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Research Article

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Posted Date: September 23rd, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10598377/v1>

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Additional Declarations: No competing interests reported.

Assessment of Metal-Organic Framework Incorporated Thin Film Nanocomposite Membrane in Real Seawater Desalination Via Pressure Assisted Osmosis

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Abstract This study presents the fabrication, characterization, and real seawater desalination performance of a microporous aluminium fumarate metal–organic framework (Al-Fumarate MOF) incorporated thin film nanocomposite (TFN) membrane synthesized for pressure assisted osmosis (PAO) applications. The membranes were fabricated through interfacial polymerization on a polyethersulfone support layer having nonwoven fabric support. The MOF was characterized using SEM, BET analysis while its stability in salt medium was confirmed using XRD analysis. The membranes were characterized by ATR-IR, SEM, XPS, AFM, contact angle and mechanical strength analysis. The membrane showed significantly better intrinsic transport features with a water permeability of $3.8 \pm 0.22 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$, NaCl rejection of $98.9 \pm 1.1\%$, and a low B/A ratio of 8.9 kPa compared with the control membrane and conventional forward osmosis membranes. Real seawater PAO testing with 2M NaCl as the draw solution showed reliable performance at hydraulic pressures between 0 and 2 bar. The membrane with 0.05wt% of MOF attained a superior permeability-selectivity balance with stabilized flux of $9.35 \text{ Lm}^{-2}\text{h}^{-1}$. The improved desalination performance was ascribed to the hydrophilic microporous framework of Al-Fumarate MOF that boosted water transport, reduced internal concentration polarization and improved membrane structural stability indicating potential candidate for seawater PAO desalination in high salinity seawater settings.

Keywords Hydrophilic nanofillers • Interfacial polymerization • Permeability–selectivity trade-off • Reverse salt flux

1 Introduction

Over the last decade, a great deal of efforts has been devoted to solve the intrinsic limitations of traditional forward osmosis (FO) membrane systems such as low water productivity owing to severe internal concentration polarization (ICP) and gradual decrease of effective osmotic driving force during operation (McCutcheon et al. 2005; Cath et al. 2006). Despite the clear advantages of FO such as low fouling propensity and low hydraulic energy consumption, practical application of FO for seawater desalination is limited by relatively low permeate flux, especially when applied to high salinity feed waters. To overcome these constraints, researchers have investigated several advanced versions of FO such as pressure-retarded osmosis (PRO), pressure-assisted osmosis (PAO) and FO–RO integrated systems (Chung et al. 2012; Achilli et al. 2009; Yip et al. 2012).

Among these approaches, PAO has been recognized as one of the most promising developments which combines the osmotic driving power of FO with a moderate hydraulic pressure provided to the feed side, and so enhances net water transport while avoiding the extraordinarily high pressures required in reverse osmosis systems (Chou et al. 2012). Unlike PRO, where hydraulic pressure is applied on the draw side to generate energy, PAO primarily uses feed-side pressure to improve desalination performance and water recovery (Han et al. 2013). It has been shown in recent studies that using relatively low hydraulic pressures (<5 bar) can dramatically increase the permeate flux, lessen the influence of ICP and improve the membrane use efficiency without significantly increasing the energy consumption (Blandin et al. 2015). Computational and experimental investigations have also shown that PAO can achieve better water recovery and lower specific energy consumption than standard FO systems while preserving good salt rejection features (Altaee et al. 2014). Thus,

membrane development has steadily transitioned from membranes specifically developed for FO applications to mechanically strong membranes that can resist simultaneous osmotic and hydraulic driving pressures under PAO operation. This change has produced a demand for advanced membrane materials that are characterized by high permeability, low reverse salt diffusion, good structural integrity, and resistance to compaction under long-term hydraulic loads (Wang et al. 2007). It has been shown in several studies that PAO can achieve much higher water productivity and recovery than standard FO with relatively low specific energy consumption (Altaee et al. 2014; Bou-Rabee et al. 2026). Moreover, moderate hydraulic pressure has been shown to minimize the effects of concentration polarization and improve the efficiency of membrane use (McCutcheon et al. 2005). Nonetheless, the successful deployment of PAO technology is highly dependent on the preparation of membranes with high water permeability, strong salt rejection, low reverse salt flux, and sufficient mechanical stability to survive long-term hydraulic loading conditions (Cath et al. 2006).

Thin-film composite (TFC) membranes are now regarded as the most efficient membrane structure for FO and PAO applications, owing to their good permeability-selectivity features (Lee et al. 2011). TFC membranes usually consist of a porous support layer that is coated with a very thin polyamide selective layer, formed via interfacial polymerization between aqueous and organic monomers (Cadotte 1981). Although TFC membranes have shown better performance compared to traditional cellulose-based membranes, their practical applicability is limited by the intrinsic permeability-selectivity trade-off (Park et al. 2015). However, increasing water permeability often leads to increase of salt transport through the membrane, whereas improving selectivity usually leads to decrease of water flux. Moreover, the dense polyamide structure and the topology of the support layer provide resistance to the mass transfer and ICP, which restrict the membrane efficiency in osmotic desalination processes (Li et al. 2010). Therefore, numerous research efforts have been concentrated on changing membrane architectures to enhance permeability, selectivity and structural robustness concurrently.

Among the reported membrane modification approaches, incorporating nanoparticles into the polyamide selective layer to produce thin-film nanocomposite (TFN) membranes has gained much attention (Fadel et al. 2026). The incorporation of nanomaterials can lead to the formation of additional transport paths, enhances the hydrophilicity of the membrane, modify the surface morphology, and improve the physicochemical properties of the selective layer (Lau et al. 2012). Various nanomaterials including carbon nanotubes, graphene oxide, silica nanoparticles, zeolites, MXenes and metal-organic frameworks (MOFs) have been studied for application in desalination membranes (Salman et al. 2016; Zhu et al. 2018; Dutta et al. 2024). MOFs, in particular, have emerged as extremely promising options among these materials due to their highly organized porous structures, adjustable pore topologies, huge specific surface areas and varied surface functions (Furukawa et al. 2013).

MOFs are crystalline porous materials constructed from metal ions linked by organic ligands to form three-dimensional networks with well-defined pore patterns (Li et al. 2012). Their particular structural features allow rapid molecular transport with selective separation properties, making them particularly suitable for membrane desalination applications (Kadhom et al. 2017). MOFs can be inserted in polyamide selective layers to form preferential water transport channels for the penetration of water while blocking the flow of hydrated salt ions (Ma et al. 2024). It has been shown in several studies that incorporating MOFs such as ZIF-8, UiO-66, MIL-101, MIL-53 and CAU-10-H into desalination membranes can significantly increase their water flux, salt rejection and antifouling properties (Dong et al. 2022; Wang et al. 2023; Li et al. 2009; Shi et al. 2021). Moreover, the hydrophilicity of many MOFs can increase the wettability of the membrane as well as decrease the transport resistance, thereby enhancing the overall performance of the membrane (Li et al. 2023).

Aluminium fumarate (Al-Fumarate) is one of the most studied MOFs for water applications due to its remarkable hydrothermal stability, high affinity to water molecules, low cost of synthesis, and high surface area characteristics (Cadiau et al. 2015; Canivet et al. 2014). Al-Fumarate has a highly structured microporous design

with interconnecting channels that allow fast adsorption and passage of water (Rubio-Martinez et al. 2017). Previous investigations have shown its remarkable durability in aquatic conditions, which is of particular interest for desalination and water purification applications where long-term structural integrity is needed (Velte et al. 2023). Unlike many MOFs, which undergo breakdown of the framework after extended contact to water, Al-Fumarate retains its crystalline structure and adsorption properties under saline conditions (Splith et al. 2018). Moreover, studies on water transport pathways of Al-Fumarate have showed fast diffusion kinetics and favorable water-framework interactions, indicating its potential to improve membrane permeability without compromising separation efficiency (Rieth et al. 2017).

The recent development of MOF-incorporated TFN membranes has shown promising improvements in intrinsic membrane transport properties, such as water permeability coefficient (A), salt permeability coefficient (B), and B/A ratio, which are widely accepted as important parameters for evaluating membrane performance in osmotic desalination processes (Tiraferri et al. 2011; Yip et al. 2010). However, most of the reported investigations have been mostly on laboratory-scale FO trials with deionized water or synthetic saline feed solutions (Lee et al. 2023). There is, however, less research on membrane performance with real seawater feed streams under PAO working conditions. For several MOF-based TFN membranes, the influence of hydraulic pressure on membrane transport behavior, reverse salt diffusion, concentration polarization, and structural stability is still unclear (Abdelrasoul et al. 2024). However, the investigations on the application of the Al-Fumarate -incorporated membranes for real saltwater PAO desalination are limited, despite the promising physicochemical properties of this MOF material.

Therefore, this study assess feasibility of using Al-Fumarate incorporated TFN membranes specifically tailored for PAO saltwater desalination. The membranes were prepared using interfacial polymerization on a polyethersulfone support layer reinforced by a nonwoven fabric substrate. The membranes were fully characterized by attenuated total reflectance infrared spectroscopy (ATR-IR), X-ray photoelectron

spectroscopy (XPS), scanning electron microscopy (SEM), atomic force microscopy (AFM), contact angle measurements, and mechanical strength analysis, to investigate the influence of MOF incorporation on the membrane structure and surface properties. Then the intrinsic transport properties of the manufactured membranes were studied and compared to a control membrane and commercial forward osmosis membranes. Desalination experiments with genuine seawater and 2 M NaCl as the draw solution were also done at hydraulic pressures of 0 - 2 bar. Special attention was paid to the study of Al-Fumarate incorporation impacts on water transport, salt rejection, reverse salt diffusion, concentration polarization mitigation as well as membrane stability during PAO operation. The findings contribute to the creation of high-performance osmotic membranes and offer fresh insights into the role of hydrophilic microporous MOFs in improving the next generation of desalination technologies.

Materials and methods

2.1 Materials

The membrane support layer consisted of polyethersulfone (PES, from Godfellow Advanced Materials). The polyamide selective layer was synthesized via interfacial polymerization of meta-phenylenediamine (MPD, from Alfa Aesar) and trimesoyl chloride (TMC, from Alfa Aesar). The membrane surface was functionalized with metal-organic Al-Fumarate procured by MOF Technologies (UK) to improve water transport and separation performance. Analytical grade *N,N*-dimethylformamide (DMF), *N*-methyl pyrrolidone (NMP), polyethylene glycol (PEG, $M_w = 600$ Da), *n*-hexane and sodium chloride were utilized for membrane production and performance evaluation. For comparison, commercial FO membranes from Hydration Technology Innovations (HTI) and Fluid Technology Solutions Inc. (FTSI) were utilized.

2.2 Membrane Synthesis Procedure

The PES supports membrane (code: M0) were prepared by the phase inversion approach over layer of nonwoven fabric by casting solution containing 15.0 wt % PES and 2.0 wt % PEG, $M_w = 600$ Da) in DMF/NMP solvent mixture. The coated substrate

was coagulated in deionized (DI) water, rinsed, and dried under ambient conditions. Then, a thin selective polyamide layer was coated on the surface of the substrate by interfacial polymerization between an aqueous 2.0 wt% MPD solution and a 0.1 wt% TMC solution in n-hexane, followed by thermal curing at 80°C for 5 min. The TFN membrane was fabricated by incorporating Al-Fumarate MOF nanoparticles into the MPD solution at 0.0125, 0.050, and 0.10 wt% concentrations and then ultrasonicing and stirring to obtain a uniform dispersion before interfacial polymerization to obtain homogeneous distribution in the polyamide layer. The prepared membranes were washed and stored in DI water before characterization and desalination testing. The membranes were denoted as M0 (control), M0.0125, M0.050, and M0.10 based on the Al-Fumarate MOF loading.

2.3 Characterization Techniques

The prepared membranes were fully characterized for their structural, surface, chemical, and mechanical properties. The surface and cross-section morphologies were studied by scanning electron microscopy (SEM), and the surface topography and roughness were evaluated by atomic force microscopy (AFM). The membrane hydrophilicity was measured by the water contact angle equipment from KINO-USA. The results provided are the average of at least three separate measurements. Brunauer-Emmett-Teller (BET studies) of Al-Fumarate were performed on a BELSORP-miniX instrument with N₂ as adsorptive at the adsorption temperature of 77.35K. The X-ray diffraction (XRD) spectra of the MOF before and after exposure to salt water proved the water stability. Furthermore, the mechanical strength of the membrane substrates was evaluated by tensile testing based on the ASTM D882-10 standard. The results presented are the average values obtained from three specimens.

2.3 PAO Experimental Procedure

PAO studies were performed in a laboratory-scale cross-flow PAO system (Alambi et al. 2025) equipped with flow control devices, conductivity monitoring sensors and a hydraulic pressure regulation unit. The feed solution was actual seawater taken from the beachwell and the draw solution was 2 M NaCl solution. The pressure on the feed

side was varied from 0 to 2 bar. The water flux and RSF were measured throughout the studies. The flux and the RSF of the membranes were measured during the PAO tests in FO mode. The FS was a deionized water and the DS was 2.0 M sodium chloride solution. The RSF and flux values were also measured at room temperature, with the FS and DS flow rates (8.5 cm/s) over the membrane kept in cross-flow mode. According to Oh et al. 2014, the input feed pressure was adjusted to a range of 1-6 bar and its stable value was recorded during the experiment. In the PAO process utilizing flat-sheet membranes, spacers are generally required to reinforce the membrane against the applied hydraulic pressure. Therefore, 1.75 mm thick porous stainless-steel spacers were used across the membrane to allow unimpeded water flow. By analyzing the change in weight of the DS (ΔV), the FO water flow J_v ($\text{Lm}^{-2}\text{h}^{-1}$) was calculated using equation (1).

$$J_v = \frac{\Delta V}{A_m \cdot \Delta t} \dots\dots\dots(1)$$

The effective membrane area is represented by the variable A_m .

To determine the RSF (J_s) at 20-min intervals, the FS's salt content was evaluated. Once the membrane reached flux stability, which usually took around 30 min, the RSF was calculated using the following equation.

$$J_s = \frac{\Delta(C_t V_t)}{A_m \cdot \Delta t} \dots\dots\dots(2)$$

At the end of the FO test, C_t and V_t denote the salt concentration and feed volume, respectively.

3 Results and Discussion

3.1 Characterization of the Al-Fumarate MOF

The BET analysis of Al-Fumarate MOFs in Fig. 1 revealed Microporous structures with avg. pore diameter 1.09 nm, surface area (BET) $802.34 \text{ m}^2\text{g}^{-1}$, and total pore volume of $0.439 \text{ cm}^3\text{g}^{-1}$. BET characteristics can affect transport and selectivity

behavior when integrated into membranes, the actual impact on desalination performance depends on their effective dispersion within the polymer matrix.

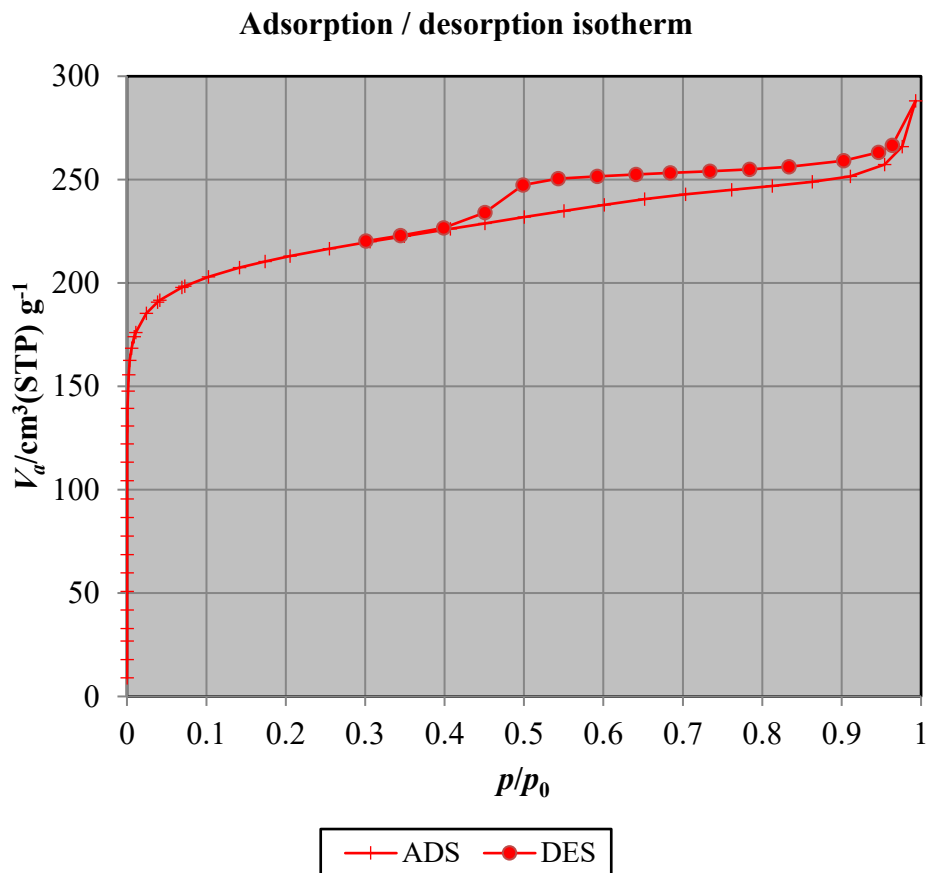


Fig. 1. N₂ Adsorption-desorption curves for Al-Fumarate MOF.

Fig. 2 (a & b) shows SEM images of the Al-Fumarate MOFs, which present well-defined crystalline particles with a typical polyhedral morphology, in agreement with the usual octahedral structure reported for aluminium-based Al-fumarate frameworks (Karmakar et al. 2016).

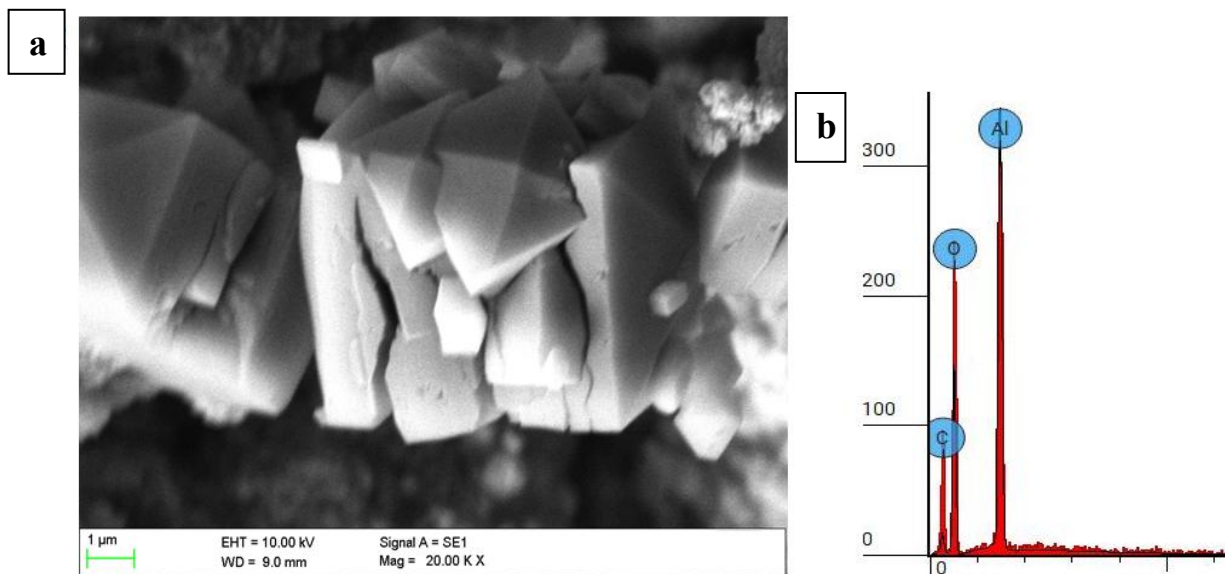


Fig. 2. a) SEM and b) EDS images of Al-Fumarate MOF.

The particles appear to have a fairly uniform shape with sharp edges and smooth crystal faces and some surface imperfections are seen and clumping. In general, the morphology shows that Al-fumarate MOF is extremely crystalline and can be used for applications that need stable porous materials like membrane modification and adsorption in water treatment systems.

3.2 Saltwater Stability Test for MOFs

The water stability of five different MOFs was assessed by dispersing the MOF powders in a 3.5 wt% sodium chloride solution—commonly used in the literature to simulate natural seawater (Zhang et al. 2013)—at a concentration of 0.1 wt%, corresponding to the maximum expected loading on the polyamide surface. The resulting MOF–saltwater suspensions were continuously stirred at room temperature for 72 h. After exposure, the suspensions were filtered using a $\sim 0.2 \mu\text{m}$ microfilter membrane, and the recovered solids were dried in a vacuum oven at 60°C . Finally, XRD analysis was performed to evaluate the structural stability of the MOFs before and after seawater exposure.

In Fig. 3, the XRD patterns of Al-Fumarate MOFs prior to saltwater exposure exhibit characteristic diffraction peaks that are in good agreement with those reported in the literature (Thuy et al. 2024).

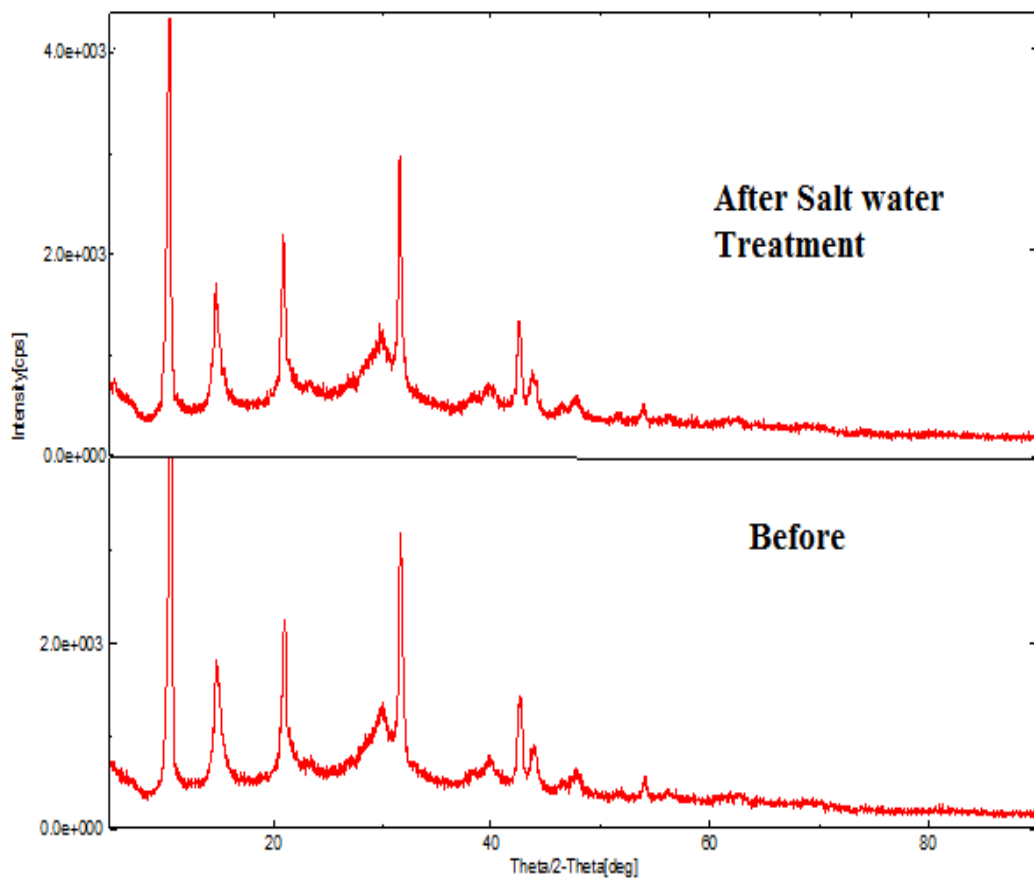


Fig. 3. Characterization of the Al-Fumarate MOF impregnated TFN membranes

Further, the XRD patterns of Al-Fumarate MOFs indicate a well-defined crystalline nature. The XRD profiles before and after saltwater exposure indicates that the crystalline structure of the MOFs was largely preserved under the tested conditions.

3.. ATR-IR Analysis

Fig. 4 shows the ATRIR spectra of three distinct membranes; the PES substrate membrane (M0), the control TFC membrane (M1), and the M3 membrane containing 0.5 wt% of Al-Fumarate MOF.

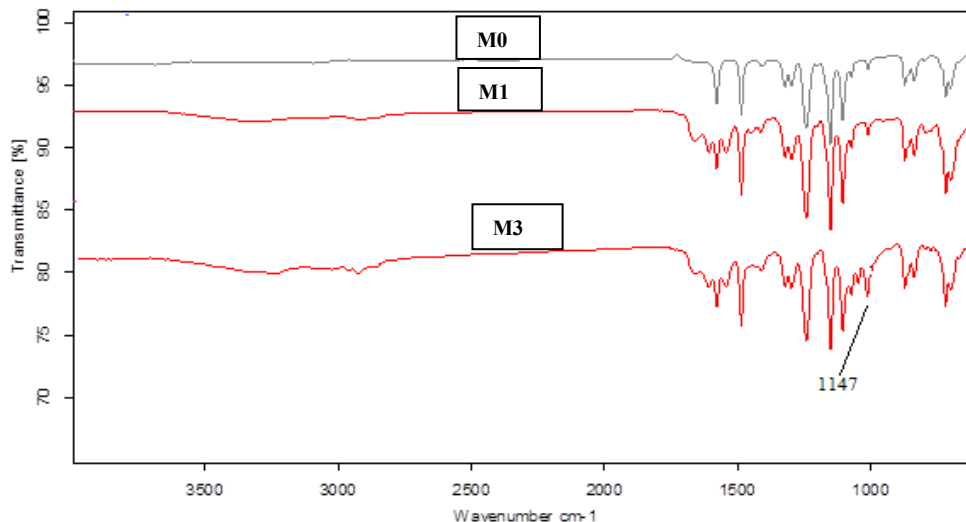


Fig. 4. The ATRIR spectra of PES support (M0), M1, and M3 membranes

The main difference in the spectra of M3 than M0 and M3 was the presence of the Al-O-H vibrational peaks at 1147 cm^{-1} in M3 spectra, which corresponds to the Al-fumarate MOF present on the surface of the membrane.

3.4 SEM Analysis of Al-Fumarate Based Membranes

As revealed from Fig. 5, the surfaces of Al-Fumarate based M2, M3 and M4 membranes displayed leaf-like or nodules and globules on their surfaces with spherical voids. The SEM images also illustrate the cross-sectional morphologies of Al-Fumarate MOF-incorporated membranes at different loadings (0.0125–0.1 wt%). At 0.0125 wt% Fig. 5 (a,d), the membrane exhibits a relatively smooth and uniform ridge-and-valley surface with a well-defined asymmetric cross-section, indicating good MOF dispersion without disturbing membrane formation.

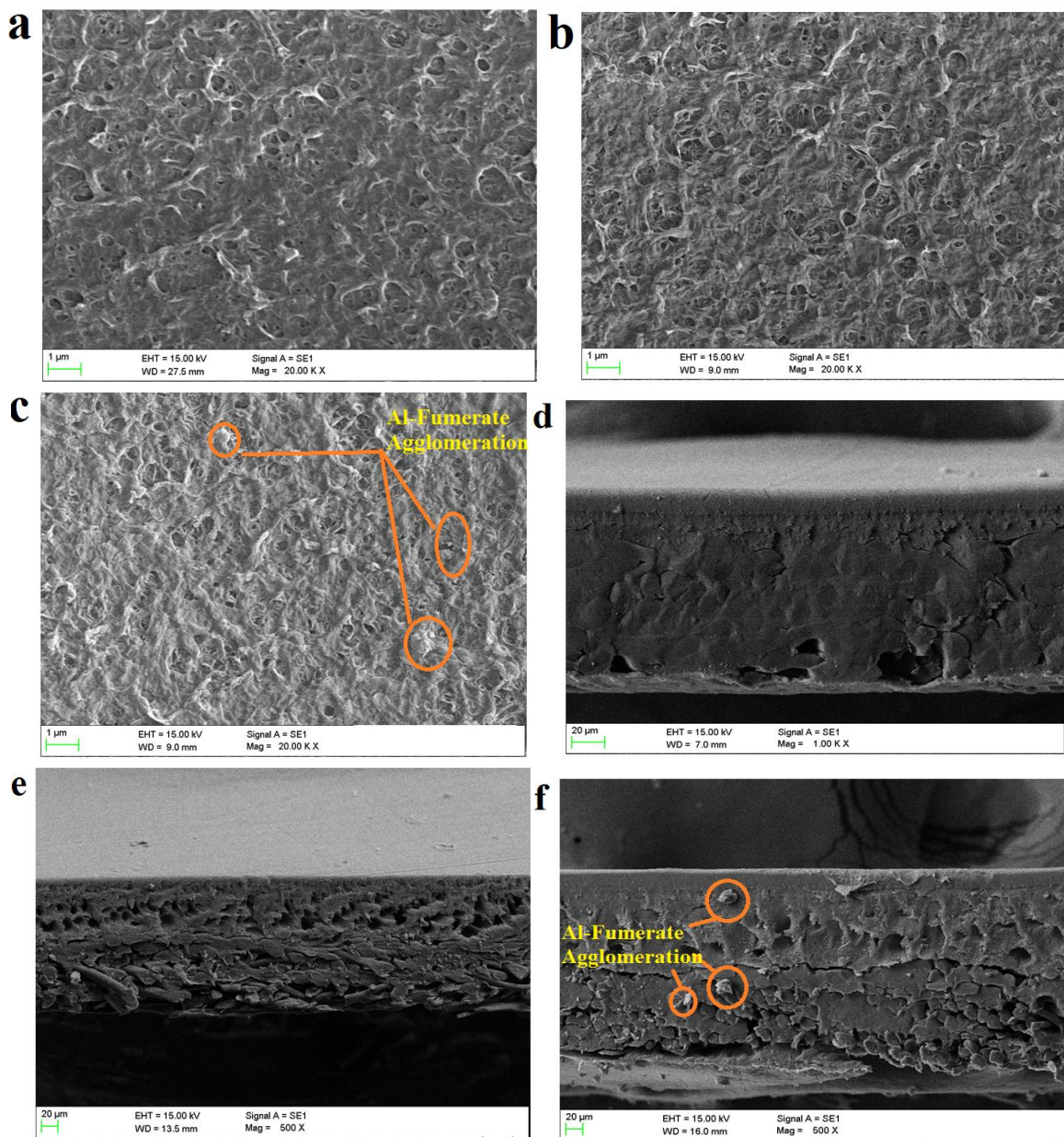


Fig. 5. SEM images of membranes : a, b, and c) surfaces of M2, M3, and M4 and d, e, and f cross sections of M2, M3, and M4 membranes, respectively.

Increasing the loading to 0.05 wt% Fig. 5 (b, e) results in slightly higher surface roughness and a more porous substructure, suggesting enhanced interaction between the MOF and polymer matrix. The surface morphology of M3 indicates a relatively good dispersity of Al-Fumarate MOF in the polyamide layer. While at higher cocentration of Al-Fumarate formed the agglomerated partciles on the membrane surface and cross-sections as highlighted in Fig. 5 (c, f). Overall, moderate Al-

Fumarate MOF incorporation improves membrane morphology, whereas higher loading promotes aggregation that may affect membrane performance.

3.5 Contact Angle Study

Membrane hydrophilicity is an important factor affecting filtration efficiency. As shown in Fig. 6, the addition of Al-Fumarate into the selective layer resulted in a increase in hydrophilicity as demonstrated by the decreasing of contact angle to 49.8° when the loading composition of Al-Fumarate was maximum (0.1 wt%) for M4 membrane in Fig. 6d.

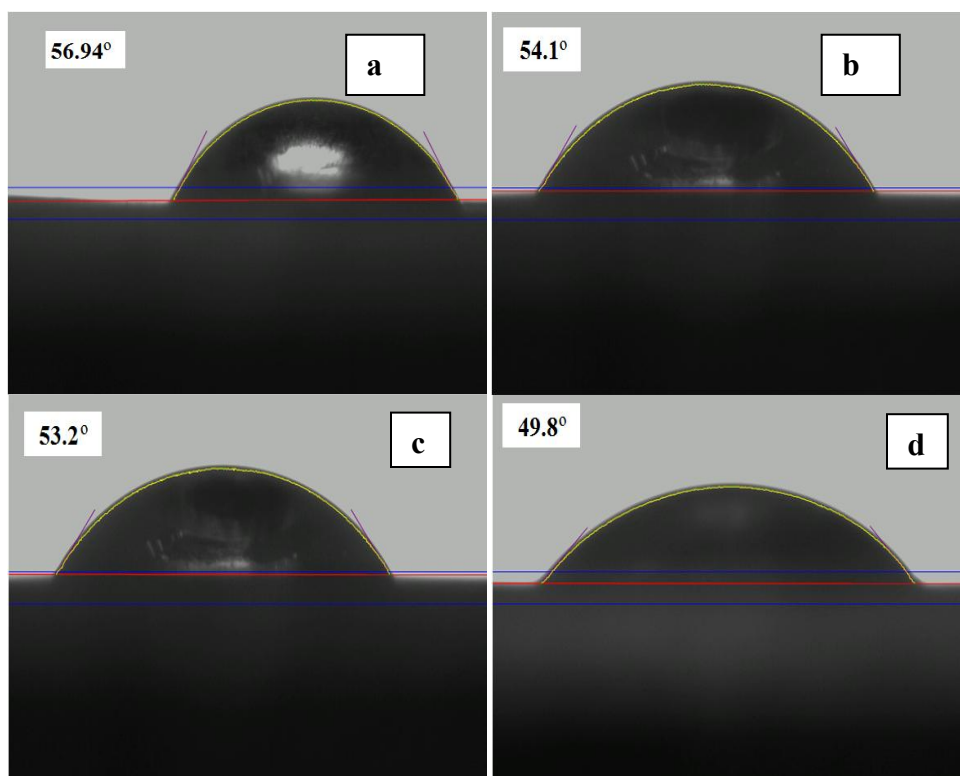


Fig. 6. Surface contact angles of a) Control M1 and Al-Fumarate MOF based b) M2, c) M3 and d) M4 membranes.

This enhancement is due to the hydrophilic nature of Al-Fumarate that improves the surface affinity towards water relative to the unmodified TFC membrane (Elsayed et al. 2021). The contact angle reduction may be also attributed to the appearance of more pronounced nodule-type surface structures detected in SEM

images, which were found MOF-modified membranes, contributing to surface roughness (Ma et al. 2024). Moreover, the greater deposition of Al-Fumarate caused less uniform dispersion of MOF leading to partial agglomeration and subsequently decreased the surface contact angle for M4 membrane.

3.6 AFM Analysis

The surface roughness of the Al-Fumarate-MOF based M2, M3 and M4 and control M1 membranes were analyzed by AFM and the results are displayed in Fig. 7.

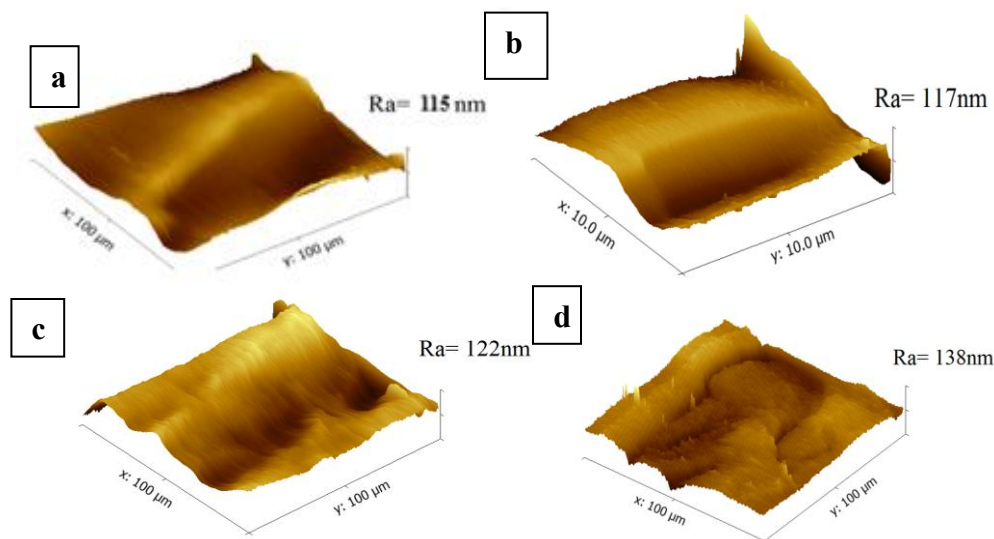


Fig. 7. Three-dimensional AFM images depicting the membranes: (a) M1, (b) M2, (c) M3 and d) M4 membranes.

Membranes with Al-Fumarate-MOF showed greater roughness values. This observation is in agreement with the SEM results where the presence of the Al-Fumarate-MOF resulted in the creation of more nodular structures. The effect is most pronounced in the M4 membrane, which showed significantly elevated Ra value of 138nm. Thus, AFM analysis further confirmed the formation of more nodular structure after the incorporation of Al-Fumarate-MOF consistent with the SEM analysis.

3.7 Tensile Strength Measurements

Although FO is inherently a non-pressure-driven process, its advanced configuration PAO requires membranes with adequate mechanical robustness to withstand the applied hydraulic pressure during desalination performance evaluation (Widjojo et al. 2013). As summarized in Table 1, a PES substrate membrane was newly fabricated following the same procedure described in the section 2.2, except that the nonwoven fabric support was deliberately excluded. This modification was implemented solely to investigate the role of the nonwoven fabric support in enhancing the mechanical strength of the UF substrate layer.

Table 1 Mechanical properties of control M1 and Al-Fumarate based membranes

<i>Membrane Code (type)</i>	<i>Young's modulus (MP)</i>	<i>Tensile strength (MP)</i>
PES Membrane (Without Fabric Support)	17.33±1.5	0.92±0.30
M0	40.32±1.0	1.28±0.05
M1	42.66±1.2	1.34±0.05
M3	46.82±1.8	2.78±0.10

The mechanical parameters shown in Table 1 clearly indicate the necessity of fabric support to improve the membrane strength for PAO operation. The unsupported PES UF membrane had the lowest Young's modulus (17.33 ± 1.5 MPa) and tensile strength (0.92 ± 0.30 MPa), demonstrating its relatively weak mechanical stability and restricted use for processes involving hydraulic pressure. The incorporation of the nonwoven fabric support considerably enhanced the mechanical properties as displayed for M0 in which the Young's modulus increased to 40.32 ± 1.0 MPa and the tensile strength increased to 1.28 ± 0.05 MPa. This confirms the importance of the fabric layer in strengthening the membrane structure, increasing stiffness, load capacity and resistance to deformation during the PAO operation. The control TFC membrane (M1) showed a further increase in Young's modulus to 42.66 ± 1.2 MPa and tensile strength to 1.34 ± 0.05 MPa, indicating that formation of the polyamide selective layer contributed additional structural integrity to the supported substrate. Further improvement was observed for the TFN membrane containing 0.05wt% of Al-Fumarate nanofillers with Young's modulus (46.82 ± 1.8 MPa) and the tensile strength

(2.78 ± 0.10 MPa) indicating that the embedded nanomaterials partly contributed towards the enhanced mechanical properties.

3.8 Real Seawater PAO Performance of M3 Membrane

The synthesized membranes were first tested for FO water flux and RSF characteristics before the actual seawater desalination performance testing. The membranes exhibited much enhanced PAO desalination performance with the addition of Al-fumarate MOF (Fig. S1-S3). As shown in Fig. S1, water flux increased from approximately $11 \text{ Lm}^{-2}\text{h}^{-1}$ for the control membrane (M1) to $17\text{--}23 \text{ Lm}^{-2}\text{h}^{-1}$ for M2–M3 and reached $33\text{--}35 \text{ Lm}^{-2} \text{ h}^{-1}$ for M4, confirming that MOF incorporation enhanced membrane permeability through the formation of hydrophilic surface formation. Although RSF also increased with MOF loading, indicating a permeability–selectivity trade-off, M2 and M3 achieved a more balanced performance than both the control and commercial membranes. Figure S2 further demonstrates that the water flux increased steadily with applied pressure for all membranes with the performance ranking of $M4 > M3 > M2 > M1$, showing the good influence of optimized MOF loading on pressure-assisted water transport. As shown in Fig. S3, RSF decreased with increasing applied pressure for all membranes, indicating enhanced selectivity at PAO conditions. Although M4 presented the highest RSF at low pressure, it had a significant decrease at higher pressures, whereas M3 consistently presented lower RSF values and better salt rejection. Overall, the results show that the addition of Al-fumarate MOF successfully improved the membrane permeability and PAO performance. M3 provides the best tradeoff between water flux and salt rejection.

In Fig. 8, for M3 membrane the FS conductivity increases nearly linearly with time under all pressures, rising from $\sim 57.4\text{--}58.0 \text{ mS/cm}$ initially to $\sim 58.5\text{--}60.2 \text{ mS/cm}$ at 150 min, indicating continuous RSF and feed concentration.

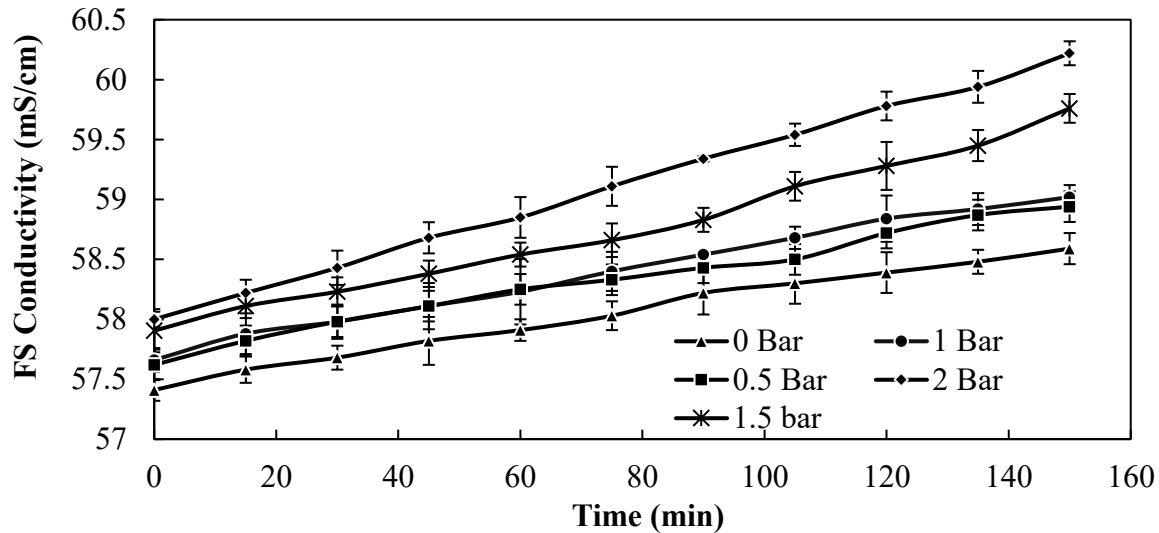


Fig. 8. Time-dependent variation of fs conductivity under different applied pressures for the M3 membrane. (Test Conditions: FS: Seawater DS: 2 M NaCl)

The largest increase (60.2 mS/cm) is obtained at 0 bar, confirming the major diffusive salt transport in FO mode. The smallest increase (58.5–58.6 mS/cm) is observed at 1 bar, demonstrating enhanced selectivity in mild PAO circumstances. At greater pressure (1.5–2 bar) the conductivity is increased to 59.5–60.0 mS/cm indicating some contribution of convective salt transport at high flux. The TFN membrane incorporated with Al-Fumarate-MOF enhances the performance owing to the hydrophilic surface structure, leading to the improved water transport and reduced internal concentration polarisation, suppressing the FS conductivity increase and achieving a balance between the flux and selectivity at 1 bar.

Fig. 9 shows a constant decline of the DS conductivity with time, showing a growing dilution of the 2 M NaCl DS by water permeation. The reduction in DS conductivity is directly proportional to the increase in FS conductivity, as both trends correspond to the concurrent water permeation and reverse salt diffusion during the PAO operation.

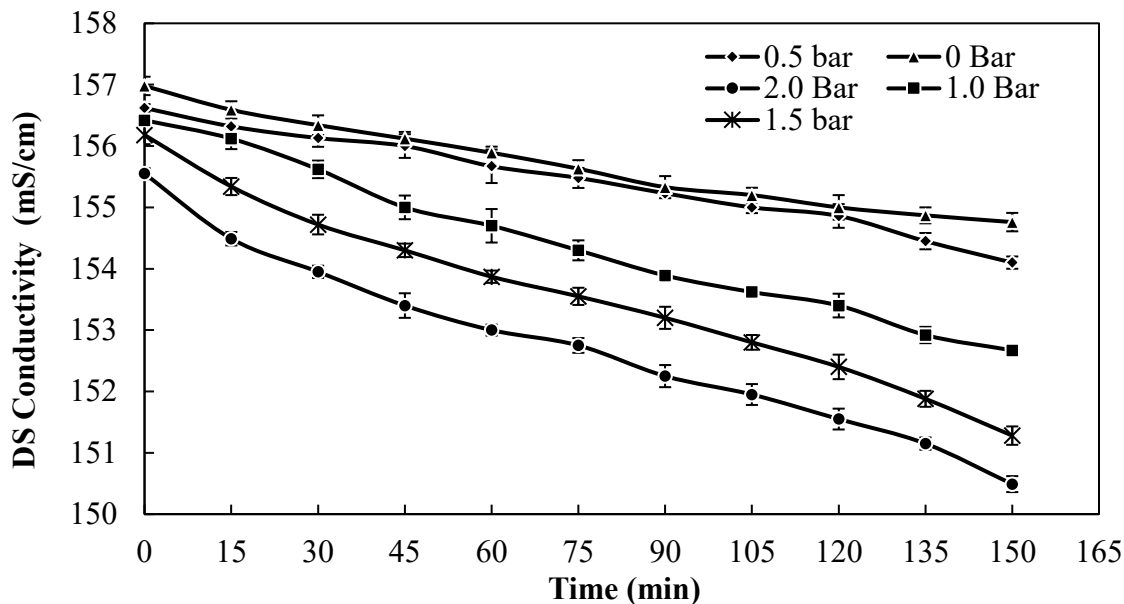


Fig. 9. Time-dependent variation of ds conductivity under different applied pressures for the M3 membrane. (Test Conditions: FS: Seawater DS: 2 M NaCl)

The major decrease is at 2.0 bar (155.5 to 150.5 mS/cm), then at 1.5 bar (156 to 151.2 mS/cm) and 1.0 bar (156 to 152.7 mS/cm), implies higher applied hydraulic pressure improves water flux. The Al-Fumarate MOF embedded in TFN membrane enhances this behaviour by offering hydrophilic membrane surface thus minimising internal concentration polarisation (Abdi et al. 2019) and permitting increased water flux and more efficient draw dilution especially at 1.5-2.0 bar.

For the M3 membrane (Fig. 10), the ΔC drops steadily with time from ~99-100 to ~90-96 mS/cm, showing depletion of the osmotic driving power due to draw dilution and feed salinity rise. The fall is more significant at higher pressures, with ΔC decreasing to ~90.2 mS/cm at 2 bar and ~91.5 mS/cm at 1.5 bar, whereas lower pressures (0–0.5 bar) maintain higher values (~95.5–96.2 mS/cm) due to reduced permeation. This is consistent with the idea that higher pressure increases water flux and gradient depletion. Overall, the MOF embedded membrane showed higher flux but faster ΔC reduction especially at 1.5–2 bar owing to its improved hydrophilic properties.

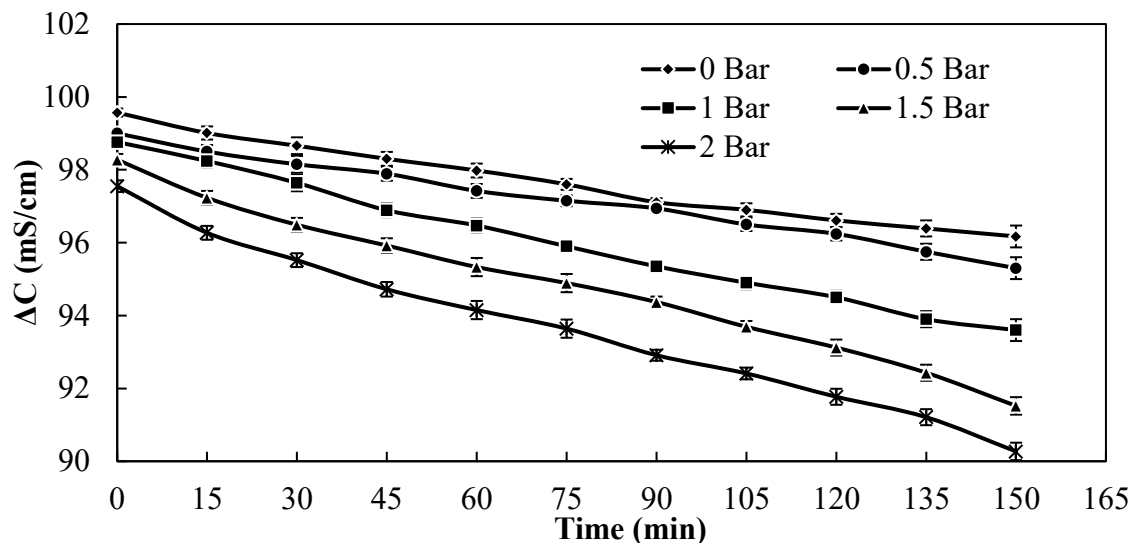


Fig. 10. Time-dependent variation of conductivity difference (ΔC) across the M3 membrane under different applied pressures. (Test Conditions: FS: Seawater DS: 2 M NaCl)

In Fig. 11, for the Al-Fumarate incorporated M3 membrane the flux initially declines rapidly (first 30–60 min) due to dilution of the 2 M NaCl draw solution followed by a gradual stabilization. Increasing hydraulic pressure from 0 to 2 bar significantly enhances water flux, with the highest initial value observed at 2 bar ($\sim 20 \text{ Lm}^{-2}\text{h}^{-1}$), confirming the positive contribution of pressure to the net driving force; however, higher pressures also accelerate draw dilution, leading to a more pronounced flux decline over time and convergence of flux values at longer durations.

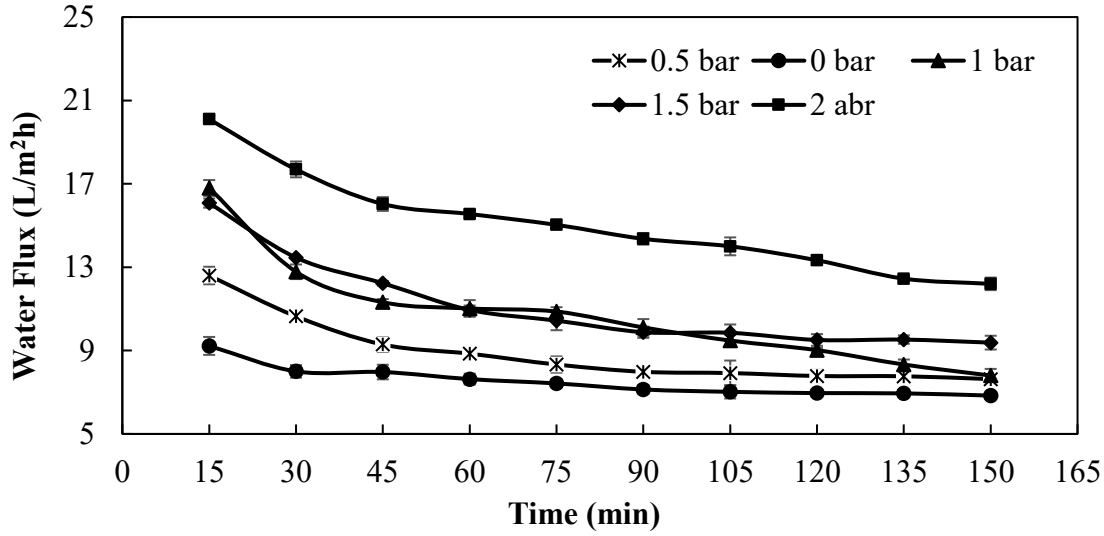


Fig. 11. Time-dependent variation of water flux under different applied pressures for the M3 membrane. (Test Conditions: FS: Seawater DS: 2 M NaCl).

In contrast, lower pressures give more stable but lower flow patterns. The integration of Al-Fumarate-MOF in the TFN membrane is critical to enhance the overall performance, by offering a highly porous and hydrophilic framework that boost water transport, decrease structural resistance and alleviate internal concentration polarization (Han et al. 2024), resulting in higher flux. Also from Fig. 11, at intermediate pressure values (~1-1.5 bar) at which there is an optimal trade-off between productivity and stability.

The RSF profiles with the greatest values under FO mode (0 bar) are shown in Fig. 12, and a noticeable reduction with the applied pressure, showing the better selectivity under PAO conditions. Initially RSF falls rapidly due to dilution by draw, but eventually levels off with time. The lowest and most stable RSF are obtained at moderate pressures (1.0–1.5 bar), however at higher pressure (2.0 bar) a minor increase in RSF is observed at later stages, probably due to the increase in convective salt transport. The better performance was due to the hydrophilic and porous nature of Al-Fumarate-MOF integrated TFN membrane that facilitated water transport and decreased reverse salt diffusion (Prasetya et al. 2020).

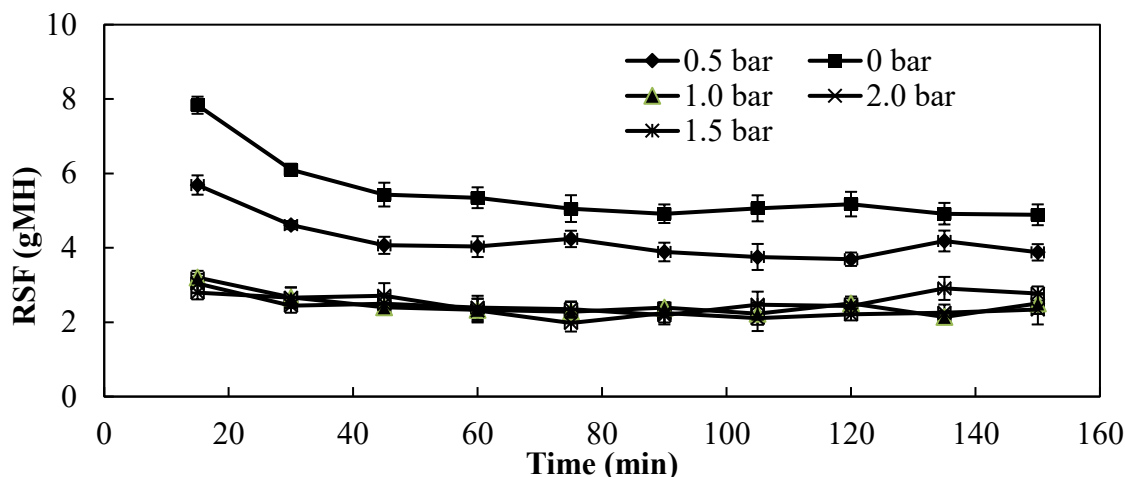


Fig. 12. Time-dependent variation of RSF under different applied pressures for the M3 membrane. (Test Conditions: FS: Seawater DS: 2 M NaCl).

3.9 Relationship Between Membrane Intrinsic Transport Properties and Performance

The relationship between membrane intrinsic transport properties (Table S1, Supporting Information) and PAO performance using real seawater was evaluated by correlating water flux and reverse salt flux (RSF) with the B/A ratio, surface roughness, wettability, and MOF porosity characteristics of the TFN membranes. Overall, membranes exhibiting lower B/A values demonstrated superior selectivity with reduced RSF and enhanced water permeability under both 1 and 2 bar operating conditions, confirming that intrinsic transport resistance strongly governs PAO performance.

3.10 Correlation of the Membrane Characterization with the PAO Performance

In this study, the correlation of membrane characterization with PAO performance is determined by the interplay of membrane morphology, surface characteristics, pore structure and intrinsic transport parameters. The inclusion of Al-Fumarate into the PA selective layer brought about considerable changes in the properties of the membrane, leading directly to improved PAO performance. Morphological characterization using SEM and AFM revealed that MOF incorporation altered the classical ridge-and-valley structure of the PA layer by increasing surface roughness and creating additional nodular features. This increased roughness for all the high-performance MOF

incorporated membranes, particularly at optimal loadings (e.g., ~0.05 wt%), facilitated greater water–membrane interaction, leading to higher initial flux under PAO conditions. BET analysis showed that the selected MOFs having microporous structures which contributed to the favorable water flux under the applied hydraulic pressure. Better salt rejection and selectivity were obtained with microporous MOFs. Surface chemical analysis using ATR-IR confirmed successful incorporation of MOFs and the presence of hydrophilic functional groups such as –OH, and –COOH functionalities from Al-Fumarate. These groups improved membrane hydrophilicity, as supported by reduced contact angle measurements across all TFN membranes. Enhanced hydrophilicity promoted rapid water sorption and diffusion through the selective layer, which is reflected in the higher PAO flux and improved flux stability over time. Additionally, the hydrophilic surface reduced foulant adhesion, contributing to improved antifouling performance and higher FRR, which indirectly supports sustained PAO performance. XRD and stability studies demonstrated that all selected MOFs retained their crystalline structure after prolonged exposure to saline conditions, confirming their chemical and hydrolytic stability. This structural integrity is crucial for maintaining consistent membrane performance during PAO operation, particularly under hydraulic where mechanical and chemical stresses are significant. The use of a nonwoven-supported PES substrate further enhanced mechanical strength, ensuring that the membranes could withstand applied pressures up to 2 bar without structural deformation, thereby enabling stable operation in PAO mode. Furthermore, time-dependent PAO performance trends (flux decline, FS/DS conductivity changes, and ΔC reduction) are consistent with the characterized structural and surface properties. Overall, the study demonstrated a direct correlation between membrane characterization parameters and PAO desalination performance.

3.11 Physicochemical Analysis of Water Streams During PAO Experimentation

In table 2, the physicochemical characterization of the FS and DS during the PAO experiments particularly at 0 - 2 bar using M3 membrane showed significant pressure dependent changes in conductivity and ionic composition when seawater was used as the FS and 2 M NaCl was used as the DS. The baseline seawater had an electrical

conductivity (EC) of about 60,200 $\mu\text{S}/\text{cm}$ and the concentrated 2M NaCl DS had a much higher EC of over 155,000 $\mu\text{S}/\text{cm}$, which acted as the osmotic driving force for water transport across the membrane.

Table 2 The physicochemical change in FS and DS conductivities for M3 membrane at different operating pressures during the PAO experiments using seawater as FS and 2M NaCl as the DS

<i>Parameter (Unit)</i>	<i>BWSW</i>	<i>FS (0bar)</i>	<i>FS (1bar)</i>	<i>FS (1.5 bar)</i>	<i>FS (2bar)</i>	<i>DS (0bar)</i>	<i>DS (1bar)</i>	<i>DS (1.5 bar)</i>	<i>DS (2bar)</i>
EC ($\mu\text{S}/\text{cm}$)	60200	58590	59100	59800	60220	154,760	152,610	151,280	150,490
F ⁻ (mg/L)	4	3.9	4.4	4.45	4.5	5.59	5.66	6.57	7.52
Cl ⁻ (mg/L)	24322	25972	24874	24080	23279	77866	76009	73809	71863
Br ⁻ (mg/L)	54.9	57.7	54.6	53.1	51.5	3.10	3.64	3.54	3.45
NO ₃ ²⁻ (mg/L)	47.5	49.5	44.6	44.4	44.1	83.67	80.70	80.39	80.38
SO ₄ ²⁻ (mg/L)	3389	3569	3361	3277	3193	762.42	791.53	1,302	1,820
Li ⁺ (mg/L)	0.2	0.3	0.8	0.5	0.2	<0.01	<0.01	<0.01	<0.01
Na ⁺ (mg/L)	12706	13555	13028	12610	12199	47,817	46,619	45,333	44,205
K ⁺ (mg/L)	394	418	392.2	380	369	10.68	8.58	9.30	10
Ca ²⁺ (mg/L)	926	976	931	940	949	580	696	1,085	1,480
Mg ²⁺ (mg/L)	1452	1533	1443	1403	1363	17.77	34.24	34.38	35
Silica (mg/L)	1.92	2.18	2.16	2.11	2.04	<0.01	<0.01	<0.01	<0.01

BWSW: Beachwell seawater; FS: Feed Solution; DS: Draw Solution; EC: Electrical Conductivity

During FO operation (or at 0bar), the FS conductivity marginally fell to 58,590 $\mu\text{S}/\text{cm}$ but the DS conductivity remained high at 154,760 $\mu\text{S}/\text{cm}$. This indicates limited dilution of the DS under purely osmotic driven working state. With the application of the hydraulic pressure, the DS conductivity gradually dropped from 152,510 $\mu\text{S}/\text{cm}$ at 1 bar to 151,280 $\mu\text{S}/\text{cm}$ at 1.5 bar and 150,490 $\mu\text{S}/\text{cm}$ at 2 bar, respectively, which confirmed the improved water permeation and dilution of the DS under PAO operation. In contrast, the FS conductivity was steady (58,590–60,220 $\mu\text{S}/\text{cm}$) during the trials, implying that the membrane had good salt rejection and the feed concentration polarization was well controlled.

The ionic concentration profiles also supported the conductivity changes during the PAO operations. The Na^+ concentration in the DS fell gradually from 47,817mg/L at 0 bar to 46,619 mg/L at 1 bar, 45,333mg/L at 1.5 bar and 71,863mg/L at 2 bar, whereas the corresponding Cl^- concentration decreased from 77,866mg/L to 76,009mg/L, 73,809mg/L and 71,863mg/L, respectively. The reductions clearly demonstrate gradual dilution of the concentrated NaCl DS resulting from increased water transfer from the seawater feed. At the same time, the FS Na^+ concentration declined slightly from 13,555 mg/L at 0 bar to 12,199 mg/L at 2 bar, and the FS Cl^- concentration from 25,972 mg/L to 23,279 mg/L, indicating sustained membrane selectivity and limited RSF. The behavior of the multivalent ion also revealed important transport properties during the PAO operation. The Mg^{2+} concentration in the FS fell progressively from 1,533 mg/L at 0 bar to 1,363 mg/L at 2 bar, while the Mg^{2+} concentration in the DS increased from 17.77 mg/L to about 34 mg/L at elevated pressures showing a modest ion movement across the membrane. Similarly, the DS Ca^{2+} concentration increased from 580 mg/L at 0 bar to 1,480 mg/L at 2 bar, which can be attributed to the pressure-enhanced convective ion transport. The sulfate content in the DS increased from 763.6 mg/L at 0 bar to 1,792 mg/L at 2 bar, which supports the possible increase of ion migration under high hydraulic pressure. However, the total ionic composition of the FS was largely steady, indicating that the M3 membrane showed good rejection ability even under the pressured operating situation. The results clearly show that the optimal operating pressure of ~ 1.5 bar showed a balanced physicochemical behavior with substantial dilution of the draw solution without excessive leakage of ions or instability, which proved the applicability of PAO operation for efficient seawater desalination applications.

3.12 Long Term Performance Test for M3 Membrane at 1.5 bar

In Fig. 13, the long-run PAO performance study of the M3 membrane over 1500 min revealed a significantly enhanced operational stability, validating the membrane's applicability for long-term desalination applications under PAO circumstances. The

M3 membrane had a very stable flux following the initial drop stage in the long-run PAO experiment.

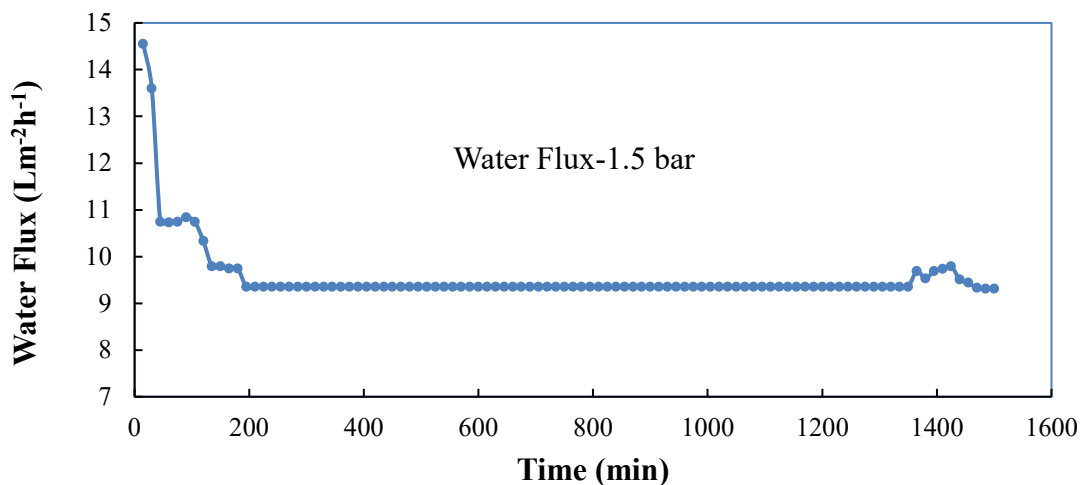


Fig. 13. Long run experimental water flux under different applied pressures for the M3 membrane. (Test Conditions: FS: Seawater DS: 2 M NaCl).

The water flux was stable at about $\sim 9.35 \text{ Lm}^{-2}\text{h}^{-1}$ for the most part of the operational period at 1.5 bar from $\sim 180 \text{ min}$ to $\sim 1350 \text{ min}$ with a small fluctuation in the flux was noticed near the end of the experiment ($\sim 9.3\text{--}9.7 \text{ Lm}^{-2}\text{h}^{-1}$). This behavior demonstrated the long-term operational stability and steady transport characteristics of the membrane. The long-term RSF behavior in Fig. 14 further validated the stability of the M3 membrane. The RSF remained consistent at $\sim 1.77 \text{ gMH}$ for much of the 1500 min run after the initial reduction phase, significantly lower and more stable than the initial short-run readings.

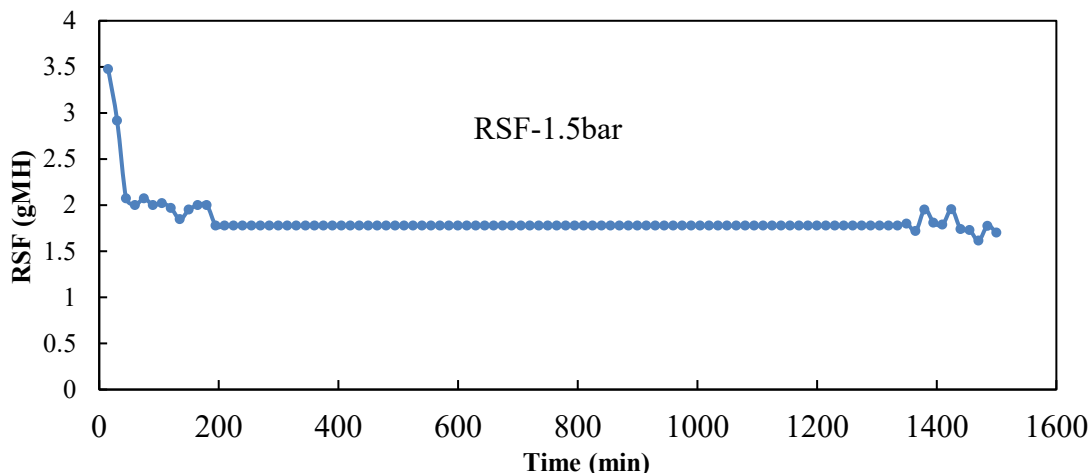


Fig. 14. Long run experimental RSF under different applied pressures for the M3 membrane. (Test Conditions: FS: Seawater DS: 2 M NaCl).

The long-term experimental results clearly showed that the M3 membrane with Al-Fumarate MOF could retain a balanced combination of stable flux, controlled RSF and sustained osmotic performance successfully for 1500 min, confirming the potential of Al-fumarate MOF-based TFN membranes for long-term PAO desalination applications under practical operating conditions.

4 Conclusions

In the present study, the synthesis and assessment of Al-Fumarate MOF integrated TFN membranes for PAO desalination of real seawater were effectively established. The hybridization of Al-Fumarate MOF into the polyamide selective layer enhanced the membrane hydrophilicity, surface structures, mechanical strength, and intrinsic transport properties than the control membrane. The optimized membrane with 0.05 wt% Al-Fumarate MOF (M3) showed a good permeability–selectivity balance with a water permeability of $3.8 \pm 0.22 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$, NaCl rejection of $98.9 \pm 1.1\%$, and a low B/A ratio of 8.9 kPa. SEM, AFM, ATR-IR, and contact angle analyses confirmed the successful incorporation and uniform distribution of the MOF within the polyamide layer, and tensile strength measurements showed enhanced structural robustness suitable for PAO operation. PAO desalination tests with actual seawater and 2 M NaCl

DS showed that the Al-Fumarate-incorporated membrane can maintain a stable performance under hydraulic pressures from 0 to 2 bar. The membrane showed better water flux, less internal concentration polarization, controlled RSF, and stable conductivity data throughout operation. M3 membrane revealed the balanced performance, which provided a consistent flux of $9.35 \text{ Lm}^{-2}\text{h}^{-1}$ without significant salt leakage in the long run experiment using real seawater as feed. Such high performance derived from the hydrophilic microporous structure of Al-Fumarate MOF, which provided preferred transport channels for water, while retaining the selectivity and mechanical stability of the membrane.

Acknowledgements

This study is financially supported by the Kuwait Foundation for Advancement of Sciences (grant code: PN23-25EC-1790) and Kuwait Institute for Scientific Research (KISR) and the project team expresses their gratitude for their continued financial aid towards the related research.

Data Availability The data that support the findings of this study are available upon request.

Competing Interests The authors declare no competing interests.

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