}$ from $\text{Mg}(\text{OH})_2$ and $\text{C}=\text{O}$ from PVP) to the membrane surface, increasing water affinity.

The lower WCA in PPM membranes is consistent with FTIR findings that revealed

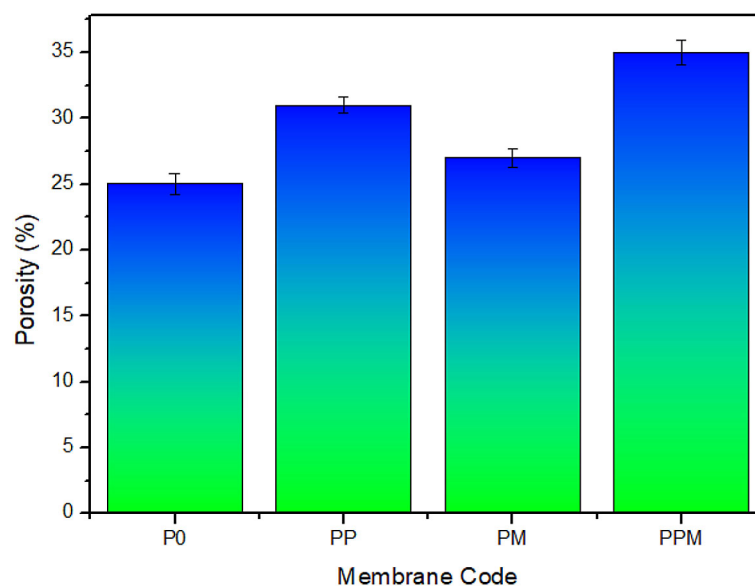


Figure 3. Porosity of the prepared membranes

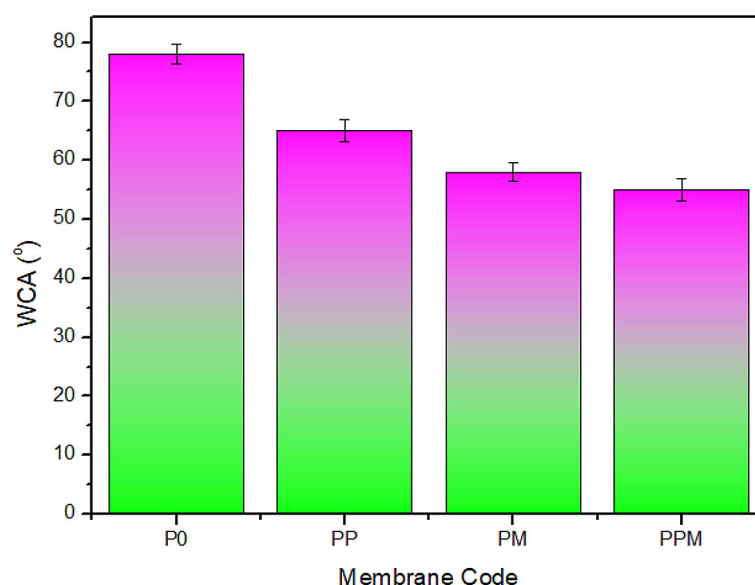


Figure 4. Water contact angle of the prepared membranes

the presence of polar functional groups. This strong correlation between FTIR peak intensity and WCA underscores the role of chemical functionality in enhancing hydrophilicity, which is a critical determinant of membrane antifouling performance (El-Zahhar et al., 2022; Irfan et al., 2015). Improved wettability helps prevent adhesion of organic foulants, thereby prolonging membrane lifespan and efficiency.

Together, the FTIR, SEM, porosity, and WCA analyses paint a coherent picture: blending PES with PVP and $\text{Mg}(\text{OH})_2$ yields membranes with optimized pore structure and enhanced

surface hydrophilicity. This tailored design is expected to improve water permeability and reduce fouling tendencies, key requirements for efficient and sustainable membrane-based water treatment systems.

Membrane performances

Pure water permeability

The PWP results, as shown in Figure 5, demonstrate a clear relationship between membrane composition and water transport efficiency. The P0 membrane exhibited the lowest permeability

(17.5 L/m²·h), which increased significantly to 55.2 L/m²·h with the addition of PVP (PP membrane), confirming that enhanced porosity facilitated water transport. The PM membrane exhibited a higher flux (69.2 L/m²·h), suggesting that the presence of hydroxyl-rich Mg(OH)₂ nanoparticles improved membrane wettability, thereby enhancing water permeability. The PPM membrane displayed the highest permeability (90.6 L/m²·h), indicating a synergistic effect between PVP-induced porosity and Mg(OH)₂-enhanced hydrophilicity, which optimized water transport through the membrane structure. While increased permeability is beneficial for improving filtration efficiency, excessive porosity may reduce selectivity, an aspect that will be further analyzed in the rejection study.

WCA measurements further validate the influence of hydrophilicity on permeability. A lower WCA corresponds to higher hydrophilicity, allowing water molecules to spread more easily across the membrane surface, reducing resistance to flow. The unmodified PES membrane had the highest WCA (78°), confirming its hydrophobic nature and low permeability (17.5 L/m²·h). As PVP was introduced, WCA decreased to 65°, while permeability increased to 55.2 L/m²·h, demonstrating the direct impact of enhanced surface wettability on water transport. Similarly, Mg(OH)₂-modified membranes exhibited a WCA reduction to 58°, contributing to an increase in

permeability (69.2 L/m²·h). The PPM membrane, with the lowest WCA (55°), achieved the highest permeability (90.6 L/m²·h), confirming that increased hydrophilicity significantly improved membrane efficiency.

Porosity plays an equally critical role in determining membrane permeability, as a higher porosity provides more pathways for water transport. The P0 membrane exhibited the lowest porosity (25%), which correlated with its low permeability, confirming that a dense structure restricts water flow. In contrast, PVP-modified membranes exhibited increased porosity (31%), which directly corresponded with the higher permeability of 55.2 L/m²·h, reinforcing the idea that the formation of additional pores improves water transport. The PM membrane had slightly lower porosity (27%) than the PVP-modified membrane, but still exhibited higher permeability (69.2 L/m²·h), suggesting that the improved hydrophilicity of Mg(OH)₂ compensated for the slightly denser structure. The PPM membrane, with the highest porosity (35%), exhibited the highest permeability, demonstrating that both porosity and surface hydrophilicity work in tandem to optimize water flux.

The relationship between WCA, porosity, and permeability is clearly demonstrated in the PPM membrane, which exhibited the lowest WCA, highest porosity, and highest permeability. The synergistic effect of hydrophilic functional groups

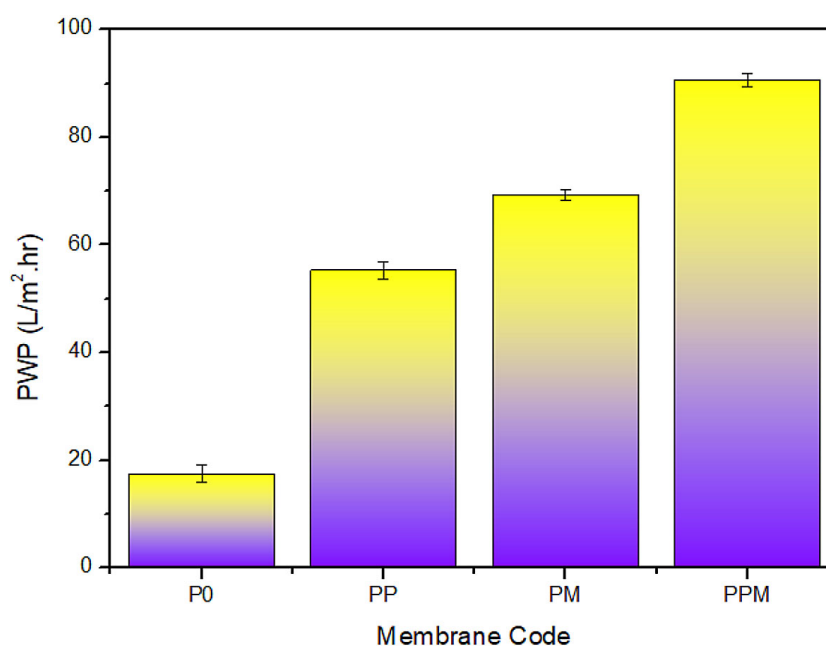


Figure 5. Pure water permeability of the prepared membranes

(from PVP and $\text{Mg}(\text{OH})_2$) and an optimized porous structure (from polymer blending and controlled phase inversion) contributed to superior water permeability. These results validate literature findings that increased porosity and hydrophilicity collectively enhance permeability (Roslan et al., 2024; Liu et al., 2016).

Humic acid rejection

The rejection performance for humic acid is shown in Figure 6. The P0 membrane demonstrated the highest rejection rate of 77.1%, consistent with its compact structure and smaller pore size, which effectively blocked larger organic molecules. However, this came at the cost of reduced permeability. The PP membrane exhibited a slightly lower rejection (74.2%), likely due to the enlarged pore sizes associated with higher porosity, allowing partial humic acid penetration. The PM membrane retained 75.6% of humic acid, indicating a balanced performance due to moderate porosity and hydrophilic improvements.

The PPM membrane had the lowest rejection rate of 70.5%, attributable to its highly porous structure. While this composition maximized permeability, it did so at the expense of selectivity, echoing the well-known trade-off between flux and rejection (Jo et al., 2016; Alkhatabi et al., 2025). This highlights the importance of optimizing additive ratios to

balance transport efficiency with contaminant filtration, especially in wastewater treatment applications (Man et al., 2020).

Scanning electron microscopy (SEM) images support this interpretation. The P0 membrane showed a dense morphology with limited finger-like macropores, aligning with its low permeability and high rejection. The PP membrane displayed a more open structure with pronounced finger-like pores, improving permeability but slightly compromising rejection. The PM membrane had a denser structure compared to PP membrane, contributing to moderate rejection with enhanced water transport. In PPM membrane, SEM revealed a well-developed network of macropores, responsible for its excellent water flux and decreased rejection.

This inverse correlation between permeability and rejection efficiency reflects the structural-functional balance in membrane engineering. The PPM membrane exemplifies this trade-off, achieving superior water permeability while moderately reducing filtration performance. Thus, membrane design must consider specific application requirements, tailoring porosity and hydrophilicity to achieve optimal operational outcomes.

In this study, humic acid was selected as the model contaminant because it is one of the most representative fractions of natural organic matter (NOM) commonly present in surface waters and

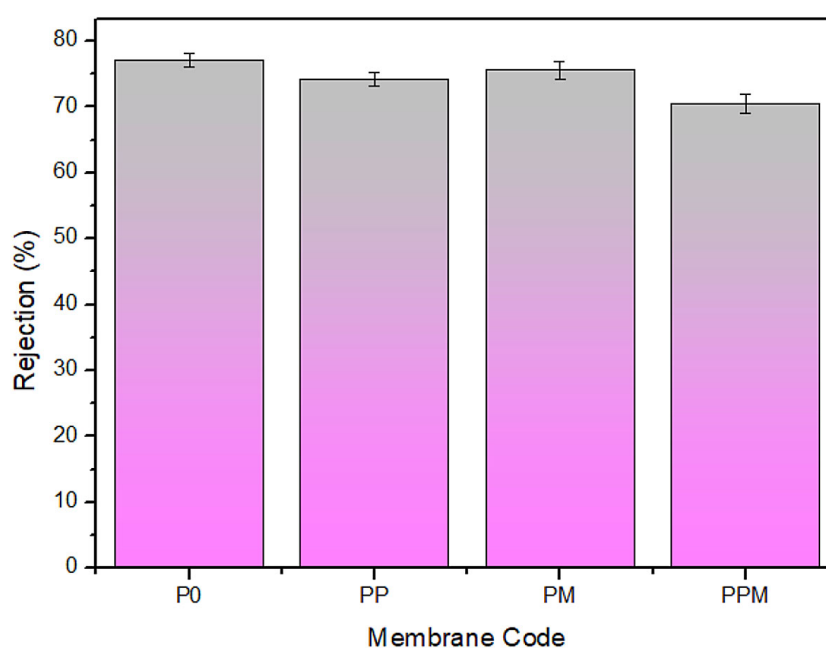


Figure 6. Humic acid rejection of the prepared membranes

is widely used as a benchmark foulant in membrane performance evaluation (Xie et al., 2019; Kywe et al., 2022). While humic acid rejection provides valuable insight into organic fouling resistance, it does not encompass the full spectrum of contaminants encountered in practical applications. For example, proteins and polysaccharides, which are abundant in biological wastewater, are known to strongly adhere to hydrophobic surfaces; increasing membrane hydrophilicity reduces this adhesion by forming a hydration layer that repels foulants. Similarly, oil emulsions and other hydrophobic organics have been shown to cause severe fouling in unmodified membranes, but hydrophilic surfaces mitigate this effect by preventing droplet adsorption and enhancing flux recovery (Sisay et al., 2023). For inorganic foulants such as heavy metals or colloidal silica, the increased porosity and hydrophilicity of modified membranes improve cleanability and flux recovery, thereby reducing irreversible fouling (Mazumdel et al., 2020). Thus, while humic acid served as a relevant model foulant in this study, the structural and surface modifications introduced are anticipated to enhance performance against a broader range of organic and inorganic contaminants, although further systematic evaluations remain necessary.

Antifouling mitigation

The antifouling performance of the membranes was evaluated using the flux recovery ratio (FRR), a widely accepted metric for assessing the ability of membranes to regain permeability following exposure to fouling agents. As depicted in Figure 7, the P0 membrane exhibited the lowest FRR (42.6%), indicative of a high degree of irreversible fouling. This result aligns with its hydrophobic character, which facilitates foulant adhesion. In contrast, membranes modified with hydrophilic agents showed markedly higher FRR values, with PP membrane and PM membrane achieving FRRs of 67.8% and 60.4%, respectively. The highest FRR (87.2%) was obtained for the PPM membrane, demonstrating a superior resistance to fouling due to the synergistic effects of both PVP and $\text{Mg}(\text{OH})_2$.

The enhancement in antifouling capacity is directly related to modifications in membrane surface chemistry and structure, which were characterized using FTIR and WCA measurements. FTIR spectra confirmed the

incorporation of functional groups associated with increased hydrophilicity. For instance, the PP membrane displayed an additional absorption peak at approximately 1660 cm^{-1} , corresponding to the carbonyl ($\text{C}=\text{O}$) stretching vibration from PVP, indicating the presence of polar groups. Similarly, the PM membrane exhibited a peak around $3000\text{--}3600\text{ cm}^{-1}$, indicating the presence of OH bonds from $\text{Mg}(\text{OH})_2$, which are likely associated with hydroxyl groups contributing to hydrophilic properties (Acarer et al., 2024). The PPM membrane showed both these peaks, confirming the successful integration of both additives and suggesting the formation of a more hydrophilic surface, which is beneficial in mitigating organic fouling.

The hydrophilic nature of the membrane surfaces, quantified by WCA measurements, further supports these findings. The WCA of the P0 membrane was measured at 78° , while that of PP membrane, PM membrane, and PPM membrane decreased to 65° , 58° , and 55° , respectively. These lower WCA values signify enhanced surface wettability, which facilitates the formation of hydration layers on the membrane surface, thereby reducing foulant adhesion (Irfan et al., 2015) (Febriasari et al., 2021). The data clearly demonstrate that a decrease in WCA correlates with an increase in FRR, emphasizing the critical role of surface hydrophilicity in antifouling performance.

The correlation between FTIR-detected functional groups, WCA, and FRR values is consistent with findings in membrane science literature. Membranes exhibiting functional groups such as hydroxyl ($-\text{OH}$) or carbonyl ($\text{C}=\text{O}$) have demonstrated enhanced antifouling capabilities by promoting hydrophilicity and forming hydration barriers (Salim et al., 2022; Liu et al., 2019). The PPM membrane, with its dual-functional modification, benefitted from both the structural attributes of PVP and the hydrophilic contribution of $\text{Mg}(\text{OH})_2$. The resulting surface chemistry effectively minimized foulant-membrane interactions and allowed better cleaning, leading to an exceptional FRR of 87.2%.

The high flux recovery ratio (FRR) of 87.2% provide indirect evidence of the long-term stability of the modified membranes, as it indicates that the PPM membrane can effectively recover permeability after a fouling–cleaning cycle, suggesting resilience under repeated

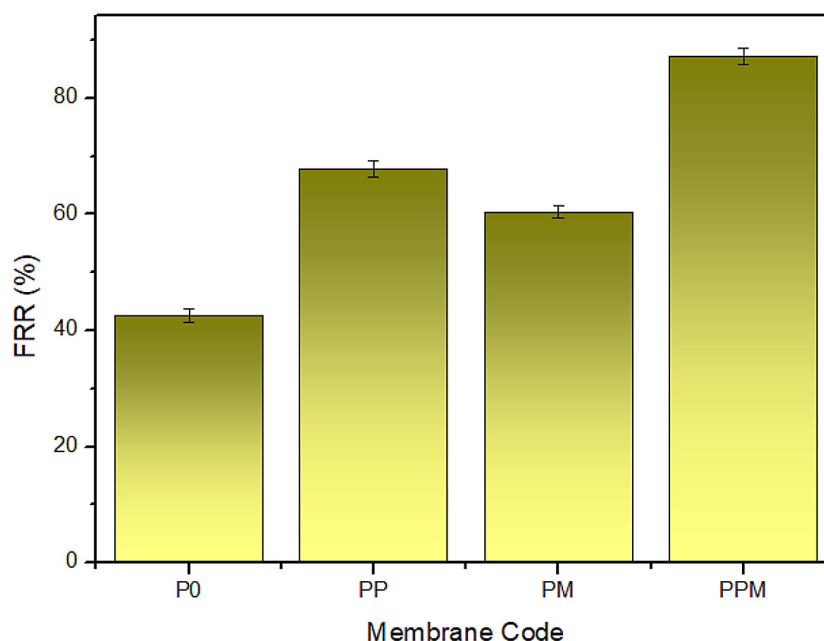


Figure 7. FRR of the prepared membranes

operation. In addition, SEM analysis revealed a well-distributed pore structure in the PPM membrane, which is less prone to compaction under pressure compared to highly porous single-additive systems. The FTIR spectra also confirmed the presence of stable hydrophilic functional groups (-OH from Mg(OH)_2 and C=O from PVP) covalently or strongly associated with the PES matrix, which reduces the likelihood of rapid additive leaching. Together, these findings suggest that the dual incorporation of PVP and Mg(OH)_2 enhances not only the initial performance but also the potential operational stability of the membrane, even though extended continuous tests will be required to fully confirm long-term durability.

This observation aligns with earlier findings that dual modification strategies involving both organic and inorganic additives can synergistically enhance long-term membrane performance. Studies have shown that such dual-modified membranes not only improve antifouling resistance but also maintain structural stability and performance over prolonged filtration operations, especially under complex feed conditions (Lakshmanan et al., 2025; Man et al., 2020). The high FRR achieved by the PPM membrane validates this approach, indicating its potential suitability for challenging filtration scenarios such as wastewater treatment or industrial effluent purification.

These results underscore the pivotal role of membrane surface modification in mitigating fouling, with FTIR, WCA, and FRR providing complementary insights into the mechanisms at play. The combined use of PVP and Mg(OH)_2 not only improved membrane hydrophilicity but also enhanced recovery performance after fouling, thereby addressing one of the most critical challenges in membrane filtration systems.

Performance comparison

As shown in Table 2, several studies have investigated hybrid modifications of PES/PVP membranes using inorganic nanoparticles. For instance, PVP + TiO_2 systems have demonstrated a two- to three-fold increase in permeability ($55\text{--}66 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$) while maintaining high humic acid rejection ($\sim 95\text{--}96\%$) and achieving flux recovery ratios of $83\text{--}89\%$. Incorporation of graphene oxide (GO) into PES/PVP membranes produced even greater permeability improvements, with reported fluxes of $\sim 150.2 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ (about eight times pristine PES) and Pb^{2+} rejection enhanced from 38.9% to 80.6% . Similarly, PVP-functionalized carbon nanotubes (CNTs) significantly improved antifouling, yielding $\sim 93.4\%$ BSA rejection and an FRR of $\sim 81.7\%$. In comparison, the dual PVP + Mg(OH)_2 (PPM) membranes developed in this study achieved a flux of $90.6 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ (five times pristine PES)

Table 2. Performance comparison with other PVP-based hybrid additive systems

Hybrid system (Additives)	Pure water flux / Permeability	Rejection (model contaminant)	Antifouling (FRR)	Reference
PES/PVP + TiO ₂	55–66 L·m ⁻² ·h ⁻¹ (≈2–3× pristine PES)	~95–96% (Humic Acid)	83–89% (vs 77% pristine PES)	Ahmad et al., 2022
PES/PVP + GO	~150.2 L·m ⁻² ·h ⁻¹ (≈8× pristine PES)	~80.6% (Pb ²⁺ ions) vs 38.9% pristine	Good fouling resistance (easy cleaning)	Poolachira et al., 2022
PES/PVP + CNT	(Not directly reported for water flux)	~93.4% (BSA, 66 kDa protein)	~81.7% FRR; ~80% fouling reversible	Irfan et al., 2015
PES/PVP + Mg(OH) ₂ (PPM, this study)	90.6 L·m ⁻² ·h ⁻¹ (≈5× pristine PES)	70.5% (Humic Acid)	87.2% FRR	This study

and an FRR of 87.2%, which is higher than most reported systems. Although humic acid rejection (70.5%) was lower than in TiO₂ or CNT-based hybrids, the PPM membranes provide a strong balance between permeability and antifouling, underscoring their potential for practical water treatment applications where fouling resistance and operational stability are critical.

CONCLUSIONS

This study systematically evaluated the synergistic effects of PVP and Mg(OH)₂ as dual additives in polyethersulfone membranes fabricated via non-solvent induced phase separation. The modified membranes demonstrated significant enhancements in water permeability, rejection performance, and antifouling resistance compared to unmodified PES. Among all variations, the PPM membrane displayed the highest pure water permeability of 90.6 L/m²·h, attributable to improved porosity and surface hydrophilicity. Although it showed a moderate decline in humic acid rejection (70.5%), the membrane's antifouling capability improved markedly, as indicated by a flux recovery ratio of 87.2%. The study highlighted clear correlations between structural characteristics (WCA, FTIR signatures) and membrane performance. FTIR confirmed the integration of hydrophilic groups (C=O and OH) while WCA analysis revealed lower contact angles for modified membranes, demonstrating increased wettability. These attributes collectively contributed to enhanced antifouling behavior. Overall, this study validates that organic–inorganic dual-additive strategies can be effectively employed to tailor permeability and antifouling properties of PES membranes. Future research may focus on optimizing additive concentrations, conducting extended long-term stability tests, and

benchmarking performance under diverse real wastewater conditions to further enhance selectivity and durability.

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