

## TUTORIAL REVIEW

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## Emerging membrane technologies for sustainable water treatment: a review on recent advances†

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The growing scarcity of freshwater resources, coupled with industrial pollution, necessitates the development of efficient and sustainable water treatment technologies. Membrane-based desalination and heavy metal removal processes are at the forefront of these technologies, providing efficient and reliable solutions to meet the growing demand for clean water. This study provides a comprehensive review on recent advancements in desalination technologies, focusing on emerging materials that have significantly influenced desalination and heavy metal removal performances. A meticulous screening of recent review papers on both along with experimental studies published within the last year is provided, thereby offering an updated perspective on the ongoing experiments dedicated to water treatment using membranes. Notably, this review considers various membrane types, including nanocomposites, biomimetic, thin-film composites, hybrids, and membranes associated with forward osmosis. Results indicate that nanocomposite membranes, thin-film composite membranes, and forward osmosis membranes are widely used for desalination and heavy metal removal compared to hybrid and biomimetic membranes. This widespread utilization can be attributed to their well-established fabrication techniques, robust mechanical properties, high removal%, and better scalability for industrial applications. In contrast, while hybrid and biomimetic membranes are promising, they are still under development and facing challenges pertaining to material synthesis, cost, and integration into existing systems.

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### Environmental significance

Water scarcity and contamination by heavy metals pose serious threats to environmental and public health globally. Current desalination and heavy metal removal technologies often suffer from limitations in energy efficiency, sustainability, and effectiveness. This review examines the recent advances in membrane technologies, focusing on innovations that enhance the efficiency and environmental compatibility of desalination and heavy metal removal processes. The key findings highlight breakthroughs in material design and process optimization, presenting implications for reducing environmental impacts and improving access to clean water. Thus, this work underscores the need for continued innovation in membrane technologies to address critical water quality issues and supports sustainable environmental management.

## 1. Introduction

The past century has witnessed a rapid surge in global population, alongside explosive industrial development and escalating energy requirement. Consequently, water scarcity has emerged as a formidable global challenge, with projections indicating a worsening scenario in the future.<sup>1,2</sup> The World

Health Organization (WHO) reports a persistent rise in water pollution, identifying it as a significant contributor to the widespread illnesses and fatalities worldwide.<sup>3,4</sup> Freshwater resources are limited, with roughly 97% of the global water reservoirs consisting of seawater, necessitating desalination for most applications and generally <1% of the world's water supply is readily available as freshwater.<sup>5,6</sup> In this context, desalination technologies, offering the capability to harvest freshwater from saline sources, stand as a promising avenue for increasing freshwater supply and achieving global water security.<sup>7</sup> Two primary approaches, namely, thermal/distillation and membrane separation, are mainly used for desalination, where membrane separation technology has garnered widespread attention over its counterpart owing to its high efficiency and low energy demand.<sup>8,9</sup> A diverse range of water and wastewater filtration systems, including conventional pressure-driven seawater and brackish water reverse osmosis (RO),

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nanofiltration (NF), ultrafiltration (UF), and microfiltration (MF), have been employed in industrial plants. Additionally, osmotically driven technologies, such as forward osmosis (FO) and pressure retarded osmosis (PRO), have been extensively developed.<sup>10</sup>

Apart from the salt and mineral content of saline water, the escalating pace of industrialization and population growth has resulted in heavy metal contamination attributed to its widespread prevalence, significant toxicity, and facile mobility.<sup>11,12</sup> The contemporary heavy metal pollution is predominantly driven by anthropogenic activities, such as electroplating, petroleum refining, and metal smelting. Excessive discharge of heavy metal ions, including Hg, Cd, Pb, As, and Cr, into water bodies, such as drinking water sources, poses significant health risks to humans.<sup>13,14</sup> In this context, membrane separation



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technologies have also emerged as a promising route for large-scale applications owing to its outstanding heavy metal rejection capability and high operational efficiency.<sup>15,16</sup>

In general, the pressure-driven membrane technology using MF, UF, NF, and RO represents the most widely employed technique, wherein transmembrane pressure is used to facilitate the transport of feed stream across the membrane, while non-pressure-driven membrane processes such as FO present notable advantages for efficient separation, characterized by operation under mild conditions (atmospheric pressure) and potential for *in situ* separation during product synthesis.<sup>17</sup> While membranes have been extensively employed for heavy metal removal and desalination, there remains room for improvement and challenges to overcome. These challenges include membrane fouling, material-based limitations, capital



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costs, reproducibility issues, detachment of membrane layers, low selectivity, and water flux drop. Addressing these challenges will be crucial for further advancements in membrane-based separation approaches for desalination and heavy metal removal.

In the rapidly evolving field of wastewater treatment using membranes, multiple review studies have summarized the experimental findings. It is crucial to compile current knowledge for ongoing and future research in wastewater treatment and environmental protection. However, many existing studies are still in the research phase and often lack comprehensive documentation of membrane properties. This gap poses challenges in selecting the most suitable membrane for specific wastewater conditions including pollutant type, concentration, temperature, pressure, and desired purity of water. To address these challenges, an updated database has been compiled, focusing on removal percentages and other key properties of commonly used membranes such as nanocomposites, thin-film composites, biomimetic membranes, forward osmosis membranes, and hybrid organic-inorganic membranes. This compilation aims to explore potential correlations among the properties, with a specific focus on developments from 2023 to 2024. Given the inconsistent reporting of key parameters such as removal efficiency, permeability, cost, long-term stability, durability, and fouling resistance, along with the interdependence of structural properties and surface chemistry, identifying a promising membrane becomes a complex task. Considering the methodology adopted in our previous study,<sup>18</sup> this study provides a comprehensive literature review and screening of both review papers and experimental studies. The initial screening and survey are conducted based on removal efficiency as the primary criterion, and top-performing membranes are identified. The discussion further explores membrane performance and key properties including permeability, economic viability, fouling resistance, comparisons across various membrane types, and considerations of environmental impact and sustainability. Additionally, the role of artificial intelligence (AI) and machine learning (ML) in enhancing membrane-based processes is examined. Finally, the challenges facing the field and potential future directions are thoroughly analyzed.

## 2. Separation mechanisms

The membranes facilitate selective removal and separation using the unique physicochemical properties of solutes, including size, charge, and chemical composition. The interaction between solutes and the membrane matrix dictates which solutes are permeable and which are rejected.<sup>19</sup>

### 2.1. Size-based separation

Size exclusion is a fundamental mechanism in membrane-based separations, crucial for filtering particles based on their size, relative to the pore size of the membrane (Fig. 1). As represented in Fig. 2(a), particles smaller than the membrane pores can permeate through the membrane, while larger particles are

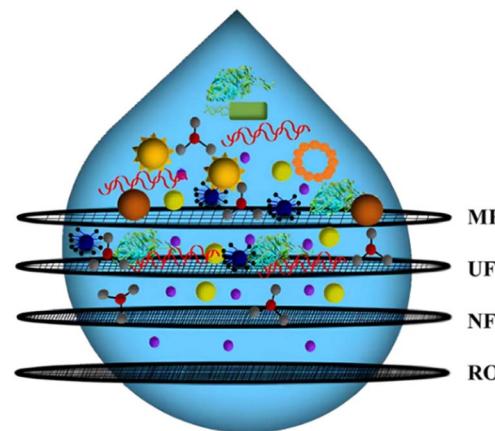


Fig. 1 Schematic of particle separation via size-sieving using membranes (reprinted with permission from ref. 20, Elsevier 2023).

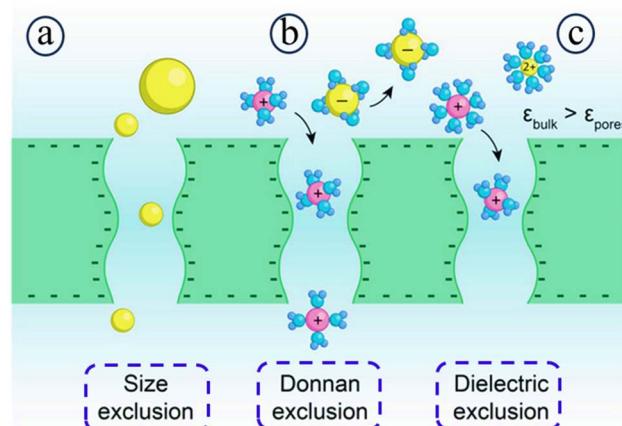


Fig. 2 Three primary membrane separation mechanisms: (a) size exclusion, (b) Donnan exclusion, and (c) dielectric exclusion (reprinted with permission from ref. 21, Wiley 2023).

excluded. In the context of hydrated ions and salts, steric hindrance plays a pivotal role: ions with a hydrated diameter exceeding the membrane pore size encounter significant resistance and are effectively rejected.<sup>22</sup> This mechanism underscores the importance of pore size in determining the selectivity and efficiency of the membrane. For neutral solutes, size exclusion remains the primary mode of separation, highlighting its universal applicability in membrane filtration processes.<sup>23</sup> As shown in Table 1, the sizes of common metal and salt ions are all less than 1 nm. Despite their small size, these ions can be effectively removed through size exclusion, provided that the membrane pore size is sufficiently small. This highlights the importance of precise pore size control in membrane fabrication to ensure high rejection rates of these ions.

One limitation of this model is its failure to consider concentration polarization (CP), which is crucial in membrane design. CP involves the accumulation of retained solutes in the boundary layer of the membrane, leading to a higher solute



Table 1 Size of bare and hydrated ions

Ion	Bare ion size (Å)	Ref.	Hydrated ion size (Å)	Ref.
Li <sup>+</sup>	0.60	24	3.82	24 and 25
Ni <sup>2+</sup>	0.69	26	4.04	27
Na <sup>+</sup>	0.95	24	3.58	24 and 25
K <sup>+</sup>	1.33	24	3.31	24 and 25
Mg <sup>2+</sup>	0.72	25 and 28	4.28	24 and 25
Ca <sup>2+</sup>	1.00	25	4.12	24 and 25
Cl <sup>-</sup>	1.81	24 and 28	3.32	24 and 25
SO <sub>4</sub> <sup>2-</sup>	2.90	24	3.79	24
NO <sub>3</sub> <sup>-</sup>	2.64	24	3.35	24
Pb <sup>2+</sup>	1.63	29	4.01	24
Zn <sup>2+</sup>	0.74	30	4.30	24
Mn <sup>2+</sup>	0.80	30	4.38	24
Cr <sup>3+</sup>	0.62	31	4.61	24
Cu <sup>2+</sup>	0.73	32	4.19	24
Cd <sup>2+</sup>	0.95	32	4.26	25

concentration at the membrane surface compared to the bulk solution. This concentration gradient is critical for both fouling and solute retention. Additionally, the separation of ionic species relies not only on size exclusion but also on the charge of the membrane, which plays a vital role in the separation process.<sup>23</sup>

## 2.2. Charge-based separation

In liquid-phase separations, membranes often incorporate charged functional groups that selectively bind to solutes with opposite charges (counterions) while repelling those with similar charges (co-ions) *via* the Donnan exclusion<sup>33</sup> (Fig. 2(b)). Neutral solutes, which lack a charge, typically experience minimal interaction with these membranes.<sup>34</sup> The Donnan exclusion, proposed in 1911, remains as a foundational theory for understanding ion distribution across semi-permeable membranes.<sup>35-37</sup> This is particularly significant in ion-exchange membranes where electrical forces drive the process, and in nanofiltration membranes where pressure differentials play a crucial role.<sup>38</sup>

The Donnan exclusion relies on electrostatic interactions between the membrane's fixed charge groups and the ionic species. Membranes with negatively charged surfaces strongly repel anions, and the degree of exclusion increases with ionic charge density. Multivalent ions, possessing a higher charge density than their monovalent counterparts, generate stronger electrostatic interactions, leading to greater rejection.<sup>39,40</sup> For instance, as shown by Epsztein *et al.*,<sup>39</sup> fluoride ions with high charge density were rejected more effectively than chloride or nitrate ions under certain pH conditions due to the Donnan exclusion effects. Similarly, Balster *et al.*<sup>41</sup> demonstrated that the transport of Ca<sup>2+</sup> ions through sPEEK/PES blend membranes is significantly affected by both the conductivity and charge density of the membrane, where higher conductivity and charge density led to enhanced transport of these multivalent ions. Gilron *et al.*<sup>42</sup> found that NF200 and NF45 membranes exhibited significant divalent ion rejection of >90% for MgSO<sub>4</sub>, while NaCl rejection remains comparatively low,

often between 60 and 80%. Asante-Sackey *et al.*'s<sup>43</sup> review highlighted the Donnan membrane process (DMP) as an efficient, energy-free method for the recovery and removal of multivalent ions such as Al<sup>3+</sup>, Fe<sup>3+</sup>, and Mg<sup>2+</sup>. Using Nafion 117 membranes, Mg<sup>2+</sup> and Ca<sup>2+</sup> removal rates of 50 and 20%, respectively, were reported, while Au<sup>+</sup> recovery from electronic waste reached up to 89%.<sup>44-47</sup> Seidel *et al.*<sup>48</sup> investigated the impact of surface charge and pore size on the rejection of NaCl, CaCl<sub>2</sub>, and Na<sub>2</sub>SO<sub>4</sub>. Findings revealed that the rejection rates followed the order of Na<sub>2</sub>SO<sub>4</sub> > NaCl > CaCl<sub>2</sub>, attributed to the Donnan exclusion principles, where ion rejection increases with higher charged co-ions and decreases with higher charged counter-ions. Specifically, Na<sub>2</sub>SO<sub>4</sub> exhibited the highest rejection with a significant negative charge of co-ions. Conversely, CaCl<sub>2</sub> showed the lowest rejection rate with a higher charge of counterions. These results indicate that ion separation is primarily governed by the combination of size and Donnan exclusion, whereas the observed rejection trends do not correspond to the sizes of the hydrated ions.

Nicolini *et al.*<sup>49</sup> investigated the saline rejection performance of NF membranes, observing varying degrees of rejection for different salts in the following order: Na<sub>2</sub>SO<sub>4</sub> > K<sub>2</sub>SO<sub>4</sub> > CaSO<sub>4</sub> > MgSO<sub>4</sub> > NaCl. This sequence reflects the interactions of membranes with ions, where stronger rejection of sulfate salts (SO<sub>4</sub><sup>2-</sup>) is due to electrostatic repulsion with the negative charge of the membrane. Conversely, divalent cations (e.g., Ca<sup>2+</sup> and Mg<sup>2+</sup>) exhibit greater attraction to the membrane, leading to higher rejection rates than that of monovalent cations such as Na<sup>+</sup>. Moreover, the concentration distribution of ions within the electrical double layer is significantly influenced by the surface potential, which regulates the partitioning of ions within the membrane, thereby determining ion concentrations and impacting their subsequent diffusion through the pores.<sup>38</sup>

Despite these insights, experimental data on the nuanced behavior of specific ions remain sparse, especially concerning the variable performance of membranes favoring monovalent or multivalent salts. Factors such as feedwater composition, membrane surface charge heterogeneity, and dynamic operating conditions introduce additional complexities.<sup>50-52</sup> Addressing these gaps requires systematic studies that integrate advanced modeling approaches such as the Donnan steric pore model (DSPM) with dielectric exclusion, alongside empirical validations.<sup>38,53</sup>

## 2.3. Further mechanisms and considerations

Chemical properties of solutes play crucial roles in their transport and selectivity across membranes, extending beyond considerations of size and charge. Factors including hydrophobicity/hydrophilicity, polarity, polarizability, hydrogen bonding capabilities (both donating and accepting), and interactions governed by van der Waals forces have all been identified as influential in determining the solute behavior during membrane processes.<sup>54-59</sup> Dielectric exclusion (Fig. 2(c)) refers to the phenomenon where ions interact with the bound electrical charges at the interface of materials with different dielectric constants such as the membrane matrix and the surrounding solvent. This mechanism



is independent of ionic charge sign but enhances the rejection of ions with a higher valence due to their stronger polarization effects. This property is especially pronounced in confined membrane environments, where the altered dielectric properties of water further enhance ion rejection.<sup>38</sup> Studies including that conducted by Suhalim *et al.*<sup>23</sup> highlight the role of dielectric exclusion in supplementing the Donnan and size exclusion mechanisms, particularly for high-valence ions. This interaction induces polarization within the two media according to their dielectric properties, leading to the formation of polarization charge distribution at the interface surface.<sup>23</sup> Zhu *et al.*<sup>60</sup> investigated how dielectric exclusion affects the relationship between fixed charge distribution and electrolyte rejection performance. The findings indicated that reducing the dielectric constant enhances the rejection performance.

Despite extensively studied size and Donnan exclusion mechanisms, hydration-based mechanism has received relatively less attention in the literature. This approach relies on the affinity of water molecules to ions dissolved in the solution (Fig. 3(a)). Specifically, hydrated ions (ions surrounded by water molecules) exhibit different sizes and affinities towards the membrane matrix compared to their dehydrated counterparts (Table 1). This difference in hydration shell size can influence their transport through the membrane. For instance, larger hydrated ions may face steric hindrance within smaller membrane pores, leading to reduced permeation rates. Additionally, the hydration shells of ions can alter their effective charge and interactions with the membrane surface, influencing their rejection or permeation behavior<sup>23</sup> (Fig. 3(b)). Chen *et al.*<sup>62</sup> studied the mechanism of water transport and ion movement across the multilayer GO membrane. The results revealed that the difference in hydration radius between Mg(II) and Ca(II) ions influences their ability to penetrate GO membrane. Due to its smaller hydration radius, Mg(II) ions can more easily infiltrate bilayer GO membranes than Ca(II), which has a larger hydration radius.

Concentration polarization (CP) plays a pivotal role in the performance and sustainability of membrane-based separation processes, significantly influencing fouling and rejection efficiency. CP refers to the accumulation of solutes near the membrane surface due to selective rejection. This localized concentration gradient reduces the driving force for separation,

impacting the overall solute rejection and increasing the energy demand for maintenance.<sup>63,64</sup> The build-up of solutes exacerbates fouling by promoting the formation of a cake layer, a phenomenon termed cake-enhanced concentration polarization (CECP), comprising organic, inorganic, or biological foulants, not only acting as a secondary barrier to solute rejection but also enhancing the solute accumulation near the membrane surface while accelerating fouling.<sup>65</sup>

CP also influences the performance of FO membranes, particularly in terms of fouling and rejection efficiency. This process impacts both the osmotic driving force and the membrane's long-term efficiency. In this context, CP can be categorized into external concentration polarization (ECP)<sup>66</sup> and internal concentration polarization (ICP).<sup>67</sup> ECP occurs at the surface of the active layer, where solutes accumulate or are diluted, depending on the flow direction, and can be mitigated by effective crossflow or mixing. This phenomenon can be partially controlled through hydrodynamic modifications such as increasing flow velocity or turbulence. However, in long-term applications, it still contributes to fouling by facilitating the deposition of colloids, organic materials, and layers onto the membrane surface, further hindering the performance.<sup>68</sup> However, ICP occurs within the porous support layer of asymmetric membranes with a more profound effect on performance, as it reduces the effective osmotic pressure differential, which in turn reduces the water flux.<sup>69</sup> The structural characteristics of the support layer, such as tortuosity, thickness, and porosity, are pivotal in controlling the degree of ICP level.<sup>69,70</sup> Additionally, reverse solute diffusion, where draw solutes migrate back into the feed solution, can interact with feed impurities to aggravate fouling, compounding the challenges posed by CP.<sup>71</sup> Innovations such as electrospun nanofiber supports, which offer low tortuosity, high porosity, and minimal thickness, have demonstrated potentials in ICP reduction and maintaining high water flux over extended operational periods.<sup>72,73</sup>

### 3. Literature survey, analysis, and data extraction

#### 3.1. Nanocomposite membranes

Membrane materials are classified into organic (polymeric) and inorganic (ceramic) types. Organic membranes are desirable for

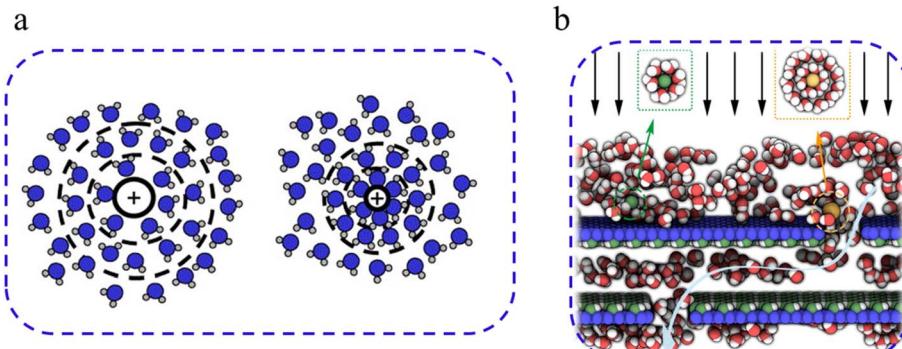


Fig. 3 (a) Hydration shells around a large and a small ion (reprinted with permission from ref. 61) and (b) hydrated ions passing through the bilayer GO membrane (reprinted with permission from ref. 62).



water treatment due to their ease of processing, low cost, and flexibility for surface modifications to enhance separation and antifouling properties. However, their major drawback is reduced flux at high temperatures due to polymer chain degradation.<sup>74</sup> To address these issues, nanoparticles have been incorporated into polymeric membranes, resulting in superior properties, including reduced fouling and improved performance. Various types of nanocomposite membranes including mixed-matrix, thin-film, and surface-located nanocomposites, which offer enhanced thermal stability, mechanical strength, and overall efficiency in water treatment applications have been developed.<sup>75</sup> Generally, the performance of nanocomposite membranes is highly influenced by the properties of the support layer, inner layer, and active layer. The support layer, which provides mechanical strength and structural integrity, should be highly porous and hydrophilic to minimize resistance to water flow and enhance permeability. The inner layer, often a polymeric matrix, is designed to reduce ICP, thereby improving flux and selectivity. The active layer, typically composed of polyamide or other selective polymers, is known for its selective rejection properties. Its thickness, surface morphology, and chemical functionalization determine the membrane's efficiency in rejecting salts and heavy metals while minimizing fouling (Fig. 4). By carefully optimizing these parameters, nanocomposite membranes can achieve enhanced performance in water treatment applications.

In a recent review, Cheng *et al.*<sup>79</sup> studied the development of polymeric nanocomposite membranes and found that the sodium titanate nanobelt (Na-TNB) membrane showed 97.5% and 57.5% removal of Cs(I) and Sr(I), respectively,<sup>80</sup> and (anatase titania/hydrous MgO)@PVC UF mixed matrix membrane (MMM) exhibited 97% and 98% removal of Cu(II) and Cd(II), respectively.<sup>81</sup> In another review, Aryanti *et al.*<sup>82</sup> surveyed ultra-low-pressure RO membranes for desalination and revealed that among a range of nanomaterial-incorporated TFN membranes, the polyamide TFC RO membrane prepared using nano-TiO<sub>2</sub> showed a promising NaCl rejection up to 99.83% and 2.59 L m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup> permeability,<sup>83</sup> while the NaY zeolite-incorporated TFN membrane showed lower NaCl rejection (98.80%) and higher permeability (4.79 L m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup>).<sup>84</sup> Another literature survey reported by

Valamohammadi *et al.*<sup>85</sup> considered the effects of carbon nanotubes (CNTs) on the performance and properties of nanocomposite membranes for wastewater treatment. Screening the reported literature revealed that the highest removal of salts and heavy metals is as follows: Na<sub>2</sub>SO<sub>4</sub> (99%, 6.98 L m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup> permeability) with CNT-enhanced TFN membrane,<sup>86</sup> MgCl<sub>2</sub> (97.36%, 7.57 L m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup> permeability) with hyperbranched polyethyleneimine-modified multi-walled CNT (MWCNT)-incorporated NF,<sup>87</sup> NaCl (98%, 1.50 L m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup> permeability) with zwitterion-functionalized CNT nanocomposite membrane,<sup>88</sup> MgSO<sub>4</sub> (97.60%, 14.03 L m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup> permeability) with modified hydroxyl-containing MWCNT-incorporated NF,<sup>89</sup> as well as Zn(II) (99.06%), Cd(II) (96.72%), Cu(II) (95.84%), Ni(II) (94.63%), and Pb(II) (93.39%) with 7.57 L m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup> permeability using a hyperbranched polyethyleneimine-modified MWCNT-incorporated NF membrane.<sup>87</sup> Yu *et al.*<sup>90</sup> reviewed studies reported on TFN membranes with a 2D nanomaterial interlayer. Regarding their literature survey on various pollutants, hierarchical flower-like MoS<sub>2</sub>-incorporated TFN membrane with >98% removal of Na<sub>2</sub>SO<sub>4</sub> and MgSO<sub>4</sub>, and 18.3 L m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup> permeability,<sup>91</sup> GO-incorporated TFN membrane with >99.7% removal of NaCl and 3 L m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup> permeability,<sup>92</sup> and PEI/MOF-incorporated TFN with 95.50% removal of MgCl<sub>2</sub> and 4.60 L m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup> permeability<sup>93</sup> delineated the highest removals. Here, the effect of GO and its 2D structure on the tortuosity of the pores and the improvement of water channels is prominent. Moreover, charge modification can help ionic removal. The effect of nanoparticles on the mechanical properties of the sublayer has also been reported in some studies.<sup>94</sup> Nanoparticles in the membrane structure can affect hydrophilicity as well as the size and tortuosity of membrane pores and channels by intervening the structure formation process.<sup>95-97</sup> This and similar studies provide valuable insights into selecting hydrophilic nanomaterials for incorporation into the support, interlayer, or active layer of NC membranes. Integrating these materials can significantly enhance the membrane flux and improve rejection rates through the combined effects of hydrophilicity and charge modification. This strategy effectively regulates membrane charge relative to the charge and size of the ions to be removed, offering a promising route for optimizing NC

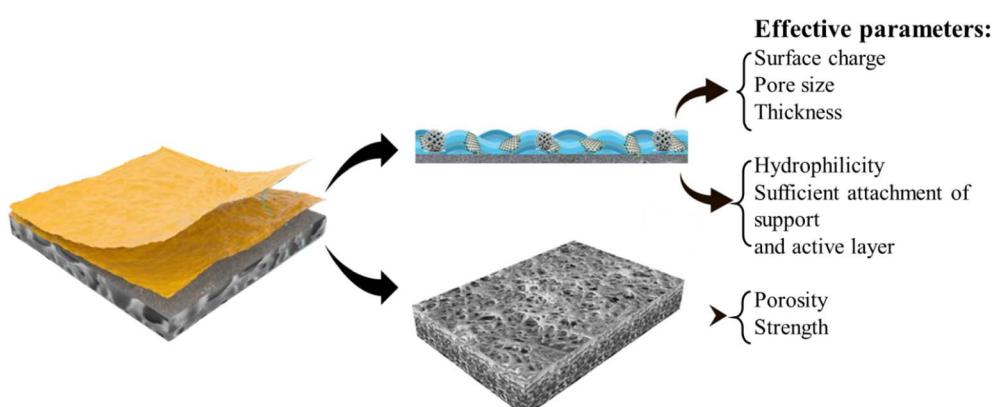


Fig. 4 Schematic structure of thin-film nanocomposite membranes with effective parameters of each layer (reproduced with permission from ref. 76 Elsevier 2021, ref. 77 Elsevier 2020, and ref. 78 RSC 2018).



membrane performance. Proper selection of nanomaterials added to the active PA layer can result in thinner layers, leading to higher water flux values and improving membrane fouling performance.<sup>95,96</sup>

Table S1<sup>†</sup> summarizes the most recent studies on desalination and heavy metal removal using NC membranes in the 2023–2024 range. It can be noted that polysulfone (PSF) is one of the most common substrates or support materials due to promising properties including high thermal, mechanical, and hydrolytic strength.<sup>98</sup> Besides, poly(*m*-phenylene isophthalamide),<sup>99</sup> poly(-vinylidene fluoride)-grafting-poly(acrylic acid),<sup>100</sup> poly(vinyl butyral),<sup>101</sup> cellulose acetate,<sup>102–104</sup> polyamide 66,<sup>105</sup> poly vinylidene fluoride,<sup>106</sup> cellulose diacetate,<sup>107</sup> polyphenylsulfone and polyvinylpyrrolidone,<sup>108,109</sup> polyacrylonitrile,<sup>95,110,111</sup> polyethylene,<sup>96</sup>

polyphenylsulfone,<sup>112,113</sup> polyurethane,<sup>94</sup> polyvinylidene fluoride,<sup>114,115</sup> and poly(vinyl alcohol)<sup>116</sup> have been used. Regarding Table S1,<sup>†</sup> Fig. 5(a) and (b) summarize the number of publications focused on salt and heavy metal removal using NC membranes in the 2023–2024 range. Moreover, the highest removals have been reported in these figures. In terms of salt removal, it can be observed that NaCl and Na<sub>2</sub>SO<sub>4</sub> are mainly used as the common salts, while MgSO<sub>4</sub> and MgCl<sub>2</sub> are in the second place. Fewer studies are also focused on KNO<sub>3</sub>, CaCl<sub>2</sub>, and LiCl. According to Table 2, the highest removals of NaCl,<sup>114</sup> Na<sub>2</sub>SO<sub>4</sub>,<sup>96</sup> and MgSO<sub>4</sub>,<sup>95,96</sup> were found to be 99.88, 99.80, and 99.50%, respectively. In terms of heavy metals, Pb(II), Cd(II), and Cu(II) are the most common species as the most abundant heavy metal pollutants in industrial wastewaters, where the highest

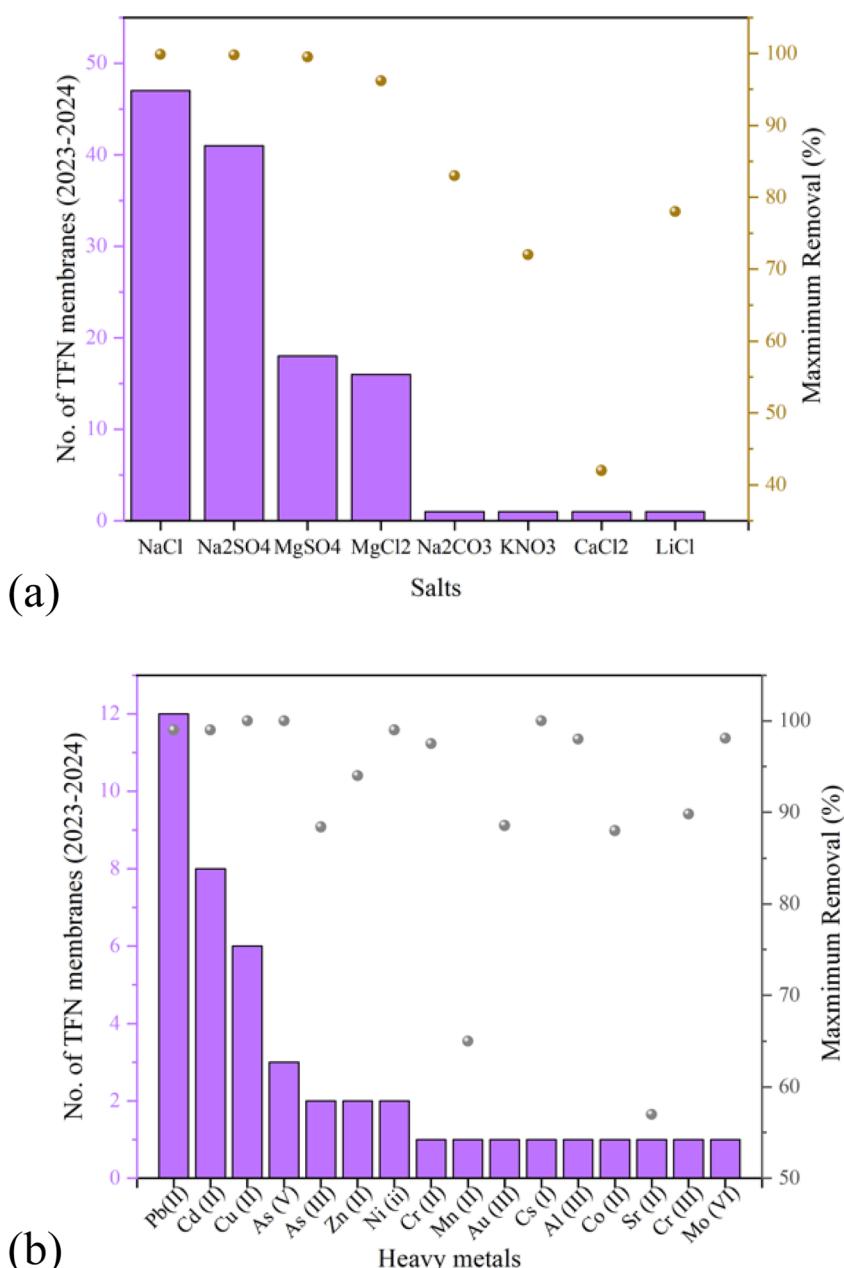


Fig. 5 Most recent publications in the field of (a) salt and (b) heavy metal removal using NC membranes with the maximum removal%.



Table 2 Top NC membranes with the most promising salt and heavy metal removal%

Membrane matrix	Nanoparticle	Water permeability ( $\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$ )	Pollutant	Removal%	Ref.
PVDF	Perfluorooctylamine-graphene nano-sheets	~1.28	NaCl	99.86	114
PE/PA	TiO <sub>2</sub>	5	Na <sub>2</sub> SO <sub>4</sub>	99.80	96
PE/PA	TiO <sub>2</sub>	5	MgSO <sub>4</sub>	99.50	96
PES	WO <sub>3</sub> @GO	445	Ni(II)	99	117
PES	MoO <sub>2</sub> @GO	410	Ni(II)	99	117
PES	Amine, thiol-SiO <sub>2</sub>	6.70	Pb(II)	99	118
CA	Amine-SiO <sub>2</sub>	—	Cd(II)	99	103
PES/PA	MCM-41	4.05	Cu(II)	100	119
PES/PA	Titania nanosheet	1.57	Cs(I)	100	120
PE/PA	TiO <sub>2</sub>	5	As(V)	100	96

removals belong to Cu(II),<sup>119</sup> Cs(I),<sup>120</sup> and As(V)<sup>96</sup> with 100%, Zn(II) with 92.23% removal,<sup>121</sup> and Cd(II),<sup>103</sup> Pb(II),<sup>118</sup> and Ni(II)<sup>117</sup> with 99% removal.

Generally, the membrane separation efficiency relies on achieving a delicate balance between high rejection rates and permeability while maintaining low costs, which presents a great challenge in developing a sustainable membrane filtration system. However, literature review and screening highlight that the efforts to enhance removal rates often coincide with a decrease in permeability<sup>111,122-124</sup> and *vice versa*.<sup>125,126</sup> Overall, it is verified that nanoparticle incorporation help improve the porosity, hydrophilicity,<sup>127</sup> and surface charge. Hence, high salt rejection can be attributed to the enhanced surface charge or dilution effect caused by water permeability enhancement.<sup>128,129</sup> The highest improvement in NaCl rejection was observed using the membrane-incorporated PVA/attapulgite nanocomposite<sup>95</sup> and MoO<sub>2</sub>@GO.<sup>117</sup> Conversely, the overall removal of Na<sub>2</sub>SO<sub>4</sub> was found to be higher than that of NaCl when using NC membranes. In this context, g-C<sub>3</sub>N<sub>4</sub>/CuFe<sub>2</sub>O<sub>4</sub>,<sup>130</sup> chitosan/MWCNT,<sup>131</sup> and rGO@Au<sup>111</sup> demonstrated the highest improvement in Na<sub>2</sub>SO<sub>4</sub> removal. In terms of MgSO<sub>4</sub>, nanoparticles of GO-ZnO<sup>122</sup> and TiO<sub>2</sub> (ref. 132 and 133) posed a higher impact on removal. Regarding MgCl<sub>2</sub> removal, O-MoS<sub>2</sub>,<sup>134</sup> SiO<sub>2</sub>,<sup>135</sup> and (ZnFeCe) layered double hydroxide<sup>136</sup> exhibited the most notable surge.

The highest improvement and change in permeability were observed with the addition of LAPONITE®/GO,<sup>94</sup> GO,<sup>137</sup> and cellulose NC.<sup>107</sup> Upon closer analysis of these studies, it was observed that the addition of LAPONITE®/GO resulted in improved porosity and hydrophilicity, consequently enhancing permeability.<sup>94</sup> The incorporation of GO into the polymeric hydrogel layer led to the improvement of hydrophilicity and reduction of surface roughness, along with a further decrease in surface charge. These properties combined with a reduction in layer thickness yielded a promising enhancement in water permeability.<sup>137</sup> Additionally, the inclusion of high-aspect-ratio cellulose nanocrystals improved the hydrophilicity and water permeability due to the nanorods' percolation-induced nanochannels.<sup>107</sup> Moreover, the polyamide layer is often charged and effectively rejects divalent ions and most organic solutes based on the Donnan repulsion and pore sieving approach.<sup>138,139</sup> In

this context, it was found that some studies have considered the cytotoxicity of the membranes caused by the possible detachment of nanomaterials<sup>94</sup> and their entry into the flow, while others have remained silent on the subject.

Regarding Table S1,† it was noted that the addition of 2D nanoparticles to the membrane matrix led to the most promising improvement in permeability and rejection rates. It is reported that the selective mass transport using 2D nanomaterials is attributed to size and Donnan electrostatic exclusion.<sup>140</sup> It is suggested that surface electrostatic charges block ions either on the pore edges of the nanopores or on the line edges and surfaces of nanosheets. Table 1 summarizes the size of bare and hydrated ions, which, together with the surface charge and pore size of the membranes documented in Table S1,† further confirm the removal mechanism of the membranes. Besides, other than tuning pore size and surface charge, decreasing membrane thickness can improve membrane permeability through diminishing solute diffusion friction.<sup>140</sup>

### 3.2. Thin-film composite (TFC) membranes

Thin-film composite (TFC) membranes stand as the premier technology for pressure-driven RO and NF water treatment processes. The promising separation performance, high water flux, and robust durability make them the leading choice for efficient water purification.<sup>141</sup> In a recent review, Kadhom<sup>127</sup> discussed the synthesis steps, basics, and alternatives of PA TFC membranes for desalination. They highlighted the cost-effectivity, easy preparation procedure of the active PA layer, and long-term operation of TFC membranes as the most promising advantage, while fouling and low thermal stability have been recognized as the most prominent shortcomings. Park *et al.*<sup>142</sup> studied polyester-based TFC membranes for desalination. They considered polyester as a promising alternative to PA membranes with enhanced water permeability, chlorine resistance, oxidation stability, and efficient separation of multivalent ions. Regarding their survey, CD polyester/DMAP-reconstructed the β-CD-EDA/PAN membrane with 98.75–98.88% NaCl rejection and  $4.94\text{--}5.33 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$  permeability,<sup>143</sup> PA TFC membrane with 99.6% of Na<sub>2</sub>SO<sub>4</sub> rejection and  $4.2 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$  permeability,<sup>144</sup> and resorcin 4 arene macrocycle/PSF membrane<sup>145</sup> with 94.80% KOH,



93.85% LiOH, and 89.03% NaOH rejections and 8.14, 9.57, and 14.73  $\text{L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$  permeability, respectively, which exhibited the highest salt removal. In another recent review by Sarkar *et al.*,<sup>146</sup> PA nanofilm composite NF membranes with 99.99%  $\text{Na}_2\text{SO}_4$  removal and 32.1  $\text{L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$  permeability<sup>147</sup> and dual-layer slot coating/polydopamine-coated PE membrane with 99.5% NaCl removal and 2.6  $\text{L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$  permeability<sup>148</sup> showed the highest removal rates. Another review by Wu *et al.*<sup>149</sup> reported that the PIP/PSF membrane with 99.7%  $\text{Na}_2\text{SO}_4$  rejection and 17.5  $\text{L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$  permeability,<sup>150</sup> ZCD-based TFC membrane with 99.8 and 98.9% rejection of  $\text{CrCl}_3$  and  $\text{FeCl}_3$ , respectively,<sup>151</sup> PHMTBA/PSF with 99% rejection of  $\text{Na}_2\text{SO}_4$  and 43.1  $\text{L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$  permeability,<sup>152</sup> and PVA/PIP/PSF membrane with 97.6%  $\text{MgSO}_4$  rejection and 35.5  $\text{L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$  permeability<sup>153</sup> depicted the highest rejections. The literature survey compiled by Zhang *et al.*,<sup>154</sup> revealed that *m*-phenylenediamine/trimesoyl chloride/PSF membrane with 99.4% NaCl rejection and 2.96  $\text{L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$  permeability,<sup>155</sup> and piperazine/4-hydroxybenzenesulfonic acid sodium salt/PSF membrane with 99.1%  $\text{Na}_2\text{SO}_4$  rejection and 34.4  $\text{L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$  permeability<sup>156</sup> represented as the most promising membranes with the highest removal. An *et al.*<sup>157</sup> studied *in situ* modification of NF and RO membranes through the incorporation of thin films and it was verified that the P(NIPAM-*co*-Am)/TFC with 98.6–98.8% NaCl rejection and  $\sim$ 5.5  $\text{L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$  permeability<sup>158</sup> showed the highest salt rejection. Liu *et al.*<sup>159</sup> studied the effect of interlayer on the TFC performance. It was observed that the MXene/PIP/PSF membrane with 99.9%  $\text{Na}_2\text{SO}_4$  rejection and 27.8  $\text{L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$  permeability,<sup>160</sup> and MXene/Fe<sub>3</sub>O<sub>4</sub>/PS/PIP/PSF membrane with >97%  $\text{MgCl}_2$  rejection and 9.48  $\text{L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$  permeability<sup>161</sup> represented the highest rejection values.

Improving water permeability without compromising the high rejection rate remains a major challenge in membrane-based technologies. To address this, recently, Sun *et al.*<sup>162</sup> have developed TFC membranes using a tannic acid (TA)-MXene interlayer. The straightforward synthesis process involved incorporating tannic acid-functionalized MXene nanosheets onto a polyether sulfone (PES) substrate, followed by the interfacial polymerization of piperazine and trimesoyl chloride (Fig. 6). The resulting membrane demonstrated a 96% rejection rate for divalent ions and a water permeability of 22.3  $\text{L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ . Additionally, the membrane exhibited sustained performance in filtration tests lasting up to 140 h. These promising results indicate that the membrane has potential for high-efficiency applications. Further studies focusing on the fouling behavior and stability of the coated layer would be beneficial to ensure long-term operational stability.

Table S2<sup>†</sup> summarizes the most recent studies focused on salt and heavy metal removal using composite membranes in the 2023–2024 range. Regarding the documented results, PSF is mainly used as the substrate, while polyacrylonitrile stands out as the second common substrate. Considering Table S2,<sup>†</sup> Fig. 7 summarizes the number of publications focused on salt and heavy metal removal using TFC membranes in the 2023–2024 range. Moreover, the highest removals are reported in Fig. 7 and Table 3. Similar to nanocomposite membranes, it can be observed that NaCl and  $\text{Na}_2\text{SO}_4$  are the most common salts for such studies, while  $\text{MgSO}_4$  and  $\text{MgCl}_2$  are in the second place. Fewer studies are also focused on  $\text{CaCl}_2$  and  $\text{LiCl}$ . According to Table S2,<sup>†</sup> the highest removals of these salts were found to be NaCl with >99%,<sup>155,163</sup>  $\text{Na}_2\text{SO}_4$  with 99.7%,<sup>164</sup>  $\text{MgSO}_4$  with 99.3%,<sup>165</sup> and  $\text{MgCl}_2$  with 99.7%.<sup>166</sup> In terms of heavy metal removal, it was noted that less focus has been devoted to TFC

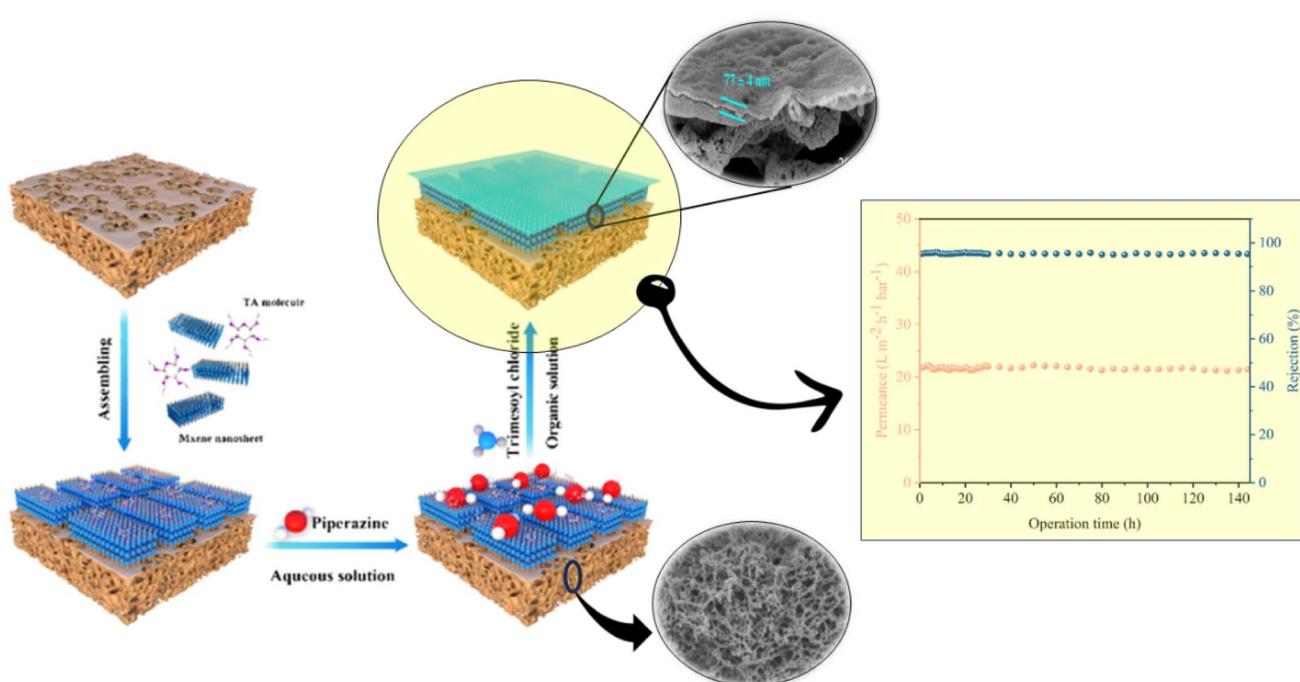


Fig. 6 Process of fabricating an interlayer-enhanced TFC membrane (reproduced with permission from ref. 162, ACS 2024).



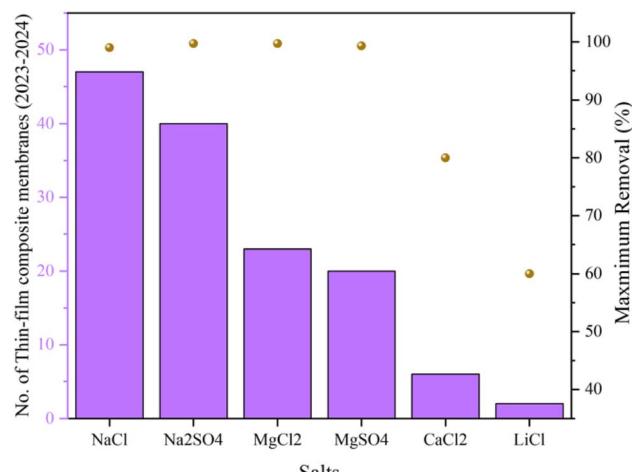


Fig. 7 Most recent publications in the field of salt removal using TFC membranes with the maximum removal%.

compared to TFN membranes for this purpose. However, the highest improvement/change in permeability was observed for PSF/l-arginine/polyamide,<sup>170</sup> PSF/sulfonated GO/polyamide,<sup>171</sup> and PSF/UiO-66-SO<sub>3</sub>H/polyamide,<sup>172</sup> while the highest rejection improvement was obtained from GO-PVDF/CS,<sup>173</sup> plasma-treated PE/PA/SDS,<sup>174</sup> and PSF/PMMA grafted silica.<sup>163</sup> Besides, from Table S2,† it was found that not all the reported studies have considered surface roughness, pore size, and surface charge of the membranes and their effect on removal rates. However, almost all of the reported membranes except that reported in ref. 175–178 exhibited a negative charge. Positive-charged membranes performed salt removal through size sieving combined with Donnan exclusion (repulsion), while negative-charged membranes fulfilled the removal *via* the combination of size sieving with the Donnan exclusion (attraction).

### 3.3. Biomimetic membranes

Biomimetic membranes are typically composed of synthetic materials incorporating key features of biological membranes,

such as ionic channels, aquaporins, and selective transport proteins. To this end, potential biomimetic membrane materials include lipid bilayers, aquaporins, and a variety of membrane proteins, which can be integrated into membranes to enhance the permeability, selectivity, and resistance toward fouling.<sup>179</sup> Aquaporins (AQPs) are transmembrane proteins found in mammalian and microbial cell membranes, facilitating water transport.<sup>180</sup> Integrated into liposomes or polymersomes, they enhance the synthetic membrane performance by increasing both water permeability and selectivity.<sup>181</sup> These membranes can be fabricated *via* assembling aquaporins into lipid membrane layers on a porous support or integrating aquaporin-containing vesicles into a thin-film rejection layer of the membrane.<sup>182</sup> Fig. 8(a–c) depicts the schematic of biomimetic membranes with sub-nanometer channels made by either aquaporin or synthetic nanochannels. Beyond their role as selective agents in membranes, aquaporins offer valuable insights into the synthetic channel design, showcasing an improved transport performance.<sup>186,187</sup> While aquaporins and other protein nanochannels can be synthesized using established bioprocessing techniques, they are prone to denaturation and loss of functionality, and the channels often face stability challenges during membrane synthesis and utilization and may not offer the optimal pore-loading efficiency and functionality. Furthermore, synthetic bioinspired channels can address the instability and poor processability issues inherent in their biological counterparts. Porter *et al.*<sup>187</sup> investigated the challenges and advancements in biomimetic desalination membranes. They identified aquaporins such as human Aqp1 and bacterial AqpZ as promising biological channels. Additionally, the study highlighted several innovative synthetic channels including cyclic peptide nanotubes, carbon nanotube porins, imidazole-derived quartet channels, pillararene-based channels, and aquafoldamer-based synthetic water channels as promising alternatives for improved desalination performance.

Regarding the literature review and screening, it was noted that in the last year minor attention has been paid to the utilization of biomimetic membranes for desalination and heavy metal removal. Moreover, as expected, TFC and TFN membranes have been widely used for this purpose showing

Table 3 Top TFC membranes with the most promising salt and heavy metal removal%

Membrane matrix	Nanoparticle	Water permeability ( $\text{L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ )	Pollutant	Removal%	Ref.
PSF	Polymethyl acrylate grafted silica nanoparticles	2–5	NaCl	>99	163
PES	PA (piperazine, TMC, 2-acrylamido-2-methyl-1-propanesulfonic acid)	30.5	Na <sub>2</sub> SO <sub>4</sub>	99.7	164
PES	PA (piperazine, 1,3,5-benzenetricarbonyl trichloride)	15.80	MgSO <sub>4</sub>	99.3	165
PES	PA (branched PEI, 1,4-phenylene diisocyanate, cyanuric chloride)	1.25	MgCl <sub>2</sub>	99.7	166
Commercial PA-TFC BWRO	Poly(acrylic acid)-polyamide	1.69	As(III), As(V)	96, 99.6	167
PSF	Polyamide (polyethyleneimine, terephthaloyl chloride, piperazine)	11	Heavy metals	98–99	168
PSF	Polyamide ( <i>m</i> -phenylenediamine, trimesoyl chloride), Fe-TA complex	3.58	Boron	98.37	169



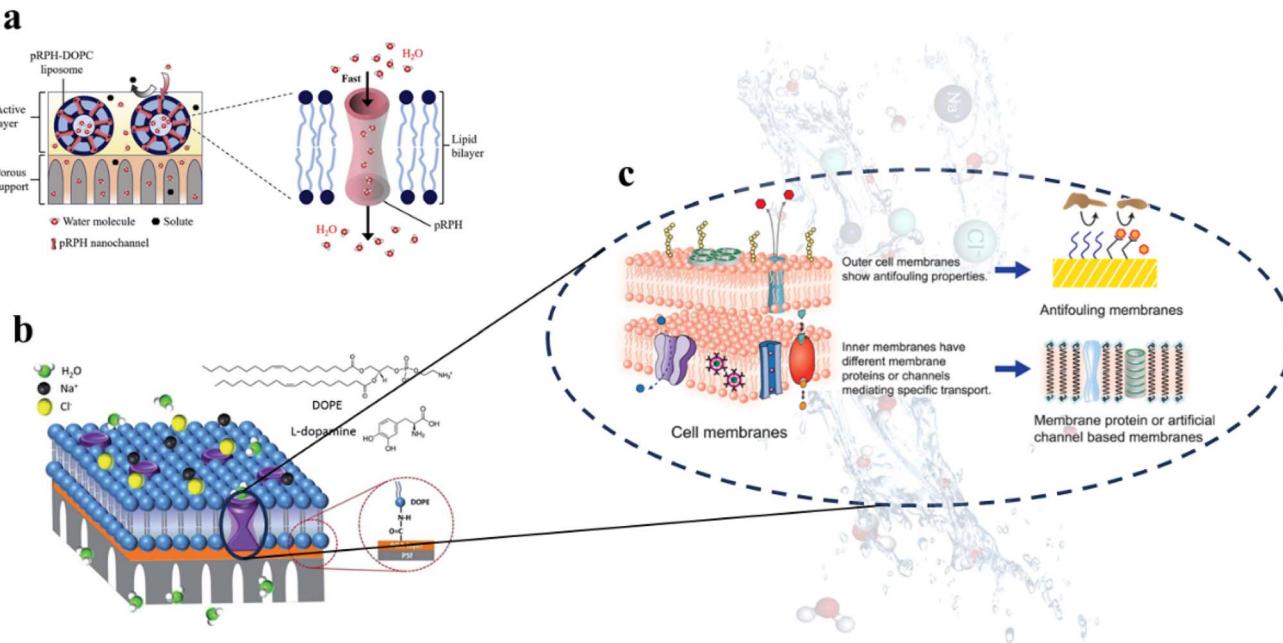


Fig. 8 (a) Biomimetic desalination membranes (reproduced with permission from ref. 183, Elsevier 2021), (b) structure of the lipid bilayer membrane incorporating aquaporins with covalent bond (reproduced with permission from ref. 184, RSC 2015), and (c) common nanochannels for desalination from biological aquaporin and gramicidin to bioinspired channels (reproduced with permission from ref. 185, Elsevier 2014).

promising results. In 2023, Azarafza *et al.*<sup>188</sup> considered protein-based membranes fabricated using aquaporin for desalination and separation purpose. They characterized these membranes by their high osmotic water permeability and excellent ability for small molecules removal. Based on their literature survey, PMOXA-PDMS-PMOXA/PCTE<sup>189</sup> and AQP-DOPC/PSF<sup>181</sup> membranes with 99% removal of NaCl, DOPC-PDA-PEI/PAI<sup>190</sup> and POPC-POPG-Chol/bilayer polyelectrolyte-coated H-PANI UF<sup>191</sup> membranes with 95% removal of MgCl<sub>2</sub>, and DOPC/DOTAP/liposome-embedded TFC with 95.9% MgCl<sub>2</sub>, 94.5% MgSO<sub>4</sub>, and 88.5% Na<sub>2</sub>SO<sub>4</sub> rejections<sup>192</sup> exhibited the highest removal rates. Table S3† summarizes the last published papers in the 2023–2024 period. Regarding the documented results, it can be observed that the overall salt and heavy metal removal of biomimetic membranes was found to be less than that of TFC and TFN membranes, while NaCl was the most common salt considered for treatment using biomimetic membranes. The analysis of Table S3† reveals that the PAN-PA-peptoid membrane exhibited the highest NaCl removal of 99.5%.<sup>193</sup>

One of the central challenges in fabricating biomimetic membranes is the integration of biological components into the membrane structure.<sup>188</sup> The substrates for biomimetic membranes must provide mechanical strength, chemical stability, and biocompatibility while being compatible with protein compounds.<sup>194</sup> For instance, the utilization of aquaporins necessitates stabilizing these proteins as functional groups, ensuring structural integrity under operational conditions.<sup>195</sup> Various techniques such as vesicle fusion, interfacial polymerization, and covalent attachment have been employed to achieve this, each addressing specific hurdles such as protein denaturation and membrane fouling.<sup>188,194,196</sup> Advanced

polymeric materials, often modified with hydrophilic or zwitterionic groups, are increasingly employed to generate the desired interface.<sup>197,198</sup>

The realization of defect-free, cohesive, and industrial-scale production remains a formidable challenge, particularly in terms of aligning nanoscale biological features *via* macroscopic fabrication processes.<sup>199</sup> Recent innovations have been sought to overcome these barriers. For instance, the incorporation of aquaporin proteins into TFC membranes has led to improved desalination efficiency, combining high water flux along with significant salt rejection.<sup>200</sup> Innovations in nanocomposite materials such as integrating block copolymers with engineered channels have resulted in membranes exhibiting improved stability and reduced fouling tendencies. Nevertheless, achieving consistency in membrane performance during scale-up continues as a challenge.<sup>196,201</sup>

Ensuring the functional integrity of aquaporins into membranes during extraction and incorporation into the membranes is critical. Traditional lipid bilayers, while effective in mimicking the aquaporin natural environment, lack the mechanical robustness and stability required for industrial applications. Consequently, synthetic amphiphilic block copolymers have emerged as more viable alternatives, offering superior durability and flexibility.<sup>202</sup> However, the compatibility of these polymers with aquaporins and the precision required in forming defect-free membranes pose additional complexities. The delicate balance of maintaining the native functionality of aquaporins while being integrated into a stable, scalable synthetic matrix remains a formidable barrier.<sup>203</sup> Techniques such as vesicle embedding, interfacial polymerization, and chemical crosslinking have been developed to immobilize



aquaporins effectively. However, these methods often encounter difficulties in the realization of defect-free, large-scale membranes.<sup>196,201,202</sup>

Recent advancements in artificial water channels (AWCs) offer a promising alternative, replicating the selectivity and efficiency of biological water channels through synthetic means. AWCs, such as carbon nanotube porins and imidazole-based channels, have shown comparable performance to aquaporins in laboratory settings. These structures are engineered to maintain molecular-scale precision, enhancing water permeability while preventing ion transport. However, replicating the precise structural and functional attributes of natural channels remains a concern.<sup>199</sup>

The path toward the widespread adoption of biomimetic membranes in practical applications is under considerations. The synthesis of biomimetic membranes involves a multi-step process, remaining as a unique technical obstacle.<sup>196</sup> First, the production of aquaporins, either through natural extraction or recombinant techniques, is constrained by low yield, instability, and the hydrophobic nature. While advancements in recombinant protein technology have enabled higher yields, production remains costly and time intensive. Continued research into scalable fabrication techniques, such as roll-to-roll processing and advanced polymer blending, is essential for transitioning these membranes from experimental stages to industrially viable visions. Additionally, exploring hybrid designs merging the advantages of biological and artificial channels may pave the way for more robust and versatile systems.<sup>199</sup> Another promising avenue is the hybrid integration of aquaporins with nanomaterials such as GO and CNT, which enhance the mechanical properties and fouling resistance of the membranes. These hybrid systems harness the strengths of both biological and synthetic components, providing a pathway toward more durable and efficient water purification systems. Furthermore, the use of advanced computational modeling and machine learning is enabling the optimization of membrane design at the molecular level, accelerating the development of next-generation biomimetic membranes.<sup>204–206</sup> Additionally, the economic feasibility of large-scale production and deployment must be addressed for laboratory-to-industry transition of these technologies.<sup>188,207</sup>

#### 3.4. Forward osmosis (FO) membranes

To address the limitations of conventional RO, forward osmosis (FO) technology has been proposed for seawater desalination.<sup>208</sup> While FO offers the advantage of reduced energy consumption and appears well-suited for applications in arid regions where conventional energy sources may be scarce or costly, it confronts several significant challenges. Foremost among these challenges is the selection of an appropriate draw solute type and concentration. The draw solute must generate adequate transmembrane pressure to facilitate water transport while minimizing reverse salt flux, which can compromise process efficiency. Additionally, the choice of the membrane material is critical; it must exhibit high flux values to maximize water throughput while maintaining a low reverse solute flux to

prevent contamination of the feed solution. Furthermore, the orientation of the membrane's active layer whether facing the draw solution or the feed solution poses a crucial consideration, as it can influence overall system performance. Moreover, the behavior of the membrane when exposed to feed solutions of different concentrations is a key area of concern. Understanding membrane performance, defined by water flux and reverse solute flux, is crucial for optimizing FO processes across diverse applications and environmental conditions.<sup>209</sup> Addressing these challenges is imperative for unlocking the full potential of FO technology and expanding its practical applicability in diverse settings.

To date, substantial research has been devoted to improving the efficiency, reliability, and overall performance of FO technology. Abounahia *et al.*<sup>209</sup> reviewed the commercially available FO membrane characteristics and the development of laboratory scale fabricated membranes based on cellulose triacetate and TFN membranes together with various draw agents and their effects on FO performance. The study highlighted that asymmetric membranes often underperform in FO processes. Moreover, the characteristics of the draw solute are critical, as ICP can lead to a reverse solute flux and a reduced water flux if the draw solute concentration decreases within the dense support layer. A promising approach to mitigate these issues involves utilization of highly porous, thin, and water-permeable support to enhance permeability. The ideal FO membrane should exhibit low ICP, high permeance, antifouling properties, chemical stability, sustained mechanical strength, and minimal reverse solute flux.<sup>210,211</sup>

In the pursuit of finding an ideal FO membrane, Abdul-Hussein *et al.*<sup>212</sup> reviewed the most recent design and deployment of FO desalination technologies, their applications, and the remaining challenges and prospects. In this review, cellulose acetate, polyamide, and TFC membranes are considered as the common FO membranes for seawater desalination. NaCl and MgSO<sub>4</sub> are highlighted as the primary minerals that can be effectively removed through the FO process. For high-salinity feed solutions, the state-of-the-art draw solutions including sodium sulfate, sodium chloride/magnesium chloride mixtures, calcium chloride, potassium phosphate, ammonia–carbon dioxide, polyethylene glycol, lithium chloride, and sodium alginate were recommended. In Ibraheem *et al.*'s<sup>213</sup> review and screening, among a range of nanoparticles used for TFC membrane fabrication, including GO, TiO<sub>2</sub>, zeolite, SiO<sub>2</sub>, ZnO, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, and MOF, the FO membrane made by PSF as support and MPD/TMC/GO as polyamide active layer with NaCl as a draw solute exhibited the highest NaCl removal of 98.71%,<sup>214</sup> and FO membrane consisting of PSF/PEG/NMP support and MPD/GO as the active layer with NaCl as the draw solute showed the highest Pb, Cd, and Cr removal of 99.9, 99.7, and 98.3%, respectively.<sup>215</sup> Reddy *et al.*<sup>216</sup> reviewed the design, synthesis, and application of thermally responsive draw solutes used in the FO system. This paper considered ionic liquids (ILs) and hydrogels as advanced thermally responsive draw solutes. Kanagaraj *et al.*<sup>217</sup> studied the TFC and TFN membranes used in the FO system. The results confirmed that the surface hydrophilicity, roughness, porosity, water



permeation, solute retention, reverse solute permeation (RSP), and specific reverse salt permeation (SRSP) were significantly influenced by the alteration of the skin layer structure in FO membranes. Besides, TFN membranes demonstrated enhanced salt rejection and FO water flux, along with superior fouling resistance properties. Piash and Sanyal<sup>218</sup> reviewed the strategies developed for FO support layer design. Among the screened membranes, the  $\text{Al}_2\text{O}_3$ /PSF membrane with 1 M of NaCl as the draw solute,<sup>219</sup> Oasys TFC flat sheet membrane,<sup>220</sup> sPPSU membrane with 2 M of NaCl as the draw solute,<sup>221</sup> and PSF/PAN membrane with 1 M of NaCl as the draw solute<sup>222</sup> showed the highest permeability of 8.43, 4.25, 3.7 and 3.68  $\text{L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ , respectively. Kallem *et al.*<sup>223</sup> reviewed and screened the recent developments in electrospun nanofiber-based substrates used for the fabrication of composite membranes in the FO system. Documented data verified that PVDF-SiO<sub>2</sub> depicted the highest salt removal of 99.7% (ref. 224) and PDA-modified electrospun nanofiber mat<sup>225</sup> exhibited the complete removal of Zn(II), Fe(III), and Cr(VI). Tharayil *et al.*<sup>226</sup> analyzed the current research trend on the FO system used in various fields including desalination, fertigation, pharmaceutical, dye and textile industries, algae dewatering, and dairy processing. In terms of desalination, the TFN membrane with *p*-aramid nanofibers (ANFs) and sucrose solution as the draw solute showed the highest salt rejection of 98.6% (ref. 227) and NIPS TFN membrane<sup>215</sup> exhibited the highest removal of 99.9, 99.7, and 98.3% for Pb, Cd, and Cr.

Selecting the appropriate draw solute is a critical challenge in FO. Extensive research has been dedicated to identifying novel draw solutes that can generate high transmembrane pressures while minimizing the reverse salt flux. Recent investigations have explored various promising alternatives including ILs,<sup>228–232</sup> deep eutectic solvents (DES),<sup>233</sup> magnetic nanoparticles (MNPs) coated with polymers,<sup>234</sup> thermo-responsive nonionic amphiphilic copolymers,<sup>235</sup> sugars,<sup>236</sup> polyelectrolytes,<sup>237,238</sup> hydrogels,<sup>239</sup> surfactants,<sup>240–242</sup> and carbon quantum dots (CQDs).<sup>243</sup> Despite these advancements, many studies continue to evaluate the efficacy of FO membranes using 1 M NaCl as a standard draw solution, while novel draw solutes are often tested with commercial membranes. This highlights the need for more comprehensive evaluations that pair innovative draw solutes with specifically designed FO membranes to fully assess their potential and optimize FO performance.

The improvement of FO membrane characteristics remains an active area of research. Strategies to enhance the membrane performance often involve adjusting the hydrophilicity of various membrane layers. PES, PSF, and cellulose acetate (CA) are the primary polymers as the substrate, while PA serves as the top layer. Various approaches have been implemented to address these challenges. One promising method is the support-free preparation of the PA selective layer with a tunable thickness, combined with a highly porous support, to mitigate ICP as a major source of flux reduction.<sup>244–247</sup> Additionally, the introduction of interlayers into composite structures has been proposed to minimize the structural parameter by creating tortuous paths, thereby reducing ICP. These interlayers include materials such as alginate hydrogel@MXene,<sup>248</sup> cellulose

nanocrystal (CNC),<sup>249</sup> PVA-glutaraldehyde (GA) hydrogel,<sup>250</sup> PDA/PEI/UiO-66,<sup>251</sup> PDA/GO-Fe<sup>3+</sup>-TA,<sup>252</sup> SA/UiO-66-NH<sub>2</sub>,<sup>253</sup> chitosan/tannic acid,<sup>254</sup> MoS<sub>2</sub>@NH<sub>2</sub>-UiO-66,<sup>255</sup> alginate/Ca(II),<sup>256</sup> aluminum tetra-(4-carboxyphenyl)porphyrin (Al-MOF),<sup>257</sup> and polydopamine/GO.<sup>258</sup> These materials enhance the membrane performance by reducing ICP and improving overall flux and solute rejection. By continuously refining these strategies and developing new materials, the efficiency and effectiveness of FO membranes can be significantly improved, paving the way for more practical and scalable applications.

The addition of hydrophilic nanostructures to the membrane support or the active layer such as sulfonated graphene oxide (SGO),<sup>259</sup> CuBTC MOF,<sup>260</sup> MAX phase (Ti<sub>3</sub>AlC<sub>2</sub>),<sup>261</sup> NH<sub>2</sub>-GOQDs,<sup>262</sup> PAM-grafted ZnO,<sup>263</sup> ZnO,<sup>264</sup> poly(sulfobetaine methacrylate) (PSBMA)-cellulose nanofibers (CNFs),<sup>265</sup> NCQDs,<sup>266,267</sup> MIL-53(Fe),<sup>268</sup> covalent organic frameworks (COF) modified with TA,<sup>269</sup> polyoxometalate-LDH,<sup>270</sup> APTMS-TiO<sub>2</sub>,<sup>271</sup> PAMAM-MNPs,<sup>234</sup> and PEI:rGO/PDA,<sup>236</sup> is proposed to obtain high water flux and retention rate. ICP reduction is also targeted by the integration of hydrophilic fillers such as Ag@NH<sub>2</sub>-UiO-66,<sup>272</sup> MIL-53(Fe)@γ-Al<sub>2</sub>O<sub>3</sub>,<sup>273</sup> and WS<sub>2</sub>-Cys-MOF nano-sheets<sup>274</sup> by introducing water specific channels and antibacterial property into the molecular structure of the selective layer matrix. Antifouling and anti-biofouling characteristics comprise another approach, which can be achieved by the addition of photocatalytic nanostructures such as MoS<sub>2</sub>/PDIsm heterostructured photo-catalysts,<sup>275</sup> anatase TiO<sub>2</sub>,<sup>276</sup> MoS<sub>2</sub>-Ag,<sup>277</sup> and MoS<sub>2</sub>@zeolite X<sup>278</sup> to the selective layer. Surfactant-induced intervention in interfacial polymerization using hexadecyltrimethylammonium toluene-*p*-sulphonate (CTAT) and the amine aqueous solution<sup>279</sup> is also implemented to obtain highly permeable TFC membranes with promising selectivity. One promising approach to enhance water treatment performance is reported by Sun *et al.*,<sup>280</sup> where a TFN PA layer was coated over the ceramic substrate using *in situ*-grown Zr-MOF (UiO-66-NH<sub>2</sub>) as the interlayer (Fig. 9). The results revealed that the interlayer decreased the film thickness, improved the cross-linking degree, enhanced the surface roughness, and resulted in an improved water flux (27.38  $\text{L m}^{-2} \text{ h}^{-1}$ ) with less reverse salt flux

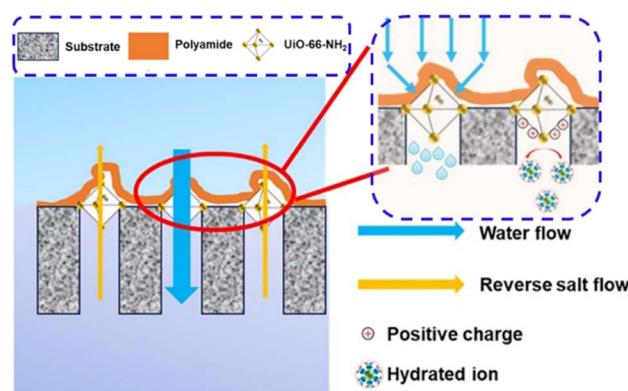


Fig. 9 PA/Zr-MOF (UiO-66-NH<sub>2</sub>)/ceramic-based FO membrane (reprinted with permission from ref. 280, Elsevier 2024).



Table 4 Top FO membranes with the most promising salt and heavy metal removal%

FO membrane material	Draw solute	DI water flux ( $\text{L m}^{-2} \text{ h}^{-1}$ )	Solution water flux ( $\text{L m}^{-2} \text{ h}^{-1}$ )/specific salt flux ( $\text{g L}^{-1}$ )	Reverse salt flux ( $\text{g m}^{-2} \text{ h}^{-1}$ )	Ref.
CTA and CA FO	NaCl	—	1464.21–1627.12	164.79–870.44	281
Chitosan nanofibers/PA	NaCl	—	95	~7	282
			107.53	~28	
			125	~37	
			131.13	~42	
PES-PA aquaporin TFC FO (A/S, Denmark)	Zinc sulfate	6.5 6.5 8.2 8.2 8.8 8.8	6.5 11.5 8.1 14 8.8 21.5	4 4.5 4.6 5 5.8 6.6	283 283 283 283 283 283
MWCNT10-PVA/PA	NaCl	—	~14	~3	245
MWCNT20-PVA/PA			~10.3	~2.5	245
MWCNT30-PVA/PA			~8.5	~2.7	245
pCNT5-PVA/PA			~21	~4	245
pCNT10-PVA/PA			~15.7	~2.5	245
pCNT20-PVA/PA			~13	~2.3	245
pCNT30-PVA/PA			~10.5	~2.2	245
PVA1pCNT3-PA			~22.5	~6.75	245
PVA1pCNT5-PA			~21.5	~7.3	245
PVA1pCNT10-PA			~16	~4	245
PVA0.25pCNT3-PA			22.57 (0.45)	10.12	245
PVA0.25pCNT3-PA			30.16 (0.3)	9.34	245
PVA0.25pCNT3-PA			55.53 (0.46)	25.37	245
PVA0.5pCNT3-PA			~27	~6.5	245
PVA2pCNT3-PA			17.47	~7.2	245

(3.45  $\text{g m}^{-2} \text{ h}^{-1}$ ). Besides, promising ion rejection (>94%) was observed using the as-prepared membranes.

Although salt rejection and removal efficiency are crucial parameters for evaluating FO membranes, many studies have prioritized reporting high water flux and low reverse solute flux. High water flux indicates the efficiency of the membrane in permeating water, enhancing throughput and reducing costs. Low reverse solute flux, however, is crucial to prevent contamination and maintain the osmotic pressure gradient, ensuring the process efficiency and cost-effectiveness. Given these considerations, the top-performing membranes are selected based on their higher water flux and lower reverse solute flux and summarized in Table 4.

### 3.5. Energy requirement

Using osmotic pressure gradients to transport water across a semi-permeable membrane, FO offers potentially more energy efficiency than RO, which relies on high pressures.<sup>284,285</sup> However, understanding the energy dynamics of FO, particularly the draw solution regeneration requirement to recover fresh water, is crucial for evaluating its feasibility and scalability within the integrated systems.<sup>286</sup> While the osmotic pressure gradient eliminates the need for external pressure application, the energy-intensive draw solution regeneration step can offset these savings if not optimized. The reports indicated that FO can operate with energy requirements of almost 0.25  $\text{kW h m}^{-3}$ , significantly lower than the typical 5  $\text{kW h m}^{-3}$  required for RO.<sup>287–289</sup> This represents an energy reduction of up to 80% for

the separation. Comparatively, thermal desalination processes such as multi-stage flash (MSF) demand even higher energy inputs, often exceeding 10  $\text{kW h m}^{-3}$ , making FO particularly attractive in scenarios where energy is expensive.<sup>287</sup>

However, the energy profile of FO must also account for the method and efficiency of draw solution regeneration. The regeneration of draw solutions can be achieved through various methods including RO, NF, or thermal processes, each with distinct energy profiles. For instance, studies highlight that energy consumption in FO coupled with membrane distillation or NF ranges between 0.6 and 2.5  $\text{kW h m}^{-3}$  of produced water, depending on the feedwater salinity and operational conditions.<sup>290,291</sup> These values often place FO systems competitive with RO, particularly for brackish water desalination, where FO benefits from reduced fouling and maintenance demands. For example,  $\text{NH}_3$  and  $\text{CO}_2$  (ref. 292–294)-based draw solutions are thermally regenerated, demanding ~2–3  $\text{kW h m}^{-3}$ . This brings the total energy consumption closer to 3–5  $\text{kW h m}^{-3}$ , depending on operational parameters and specific system designs.<sup>295–297</sup> In contrast, magnetic nanoparticle-based draw solutions, which can be regenerated using external magnetic fields, show promise for reducing energy costs, although their scalability is challenging.<sup>298</sup>

Studies have demonstrated that advanced draw solutes, such as multi-functional ones can also optimize regeneration energy, achieving osmotic pressures >3000 mOsm per kg with manageable recovery requirements.<sup>298</sup> The FO process inherent energy efficiency is further amplified in hybrid systems combining FO and RO. In such configurations, FO is used for



feed-water pre-concentrate, reducing the osmotic pressure gap the RO system must overcome. Hybrid FO-RO systems have demonstrated energy reductions of up to 25% compared to standalone RO, with the overall consumption decline of  $\sim 1.5$  kW h m $^{-3}$ .<sup>295,299</sup> This approach not only optimizes energy consumption but also mitigates the fouling and scaling issues that typically plague high-pressure systems, enhancing long-term operational efficiency and reducing maintenance costs.<sup>297</sup> Unlike pressure-driven processes, FO benefits from reversible fouling behavior due to the absence of significant hydraulic forces on the membrane surface. This reduces the frequency and cost of membrane cleaning and replacement, further improving its lifecycle cost-effectiveness. Various structures of FO, TFC or double-skinned membranes have also demonstrated enhanced performance, achieving water flux rates of 10–20 L m $^{-2}$  h $^{-1}$  under typical conditions, depending on the draw solution and feedwater salinity.<sup>296,300</sup>

### 3.6. Hybrid organic–inorganic membranes

Hybrid organic–inorganic membranes represent a promising advancement in the field of desalination and heavy metal removal. By synergistically integrating the advantageous properties of both organic polymers and inorganic materials, these membranes deliver superior performance, enhanced stability, and resistance to fouling. It is suggested that hybrid adsorptive membranes outperform conventional polymer membranes in removing pollutants from aqueous media. These advanced membranes facilitate rapid solute transport by replacing molecular diffusion mechanisms with high filtration rate systems, thereby improving the overall performance in water purification applications.<sup>301</sup> In terms of FO system, studies have confirmed that organic–inorganic hybrid nanocomposite membranes exhibit substantially higher water flux, mechanical strength, chemical stability, selectivity, and hydrophilicity than the conventional polymeric FO membranes.<sup>302</sup> The incorporation of inorganic nanomaterials into FO membranes aims to optimize the membrane structure, reduce ICP, mitigate fouling, and overcome performance trade-offs. Enhanced membrane performance results from the interactions between nanomaterials and polymer molecular linkers, along with the functional groups present on the nanomaterial surfaces.<sup>303</sup> In Song *et al.*'s study,<sup>304</sup> high-performance double-skinned FO membranes were developed with promising solute rejection *via* the incorporation of polydopamine and CNTs through interfacial polymerization in the active layer. The results underscored the significant influence of CNTs on the membrane characteristics and the hybrid membranes exhibited a higher FO water flux and remarkable antifouling capacity compared to the conventional membranes. In 2017, Sun *et al.*<sup>302</sup> reviewed the organic–inorganic nanocomposite FO membranes fabricated using CNTs, GO, halloysite nanotubes, as well as TiO<sub>2</sub>, silica, and Ag nanoparticles. Besides, the effect of modification methods on the FO performance was studied. Studies revealed that although there have been notable improvements in performance, achieving practical applications and commercialization remains a challenge owing to the high cost of

nanomaterials, non-homogeneous dispersion by aggregation, weak bonds between membrane matrix and the nanoparticle, long-term stability, *etc*. Despite the diverse research focus in this area, there remains a noticeable scarcity of comprehensive review papers that systematically analyze and consolidate the advancements in hybrid materials for water treatment.

The long-term stability and cost-effectiveness of hybrid membranes are pivotal in the advancement of desalination technologies. Hybrid membranes integrating materials such as mesoporous silica and organo-silica as common samples have demonstrated promising results in terms of durability, operational stability, and economic viability. For example, a study evaluating silica-P123 membranes for brackish water desalination highlighted their excellent robustness and salt rejection, achieving >99% rejection while maintaining structural integrity over prolonged utilization.<sup>305</sup> The hybrid organo-silica species, in particular, displayed superior hydrostability due to reduced silanol content, a critical factor in maintaining membrane performance under harsh conditions.<sup>306</sup> Similarly, the integration of UF and NF in hybrid systems for brackish water treatment, as tested in remote Australian national parks, underscores the viability of hybrid membranes in resource-limited environments. These systems effectively managed high turbidity and salinity levels, ensuring water quality while operating under variable energy inputs such as solar power. Specific energy consumption was maintained below 5 W h L $^{-1}$ , showcasing their efficiency.<sup>307</sup> Large-scale implementations of hybrid systems further illustrate their cost-effectiveness. In regions such as the Middle East, where water scarcity is acute, hybrid RO-multistage flash (MSF) systems have been successfully deployed, achieving significant reductions in freshwater production costs. These systems optimize energy use and enhance water recovery rates, addressing key limitations of standalone membrane or thermal technologies.<sup>308,309</sup>

The integration of organic and inorganic materials in hybrid membranes offers a balance between performance and cost, with substantial cost reductions compared to pure inorganic membranes. Organic membranes, primarily polymeric, are known for their flexibility, cost-effectiveness, and ease of fabrication.<sup>310</sup> In contrast, inorganic membranes, particularly ceramic-based ones, exhibit exceptional mechanical, thermal, and chemical stability, albeit at significantly higher costs, ranging from 500 to 3000 \$ per m $^2$  (ref. 311 and 312) compared to 20–200 \$ per m $^2$  for polymeric membranes.<sup>313,314</sup> Hybrid membranes achieve cost-effectiveness by addressing the limitations of individual components. For instance, ceramic membranes fabricated from natural minerals or industrial waste materials can reduce material costs to 2–130 \$ per m $^2$ .<sup>315</sup> By combining these with polymeric materials, hybrid membranes can achieve enhanced performance at a fraction of the cost associated with pure ceramic membranes. For example, hybrid membranes such as those combining a low-cost Daramic framework (31.52 \$ per m $^2$ ) with Nafion resin achieved a cost of <50% of pure Nafion membranes. However, it is important to note that not all reported studies have considered the price of the membranes or conducted a detailed techno-economic analysis.<sup>316</sup>





Table 5 Top hybrid organic–inorganic membranes with the most promising salt and heavy metal removal%.

Membrane matrix	Feature	Pollutant	Permeability ( $\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$ )	Rejection (%)	Ref.
Graphene oxide hybrid membrane- $\text{Fe}_3\text{O}_4$ @amyloid fibrils nanoclusters intercalated into the GO sheets	Heavy metal removal	As(III), Pb(II), Cd(II), Hg(II), Cu(II), $\text{Zn}(\text{II})$ , $\text{Ni}(\text{II})$ , $\text{Co}(\text{II})$ and $\text{Cr}(\text{III})$	—	>99.9	317
ML-101(Cr) and ML-101(Cr)@GO doped PVA	Desalination by pervaporation	NaCl	9.7 $\text{kg m}^{-2} \text{h}^{-1}$	>99.99	318
$\text{SiO}_2$ /PVDF-TMC	Membrane distillation High permselectivity	NaCl $\text{Mg}(\text{II})$ , $\text{Ca}(\text{II})$	16.08 $\text{kg m}^{-2} \cdot \text{h}^{-1}$ 53.4	>99.9 >99	319 320
PVDF/SM@ polyvinylamine (PVAM)- tannic acid (TA)-metal ion Carboxyl functionalization of hybrid organosilica RO	Desalination	NaCl, $\text{MgCl}_2$ , $\text{MgSO}_4$	~3.5, 3.2, 3 ( $\times 10^{-13} \text{ m}^3 \text{ m}^{-2} \text{ s Pa}$ )	~97–99	321
Graphene QDs doped PVA hybrid membranes	Desalination <i>via</i> pervaporation	NaCl	17.09 $\text{kg m}^{-2} \text{h}^{-1}$	>99.6	322
PES-PTL	Antifouling properties	Cu(II), Ni(II), Cd(II), Pb(II)	39.5	>99	323
TA-ZIF-8	Improved permeation $\text{Cr}(\text{III})$ removal	NaCl $\text{Cr}(\text{III})$	56 $\text{L m}^{-2} \text{h}^{-1}$ —	~99	324
PES-Na-A zeolite/oxycut residue NF Covalent organic framework (COF) membrane	$\text{Na}^+$ / $\text{Mg}^{2+}$ permselectivity	$\text{Na}^+$ , $\text{Mg}(\text{II})$ , $\text{Cl}^-$	$\text{Na}(\text{I})$ permeance $13 \times 10^5$ – $14.2 \times 10^5$ $\text{mol m}^{-2} \text{h}^{-1}$	98 $\text{Mg}(\text{II})$ 85–97	325 326

The most recent organic–inorganic hybrid membranes are summarized in Table S5.† Among them, Table 5 highlights the membranes that outperform others in terms of high salt and heavy metal removal percentages. The analysis of these tables reveals a predominant focus on the use of hybrid organic–inorganic membranes for heavy metal removal compared to salt removal in recent studies. This trend probably reflects the specific affinity and effectiveness of hybrid membranes in capturing heavy metal ions through tailored surface functionalization and enhanced adsorption mechanisms.

One of the most critical hurdles lies in achieving the uniform dispersion of inorganic fillers within the polymeric matrix. Poor dispersion often leads to nanoparticle aggregation, resulting in non-uniform material distribution that adverse impacts the mechanical strength and functional performance of the membranes. Mendes-Felipe *et al.*<sup>327</sup> emphasized that ensuring compatibility between the polymeric matrix and the inorganic nanoparticles, such as  $\text{TiO}_2$  or MOFs, frequently requires surface modification of the fillers to improve interfacial bonding. For instance, MXenes, characterized by high surface area, tunable functional groups, and exceptional electrical conductivity, are prone to restacking or oxidation under ambient conditions, diminishing the availability of active sites which compromise mechanical flexibility.<sup>328,329</sup> To address these issues, researchers have employed surface engineering techniques such as functionalization of MXenes by hydrophilic/phobic groups or intercalating molecules to prevent restacking. These modifications enhance chemical interactions between MXenes and polymer matrices, resulting in more stable and efficient hybrid membranes.<sup>330–332</sup>

Similarly, nanocellulose-based hybrid membranes offer an environmentally sustainable alternative by enhancing the renewable and biodegradable properties of cellulose nanomaterials. Cellulose nanocrystals (CNCs) and cellulose nanofibers (CNFs) provide exceptional mechanical strength and hydrophilicity, significantly enhancing the antifouling properties and water flux of hybrid membranes. However, the inherently hydrophilic nature poses integration challenges when combined with hydrophobic polymer matrices, often leading to phase separation or compromised structural integrity.<sup>328</sup> To address this, surface modifications such as acetylation or the grafting by functional groups have been implemented to improve the compatibility of nanocelluloses with the polymeric matrix.<sup>333,334</sup> These strategies not only facilitate uniform dispersion but also enable the development of membranes with tailored functionalities, such as enhanced selectivity or antimicrobial properties.

Another innovative direction involves the incorporation of metallic or photocatalytic nanoparticles, such as Ag and  $\text{ZnO}$ , into hybrid membranes, providing antimicrobial activity and photocatalytic degradation of pollutants. For example, Ag nanoparticles have been widely utilized to impart antibacterial properties to ref. 335, while  $\text{TiO}_2$  nanoparticles induce photocatalytic activity under UV.<sup>336</sup> However, challenges such as nanoparticle leaching, secondary contamination, and limited stability under harsh operational conditions must be addressed to ensure long-term effectiveness and environmental safety.<sup>329</sup>

Recent advancements in fabrication techniques have also been instrumental in overcoming the challenges. Approaches such as interfacial polymerization, electrospinning, and phase inversion have enabled precise control over membrane structure and the distribution of additives within the matrix. Interfacial polymerization, for example, has been employed to fabricate TFC membranes characterized by exceptional uniformity and functional integration. Similarly, electrospinning has facilitated the fabrication of membranes with hierarchical pore structures, significantly enhancing permeability and selectivity. Additionally, layer-by-layer assembly has emerged as a promising method for designing hybrid membranes with tailored functionalities such as pH-responsive or stimuli-sensitive separation features.<sup>328,329</sup>

Another challenge lies in maintaining the structural integrity and mechanical robustness of hybrid membranes, especially in higher-filler-content condition. High filler loads, although beneficial for improving catalytic or adsorptive properties, often compromise the flexibility and durability of the membrane. The development of novel polymeric matrices such as PES or PVDF, known for their inherent mechanical strength and thermal stability, has shown promise in overcoming these limitations. In this context, researchers have suggested strategies such as cross-linking or blending different polymers to achieve an optimal balance between flexibility and rigidity.<sup>337</sup>

Scalability is another hurdle in the commercialization of hybrid membranes. While laboratory-scale studies have demonstrated their potential, scaling up to industrial production often encounters issues such as reproducibility, cost-effectiveness, and material stability. For instance, the fabrication of MXene-based membranes involves intricate etching and intercalation processes not easily adaptable for large-scale manufacturing. Similarly, the use of high-cost precursors, such as noble metal nanoparticles, poses economic challenges limiting widespread adoption. Addressing these issues requires innovations in synthesis methods, such as greener and more cost-effective fabrication routes, as well as the development of robust and scalable production systems.<sup>328,329</sup>

## 4. Comparison and discussion

The application of membrane-based technologies in water treatment has gained substantial traction due to their efficiency in removing contaminants such as salts and heavy metals. These technologies have revolutionized water purification processes, providing high selectivity and permeability. However, despite their widespread use and established benefits, significant challenges and gaps persist within each type of membrane that must be addressed to further enhance their performance and broaden their applicability.

### 4.1. Removal efficiency

Traditional RO and FO membrane technologies have undergone extensive evaluation for eliminating trace contaminants from wastewater.<sup>338</sup> The significantly low content of pollutants necessitates high pressure in RO processes for an effective

removal, rendering such operations economically unfeasible in many regions. Furthermore, FO membranes with low operational pressure requirement demonstrate limited efficacy in rejecting small neutral organics.<sup>339</sup> Biomimetic membranes present a more cost-effective solution for eliminating trace organic contaminants due to their ability to enhance freshwater permeability and accommodate low-pressure operations. In terms of aquaporin-based biomimetic membranes as promising candidates in this category, the main challenge would be the extraction of aquaporin and fabrication of related biomimetic membrane, offering durability and long-term stability against saline water and cleaning procedure. Besides, the upscaling of these membranes is a challenge due to not commercially available aquaporin, difficult production procedure, and compatibility requirement of the host membrane with the protein, which limits the options.<sup>340,341</sup>

### 4.2. Permeability

The substrate plays a crucial role in membrane permeability. An optimal substrate should exhibit hydrophilicity to ensure high water flux. However, excessively high substrate hydrophilicity can diminish adhesion between the active layer and the substrate. Besides, substrates with significant variations in pore size may lead to uneven active layer thickness due to preferential penetration of the polymer solution into larger pores compared to smaller ones.<sup>342,343</sup> The selection of the right substrate involves ensuring high flux, compatibility for uniformity and defect-free performance, and strong adhesion within the active layer. As expected, the incorporation of nanomaterials in various membranes systems, whether in RO or FO systems, has significantly improved water permeability and desalination rates. Among a range of nanomaterials, carbon-based ones, in particular, have been extensively researched. However, these materials are not optimal for commercial use since their expensive manufacturing processes hinder large-scale production and economic feasibility in desalination. There is often a trade-off between membrane permeability and selectivity, with improvements in one typically resulting in compromises in the other. However, membranes incorporating nanostructured materials such as mixed-matrix nanocomposite membranes (MMNMs) and TFN have shown exceptional properties. These nanostructured membranes offer synergistic benefits, including enhanced permeability, elevated rejection rates, high thermal and mechanical stability, and antifouling/biofouling characteristics, making them highly effective for water treatment applications. However, the primary challenge in this context lies in uniformly dispersing inorganic nanoparticles within the polymer matrix. Aggregation is a frequent issue, which obstructs the consistent distribution of nanomaterials throughout the polymer structure.<sup>344</sup> Selecting the best filler for nanocomposite membranes is a challenge due to improving specific membrane features while negatively affecting others. Therefore, based on the desired characteristics of the outflow, and considering the stability, durability, and cost of the membrane, the optimal nanocomposite can be selected to improve desired properties without compromising the overall



membrane performance. In spite of significant progress in developing nanocomposite membranes for water treatment, further gaps still need to be addressed. The fabrication of nanocomposite membranes is a complex and meticulous process. Researchers have primarily adopted two different approaches for this purpose,<sup>345–347</sup> such as (i) entrapment of nanoparticles into the polymer matrix during the fabrication process using the phase inversion method and (ii) applying a nanoparticle coating to the surface of the membrane. Future research should focus on refining the fabrication techniques to improve the performance and stability of nanocomposite membranes. Additionally, investigating new types of nanoparticles and their interactions with various polymer matrices could yield better fouling resistance, higher selectivity, and increased mechanical strength.

The permeability of the selected TFN, TC, and biomimetic membranes is summarized in Fig. 10. As depicted in the figure, with the exception of one biomimetic membrane (GSNA<sup>348</sup>) exhibiting the highest permeability of  $2900 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ , the average permeability of TFN membranes surpasses that of TC and biomimetic membranes. The enhanced permeability of TFN membranes can be attributed to (i) the hydrophilicity of the membrane matrix caused by the incorporation of nanoparticles, facilitating water transport and permeation through the membrane, (ii) more porous and interconnected structure compared to TC and biomimetic membranes, and (iii)

increased surface roughness due to the presence of nanoparticles, which can also contribute to improved fouling resistance. Reduced fouling can maintain the membrane's permeability over extended periods of operation, as the accumulation of foulants on the membrane surface is minimized. Moreover, to improve the performance of FO system, a diverse array of draw solutes have been explored, including organic and inorganic solutions, functional nanoparticles, ILs, thermolytic solutions, switchable polarity solvents, thermo-responsive draw solutes, hydrogels, dendrimers, and fertilizers. Despite these advancements, identifying an optimal draw solute that is cost-effective while generating sufficient osmotic pressure remains a significant challenge.<sup>209</sup>

#### 4.3. Economic viability

The economic feasibility of advanced membrane technologies plays a critical role in their adoption and scalability across water treatment applications. Costs associated with different membrane types vary significantly, reflecting differences in material composition, fabrication processes, and operational requirements. Among these, ceramic membranes, while having higher upfront costs, ranging from 500 to 3000 \$ per  $\text{m}^2$  compared to 20–400 \$ per  $\text{m}^2$  for polymeric membranes, offer unparalleled long-term advantages. Their lifespan of 15–20 years, compared to 5–8 years for polymeric membranes, reduces

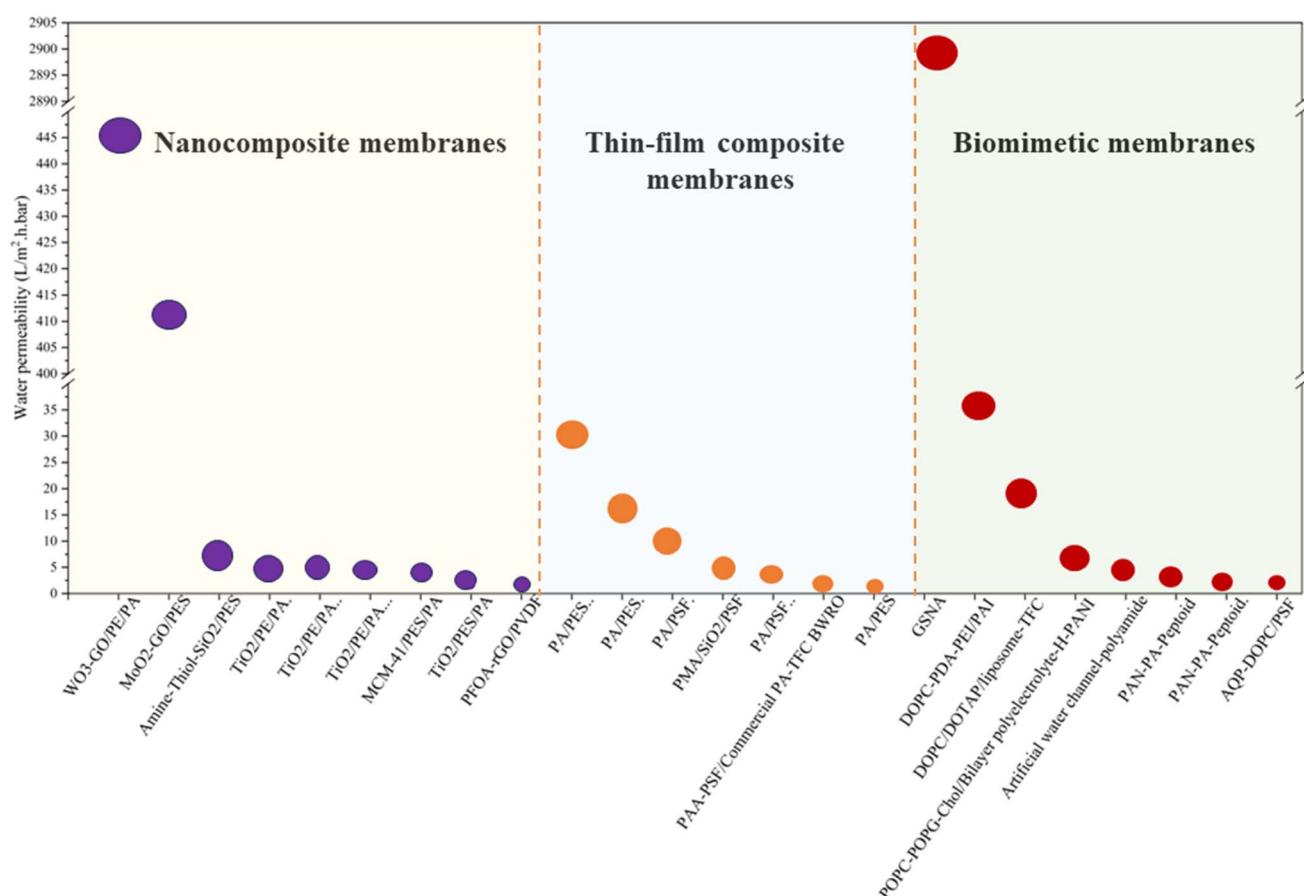


Fig. 10 Permeability of the selected membranes obtained through literature survey and screening in the present study.



the frequency of replacements and lowers overall capital expenditures.<sup>310,349–352</sup> Nanostone Water Inc. conducted a comprehensive 10 years study comparing ceramic and polymeric membranes, revealing that ceramic membranes can achieve ~55% reduction in overall system costs.<sup>353</sup> Moreover, their robust structure, resistance to fouling, and compatibility with aggressive cleaning agents result in lower maintenance costs and increased operational reliability.<sup>351,352,354,355</sup> Ceramic membranes also demonstrate superior operational efficiency, with flux capacities exceeding  $200 \text{ L m}^{-2} \text{ h}^{-1}$  and reaching up to  $381 \text{ L m}^{-2} \text{ h}^{-1}$  in some cases, substantially higher than the typical  $68 \text{ L m}^{-2} \text{ h}^{-1}$  of polymeric membranes.<sup>351,352,354</sup> This enhanced throughput capacity translates to fewer membranes required per system, reducing the footprint and infrastructure costs. These benefits are especially pronounced in challenging water treatment scenarios, such as the treatment of saline water, where ceramic membranes outperform polymeric alternatives in both efficiency and durability.<sup>310,351,352,354</sup>

In comparison, other advanced membrane technologies such as FO, TFC, and nanocomposite membranes also exhibit distinct cost and performance profiles. FO membranes, for instance, consume less energy due to their low-pressure operation but may incur higher overall costs due to the need for draw solution regeneration and susceptibility to fouling.<sup>127</sup> TFC membranes, which pair an affordable support layer with a thin PA selective layer, offer a balance between cost and performance. However, issues related to fouling and material stability persist, prompting the ongoing research into improved formulations and coatings.<sup>127</sup> Additionally, real-world case studies have shown that advanced TFC membranes reduce energy consumption by 15–45% and require smaller infrastructure footprints due to high water permeability and selectivity.<sup>356,357</sup> The scalability of TFC membranes is also evidenced by their successful integration into existing manufacturing lines, enabling adaptation to industrial processes.<sup>127</sup> For instance, Low *et al.*<sup>358</sup> demonstrated the feasibility of large-scale manufacturing by scaling up the fabrication of PES hollow fibers and the TFC coating process from the laboratory to the industrial scale. Furthermore, pilot-scale implementations, such as those employing 4- and 8-inch TFC membrane modules, have further validated their scalability and operational viability in real-world settings. These implementations not only showcase consistent salt rejection rates >97% but also achieve power densities of up to  $5 \text{ W m}^{-2}$  in pressure-retarded osmosis applications, underscoring their practical viability.<sup>359</sup> Additionally, advancements in TFC manufacturing techniques have enabled promising integration into large-scale desalination systems, with modules featuring diameters of up to 8-inch and capacities reaching  $24 \text{ m}^3 \text{ per day}$ , demonstrating operational feasibility in real-world industrial setups.<sup>358,360</sup>

Nanocomposite membranes, while offering enhanced selectivity and permeability, are associated with higher costs due to the expense of nanomaterials and the precise fabrication techniques required.<sup>127,361</sup> Biomimetic membranes, designed to mimic natural biological processes, exhibit remarkable efficiency but remain prohibitively expensive due to their complex fabrication and reliance on sophisticated biological

materials.<sup>127</sup> Traditional water treatment methods such as coagulation, sedimentation, and sand filtration may have lower initial capital costs but often involve higher operational expenditures due to significant chemical inputs, frequent media replacement, and extensive sludge management. In contrast, ceramic membranes, especially when integrated with advanced processes such as oxidation or electrochemical treatments, deliver superior contaminant removal efficiencies with reduced post-treatment requirements.<sup>310,351,354</sup> This combination of high performance and lower long-term costs positions ceramic membranes as competitive alternatives for industrial and municipal water treatment.<sup>351,352,362</sup> From a sustainability standpoint, ceramic membranes present clear environmental advantages. Their extended lifespan minimizes waste from replacements, and their resistance to fouling reduces the need for intensive cleaning chemicals, thereby lowering environmental impact. These attributes align with global efforts to enhance resource efficiency and adopt sustainable water treatment practices.<sup>351,361,363</sup> Lifecycle cost analyses have shown that ceramic membranes can achieve a net cost benefit of 7–15% over polymeric membranes when considering their extended lifespan, higher flux capacity, and reduced maintenance requirements.<sup>352–354</sup>

#### 4.4. Fouling

Fouling of membranes arises from the accumulation or adsorption of solutes/solvents on both the membrane surface and within its pore structure.<sup>364</sup> RO membrane fouling remains a significant challenge, prompting extensive research into nanotechnology for developing fouling-resistant TFN-RO membranes. Despite promising advancements, concerns persist over the high costs, scalability issues, and health and safety implications associated with nanoparticle additives. Further exploration of surface modification techniques is essential to confirm their efficacy in prolonged operational scenarios. Future research should prioritize long-term fouling tests to assess the durability of modified RO membranes. Additionally, optimizing the balance between membrane transport properties and antifouling capabilities is crucial for enhancing membrane performance.<sup>365</sup> One significant limitation of currently developed nanomaterial-based desalination membranes is their susceptibility to biofouling. Biofouling occurs when biological materials, such as bacteria, algae, and other microorganisms, accumulate on the membrane surface, leading to a decline in performance and an increase in maintenance costs. To address this challenge, researchers have suggested the application of nanomaterials with antimicrobial properties, such as Ag and Cu, as coatings on desalination membranes. These nanomaterials can inhibit the growth and adhesion of microorganisms on the membrane surface, thereby enhancing the membrane's longevity and efficiency. The integration of Ag- and Cu-based nanomaterials as antimicrobial coatings offers a promising solution to mitigate biofouling, ensuring more sustainable and effective desalination processes.<sup>366</sup> Bioinspired approaches used for fouling mitigation offer promising research directions, particularly by



incorporating biological molecules that have evolved to resist severe fouling. For example, lysozyme, a natural and inexpensive source of L-arginine, can be grafted onto the polyamide surface *via* chemical reactions, demonstrating excellent anti-fouling properties. However, common modification approaches may increase membrane resistance or deteriorate the cross-linking structure of the PA layer. Additionally, the integration of biological materials with synthetic components is still in its early stages, primarily involving simple biological molecules and proteins within basic polymers. Recent discoveries of new proteins with unique functions and detailed atomic structures present opportunities for the fabrication of advanced membrane systems. Future research should focus on optimizing these bioinspired modifications to balance antifouling capabilities with membrane transport properties and stability.<sup>367,368</sup> To decrease the fouling of the membranes, studies have used either a wide variety of materials, including dopamine,<sup>369</sup> Mxene,<sup>370</sup> layered double hydroxides (LDH) nanosheets,<sup>371</sup> graphene quantum dots (GQDs),<sup>372</sup> and chitosan/graphene oxide,<sup>373</sup> or physical/chemical cleaning approaches.

Besides, enhancing the efficiency of desalination processes can be achieved through the design of suitable pretreatment methods, making the overall process more economic. Membrane-based pretreatment stands out as a competitive technological alternative to conventional methods, particularly in RO desalination, which can reduce the production cost of produced water. Ceramic filters are particularly advantageous due to their durability, ease of use, and resistance against operational pressure. Moreover, pretreatment methods can be effectively combined with conventional pretreatment techniques to enhance the overall system performance. Additionally, integrating renewable energy sources can further reduce energy costs, making membrane-based desalination technologies more cost-effective. Future research should explore various pretreatment design configurations such as combining conventional processes with MF, UF, FO, RO, membrane distillation (MD), *etc.*, to optimize the efficiency and economic viability of desalination system.<sup>374</sup>

Conventional strategies such as membrane pretreatment, careful selection of membrane materials, and maintaining optimal operating conditions have proven insufficient to fully resolve this issue. Hence, antifouling techniques have emerged as essential solutions to address fouling by targeting membrane properties such as pore size, hydrophilicity, and porosity.<sup>375</sup> Antifouling approaches can be broadly categorized into passive antifouling, active antifouling, and surface modification techniques.<sup>376</sup> Among these, surface modification has garnered significant attention due to its cost-effectiveness and ability to alter membrane surface characteristics to substantially enhance performance. By reducing foulant adhesion and deposition, surface modifications not only improve operational efficiency but also extend membrane lifespan, thereby lowering overall maintenance costs.<sup>377</sup> These modifications also minimize protein and particle adsorption on the membrane surface, a critical factor in maintaining consistent filtration performance.<sup>378</sup> Surface modification techniques are further divided into physical, chemical, and hybrid (combined) methods, each

offering unique advantages. Physical modifications involve techniques such as blending, coating, and adsorption, while chemical modifications include advanced approaches such as grafting and plasma treatments. Hybrid methods combine elements of both physical and chemical modifications, enabling tailored solutions for specific fouling challenges.<sup>377</sup>

A comprehensive analysis of contemporary approaches reveals considerable progress in the use of nanomaterials, polymeric modifications, and bioinspired designs. Nanomaterials have become pivotal in antifouling research due to their unique surface properties, scalability, and multifunctionality. GO and CNTs are among the most explored materials for improving hydrophilicity and fouling resistance.<sup>379</sup> GO, with their abundant functional groups such as hydroxyl, carboxyl, and epoxy, enhances membrane hydrophilicity and provides antimicrobial properties.<sup>380</sup> These features reduce foulant adhesion and biofilm formation while improving permeability. Similarly, CNTs, when incorporated into polymer matrices, enhance mechanical robustness and provide a smooth surface that reduces the accumulation of biofoulers. Studies have demonstrated that CNT-modified membranes show significant reductions in biofouling while maintaining high separation performance.<sup>381,382</sup> MOFs contribute to anti-fouling by enhancing surface charge, hydrophilicity, and selective rejection properties, particularly for heavy metals such as lead and cadmium. Nanodiamonds, with their superior hydrophilic characteristics, not only mitigate biofouling but also improve the flux recovery ratio after fouling, making them highly effective for sustainable operations.<sup>383,384</sup>

Another area of innovation lies in zwitterionic and biomimetic surfaces. Zwitterionic polymers mimic the antifouling mechanisms of natural membranes by creating a hydration layer that resists the adhesion of organic and biological foulants.<sup>385-387</sup> This approach is particularly effective against protein fouling, a common issue in desalination membranes. Biomimetic surfaces inspired by natural antifouling systems, such as fish scales and marine organisms, are gaining traction, utilizing hierarchical micro- and nano-structures to physically prevent the attachment of foulants while maintaining high permeability.<sup>388,389</sup>

Functionalized surface modifications further expand the scope of antifouling strategies. By grafting hydrophilic polymers or embedding antimicrobial agents onto the membrane surface, researchers have achieved membranes that exhibit dual antifouling and antibacterial properties. Functionalized GO, for instance, has been used to improve fouling resistance and microbial inhibition by incorporating active sites that disrupt microbial adhesion and growth.<sup>390-393</sup> Similarly, carboxylated nanodiamonds enhance hydrophilicity and reduce interactions with biofoulers.<sup>384</sup> Photocatalytic coatings offer an active mechanism to mitigate fouling. Materials such as TiO<sub>2</sub> are incorporated into membranes to provide self-cleaning capabilities under UV light. These coatings actively degrade organic contaminants and biofilms, reducing the need for chemical cleaning and prolonging membrane life. Emerging research on photocatalytic membranes focuses on enhancing their efficiency under visible light, broadening their applicability in



diverse water treatment settings.<sup>394,395</sup> Despite these advancements, challenges remain in translating laboratory-scale innovations to large-scale applications.

Scalability, cost, and long-term stability of these antifouling strategies are critical concerns. Additionally, the environmental impact of certain nanomaterials necessitates the development of greener, more sustainable alternatives.<sup>381</sup> Future research must prioritize the synthesis of multifunctional coatings that address not only fouling resistance but also mechanical durability and compatibility with existing membrane production processes.<sup>396</sup> Moreover, the integration of smart materials capable of real-time fouling detection and self-cleaning mechanisms could revolutionize the field.<sup>397</sup>

#### 4.5. Comparison across different types of membranes

Based on the literature review performed, Table 6 summarizes the key performance metrics for widely recognized membranes used in water/wastewater treatment. While direct comparative analysis across all membrane types is challenging due to variability in operating conditions, feedwater characteristics, and test protocols reported in the literature, this table documents the available data and findings to provide an overall perspective. RO and NF are highly effective for salt and heavy metal removal but are hindered due to low permeability and high fouling potential. FO represents a versatile option with moderate removal% and permeability while highly influenced by the draw solution. Furthermore, UF and MF are indispensable as pretreatment techniques, offering high permeability and fouling resistance but limited selectivity for dissolved solutes. Fouling resistance varies significantly among the membranes. FO membranes generally exhibit moderate fouling due to the low operational pressure. RO membranes, while highly selective, are prone to scaling and biofouling, necessitating rigorous pretreatment stages. NF membranes demonstrate a moderate fouling tendency, particularly from organic and biological fouling. In contrast, UF and MF membranes offer the highest fouling resistance, as their larger pore sizes allow easy backwashing and cleaning to restore performance.

#### 4.6. Environmental impact and sustainability consideration

The environmental sustainability of membrane technologies spans the entire lifecycle, from fabrication to operational implementation and eventual disposal. While membranes play a pivotal role in water purification systems, their production processes often rely on energy-intensive methods and fossil-derived materials, raising concerns about carbon emissions and resource depletion.<sup>403,404</sup> Similarly, end-of-life management poses challenges, as many membranes are non-biodegradable and require innovative disposal or recycling strategies to mitigate environmental harm. Addressing these issues is critical to aligning membrane technologies with global sustainability goals, ensuring their continued contribution to water security without compromising ecological integrity.

**4.6.1 Environmental footprint.** The production of membranes predominantly relies on polymeric or ceramic materials, each with distinct environmental implications.

Table 6 Comparison of the recognized membrane separation technologies<sup>70,398–402</sup>

Membrane matrix	MF	UF	NF	RO	FO
Monovalent ions removal% (Na, K, Cl, NO <sub>3</sub> )	<5	<40	<50	>98	50–90% (depends on draw solute)
Bivalent ions removal% (Ca, Mg, SO <sub>4</sub> , CO <sub>3</sub> )			>90	>99	
Heavy metal removal% (L m <sup>-2</sup> h <sup>-1</sup> bar <sup>-1</sup> )	<10	20–50	50–95	98–99.9	60–90
Permeability (L m <sup>-2</sup> h <sup>-1</sup> bar <sup>-1</sup> )	>1000	10–1000	1.5–30	1–10	5–50
Pressure (bar)	0.1–3	0.5–10	2–40	10–75	Osmotic pressure
Fouling resistance	Very high	High	Moderate	Low	Moderate
Typical indicator of fouling behavior	Flux recovery: >95% after backwashing or chemical cleaning	Flux recovery: >90% after chemical cleaning	Flux decline: 10–50%; less prone to scaling compared to RO	Flux decline: 30–70% (depending on pretreatment)	Flux decline: 20–40% over time; higher tolerance to organic fouling but sensitive to scaling



Polymeric membranes, such as those fabricated from PVDF, PSF, or CA, are synthesized through energy-intensive processes involving organic solvents and non-renewable petrochemical feedstocks. The widespread use of volatile organic compounds (VOCs) during fabrication not only elevates the carbon footprint but also poses risks to air quality and human health if improperly managed.<sup>405,406</sup> Ceramic membranes, often derived from metal oxides or carbon-based materials, involve high-temperature sintering processes that result in elevated energy consumption and greenhouse gas (GHG) emissions. However, their longer operational lifespan and durability offset these initial environmental costs in long-term applications.<sup>354,405,407</sup> For example, modern seawater reverse osmosis (SWRO) plants typically exhibit energy consumption rates in the range of 3–4 kW h m<sup>-3</sup>, corresponding to net CO<sub>2</sub> emissions of 0.4–1.8 kg m<sup>-3</sup>.<sup>403</sup> Recent advancements such as incorporating nanostructured materials including graphenes or MOFs have enhanced the separation performance and fouling resistance, potentially reducing the need for frequent replacements and chemical cleaning.<sup>408,409</sup> Bio-based membranes are emerging as green alternatives, utilizing renewable feedstocks such as nanocellulose or chitosan. These materials exhibit low environmental footprints during fabrication and biodegradability. However, achieving scalability while maintaining performance is still a challenge.<sup>410,411</sup>

Desalination technologies generate substantial volumes of brine, characterized by elevated total dissolved solids (TDS). For instance, the Ashkelon desalination plant, one of the largest facilities globally and the most prominent in the Levant Basin, processes ~315 million m<sup>3</sup> (MCM) of seawater annually. The plant discharges brine with a TDS concentration of 7.35%, ~1.86 times higher than that of seawater, at a rate of 160 MCM per year.<sup>412</sup> Brine reject often contains residues of pretreatment and cleaning chemicals employed to mitigate biofouling, suspended solids, foaming, and corrosion. Additionally, side reactions between these chemicals can result in the formation of halogenated organics and trace heavy metals from corrosion processes. These contaminants, albeit typically at low concentrations, are continuously discharged into the marine environments.<sup>404</sup> Of particular concern is the release of toxic antifoulants and anti-scalants. For instance, 10–25% of the Cl<sub>2</sub> used as antifoulant during desalination is residual, posing a significant hazard to aquatic ecosystems. Furthermore, cleaning chemicals and their additives such as dodecylbenzene sulfonate and sodium perborate can adversely affect marine life in case of untreated discharge. The environmental implications of such chemical discharge underscore the need for more sustainable and ecologically responsible brine management practices.<sup>404,413</sup>

**4.6.2 Lifecycle assessments.** Operational energy consumption is a critical factor in the environmental impact of membrane separation technologies, particularly for energy-intensive processes such as RO desalination. TFC membranes, widely used for RO, require substantial energy inputs to maintain high operational pressures due to the high flux and salt rejection. While these systems have improved energy efficiency through innovations such as energy recovery devices and

pressure exchangers, the energy demands remain high.<sup>408,414,415</sup> Fouling, a common operational challenge, exacerbates environmental impacts by necessitating frequent cleaning with harsh chemicals which shortens membrane lifespan and generates secondary pollutants.<sup>416</sup> Advances in surface modification techniques such as grafting hydrophilic or nanocomposite layers have shown promise in mitigating fouling and extending operational stability.<sup>417,418</sup> Nanocellulose-based membranes are a notable breakthrough, offering biodegradability, mechanical robustness, and enhanced hydrophilicity. These membranes operate with minimal chemical additives, making them environmentally friendly. However, concerns on biofouling limit their broader adoption.<sup>405</sup>

**4.6.3 Sustainable disposal and recycling pathways.** The disposal of membranes, particularly polymeric ones, poses substantial environmental challenges. These materials are often non-biodegradable, contributing to persistent waste when disposed in landfills. Incineration, while capable of energy recovery, emits CO<sub>2</sub> and other pollutants, further aggravating environmental concerns.<sup>406</sup> Recycling polymeric membranes is difficult due to their complex compositions, complicating material separation and reuse.<sup>354</sup> Ceramic membranes offer a more sustainable end-of-life trajectory. Their inert nature allows for repurposing into construction materials or recycling via pyrolysis to recover the embedded components. Hybrid membranes containing nanomaterials such as GO may also benefit from advanced recovery methods, although all remain in early development stages.<sup>405</sup>

**4.6.4 Toward sustainable membrane systems.** Achieving sustainability in membrane technologies necessitates a shift toward circular economy principles. This includes adopting greener fabrication techniques, such as water-based solvents or bio-based precursors, and designing membranes with extended operational lifespans. Lifecycle assessment (LCA) frameworks should guide the development of new membranes to ensure environmental impacts to be minimized in all stages.<sup>405</sup> Emerging innovations including biodegradable membranes and low-energy fabrication processes highlight the potential for reducing the environmental footprint of membrane separation systems. Integrating renewable energy sources with hybrid systems and promoting fouling-resistant technologies can further contribute to sustainability. By addressing the full lifecycle, from raw materials to disposal, membrane technologies can evolve into environmentally responsible solutions for water purification and resource management.<sup>354,419</sup>

## 5. Artificial intelligence (AI) and machine learning (ML)

Membrane-based desalination technologies have made significant advancements, while fouling, high energy consumption, and operational inefficiencies continue to impede the effectiveness and scalability, stemming from the complex, nonlinear interactions between operational parameters, membrane properties, and environmental factors. Traditional



experimental approaches, while valuable, are constrained in their ability to comprehensively model these dynamic processes. Consequently, they often fail to predict long-term system behavior or optimize performance across varying operational conditions, particularly in large-scale applications where real-world variability plays a crucial role.

The incorporation of artificial intelligence (AI) and machine learning (ML) into membrane-based technologies is transforming the field, offering innovative solutions to key challenges such as fouling mitigation, energy efficiency, and system optimization.<sup>420</sup> These computational tools excel in analyzing complex, nonlinear interactions inherent to desalination systems, enabling accurate predictions, efficient designs, and real-time adjustments, surpassing traditional modeling techniques. A critical contribution of AI lies in the prediction and management of fouling, a persistent challenge in desalination processes. Advanced algorithms such as artificial neural networks (ANNs), fuzzy logic (FL), and genetic programming (GP) effectively model nonlinear relationships between operational parameters such as transmembrane pressure, permeate flux, and feedwater characteristics. ANNs have achieved prediction accuracies >95%, enabling the anticipation of fouling events and the implementation of proactive strategies to maintain membrane performance and extend operational lifespan.<sup>421–424</sup> Deep learning models and hybrid systems have further advanced fouling control, dynamically adapting operational parameters such as feed flow rates and pressure, which has been shown to reduce fouling rates by up to 25%.<sup>422,425</sup> AI and ML also play a transformative role in optimizing energy efficiency and operational parameters. Algorithms such as particle swarm optimization (PSO) and genetic algorithms (GA) analyze large datasets to identify optimal feed pressure, recovery rates, and energy consumption strategies, resulting in a 20% reduction in energy demand for RO systems.<sup>423,426–428</sup> Hybrid models that combine empirical data with AI algorithms enhance adaptability, enabling real-time adjustments to sustain system efficiency under varying conditions. These methods not only lower energy requirements but also reduce operational costs, aligning with sustainability goals in the desalination industry.<sup>423,427</sup>

In addition to operational optimization, AI has contributed to the design of next-generation membranes. By integrating convolutional neural networks (CNNs) with molecular dynamics simulations, researchers have developed nanoporous membranes with superior ion selectivity and water flux, achieving up to a 30% performance improvement compared to conventional membranes.<sup>421,426,427</sup> These advancements highlight the potential of AI-driven tools in advancing material science for desalination applications. Real-time monitoring and control of desalination systems have also been revolutionized by AI-powered sensors and reinforcement learning algorithms. These systems dynamically adjust feed flow rates, pressures, and operational strategies, reducing response times and minimizing maintenance needs. Such improvements have been instrumental in achieving sustainable operation, with hybrid models reducing prediction errors to <5%, compared to 12% for traditional mathematical models.<sup>423,425</sup> Moreover, AI has been

increasingly integrated into renewable energy-driven desalination systems, optimizing both energy input and water production to create economically viable solutions for large-scale applications. These systems demonstrate AI potential in both addressing technical challenges and promoting environmentally friendly desalination practices.<sup>424,427</sup> Despite the significant progress, challenges remain in scaling AI applications for large desalination plants and improving the interpretability of complex models.<sup>429,430</sup> Future efforts are expected to focus on hybrid systems that combine multiple ML techniques with mechanistic models, offering enhanced robustness and scalability. Additionally, as AI evolves, its role in automating real-time operations and developing next-generation membranes is likely to revolutionize the desalination industry further, making it more efficient, cost-effective, and sustainable.

## 6. Future perspective

Material innovations hold immense promise in overcoming current challenges in membrane performance and durability. The integration of nanomaterials such as TiO<sub>2</sub> has demonstrated promising improvements in water flux and salt rejection due to their hydrophilicity, mechanical stability, and anti-fouling properties, creating a conducive environment for extensive hydrogen bonding with membrane polymers, enhancing permeability and selectivity.<sup>431</sup> Future work could explore alternative metal oxides, graphene derivatives, or hybrid nanostructures to further optimize the membrane properties.<sup>432,433</sup> Polymeric membranes, while cost-effective and widely used, face challenges such as fouling and limited chemical resistance. Advanced materials such as GO, nanocomposites, and hybrid polymer-ceramic membranes offer promising solutions. GO, for instance, has shown potential in enhancing membrane hydrophilicity and anti-fouling properties, thereby improving performance and durability.<sup>431</sup> Similarly, research into ceramic membranes should focus on reducing production costs and improving scalability, as these membranes provide superior thermal and chemical resistance, making them suitable for harsh feedwater conditions.

Additionally, natural polymers such as CA, when combined with nanomaterials, provide a sustainable and efficient pathway for FO membrane development. These materials not only enhance the hydrophilic characteristics but also offer scalable fabrication potential through phase inversion and other nanocomposite techniques.<sup>434,435</sup> Developing modular and scalable FO systems using membranes optimized with innovative materials will allow for comprehensive performance evaluations under real-world conditions. Pilot studies should address key parameters such as flux stability, fouling resistance, and energy efficiency to validate their feasibility in wastewater treatment and desalination processes.<sup>433,436</sup> Moreover, testing FO systems with diverse feed solutions, ranging from industrial wastewater to brackish water, will help determine the robustness of these technologies across various applications. Incorporating modeling techniques such as response surface methodology (RSM) could also guide the optimization of



process conditions and reduce experimental overheads during scale-up.<sup>437–439</sup>

In terms of biomimetic membranes, emerging materials such as aquaporins, aligned CNTs, graphene-based membranes, and MOFs present promising opportunities to enhance membrane performance.<sup>435,440</sup> Self-assembled block copolymers and nanofabrication techniques could enable the precise customization of membrane properties, creating modular designs tailored for specific applications.<sup>441,442</sup> Additionally, the development of renewable polymers and the adoption of environmentally benign solvents in membrane fabrication will help align with sustainability goals, reducing environmental impacts during production and disposal.<sup>440</sup> To translate laboratory-scale successes into practical solutions, pilot-scale studies are essential. These efforts should validate the scalability and robustness of novel membranes under diverse operational conditions. For example, ultrathin PA membranes require further exploration of substrate-induced limitations and defect-free fabrication processes to realize their full potential in achieving high water permeance and selective ion transport.<sup>443</sup>

Sustainability considerations are also critical for future advancements in membrane technology. Lifecycle analysis of membrane modules including strategies for recycling and reuse must be prioritized to ensure long-term environmental benefits.

## 7. Conclusion

Water treatment is of paramount importance for ensuring access to clean and safe water, as a critical resource for public health, agriculture, and industry. The present study systematically reviewed and screened recent literature, both review papers and experimental research, on desalination and heavy metal removal using various advanced membrane technologies, including nanocomposites, thin-film composites, biomimetic materials, forward osmosis, and hybrid membranes. The screening process revealed a significant number of studies being published annually, highlighting the rapid advancements and the necessity for continuous updates to previous reviews. This review has consolidated the most recent findings, identifying the top 10 membranes with the highest removal efficiency as the primary criterion from each category. An updated assessment of the state-of-the-art membrane technologies for water treatment is provided. The performance of each membrane type is discussed, emphasizing the need for further research to address existing challenges and optimizing the trade-offs between different determining factors including economic viability, permeability, removal efficiency, fouling, comparison across different types of membranes, and environmental impact and sustainability consideration. The incorporation of artificial intelligence (AI) and machine learning (ML) into membrane-based desalination technologies has also been studied. Future advancements in materials science, fabrication techniques, and long-term testing will be crucial for developing next-generation membranes that are more efficient,

cost-effective, and sustainable for large-scale water treatment applications.

## Data availability

No primary research results, software or code have been included and no new data were generated or analyzed as part of this review.

## Author contributions

Sahar Foorginezhad contributed to the writing of the original draft, review and editing, investigation, and methodology. Dr Mohammad Mahdi Zerafat was responsible for the writing of the original draft, review and editing, investigation, and supervision. Prof. Ahmad Fauzi Ismail and Dr Pei Sean Goh provided supervision, administration, review and editing support, and fund acquisition.

## Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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