

Fabrication of Thin-Film Composite Nanofiltration Membrane Employing Polyelectrolyte and Metal–Organic Framework (MOF) via Spin-Spray-Assisted Layer-by-Layer Assembly [†]

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Abstract

Spin-spray-assisted layer-by-layer (LbL) assembly is an innovative method for producing nanostructured thin films due to its rapid assembly and extensive coverage of substrates. In this study, a nanofiltration (NF) membrane consisting of multilayers of polyethyleneimine (PEI) and poly(sodium-4-styrene sulfonate) (PSS) was fabricated on a polysulfone (PSF) support. The resulting membrane was further coated with a metal–organic framework (MOF303). The resulting (PEI/PSS)₅-MOF303 showed a rejection rate of $18.94 \pm 1.58\%$ and a permeability of $0.91 \pm 0.13 \text{ L}/(\text{h} \cdot \text{bar} \cdot \text{m}^2)$ while also showing enhanced antifouling properties. This work explores the possibility of spin-spray-assisted LbL assembly as a promising method for fabricating membranes.

Keywords: layer-by-layer; nanofiltration; membrane; thin-film composite; TFC; reverse osmosis; polyelectrolyte; spin coating; spray coating; MOF303

1. Introduction

Nanofiltration (NF) membranes have been increasingly used in water treatment and industrial applications over recent decades due to their selectivity and lower energy consumption compared to other filtration methods [1,2]. However, membrane fouling remains a significant challenge, reducing performance and increasing operational costs [3]. Various strategies have been developed to enhance NF membrane selectivity and mitigate fouling, including improved fabrication methods, process intensification, and surface modifications [4,5]. Antifouling modifiers such as nanoparticles, polymers, and composite materials have been explored to improve membrane resistance to fouling [6]. Many nanoparticles have been studied, including silver [7,8], titanium [9], zinc [10], graphene oxide [11], carbon nanotubes [12], and functionalized CNT with functional groups such as amine [13], sulfonate [14], and zwitterion [15]. One of the materials proven to show biocidal properties is metal–organic frameworks (MOFs), which combine both biocidal metal and the organic ligand.

MOFs exhibit biocidal activity through various mechanisms, including the release of metal ions, the photocatalytic generation of reactive oxygen species, and strong interactions with the bacterial membrane [16]. The topic of MOF properties is indeed a vast subject. However, it is essential to note that to utilize MOFs in NF applications, the MOF must be stable in water and possess biocidal characteristics. When these criteria are satisfied, the selection of MOFs can be narrowed down. Recent investigations have shown that



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MOF303 exhibits stability in the aqueous environment [17] and moderate antibacterial properties [18], and has been successfully used to develop a membrane for desalination fabricated entirely from MOF303 [19].

In this work, we use polyethyleneimine (PEI) and poly(sodium 4-styrenesulfonate) (PSS) to fabricate a thin-film composite NF membrane. MOF303 is also used to increase membrane fouling resistance. The film is manufactured using spin-spray layer-by-layer assembly, as the method is considered the fastest and is scalable to prepare a uniform, defect-free membrane of a large size.

2. Materials and Methods

2.1. Materials

A weak polycation, i.e., branched PEI with a molecular weight of 25,000, and a strong polyanion, i.e., PSS with a molecular weight of 70,000, were purchased from Sigma-Aldrich (St. Louis, MO, USA). Both are available from Sigma-Aldrich in 30% wt in H₂O. PES ultrafiltration (UF) membranes (YMPWSP3001, Sterlitech Corp. (Auburn, WA, USA) with a pore size corresponding to a molecular weight cut-off of 10 kDa were used as the support layer. All of the polyelectrolytes were used without further purification. All solutions were prepared using ASTM Type 1 water (18.2 MΩ, 0.055 mS/cm). In addition, MOF303 characterized by a hole volume of 0.54 cm³/g was purchased from CD bioparticles (Shirley, NY, USA).

2.2. Polyelectrolyte Membrane (PEM) Thin-Film Composite (TFC) Fabrication

Before depositing polyelectrolytes, the PES support was activated using a plasma cleaner (PDC-32-G-2, Harrick Plasma Inc. (Ithaca, New York, NY, USA)) to introduce oxygen-containing groups, making the surface more hydrophilic and negatively charged.

PEI and PSS solutions with a concentration of 0.02 M, and additional 0.05 M NaCl (pH 8), were prepared from 30% stock as per the received chemicals. The deposition was conducted by alternately spraying PEI and PSS onto the PES support at 0.2 mL/s for 10 s at 3000 rpm, followed by spin-drying and rinsing with DI water. Each layer was applied in the same manner, and the cycle was repeated as needed (see Figure 1 for schematic diagram) [20].

After completing the desired cycle, MOF303 was injected in a similar manner. Aqueous solution containing MOF303 with a concentration of 0.05% wt. was prepared and dispersed using sonication. Two types of sonication were employed: bath sonication and probe sonication. Sonication was performed for 30 min, followed by the injection of an MOF solution, which was then applied to a spinning PEI/PSS membrane. After the deposition, the PEM was rinsed and stored in distilled water until the permeation test was conducted.

2.3. Characterization

2.3.1. Scanning Electron Microscopy

The sample's surface morphology was analyzed using an SEM S3400 from Hitachi. All membrane samples were gold-coated for 30 s before characterization.

2.3.2. Hydrophilicity

Membrane hydrophilicity was analyzed using a Biolin Theta Flex[®] optical tensiometer by applying a 10 µL of water droplet at 20 °C to the membrane. The contact angle was recorded for 10 s and measured with OneAttension (software version 4.1.3) from Biolin Scientific and sent to layout in advance. If accept it, please help to send it for English Editing! to obtain the average angle.

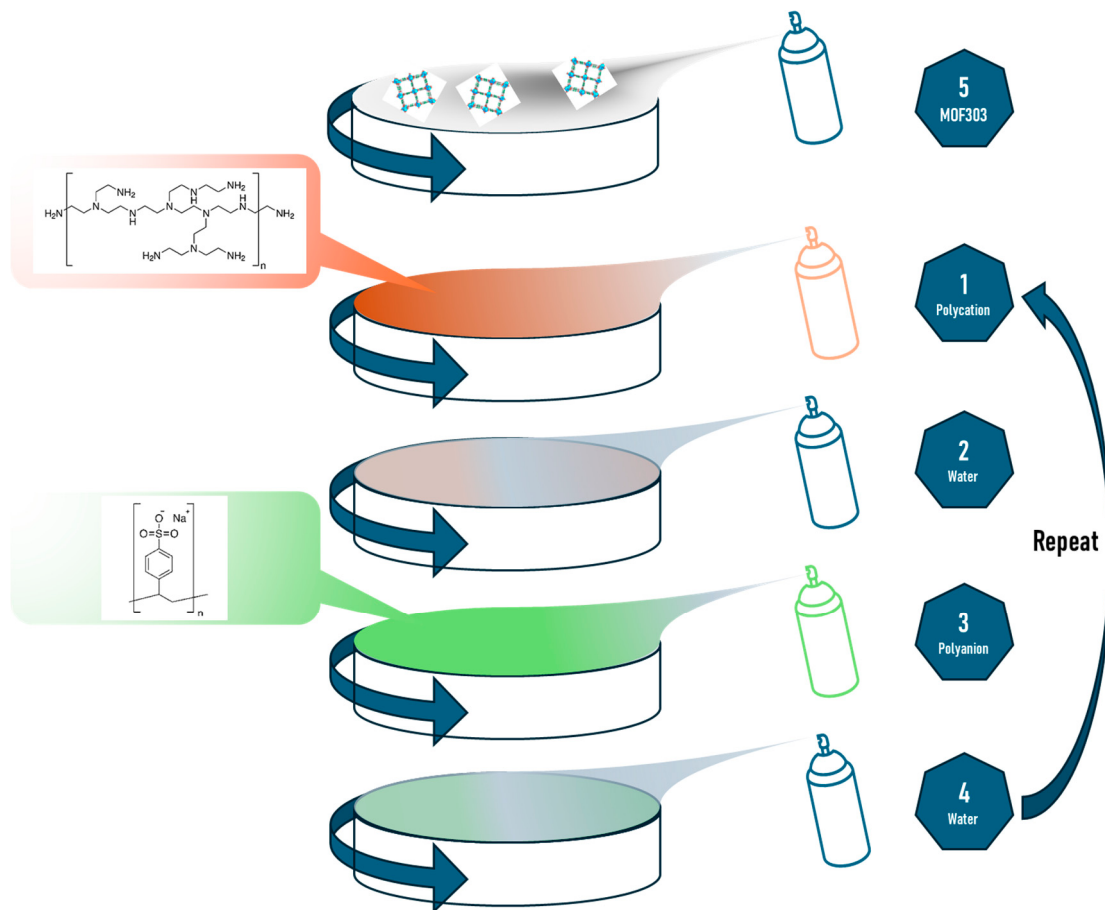


Figure 1. Schematic diagram for preparing (PEI/PSS)-MOF303 membrane.

2.3.3. Surface Charge

The surface charge required for NF membranes due to the Donnan exclusion mechanism was determined using an Anton-Parr Surpass 3 analyzer (software version 2.20.0.5155) in a 0.01 M KCl solution (pH 5.72) at 24 °C with an interfacial double layer thickness of 100 µm.

2.3.4. Atomic Force Microscopy

The sample was also analyzed using TOSCA[®] AFM (software version 1.10.119.30673) from Anton-Parr utilizing silicon AP-Arrow-Contr-10 cantilever with force constant of 0.2 N/m, for contact mode measurement. We presented lateral image in this work to show surface inhomogeneities appear in the image.

2.4. Membrane Performance Test

Two permeation tests were conducted on the prepared membrane: short-term and long-term fouling tests. The short-term test lasted 5 h under controlled conditions (10 bar pressure, 25 °C, 0.65 m/s crossflow velocity, and 2000 ppm NaCl feed). The membrane was pre-soaked in distilled water overnight and tested in a crossflow cell (CF016 from Sterlitech Inc.; active area: 20.6 cm²).

The long-term fouling test used the same setup but 20 ppm BSA was added as an organic foulant. A compaction stage at 15 bar for 48 h was performed beforehand to eliminate effects unrelated to fouling. To ensure turbulent flow, a low-fouling feed spacer increased the crossflow velocity to 1.03 m/s. BSA was introduced after equilibration for 24 h at 10 bar, and the test was run for ~2 days. Membrane performance was evaluated via salt rejection and water permeability.

3. Results and Discussion

3.1. MOF303 Sonication

Prior to the deposition of MOF303, it is necessary to disperse MOF303 in water. It is also important to emphasize that stable MOF303 is needed to form a uniform distribution during the deposition process. For our experiment, we employed two types of sonication, bath and probe sonication, to disperse MOF303. The outcomes of the two sonication methods are presented in Table 1.

Table 1. Effect of sonication on the particle size of MOF303 in aqueous solution.

Time, min	Particle Size, nm	
	Bath Sonication	Probe Sonication ¹
5	-	1053.6 ± 163.31
10	2502 ± 450.36	961.8 ± 126.96
15	-	969.8 ± 135.77
20	1477.4 ± 217.12	913.0 ± 127.82
30	1251.2 ± 137.63	826.5 ± 99.18
40	1406.5 ± 196.84	995.5 ± 129.42

¹ Power density 0.275 J/mL.s.

As shown in the table, probe sonication is quite effective in breaking apart the MOF agglomeration. We were able to reach 826.5 nm size during 30 min of sonication. The extended periods of sonication do not always perform better because the particles start to re-agglomerate, and this phenomenon was observed in both cases. Based on this observation, we sonicated MOF303 in aqueous solution for 30 min. Our observation over 24 h showed that the MOF303 dispersed quite stably, as shown in Figure 2. However, MOF303 is unstable in PEI and PSS solution and completely degrades in PSS within a few minutes. Thus, we only dispersed this in water and deposited it as the outermost layer in our study.

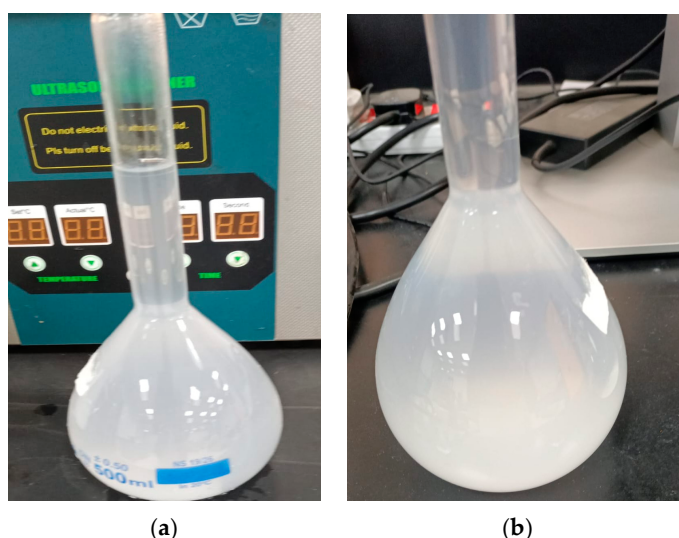


Figure 2. MOF303 dispersion in water: (a) immediately after sonication and (b) 24 h after sonication.

3.2. Performance of (PEI/PSS)₁₀-MOF303 NF Membrane

After obtaining stable MOF303 dispersion, we deposited it on the (PEI/PSS)₅ NF membrane. As shown in Figure 3, the MOF, indicated by white particles spread on the membrane surface, remained intact even after the 5-h permeation test, which suggests quite stable attachment.

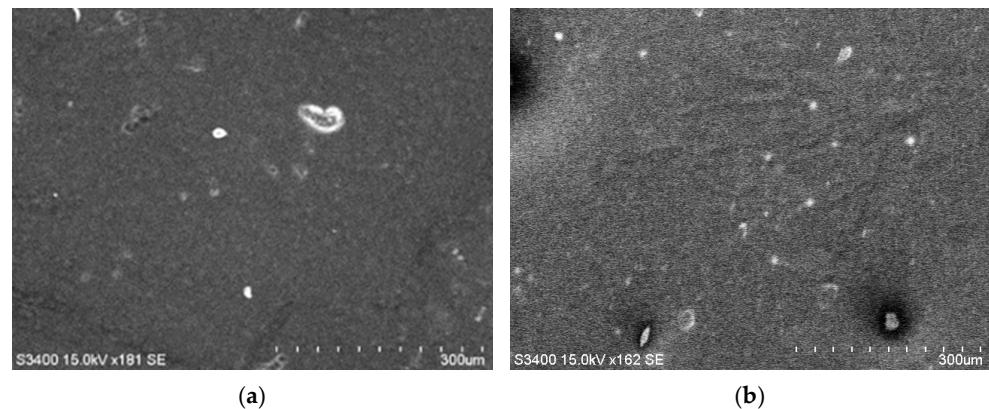


Figure 3. Scanning electron microscope image of PEM: (a) (PEI/PSS)₅ and (b) (PEI/PSS)₅-MOF303 after permeation.

Figure 4 shows the lateral retrace figure of AFM that shows the inhomogeneity of the surface which clearly indicates the particles and the polyelectrolyte layer. The manual size measurement using AFM (see right figure of Figure 4) also confirm the particle size presented in Table 1.

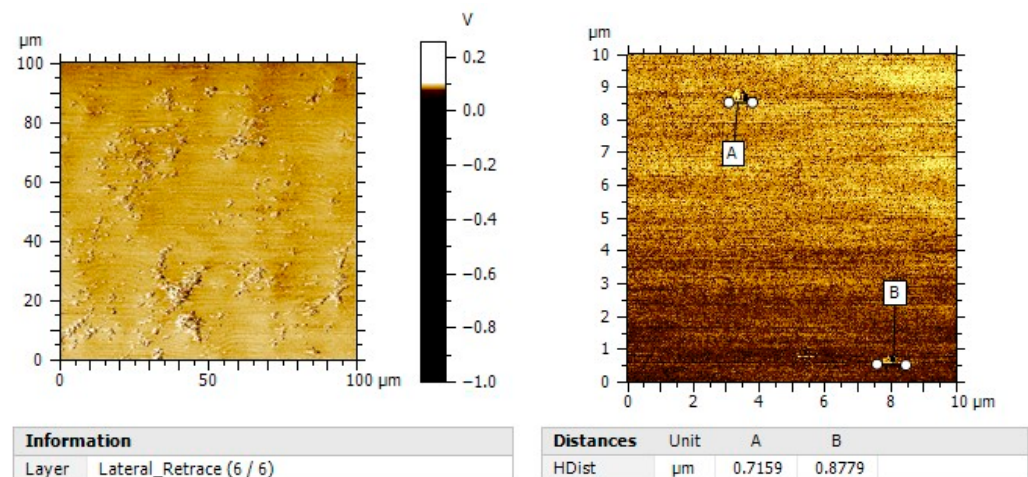


Figure 4. Atomic Force Microscope image ((left): lateral retrace (scan size 100 × 100 μm), (right): particle size (scan size: 10 × 10 μm)).

Successful deposition can also be concluded from the alteration in the surface properties before and after deposition, as listed in Table 2. The value reported in the literature for MOF303 is around 30° [21] and positive surface charge at pH 5.7 [22]. The increase in surface charge is noticeable, and it helps the MOF-modified (PEI/PSS) reject the ions better than the unmodified sample, as depicted in Table 3.

The size of the MOF303 particles affects the membrane structure, which may have an impact on the active layer's porosity, surface roughness, and homogeneity, all of which have an impact on membrane performance. According to the result in Table 3, both the permeability and rejection rate decreased due to the larger MOF particle sizes. The bigger the MOF particles, the more deeply the MOF penetrates the ultrathin (PEI/PSS) layer. Moreover, its surface charge decreases with increasing particle size. This might create channels allowing the salt or ion to permeate the dense PEI/PSS layer. On the other hand, a smaller size results in a higher surface charge because of only slight penetration. As a result, the salt and ions no longer have channels. These ions must pass through a dense layer of PEI/PSS and must also encounter a stronger repulsive force due to a higher PEI/PSS-MOF surface charge.

Table 2. Surface properties of PEM.

Surface Properties	(PEI/PSS) ₅	(PEI/PSS) ₅ -MOF303
Surface charge, mV	2.43	18.7
Contact angle, °	17.88 ± 0.61	25.60 ± 2.61

Table 3. Effect of MOF303 particle size on membrane performance.

Performance *	(PEI/PSS) ₅	(PEI/PSS) ₅ -MOF303	
MOF303 size, nm		1251.2 (dispersed by bath sonicator)	826.0 (dispersed by probe sonicator)
Rejection rate, %	42.61 ± 2.58	18.94 ± 1.58	47.01 ± 0.63
Permeability, L/m ² ·h·bar	9.46 ± 0.46	0.91 ± 0.13	8.33 ± 0.11

* Testing condition: 2000 ppm NaCl, T = 25 °C, P = 10 bar.

In Table 4, we compare the results of this work with several studies that employed polyelectrolyte multilayer membranes used directly as nanofiltration membranes. While there are also recent publications focusing on the modification of existing commercial nanofiltration membranes—particularly polyamide-based ones—with polyelectrolyte multilayers. These studies fall outside the scope of our comparison, as our focus is on membranes constructed entirely from polyelectrolyte layers.

Table 4. LbL membrane performance comparison.

Membrane	Method	Testing Condition	Result (Rejection; Permeability)	Ref.
(PDAC/PSS) ₈	Dip LbL	5 mM NaCl (292.5 ppm); 5 bar	40%; 12 L/h·m ² ·bar	[23]
(PAA/PSS) ₆	Dip LbL	5 mM NaCl (292.5 ppm); 25 °C 5 bar	38%; 10 L/h·m ² ·bar	[24]
(PEI/PSS) ₅ -MOF303	SSA-LbL	2000 ppm NaCl; 25 °C; 10 bar	47%, 8.3 L/h·m ² ·bar	This work

3.3. Long-Term Permeation Test (BSA Fouling Test)

As mentioned earlier, the aim of this study is to enhance the biofouling resistance of PEMs further; thus, it is important to test the MOF-modified PEM for biofouling to determine how this membrane performs against a biofoulant representative, i.e., BSA.

As illustrated in Figure 5, MOF303 (PEI/PSS) membranes still exhibit moderate fouling, with permeability dropping to ~0.74 (26% reduction from initial flux) and remaining stable afterward, i.e., up to 100 h (4 days). Unlike commercial NF90 and NF270 membranes, for example, the performance gap becomes pronounced over the longer term. After ~4 days (~96 h) of continuous BSA filtration, NF270's permeate flux had declined by 30–40% from its initial value, whereas NF90's flux had fallen by roughly 50%. In other words, NF90 ended up with only ~50% of its initial flux, while NF270 retained ~60–70% under the same conditions [25,26].

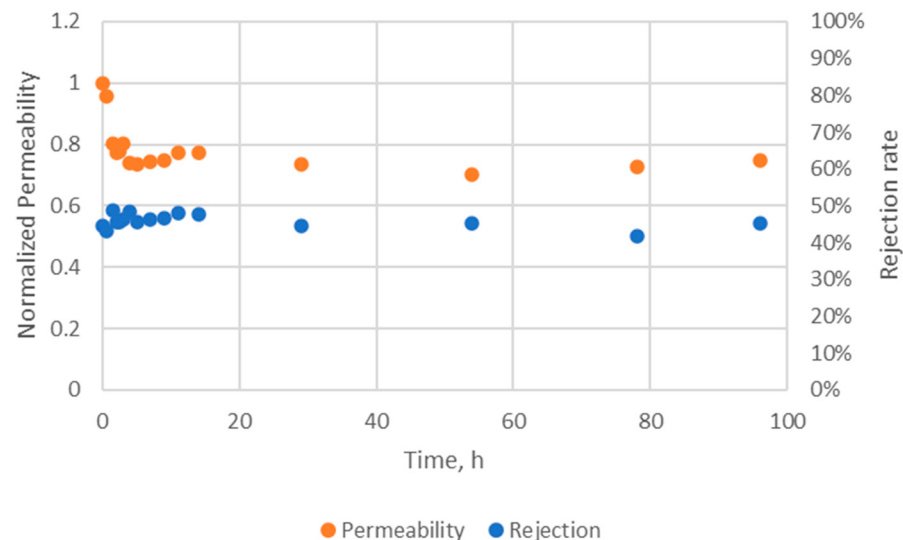


Figure 5. Long-term permeation test for MOF303-modified PEM.

4. Conclusions and Future Work

In this study, we successfully fabricated a MOF303-modified (PEI/PSS) PEM NF membrane. The resulting membrane is characterized by slightly increased hydrophobicity and an improved ion rejection rate compared to pristine (PEI/PSS). In addition, this membrane exhibited promising long-term antifouling behavior under BSA exposure, maintaining 74% of its initial permeability after 100 h, slightly higher than NF270 (60–70%) and outperforming NF90 (50%) under similar conditions.

Based on these results, important areas for further study are as follows: conducting layer optimization by studying the effect of MOF layer position (e.g., middle layer vs. outermost) on performance; performing more characterization to achieve higher structure-related performance, such as using advanced tools (e.g., AFM, zeta potential mapping, or XPS) to study MOF-PEM interaction mechanisms; and conducting and extending biofouling tests to include multiple foulants (e.g., humic acids, polysaccharides, and real wastewater samples) to more accurately simulate realistic conditions.

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References

1. Macedo, A.T.Z.N.; Pulido, J.M.O.; Fragoso, R.; Duarte, E.d.C.N.F.D. The Use and Performance of Nanofiltration Membranes for Agro-Industrial Effluents Purification. In *Nanofiltration*; InTech: London, UK, 2018. [\[CrossRef\]](#)
2. Tul Muntha, S.; Kausar, A.; Siddiq, M. Advances in Polymeric Nanofiltration Membrane: A Review. *Polym.-Plast. Technol. Eng.* **2017**, *56*, 841–856. [\[CrossRef\]](#)
3. Mulyanti, R.; Susanto, H. Wastewater Treatment by Nanofiltration Membranes. In Proceedings of the 4th International Conference on Sustainable Agriculture and Environment (4th ICSAE), Surakarta, Indonesia, 10–12 August 2017; IOP Publishing Ltd.: Bristol, UK, 2018; Volume 142, p. 012017. [\[CrossRef\]](#)

4. Zhang, H.; He, Q.; Luo, J.; Wan, Y.; Darling, S.B. Sharpening Nanofiltration: Strategies for Enhanced Membrane Selectivity. *ACS Appl. Mater. Interfaces* **2020**, *12*, 39948–39966. [\[CrossRef\]](#)
5. Yadav, D.; Karki, S.; Ingole, P.G. Current Advances and Opportunities in the Development of Nanofiltration (NF) Membranes in the Area of Wastewater Treatment, Water Desalination, Biotechnological and Pharmaceutical Applications. *J. Environ. Chem. Eng.* **2022**, *10*, 108109. [\[CrossRef\]](#)
6. Ahmad, N.N.R.; Mohammad, A.W.; Mahmoudi, E.; Ang, W.L.; Leo, C.P.; Teow, Y.H. An Overview of the Modification Strategies in Developing Antifouling Nanofiltration Membranes. *Membranes* **2022**, *12*, 1276. [\[CrossRef\]](#)
7. Liu, S.; Fang, F.; Wu, J.; Zhang, K. The Anti-Biofouling Properties of Thin-Film Composite Nanofiltration Membranes Grafted with Biogenic Silver Nanoparticles. *Desalination* **2015**, *375*, 121–128. [\[CrossRef\]](#)
8. Zhang, Y.; Wan, Y.; Shi, Y.; Pan, G.; Yan, H.; Xu, J.; Guo, M.; Qin, L.; Liu, Y. Facile Modification of Thin-Film Composite Nanofiltration Membrane with Silver Nanoparticles for Anti-Biofouling. *J. Polym. Res.* **2016**, *23*, 105. [\[CrossRef\]](#)
9. Bilal, A.; Yasin, M.; Akhtar, F.; Gilani, M.; Almohamadi, H.; Younas, M.; Mushtaq, A.; Aslam, M.; Hassan, M.; Nawaz, R.; et al. Enhancing Water Purification by Integrating Titanium Dioxide Nanotubes into Polyethersulfone Membranes for Improved Hydrophilicity and Anti-Fouling Performance. *Membranes* **2024**, *14*, 116. [\[CrossRef\]](#) [\[PubMed\]](#)
10. Purushothaman, M.; Arvind, V.; Saikia, K.; Vaidyanathan, V.K. Fabrication of Highly Permeable and Anti-Fouling Performance of Poly(Ether Ether Sulfone) Nanofiltration Membranes Modified with Zinc Oxide Nanoparticles. *Chemosphere* **2022**, *286*, 131616. [\[CrossRef\]](#)
11. Bano, S.; Mahmood, A.; Kim, S.-J.; Lee, K.-H. Graphene Oxide Modified Polyamide Nanofiltration Membrane with Improved Flux and Antifouling Properties. *J. Mater. Chem. A* **2015**, *3*, 2065–2071. [\[CrossRef\]](#)
12. Long, L.; Wu, C.; Yang, Z.; Tang, C.Y. Carbon Nanotube Interlayer Enhances Water Permeance and Antifouling Performance of Nanofiltration Membranes: Mechanisms and Experimental Evidence. *Environ. Sci. Technol.* **2022**, *56*, 2656–2664. [\[CrossRef\]](#)
13. Zarrabi, H.; Yekavalangi, M.E.; Vatanpour, V.; Shockravi, A.; Safarpour, M. Improvement in Desalination Performance of Thin Film Nanocomposite Nanofiltration Membrane Using Amine-Functionalized Multiwalled Carbon Nanotube. *Desalination* **2016**, *394*, 83–90. [\[CrossRef\]](#)
14. Zheng, J.; Li, M.; Yu, K.; Hu, J.; Zhang, X.; Wang, L. Sulfonated Multiwall Carbon Nanotubes Assisted Thin-Film Nanocomposite Membrane with Enhanced Water Flux and Anti-Fouling Property. *J. Membr. Sci.* **2017**, *524*, 344–353. [\[CrossRef\]](#)
15. Chan, W.-F.; Marand, E.; Martin, S.M. Novel Zwitterion Functionalized Carbon Nanotube Nanocomposite Membranes for Improved RO Performance and Surface Anti-Biofouling Resistance. *J. Membr. Sci.* **2016**, *509*, 125–137. [\[CrossRef\]](#)
16. Li, R.; Chen, T.; Pan, X. Metal–Organic-Framework-Based Materials for Antimicrobial Applications. *ACS Nano* **2021**, *15*, 3808–3848. [\[CrossRef\]](#) [\[PubMed\]](#)
17. Zheng, Z.; Nguyen, H.L.; Hanikel, N.; Li, K.K.-Y.; Zhou, Z.; Ma, T.; Yaghi, O.M. High-Yield, Green and Scalable Methods for Producing MOF-303 for Water Harvesting from Desert Air. *Nat. Protoc.* **2023**, *18*, 136–156. [\[CrossRef\]](#) [\[PubMed\]](#)
18. Pal, A.; Suresh, S.; Khan, A.; Kuo, L.H.; Chi, L.T.; Ganguly, A.; Kao, C.-Y.; Sharma, M.K.; Wang, T.-S.A.; Kang, D.-Y.; et al. Metal-Organic Frameworks as Thermocatalysts for Hydrogen Peroxide Generation and Environmental Antibacterial Applications. *Sci. Adv.* **2025**, *11*, eads4711. [\[CrossRef\]](#) [\[PubMed\]](#)
19. Cong, S.; Yuan, Y.; Wang, J.; Wang, Z.; Kapteijn, F.; Liu, X. Highly Water-Permeable Metal–Organic Framework MOF-303 Membranes for Desalination. *J. Am. Chem. Soc.* **2021**, *143*, 20055–20058. [\[CrossRef\]](#)
20. Alghamdi, A.M. Fast and Versatile Pathway in Fabrication of Polyelectrolyte Multilayer Nanofiltration Membrane with Tunable Properties. *J. Chem.* **2021**, *2021*, 9978596. [\[CrossRef\]](#)
21. Siahkamari, L.; Bakhtiari, O. Preparation of Post-Synthesized MOF-303@ Graphene Oxide (GO) Composite Membrane for Pervaporative Dehydration of Ethanol. *Sep. Purif. Technol.* **2025**, *359*, 130564. [\[CrossRef\]](#)
22. Li, H.; Su, P.; Fan, H.; Liu, J.; Xin, B.; Chen, T.; Zhong, G.; Xie, J.; Li, J.; Deng, J.; et al. Regulating Positively Charged MOF-303 Membranes for Enhanced Ion Selectivity. *Chem. Eng. J.* **2025**, *517*, 164373. [\[CrossRef\]](#)
23. Elshof, M.G.; De Vos, W.M.; De Groot, J.; Benes, N.E. On the Long-Term pH Stability of Polyelectrolyte Multilayer Nanofiltration Membranes. *J. Membr. Sci.* **2020**, *615*, 118532. [\[CrossRef\]](#)
24. Junker, M.A.; Regenspurg, J.A.; Valdes Rivera, C.I.; Brinke, E.T.; De Vos, W.M. Effects of Feed Solution pH on Polyelectrolyte Multilayer Nanofiltration Membranes. *ACS Appl. Polym. Mater.* **2023**, *5*, 355–369. [\[CrossRef\]](#) [\[PubMed\]](#)
25. Maeda, Y. Fouling of Reverse Osmosis (RO) and Nanofiltration (NF) Membranes by Low Molecular Weight Organic Compounds (LMWOCs), Part 1: Fundamentals and Mechanism. *Membranes* **2024**, *14*, 221. [\[CrossRef\]](#) [\[PubMed\]](#)
26. Wang, Y. Fouling of Nanofiltration and Reverse Osmosis Membranes by Organic Macromolecules and Their Mixtures. Ph.D. Dissertation, Nanyang Technological University, Singapore, 2011.

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