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REVIEW PAPER

Polyamide (PA)- and Polyimide (PI)-based membranes for desalination application

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Abstract

In recent years, water purification by membrane desalination techniques has been growing drastically; after all, water scarcity is a significant issue to deal with in some parts of the world. To put one step forward toward resolving the issue of water scarcity, the best way is to upgrade the current desalination technique and membranes so that the output of clear water will be improved. In this review, we will focus on enhancing some crucial properties of the Polyamide (PA) and Polyimide (PI) membranes by incorporating some functional additives. Ag NPs (Silver nanoparticles), Cu NPs (Copper nanoparticles), GO (Graphene oxide), SWCNT (Single-walled carbon nanotube), and MWCNT (multi-walled carbon nanotube) are some of the additives which can be used with PA/PI active layer to improve some essential properties of membrane-like antifouling, biofouling, low water flux, selectivity, permeability, hydrophilicity, hydrophobicity, etc. The deposition of such additives onto the surface of the Polyimide/Polyamide coat or membrane can be done using interfacial polymerization or phase inversion. Membrane filtration can be done using reverse osmosis and electrodialysis techniques. A thin-film composite membrane comprising PA and MWCNTs, yielded a water flux of almost 25.9 L m^{-2} h^{-1}, with a salt rejection of 98.1% exhibiting excellent hydrophilicity with a water contact angle of 59.6°.

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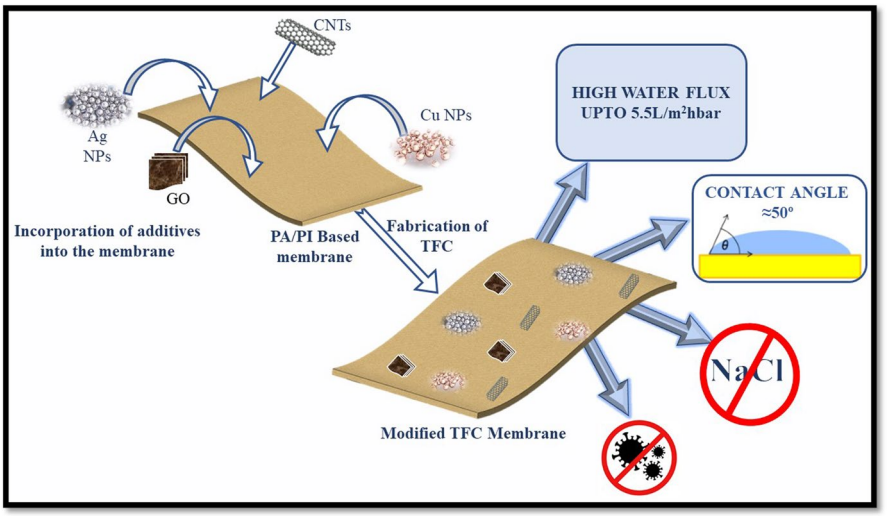
Graphical abstract



Keywords Desalination membrane · Polyamide · Polyimide · Additives · Thin-film composite

Abbreviations

aCN/AP	Silver phosphate-loaded acidified graphitic carbon nitride
Ag	Silver
Ag NPs	Silver nanoparticles
$AgNO_3$	Silver nitrate
CNT	Carbon nanotube
Cu	Copper
$CuCl_2{\cdot}2H_2O$	Dehydrated copper chloride
CuNPs	Copper nanoparticles
DAPPC	1,4-Bis(3-aminopropyl)-piperazine propane carboxylate
ED	Electrodialysis
GO	Graphene oxide
GO NPs	Graphene oxide nanoparticles
GOQD	Graphene oxide quantum dots
IP	Interfacial polymerization
MED	Multi-effect desalination
MOF	Metal organic framework
MSF	Multistage flash desalination
MTFN	Multifunctional thin-film nanocomposite
MMM	Mix matrix membrane
MPD	M-phenylene diamine
MWCNT	Muti-walled carbon nanotube

Na_2SO_3	Sodium sulfite
Na_2SO_4	Sodium sulfate
NaCl	Sodium chloride
PA	Polyamide
PAN	Polyacrylonitrile
PEI	Polyethyleneimine
PES	Polyethersulfone
PI	Polyimide
PIP	Piperazine
PSF	Polysulfone
PVDF	Polyvinylidene fluoride
PVP	Polyvinyl pyrrolidone
RO	Reverse osmosis
SPI	Sulfonated polyimide
SWCNT	Single-walled carbon nanotube
T (°C)	Temperature
TFC	Thin-film nanocomposite
TiO_2	Titanium dioxide
TMC	Trimesoyl chloride
TNT	Titania nanotubes

Introduction

Water scarcity is a significant issue in the upcoming days which means deficient availability of water resources to satisfy the amount of water usage within a particular country. This water scarcity results in more demand for water desalination [1, 2] as seawater is a significant source of salinated water [3]. So it is essential to have evolution in the current desalination processes as well as membranes employing upgrading technology or improving membrane properties by adding particular additives. The desalination process is a consumable energy process that utilizes non-conventional energy sources for operations. There are two main categories of desalination techniques: [4] membrane-based desalination and thermal desalination. The thermal desalination process has many sub-types like multistage flash (MSF) desalination, solar desalination, multi-effect distillation (MED), etc. Membrane desalination processes can be categorized into three major types, including forward osmosis, electrodialysis (ED), and reverse osmosis (RO) [5]. The desalination process involves the elimination of salts or unwanted minerals and impurities from water sources (which can be seawater, wastewater, etc.) [6], and it serves as an effective remedy for obtaining clean water for daily use for humans [5]. Membrane technology has brought about essential enhancements to the desalination sector, as it tends to be an energy-saving technique and is easily upgradable as compared to the thermal desalination process [7]. The reverse osmosis process is generally used for seawater desalination, while electrodialysis is widely used for brackish water [7]. Several examples of polymeric materials extensively used as desalination membranes,

along with their chemical structures and desalination properties (salt rejection and flux), are enlisted in Table 1.

Membranes [4] made of polymeric materials have ruled the commercial market of desalination membranes since the initial stages of desalination [8]. A polymeric membrane comprising technical feasibility [9] enhances desalination membranes' performance in terms of permeability and selectivity [10]. An extensive array of materials capable of efficacious waste water treatment have been explored by researchers in this domain [4, 6, 11–23].

Desalination membranes can also be made of ceramics or inorganic substances, as well as mix matrix membranes (MMM). Mix matrix membrane (MMM) is a membrane consisting of both organic as well as inorganic elements in it, for example, nanoparticles/polymer (TiO_2/Polyamide, etc.), carbon nanotubes/polymer (CNT/Polyimide) [8, 25], as illustrated in Fig. 1. Incorporating inorganic substances within organic desalination membranes significantly improves various membrane properties discriminatingly rendered by the individual component like exceptional biological, thermal and chemical stability of inorganic membranes combined with the favorable permselectivity, extended operation and greater packing density of polymeric membranes [10, 26–28].

This review emphasizes on specific polymers, including Polyamide (PA) and Polyimide (PI), and the mix matrix membrane (MMM) employing these polymers as desalination membranes [29]. The property alteration of these polymers through incorporation of some organic additives into the matrix material of the membrane to enhance various membrane properties [30–32] will be explored [1, 33] effectively without hindering the basic properties of the membrane. There can be many more permutations and combinations of these polymers with other additives [34] to achieve more enhanced desalination, on which further research can be done. A literature survey for this review article has been done in accordance with the SCOPUS data, Fig. 2 represents the number of yearly published articles based on Polyamide and Polyimide desalination membranes.

Polyamide-based system

Polyamide (PA) desalination membranes that are prepared through IP (interfacial polymerization) have played a significant role for the drastic growth of desalination techniques [35–37]. The inovation of a thin-film composite membrane made from Polyamides demonstrated excellent desalination performance, removing salt up to 99% from seawater by desalination through reverse osmosis. Cadotte and his coworkers, who discovered thin-film membrane in the late 70s, concluded that PA desalination membranes exhibited better performance compared to cellulosic desalination membranes [36, 38]. Interfacial condensation between *m*-phenylene diamide (MPD) and trimesoyl chloride (TMC) results in a wholly aromatic polyamide membrane [36, 37]. The interfacial polymerization technique consists of multiple condensation chemistries, involving the synthesis of Polyamide, Polyurethanes, Polycarbonate, etc. [37, 39, 40]. Polyamides also referred to as Nylons are primarily utilized for manufacturing synthetic fibers. Polyamides

Table 1 Examples of polymeric materials extensively used as desalination membranes along with their chemical structures and desalination properties [10, 24]

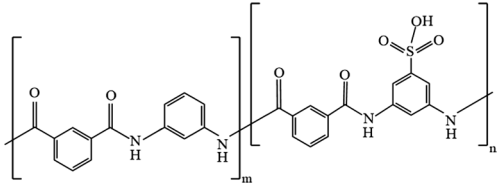
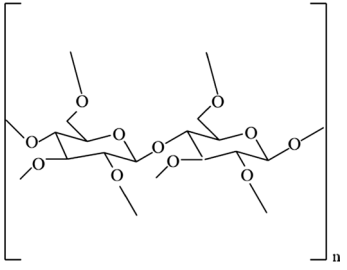
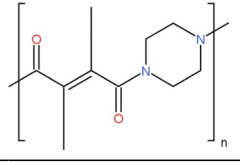
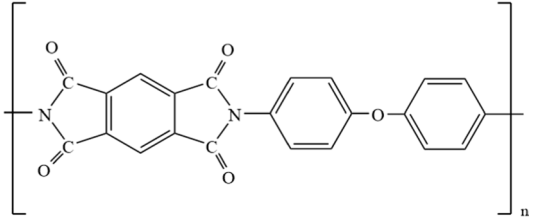
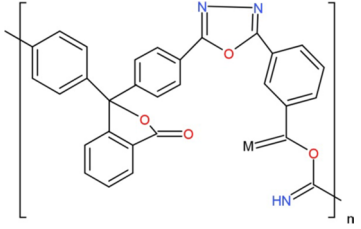
S. no	Name of polymer	Chemical structure	Salt rejection (%)	Flux (L m^{-2} h^{-1})
1	Polyamide-hydrazide (aromatic Polyamide)		99.5	27.91
2	Cellulose acetate		99	12.91
3	Polypiperzineamide		97.2	27.91

Table 1 (continued)

S. no	Name of polymer	Chemical structure	Salt rejection (%)	Flux (L m^{-2} h^{-1})
4	Polyimide		99	26
5	Polyoxadiazole		92	2.91

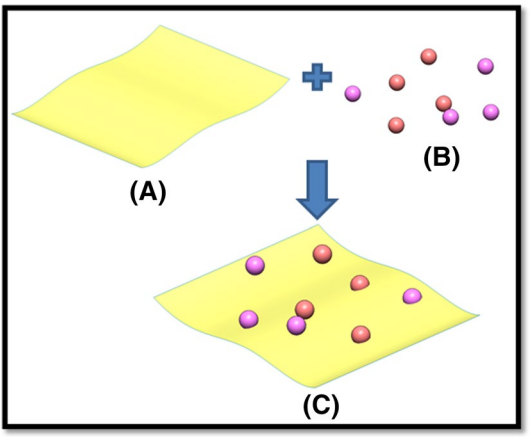


Fig. 1 Illustration of the concept of mix matrix membrane (MMM) [A]-polymeric membrane, [B]-particles of additives, [C]-MMM

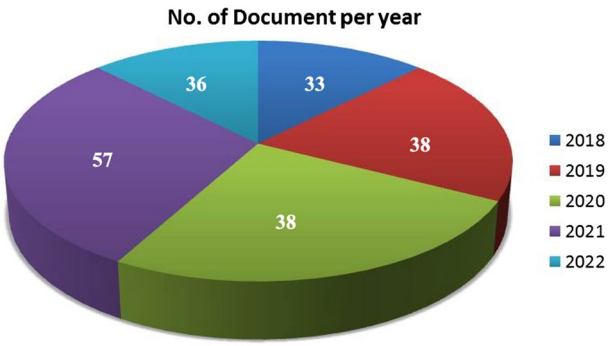


Fig. 2 SCOPUS analysis of the number of documents published in the domain of Polyamide and Polyimide desalination membranes from 2018 to 2022

Table 2 Properties of multifunctional thin-film nanocomposite (MTFN) membranes [53]

S. no	Name	Percent of additive	Water flux (L m^{-2} h^{-1})	$CaCl_2$ rejection (%)	Antibacterial properties
1	MTFN-1	0.05	45	71	Good
2	MTFN-2	0.2	52	76	Better
3	MTFN-3	0.4	55	73	Best (100%)

MTFN-1: TFN membrane comprising 0.05 wt% Ag@rGO@TiO_2; MTFN-2: TFN membrane comprising 0.2 wt% Ag@rGO@TiO_2; MTFN-3: TFN membrane comprising 0.4 wt% Ag@rGO@TiO_2

can be synthesized through self-condensation of amino acids or their cyclic lactum or via ring-opening polymerization and polycondensation of diamines and dibasic acids. Polyamides are a class of thermoplastic polymers. Recently many researches have been carried out on Polyamide, leading to the development of

their nanocomposites. Newly developed Polyamides are filled with nanofibers resulting in the enhancement of various polymer properties [41].

Polyamide with metal-based additives

PA is compounded with different additives, resulting in the enhancement of performance [23] and efficiency of desalination membranes [42]. PA can be blended with an extensive array of additives while this review will be focusing on silver (Ag), copper (Cu), graphene oxide (GO), and carbon nanotubes (CNTs): Single-walled carbon nanotube (SWCNT) and multi-walled carbon nanotube (MWCNT) nanoparticles (NPs). Silver nanoparticles possessing very good bactericidal properties are employed in the manufacturing of anti-biofouling thin-film composite-membranes to enhance the antibactericidal capacities of the membrane material. It has been recorded that silver ions and silver nanoparticle compounds can hinder intracellular protein transportation and force the active bacteria to be inactive. Also, whenever the light is used as a catalyst in a reaction, Ag ions might form oxygen sensitive species, which helps in the application of membrane sterilization [3, 43].

Ming Qiu and his coworkers have studied the Zwitterion-silver nanocomposite used for forward osmosis technique in order to enhance the water flux as well as biofouling resistance properties of desalination membranes, in which they firstly synthesized a Polyethersulfone membrane by a non-solvent induced phase separation methodology [44]. The thickness of casted membrane was kept up to 150 µm. They synthesized a PA coat onto the exterior face of the support membrane via interfacial polymerization [45] with subsequent deposition of silver nanoparticles onto the Polyamide active layers via in-situ formation [46]. As a result of this experiment, the water flux was improved from 4.92 to 7.26 L m^{-2} h^{-1} while the hydrophilicity and water bounding properties of membrane were also ameliorated. Both membranes mean normal TFC membrane, and the Zwitterion-silver thin-film composite-membrane was suspended into bacteria for 2 h. The pristine thin-film membrane showed 58% *E.coli* retention, whereas the zwitterion-silver thin-film membrane showed *E.coli* retention of about only 4% and the antimicrobial efficiency was found to be greater than 96% [46]. Similar to this work, one group of researchers studied the incorporation of hydrophilic silver NPs onto the TFC Polyamide membrane which included the primary manufacturing of Polysulfone substrate by conventional phase inversion technique [47]. Silver nanoparticles were deposited onto the Polysulfone substrate via in-situ formation [48], leading to the generation of Polysulfone-silver nanoparticle substrates. The thin-film composite was prepared by interfacial polymerization [49] involving reactions on normal Polysulfone membrane as well as the Polysulfone-silver substrate. According to the concentration of $AgNO_3$, they categorized membrane as TFCAg1, TFCAg5, TFCAg20, TFCAg50 and TFCAg100. TFC-Ag20 showed a water flux of 50 ± 4.2 l/m^2h, 170% more than a thin-film membrane without an additive, silver. TFC-Ag20 demonstrated NaCl rejection up to 99.1 ± 0.1%, while membranes without any additives showed rejection of 97.4 ± 0.5%. The size of the nano-channel produced was about 2.5 nm. Overloading silver nanoparticles (TFC-Ag100) resulted in lower water permeability as

well as poor salt rejection [50]. Also, graphene oxide (GO), silver (Ag), and titanium dioxide (TiO_2) NPs can also be combined to form a nanocomposite of Ag@rGO@TiO_2 and desalination membrane having an active Polyamide layer. Hamidreza Abadikhah and his colleagues performed research on the similar topic in which graphene oxide was synthesized via the Hummer's method [51]. They prepared a suspension of TiO_2 and $AgNO_3$ in ethylene glycol solution followed by the subsequent incorporation of the GO susupension (prepared via Hummer's method) to the suspension containing TiO_2 and $AgNO_3$ nanoparticles. Following the homogenization of these two suspensions, the mixture of these suspensions was subjected to microwave irradiation at 600 W for 5 min. Figure 3 depicts various stages involved in the synthesis of Ag@rGO@TiO_2 composite via microwave irradiation technique.

The synthesis of Si_3N_4/Polyethersulfone substrate via phase inversion technique was reported [52]. In order to fabricate the TFC membrane, interfacial polymerization between m-Phenylenediamine (MPD) and Trimesoyl chloride (TMC) onto the deposited active layer of Polyamide on the PES/Si_3N_4 surface layer was performed resulting in the generation of a multi-functional thin-film membrane. Membrane nanofiltration experiments revealed that the flux of the multi-functional thin-film membrane was 1.7 times higher than the new TFC membrane. The as-prepared membrane exhibited an Na_2SO_3 salt rejection capacity of upto 96% [53]. Table 2 enlists the characteristics of MTFN membranes comprising 0.05–0.4 wt% Ag@rGO@TiO_2.

Incorporation of metal–organic frameworks (MOFs) [54] into the membrane comprising of Polyamide can also improve the membrane properties. Alireza Zirehpour and his co-workers focused on studying the performance of desalination membranes along with their structural properties. They fabricated nano-scaled metal–organic framework particles by combining 1,3,5,-benzene tricarboxylic acid and silver to enhance forward osmosis technique. Firstly, the substrate membrane was synthesized using Polyvinylpyrrolidone (PVP) and Polyethersulfone. Then

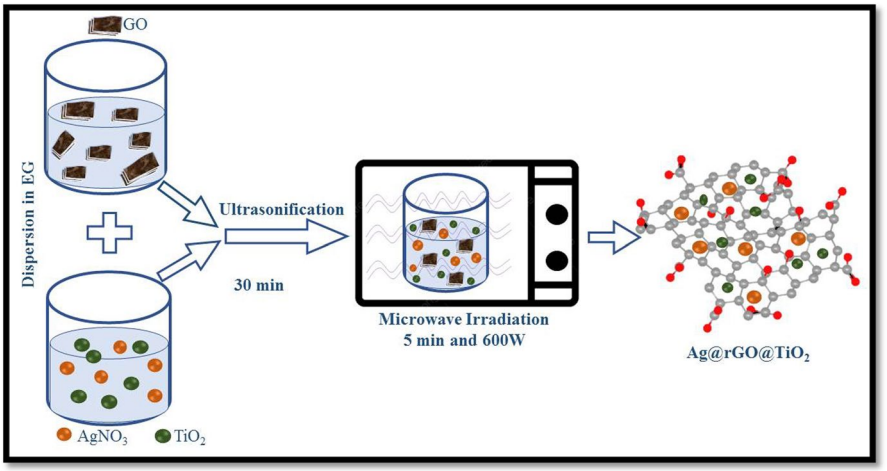


Fig. 3 Schematic illustration of the preparation of Ag@rGO@TiO_2 composite by microwave irradiation technique

thin-film membrane of Polyamide was manufactured onto the surface of the Polyethersulfone layer via IP technique followed by the subsequent deposition of MOFs onto the surface of the Polyamide active layer through interfacial polymerization. It was ascertained that the water permeability was improved by 126% when the membrane consisted of 0.04% MOF (metal–organic frameworks). Modified TFN membranes showed enhanced desalination through forward osmosis. Table 3 enlists the water flux of TFN membranes incorporating MOF in different proportions.

Also, the surface of the Polyamide layer has become more hydrophilic in nature, thereby improving the fouling resistance of the membrane [55]. Silver nanoparticles can also be combined with some carbon nitrides to enhance the forward osmosis technique; Dong wang and his coworkers tried to improve the forward osmosis performance by using a triple-layered TFN (thin-film nanocomposite) membrane. They prepared carbon nanotube dispersion according to the following method [56, 57]: aCN/AP (Silver phosphate-loaded acidified graphitic carbon nitride) was synthesized by mixing carbon nitride with AP solution [3] followed by the deposition of carbon nanotubes (CNT) onto the Polyethersulfone substrate membrane by mixing distinct amount of CNT dispersion solution onto the substrate membrane. Polyamide active coat was formed on the upper surface of the support membrane, resulting in the generation of TFN membrane. With a similar process, i.e., interfacial polymerization, they prepared TFN-aCN/AP membrane. The hydrophilic nature of membrane was enhanced by this technique. The optimized TFN-aCN/AP membrane demonstrated greater water flux of 67.0 L m^{-2} h^{-1} while the backward salt flux was found to be lower than 3 g m^{-2} h^{-1}. TFN-aCN/AP membrane exhibited very good antimicrobial properties toward both *E. coli* as well as *S. aureus* with sterilization rates of 99% and 92%, respectively [3]. Graphene oxides' quantum dots could also be used in conjunction with silver NPs, this is another viable way for altering the properties of TFC membrane, and work contingent with this combination has been reported in this domain. Shuya li and their team worked on improving the antibacterial properties of Polyamide TFN. They added GOQD (graphene oxide quantum dots) filled with silver phosphate (GOQD/AP) into a PA active coat. The AP/GOQD nanocomposite was fabricated facilely via an electrostatically driven technique [58, 59]. They prepared thin-film nanofiltration (TFN) membranes and thin-film nanocomposites comprising AP/GOQD nanocomposite membranes via interfacial polymerization carried on Polyethersulfone (PES) membrane. The final structure included a base layer of PES substrate membrane onto a Polyamide active layer with a subsequent PA active layer on its top, deposited with GOQD/AP nanocomposite through interfacial polymerization. TFN containing GOQD/AP exhibited

Table 3 Water flux of TFN membranes with different concentrations of MOF [54]

S. no	Membrane type	Concentration of MOF incorporated (%)	Water flux (compared with the flux of pristine TFN)
1	TFN-1	0.02	–
2	TFN-2	0.04	129
3	TFN-3	0.08	238

a good water flux of 39.6 L m^{-2} h^{-1} at the pressure of 15 bar. Salt rejection was retained at 98.2%. TFN membrane consisting of 50 mg L^{-1} GOQD/AP membrane exhibited robust antibacterial properties toward *E.coli* when the rate of sterilization was 99.9%. Furthermore, TFN-GOQD/AP50 demonstrated excellent anti-biofouling performance while performing RO technique [60]. Addition of silver NPs on the surface of TFC membrane showed ameliorated antifouling properties [61]. In this work, Ulrike M. Hirsch and their colleagues focused on improving the antifouling properties of the TFC membrane with help of plasma-enhanced magnetron sputtering for easing the reverse osmosis technique. They coated an active layer of Polyamide onto TFC membrane followed by plasma-activation to incorporate functional groups onto the membrane surface. Employing radio frequency magnetron sputtering at 13.56 MHz, Ag NPs were incorporated from a spherical sputter target onto the TFC membrane. The average diameter size of Ag NPs was around 30 nm. As a result of this experiment, the formation of biofilm consisting of *Pseudomonas* sp. was decreased by 64.6% at an average after a cultivation period of 14 days [62].

Table 4 enlists the properties demonstrated by Polyamide-based membranes integrated with different forms of functionalized silver nanoparticles.

Many researchers have concluded that incorporating metal nanoparticles like copper, etc., into polymeric membranes improved the antibacterial, fouling resistance, and anti-biofouling properties. Copper has been well known for its antibacterial activities for ages. Also, it is economically affordable. It is a perfect option as a biocidal agent [42]. Similar to silver, copper can also used in desalination membranes due to its various advantageous properties. In 2018, B. Rodrigues and his group members studied the incorporation of copper (Cu) nanoparticle and m-Phenylenediamine (MPD) onto the active coat of the TFC membrane to enhance their anti-biofouling properties, in which they firstly prepared a Polysulfone support membrane by using the phase inversion technique [63–65]. The TFC membrane was fabricated by interfacial polymerization of MPD and TMC onto the base membrane according to their methodology [65–67]. The modified membrane was fabricated by incorporating Cu-MPD by in-situ formation. Then the membrane was dipped into TMC solution, and interfacial polymerization was carried out, thereby curing the membrane. The modified membrane showed a decrease in hydrophilicity but had higher surface roughness. The membrane will possess copper toxicity because of its ability to release Cu^{2+} ions from the surface. Hence, while showing excellent antibacterial properties [68], it also possesses good anti-adhesion properties. Modified membrane showed salt removal of 97%. Modified membrane permeates the flux of 1.6 L m^{-2} h^{-1} bar^{-1}, which is 1.3 times higher than that of the pristine TFC membrane [69]. In a similar way as silver, copper could also be used with GO to improve various particular properties of the fabricated membrane. E. A. Ali and his group of researchers focused on improving membrane performance via surface modification and chelation to improve desalination. Firstly, they prepared a thin-film membrane containing PA active layer by IP onto the commercial PS support membrane. Employing the similar process, i.e., IP, they incorporated GO onto the surface of Polyamide active layer. Then, this modified membrane was immersed in the aqueous solution of dehydrated copper chloride ($CuCl_2 \cdot 2H_2O$). In conclusion, the PA-Cu^{2+}-GO membrane possessed greater clean water permeability of 44.25 L m^{-2} $h^{-1}$and

Table 4 Characteristics of polyamide-based desalination membranes incorporating different functionalized silver nanoparticle additives

S. no	Polymer name	Additive	Application	Synthesis	Mechanism	T (°C)	Thermo-dynamic reaction	Functional group	Result	References
1	Polyethersulfone (PES)-Polyamide	Silver DAPPC	For antimicrobial TFC Improving water flux	Interfacial polymerization	Forward osmosis	60	Exothermic	Carboxylic	• Water flux—7.261 L m^{-2} h^{-1} • Increase in hydrophilicity • *E.coli* retention only 4% • Antimicrobial efficiency > 96%	[46]
2	Polyamide	Silver	Seawater desalination Waste water reclamation	Interfacial polymerization	Reverse osmosis	60	Exothermic	Amide	• Water flux—50 ± 4.2 L m^{-2} h^{-1} • NaCl rejection – 99.1 ± 0.1% • Excess loading of additive will result in property distortion	[50]
3	Polyamide	Graphene oxide Silver NPs Titanium dioxide	Improving antimicrobial properties Membrane performance	Interfacial polymerization Microwave-assisted irradiation process	High-pressure crossflow filtration	60	Exothermic	–	• Water flux is 70% higher than that of pristine TFN membrane • Na_2SO_3 rejection –96% • MTFN-2 shows 76% $CaCl_2$ rejection • MTFN-3 exhibits a water flux of L m^{-2} h^{-1}	[53]

Table 4 (continued)

S. no	Polymer name	Additive	Application	Synthesis	Mechanism	T (°C)	Thermo-dynamic reaction	Functional group	Result	References
4	PES-Polyamide	Silver NPs	Improving structural properties Desalination performance	Interfacial polymerization	Forward osmosis	80	Exothermic	Carboxylic	• Pure water permeability—126% greater than pristine TFN modified membrane showed enhanced desalination • Water flux of TFN-3—238% of pristine TFN membrane • Hydrophilicity got improved • Fouling resistance increased	[55]
5	Polyether sulfone Polyamide	Silver phosphate-loaded acidified graphitic carbon nitride	Desalination membranes	Interfacial polymerization	Forward osmosis	60	Exothermic	–	• Water flux—67.01 L m^{-2} h^{-1} • Reverse salt flux < 3 g m^{-2} h^{-1} • Very good antibacterial properties towards both *E. coli* and *S. aureus*	[3]

Table 4 (continued)

S. no	Polymer name	Additive	Application	Synthesis	Mechanism	T (°C)	Thermodynamic reaction	Functional group	Result	References
6	Polysulfone Polyamide	Silver phosphate Graphene oxides Quantum Dots	Desalination and wastewater reclamation	Interfacial polymerization	Reverse osmosis	80	Exothermic	Amides and phosphorous	• Water flux – 39.6 L m^{-2} h^{-1} (pressure of 15 bar) • Salt rejection—98.2% • GOQD/AP50 possesses excellent antibacterial properties against *E. coli* • GOQD/AP50 also have robust antifouling property	[60]
7	Polyamide TFC	Silver NPs	Water desalination and water reclamation	Plasma-enhanced magnetron sputtering	Reverse osmosis	–	Exothermic		• The formation of biofilm having *Pseudomonas* sp. decreased by 64.6%	[62]

solute water flux of 33.77 L m^{-2} h^{-1}, whereas the unmodified membrane exhibited a clean water permeability of 21.36 L m^{-2} h^{-1}. Modified membrane showed excellent salt rejection of ≥98.5% while improving the chlorine resistance as well as fouling resistance property of TFC membrane [70]. In 2014, Moshe Ben-Sasson and his coworkers tried to functionalize the surface of the TFC membrane with Cu nanoparticles to incorporate anti-microbial properties [71]. A thin-film composite membrane of Polyamide [72], was then impregnated into isopropanol and deionized water solution, followed immersion of the membrane into a Cu NPs dispersion solution in order to functionalize the membrane surface. Salt rejection of Cu-modified membrane was found to be 98.86 ± 0.27%. The water contact angle of the functionalized membrane was 45.6 ± 8.4°, while the pristine membrane showed a contact angle of 52.6 ± 5.3° thereby slightly improving its hydrophilicity. The surface roughness of the TFC membrane got enhanced from 95 ± 11 nm to 102 ± 17 nm [42]. Table 5 summarizes the antibacterial characteristics (% bacterial removal) of functionalized TFC membranes.

Polyamide with graphene oxide nanoparticles (GO NPs)

Shahrzad Shokrgozar Eslah and his team attempted to improve the forward osmosis water desalination technique by incorporating GO (graphene oxide) nanosheet into polyamide TFC membrane. Firstly, a TFC support substrate was prepared via the phase inversion technique. Then, a PA active coat was incorporated onto the surface of the base substrate via interfacial polymerization, followed by the integration of GO nanosheets onto the surface of the TFC membrane via the same process, i.e., IP. As per the loading of the GO nanosheet, the properties of the modified membrane were altered. As a result of this experiment, water permeability was improved upto 2.02 L m^{-2} h^{-1} by incorporating 0.1 wt% GO, but the addition of 0.2 wt% of GO into the membrane resulted in lower water flux values. The surface roughness of the TFC membrane increased with GO loading [73, 74]. Salt rejection was improved up to 88% with the GO loading of 0.1 wt%, and the salt reverse diffusion was decreased upto 39% [75, 76].

Research on "PA/ GO composite membrane for enhancing pervaporation desalination process" was performed by Xiaoying Zhao and his fellow researchers. GO in its nanoform was deposited onto the Polyacrylonitrile (PAN) substrate via pressure-assisted ultra-filtration with consequent interfacial polymerization. After deposition of GO on the membrane, the PA active layer was formed onto the GO composite membrane through IP. Figure 4 illustrates different layers present in the synthesized PA/GO/PAN-thin-film composite membrane.

Table 5 Antibacterial properties of functionalized TFC membrane [42]

S.no	Name of bacteria	Bacterial removal (%)
1	*E.coli*	87 ± 02
2	*P.aeruginosa*	96 ± 3
3	*S.aures*	79.5 ± 12

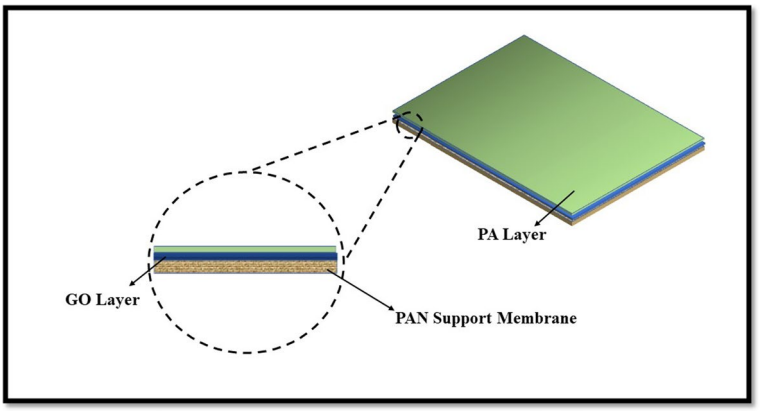


Fig. 4 Schematic representation of PA/GO/PAN-thin-film composite membrane

Through experimental analysis it was ascertained that the hydrophilicity of the TFC membrane was ameliorated. The maximum water flux recorded was upto 37.1 L m^{-2} h^{-1}. With a 50 nm layer of GO, the salt rejection was 99.80%, but the flux decreased to 28.1 L m^{-2} h^{-1} [77]. Coating of GO could be done on the support substrate in order to improve the hydrophilicity [78]. Saira Bano and her teammates were working on increasing the flux as well as the antifouling properties of the PA TFC membrane by the addition of GO NPs. GO was synthesized via Hummer's method and a coat of PA was incorporated via IP on the PSF ultrafiltration membrane [79]. Table 6 represents various characteristics of Polyamide-based composites incorporating functionalized copper nanoparticles.

Figure 5 illustrates the various stages involved in the fabrication of PA/GO TFC membranes. The blue-colored beads represented the GO particles depicting a color change of the membrane, while the IP shows the curing of the PA/GO TFC membrane.

The synthesized membrane with 0.3 wt% loading of GO showed a contact angle of $60 \pm 1°$, resulting in an enhancement of the hydrophilicity. Roughness (R_a) of the modified membrane was up to 16.38. Salt rejection of GO/PA TFC membrane was 87% and 97% for NaCl and $MgSO_4$, respectively. The water flux of the modified TFC membrane was maintained above 80 L m^{-2} h^{-1} [80]. Polyamide can also be functionalized with bactericidal graphene quantum dots; S.Fatemeh Syedpour and their teammates focused on improving the shortcomings associated with the forward osmosis method like biofouling detrimentally impacting the operational expenses, the lifetime of membrane and flux efficiency through the incorporation of bactericidal graphene quantum dots (GQDs). GQD was synthesized by the direct pyrolysis of CA [81]. Polyethersulfone membrane was manufactured via the conventional phase inversion method, and an active Polyamide coat was formed onto the surface of the membrane via IP. As a result of incorporating GQD, the hydrophilic nature of the membrane was improved, and the contact angle decreased from 72.9° to 51° (for TFC with 0.5wt.% loading of GQD). The antibacterial properties of the modified membrane is shown

Table 6 Properties of polyamide and based composites incorporating functionalized copper nanoparticles

Sr. no	Polymer name	Additive	Application	Synthesis	Mechanism	T (°C)	Thermodynamic reaction	Result	References
1	Polysulfone m—phenylenediamine	Copper chloride	Antifouling properties	Interfacial polymerization	Reverse osmosis	65, 70	Exothermic	• Increase in hydrophilicity and surface roughness • Excellent antibacterial properties • Good anti-adhesion properties • Salt removal—97%	[69]
2	Polyamide	Graphene oxide Cupric chloride	Desalination membranes	Interfacial polymerization	Membrane desalination	65	Exothermic	• Pure water permeability 44.25 L m^{-2} h^{-1} bar^{-1} • Solute water flux—33.77 L m^{-2} h^{-1} • Increase in chlorine and biofouling resistance	[70]
3	Polyamide	Copper	Antibacterial surface	Dipping membrane in Cu-NPs suspension	Reverse osmosis	–	–	• Water permeability—2.54 ± 0.19 L m^{-2} h^{-1} bar^{-1} • Salt rejection—98.86 ± 0.27% • Increase in hydrophilicity • Contact angle—45.6 ± 8.4° • Surface roughness—102 ± 17 nm	[42]

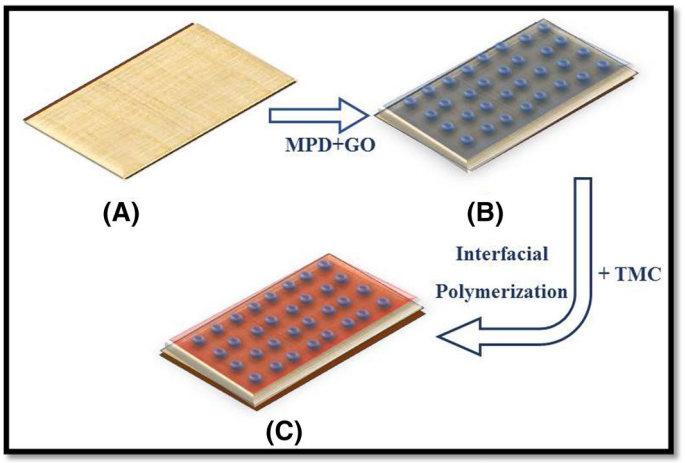


Fig. 5 Steps involved in the synthesis of PA/GO TFC membrane. (**A**) Polysulfone support membrane, (**B**) substrate with MPD and GO, (**C**) synthesized PA/GO-TFC membrane

in Table 7. When GQD loading was 0.1 wt%, the water permeability was 150% higher than that of the pristine TFC membrane [82].

Table 7 enlists the bacterial inactivation (%) of the TFC membranes modified with GQD.

Table 8 depicts the characteristics of Polyamide-based membranes encompassing functionalized GO nanoparticles.

Polyamide with carbon nanotube (CNT)

Hao Sun and his team of researchers were concentrated on improving the permeability of the TFC membrane by adding a Polyamide matrix to the MWCNT framework. They initially prepared PVDF [88] (Polyvinylidene fluoride) via a non-solvent-induced phase separation technique, followed by the production of a TFC membrane by synthesizing an active layer of PA onto the MWCNT framework. A framework of MWCNTs was deposited onto the substrate via vacuum filtration of the MWCNT suspension, with subsequent precipitation of the PA layer onto the support layer through IP. After analyzing the test results, they found out that the modified membrane demonstrated an excellent salt rejection of ≥ 99%. The contact angle property shown by the PA/MWCNT-TFC was 55.5°, whereas the pristine membrane showed

Table 7 Antibacterial property (% bacterial inactivation) of GQD-modified membrane [82]

Sr. no	Name of bacteria	Bacterial inactivation (%)
1	*E.coli*	90
2	*S.aureus*	95

Table 8 Characteristics of Polyamide-based composites incorporating GO and functionalized GO nanoparticles

S. no	Polymer name	Additive	Application	Synthesis	Mechanism	T (°C)	Thermodynamic reaction	Functional group	Result	References
1	Polysulfone (PSF) Polyamide	Graphene oxide (GO)	Improving desalination	Phase inversion	Forward osmosis	60°	Endothermic	Amide	• Water permeability—2.02 L m^{-2} h^{-1} bar^{-1} • Water Flux—34.7 L m^{-2} h^{-1} • Surface roughness increases • Salt rejection—88% • Salt reverse diffusion—39%	[75]
2	Polyamide-PAN	GO	Desalination performance	Interfacial polymerization	Dispersion	150°	–	Amide	• Increase in hydrophilicity • Water Flux—37.1 L m^{-2} h^{-1} • Salt rejection—99.80% • Water flux of 50 nm GO layer membrane—28.1%	[77]

Table 8 (continued)

S. no	Polymer name	Additive	Application	Synthesis	Mechanism	T (°C)	Thermodynamic reaction	Functional group	Result	References
3	PSF Polyamide	GO	Improving nanofiltration	Interfacial polymerization	Nano-filtration membrane	60°	Exothermic	Amides	• Contact angle—$60 \pm 1°$ • R_a roughness—16.38 • NaCl rejection—87% • $MgSO_4$ rejection—97% • Water flux- ≥ 80 L m^{-2} h^{-1}	[80]
4	PES Polyamide	Bactericidal graphene quantum dots	Improving desalination	Interfacial polymerization	Forward osmosis	80°	Exothermic	Amides	• Hydrophilicity increased • Contact angle—51° • Water permeability is 50% higher than that of the pristine membrane	[82]
5	Polyamide	AGO nanosheet	Desalination membrane	Dispersed into ethanol	Membrane filtration	–	–	Amides	• Water permeability—5.62 L m^{-2} h^{-1} bar^{-1} • Salt rejection—97.9%	[83]
6	Polyamide	GO	Improving desalination	Interfacial polymerization	Reverse osmosis	–	Exothermic	Amides	• With the loading of 80 µg of GO-salt rejection—99.7%	[84]

Table 8 (continued)

S. no	Polymer name	Additive	Application	Synthesis	Mechanism	T (°C)	Thermodynamic reaction	Functional group	Result	References
7	Polyamide	GO	Desalination membrane	–	Membrane desalination	–	–	Amides	• RMS roughness—52 ± 8 nm • Contact angle—63° • Water permeability—2.3 ± 0.4 L/m^2h.bar	[85]
8	Polyamide	Graphene oxide nanoplatelets	Desalination membrane	–	Membrane desalination	–	–	Amide	• NaCl rejection—89.3 ± 2.6% • Water flux—13.9 ± 1.2 L m^{-2} h^{-1}	[86]
9	Polyamide	Graphene quantum dots	Desalination membrane	–	Reverse osmosis	–	–	Amide	• Water Flux—40.02 L m^{-2} h^{-1} • NaCl Rejection—96.2%	[87]

a contact angle of 91.2° and the surface roughness was increased upto 53.11 nm [89]. A similar combination of materials could be used to improve the chlorine resistance and other important properties of the membrane. Junwo park and their teammates performed research on improving chlorine immunity of reverse osmosis membranes by incorporation of CNTs and they fabricated a TFC membrane encompassing MWCNT/PA via the interfacial polymerization technique.

The experiment resulted in a membrane permeate flux of 13.4 L m^{-2} h^{-1} and salt rejection of upto 92.5%. The chlorine resistance was determined by the decrease in the rejection after immersing the membrane in NaOCl (3000 ppm) solution for 4 h, after the test, the salt rejection had decreased from 92.5 to 76.5% [90]. CNTs could also be used in conjunction with titania nanotubes. I.wan Azelee and their coworkers focussed on improving the desalination of the Polyamide-TFC membrane by incorporating acid-treated carbon nanotubes-titania nanotubes (TNT). Initially, they had prepared the MWCNT and TNT hybrid composite via the hydrothermal method, after which, these hybrid composites were incorporated onto the surface of the support membrane simultaneously during IP of the polyamide coat. As a result of this experiment, researchers found NaCl salt rejection to be 97.9%. The contact angle property shown by the membrane was $69.66 \pm 4.79°$ [91].

Table 9 represents various characteristics of Polyamide-based membranes encompassing functionalized CNTs.

In 2017, Javad Farahbaksh and his colleagues studied the effect of incorporating pristine and oxidized MWCNT onto a PA membrane to enhance the antifouling properties and performance efficiency. Pristine and oxidized MWCNTs were embedded within Polyamide reverse osmosis membranes via IP technique. Membranes with pristine MWCNT exhibited a water flux of 25.9 L m^{-2} h^{-1}, while the membranes modified with oxidized MWCNT demonstrated a water flux of 28.9 L m^{-2} h^{-1}. 98.1% and 97.8% were the salt rejection of membrane when modified with pristine and oxidized MWCNT, respectively. The membrane modified with oxidized MWCNT showed a water contact angle of 59.6° [92].

Polyimide (PI)-based system

Bo Feny and his team of researchers synthesized a mixed matrix membrane (MMM) of graphene oxide/Polyimide for desalination. An aqueous suspension solution of GO was prepared, and it was synthesized by the modified Hummer's method [97] by utilizing graphite as the starting material. PI composite membranes integrating asymmetric GO/PI MMMs were fabricated using the water bath technique. Modifying the as-prepared membrane with GO/PI, rendered a water contact angle of 59°. At 90 °C, water flux becomes 36.1 L m^{-2} h^{-1}, and the salt rejection stays unchanged at 99% [98]. Additionally, Chaoyi Ba and co-workers modified P84 co-Polyimide membrane with Polyethyleneimine (PEI) to enhance nanofiltration. The P84 membrane was synthesized by the solution casting technique, followed by phase inversion. The chemical modification of P84 membrane within PEI solution engendered the formation of TFC membrane. As a result of this trial, the optimized membrane demonstrated salt rejection of $50.9 \pm 5.1\%$ and flux of 54.16 L m^{-2} h^{-1} at 13.88 bar

Table 9 Characteristics of Polyamide-based membrane encompassing pristine and functionalized CNTs

Sr. no	Polymer name	Additive	Application	Synthesis	Mechanism	*T* (°C)	Thermodynamic reaction	Functional Group	Result	References
1	PA	MWCNT	Desalination membrane	Interfacial polymerization	Reverse osmosis	75	Exothermic	Amide	• Good chlorine resistance • Water flux—13.4 L m^{-2} h^{-1} • Salt rejection—92.5%	[93]
2	PA	Raw MWCNT Oxidized MWCNT	Water desalination	Interfacial polymerization	Reverse osmosis	50	Exothermic	Amide	• Water flux (L m^{-2} h^{-1})- • Raw MWCNT-25.9 • Oxidized MWCNT-29 • Salt rejection (%)- • Raw MWCNT-98.1 • Oxidized MWCNT-97.8 • Contact angle—59.6°	[92]

Table 9 (continued)

Sr. no	Polymer name	Additive	Application	Synthesis	Mechanism	*T* (°C)	Thermodynamic reaction	Functional Group	Result	References
3	• Piperazine • PA	Raw MWCNT Oxidized MWCNT	Water desalination	Phase inversion	Membrane desalination	70	Endothermic	–	• Surface roughness (nm) • Raw MWCNT-17–27 • Oxidized MWCNT-14–23 • Contact angle (°) • Raw MWCNT-62 • Oxidized MWCNT-51.4 • Water flux (L m^{-2} h^{-1}) at 10 Bar- • Raw MWCNT-58.8 • Oxidized MWCNT-65.7 • Na_2SO_4 rejection (%)- • Raw MWCNT-97.7 • Oxidized MWCNT-97.9	[94]

Table 9 (continued)

Sr. no	Polymer name	Additive	Application	Synthesis	Mechanism	T (°C)	Thermodynamic reaction	Functional Group	Result	References
4	PA polysulfone	Carboxylated MWCNT	Desalination purpose	–	Forward osmosis	–	–	Amide	• Water flux—73.15 L m^{-2} h^{-1} • Salt rejection-90.1% • Contact angle-41.85° • Surface roughness (*Ra*)- 67.30 nm • Reverse solute flux-2.76 ± 1	[95]
5	Polyamide	MWCNT	Desalination membrane	Interfacial polymerization	Reverse osmosis	–	–	Amide	• Water flux -68.3 L m^{-2} h^{-1} • NaCl rejection—96% • Increase in surface negative charges • Contact angle-29° • Increase in hydrophilicity	[96]

pressure [99]. Apart from pristine Polyimide system, modified Polyimides were also studied, for instance, Geetanjali Shukla and her teammates focused on enhancing the desalination performance of the membrane by adding phosphorylated GO-sulfonated Polyimide (SPI) composite. Phosphorylated GO was synthesized by treating oxygenated GO with 3-aminopropyltrimethoxysilane [100]. Sulfonated Polyimide (SPI) was manufactured by sulfonation of 4,4'-bis(4-aminophenoxy)biphenyl as per their technique[101]. Finally, SPI/PGO -TFC membrane was fabricated via solution casting. Encompassing PGO with the membrane improved the membrane's oxidative, mechanical, and thermal resistant characteristics. The optimum SPI/PGO membrane possessed an ionic conductivity of 6.8×10^{-2} S/cm, which was most suitable for electrodialytic water desalination [102]. Chengyu Yan and their coworkers researched on improving the desalination of nanofiltration membranes by crosslinking PI with PA (MPD). Nanofiltration TFN membranes were synthesized via IP of Piperazine (PIP) and MPD [38, 103–105]. The as-prepared modified membranes demonstrated Na_2SO_4 and NaCl rejection upto 99.13% and 97.45%, respectively. The modified membranes also exhibited a water contact angle of 54.28° indicating hydrophilicity of the prepared membranes. After soaking the membrane insolvent for several weeks, the membrane showed more than 90% rejection of Na_2SO_4, indicating excellent solvent resistance [106]. Table 10 represents the characteristics of Polyimide-based composite desalination membranes incorporating different additives.

Conclusion and future scope

In upcoming days, the central issue of shortage of drinking and usable water will arise someday since there are minimal resources of usable water. So, in the future, there will be a significant need to improve desalination technology and apply desalination techniques on a large scale to meet the necessary water supply for daily use in the world. The heart of the desalination technique is at its membrane use since the actual salt removal is caused by a membrane only. Polymeric membranes are predominantly employed for desalination applications. Being lightweight, polymeric membranes provide better strength-to-weight ratio, and most importantly, they are corrosion resistant and readily available. In order to enhance the membrane characteristics, many researchers have combined various polymeric materials to synthesize a TFC membrane, for example, PSF/PA, PSF/PI, PAN/PA, etc. Another way to alter the membrane properties is to incorporate various functional additives into the membrane like silver, copper, CNTs, GO nanoparticles etc. These additives can be added to the surface of the membrane via a particular process to improve a particular property/set of properties of TFC membranes.

In this review, we have deeply emphasized on desalination membranes comprising Polyamide and Polyimide. Polyamide and Polyimide are used in combination with certain additives that are deposited on the surface of the membrane to improve a diverse array of membrane properties like water flux, salt rejection, hydrophilicity, fouling resistance, anti-bactericidal properties, etc. The following conclusions can be drawn from this review:

Table 10 Characteristics of Polyimide-based composite desalination membranes integrating different additives

S. no	Polymer name	Additive	Application	Synthesis	Mechanism	T (°C)	Thermodynamic reaction	Result	References
1	Polyimide	Graphene oxide	Desalination membrane	Wet phase inversion	Membrane desalination	60	Endothermic	• Contact angle—59° • Water flux—36.1 L m^{-2} h^{-1} • Salt rejection—99%	[107]
2	Polyimide	Polyethylenimine	Nano-filtration	Phase inversion	Membrane filtration	70	Endothermic	• Salt rejection—50.9 ± 5.1% • Water flux—54.16 L m^{-2} h^{-1} at 13.88 bar	[99]
3	Sulfonated Polyimide	Phosphorylated graphene oxide	Water desalination	Sulfonation	Membrane filtration	–	–	• Ionic conductivity—6.8×10^{-2} S/cm	[102]
4	Polyimide	PA	Solvent-resistant nanofiltration	Interfacial polymerization	Membrane filtration	80	Exothermic	• Na_2SO_4 rejection—99.13% • NaCl rejection—97.45% • Contact angle—54.28° • Excellent chlorine resistance	[106]
5	Polyimide	Graphene oxide	Salt removal	–	Membrane desalination	60	–	• Salt rejection—99% • High water permeability • Surface roughness—1.14 nm (R_a) • Contact angle—68° • Water flux—≥ 26 L m^{-2} h^{-1}	[24]

Table 10 (continued)

S. no	Polymer name	Additive	Application	Synthesis	Mechanism	*T* (°C)	Thermodynamic reaction	Result	References
6	Polyimide	Grapheneoxide	Seawater desalination	Phase inversion	Membrane filtration	60	Endothermic	• Water flux at 90°C—36.1 L m^{-2} h^{-1} • Salt rejection—99% • Tensile strength—8.41 MPa	[98]
7	Polyimide	Graphene oxide	Water desalination	Interfacial polymerization	Reverse osmosis	–	Exothermic	• Water flux—31.80 L m^{-2} h^{-1} • Salt rejection—98.8% • Very good antifouling properties • Enhanced chlorine resistance with flux of 36.3 L m^{-2} h^{-1} and salt rejection of 98.5%	[108]

- Anti-bacterial capabilities of silver NPs and copper NPs are the best, resulting in improved anti-biofouling properties.
- The addition of graphene oxide to the TFC membrane enhances mechanical strength and increases hydrophilicity.
- Incorporating CNT onto the membrane improved desalination at slightly higher temperatures without any membrane distortion.
- Even a little excess loading of GO and CNTs in the TFC membrane can result in a significant reduction in permeability.
- A life cycle evaluation of any modified TFC membrane may be performed to determine the membrane's effective life duration.
- There can be desalination consisting of two different mixed matrix membranes, for example, the system containing PA/GO/PSF TFC membrane and A/PI/PSF TFC membrane arranged in an alternating manner to achieve maximum rejection or other requirements through a single system.
- In most cases, Polysulfone, Polyethersulfone, Polyacrylonitrile and Polyvinylidene fluoride have been used as membrane support materials.

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