



# Forward osmosis desalination via laminar graphene oxide-based membranes: A comprehensive review of principles, current state-of-the-art, challenges, and perspectives

Mohamed Edokali<sup>1</sup>, Alexander Massey<sup>2</sup>, David Harbottle<sup>1</sup>, Robert Menzel<sup>2</sup>, Ali Hassanpour<sup>1,a)</sup>

<sup>1</sup>School of Chemical and Process Engineering, Faculty of Engineering and Physical Science, University of Leeds, Leeds LS2 9JT, UK <sup>2</sup>School of Chemistry, Faculty of Engineering and Physical Science, University of Leeds, Leeds LS2 9JT, UK

<sup>a)</sup>Address all correspondence to this author. e-mail: A.Hassanpour@leeds.ac.uk

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As freshwater demand rises, innovative water treatment technologies are sought. Forward Osmosis (FO) has emerged as a promising membrane-based method for desalination and purification, overcoming challenges of traditional methods. FO membranes demand optimal water permeability, salt rejection, and stability. Despite its potential, FO faces issues including reverse solute flux (RSF) and internal concentration polarisation (ICP), reducing water flux. Carbon-based nanomaterials, especially graphene oxide (GO) laminar sheets, exhibit excellent desalination performance as FO membranes. However, scaling up GO-based FO membranes presents challenges in balancing water flux, salt rejection, and stability for industrial desalination application. This review discusses the ideal FO membrane design criteria, focussing on the state-of-the-art development of GO-based laminar FO membranes in terms of water permeation, salt rejection, scalability, stability, and fouling resistance. Current challenges and perspectives for enhancing laminar GO-based FO membranes are outlined.

Abbreviations		MPD	Meta-phenylenediamine
AgNPs	Silver nanoparticles	NF	Nano-filtration
APS	Ammonium persulfate	NH <sub>4</sub> OH	Aqueous ammonia solution
BSA	Bovine serum albumin	NIPAM	N-isopropylacrylamide
CS	Chitosan	OCNTs	Oxidised carbon nanotubes
СТА	Cellulose triacetate	PA	Polyamide
DMF	N, N-dimethylformamide	PAA	Poly (acrylic acid)
EDA	Ethylenediamine	PAH	Poly(allylaminehydrochloride)
FO	Forward osmosis		Chitosan
GN	Graphene	PAN	Polyacrylonitrile
GO	Graphene oxide	PCA	Poly (carboxylic acid)
GQDs	Graphene oxide quantum dots	pDA	Polydopamine
ICP	Internal concentration	PDDA	Poly dimethyl diallyl ammo-
	polarisation		nium chloride
LBL	Layer-By-Layer assembly	PDMAEMA@BL	Poly (2-(dimethylamino)ethyl
LDHs	Layered double hydroxides		methacrylate) and blue lemon
MBA	N, N'-methylenebisacrylamide		polyoxometalate
MCE	Mixed cellulose ester	PEI	Polyethyleneimine
МО	Methylene orange	PES	Polyethersulfone
MOF	Metal–organic framework	PLC	Polycarbonate



PPA	Propanedioic acid
PSF	Polysulfone
PSS	Polystyrene sulfonic acid
PTFE	Polytetrafluoroethylene
PVA	Polyvinyl alcohol
PVDF	Polyvinylidene difluoride
RB	Rhodamine B
RO	Reverse osmosis
SEM	Scanning electron microscope
TFC	Thin-film composite
ТМС	1,3,5-Benzenetricarbonyl
	chloride
UiO-66	UiO stands for University of
	Oslo
V	Crossflow velocity
XRD	X-ray powder diffraction
Symbols	
$\pi$ (bar)	Bulk osmatic pressure
$\rho$ (Kg/cm <sup>3</sup> -g/m <sup>3</sup> )	Density
τ	Tortuosity
$\Delta t (min-h)$	Interval time
M (g)	Mass
A <sub>p</sub> (LMH/bar)	Water permeability coefficient
A ( $cm^2$ - $m^2$ )	Area
B (LMH)	Salt permeability coefficient
$C \left(mg/mL - g/L - mol/L - ppm\right)$	Concentration
D (m/s)	Mass transfer coefficient
K (S/m)	Solute resistivity
FRR (%)	Flux recovery ratio
Rt (%)	Total flux decline ratio
J <sub>R</sub> (LMH)	Recovery flux
J <sub>0</sub> (LMH)	Initial flux
J <sub>steady</sub> (LMH)	Steady flux
$J_s (g/m^2.h-mol/m^2.h-gMH)$	Reverse solute flux
$J_{sp}(g/L)$	Specific salt flux
$J_w (L/m^2.h-LMH)$	Water flux
$J_{wp}$ (L/m <sup>2</sup> .h-LMH)	Pure water flux
P (bar)	Hydraulic pressure
ε (%)	Porosity
$D_s (cm^2/s)$	Salt diffusion coefficient factor
R (%)	Salt rejection
W (g)	Weight
S (μm)	Structural parameter
t (µm-nm)	Thickness
•	

# Introduction

Water scarcity is increasingly intimidating communities worldwide due to population growth and rising demand for clean water. Forecasts from United Nations (UN) indicate that by

2025, two-thirds of the global population may face water supply shortages [1]. This urgency has prompted researchers to explore economically viable technologies for clean water production, including desalination of unconventional sources such as drainage water, waste-water, brackish water, and seawater [1-3]. Desalination, which is defined as the removal of salts from saline water, offers a promising solution to freshwater scarcity by extracting potable water from abundant seawater [4]. Membrane-based separation technologies have proven highly advantageous in desalination for decades, providing energy efficiency and economic benefits over conventional methods [5]. Reverse osmosis (RO)- and nanofiltration (NF)-based membranes, widely used for treating saline water, face challenges such as chemical use, energy consumption, high costs, membrane fouling, and limited water permeability, highlighting the need for efficient, and low-energy approaches in seawater desalination [6].

Recently, forward osmosis (FO) has emerged as a competitive membrane process with notable advantages for addressing high brine water challenges compared to existing membranebased technologies such as RO and NF [7, 8]. Benefits of FO include low-energy consumption, versatility in using different feed and draw solutions, and the ability to recover low osmotic pressure feed solutions by concentrating draw solutions [9]. However, the FO membrane development for desalination faces challenges such as low permeability and selectivity, concentration polarisation (CP), reverse solute flux (RSF), and membrane fouling due to impurities accumulation [10]. Polymeric materials including cellulose acetate (CA), polysulfone (PSF), and polyamide (PA) have been widely used and commercialised for fabrication of FO desalination membranes. On the other hand, these FO membranes have drawbacks including a trade-off between permeability and selectivity, and limited mechanical stability, affecting separation performance and durability [11].

Recent research has emphasised the integration of carbonbased nanomaterials such as carbon nanotubes (CNTs) and graphene oxide (GO) into FO water desalination membranes to address fouling and CP issues [12]. These nanomaterials offer strong nanostructures, accessibility, mechanical stability, chemical resistance, and potential for improved separation performance. Amongst these, graphene-based materials stand out as promising options for FO membranes. Graphene, an atomically thin material with hexagonally arranged sp<sup>2</sup> hybridised carbon atoms, possesses unique properties such as high stiffness, tensile strength, flexibility, surface area, and chemical stability [13]. Graphene oxide (GO), as an oxidised form of graphene, contains various oxygen functional groups (i.e. hydroxyl, epoxy, carboxyl, and carbonyl) across its basal surface and edges [see Fig. 1(a), (b), and (c)], enhancing its hydrophilicity and dispersibility in water [13]. Reduction methods can convert GO to



reduced graphene oxide (rGO), where some oxygen remains, introducing defects in the sp<sup>2</sup> structure, distinguishing it from the pristine graphene [14]. rGO differs from pristine graphene as some oxygen remains, and that defects in the sp<sup>2</sup> structure exist where oxygen functionality is removed. This states that the perfect graphitic structure never totally reforms [see Fig. 1(d) and (e)] [15].

The oxygen functional groups in GO serve as reactive sites for chemical modification and surface functionalisation with other nanomaterials, enhancing the desalination performance of resulting membranes [18]. GO's high hydrophilicity allows for the preparation of well-exfoliated aqueous suspensions, ideal for thin-film formation [19]. By widening interlayer spacing, GO's hydrophilic nature highly creates water-permeable channels through pores on the basal plane [20]. GO's amphiphilic nature, with oxidised (hydrophilic) and non-oxidised (hydrophobic) regions, forms wrinkles, stacked structures, and structural defects on the basal plane, forming frictionless nano-channels for water molecule transport across GO laminates [21].

The GO-based nanomaterial, known for its ease of functionalisation, high wettability, mechanical strength, structure, and antifouling properties, has significantly enhanced the performance of FO desalination membranes [22]. Over the past ten years, there has been a substantially growth in the research interest in laminar GO-based membranes for FO desalination and water purification, as illustrated in Fig. 2. Recent reviews by several research groups [23–26] have highlighted the advancements in GO-based FO membranes for water treatment. The synthesis of GO-based laminar membranes has been a focal point for water desalination and purification in the FO process due to their straightforward fabrication and high efficiency in sieving monovalent and di-valent hydrated salts [13, 22]. However, these membranes face challenges that limit their use in large-scale desalination processes, including GO structural instability, re-dispersion of GO nanosheets in aqueous environments, scalability issues, challenges in precisely tuning interlayer spacing, and low water permeability, which impact their separation performance and economic viability [27, 28].

This review summarises the physical and theoretical transport phenomena involved in FO processes for water desalination and purification, along with theoretical design criteria for ideal GO-based membranes used in FO-based water treatment applications. The review also covers designated fabrication techniques for laminar GO-based FO membranes and offers detailed insights into recent theoretical and experimental studies involving these membranes for water desalination and purification. Additionally, the review discusses current challenges, limitations, and future perspectives associated with those membranes, providing a thorough evaluation of the field.



Figure 1: Structural models of (a) single-layer GN, (b) GO and (c) rGO. Reproduced from Ref. 16 with permission from RSC Publications. Structures of rGO prepared by thermal annealing of GO with initial oxygen contents of (d) 20% and (e) 33%, generated via molecular dynamic simulations (grey spheres represent carbon and red spheres represent oxygen) [17].





Figure 2: Number of published research works of laminar GO-based membranes for FO desalination and water treatment in recent years. The data obtained from SCOPUS® based on the keyword search "laminar graphene oxide and forward Osmosis for water desalination". Note: The data of 2024 is incomplete.

# Membrane science and design criteria in FO process for desalination and water treatment

# Physical transport phenomena of desalination membrane in FO technology

The main concept of the membrane in FO desalination process can simply be defined as the semi-permeable and selective interface that allows only the permeation of water molecules from a feed solution side (Brine) using a highly concentrated salty draw solution (low water chemical potential solution), while rejects the salts from the feed solution and draw solution sides, simultaneously, as shown in Fig. 3 (a) [29]. The transportation phenomena across the FO membrane are driven by the difference in the osmotic pressure between the draw and feed solutions. The latter statement agrees with the 2nd law of thermodynamics,<sup>1</sup> as far as water molecules transported across the membrane are to imply the equilibrium state between feed and draw solution, which is explained theoretically in more details in Sect. "Theoretical background of transport phenomena across FO membranes". Herein, water molecules which pass through the membrane are so-called permeates, whereas the rejected salts are called retentates [30].

## Theoretical background of transport phenomena across FO membranes

Osmosis is defined as the diffusion-driven movement of water molecules from a region of low solute concentration (*Feed water/brine*) to a region of high solute concentration (*Draw solution*) across a selectively permeable membrane, as shown in Fig. 3(a), with the objective of equalising the chemical potential (*solute concentrations*) on both sides. In the context of FO, the transport of water across the membrane can be linked to Fick's laws through the concept of concentration gradients and fluxes. Fick's law of diffusion describes the flux of a solute moving through a solvent due to a concentration gradient. There are two forms of Fick's law: the first law, which applies to the steady-state diffusion where the diffusive flux is proportional to the concentration gradient, and the second law, which applies to the non-steady-state diffusion which describes how diffusion causes the concentration to change with time [31]. According to this theory, water is transported across the membrane to equalise the chemical potential on both sides [see Fig. 3(b)]. The pressure differential across the membrane allows for the concentration of liquid without a phase change. The osmotic pressure gradient across FO membranes between feed and draw solutions drives the movement of water from the feed solution to the draw solution, thereby concentrating the feed solution [see Fig. 3(c)] [32].

The relationship between the water flux, osmotic pressure, and hydraulic pressure across FO membranes can be expressed as follows [33]:

$$J_w = A_p \cdot (\Delta P - \Delta \pi) \tag{1}$$

where  $(J_w)$  represents the water flux (in LMH),  $(A_p)$  denotes the membrane permeability (in LMH/bar), and  $(\Delta P)$  signifies the difference in hydraulic pressure which is negligible in an FO process since it is driven by the osmatic pressure difference  $(\Delta \pi)$  between draw and feed solutions.

Concentration polarisation (CP) occurs when retained molecules accumulate at the membrane surface, leading to a decrease in the osmotic pressure difference across the membrane. For a dense FO symmetric (*free-standing*) membrane, CP can occur on both sides of the membrane, affecting both feed and draw solutions. This results in solute concentration on the feed side and dilution on the draw solution side, known as concentrative and dilutive external concentration polarisation (ECP), respectively [see Fig. 3(d)]. The flux equation for FO is expressed as [34]

$$J_w = A_p \cdot (\pi_d^* - \pi_f^*) \tag{2}$$

Equation (2) can be adjusted for higher fluxes to account for both dilutive and concentrative ECP on the feed and draw sides, as follows [34]:

$$J_w = A_p \cdot (\pi_d^* - \pi_f^*) = A_p \cdot \left[\pi_d \exp\left(\frac{J_w}{D_d}\right) - \pi_f \exp\left(\frac{J_w}{D_f}\right)\right]$$
(3)

where  $(D_f)$  and  $(D_d)$  are mass transfer coefficients (in m/s) for feed and draw solution sides, respectively. The symbols  $(\pi_f)$  and  $(\pi_d)$  denote the bulk osmotic pressures (in bar) of feed and draw solutions, respectively. The expressions  $[\pi_d^* = \pi_d \exp(\frac{J_w}{D_d})]$  and  $[\pi_f^* = \pi_f \exp(-\frac{J_w}{D_f})]$  represent osmotic pressures of feed and draw solutions, respectively, adjusted for ECP.

<sup>&</sup>lt;sup>1</sup> "The total entropy of an isolated system always increases over time, or at best remains constant.".





Figure 3: (a) Typical representation of FO-based membrane process for saline water desalination, operating under the difference of osmotic pressure between feed stream (brine) and draw solutions [30]. The movement of water is depicted in (b) osmosis, and (c) forward osmosis, with arrows indicating the direction of mass transfer [36]. Mechanism of FO involves water transport in different membrane configurations: (d) using a dense symmetric (free-standing) membrane, and (e) with an asymmetric (supported) membrane where the feed solution moves towards the active layer (FO mode for desalination application) [36].

The FO asymmetric (*supported*) membrane, consisting of a loosely bound support layer and a compacted active layer, can be utilised in the configuration where the feed solution is directed towards the active layer (FO mode) [see Fig. 3(e)] [34]. In water desalination FO mode, when the feed is on the side of the active layer, dilutive ICP occurs towards the permeate side. The movement of water towards the draw solution side increases the solute concentration on the active layer of the membrane, thereby increasing the osmotic pressure and reducing the driving force. This reduction in the osmotic driving force is significant and cannot be mitigated by hydrodynamic measures such as turbulence. No ECP occurs on the draw side [see Fig. 3(e)] [35].

The FO flux through an asymmetric membrane for FO desalination mode (feed towards the active layer) is described in the following equation [34]:

$$J_w = A_p \cdot (\pi'_d - \pi_f^*) = A_p \cdot \left[ \pi_d \exp\left(-J_w \cdot k_d\right) - \pi_f \exp\left(\frac{J_w}{k_f}\right) \right]$$
(4)

where  $(\pi_{f}^{*})$  and  $(\pi_{d})$  denote osmotic pressures of feed and draw solutions, respectively, inside the active layer and within the

porous support, corresponding to dilutive ICP on the draw side for FO mode:  $[\pi_d = \pi_d \exp(-J_w k_d)]$  and  $[\pi_f^* = \pi_f \exp(\frac{J_w}{k_f})]$ . The terms  $(k_d)$  and  $(k_f)$  represent the draw and feed solute resistivities, respectively, (in S/m) within the porous support layer for FO water desalination mode. Herein, dilutive ICP and concentrative ECP occur concurrently.

Considering transport phenomena across FO-based membranes, this comprehensive approach combines theoretical and practical aspects to optimise FO desalination performance, focussing on maximising water flux while minimising reverse solute flux and fouling. The following are critical parameters for evaluating and improving the performance of FO membranes, which are widely employed in laboratory-scale operations, as described:

# Water flux (J<sub>w</sub>)

Water flux (in LMH) is the rate at which water permeates through the membrane per unit area. It is driven by the osmotic pressure difference ( $\Delta \pi$ ) between draw and feed solutions and can be expressed as [37]



$$J_w = \frac{\Delta m}{\rho.A.\Delta t} \tag{5}$$

where ( $\Delta m$  in g) is the mass change of the feed solution using a constant density of DI water ( $\rho$  in g/cm<sup>3</sup>), measured over a time interval ( $\Delta t$  in h) and permeated across the effective area of the membrane (A in cm<sup>2</sup>).

#### Reverse solute flux (J<sub>s</sub>)

Reverse solute flux (RSF in gMH) represents the rate at which solutes permeate from the draw solution back into the feed solution. It is typically undesirable as it reduces the osmotic driving force. It can be described using Fick's first law of diffusion [38]:

$$J_s = \frac{(C_t m_t) - (C_0 m_0)}{\rho \cdot A \cdot \Delta t} \tag{6}$$

Where ( $C_0$  in g/cm<sup>3</sup>) and ( $m_0$ ) are the initial salt concentration and the mass of feed solution, respectively, and ( $C_t$  in g/cm<sup>3</sup>) and ( $m_t$ ) are the corresponding values of salt concentration and feed solution over the FO operation time ( $\Delta t$ ).

### Specific solute flux (J<sub>sp</sub>)

Specific solute flux (in g/L) is the ratio of reverse solute flux to water flux, indicating the efficiency of solute rejection relative to water transport. The specific solute flux (perm-selectivity) of membranes can be obtained as follows [39]:

$$J_{sp} = \frac{J_s}{J_w} \tag{7}$$

#### Salt rejection (R)

Salt rejection (in %) is the percentage of salts that are retained by the membrane. It is defined as [37]

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\tag{8}$$

Where ( $C_p$  in g/cm<sup>3</sup>) denotes the concentration of permeated salt, and ( $C_f$  in g/cm<sup>3</sup>) is the initial concentration of the feed solution.

#### Water permeability coefficient (A)

The water permeability coefficient (in LMH/bar) measures the membrane's ability to transport water under an osmotic pressure difference, as follows [40]:

$$A_p = \frac{J_{wp}}{(\Delta P - \Delta \pi)} \tag{9}$$

where  $(J_{wp} \text{ in LMH})$  represents the pure water permeation flux and  $(\Delta P \text{ in bar})$  is the transmembrane pressure.

#### Salt permeability coefficient (B)

The salt permeability coefficient (in LMH) measures the membrane's ability to transport solutes. Subsequently, the intrinsic membrane property of (B) was acquired according to the solution-diffusion theory as following [40]:

$$B = [A_p \cdot (\Delta P - \Delta \pi)] \times \left(\frac{1 - R_s}{R_s}\right)$$
(10)

where ( $\Delta \pi$  in bar) represents the difference in the osmatic pressure across membranes. In this equation, the term [A. ( $\Delta P$ — $\Delta \pi$ )] represents the pure water permeation flux ( $J_{wp}$ ) and ( $R_s$  in %) is the salt rejection rate.

#### Porosity of membranes (ε)

Porosity (in %) is the volume fraction of void spaces in the membrane. Gravimetrically, it can be determined by measuring the mass of a dry membrane ( $W_d$  in g) and its mass when saturated with a liquid ( $W_w$  in g) [41]:

$$\epsilon = \frac{(W_{w-}W_d)/\rho_e}{\left[\frac{W_w-W_d}{\rho_e}\right] + \left[\frac{W_d}{\rho_m}\right]} \tag{11}$$

where ( $\rho_e \text{ in g/cm}^3$ ) and ( $\rho_m \text{ in g/cm}^3$ ) represent densities of the liquid used for saturation and membrane, respectively.

#### Structural parameter (S)

The structural parameter (in  $\mu$ m) of the membrane describes the resistance to water flow within the membrane's support layer. It can be determined using the following equation [38]:

$$S = \frac{D_s}{J_{wp}} \times \ln\left(\frac{A_p \times \pi_{permeate} \times B}{A_p \times \pi_{feed} + B + J_w}\right) \tag{12}$$

where ( $D_s$  in m/s) is the salt diffusion coefficient factor, and ( $\pi_{permeate}$  in bar) and ( $\pi_{feed}$  in bar) denote the osmatic pressure of permeate and feed solutions, respectively.

#### Tortuosity (τ)

Tortuosity describes the convoluted nature of pathways through the membrane. The tortuosity of the membranes is accordingly determined from the acquired values of (*S*) and ( $\epsilon$ ), and the measured thickness (*t* in  $\mu$ m) of membranes, as follows [42]:

$$\tau = S \times \frac{\varepsilon}{t} \tag{13}$$

## Fouling propensity in FO

Fouling refers to the accumulation of particles, solutes on the membrane, reducing its performance. The total flux decline ratio (*i.e. a parameter used to quantify the reduction in membrane flux over time, particularly in the context of fouling during membrane* 



processes. It is an important metric for assessing the performance and durability of membranes under operational conditions), and the total flux recovery ratio (i.e. a measure used to evaluate the effectiveness of cleaning processes in restoring the water flux of a membrane to its original performance after fouling. It indicates the ability of a membrane to recover its initial flux after being subjected to a cleaning protocol) are used to quantify fouling impacts. The flux recovery ratio (*FRR*, %) and total flux decline ratio (*R<sub>n</sub>*, %) are calculated using [43, 44]:

$$FRR = \frac{J_R}{J_0} \times 100 \tag{14}$$

$$R_t = \frac{J_0 - J_{steady}}{J_0} \times 100 \tag{15}$$

where  $J_R$  (in LMH) denotes the recovery flux after backwashing of membrane,  $J_0$  (in LMH) represents the initial water flux, and  $J_{steady}$  (in LMH) indicates the steady water flux obtained during fouling tests.

In the FO-based membrane desalination, the above parameters are interrelated. The water and solute permeability coefficients (*A* and *B*) determine the membrane's intrinsic transport properties. The structural parameter (*S*) affects ICP within the membrane support layer, which reduces the effective osmotic pressure. Moreover, porosity ( $\varepsilon$ ) and tortuosity ( $\tau$ ) impact the water flux and solute transport. Fouling affects water flux and solute rejection, quantified by (*FRR*) and (*R*<sub>t</sub>).

## Configurational categories of water desalination-based membranes in the FO process

The selection of appropriate materials for fabricating FO desalination membranes is a critical area that requires further investigation, as material choice directly influences the interactions between feed ions and the membrane [45, 46]. The material factors such as packing density and polymer chain mobility, affect the solid regions of the membrane. Both material selection and preparation techniques shape membrane stability, performance, and transport mechanisms, though the latter is also affected by membrane morphology, which impacts permeation rates, e.g. through steric hindrance [26, 45].

FO membranes can exhibit symmetric or asymmetric structures. Symmetric membranes are characterised by uniform pores, which can take various forms such as cylindrical, sponge-like, or slit-like. In contrast, asymmetric membranes feature variable pore sizes throughout their structure and can be categorised into types such as porous, thin-film composites or integral-asymmetric membranes with dense skin layers. FO membranes may also be classified as homogeneous or heterogeneous, thick, or thin, depending on their structural and transport properties, which can be passive, active, or reactive [26, 46]. FO membranes are made from a broad range of materials, including organic, inorganic, and hybrid combinations. Inorganic materials such as carbon, graphene oxide, alumina, and zeolites have been utilised, but most commercially available FO membranes are fabricated from polymers and liquids, with cellulose acetate being a notable organic material. These materials offer high mechanical strength, thermal stability, and long-term separation capabilities, making them ideal for industrial applications [26, 47, 48].

FO membranes made from organic materials, particularly polymers, are widely used in industrial applications due to their high performance and flexibility in design. Organic membranes, which cover a range of materials, are typically classified as either dense (non-porous) or porous (symmetric or asymmetric) [47, 48]. However, selecting the right polymer for membrane fabrication is a complex task, as it must meet specific requirements for the intended application, such as water desalination. The chosen polymer must exhibit chemical and mechanical stability, effective separation properties, and low binding affinity for the molecules it separates [26]. It also needs to withstand rigorous cleaning conditions and be compatible with membrane fabrication technologies. Furthermore, the polymer should possess suitable chain rigidity, interactions, and functional group polarity, while being cost-effective and readily available for large-scale use [46].

Inorganic FO membranes, similar to their organic counterparts, can be classified into dense (non-porous) and porous (symmetric and asymmetric) types. Dense membranes are used in gas separation but face limitations in industrial applications due to low permeability [25, 26, 45, 49]. Porous membranes, on the other hand, are favoured in applications such as seawater filtration, where their molecular sieving properties, chemical resistance, and high permeability are advantageous. These membranes also withstand harsh cleaning agents and elevated temperatures, making them suitable for FO desalination processes. Recently, porous membranes, particularly those based on graphene oxide (GO), have gained attention for their potential in real-world desalination applications [26].

Hybrid FO membranes, created by embedding inorganic particles into polymer matrices, are increasingly being explored for molecular separations, such as filtering hydrated salts from seawater. These nanomaterial-polymeric membranes combine the benefits of both polymers and inorganic materials while also exhibiting unique properties resulting from their interactions [26, 45]. For instance, incorporating GO into polyamide-based thin-film membranes can enhance selectivity and antifouling properties, making hybrid membranes a promising solution for improving the efficiency of FO processes [25, 49].

In the FO desalination process, two membrane configurational types, flat-sheet and hollow-fibre, are typically used as follows [50]:



*Flat-sheet membranes* are utilised in FO desalination of diverse sizes and shapes, treating moderately saline streams such as brackish water and medium concentrated seawater. These types of membranes offer high solid processability, low defects, and easy replaceability [35, 51]. Limitations include low packing density which increases costs, and the lack of fabric support, restricting operation at higher pressures in large-scale desalination [51].

*Hollow-fiber membranes* find extensive use in high salinity water treatment, such as seawater desalination [52]. Their high packing density allows direct packing into large vessels [35, 52]. However, they are prone to deformation and are challenging to clean, resulting in higher system carbon footprints and increased capital costs [52].

Table 1 categorises FO-based desalination membranes, depending on their synthetic nature, structure, and configuration [26]. These membranes can be organic polymers, inorganic materials such as graphene derivatives, or hybrid compositions [45]. These membranes can have symmetric or asymmetric physical structures, encompassing porous and non-porous symmetric membranes, as well as thin-film composite or integrally skinned asymmetric membranes [26].

## Design criteria for an ideal membrane in FO desalination process

In the field of FO desalination, the membrane stands as a pivotal element, similar to other membrane-based technologies such as RO and NF. However, the primary challenge faced in FO desalination lies in the membrane development [34]. This development is impeded by multiple issues, encompassing the scarcity of efficient and economical membrane materials, concerns regarding the membrane structure, orientation, reverse solute diffusion, membrane fouling, and the impact of internal concentration polarisation (ICP) on the membrane efficacy [53]. ICP refers to the buildup of solutes within the porous support layer or structure of the membrane itself. As water moves through the membrane, solutes can become trapped or concentrated within the membrane material, creating an additional resistance to water transport. It significantly undermines membrane performance by affecting osmotic pressure, resulting in up to 80% reduction in water permeability and increased reverse solute flux (RSF) [53]. Additionally, it contributes to the membrane fouling, further deteriorating performance [53].

For FO desalination, the porosity of membrane materials holds critical significance, with different applications relying on porous or non-porous membranes [26]. Symmetric and asymmetric membranes find wide usage. They are made from dense or semi-permeable materials, while the thickness of dense membrane layers is determined by permeability-selectivity

coefficients [26, 35]. One of the most significant challenges emphasised by researchers in FO-based membrane processes is the nature of the feed solution (FS) and draw solution (DS). In conventional FO desalination systems, the active layer (AL) interfaces with the feed solution, while the support layer (SL) is in contact with the draw solute. For example, optimising the viscosity and concentration of the DS is crucial to mitigate ICP effects, which can severely impair membrane performance [54]. To further prevent salt back diffusion from the support layer into the active layer, improving membrane selectivity is vital. Without advancements in membrane materials, achieving a commercially viable FO-based desalination process remains difficult. These constraints underscore the need for continued research focussed on modifying the structural properties of FO membranes to maximise their overall efficiency [29]. Investigating how membrane structure influences mass transport is also critical for improving system performance and scaling up for real-world applications. Various membrane materials and designs have been employed in the FO process, including flat-sheet and hollow-fibre configurations. These include polymer-based membranes such as cellulose acetate (CA), cellulose triacetate (CTA), polyamide thin-film composites (TFC), and carbon-based membranes, particularly graphene-based films [29]. Amongst FO membranes, cellulosic membranes have been extensively used in FO processes, but these membranes face various limitations, including low selectivity and vulnerability to biological fouling and chemical degradation. Consequently, desalination researchers have turned their focus to asymmetric composite FO membranes, which can offer superior water permeability and selectivity due to their unique structure; a porous sub-layer coupled with a thin active layer [26, 29]. This structural configuration enables the optimisation of both the active layer and porous support independently, presenting opportunities to develop high-performance FO membranes for enhanced desalination technologies. Therefore, the ideal FO-based membrane for desalination should possess high water permeability, selectivity to salts, resistance to fouling and CP effects, improved stability, recyclability, ease of manufacture, and cost efficiency [55]. Ideally, such membranes should comprise an active-dense layer allowing high water permeability and low reverse solute permeability, along with a support layer featuring enhanced mass transfer, low concentration polarisation (CP), high mechanical strength, and resistance to chemicals and fouling [26, 55]. Figure 4 illustrates essential design prerequisites crucial for forming viable FO desalination membranes, emphasising morphology, material selection, and factors influencing optimal membrane performance.

Each category of FO membranes has distinct characteristics and advantages for different applications and operational conditions in FO desalination and water treatment applications. These categories are summarised in Table 2. Commonly used polymers



 Table 1:
 Summary of materials nature, and practical and configurational structures of FO-based membrane for desalination processes (adapted from Ref. 47, 48).

Synthetic Nature	Organic	Inorganic	Hybrid
	Symmetric	Porous	Non-Porous
Physical		99999999999999999999999999999999999999	
Structure		Integral-skinned asymmetric	Composite formation
	Asymmetric		
		Flat-Sheet Feed Stream	
		(water with suspended particles) Polymer-Supp	oort Membrane
		Permeated	
Configuration		Clear Water	
8		[Flat Sheet Membrane]	
		Hollow-Fiber	
	Feed Stream (water with suspended particles)		Retentate
		[Hollow Fiber Men	Permeated Clear Water hbrane]

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Figure 4: Summary of the most crucial properties to be considered when proposing to fabricate an ideal membrane for FO water desalination and purification processes [29].

for the fabrication of FO-based membranes encompass CTA/ CA, Polyetherimide (POEI), Polysulfone (PSF)/Polyethersulfone (PES), Poly(vinylidene fluoride) (PVDF), and Polyacrylonitrile (PAN), alongside widespread use of inorganic materials for similar purposes [56, 57]. In addition, Table 2 outlines advantages and disadvantages of these commonly employed materials for fabricating FO desalination substrates.

Asymmetric FO-based desalination membranes should have a thin active layer resistant to solute diffusion from feed and draw solutions. The design of this active layer should align with specific pore size requirements for efficient salt rejection, such as sodium chloride (NaCl) ions in seawater, necessitating pore sizes between 0.3 and 0.7 nm radius for dominant rejection [27, 33]. Meanwhile, the support layer should offer high porosity while maintaining excellent mechanical stability [26, 33]. The pore structure and hydrophilicity of the support layer are critical properties for improving resistance to fouling and enhancing water flux [38].

# Graphene oxide for laminar structure-based membranes

### Fabrication methods of laminar GO-based membranes

Laminar graphene oxide (GO) membranes are extensively explored for FO water desalination due to their potential for nearly 100% salt rejection and high water permeation [13]. These membranes can exist as free-standing or composite structures, with GO nanosheets forming tightly packed, interlocked layers on flat substrates in a parallel laminate sequence [21].

Recently, the emergence of laminated GO-FO membranes has driven advancements in ion/molecule separation, prompting the development of various techniques for their fabrication. Modified GO and reduced graphene oxide (rGO) membranes for FO desalination, ensuring stable dispersity and improved structure, are commonly produced using wet chemical techniques involving vacuum/pressure-assisted filtration (VF), spin-coating (SC), drop-casting (DCS), layer-by-layer assembly (LBL), and electrophoretic deposition (EPD) (refer to Fig. 5) [12, 25]. Electrostatic interaction and van der Waals forces play crucial roles in the orderly deposition of GO flakes in these methods. Herein, the selection of the appropriate method amongst those for the fabrication of laminar GO-based FO membranes relies on the desired membrane properties, including membrane scalability, thickness, uniformity, mechanical strength, and porosity (i.e. interlayer spacing). However, VF, SC, DCS, and LBL methods often encounter some challenges regarding uncontrollable GO dispersion amounts and uneven interlayer spacing between GO sheets during fabrication [28]. Scaling up these methods for practical FO applications remains a challenge. On the other hand, the EPD technique shows promise in depositing GO sheets into thin films using an external electric field, exhibiting the potential for scaling up GO-FO membranes with excellent microstructure and high packing density [38, 60]. Given challenges associated with VF, SC, DCS, and LBL methods, such as uncontrollable dispersion

		Significar	nt Factors				Selectio	n Factors				Discherce
Membra Materia	ne ul Morphology	Roughness	Porosity	Structural parameter	Water per- meability	Salt rejec- tion	Stability	ICP effects	Mechanical strength	Cost	Advantages	Disadvan- tages
Typically, such as Ps PES, PVDF PAN	Asymmetric structure, sponge-like	Moderate tr high (10 – 200 nm)	o High (30- 80%)	<ul> <li>Moderate tc</li> <li>high (300 –</li> <li>1500 µm)</li> </ul>	) Moderate tr high (1 – 10 LMH/bar)	o Moderate t high (90 – 99%)	o Good to excellent	Significant	Moderat to high (2 – 20 MPa) 20 MPa)	e Moderate (£ 10-£1 00 per m²)	*Chemically robust wWide tolerance for pH (2–13). *Excellent stability *Goob pro- cessability antifouling property	*Extremely hydrophobic strong fouling #Highly sensitive to Alkaline- based groups with common solvents, such as dimethyl- formamide (DMF) *Highly sensitive to Alkaline- based groups based groups
Proteins, peptides, biopolym POEI, CTA CA	Structured or to mimic ers, biological membranes	Low to moder ate (5 – 50 nm	- Moderate tr ) high (25 – 70%)	ate (100 – ate (100 – 600 µm)	-Low to moder ate (0.5 – 5 LMH/bar)	- Moderate t high (90 – 95%)	o Good to excellent	Minimal to moderate	Moderate (3. 15 MPa)	– High (£100- £500 per m²)	*Cheaper *Highly hydrophilic *Strong resistance to fouling *Long-term applicability *Excellent tchemical stability *More tydrophilic *Excellent antifouling property	*Highly reactive with amine groups at elevated temperatures *Highly sensitive to Alkaline- based groups *Narrow pH range (3–8) *Poor chemi- cal stability (i.e. acids, organic solvents and etc.)
y Thin-fill composi es (TFC), Po amide, sil xerogel: nano-ce bons	n Thin and te dense selec- ly- tive layer ica over support s,	Low (1 – 30 mn)	Low to moderate (20 – 50%)	High (200 – 800 µm)	High (5 – 15 LMH/bar)	High (95 – 98%)	Good to excellent	Significant	High (5 – 25 MPa)	High (£60- £300 per m <sup>2</sup> )	*Excellent thermal and chemical strength *More hydrophilic	*Very Expen- sive Complicated *Synthesis process





Figure 5: Schematic diagram showing the associated mechanisms of the fabrication techniques for GO-based FO laminar membranes; (a) Vacuum/ pressure-assisted filtration [58]. (b) Spin-coating [28]. (c) Drop-casting [59]. (d) LBL self-assembly process [18]. (e) Electrophonic deposition technique [60].

and uneven spacing, these techniques may be less suitable for large-scale production. In contrast, EPD offers a more controlled approach to depositing GO sheets, considering an external electric field to achieve a uniform and densely packed structure. The ability of such method to produce high-quality membranes with consistent performance makes it a favourable option for scaling up GO-FO membrane production. Table 3 summarises the description of each GO-FO membrane's fabrication method, along with their advantages and disadvantages, and remarks for selecting the appropriate method during the fabrication process.

The upcoming section "Recent developments of laminar r(GO)-based FO membranes for desalination" will comprehensively explore into the recent research on fabricating laminated GO-FO membranes for desalination, outlining their performance and practical limitations.

# Molecular separation mechanisms of laminar GO membranes

Within the recent developments of desalination-based membranes, GO laminates can serve as an ultra-thin selective layer, filtering small hydrated ions [77]. GO's individual nanosheets maintain specific interlayer spacings determined by the concentration of oxygenated functional groups, which control the size of these gaps [78]. The interlayer spacing can vary from approximately 0.4 to 1.0 nm, impacting the formation of a network of graphene nano-capillaries amongst GO nanosheets, facilitating low friction water flow [79, 80].

Laminar GO-based membranes significantly contribute to sieving small, hydrated ions found in mono- and di-valent salts of seawater [83, 84]. GO, ideally, possesses distinct properties such as dense graphene nano-slits and delocalised electron clouds, acting as barriers within aromatic carbon networks

Fabrication Method	Description	Advantages	Disadvantages	Selection Remarks
Vacuum/Pressure-assisted filtration	Filtration-based methods, such as vacuum-assisted and pressure-assisted techniques, referenced in Fig. <b>5 (a)</b> , stand as common and direct approaches for crafting laminar GO membranes [12, 28]. These methods enhance GO's dispers- ibility in water, proving highly effective as through a porous substrate to create either free-standing or supported GO membranes [19, 61]	*Benefits of filtration methods include a high degree of structured lamination, low surface roughness, and adjustable separation performance through the rate of GO deposition [1 2, 58, 62] *The thickness of these membranes can be adjusted by altering the concentration and volume of the GO dispersions [63]	*Vacuum filtration, in particular, yields laminar GO membranes with time-con- suming, depositing GO sheets randomly or semi-uniformly parallel to base mem- branes [64] *Drawbacks encompass challenges in scaling up membrane production-limited studies focus on scaling up vacuum filtra- tion for GO membrane fabrication-and poor stability under operational condi- tions, such as rapid disintegration of the GO film in aqueous solutions [65]	*This method is the most appropriate for the lab-scale where small membrane sixes, with thin, smooth, and porous coatings, are required for research purposes
Spin-Coating	To produce laminar GO-based mem- branes, spin-coating, as depicted in Fig. 5 (b), stands as another prevalent, straightforward, and widely employed technique [12, 66]. It involves deposit- ing a GO suspension drop onto various substrates (such as copper foil, polymers, or silicon nitride) followed by rotating the substrate at different speeds and durations, creating a thin, stacked liquid layer driven by centrifugal force [12, 21, 67]. Free-standing membraness are then obtained by peeling off substrates or through an etching process	*Spin-coating offers advantages such as cost-effectiveness, rapid processing, and adjustable membrane thickness by manipulating the GO suspension amount, quick fabrication, and highly stacked membrane formation [12, 28, 63] *Washing with deionised water and mild temperature drying completes the fab- rication, resulting in highly stacked and dense GO membranes [12, 28, 63]	*Challenges related to uncontrollable dispersion, uneven spacing and scal-ability regarding substrate shape and size hinder its application in large-scale industries [28]	*Similar to filtration-based methods, it is highly suitable to quickly fabricate thin and uniform coatings with fine surface features on small substrates. This is only limited for researchers and lab environments by adjusting spin speeds
Drop-Casting	Drop-casting, illustrated in Fig. 5 (c), stands as a simple and direct technique for crafting uniform and highly stacked free-standing GO membranes [28, 63]. This process involves casting a GO col- loidal suspension onto a smooth surface substrate, such as silica or filter paper, and subsequently drying it at room temperature [68]. Notably, due to water's low vapour pressure and high surface tension, alternative solvents such as alcohol, hexane, or toluene are preferred for dispersing GO particles during drop- casting [28]	*This technique gains attention due to its simplicity, ease of operation, and rapid production of thin GO layers on relatively small support surfaces [18]	*Significant challenges lie in the uncon- trollable dispersion, uneven spacing, and potential alteration of film thickness or microstructure due to substantial dif- ferences in evaporation rates across the substrate [18]	*This method is also highly suitable for preparation of thicker laminar GO mem- branes for lab use. It can also be suitable for scaled up membranes with limitations by increasing the volume of the GO suspen- sion and the size of the substrate but with less uniform layers and potential variations in the porosity and mechanical stability due to the thickness differences across the surface

Table 3: Summary of fabrication methods of GO-based FO membranes, with their advantages and disadvantages and selection remarks.

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Table 3:       (continued)				
Fabrication Method	Description	Advantages	Disadvantages	Selection Remarks
Layer-By-Layer (LBL) Assembly	LBL assembly, as depicted in Fig. 5 (d), represents a common and effective strat- egy for thin crafting films and laminar GO- based membranes [12, 18, 28, 65]. This approach relies on electrostatic attraction forces between negatively charged GO fakes (Poly-anions) and positively charged, hydrophilic substrates (Polyca- tions) to deposit GO sheets [69]. Hydroxyl and carboxyl acid groups further enhance this process by facilitating reactions with various nanomaterials [70, 71]	*Compared to spin-coating-, casting- and filtration-based methods, LBL assembly offers greater stability and structural integrity in bonding GO nanosheets [65]. It enables precise control over laminate thickness by regulating LBL deposition cycles at the molecular level [12, 28, 65]. Additionally, it could be scalable and cost-effective [18, 65]	*Drawbacks include the potential for lengthy processes, difficulties in scaling up, uncontrollable dispersion, uneven spacing, and altering the interlayer spac- ing of GO (crucial for controlling desalina- tion efficiency) [72]	*LBL assembly is also perfect for precise, controlled over thickness at the nanoscale for research at the lab-scale, allowing researchers to prepare multi-layered composite GO membranes with specific functionalities. It is still challenging to be implemented for large-scale GO mem- branes unless automation is introduced
Electrophoretic Deposition	Electrophoretic deposition (EPD) is a colloidal technique shaping materials directly from a stable suspension using a direct current electric field, as illustrated in Fig. <b>5 (d)</b> . It involves two connected processes: electrophoresis and deposition [73, 74]. The deposition process mitigates relying on complex interactions. Higher electro-lyte concentration near the deposition lyte concentration near the deposition electrode reduces the zeta potential, causing particle flocculation, notably in water-based suspensions [75]. Sarkar and Nicholson [76] proposed a framework elucidating positively charged oxide particle migration towards the cathode in EPD	*Compared to all other GO-based fabrica- tion methods, EPD is a versatile technique used for fabricating thin films from colloi- dal suspensions, ensuring microstructural uniformity and high packing densities for fluid flow. In aqueous environments, GO nanosheets retain negative charges due to deprotonation of hydrophilic groups. Thus, GO nanosheets can be easily depos- ited on an anode surface using an electric field [25]	*During the EPD process, water elec- trolysis in the dispersible GO leads to the release of hydrogen (H <sub>2</sub> ) and oxygen (O <sub>2</sub> ) gases at the respective electrodes. The formation of gas bubbles during this process sometimes introduces defects in the synthesis of membranes. Neverthe- less, these drawbacks can be mitigated by reducing the ionic conductivity of the water or by employing alternating current, both of which can optimise the deposition process and enhance mem- brane quality [25]	*Unlike the other fabrication methods, it is suitable to fabricate small, uniform, and highly porous GO films on conductive sub- strates. Additionally, it is highly suitable for production of consistent, uniform, porous, and large area GO membranes by control- ling the deposition parameters, such as voltage and time











**Figure 6:** (a) Schematic of permeation of water molecules and small-sized ions between GO nanosheets, while large species are hindered by interlayer spacing. (b) The separation capability of interlayer spacing between two stacked GO nanosheets for desalination. Reproduced from Ref. 81 with permission from the Science. (c) Main separation mechanisms in the stacked GO membranes, including size of pores as a function of inter-laminar spacing between GO nanosheets, besides the size exclusion, selectivity mechanism can be performed by electrostatic interactions and ionic adsorption of hydrated species. Reproduced from Ref. 82 with permission from WILEY Online Library.

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to separate ions from seawater [77]. Figure 6(a) and (b) illustrates ionic/molecular separation mechanisms of GO laminar membranes, reliant on the arrangement of highly laminated GO nanosheets and the interlayer spacing [70, 81, 85]. The selective permeation of water and rejection of small hydrated ions such as Na<sup>+</sup> and Cl<sup>-</sup> depend on maintaining the interlayer spacing (e.g. pore size) within the range of 0.3 to 0.7 nm [27, 86]. Strategies to control swelling issues and maintain this spacing involve modifying functional groups or bonding GO nanosheets with molecules/nanoparticles. The selectivity of laminar GO-based membranes is based on size exclusion and ion adsorption effects [82, 87]. While the former depends on the interlayer spacing, the latter involves electrostatic binding, cation– $\pi$  interaction, and metal coordination to the functionalised GO nanosheets [82].

In this context, laminar GO membranes utilise their unique structure and chemical properties to effectively separate hydrated salt ions, such as NaCl, from water during FO desalination. Separation mechanisms involve size exclusion, charge repulsion, and selective permeability, influenced by the degree of oxidation and chemical cross-linking of GO layers, which are explained in Sects. "Size exclusion and selective permeability" and "Charge repulsion (or Adsorption effects" below.

#### Size exclusion and selective permeability

The primary mechanism for salt ion separation in laminar GO membranes is size exclusion. GO sheets are stacked in a way that creates nano-channels with controlled interlayer spacing, as shown in Fig. 6c. These nano-channels are small enough to allow water molecules to pass through while blocking larger salt ions. The typical size of these nano-channels is less than 1.0 nm, making them effective at excluding hydrated ions such as Na<sup>+</sup> and Cl<sup>-</sup> [27, 82, 86, 87].

#### Charge repulsion (or Adsorption effects)

GO is inherently negatively charged due to the presence of oxygen-containing functional groups such as hydroxyl, carboxyl, and epoxy groups. These negatively charged groups create an electrostatic repulsion effect that further inhibits the passage of negatively charged ions (such as  $Cl^-$ ) through the membrane [see Fig. 6(c)]. This charge repulsion mechanism complements size exclusion by providing an additional barrier to ion transport [27, 82, 86, 87].

In addition, the separation mechanisms of size exclusion and charge repulsion in laminar GO membranes are closely linked to the degree of oxidation and chemical cross-linking of GO, as follows:



**Figure 7:** Schematics of the principles of major stacked multilayered GO-based FO desalination membranes. (a) GO interlayers on porous substrate. (b) GO nanosheets incorporated into the polymer surface matrix of thin-film composite membrane. (c) GO nanosheets incorporated into the support matrix of thin-film composite membrane [24].

**Role of tuning oxidation degree of GO** Tuning the oxidation degree allows for balancing water permeability and salt rejection by controlling interlayer spacing and surface charge (*explained in more details in* Sect. "Tuning oxidation degree/ or direct reduction of r(GO)-FO membranes". The degree of oxidation of GO significantly influences its structure and separation performance, including size exclusion and charge repulsion, as follows [82, 87]:

- Interlayer spacing: Higher degrees of oxidation introduce more oxygen-containing functional groups, which can increase the interlayer spacing between GO sheets. This can enhance water permeability but may reduce salt rejection if the spacing becomes too large, allowing ions to pass through.
- Hydrophilicity: An increased in oxidation enhances the hydrophilicity of GO, improving water flux. More oxygencontaining groups attract and hold water molecules, facilitating their transport through the membrane.
- Charge density: A higher oxidation degree increases the density of negatively charged functional groups, enhancing the charge repulsion mechanism. This improved charge repulsion can better reject negatively charged ions such as Cl<sup>-</sup>.

**Role of chemical cross-linking of GO membranes** Chemical cross-linking involves introducing cross-linking agents that form covalent bonds or non-covalent bonds between GO sheets (*explained in more details in* Sect. "Intercalation/or chemical cross-linking of r(GO)-based FO membranes", impacting membrane properties and performance, including size exclusion and charge repulsion, in several ways [12, 82, 87, 88]:



- Stabilising interlayer spacing: Cross-linking helps maintain consistent interlayer spacing, preventing GO sheets from swelling excessively when in contact with water. This ensures that nano-channels remain small enough to effectively exclude salt ions.
- Enhancing mechanical strength: Crosslinked GO membranes exhibit improved mechanical stability, which is crucial for maintaining structural integrity under osmotic pressure gradients encountered in FO processes.
- Reducing water permeability variation: By stabilising the GO structure, cross-linking reduces the variability in water permeability and ensures consistent performance over time.
- Improving chemical resistance: Cross-linking can also enhance the chemical resistance of GO membranes, making them more durable in various operating conditions, including different pH levels and the presence of chemical agents.

# Implication of laminated GO membranes for FO desalination

FO-based GO-enhanced membranes mainly fall into three primary categories: laminar-structure GO, GO surface modified, and GO mixed-matrix support membranes as follows [23, 25, 28, 39, 89–94]:

- Laminar-structure GO membranes: These membranes are composed of stacked GO sheets arranged in a layered, laminar structure [see Fig. 7(a)]. Several fabrication techniques, including VF, SC, DCS, LBL, and EPD (refer to Sect. "Fabrication methods of laminar GO-based membranes", are commonly employed to integrate GO-based selective layers onto membrane support layers [12, 25]. These methods induce key interactions, particularly electrostatic forces, and van der Waals interactions, to ensure the deposition of GO flakes, which is essential for achieving optimal membrane structure and functionality [28]. A comprehensive discussion of the development and refinement of these membranes is provided in Sect. "Recent developments of laminar r(GO)based FO membranes for desalination". The interlayer spacing between GO sheets creates narrow channels that allow for selective permeation of water molecules while rejecting larger solutes. The laminar structure provides high water flux and good selectivity, making these membranes effective for FO processes.
- GO surface modified membranes: In these membranes, the surface of the membrane is modified with GO to enhance its properties [see Fig. 7(b)]. This modification can involve coating or grafting GO onto the surface of the active layer to improve hydrophilicity, antifouling characteristics, and overall performance. Surface modification with GO can also

enhance the membrane's mechanical strength and chemical resistance.

• GO mixed-matrix support membranes: These membranes incorporate GO particles into the polymeric matrix of the support layer, creating a mixed-matrix structure [see Fig. 7(c)]. The addition of GO to the support layer can improve the membrane's structural integrity, increase water permeability, and enhance selectivity by providing additional pathways for water transport. This hybrid approach combines the benefits of polymeric membranes with the unique properties of GO.

In the field of GO-based surface modification and mixedmatrix support membranes, a thin active layer is typically formed on a mixed-matrix support layer, such as in TFC membranes. This approach addresses two main challenges: first, the hydrophobic nature of many membrane polymers, and second, the vulnerability of hydrophilic sub-layers to water-induced plasticisation, while the selective layer remains more rigid [26, 29]. These FO membranes are often fabricated using phase inversion techniques, which can be further divided into thermally induced phase separation, precipitation by controlled evaporation, vapour-phase precipitation, and non-solvent-induced phase separation (NIPS). Phase inversion is widely recognised as one of the most effective methods for preparing both flat-sheet and hollow-fibre FO membranes. Briefly, this process involves blending polymers and nanofillers such as GO with a solvent and casting the resulting suspension onto a support layer, followed by immersion precipitation—submerging the polymer solution into a non-solvent coagulant bath [29]. Additionally, LBL assembly technique is also used to synthesise FO membranes, where a prefabricated sub-layer is exposed to oppositely charged polyelectrolytes for limited periods, forming a uniform, ultra-thin selective film. Alternating layers of polyelectrolytes create a multi-layered structure. The selective layer itself is synthesised and integrated through interfacial polymerisation (IP), involving a reaction between m-phenylenediamine (MPD) and trimesoyl chloride (TMC) to form an extremely thin film. This membrane, characterised by its asymmetric structure and high permeability, is widely used in FO processes. However, the two-stage preparation method increases costs and introduces challenges in controlling the IP process for the selective layer [29]. A remaining issue is the compatibility between the nanofibrous substrate and the selective layer. It has been suggested that the chemistry and pore structure of the support layer influence the morphology of the selective layer, indicating a direct relationship between surface morphology, support layer structure, and selective layer performance. By optimising these factors, water transport through the sub-layer to the





Figure 8: Types of modification for recent advancements of graphene oxide-based membranes for FO desalination.

selective layer can be enhanced, ultimately improving water flux and membrane efficiency.

Despite progress in the GO-based surface modified and mixed-matrix support membranes, stacked r(GO) laminates have garnered attention for FO desalination membranes due to their ability to offer high water permeability, salt rejection, reduced fouling, and reverse salt flux, even though with concerns about mechanical robustness [22, 25, 28, 49, 89, 90, 94-104]. Laminated GO membranes for desalination exist as either free-standing or supported membranes. Free-standing GO-FO membranes, as limited to flat-sheet configurations, eliminate the impact of ICP in FO mode due to none substrate interference, but face challenges in the mechanical stability [90, 105]. Supported laminar GO-FO membranes, available as flatsheet or hollow-fibre structures, often encounter ICP due to the existence of the porous substrate in these membranes, leading to solute permeation from draw to feed sides (as depicted in Fig. S-1, and theoretically explained in Sect. "Theoretical background of transport phenomena across FO membranes" [23, 26, 29, 53, 106–108]. Researchers are still exploring modifications to support layer matrices to alleviate ICP effects by including different polymers, MOFs, NPs, conductive/carbon nanomaterials, etc. [23, 25, 26]. Compared to free-standing GO-FO membranes, supported GO laminated membranes offer acceptably higher mechanical and chemical strength for small-scale applications but face challenges in resolving practical issues for FO applications [107].

# Recent developments of laminar r(GO)-based FO membranes for desalination

Recent studies have highlighted the potential of GO-based membranes for achieving high water permeation, suggesting their practical promise in FO applications [25]. However, a specific cut-off point for water permeability in these laminar FO membranes has not been reported. Comparisons often focus on their performance relative to commercially available FO membranes such as RO-based CTA and TFC membranes [25]. The application of GO membranes for ionic separation, particularly in FO desalination, is limited by the interlayer spacing (d-spacing cut-off of 0.7 nm) between GO sheets [109]. Immersing GO membranes in water poses stability challenges, causing swelling of inter-laminar spacing, mechanical instability, and reduced performance in rejecting small salt ions in laminated GO membranes [40, 109]. Various strategies, such as partial oxygen reduction of GO (rGO), nanomaterials cross-linking, and nanoparticle intercalation, aim to control interlayer spacing, enhance stability in water and ionic solutions, and counter swelling effects in GO-based FO membranes for water desalination (See Fig. 8).

A summary table (see Table 4) outlines recent progress in laminar GO-based FO membranes for sieving common seawater salts, including fabrication techniques, materials, optimal thicknesses, modification strategies, and membrane performance metrics such as water flux, reverse solute flux, or salt rejection and stability. Next sections will explore the latest advancements

			Membrane	GO-FO Membrane		Optimal Membi	rane Perform	ance [FO MO	DEJ			
Fabrication Technique	Membrane Type	Candidate Material(s) & optimal Additive(s)	& SL Pore Size (µm)	Thickness (µm)	Modification Process	Testing Condi- tions	J <sub>w</sub> (LMH)	J <sub>s</sub> (GMH)	R <sub>s</sub> (%)	Antifouling Property	Challenges &/ Limitations	Year & Ref.
(Vacuum/ Pressure) assisted Filtration	Free-standing GOM	rGO (GO-load- ing ~ 0.4 g/m2)	Flat-Sheet (-)	(AL)~0.1 (SL) N/A	Optimising oxidation degree by chemical reduction with HI acid vapour after GOM prepa- ration	(FS) DI water (DS) 2 M NaCl (Temp.) 23 ± 1°C	57.0	č.	76.5 of NaCl	A/A	Mechanical instability, scalability, long-term stability	2015 [105]
	Free-Standing GOM	GO/PPA ratio (0.694)	Flat-Sheet (-)	(AL)~1.0 (SL) N/A	Thermally induced chemical cross-linking using Pro- panedioic acid (PPA)	(FS) Pure water (DS) 2 M NaCl Vc = 0.00075 L/s (Temp.) 25 °C	35.5	31.6	99.95 of Na+ ions	Almost no fouling with Effective rejection for organic dyes, such as (MO) & (RB)	Scalability, long-term stability for limiting effects of Na+ ions were not evaluated	2017 [90]
	MCE Sup- ported GOM	rGO (0.006 mg/ml)	Flat-Sheet (0.2)	(AL) ~0.160 (SL) COM	Optimising oxidation degree by chemical reduction with HI acid	(FS) DI water (DS) 0.6 M NaCl Vc = 0.0033 L/s (Temp.) 25 °C	20.1	4.7	96.0 of NaCl	N/A	Scalability, lower water permeation rate due to the tighten channels	2017 [22]
	MCE Sup- ported GOM	rGO-pDA (0.006 mg/ ml-2.0 g/l)	Flat-Sheet (0.2)	(AL)~0.170 (SL) COM	Tuning oxida- tion degree using HI acid & Modifi- cation of membrane surface using pDA coating	(FS) DI water (DS) 0.6 M NaCl Vc = 0.0033 L/s (Temp.) 25 °C	36.6	2.3	92.0 of NaCl	A/A	Scalability, long-term stability, and influence of heavy coat- ing of pDA on rGOM, leading to ICP	2017
	PVDF Sup- ported GOM	rGO (GO ~ 0.1 mol/ 1)—[high reduction degree (2.0-R)]	Flat-Sheet (0.45)	(AL)~0.028 (SL) COM	Partially tun- ing reduc- tion degree using vitamin C (L-AA) and crosslinked by PCA	(FS) DI water (DS) 0.3 M NaCl (Temp.) 25 °C	2.13	0.09	46.2 of NaCl	N/A	Scalability of rGO laminates, long-time stability	2017 [108]

 Table 4:
 Summary of recent progresses of laminar r(GO)-based FO membranes for water desalination and purification\*

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(continued)
Table 4:

			Membrane	GO-FO		Optimal Membr	rane Performat	nce [FO MO	DE]			
Fabrication Technique	Membrane Type	Candidate Material(s) & optimal Additive(s)	Configuration & SL Pore Size (µm)	Membrane Thickness (µm)	Modification Process	Testing Condi- tions	رالMH) رلاسلال	J <sub>s</sub> (GMH)	R <sub>s</sub> (%)	Antifouling Property	Challenges &/ Limitations	Year & Ref.
	MCE Sup- ported GOM	rGO (GO~ 0.006 mg/ ml)-AgNPs (0.5 M) -pDA	Flat-Sheet (0.2)	(AL) ~ 0.015 (SL) COM	Tuning oxida- tion degree using HI acid + Modi- fication of membrane surface using pDA coating and silver NPs	(F5) DI water (D5) 0.6 M NaCl Vc = 0.0004 2 L/s	28.9	12.3	65.6 of NaCl	Almost no observation for bacterial adhesion with excel- lent anti- biofouling resistance	Scalability, effects of n-Ag release on the GO membrane compaction led to water flux decline	2018 [89]
	MCE Sup- ported GOM	rGO (GO ~ 0.006 mg/ ml)-pDA	Flat-Sheet (0.2)	(AL) ~ 0.015 (SL) COM	Tuning oxida- tion degree using H1 acid incorporated with pDA only	(FS) DI water (DS) 0.6 M NaCl Vc = 0.00042 L/s	34.0	1.2	59.5 of NaCl	Observation of fewer bacterial activities and viable cells	Addition of pDA only to rGO resulted in salt reject decline	2018 [89]
	PVDF Sand- wich- Sup- ported GOM	GO-GQDs [3:2 ratio wt. %]	Flat-Sheet (0.125)	(AL) ~ 0.00085 (SL) 0.1 COM	Modifica- tion of GO nanosheets via covalent cross-linking with GQDs	(FS) DI water (DS) 2 M Na2504 Vc=0.0067 L/s (Temp.) 25 °C	55.0	1.6	97 of Na2504	Low fouling rate of 22% for the pollutant of BSA feed	Scalability, rapid water reduction due to intercalation of GQDs	2019 [44]
	PVDF Sand- wich- Sup- ported GOM	GO-Mg (OH)2 [3:2 ratio wt. %]	Flat-Sheet (0.125)	(AL) ~0.00103 (SL) 0.1 COM	Modifica- tion of GO nanosheets via ionic cross-linking with Mg (OH)2	(F5) DI water (D5) 2 M Na2504 Vc = 0.0067 L/s (Temp.) 25 °C	110.0	3.04	93.5 of Na25O4	Moderated fouling rate of 27% for BSA pollut- ant feed	Scalability declined salt rejec- tion due to intercalation of Mg (OH)2 NPs	2019 [44]
	Free-Standing GOM	GO-PVA (25 ppm)	Flat-Sheet	(AL)~0.222 (SL) N/A	Functionalisa- tion of GO with PVA	(FS) Dl water (DS) 2 M NaCl (Temp.) 25 °C	5.9	13.1	51.3 of NaCl	N/A	Scalability, exclusion of NaCl salt was unclear	2019 [125]
	Free-Standing GOM	GO-MPD/TMC (25 ppm)	Flat-Sheet	(AL) ~ 0.233 (SL) N/A	Functionalisa- tion of GO nanosheets covalently with cross- linking agents	(F5) DI water (D5) 2 M NaCl (Temp.) 25 °C	17.3	2.5	80.0 of NaCl	N/A	Scalability, the separation mechanism of NaCl salt was unclear	2019 [125]

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Table 4: (contin	nued)											
			Membrane	GO-FO Mombrano		Optimal Membra	ane Performa	nce [FO MO	DE]			
Fabrication Technique	Membrane Type	Candidate Material(s) & optimal Additive(s)	comiguration & SL Pore Size (µm)	Membrane Thickness (µm)	Modification Process	Testing Condi- tions	J <sub>w</sub> (LMH)	J₅ (GMH)	R <sub>s</sub> (%)	Antifouling Property	Challenges &/ Limitations	Year & Ref.
	Nylon Sandwich- Supported GOM	GO (0.01 wt. %)- MOF (UiO-66)/pDA	Flat-Sheet (-)	(AL)~0.2 (SL) COM	Modification through intercalation of nano- sized MOF- UiO-66 with positively charged PDA	(FS) DI water (FS) 2 M NaCl V = 0.00155 L/s	29.16	12.86	83.5 of NaCl	Almost no bio- fouling with excellent anti-bacte- rial property (90% bacte- riostasis)	Scalability of membrane material, limiting effects of UIO-66 over loading	2019 [134]
	PTFE Sup- ported GOM	GO (6.2 g/l)-NH4OH- DMF (doping time of reaction 24 h.)	Flat-Sheet (0.45)	(AL) ~ 65.9 (SL) COM	Eunctionalisa- tion of GO nanosheets through nitrogen- doped reac- tion with carboxylic groups	(F5) DI water (D5) 2 M NaCl Vc = 0.0033 L/s (Temp.) 25 °C	96.7	19.5	91.0 of NaCl	N/A	Scalability, precise control of pore sizes, long-term stability	2019 [123]
	PES Sup- ported GOM	rGO (GO-load- ing~10 mg)	Flat-Sheet (-)	(AL) ~ 1.2 (SL) COM	Tuning the oxidation degree of GO nanosheets using hydra- zine hydrate zine hydrate zine hydrate zine dand fabrication of electro- oxidative membrane	(FS) DI water (DS) 1 M NaCl Vc =0.0033 L/s (Temp.) 25 °C	10.9	6.8	92 of NaCl	Outstanding antifouling property against SA foulant with 2.0 V DC potential on membrane surface	Low mechani- cal stability of electro- oxidative membrane	(43]
	MCE Sup- ported GOM	GO (1 mg/ml): EDA: PAA (8.1:0.9:1 wt. ratio)	Flat-Sheet (0.2)	(AL) ~ 1.13 (SL) COM	Covalent cross-linking by ethylene- diamine monomer and poly- (acrylic acid) polymer	(FS) DI water (DS) 1 M NaCl Vc =0.0017 L/s (Temp.) 25 °C	34.9	7.0	97.0 of NaCl	NA	Scalability, fabrication technique for nano- composite membrane	2020 [37]

Table 4: (con	ntinued)											
			Membrane	GO-FO Mombrano		Optimal Memb	rane Performa	nce [FO MO	DE]			
Fabrication Technique	Membrane Type	Candidate Material(s) & optimal Additive(s)	Comiguration & SL Pore Size (µm)	membrane Thickness (µm)	Modification Process	Testing Condi- tions	J <sub>w</sub> (LMH)	J <sub>s</sub> (GMH)	R <sub>s</sub> (%)	Antifouling Property	Challenges &/ Limitations	Year & Ref.
	Nylon Sup- ported GOM	Medium-sized Flake rGO/PSS	Flat-Sheet (0.2)	(AL)~1.13 (SL) COM	Thermal reduction of GOM at 150 °C accom- plished by coating with hydrophilic PSS	(F5) DI water (D5) 1 M NaCl Vc = 0.0108 L/s (Temp.) 25 °C	34	6.2	78 of NaCl	A/A	Long-term stability hindered by pulsating crossflow	2021 [121]
	PES Sup- ported GOM	GO: PDMAEMa@ BL-0.8 (1:2 wt. ratio)	Flat-Sheet (-)	A/N (SL) N/A	Chemical cross-linking of GO nanosheets through hydrogen bonding between GO surface functional groups and amide groups of PDMAEMA	(F5) DI water (D5) 1 M NaCl Vc = 0.0033 L/s (Temp.) 25 °C	37.26	12	69 of NaCl	Excellent organic fouling resistance to sodium Alginate (SA)	Scalability of membranes and increas- ing the effects of ICP due to increasing PDMAEMA loading	[1 28]
	PLC Sup- ported GOM	GO: LDHs dispersions (1:1 ratio) 0.15 mg/ mL	Flat-Sheet (0.1)	(AL)~0.75 - 1.75 (SL) COM	Intercalation of LDHs with GO nanosheets via elec- trostatic interactions strategy to form het- erogonous GO/LDHs membrane	(F5) 0.001 - 1 M (D5) 1 M Sucrose (Temp.) 25 °C	2.1 (For stimulat	3.4 ed seawater	95.2 of NaCl	A/A	Scalability issue with fabrication method and long-term mechanical stability	2022 [1 29]
	Free -standing GOM	GO (0.1 mg/mL): PSS (1:1)/PVA (1:1)	Flat-Sheet	(AL-PCS) ~ 3.3 (AL-PVA) ~ 4.3 (SL) N/A (SL) N/A	Intercalation of PSS and PVA poly- mers with GO water dispersible sheets to form stable mixtures	(F5) DI water (D5) 2 M NaCl (Temp.) 25 °C	PVA 156.3 PVA 156.3	PSS 2.3 PVA 12.6	PSS 82.7 PVA 68.4 of NaCl	N/A	Scalability issue with fabrication and long- term FO and chemical stability, and antifouling	2022 [132]

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			Membrane	GU-FU Membrane		Uptimal Memb	rane Pertorm	iance [FU MC	JUEJ			
Fabrication Technique	Membrane Type	Candidate Material(s) & optimal Additive(s)	& SL Pore Size (µm)	Thickness (µm)	Modification Process	Testing Condi- tions	J <sub>w</sub> (LMH)	J <sub>s</sub> (GMH)	R <sub>s</sub> (%)	Antifouling Property	Challenges &/ Limitations	Year & Ref.
	Nylon Sup- ported GOM	GO-NCO/LLC (under UV-light)	Flat-Sheet	(AL) ~ 20 (SL) COM	Chemical modification of GO with NCO and LLC in the presence of DMSO under UV-light	(F5) DI water (D5) 0.017 NaCl (Temp.) 25 °C	120	0.51	99.8 of NaCl	≥ 90% removal of cationic and anionic dyes	Scalability and precise control of pore sizes	2023
	Nylon Sup- ported GOM	PEI: rGO (0.01 wt.%)/ pDA	Flat-Sheet (0.2)	(AL) ~ 0.24 (SL) COM	Chemical cross- linking, modification and reduc- tion by PEI and further modifying SL by PDA SL by PDA coating	(F5) DI water (D5) 0.6 M NaCl Vc=0.00002 L/s (Temp.) 25 °C	18.8	0.01	98.9 of NaCl	A/A	Scalability issue with fabrication and long- term FO antifouling	2023
	Nylon Sup- ported GOM	rGO (GO-load- ing ~0.25 mg with N2 atm)	Flat-Sheet (0.2)	(AL) ~ 0.132 (SL) COM	Optimising oxidation degree by hydrother- mal reduc- tion of GOM at 160 °C	(F5) DI water (D5) 1.5 M Na2SO4 (Temp.) 25 °C	5.75	0.241	92.0 of Na25O4	Improved antifouling resistance to chromate and chlorine	Water flux decrease caused by rGO deposi- tion, lower rejection for NaCI, and fouling	2024 [145]



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			Membrane	GO-FO Mombran		Optimal Membr	ane Perform	ance [FO MC	DE]			
Fabrication Technique	Membrane Type	Candidate Material(s) & optimal Additive(s)	Coniiguration & SL Pore Size (µm)	Memorane Thickness (µm)	Modification Process	Testing Condi- tions	J <sub>w</sub> (LMH)	J <sub>s</sub> (GMH)	R <sub>s</sub> (%)	Antifouling Property	Challenges &/ Limitations	Year & Ref.
Spin-coating	Nylon Sup- ported GOM	GO-(60.7 wt.% GO/ polymer)	Flat-Sheet (0.45)	(AL)~0.026 (SL) COM	Chemical cross-linking of GO cou- pled with in situ poly- merisation with NIPAM & MBA monomers and APS	(FS) Pure water (DS) 1 M NaCl Vc = 0.0083 L/s (Temp) 25 °C	25.8	<del>د</del> د	99.9 of NaCl	A/A	Increasing the GO/addi- tives ratio resulted in a non- permeable selective layer and scalability issues	2017 [107]
	Nylon–6 Supported GOM	Cationic KCl (0.8 mg)- Co-polymerisation GO (33 mg) with NIPAM + MBA + APS	Flat-Sheet (0.22)	(AL) ~ 0.044 (SL) COM	Modifica- tion of GO nanosheets through cross-linking with metal ions (K+)	(FS) DI water (DS) 0.5 M NaCl (Temp.) 25 °C	153.0	2.03	91.0 of NaCl	N/A	Water flux decline caused by increas- ing KCI deposition, long-time stability, and fouling	2019 [137]
Drop-Casting	Free-Standing GOM	GO (2 mg/ml)-POFG (2 mg/ml)	Flat-Sheet (-)	21.09	Tuning oxida- tion degree by partially oxidised GO and further modified by Acryl polymer	(FS) DI water (DS) 2 M NaCl Vc = 0.005 L/s (Temp.) 25 °C	62	8. 6	89 of NaCl	N/A	Difficult to precisely control pore sizes and inter-edges zones formed in POFG-Acryl polymer membrane	[146]

			Membrane	GO-FO		Optimal Membr	ane Perform	ance [FO MC	DE			
Fabrication Technique	Membrane Type	Candidate Material(s) & optimal Additive(s)	Configuration & SL Pore Size (µm)	Membrane Thickness (µm)	Modification Process	Testing Condi- tions	J <sub>w</sub> (LMH)	J <sub>s</sub> (GMH)	R <sub>s</sub> (%)	Antifouling Property	Challenges &/ Limitations	Year & Ref.
LBL self- Assembly	PAN Sup- ported GOM	GO: PAH (1:1 ratio), 1.0 g/L, pH 4 (10 bilayers)	Flat-Sheet (-)	(AL) 0.165 (SL) 60	LBL process by attaching positively charged PAH and negatively charged GO via electrostatic interaction	(F5) DI water (D5) 1 M MgCl2 (Temp) 25 °C	19.2	2.57	80 of MgCl2	A/A	Hydration issue of GO nanosheets in high ionic solution of MgCl2 caus- ing low sta- bility of GO interlayer spacing	2014 [140]
	PES Sup- ported GOM	GO: PAH (1:1 ratio), 0.1 wt. % (4 bilayers)	Flat-Sheet (-)	(AL) 0.165 (SL) 70	LBL process by attaching positively charged CS and negatively charged GO via electrostatic interaction	(F5) DI water (D5) 1 M Na2SO4 Vc = 0.025 L/s (Temp.) 25 °C	39.4	16.9	60.50 of Na2SO4	Excellent foul- ing resist- ance to feed solution of 200 ppm SA	Enlargement of GO inter- layer spac- ing caused by hydration effects of Na2SO4 solution causing high salt flux	2017 [141]
	PES Sup- ported GOM	GO (GO ~1 mg/ml) -OCNTS-PDDA (5 bilayers)	Flat-Sheet (-)	(AL) N/A (SL) COM	Modification of interlayer spacing between GO nanosheets by cross- linking via OCNTs	(F5) DI water (D5) 1 M NaCl Vc = 0.025 L/s (Temp.) 25 °C	5.9	0.49	70.2 of NaCl	N/A	Water flux decreases due to the increase in the thick- ness of LBL membranes to 10 bilay- ers, and fouling	2019 [143]

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			Membrane	GO-FO		Optimal Memb	Irane Perforr	nance [FO Mt	DDE]			
Fabrication Technique	Membrane Type	Candidate Material(s) & optimal Additive(s)	Configuration & SL Pore Size (µm)	Membrane Thickness (µm)	Modification Process	Testing Condi- tions	Jw (LMH)	J <sub>s</sub> (GMH)	R <sub>s</sub> (%)	Antifouling Property	Challenges &/ Limitations	Year & Ref.
Electropho- retic Deposi- tion	CNT Sup- ported GOM	rGO (GO~1 mg/ml)/ CNT	Hollow-Fibre (0.194)	(AL)~0.051 (SL) 128	Optimising oxidation degree by chemical reduction with HI acid vapour after GOM prepa- ration	(F5) D1 water (D5) 0.5 M NaCl Vc = 0.25 m/s (Temp.) 25 °C	22.6	بې ۲	94.0 of NaCl	N/A	Poor wettabil- ity of HFM, long-term stability not assessed along with antifouling property	2019 [38]
	PEDOT: PSS/ PEG Sup- ported GOM	PEL: rGO (0.01 wt:%)/ PEDOT: PSS/PEG	Flat-Sheet (-)	(AL)~0.48 (SL) 381	Chemical intercala- tion, modi- fication and reduction by double PEI layers and further modifica- tion of SL by PEG double PEG double coating	(F5) DI water (D5) 0.6 M NaCl Vc = 0.00002 L/s (Temp.) 25 °C	59.4	0.86	95.0 of NaCl	Excellent antifoul- ing to feed solution of 1,000 ppm SA, and CaCl2 and Na2SO4 under 3.0 DC voltage	Further opti- misation to enhancing the con- ductivity of membranes to mitigate potential drop issues and running proces for a long-term	2024 [144]

\*Details in the table were collected from relevant charts and figures in the literature based on actual, estimated, and calculated values

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and proposed methods to enhance the separation efficiency of these laminar GO membranes.

### Tuning oxidation degree/or direct reduction of r(GO)-FO membranes

Modulating the oxidation degree of GO sheets exerts control over crucial characteristics including thickness of GO sheets, chargeability, and hydrophilicity [110]. These factors significantly impact the performance of GO membranes in desalination, influencing nanosheet roughness, interlayer spacing, size of non-oxidised regions, and quantity and dimensions of nanopores [12, 111]. Additionally, reducing hydrophilic functional groups in GO mitigates swelling challenges in wet environments, ensuring sustained mechanical strength for long-term use in FO desalination processes [85, 86, 112].

Uncontrollable reduction of oxidation degree of GO laminates can result in reduced water permeability but improved salt rejection compared to pristine GO membranes [12]. This reduction process not only alters the membrane structure but also decreases interlayer spacing and wettability, enhancing the stability of the rGO layer [43, 113]. Since reduced interlayer spacing in GO-FO desalination membranes can lower the diffusion of small, hydrated salts, extensive research efforts have been directed towards developing and modification of GO membranes using different reduction processes. It should be noted that achieving precise control over the degree of GO reduction and its resulting hydrophobicity through chemical methods remains a formidable challenge, posing a significant hurdle to the practical implementation. To mitigate the elevated hydrophobicity following chemical reduction of GO, integrating hydrophilic modifications represents viable approaches to reestablish the hydrophilicity and improve the fouling resistance of separation membranes [22, 105, 114].

Liu et al. [105] pioneered the fabrication of a free-standing rGO membrane via vacuum-assisted filtration. Acid-based Hydroiodic acid (HI) vapour was employed as an effective reducing agent to adjust the oxidation state post-preparation of the GO membrane, as seen in Fig. S-2 (a). Removing the porous substrate eliminated the effects of ICP; however, mechanical stability of free-standing rGO membranes was lower than that of commercial CTA and supported pure GO membranes in the operational FO process. The water permeability of the resultant rGO membrane was linear to the NaCl concentration (0.5 - 2.0 M) (see Fig. S-2 (b)), with an optimal 100 nm thick membrane showing a water flux rate of 57 L/m<sup>2</sup>.h using a draw solution of 2.0 M concentration-five times higher than commercial CTA membranes in FO mode (water flux 10 L/m<sup>2</sup>.h) [5]. The rGO membrane exhibited enhanced Na<sup>+</sup> and Cl<sup>-</sup> ion rejection, attributed to small nano-channels between rGO nanosheets (see Fig. S-2 (c)).

Fan et al. [38] recently developed a dense rGO film onto the top of a CNT hollow-fibre substrate using an electrophoretic deposition (EPD). Post-composite membrane fabrication, GO was chemically and directly reduced using HI acid vapour (see Fig. S-3 (a)). EPD, known for its versatility and cost-effectiveness, applies GO nanoparticles suspensions to conductive substrates, forming novel coatings [115]. Stacked rGO sheets and the controlled interlayer spacing created a wrinkled morphology atop the CNT substrate, enhancing water permeation and mechanical stability by introducing defects for water flow and buffering spaces for membrane support, respectively (Fig. S-3 (b)). Lab-scale FO desalination tests using 0.1 M NaCl as feed solution and 1.0 M sucrose as draw solution demonstrated the resulting rGO membrane achieving a water flux of 40 L/ m<sup>2</sup>.h and approximately 94% salt rejection. This performance surpassed that of commercial CTA membranes (water flux 10  $L/m^2$ .h, reverse salt flux 12 g/m<sup>2</sup>.h) and other reported literature performances [104, 105, 116, 117].

Yang et al. [22] also developed rGO membranes, enhancing desalination performance in FO mode by coating them with a hydrophilic polydopamine (pDA) layer. Direct chemical reduction to rGO (interlayer spacing (d) = 0.345 nm), notably decreased the reverse salt flux to approximately 0.082 mol/m<sup>2</sup>.h and enhanced NaCl ion rejection to nearly 92% in contrast to pure GO membranes (with a d-spacing of 0.8 nm). Incorporating a hydrophilic pDA layer on the rGO membrane substantially improved the water permeation flux to around 36.6 L/m<sup>2</sup>.h by boosting water adsorption rates on the membrane surface. In a subsequent study by Yang et al. [89], the resultant rGO/pDA laminar membrane was further modified with silver (nAg) nanoparticles which showed an enhancement with the FO desalination performance targeting small monovalent ions and resisting biofouling. FO filtration tests aligned with their prior findings [22]. The resultant nAg@pDA-rGO membrane demonstrated improved water flux (28.9 L/m<sup>2</sup>.h), reduced reverse salt flux (0.21 mol/m<sup>2</sup>.h), and enhanced the resistance against micro-organisms and bacterial cells compared to the pristine GO membranes. Despite the improvement of FO desalination, the resultant membrane is yet required to be tested for a longterm structural stability.

Similarly, Shakeri and co-workers [43] have recently developed a partially oxidised rGO membrane via a pressure-assisted filtration, improving electro-conductive properties of the rGO. The resulting membrane exhibited enhanced the NaCl selectivity in FO desalination, displaying a reverse salt flux (RSF) of 6.8 gMH, slightly lower than the commercial TFC membrane (7.9 gMH). However, the high reduction of GO led to a reduced water permeation flux due to a small interlayer spacing (d-spacing of 0.34 nm) [43, 118–120]. Despite lower desalination performance and reduced mechanical stability compared to TFC membranes, the prepared rGO membrane showed exceptional



antifouling properties against sodium alginate (SA) foulants when a 2.0 V DC potential was applied to the membrane surface, displaying a higher flux recovery ratio of 98.7% compared to the TFC membrane's 75.4%.

Wang et al. developed an rGO laminate using partially reduced GO nanosheets [108]. Their procedure was based on using vitamin C as a mild reducing agent and crosslinked with poly (carboxylic acid) to enhance the mechanical stability. Their study demonstrated an inverse relationship between the reduction degree and the size of rGO nano-channels, affecting the reverse salt flux of monovalent ions (NaCl) in FO mode. Highly reduced rGO membranes achieved greater salt rejection due to tight nanosheet structures, while moderately reduced rGO laminates exhibited higher water flux because of abundant hydrophilic nano-channels and hydrophobic walls, allowing rapid water transport.

In a separate study, Deka et al. fabricated a novel Polystyrene sulfonic acid (PSS)-doped rGO membrane using a vacuum filtration on a nylon substrate followed by a thermal reduction at an optimal temperature of 150 °C [121]. The rGO-PSS membrane, fabricated with medium sized GO flakes, featuring an interlayer spacing of 0.77 nm, exhibited superior water flux (34 LMH) and lower reverse solute flux (6.2 gMH) compared to rGO and CTA-FO membranes in FO mode (see Fig. S-4). This study suggests a potential for the rGO-PSS membrane in FO desalination; however, its long-term stability remained uncertain.

## Intercalation or chemical cross-linking of r(GO)-based FO membranes

Chemical cross-linking or intercalation with different nanomaterials is another effective method (i.e. through covalent, or non-covalent bonding or/and combination of both) to adjust the interlayer spacing and further enhance stability of laminar GObased membranes for FO desalination [12, 88, 122]. Yan et al. developed a straightforward approach to create a free-standing crosslinked GO (F-CGO) laminar FO membrane using vacuumassisted filtration and a thermal treatment involving Propanedioic acid (PPA) with GO sheets [90]. The optimal GO/PPA ratio of 0.694 maintained excellent membrane stability while adjusting the inter-laminar spacing between GO laminates improved sieving of monovalent ions (NaCl) in the lab-scale FO process. As ICP effects were entirely eliminated in the nonsupported membrane, the resulting F-CGO membrane demonstrated a good water flux of 35.5 L/m<sup>2</sup>.h and a reverse solute flux of approximately 0.54 mol/m<sup>2</sup>.h using 2.0 M NaCl draw solution under controllable FO conditions.

Other strategies for reducing rGO include chemical functionalisation of GO with amine-containing nanomaterials. Song et al. proposed a method for fabricating a nitrogen-doped rGO membrane for improving FO desalination [123]. Their approach

involved inserting nitrogen atoms from NH4OH directly into the carbon lattice of GO nanosheets, creating a pyridinic-N bonding structure. This N-doping reaction facilitated potential tuning of the interlayer spacing, and improved hydrophilicity, and stability of the rGO membrane. The resulting membrane exhibited negatively polarised hole defects due to N-doping, enabling uniform nano-sized channels for water permeation while blocking small ions (Na<sup>+</sup> and Cl<sup>-</sup>). Simulation studies by Chena and Yang [124] supported these findings, showcasing mild free energy barriers for high water flux and substantial barriers for Na<sup>+</sup> and Cl<sup>-</sup> ions selectivity in pyridinic-N-doped graphene membranes. In FO desalination, the N-doped GO membrane demonstrated a water flux of 96.7 L/m<sup>2</sup>.h, four times higher than the commercial CTA membrane (28.4 L/m<sup>2</sup>.h), and a specific salt flux  $(J_s/J_w)$  of 0.18 g/L with 2.0 M NaCl as the DS, surpassing the commercial CTA membrane (0.55 g/L). On the other hand, the long-term stability of the as-prepared membrane was not considered.

Padmavathy et al. demonstrated a control approach for the interlayer spacing of GO sheets using chemical and ionic cross-linking methods, achieving an exceptional stability and desalination performance in FO mode [44]. Through esterification process, the addition of graphene oxide quantum dots (GQDs) effectively reduced the d-spacing in fabricated G-GQD membranes, creating a narrow nano-channel gap of 0.610 nm compared to that of 1.35 nm and 1.26 nm in Mg(OH)<sub>2</sub>-doped GO and pristine GO membranes, respectively. The functionalisation of GQDs' membrane during the esterification eliminated oxygen functional groups in GO sheets, thereby tightening the inter-laminar spacing between GO sheets. FO lab-scale assessments revealed that the resulting G-GQD membrane outperformed Mg(OH)2 and pristine GO films, exhibiting a remarkable 97% rejection towards di-valent salts (Na<sub>2</sub>SO<sub>4</sub>), surpassing the approximate rejection of 65% observed in the pristine GO membrane, even though with a slightly lower water flux.

Hung et al. [125] developed a symmetric GO membrane by adjusting the d-spacing via covalent bonding of modified GO laminates with various dicarboxylic cross-linking agents such as meta-phenylenediamine (MPD), 1,3,5-benzenetricarbonyl chloride (TMC), and polyvinyl alcohol (PVA). The interlayer spacing and stability of modified GO membranes were improved through electrostatic interactions between functional groups on GO sheets, and water molecules and monovalent Na<sup>+</sup> and Cl<sup>-</sup> ions. Besides its stability in water for 6 h during FO operation, the GO-MPD/TMC membrane demonstrated enhanced surface charges that excluded monovalent salts, making it suitable for FO desalination [126]. Similar outcomes were observed by Jang et al. who controlled the inter-laminar spacing and structural stability using cross-linking agents of Ethylenediamine (EDA) monomer and Poly(acrylic acid) (PAA) polymer chain in modifying GO membranes [37]. Recent studies highlighted the potential enhancement of GO stability by diamine



monomers and the improvement in separation efficiency and hydrophilicity when modified with PAA polymer chains. Additionally, cross-linking with the PAA improved structural integrity. Jang and colleagues proposed that GO/EDA/PAA composite membranes altered the nanostructure, forming controlled nanochannels that enhanced rejection performance towards hydrated NaCl ions while maintaining high water permeability and durability for 100 days. The as-prepared GO/EDA/PAA membrane with an optimal weight ratio of 8.1:0.9:1 exhibited a water flux of 52 L/m<sup>2</sup>.h and NaCl rejection of 97% in FO lab-scale tests compared to pristine GO membranes [88, 127]. In another study, Ghorbani et al. developed a PDMAEMA@BL-doped GO- FO membrane [128]. The membrane created by the physical cross-linking between GO nanosheets and the synthesised PDMAEMA, intercalating oxygen functional groups on GO's surface with PDMAEMA@BL's amine groups through hydrogen bonding. The membrane demonstrated a 2.5 times higher water flux compared to tested TFC-FO membranes due to the improved surface hydrophilicity from PDMAEMA@BL addition. Using 1.0 M NaCl as a DS resulted in lower salt rejection due to enlarged d-spacing, impacting the membrane's desalination performance for mono- and di-valent salt ions, nevertheless, the resulting membrane demonstrated exceptional antifouling properties against organic foulants compared to TFC-FO membranes. Despite the advancements with GO-FO membranes achieved through chemical functionalisation process in the above-mentioned literatures [37, 125] and [128], it remains challenging to upscale membrane fabrication techniques which could be applicable for the practical FO application.

Recently, Wang et al. also proposed enhancing the stability of GO-based FO membranes by introducing oppositely charged layered double hydroxide (LDHs) colloidal solutions [129]. Their proposal was to craft a sandwiched GO-LDHs membrane via a three-step vacuum filtration process (see Fig. S-5) [130, 131]. The addition of LDHs particles reduced the membrane's d-spacing, enhancing rejection rates to nearly 95.2% but with a lower water flux of about 2.1 L/m<sup>2</sup>.h for high NaCl concentrated seawater, as depicted in Fig. S-5. Additionally, Tong et al. [132] also attempted to tackle the on-going issue of performance-stability trade-off in laminar GO-FO membranes by incorporating GO nanosheets and polyelectrolyte spacers of poly(sodium 4-styrenesulfonate) (GO-PSS), comparing to the poly-(vinyl alcohol)-doped GO membrane (GO-PVA). The GO-PSS membrane exhibited superior characteristics, including higher water flux, low salt flux, and excellent selectivity. However, the long-term stability remains a consideration for the practical FO application. Moreover, Pathan and co-workers [133] introduced mechanically robust GO-modified membranes highly resistant to chlorine exposure with precise molecular sieving properties. Their concept was to use GO-lyotropic liquid crystals (GO LLCs) formed through chemical cross-linking in aqueous solutions (see Fig. S-6). These modified GO membranes outperformed shear-aligned GO membranes in salt rejection (99.8% NaCl rejection) and water flux (120 L/m<sup>2</sup>.h) due to their stable interlayer spacing. While their resultant membranes exhibit exceptional mechanical stability, the scalability is still necessary for practical FO water remediation applications.

Precisely adjusting the pore size of GO membranes proves effective in ion sieving during desalination processes, yet stability remains underexplored [26]. Pang et al. investigated the incorporation of hydrophilic nano-sized metal-organic framework particles (MOF-UiO-66) into GO laminates via electrostatic interactions with positively charged pDA molecules, as shown in Fig. S-7 [134]. The resulting GO/UiO-66 sandwich membrane demonstrated uniform 0.6 nm pores, enhancing water permeation, and significantly improving Na<sup>+</sup> ion rejection. In FO desalination, the composite membrane displayed a water flux rate of 29.16 L/m<sup>2</sup>.h (270% higher than the pure GO) and a reverse solute flux of 12.86 g/m<sup>2</sup>.h using 2.0 M NaCl draw solution, outperforming pristine GO membranes.

In the same essence, Kim et al. also proposed a straightforward method to create a thin-film GO composite membrane on a porous nylon substrate by spin-coating. Prior to the membrane fabrication, GO nanosheets were crosslinked with N-isopropyl acrylamide (NIPAM), N, N'-methylene bisacrylamide (MBA), and ammonium persulfate (APS) [107]. This approach formed a polymer network between GO layers, as illustrated in Fig. S-8. The resulting membrane, composed of hydrophilic GO nanosheets and (NIPAM-MPA) polymer, achieved a small interlayer spacing of 0.48 nm (compared to pristine GO's reported 1.04 nm [135]), leading to excellent NaCl rejection, fast water permeation, and minimised ICP effects. Notably, this intertwined polymer/GO structure exhibited robust mechanical strength and chlorine stability during FO desalination. In FO lab-scale tests, the membrane with an optimal GO/polymer ratio of 60.4 wt% demonstrated high water flux of 25.8 L/m<sup>2</sup>.h and 99.9% NaCl rejection.

The alteration of GO nanosheets using crosslinked cationic metal ions also exhibits varied effects on the properties of GO membranes and their stability in FO desalination processes [12]. Chen et al. utilised different cations ( $K^+$ ,  $Na^+$ , and  $Li^+$ ) and discovered that GO cross-linking results in varying interlayer spacing between adjacent non-oxidised regions [136]. Chen et al. discovered that potassium cationic crosslinked GO- $K^+$ membranes could obstruct  $K^+$  ions due to the hydration energy of  $K^+$ , impacting the interaction energy between hydrated cations and GO. This could potentially cause instability during passage through GO nanosheets [12, 136]. Building on this, Talar et al. [137] developed a novel nanocomposite membrane for FO desalination by adding varying amounts of potassium chloride (KCl) into a co-polymerised GO mixture, followed by spincoating on a porous nylon substrate. The resulting membrane



achieved different d-spacing values (0.4, 0.6, and 0.78 nm), enabling efficient rejection of monovalent salt ions and an average reverse salt rejection of 2.03 gMH during FO operation. Additionally, the membrane's enhanced desalination performance is attributed to GO's adsorption capacity for KCl, charge balance, and the controlled d-spacing between GO nanosheets.

In general, LBL self-assembled GO membranes can maintain excellent stability due to covalent bonding and/or electrostatic interaction between layers [138]. However, prolonged exposure to ionic solutions containing Na<sup>+</sup> ions can disrupt stacked GO nanosheets, impacting stability and interlayer spacing, consequently affecting the rejection performance of small hydrated ions, especially in desalination [139].

Mi and Hu [140], and Shakeri et al. [141] developed GO-based LBL-FO membranes employing GO-modified Poly(allylaminehydrochloride) (GO-PAH) and GO-doped Chitosan (GO-CS) bilayers through electrostatic interactions on different porous support layers, respectively. The GO-PAH-LBL membrane (see Fig. S-9 (a)) exhibited dominated GO deposition with FO performance showing a water flux of 19.2 LMH but lower ion selectivity using 1.0 M MgCl<sub>2</sub> as a DS due to the GO nanosheet hydration issues in highly ionic solutions, causing enlarged interlayer spacing and reduced mechanical stability. Similarly, the resultant GO-CS-LBL membrane (see Fig. S-9 (b)) demonstrated higher water flux in FO desalination but exhibited lower selectivity to ionic solutions, attributed to increased d-spacing between GO nanosheets, compromising membrane stability [141]. Meanwhile, the use of invertibly charged crosslinkers in oxidised carbon nanotubes (OCNTs) was proposed to limit the expansion of interlayer spacing, enhance water flux, and reduce membrane surface roughness by preventing GO agglomeration [142]. Kang et al. [143] explored the impact of OCNT intercalation for LBL-GO membranes in FO. The resulting GO-OCNTs-LBL membrane, with controlled GO interlayer spacing, displayed improved stability, higher water permeability, and 70.2% decrease in reverse solute flux towards NaCl salts compared to pristine GO-LBL in FO processes, suggesting its potential superiority in FO desalination.

In most recent studies addressing the trade-off between FO performance and chemical/mechanical stability, innovative approaches have been developed to fabricate desirable GObased nanocomposite membranes. One study utilised polyethyleneimine (PEI) to reduce GO (rGO) and crosslink and surface modify GO sheets, enhancing membrane performance. The resulting membrane, deposited on a hydrophilic nylon support layer modified with polydopamine (pDA) using vacuum filtration, demonstrated excellent water flux, high NaCl rejection, and low reverse solute flux in lab-scale tests [119]. The combination of PEI cross-linking with GO and pDA modification improved membrane hydrophilicity and structural stability, compacting nano-channels to raise molecular/ion separation. Subsequently,

the same group developed an electro-oxidative technique to fabricate graphene-based single- and double-sided GO-FO membranes (see Fig. S-10) [144]. PEI crosslinked rGO layers were constructed on scalable flat-sheet substrates functionalised with polyethylene glycol-Poly(3,4-ethylene-dioxythiophene)-poly (styrene-sulfonate) (PEDOT:PSS/PEG) via electrophoretic deposition (EPD). The resulting double-sided coated PEI:rGO membrane exhibited a superior performance compared to the single-sided PEI:rGO, achieving higher ion salt rejection and reduced specific salt flux. Under 3.0 V DC potential, PEI:rGO membranes showed improved antifouling properties, attributed to electro-oxidation mechanisms and unique nanocomposite structures. These studies highlight the effectiveness of combining PEI cross-linking with GO and surface modifications to enhance the membrane stability, hydrophilicity, and desalination performance, representing promising strategies to overcome challenges in practical FO applications.

In summary, the recent innovations of laminar GO-based membranes for FO desalination suggest that research primarily targets understanding the physico-chemical properties to address stability, permeability, and selectivity challenges in aqueous environments. Some studies have focussed on reduced GO (rGO) membranes to reinforce underwater stability and molecular sieving for saline water hydrated salts. Despite the manifesting stability of GO membranes, the drawback of the reduced GO for the decrease of water permeation, due to diminished hydrophilicity and narrowed nano-channels, is still a major concern. Recent proposals suggest creating novel GO-based FO membranes by combining different nanofillers/cross-linkers to balance water permeability and ion selectivity within GO membranes, addressing issues such as d-spacing swelling, mechanical instability, and scalability. Further investigations into longterm stability, precise control of pore sizes, and nanostructure through varying doping reaction and fabrication procedures are crucial and required for the advancements in this field.

# **Critical themes and findings**

The literature presented on laminar GO-based membranes for FO desalination demonstrates promising advancements but also highlights several critical areas for further exploration and improvements.

Firstly, while recent studies have indeed highlighted the potential of GO-based membranes for achieving high water permeation, there is a notable lack of a specific cut-off point for water permeability in these laminar-based FO membranes. This absence of a clear benchmark limits the ability to assess and compare the performance of GO membranes effectively against other commercially available FO membranes. Additionally, the focus of comparisons primarily on commercially



available membranes such as RO-based cellulose triacetate (CTA) and thin-film composite (TFC) membranes might not provide a comprehensive understanding of GO membranes' performance across various parameters. Moreover, the application of laminar GO membranes in ionic separation, particularly in FO desalination, faces significant limitations due to the interlayer spacing between GO sheets. Immersing GO membranes in water exacerbates stability challenges, leading to swelling of inter-laminar spacing, mechanical instability, and reduced performance in rejecting small salt ions. Although various strategies such as partial oxygen reduction of GO (rGO), nanomaterials cross-linking, and nanoparticle intercalation aim to address these challenges, their effectiveness in practical applications and long-term stability require further investigations. Furthermore, while studies have demonstrated innovative methods for fabricating rGO membranes with enhanced performance in FO desalination, there are notable limitations and challenges to address which are explained in the following section in more detail. For instance, some methods may compromise mechanical stability, while others may exhibit reduced water permeation due to decreased hydrophilicity and narrowed nano-channels within the GO structure. Additionally, while cross-linking methods show promise in enhancing stability and performance, there is a need for comprehensive investigations into their long-term efficacy and scalability.

Overall, while recent advancements in GO-based laminar membranes for FO desalination are promising, critical gaps and challenges remain. Addressing these gaps, including establishing clear benchmarks for performance evaluation, improving understanding of stability mechanisms, and developing scalable fabrication methods are essential for the practical implementation and further advancement of GO-based membranes in FO applications.

# **Current challenges and research perspectives**

Despite significant progresses in developing laminar-structure GO-based membranes for FO desalination, several challenges and limitations must be addressed before their practical application. This section examines these challenges in more detail and proposes potential improvements, as summarised in Table 4. Commercialising FO desalination using laminar GO-based FO membranes faces persistent challenges such as membrane fouling, ICP, and the lack of commercially suitable draw solutes [26, 38, 147]. Over the past decade, the unique 2-D structure and hydrophilic properties of GO-based laminar membranes have attracted considerable scientific and practical interests for developing FO desalination processes [148]. Layered GO sheets are essential for achieving high salt rejection efficiency by adjusting the interlayer spacing to approximately 0.6 nm through methods such as reduced GO (rGO) and functionalisation with

cross-linkers, allowing selective transport of water molecules while excluding ions. Desalination efficiency is also influenced by charge and adsorption mechanisms involving electrostatic interactions between GO nano-channels and hydrated ions [24, 25, 53].

The development of GO-based FO membranes also remains constrained by scalability issues, hindering progress in FO desalination. Recent advancements have utilised GO sheets in various fabrication approaches to enhance membrane performance, particularly water permeation rate, salt rejection, and antifouling properties, even though sometimes at the expense of the long-term stability [23]. Several challenges and knowledge gaps remain in the literature that must be addressed before scaling up these membranes for practical FO desalination processes:

Water stability in laminar GO-based FO membranes remains an unresolved issue. Herein, water stability refers to the membrane's ability to maintain its performance, and separation efficiency when exposed to water over extended periods. High water stability is crucial for the durability and reliability of GO-based membranes in FO applications [149]. Recent advancements have focussed on modifying the microstructure of GO laminates through techniques, including incorporating rGO sheets or cross-linking materials, overlooking the imperfect assembly using conventional methods. The challenges of conventional assembly techniques can heavily impact stability, mechanical strength, and performance of large-scale GO-based FO membranes. Improving membrane preparation methods to ensure uniformly stacked GO sheets is critical but challenging in largescale industrial processes. Conventional techniques such as vacuum/pressure-assisted filtration and spin-coating are commonly used and approved for fabrication of lab-scale GO flat-sheet membranes, but those methods still face challenges related to liquid volume, long-term durability, and uneven alignment of GO nanosheets. Scalability issues mainly arise due to limitations in apparatus size. Other methods, i.e. LBL-self-assembly and drop-casting, can have limited scalability but suffer from rapid membrane productivity issues. Enhancing membrane fabrication techniques to precisely control microstructure and scalability is also crucial. Employing a combined-fabrication system involving scalable processes including, for instance three-dimensional (3D) printing or electrophoretic deposition with induced electrical potential, alongside embedding novel cross-linkers (such as highly porous covalent organic frameworks (COFs)) or ionic liquids between GO sheets, could offer a solution to fabrication challenges. These would suggest reducing the water adsorption and degradation and help to maintain the membrane's separation efficiency and water stability over



extended periods. In addition, future work should focus on utilising a sun simulation process as a post-treatment for laminar-selective GO-FO films which can offer several positive potential effects [89]. This is particularly due to its ability to mimic sunlight exposure, including ultra-violet and visible lights. In comparison to the uncontrollably thermal treatment of GO laminates to reduce GO, sunlight-induced GO reduction could lead to controlled pore formation (i.e. interlayer spacing) in the laminar-selective GO layer, which can enhance water permeability and stability without significantly compromising solute rejection. Moreover, the sunlight could tune the surface chemistry of the laminar GO membrane, potentially improving the interaction between the membrane and water molecules or solutes. This can enhance specific properties such as membrane's surface charge and fouling resistance, making the membrane more effective in FO desalination.

The long-term mechanical and chemical stability of GO laminar FO membranes for desalination remains a core challenge for advancement, as FO washing processes significantly impact membrane recovery. Herein, the longterm stability refers to the membrane's ability to withstand physical stresses, such as pressure and handling, without significant deformation, damage, or loss of performance over extended periods. This includes maintaining its structural integrity and resistance to cracking, tearing, or mechanical failure during prolonged use in FO applications [25]. Future research should prioritise the search for more effective cross-linkers to enhance structural stability. Fabrication of GO-FO membranes requires strong active layers balancing desalination performance and stability. Challenges persist in creating self-supporting laminar GO-FO membranes due to hydraulic backwashing concerns. On the other hand, traditional polymeric substrates may hinder the performance of supported GO-based membranes, leading to severe performance reduction due to ICP issues. This can result in flux loss under highly concentrated ionic draw solutions. Developing sufficiently robust support layers to reduce ICP effects remains a priority. Future research should focus on creating novel, mechanically robust, and scalable substrates to mitigate the negative effects of ICP, meanwhile stimulating stability. In this context, it can be proposed that ion-exchange and conductive substrates can offer promising avenues to enhance performance and chemical and mechanical stability for long-term use in desalination and other FO applications [144]. For instance, ion-exchange films could serve as an alternative support layer for GO-based laminar FO membranes. These membranes, typically made from sulfonated polymers or other ion-conducting materials such as carbon nanotubes (CNT), can facilitate better transport of ions across the membrane, reducing ICP. This also provides enhanced mechanical stability due to their dense polymer matric and resistance to degradation in highly concentrated salt solutions, making them ideal for long-term use in FO desalination. Further, integrating conductive polymers such as polyaniline (PANI), polypyrrole (PPy) or Poly(3,4-ethylenedioxythiophene)-poly (styrene-sulfonate) (PEDOT:PSS) into the substrate structure can offer multiple benefits; (1) mechanical stability by forming robust network and hence improving membrane's ability to withstand physical stress and reducing the likelihood of damage, (2) antifouling characteristics by electron-donating ability of conductive polymers to reduce the adhesion of foulants, and (3) electrochemical backwashing through induced DC voltages and applied currents to help removing fouling and also enhancing the long-term usability and stability of the FO membrane.

• The separation efficiency of GO-based membranes is also affected by electrostatic charges from mono- and di-valent solutions such as NaCl and Na<sub>2</sub>SO<sub>4</sub>, with rejection efficiency decreasing as ionic strength increases. Assessing these membranes in long-term crossflow filtration with these solutions is crucial to understand their structural properties and durability and effects of various ionic salts. The selectivity of GO- laminar FO membranes has been a focus for synthetic seawater salts, but real seawater contains additional ions and scalants, potentially impacting membrane's water stability. Further research should explore membrane performance in real seawater conditions, including inorganic fouling, to simulate industrial desalination situations.

Future research should prioritise developing novel fabrication techniques and support layers to address these challenges and advance the practical application of laminar GO membranes in FO desalination, including testing stability of these membranes in real seawater conditions to mimic industrial desalination scenarios.

# Conclusions

The commercialisation of FO for water desalination faces challenges including lack of suitable membrane materials, reverse solute flux, membrane fouling, and CP effects. Developing an ideal FO membrane requires a robust selective layer and a highly porous support layer to optimise water flux and salt rejection. Recent efforts have focussed on using nanomaterials, particularly GO nanosheets, to achieve long-term stability and exceptional ion/water separation performance in FO membranes. This review highlighted recent developments in laminar GO-based



FO membranes for desalination, emphasising on the unique properties of GO nanosheets such as their stacked microstructure, hydrophilicity, defects, and nano-sized pores. Size exclusion mechanisms driven by narrowed nano-channels play a key role in salt rejection efficiency. The ion selectivity of GO-based laminar membranes is dominated by size exclusion, charge, and adsorption effects. Various physical techniques including vacuum/pressure-assisted filtration, spin-coating, drop-casting, and electrophoretic deposition are employed to fabricate layered r(GO)-based FO membranes with tuned inter-laminar structures. Challenges remain in achieving long-term chemical and mechanical stability, controlling membrane swelling during filtration, and addressing fabrication limitations for large-scale production. Future research should focus on understanding ion and water transport behaviours in stacked GO-FO membranes to optimise water permeability and salt rejection while overcoming trade-offs between stability and FO performance.

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# **Author contributions**

Mohamed Edokali contributed towards conceptualisation, formal analysis, resources, investigation, writing—original draft, visualisation, and review & editing. Alexander Massey contributed towards resources, investigation, and review & editing. David Harbottle contributed towards resources, review & editing, and supervision. Robert Menzel contributed towards formal analysis, resources, review & editing, and supervision. Ali Hassanpour contributed towards formal analysis, resources, review & editing, supervision, and project management. All authors discussed and reviewed the information and data included in the manuscript.

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# **Data availability**

The data and material will be made available on request.

# **Declarations**

**Conflict of interest** The authors declare that they have no known competing financial interests that could have appeared to influence the work reported in this review article.

# **Consent for publication**

All individual participants included in this review study provided informed consent prior to their participation.

# **Supplementary Information**

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