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Recent Advances in Functionalized Polymer Membranes for Biofouling Control and Mitigation in Forward Osmosis

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Abstract

Forward osmosis (FO) is an osmotically driven process widely studied for water desalination, wastewater treatment, and water reuse, as well as dilution and concentration of aqueous streams. However, its application is still hampered by the lack of ideal draw solutes, high-performance membranes, and fouling/biofouling. Biofouling is particularly challenging when FO is applied for seawater desalination and wastewater treatment. Over the last decade, many attempts have been made to exploit advances in materials science to obtain membranes with anti-biofouling properties to prevent or to reduce the detrimental effects of this phenomenon. In this review, we address the various approaches of membrane surface functionalization for biofouling control and mitigation. Recent developments in surface modification of thin-film composite and asymmetric membranes using surface coating, surface functionalization, and incorporation of tailored materials for biofouling control in FO are critically discussed. The future perspectives of anti-biofouling materials and FO membranes are reviewed to shed light on the future research directions for developing the true potential surface modification approach for the FO process.

Keywords: Advanced materials, Membrane surface functionalization, Biofouling mitigation, Forward osmosis, Water treatment, Water purification.

1. Introduction: FO Opportunities, Challenges, and Process Description

Forward osmosis (FO), introduced by Kessler and Moody in 1976, is one of the promising energy-efficient and sustainable membrane technologies for aqueous separation processes [1]. Although FO was introduced over four decades ago, research interest in FO has increased recently, with over 1700 total publications since 2006 and the numbers increasing year-on-year [2]. FO membranes are used in diverse applications, such as desalination and wastewater reuse [3], osmotic membrane bioreactors [4], power generation [5], and food processing [6]. Despite the developments achieved by membrane-based technologies, fouling is still the most challenging problem in their industrial implementation. Fouling is defined as a process in which colloidal particles, organic and inorganic matter, and biological materials deposit on the surface of the membrane or in the membrane pores during filtration. Membrane fouling results in higher feed pressures, higher operational costs, higher demand for chemical cleaning, and shorter overall membrane life. Biofouling is a specific type of fouling caused by the deposition and growth of living organisms and microorganisms on the surface [7, 8].

Filtration of biologically contaminated wastewater by membranes results in microbial cell multiplication, colonization, and attachment to the surface of the membrane. The exopolymeric substances that microorganisms typically produce form a biofilm that impairs membrane performance [9]. The intensity of biofouling differs based on wastewater characteristics, including: (1) nutrient content, (2) available biological species and concentration, (3) temperature, (4) light exposure, (5) turbidity and (6) currents (tides and waves) [10]. Depending on the interactions between microorganism and membrane surface, biofouling can be promoted or prevented. **Table 1** classifies the parameters affecting biofouling, including membrane, environment, and microbial characteristics [10, 11]. Several studies have

been published discussing advances in FO membrane fabrication and properties [12-14]. However, to the best of our knowledge, there is no comprehensive study to review the surface modification strategies of TFC FO membranes for fouling and biofouling control and mitigation.

Table 1. Parameters affecting biofouling in membrane processes [10, 15].

Affecting Parameters Category			
Microorganism	Membrane Properties	Feed Water	Draw solute
Species	Chemical composition	Temperature	Solute type
Composition of mixed population	Surface charges	pH	Concentration
Population density	Surface tension	Dissolved organic matter	Size/Size distribution
Growth phase	Hydrophobicity	Dissolved inorganics	pH
Nutrient status	Conditioning film	Suspended matter	Viscosity
Hydrophobicity	Roughness	Viscosity	Temperature
Surface charges	Porosity	Shear forces	Velocity
Physiological responses		Boundary layer	Shear Forces
		Flux/Velocity	

FO involves two streams flowing tangentially on the two sides of a semipermeable membrane. The driving force for mass transport is provided by the difference in osmotic pressure between the two sides of the membrane (feed solution (FS) and draw solution (DS)). This chemical potential difference results in a net transport of mass from the stream with lower osmotic pressure (feed solution) to the other stream (draw solution) with higher osmotic pressure. In other words, the concentrated stream or draw solution exerts a higher osmotic pressure and draws water, solvents or a targeted substance from the feed solution [16]. Since the FO process is osmotically-driven, there is no need for an external energy sources, other than a

small pressure of around 1-2 bar to overcome the frictional resistance in the flow channels. In particular, the absence of hydraulic pressure results in lower biofouling in FO compared to reverse osmosis (RO). That being said, when it comes to the production of freshwater from a contaminated feed stream, FO cannot be applied as a single unit process since it only dilutes the draw solution and concentrates the feed solution. A second separation stage is needed to regenerate the draw solution [17]. This is the reason why FO is mostly used only as a pretreatment for purification of highly contaminated waters [18, 19]. The physicochemical characteristics of the draw solution are also determinants of the FO performance. Several reviews have covered different aspects of draw solution development [20, 21]. These studies have assessed the effect of novel polymeric, organic, inorganic, and magnetic draw solution on the FO membrane performance [22, 23].

1.1. FO Membranes: Requirements and Design Criteria

FO uses polymeric membranes similar to those used in many other membrane-based separation processes. Two main types of membranes have been applied in FO: (1) thin-film composites (TFC) membranes formed by interfacial polymerization on a porous substrate, and (2) phase inversion cellulosic membranes. Both FO membrane types can come in one of three structures: flat sheet, hollow fiber, or as electrospun layers. Additionally, numerous pre- and post-modification techniques can be used to improve the membrane performance for specific applications, including mixed-matrix membrane, surface coating, surface functionalization, and incorporation of nanoparticles [24, 25].

1.1.1. Thin Film Composite Membranes (TFC)

TFC membranes used in FO are commonly formed by interfacial polymerization (IP) via the polycondensation reaction between two monomers on the surface of a porous substrate (usually an ultrafiltration membrane). The IP process starts with the immersion of the substrate into the aqueous solution containing an amine-rich monomer. Then, the amine saturated membrane is immersed into an organic solvent containing acylchloride monomers. The reaction between the monomers at the interface of the two immiscible solvents results in the formation of a thin and dense layer on top of the substrate [26, 27]. It is also worth mentioning that selecting more hydrophilic sublayers can enhance water flux and reduce internal concentration polarization (ICP) [26, 28]. Typical monomers used for IP are listed in **Table 2**, while typical supports used to fabricate TFC FO membranes are summarized in **Table 3**.

1.1.2. Cellulosic FO Membranes as Integrated Asymmetric membranes

The invention of the Loeb-Sourirajan membrane fabrication procedure in the 1960s has had a substantial and lasting impact on the application of membranes [29, 30]. Since then, cellulosic membrane attracted attention due to the simplicity of their synthesis [31, 32]. Cellulose FO membranes are commonly produced through nonsolvent-induced phase separation methods [33]. However, pH sensitivity, temperature resistance, and biofouling mitigation are three critical weaknesses of the cellulosic FO membrane [21].

Table 2. Recent monomers for the fabrication of thin film composite membranes and recent sublayers for used for FO membranes [21]. (reproduced with permission from Elsevier)

Aqueous Phase Monomer	Organic Monomer	Ref	Aqueous Phase Monomer	Organic Monomer	Ref
m-phenylenediamine (MPD), 2,5-diamino-N-(4-aminophenyl) benzamide (DABA)	trimesoyl chloride (TMC)	[34]	MMPD, MPD	Cyclohexane-1,3,5-tricarbonyl chloride (HTC), TMC	[35]
Dopamine	TMC	[36]	Bisphenol A (BPA)	TMC	37]
MPD	2,4,4',6-biphenyl tetraacyl chloride (BTAC), 2,3',4,5',6-biphenyl pentaacyl chloride (BPAC), 2,2',4,4',6,6' biphenyl hexaacyl chloride(BHAC), 3,3',5,5'-biphenyl tetraacyl chloride (BTEC), TMC	[38]	MPD ,o-aminobenzoic acid-triethylamine salt (o-ABA-TEA), m-aminobanzoic acid-triethylamine salt, (m-ABA-TEA), 2-(2-hydroxyeythyl) pyridine, 4-(2-hydroxyethyl) morpholine	TMC	[39]
Piperazine (PIP)	BETEC	[40]	MPD, 2,2'-benzidinedisulfonic acid (BDSA)	TMC	[41]
PIP	BHAC	[40]	PIP, N-aminoethyl piprazie propane sulfate (AEPPS)	TMC	[42]
Disulfonated bis[4-3 aminophenoxy)phenyl].sulfone (S-BAPS)	TMC	[43]	Triethanolamine (TEOA), N-methyl-diethanolamine (MDEOA)	TMC	[44]
Ethylenediamine (EDA), Hyperbranched polyethyleneimine (PEI), Diethylenetriamine (DETA)	TMC	[45]	Polyamide polyvinylamine (PVAm)	IPC	[46]
MPD	TMC, 5-isocyanato-isophthaloyl chloride (ICIC), Chloroformyloxyisophthaloyl chloride (CFIC)	[47]	4-aminobenzoylpiperazine (4-ABP)	TMC	[48]
MPD	CFIC, Terephthaloy chloride (TPC), Isophthaloyl chloride (IPC)	[49]	MPD	2,4,6-pyridinetricarboxylic acid chloride (PTC), TMC	[50]
m-phenylenediamine-4-methyl (MMPD), n,n"-dimethyl-m-phenylenediamine (DMMPD), MPD	CFIC, TMC	[51]	MPD, 1,2-diamino,2-hydroxypropane (DAHP)	TMC	[52]
MPD	1,2,4,5-benzene tetracarbonyl chloride (BTC), TMC	[53]	Bis-2,6-N,N-(2-hydroxyethyl) diaminotoluene	TMC	[54]
PIP, 2,2'-oxybis-ethlamine (2,2'-OEL)	TMC	[55]	melamine	TMC	[56]

Table 3. Recent sublayers used for FO membranes [52]. (reproduced with permission from Elsevier)

Support Material	Geometry	Performance	Operating Condition	Ref	Support Material	Geometry	Performance	Operating Condition	Ref

		FO Mode		Feed Solution		Feed Solution	Draw Solution	
		Water Flux (LMH)	Salt Flux (gMH) or % R	Water Flux (LMH)	Salt Flux (gMH)			
PSf	Flat sheet	9.5/12.0	2.4/4.9	18.1/20.5	6.3/5.9	10 mM NaCl	0.5 M NaCl	[57]
PSf	Flat sheet	20.1	2	33.1	2.6	DI water	0.5 M NaCl	[59]
PSf/ SPEK	Flat sheet	35	7	50	9	DI water	2.0 M NaCl	[61]
PES/ PESU-co-sPPSU	Flat sheet	21	2.2	33	2.8	DI water	2.0 M NaCl	[63]
sPPSU	Flat sheet	48	7.6	54	8.8	DI water	2.0 M NaCl	[65]
Hydrolysed CTA	Flat sheet	–	–	2.4–6.7	8.0–47.8	DI water	1.5 M NaCl	[67]
PDA-modified PSf	Flat sheet	8.2	1.4	24	1.8	DI water	2.0 M NaCl	[69]
PSf/ PES	Flat sheet	27.6	37.5	–	–	DI water	2.0 M NaCl	[71]
PES/ SPSfa	Flat sheet	26	8.3	47.5	12.4	DI water	2.0 M NaCl	[73]
Carboxylated PSf	Flat sheet	18	2.2	27	5.5	DI water	1.0 M MgCl2	[75]
PSf-PET fabric	Flat sheet	0.5–25	95.8-99.3	–	–	DI water	1.0 M NaCl	[77]
PSf-PET fabric	Flat sheet	18.2	97.4%	–	–	DI water	1.5 M NaCl	[79]
PEI/PAA-coated hydrolyzed PAN-PET fabric	Flat sheet	24.6	2. 4	32.9	3.8	DI water	0.5 M NaCl	[77]
Hydroxyl functionalized PTA-POD	Flat sheet	37.5	5.5	78.4	12.3	DI water	1.0 M NaCl	[82]
PES	Hollow fibre	16.7–18.7	1.2–2.0	43.6–49.4	2.8–4.0	DI water	0.5 M NaCl	[84]
PES	Hollow fiber	–	–	42.6	4	DI water	0.5 M NaCl	[86]
PVDF	electrospun nanofiber	30.4	6.4	–	–	DI water	1.0 M NaCl	[70]
PSf-PET fabric	Flat sheet (co-casting)	31.1	8.5	60.3	17.6	DI water	1.0 M NaCl	[58]
PSf/ silica (3 wt%)-PET fabric	Flat sheet (co-casting)	31	7.4	60.5	16	DI water	1.0 M NaCl	[60]
PSf/ TiO2(0.5 wt)	Flat sheet	17.1	2.9	31.2	6.7	10 mM NaCl	0.5 M NaCl	[62]
PSf/ rGO-modified graphitic carbon nitride (0.5 wt%)	Flat sheet	41.4	9.6	–	–	DI water	2.0 M NaCl	[64]
PSf/ zeolite (0.5 wt%)	Flat sheet	40	28	86	57	DI water	2 M NaCl	[66]
PES/MWCNTs (2.0 wt%)	Flat sheet	–	–	12	94.7	10 mM NaCl	2 M glucose	[68]
PVDF nanofiber	Flat sheet	11.6/28	3.5/12.9	47.6	6.4/21.6	DI water	1.0 NaCl	[70]
Polyketone	Flat sheet	12.6–29.3	2.0–3.8	22.6–41.5	2.8–5.0	DI water	0.6 M NaCl	[72]
PAN	Flat sheet	9.25	5.8/6.4	11.6/13.9	5.8/6.4	DI water	0.5 M NaCl	[74]
Nylon 6,6 microfiltration membrane	Flat sheet	6	0.7	21.5	0.8	DI water	1.5 M NaCl	[76]
CAP	Flat sheet	80.1	10	128.8	19.4	DI water	2.0 M NaCl	[78]
CAPa	Flat sheet	–	–	31.8/35.0	1.6/1.9	DI water	2.0 M NaCl	[80]
PES	Hollow fiber	5/14	2.1/1.8	12.9/32.2	5.0/3.5	DI water	0.5 M NaCl	[81]
PES	Hollow fiber	32.1–34.5	6.2–9.9	57.1–65.1	6.9–12.3	DI water	2.0 M NaCl	[83]
PES	Hollow fiber (double-skinned)e	14.2–17.3	3.5–4.2	32.7–38.4	3.6–4.0	DI water	0.5 M NaCl	[85]
PAI	Hollow fiber (double-skinned)e	16.9	16	41.3	5.2	DI water	2.0 M NaCl	[87]
PVDF-0.5SiO2	electrospun nanofiber	83	63.91	–	–	DI water	2.0 M NaCl	[88]

2. Biofouling in Forward Osmosis Membranes

2.1. Definition and Mechanisms

Biofouling is defined as microbial deposition onto a surface with subsequent growth to form a biofilm. Biofouling can occur in any membrane filtration unit where a membrane is submerged in a non-sterile aqueous system, even in oligotrophic environments. The membrane represents an ideal habitat for diverse microorganisms (such as *Pseudomonas*, *Aeromonas*, *Corynebacterium,* and *Fluviicola*) [89], which can attach, grow, and replicate on its surface, eventually forming mixed-species communities [90]. This phenomenon has been studied for the past decades, during which researchers have demonstrated the formation of complex biofilms on the membrane surface due to bacterial colonization [91]. The biofilm acts as an additional layer that increases the overall hydraulic resistance to mass transport, and it compromises the membrane integrity, in turn affecting system productivity [92]. Among the different fouling phenomena, biofouling is considered the most complicated and challenging phenomenon. This complexity is due to the microorganisms' capability of fast reproduction and high resilience to the surrounding environment [93]. Organic and inorganic fouling can generally be managed by reducing the concentration of the undesirable species in solution through feed pretreatments [94], but bacterial growth is usually inevitable whenever nutrients are present in the water [95, 96].

Figure 1 schematically depicts the biofilm formation and growth. Biofouling initiates with bacteria cell transportation through the solid-liquid interface and continues with the attachment of bacteria cells to the membrane surface, often as a result of electrostatic interactions between membrane and bacteria [97]. Along with electrostatic interactions, biofouling is influenced by other important factors, i.e., the membrane physical properties

(roughness, hydrophobicity, electro-kinetic charge, and pore size), the physio-chemical characteristics of the feed solution (temperature, pH, ionic strength and composition, nutrients, pollutants, and osmotic pressure), and by microbial properties (size, cell surface hydrophobicity, and charge). It is also influenced by the presence of pre-absorbed macromolecules, often generated by the bacterial cells themselves [98]. One of the major categories of biofouling precursors is transparent exopolymer particles (TEPs). TEPs are organic compounds, mostly comprising polysaccharides, dissolved in water and with typical gel-like structure and sticky properties [99]. TEPs can contribute actively to bacterial attachment providing a nutritious substratum for bacteria colonization and enhancing the adhesion of microorganisms to the membrane surface.

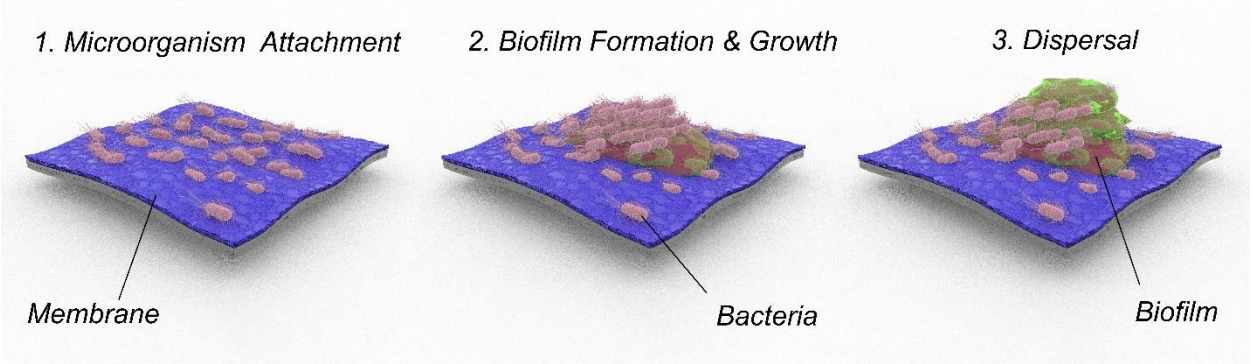

Figure 1. Biofilm formation steps, (1) attachment to the surface, often preceded by a surface conditioning step and/or by deposition of organic material (2) growth and creation of microcolonies, and (3) expansion of the biofilm to other areas, often followed by detachment of part of the biofilm and dispersal

The formation of floating proto-biofilms in water, composed by TEPs and microorganisms, can strongly enhance biofouling in membrane systems [100]. Control of organic fouling is thus essential for the prevention of biofouling in membrane-based water treatment processes. It should also be noted that synergetic biological, organic, and colloidal fouling usually leads to a more severe flux decline than the algebraic sum of flux declines by the

individual foulants. Flagellar motility can also help microorganisms overcome possible membrane repulsive forces [101].

Extracellular polymeric substances (EPSs) are organic macromolecules consisting mostly of proteins and polysaccharides that can surround the bacterial cell, embed the microorganism, and also detach from the cell [102]. EPSs prevent the direct contact of the cell with the adverse surrounding environment and are responsible for biofilm development, thanks to their aptitude of adhesion to the membrane surface [103]. EPSs are characterized by numerous functional groups and large surface area, which facilitate the attachment [103]. Not only do EPSs cause bacterial proliferation and biofilm formation, but they can also affect the membrane performance directly through pore blocking or cake-enhanced concentration polarization. If EPSs generate a stagnant liquid layer on the membrane surface, this unstirred layer lowers both the turbulence flow at the solid-liquid interface and thwarts the back-diffusion of solutes, which consequently decreases the driving force to water permeation and increases solute passage through the membrane [103].

Biofilms present heterogeneous compositions, which may vary consistently from the suspended biomass. Based on different system operating conditions, a different biomass distribution between external and internal biofilm has been reported [104]. Also, after biofilm formation, other foulants can react with the biofilm and increase the intensity of biofouling [105]. Usually, cell development at the surface contributes more to biofilm accumulation than does the adhesion of other cells from the feed suspension, leading to an exponential development of the biofilm right after bacteria attachment to the surface [106]. Therefore, pretreatment to reduce the concentration of nutrients in the feed solution is a key factor in slowing down the kinetics of biofouling. Specifically, not only more robust feed pretreatments

are necessary to remove nutrient and organic macromolecules from solution, but also periodic membrane cleaning with biocides or oxidizing agents is compulsory to extend the membrane lifetime [107, 108].

2.2. Parameters Influencing Biofouling in Forward Osmosis

It is generally accepted that fouling in osmotically driven membrane processes (ODMPs) is less problematic than in pressure-driven membrane processes (PDMPs). The fouling layer formed on the FO membrane surface is usually less compact than that formed in RO or NF, due to the lack of hydraulic pressure [109]. Therefore, fouling in FO is usually more reversible [110]. However, biofouling still represents one of the major challenges for the advancement of FO and it will be one of the most important topics for future research activity, especially considering that FO is increasingly being employed in processes treating complex feed sources, such as in bioreactor systems or microalgae separation for biodiesel production, where PDMPs are prone to irreversible fouling [111].

Unlike PDMPs, nutrients for biofilm development in FO can derive not only from the feed water but also from the draw solution, as a result of the reverse solute diffusion through the membrane into the feed solution [95]. For example, this can occur with draw solutions containing fertilizer solutes or ammonia-carbon dioxide salts. This mechanism may be particularly important when the draw solutes consist of short-chain organic molecules, such as salts of volatile fatty acids [112]. Even simple inorganic draw solutes can enhance biofilm formation (e.g., EPS secretion from the utilization of magnesium-based draw solutes) [113]. Also, cellulose triacetate (CTA) membranes used in FO membrane bioreactors can be

biologically degraded by the microorganisms during the development of their colonies and provide themselves a nutrient source [114].

The configuration of the spacer used in the FO membrane module is another important factor affecting biofouling. Valladares Linares *et al.* have studied the impact of the spacer thickness on biofilm formation, showing the benefits derived from the utilization of a thicker spacer during FO filtration. These results are rationalized with the higher turbulence flow generated at the solid-liquid interface, which decreased both the attachment and the extent of solute concentration polarization, hence the availability of nutrients [115]. This is also in accordance with organic/inorganic fouling where higher linear flow velocity at the membrane interface generally improves the system performance [116].

Experiments performed with the same membrane materials and under identical processing conditions in FO and RO have shown different biofilm characteristics. The biofilm formed in RO was thinner and more compact [117]. Also, the bacteria concentration in the biofilm was found to be 1.5 times higher in RO compared to FO. Kwan *et al.* have reported a 10% flux decline in FO, compared to a decrease of almost 30% observed during the analogous RO process as a result of a more compacted biofilm [118]. Therefore, the increase of the hydraulic resistance and the enhancement of the concentration polarization are more significant in the case of the RO system. Characterizations have shown a sparser, thicker, and more distended finger-like/mushroom structure of the biofilm developed on FO membranes [117].

One of the most promising applications for FO is its integration into membrane bioreactor systems (MBRs) to form FO-MBRs. Nevertheless, biofouling is also recognized as a challenge adversely affecting the performance of FO-MBR systems. Specifically, there are reports of large water flux decline due to biofouling in FO-MBR even with the implementation

of osmotic backwashing [119], suggesting the necessity of chemical cleaning in the presence of microorganisms and bacteria in the feed water. Several factors influence the extent of biofouling in FO-MBR. The level of aeration and the presence of soluble microbial products are arguably the most important aspects [120]. Studies have proven that increasing the overall oxygen concentration in the feed water results in less biofouling. In bioreactor systems, bacteria are also commonly producing organic compounds denoted as soluble microbial products (SMPs), which can impact the quality of the feed and permeate water [121]. Previous studies have shown higher fouling potential of SMPs compared to common organic macromolecules, such as colloidal NOM or BSA [122]. SMPs may thus act as a potential substratum, enhancing bacteria attachment and their proliferation on the membrane surface [123].

2.3. Biofouling Monitoring and Characterization Techniques

The purpose of biofouling monitoring and characterization in membrane processes is to identify the formation and growth of biofilms, as well as to monitor cell accruement and suggest the proper strategies for biofouling mitigation [10]. Moreover, characterization can help engineers to better predict membrane performance in different processes. The methods used to monitor and characterize membrane biofouling include a range of techniques, from simple primary detection via eyesight to advanced techniques, such as microscopy techniques (light microscopy, epifluorescence microscopy (EFM), electron microscopy, confocal laser scanning microscopy (CLSM), and atomic force microscopy (AFM)) and spectroscopy techniques (Raman spectroscopy, infrared spectroscopy, bioluminescence, fluorometry techniques, nuclear magnetic resonance (NMR) spectroscopy, photoacoustic spectroscopy (PAS), Fourier transform infrared spectroscopy (FTIR), and three-dimensional excitation-emission matrix fluorescence

spectroscopy (3DEEM)). However, the application of spectroscopic methods is still challenging as there are few examples of the use of spectroscopy for biofilm characterization in the literature [124]. Therefore, these methods must be combined for a better understanding of a biofilm layer formation and growth [125]. Four common techniques used to monitor the membrane biofouling are shown in Figure 2. Among these methods, confocal laser scanning microscopy (CLSM) is one of the most elegant methods to evaluate a biofilm because of its ability to provide high resolution optical images, profiles of porosity-depth, to provide a measurement of the percentage of dead bacteria, and because it also allows the recognition of different constituents of biofilms, such as polysaccharides, proteins, and dead or living cells. In the CLSM technique, the membrane is stained by fluorescent dyes. Then, a laser penetrates into the biofilm sample to excite these molecules. The fluorescence emitted from the excited molecules transforms into photons, which are then converted to electron signals, in turn transformed into three-dimensional images via the help of an image processor [126, 128].

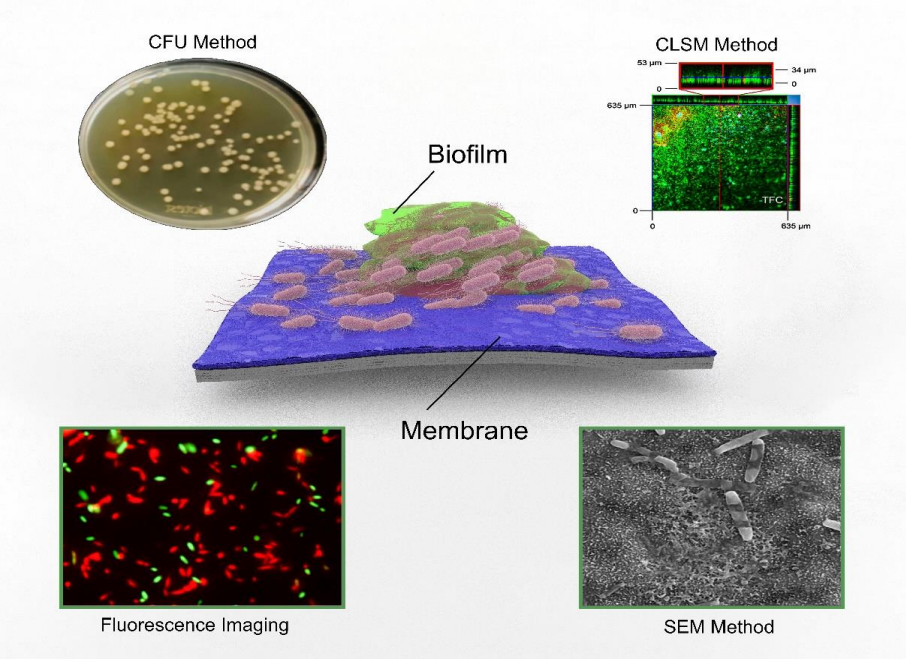

Figure 2. Biofouling characterization methods; SEM image of E. coli on top side of TFC FO membrane, CFU test of TFC FO membrane, fluorescence imaging [129], reproduced with permission from Elsevier, and CLSM method [130]. reproduced with permission from ACS Publications.

The bacterial communities on fouled membranes have also been evaluated by heterotrophic total plate count, colony-forming units (CFU) methods, and adenosine triphosphate (ATP) bioluminescence assay tests [131]. ATP is a biochemical method that indicates the biological activity of live cells and biomass. These methods are not able to provide the amount of dead bacteria cells. Also, in many biofouling investigations in MBR systems, more often molecular methods, such as clone library, polymerase chain reaction-denaturing gradient gel electrophoresis (PCR-DGGE), and fluorescence in situ hybridization (FISH), have been used to detect and describe bacterial communities [132].

2.4. Biofouling Modeling in Forward Osmosis

Numerical modeling integrated with experimental data is a helpful tool for predicting the biofouling behavior of the FO membranes. The integration of these methods also show promise for identifying feasible ways to biofouling mitigation with advanced materials. Bucs et al. evaluated the influence of biofouling on the FO membrane performance in a cross-flow system . They applied two-dimensional numerical computer simulations combined with experimental data to investigate the effects of (i) biofouling on external concentration polarization (ECP) under various FO conditions, and (ii) biofilm attributes (porosity, hydraulic permeability, and thickness), biofilm membrane surface coverage, and biofilm size (draw channel, feed channel or both) on the FO membrane performance. The results demonstrated that: (i) the biofouling surface remarkably affected the ECP and could be the controlling parameter for water permeation; (ii) the biofilm formed in the draw side decreased the water flux due to higher

internal concentration polarization (ICP); and (iii) the biofilm hydraulic resistance and membrane surface coverage also considerably affected the water flux. The authors also reported all biofilm properties, such as hydraulic permeability, average thickness, porosity, and spatial heterogeneity are important factors influencing the system productivity. Due to the dynamic behavior of biofilm, measurements should determine how the biofilm properties are evolving overtime. The geometry of the FO model, the effect of biofilm and related factors on the water flux are illustrated in **Figure 3**. Overall, the numerical models can help researchers to better understand the effect of biofilm/biofouling in FO membrane processes and to apply feasible strategies in biofouling control and mitigation. Additionally, future experimental studies should focus on the use of new modification approaches for the development of state-of-the-art anti-biofouling membranes and novel cleaning strategies. Also, it is strongly suggested to integrate numerical modeling methods with experimental data to reach a comprehensive evaluation of product quality and energy parameters [133, 134].

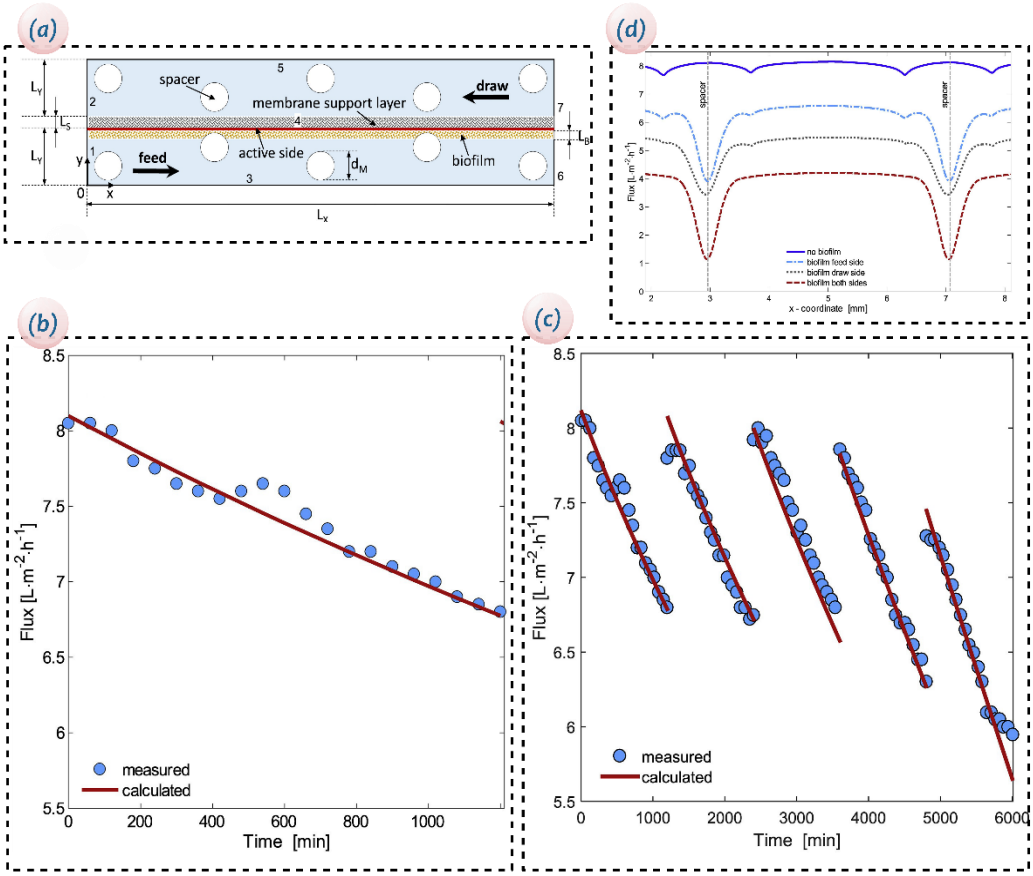

Figure 3. (a) Illustration of the forward osmosis (FO) model geometry. The model space is divided to three domains: feed and draw channels (blue color, with bold arrows indicating the flow directions), membrane support layer (woven grey) and the membrane active layer (red line) is facing the feed channel side. The biofilm (yellow dotted zone) constitutes a fourth domain. (b) Combined impact of dilution and biofilm formation on flux in forward osmosis system operated in repeated batch mode, measured (blue circles) and modeled (red lines). (c) Calculated flux decline at different biofilm thickness on the membrane feed side, with spacers in the flow channels (Effect of different biofilm porosities (εB)). (d) Calculated water flux along the membrane: without biofilms (continuous blue line), with patchy biofilm (dotted blue line and dotted black) and with continuous uniform biofilm (dashed red line), on the membrane active side. The average water flux obtained was: 7.9 (L.m-2.h-1) (no biofilm), 6.4 (L.m-2.h-1) (patchy biofilm) and 6 (L.m-2.h-1) (continuous biofilm) [135]. reproduced with permission from Elsevier.

3. Membrane Biofouling Control Strategies in Forward Osmosis

3.1. Pretreatment Technologies and Cleaning Strategies

Delaying or reducing the intensity of biofouling is typically easier than either attempting to prevent it completely or than removing an established biofilm. As mentioned in previous sections, the rate of microbial growth is dependent on nutrients and other environmental

conditions. Pretreatment of the feed solution before filtration is one of the easiest means to postpone or decrease the intensity of biofouling, but it comes with capital and operational costs. Pretreatments can be applied chemically, e.g., by oxidation or by decreasing the concentration of the nutrients by precipitation (i.e., phosphate [131]), or physically, e.g., via filtration.

Regarding membrane cleaning strategy, while physical cleaning can be effective for the removal of organic/inorganic foulants, it is largely ineffective for biofouling reduction, regardless of the nature of the driving force [117]. Chemical cleaning of the FO membrane normally yields better results in terms of flux recovery than in RO systems, and it may represent a potential treatment for FO membrane maintenance and flux restoration in future large-scale applications [117]. The major drawback of chemical cleaning is its high cost and the required disposal of undesirable by-products to the waste stream that must be treated before discharge to the environment. Additionally, many cleaning chemicals can damage membranes. However, the resistance of extracellular polymeric substance (EPS) to physical cleaning dictates that intense chemical treatment may be necessary to clean membranes encased in EPS. Wang et al. used acidic cleaners coupled with alkaline ones, and they found that a mixture of 0.1% NaOH or 0.1% sodium dodecyl sulfate (SDS) followed by 2% citric acid or 0.5% HCl can be utilized to remove foulants from the membrane surface [136]. Another method is the addition of acids, alkalis, and surfactants as well as oxidizing or chelating agents, such as chlorine, directly to the feed water before membrane treatment. Fujioka et al. applied the target concentration of 3-8 mg/L of chloramines for wastewater pretreatment before the FO process by CTA membranes. After 96 hours of continuous membrane experiment, flux reductions of 6% and 35% were observed in the chloraminated and non-chloraminated FO system, respectively [137]. Despite the potential efficacy of chlorination for biofouling control, the potential formation of harmful

and carcinogenic disinfection by-products must be considered [138]. Also, the presence of oxidants often diminishes the membrane lifetime, and therefore these substances must be removed from the feed before initiating the filtration process [137]. Wang et al. reported that H_2O_2 oxidizes the microbial community and converts them to more desirable organic substances, but high concentration and prolonged contact time of the surface with H_2O_2 can finally lead to membrane degradation. Therefore, it is of prime importance to control the concentration of oxidants and their contact time in membrane cleaning strategies. The results of SEM observations indicated that the optimum concentration of H_2O_2 and contact time for membrane cleaning should be 0.5% and 6 hours [139] .

Considering the difficulties generated by the application of biocides, other pretreatment strategies have been applied. Quorum sensing inhibition (QSI) can control biofilm growth. This method creates disturbance in a bacterial communication system. In 2017, Choi [140] used three natural organic molecules, namely, cinnamaldehyde (CIN), vanillin (VAN), and zingerone (ZIN), as QSI to control bacterial growth, resulting in decreased biomass accumulation on the membrane surface up to 68%, 41%, and 15% in the presence of CIN, VAN, and ZIN, respectively. Another biological control method is the use of bacteriophages to hinder or destroy biofilm development on membrane surfaces by infecting the host bacteria. However, bacteriophages can also inhibit the growth of bacteria necessary for wastewater treatment when the treatment train includes biological processes, and this phenomenon limits their application for pretreatment of wastewater.

Beside chemical pretreatments, physical approaches such as aerobic pretreatment are applicable. Zhang et al. investigated biofouling development in four FO stages under low (6.54 mg/l-(stage A) and 4.59 mg/l-(stage B)) and high aeration (8.95 mg/l-(stage C) and 8.53 mg/l-

(stage D)) conditions. The results of this assessment demonstrated that biofilm formation in low aeration (average of stage A and B) were 31 and 12 times higher than those in high aeration stages (average of stage C and D), respectively.

Ozonation of feed water is also an important disinfecting method. However, ozone may produce assimilable organic carbon (AOCs), especially in the case of wastewater pretreatment, and cannot be applied to feed waters containing bromate, due to the formation of carcinogenic by-products [15]. Ultraviolet (UV) irradiation is reported as a common physical pretreatment for the inactivation of microorganisms. Despite being able to reduce AOCs, the use of UV irradiation is limited in UV-absorbing or light scattering solutions, and it is not effective for microorganisms that have been deposited on the membranes [15]. Overall, despite these difficulties, FO is usually reliable for the treatment of highly polluted waters and has lower fouling propensity compared to the RO process. Its cleaning procedures are also easier and require less time and effort, which makes some pretreatment strategies unnecessary in most cases [141].

3.2. Membrane Surface Functionalization for Biofouling Mitigation

On account of polyamide (PA)-TFC membrane higher water permeability and higher salt rejection compared to CTA asymmetric membrane, their fouling behavior has been the topic of the vast majority of recent studies. Apart from the hydrodynamic operation conditions, the FO fouling tendency is closely related to the membrane surface characteristics that dictate the interaction with foulants. In general, a fouling-resistant membrane should be hydrophilic, smooth, and negatively charged to prevent attachment of foulants to its surface. TFC PA membranes are intrinsically prone to fouling (especially biofouling) owing to their inherent

chemistry in terms of relative hydrophobicity, high surface roughness, and the existence of carboxyl groups on the membrane surface [142]. Consequently, there is an essential need for the alleviation of fouling by innovative strategies to increase membrane lifespan. A variety of approaches have been implemented to functionalize the TFC PA membranes, including surface grafting of monomers or polymers, chemical coupling, and in situ growth. In these approaches, an agent chemically reacts with the functional groups of the surface, preferentially via covalent bonding. The membrane surface is initially activated with physical or chemical reactions and subsequently subjected to functionalization. It should be noted that the main feature of chemically functionalized surfaces is their long-term stability compared to those modified only by physical means [143]. In the case of application of functional nanoparticles, surface functionalization decreases the possibility of nanoparticle aggregation compared to protocol attempting to incorporate nanomaterials within the membrane structure [144, 145].

As mentioned above, the physiochemical properties of the membrane surface are the most important factor affecting cellular attachment. Surface hydrophobicity/hydrophilicity, charge and roughness are key parameters in biofouling control and mitigation, as they dictate the interaction between the membrane and the bacterial cells [146]. It is generally accepted that membranes with smoother and more hydrophilic surfaces provide better antifouling performance [147]. It has been reported that a hydrophilic surface imparts high surface tension and is prone to form hydrogen bonds with the surrounding water molecules to create a thin boundary of water between the membrane and the bulk solution. This layer can prevent the undesirable adsorption or adhesion of hydrophobic foulants on the surface of the membrane. Although the membranes with a rougher surface generally present lower hydrophilicity [148] the effect of surface functional groups on hydrophilicity is greater than that of surface

roughness. Generally, inconsistent results have been reported in the literature on the relationship between biofouling and the roughness of the membrane surface [149, 150]. Higher surface roughness increases the total surface area accessible to bacterial cell accumulation and consequently biofilm formation . On the other hand, the presence of brushes or biocidal agents can improve the anti-biofouling tendency, even when these materials increase the surface roughness [151]. Although the approaches listed above result in a significant increase in hydrophilicity and decreased foulant-membrane interfacial adhesion forces, there is an emerging paradigm shift to develop fouling resistant TFC PA FO membranes. This shift is from passive (fouling resistance and fouling release) to active (off-surface antibacterial and on-surface antibacterial) antifouling strategies, which includes binding antibacterial agents to the TFC PA active layer [120].

The surface charge of the membrane is an important parameter in membrane fouling reduction when treating a feed with charged foulants [152]. In this context, one of the frequently used methods is to induce the same sign of charge to the membrane surface as that of the foulants. This approach results in electrostatic repulsion, thus decreasing deposition of the foulant [153]. Since bacterial cells are made up of phospholipids and lipopolysaccharides, they normally carry negative electrical charges in a pH range of 4–9 [154]. A negatively-charged surface is thus less prone to bacterial deposition [155]. Accordingly, it seems that the functionalization of the TFC PA layer with negatively charged agents can provide stronger electrostatic repulsion toward bacteria cells and hence lower biofouling tendency [156]. However, strong electrostatic attraction may also inhibit biofilm formation; many bacteria deposited on positively charged surfaces show little to no growth. This mechanism has been

attributed to the strong, attractive force, hindering elongation and division necessary for bacteria growth [157].

Here, we review recent trends on the surface functionalization strategies with the aim of biofouling mitigation. Various aspects of different functionalization strategies are discussed in terms of simplicity/versatility, reproducibility, transport performance after modification, cost-effectiveness, and environmental side-effects.

3.2.1. Approaches for the Surface Functionalization of the TFC FO Membrane

There are numerous studies reporting the presence of native negatively charged moieties on the surface of the TFC PA membranes. On account of incomplete crosslinking of the MPD and TMC monomers, the two main reagents used to synthesize dense and highly cross-linked polyamide films, amine and especially carboxyl functional groups are present on the surface of the freshly prepared TFC PA membrane. When the TFC PA membrane is soaked in an aqueous solution, the residual acyl chloride groups from the unreacted TMC monomers convert to carboxyls [158]. These negatively charged moieties at the surface may serve as reactive sites for subsequent binding of functional monomers, polymers, or nanoparticles [159]. For this reason, functionalization approaches to improve antifouling properties can potentially be facilitated on the TFC PA surface [160]. TFC PA

3.2.1.1. Surface Grafting

Surface grafting is a promising method and involves the covalent binding of grafted monomers or chains onto the membrane surface. The free radical and ionic active sites are generated via initiators on the TFC PA chain, and afterward, the radical ion reactions propagate

to complete the polymerization with the target monomer. Generally, grafting reactions can be divided into two categories including grafting-to and grafting-from. The former consists of covalent attachment of reactive functional polymeric chains, while the latter comprises the initiation of grafting from the reactive species present on the surface. The grafting-from process can be chemically initiated via chemical, UV-irradiation, photochemical, and plasma-induced treatment, followed by the propagation of different reactive groups [161]. The grafting procedure depends on the chemical structure of the grafting agent, the chemistry of the surface, and the desired properties after surface treatment. Among all procedures, photochemical/redox-initiating grafting is less expensive, facile, and very convenient for industrial applications [162].

One example of grafting is discussed by Li et al [163] where cheap and efficient photosensitizer porphyrin molecules (Por) were grafted to design photodynamic antibacterial TFC PA FO membranes. The porphyrin molecules were grafted on the TFC PA surface via the reaction between the amine group of porphyrins and the barboxyl groups on the TFC membrane. Due to the strong covalent bond between the porphyrin molecules and the TFC surface, the Por-TFC membrane showed good chemical and photo stability. The key concept in this antibiofouling strategy is that, when exposed to sunlight radiation, the porphyrin molecules can produce a large amount of ROS (singlet oxygen or other reactive oxygen species), which are highly toxic to bacteria [164, 165]. In this regard, further progress in the development of the photo-bactericidal membranes offers good opportunities to address biofouling implications and pave the way towards practical FO applications.

3.2.1.2. Surface Functionalization with the Aid of EDC/NHS Coupling Reaction

N-ethyl-N′-(3-(dimethylamino)propyl) carbodimide (EDC) and Nhydroxysuccinimide (NHS) coupling reactions are widely used in membrane functionalization where amide bonds form between carboxyl groups and amine groups by the mediation of these two molecules. In these reactions, first, the carboxylic acids are activated by using carbodiimide with the aid of NHS followed by the amine addition [166]. The EDC/NHS coupling reaction has several advantages, including high conversion efficiency, mild reaction conditions, accessibility in an aqueous phase, and exceptional biocompatibility with minimal effect on the bioactivity of a target structure [167]. Applying similar strategies, a number of antibiofouling FO membranes were fabricated. Typical examples of such reactions were reported for functionalization with graphene oxide (GO) and carbon nanotubes (CNTs) [168], bound to the TFC membrane surface [169]. The GO-functionalized TFC surface exhibited considerable antibacterial activity, most likely attributed to the physical disruption of the bacterial cell membrane, membrane stress, oxidative stress, and/or release of reactive oxygen species (ROS).

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3.2.1.3. Other Chemical Coupling Approaches

Chemical coupling is a commonly used approach to tune the membrane surface with a variety of target-designed functional groups. Also in this case, free carboxylic acids and primary amine groups present on the PA layer serve as reactive sites for surface functionalization via chemical reaction or coupling. Substitution, addition, adhesion, and oxidation are the main methods applied for chemical coupling. Carboxylation [170] hydroxylation [162] and amination [171] are frequently used approaches for altering the TFC PA layer chemistry [172]. However, the main challenge of chemical functionalization is that the modification agent or the reducing

agent may deteriorate the selective layer integrity and reduce the membrane rejection [173]. A reducing agent, e.g., sodium borohydride, is a compound or element that donates an electron to another chemical species in a redox reaction. The main drawback of reducing agents is their high reactivity, which possibly pose environmental and biological risk [174]. Moreover, they may lead to surface segregation and hence deteriorate the membrane integrity by repeated usage. Therefore, the utilization of green, non-toxic, and eco-friendly chemicals for stabilizing the functional groups or nanoparticles on the surface is a major challenge associated with reducing agents. Following these criteria, green reducing agents, such as ascorbic acid [175, 176] and citric acid [177] have been reported to eliminate some side-effects and minimize the generated waste.

3.2.1.4. In Situ Growth of Metal Nanoparticles

In situ growth is a simple procedure in which metal nanoparticles (NPs) anchor on the TFC PA membrane surface. This approach is frequently applied for the functionalization with Ag [178] and Cu [179] NPs. The interaction between the metal precursor and the PA layer is of prime importance as it regulates the particle size distribution, stabilizes the interaction strength, and prevents NP release. Generally, two procedures, namely, classical generation-before and generation-after, have been reported for in situ formation of metal NPs on the membrane surface. The generation-before method involves the binding of pre-prepared metal NPs to the surface [174]. Although this method is beneficial in controlling the size and morphology of the metal NPs, the improper dispersion of NPs on the surface restricts its application. The fabrication procedure in case of generation-after is instead based on the in-situ formation of metal particle from their precursor salt solutions in the presence of a chemical reducing agent or

thermal driving force. Typically, this procedure involves two steps: (i) interaction of metal ions with the pretreated surface and then (ii) reduction of metallic ions to metal NPs with the aid of a reducing agent or an external stimulus, such as thermal inducement or UV irradiation. Before applying the chemical reducing agent, the residual amount of metal precursor should be removed from the surface to ensure the all the NPs are covalently bound to the reactive sites of the surface. Since NPs are thus present on the surface, where fouling develops, direct exposure activates two biocidal mechanisms, one based on direct contact and the second on the release of metal ions. Moreover, this approach offers a higher yield of NPs dispersion and prevents aggregation compared to attempts of NPs incorporation into the TFC membrane.

3.2.1.5. Self-Assembly via Coordination Chemistry

Self-assembly via coordination bonds is an interesting subset of in situ growth in which, e.g., metal organic frameworks (MOFs), are grown at the surface following the chemical reaction of metals and ligand species. Self-assembly offers a powerful platform for the design of the well-defined architecture of functional materials at the molecular level with various shapes and structures. The physicochemical properties of the surface play an essential role in regulating the quality of crystal formation during the heterogeneous growth of MOFs on the substrate [180]. For this reason, the substrates are usually subjected to physical or chemical pretreatment to improve the reactivity of nucleation sites [181]. Since the synthesis of MOFs involves the coordination between metal ions and organic ligands, surfaces modified with amine and carboxyl functional groups are beneficial for MOF crystal growth, as these moieties can serve as covalent ligands in the MOF structure [182, 183]. The carboxyl functional groups present on the TFC surface offer the reactive sites for subsequent nucleation and growth of MOFs. The MOF

seeds are first anchored on the reactive sites of the surface, followed by the growth of the MOF framework to form a thin film or individual crystals. Coordination and H-bonding interactions are the main mechanisms responsible for MOF structure attachment. The metal and ligand act, respectively, as the core and the linker to form coordinate covalent bonds of the MOF crystals. Most of the surface functionalized with MOFs are applied in gas separation, few reports involve water separation, and very limited research relates to TFC PA membranes for FO application [184, 185].

The emergence of these nanostructures is regarded as one of the most promising approaches for antibiofouling TFC PA membranes. MOFs are porous nanostructures in which the active cores are the same or similar to those present in metal oxide NPs [186]. The metal ion release at the boundary layer of the membrane surface acts as a source of biocides [187] and creates an inhibition zone [188]. The key advantage of MOFs compared to inorganic microporous compounds is that their structure is highly tunable by applying diverse metal centers or altering the organic ligand [186]. Antibacterial MOFs have thus the advantage of broad-spectrum antibacterial activity against both Gram-negative and Gram-positive bacteria, high efficiency, and long lasting stability [189, 190]. Nevertheless, limited approaches can be applied for MOFs functionalization since the PA layer is intrinsically sensitive to high temperature and harsh solvents [191]. As a result, developing a well-designed approach with minimal risks to membrane integrity, performed at ambient temperature, with relatively rapid precipitation, and employing green solvents, is necessary for the future of MOFs-functionalized membranes.

Surface functionalization strategies provide tailored control and target design of surface characteristics, generating valuable frameworks with improved or novel properties, such as superior antimicrobial activity. Regardless of the increasing interest in applying biocidal agents for the development of antibiofouling membranes for water purification, a practical strategy remains challenging. Moreover, the traditional contact-killing antibacterial strategy is restricted to surface accessibility, and the antibiofouling effect decreases once the membrane surface is completely covered with a fouling layer. However, compared to the bulk incorporation of antibacterial agent or nanomaterials, surface functionalization has minimal influence on the intrinsic performance of the TFC PA membranes. Additionally, the possibility of NPs regeneration after their release is practically very low when they are embedded within the polymer matrix. Considering its simplicity and prolonged stability, the surface functionalization of TFC PA membranes with antibiofouling materials is a dominant trend today and has important practical implications for water treatment. While several studies discuss the strong antibacterial activity of biocidal nanostructures, many of the proposed methods do not address all the limitations related to industrial-scale fabrication and operation of the membranes. Applying biocidal nanostructures on the TFC PA surface necessitates mild, facile, rapid, low-cost, and reproducible procedures without the need to disassemble the membrane module or sacrifice the membrane intrinsic transport properties.

3.2.2. Different Types of Materials Applied in Surface Functionalization

Generally, antibiofouling strategies can be divided into three main categories, including (i) microorganism antiadhesion, (ii) bactericidal activity, and (iii) integration of antiadhesion with bactericidal approaches [184]. Strategies to decrease adhesion forces between bacteria and

membrane surface comprise the attainment of superhydrophilic or superhydrophobic surfaces. Superhydrophilic surfaces are often obtained with zwitterionic materials by promoting the formation of a hydration layer on the surface leading to a mitigation of the bacterial adhesion due to non-specific interaction [173]. Approaches that have been developed to functionalize membrane surfaces with zwitterions include surface grafting [192, 193] and polydopamine (PDA)-assisted deposition [194]. Several studies have reported zwitterion functionalized TFC PA surfaces for antifouling FO applications without extensive characterization of the antibiofouling behavior [195-197]. Liu et al. [198] prepared a highly antifouling TFC PA membrane by grafting a controlled architecture zwitterionic polymer brush via atom transfer radical polymerization (ATRP). By bioinspired catechol chemistry, the initiator molecules of the polymerization reaction were embedded on the membrane surface and resulted in the grafting of a dense zwitterionic polymer brush layer. The functionalized membrane surface exhibited decreased roughness, improved hydrophilicity, and larger negative charge. Moreover, the zwitterionic-modified membrane presented remarkably lower (one order of magnitude) foulant-membrane interaction forces compared to that of the pristine TFC membrane. This behavior led to considerably reduced adsorption of both proteins and bacteria, providing a highly fouling resistant surface. The water permeability of the modified membrane decreased somewhat while the salt permeability increased after the formation of the zwitterionic polymer brush layer on the surface. However, precise control of the thickness of the modifying layer via ATRP allowed further optimization of the membrane transport properties without sacrificing antifouling properties **(Figure 4)**.

Other than zwitterions, several materials, such as PEG-based and natural biopolymers, e.g., polydopamine and chitosan, have been applied to prepare such hydrophilic membrane

surfaces with antibiofouling properties [199, 200]. Lu et al.[201] chemically modified the surface of the TFC membrane with Jeffamine, an amine-terminated poly (ethylene glycol), to enhance organic fouling resistance against synthetic wastewater containing alginate. Castrillón et al. [202] functionalized the TFC FO membrane surface with PEG to reduce organic (alginate) fouling, where a second interfacial reaction was adopted between ethylenediamine and free carboxyl groups to facilitate PEG grafting.

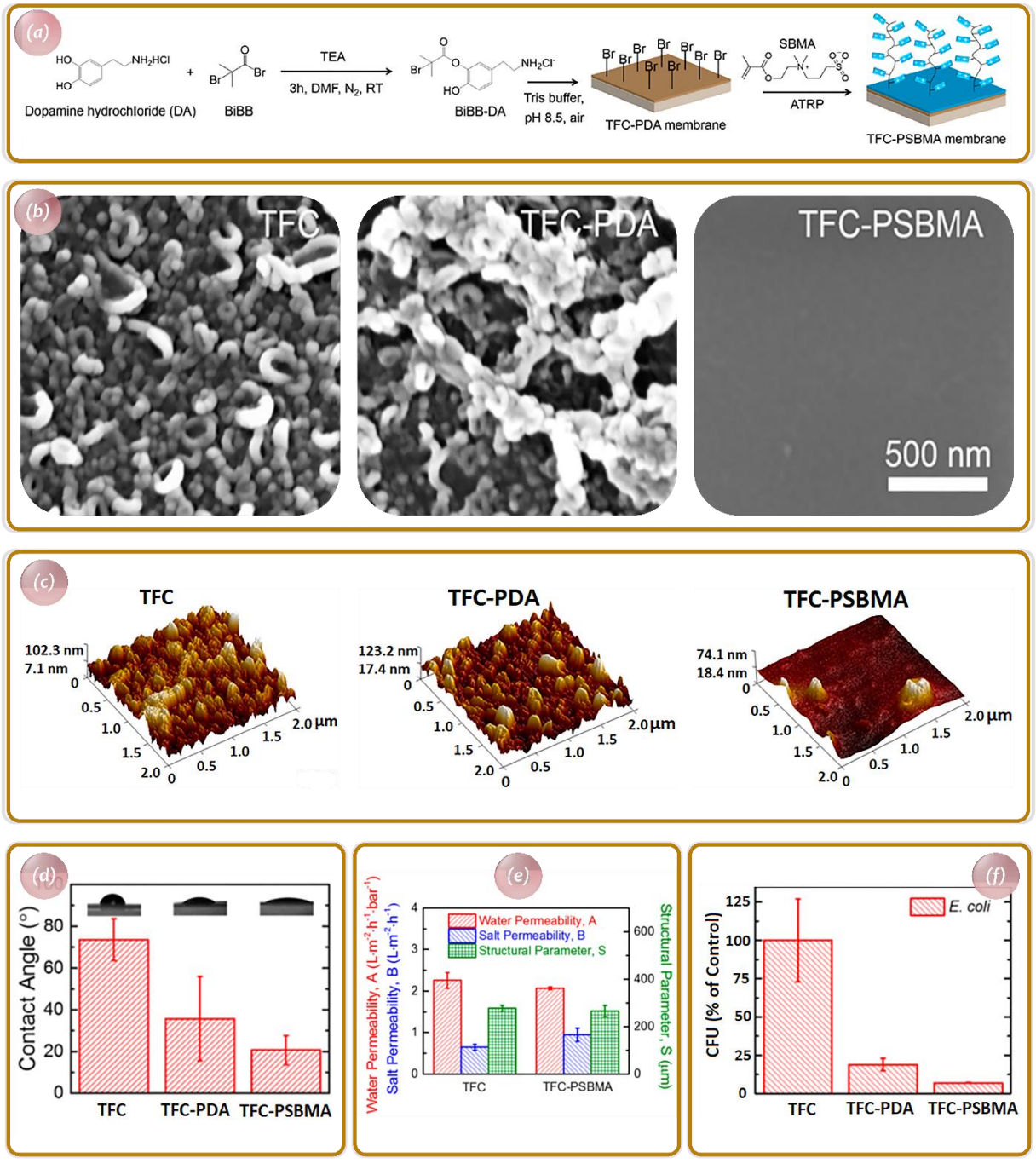

Figure 4. a) Schematic illustration of TFC membrane grafting by zwitterionic polymer via ATRP in which BiBB stands for α- bromoisobutyryl bromide, TEA for triethylamine, SBMA for [2-(methacryloyloxy)-ethyl].dimethyl-(3-sulfopropyl)ammonium hydroxide (also named sulfobetaine methacrylate), and PSBMA for poly(sulfobetaine methacrylate), b, c) SEM and 3D AFM images of the pristine TFC, TFC-PDA, and TFC-PSBMA membranes, d) Water contact angles, e) transport and structural properties of pristine TFC and TFC-PSBMA membranes, and f) E. coli adhesion of the of pristine and modified membranes after 3 h contact time [203]. reproduced with permission from Elsevier.

Liu et al. in [204] proposed a novel strategy to functionalize the TFC surface with superhydrophilic 3D hyperbranched polyglycerol for simultaneous improvement of both transport performance and antifouling properties (BSA protein adsorption). Additionally, Shen et al. [205] grafted polyethyleneimine (PEI) to the TFC FO surface to reduce alginate fouling. In a similar attempt, Bao et al. [206] prepared polyamidoamine (PAMAM) dendrimers grafted to the TFC surface to simultaneously increase ammonia selectivity and antifouling properties of the FO membrane for resource recovery from domestic wastewater.

Polydopamine (PDA) is a bio-inspired polymer that can robustly attach on the TFC PA membrane surface with strong interactions [207]. The PDA layer can form on any surface via in situ spontaneous oxidative self-polymerization of dopamine under mild conditions, via a range of interactions including covalent bonding, coordination, hydrogen bonding and π–π stacking [208, 209]. The presence of the residual catechol, quinone, and amine functional groups on PDA offer reactive sites for further treatment with functional molecules [210].

Surface modification with dendrimers, highly branched molecules with a symmetric repetitive structure, provides a high density of hydrophilic functional groups on the membrane surface and diminishes protein and bacteria adsorption [211]. Moreover, a 3D star-like nanostructure of dendrimers exerts high steric hindrance to foulants and forms an antifouling layer without significantly sacrificing the water permeability [204], as intermolecular cavities facilitate the transport of water molecules. Bao et al. [212] grafted PAMAM dendrimers (generations 0, 1, 2 and 3) with abundant easily-protonated amine functional groups on the TFC

PA FO membrane surface. The grafting approach was accomplished by forming chemical amide bonds between the unreacted carboxyl groups on the PA surface and amine groups of PAMAM dendrimer. This covalent bond rendered the TFC PA ζ-potential highly negative and imparted superior hydrophilicity, to simultaneously improve the ammonia rejection and antifouling performance of the FO membrane for treating domestic wastewater (**Figure 5**). Although providing effective ammonia selectivity is challenging because of the similar polarities and hydraulic radii of the ammonium cation and water molecules, grafting PAMAM dendrimers enabled the FO membrane to achieve high ammonia rejection of 98.2% and significantly reduced reverse salt flux due to the electrostatic repulsion between the protonated amine layer and the compound. The antifouling properties of the grafted membrane were enhanced owing to the hydrophilic nature of amine groups and the electrostatic repulsion to positively charged ions.

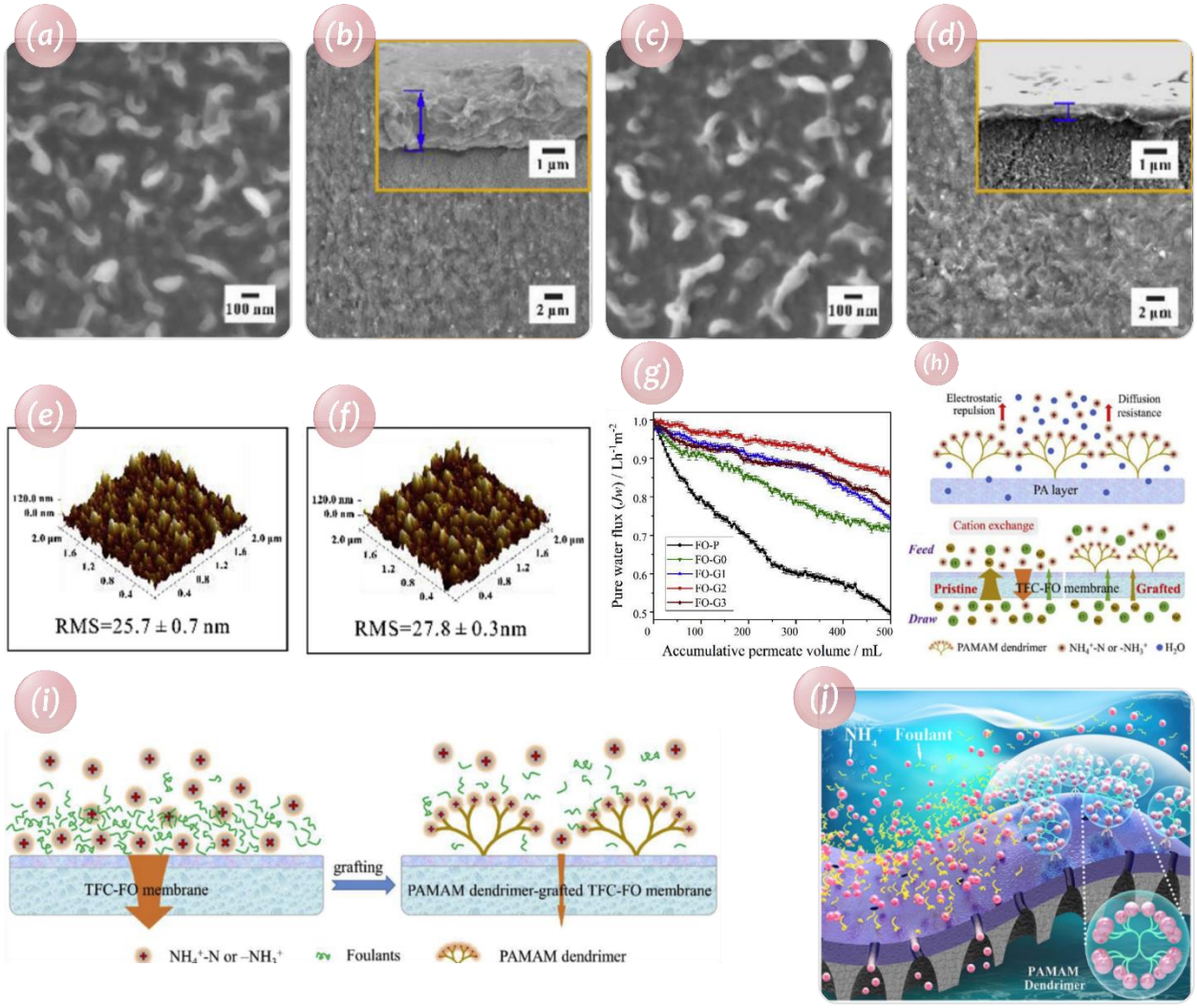

Figure 5 (a, and b) SEM images of the pristine membrane, (c, and d) SEM images of PAMAM dendrimer-grafted TFC-FO membrane, (e) AFM images of pristine membrane, (f) AFM images of the PAMAM (generation 2) dendrimer-grafted TFC-FO membranes, (g) normalized water flux reduction trend, (h) schematic illustration of the TFC-FO membrane rejection of NH4+-N and the mixture of NaCl with NH4Cl as the feed solution, (i) schematic diagram of the effect dendrimer grafting on the membrane fouling, (j) Schematic PAMAM dendrimer's grafting on the TFC-FO membrane [212]. reproduced with permission from Elsevier.

Membrane surface modification via PDA grafting can effectively alter the surface wettability [213] and decrease the adhesion energy for organic foulants' deposition [213, 214]. The protonated amine groups possibly exert antibacterial activity, as they cause cell lysis in contact with the bacteria cell membrane [215]. Owing to the simplicity of this type of

modification to improve the fouling resistance, PDA was applied to several TFC PA FO membranes to suppress biofouling [216]. Li et al. [217] evaluated the biofouling behavior of cellulose triacetate (CTA) surface-modified with PEG-grafted PDA (PDA-g-PEG) in a submerged forward osmosis membrane bioreactor (FO-MBR) over 61-days. At first, the PDA was applied to coat the CTA surface, and then mPEG-NH_2 was separately grafted on the PDA-coated CTA to improve the antifouling properties and transport performance (A of 0.45 LMH/bar and B of 1.91 $\times 10^{-8}$). The PDA-g-PEG-modified membrane displayed enhanced surface hydrophilicity, lower flux decline, and hence better antifouling ability than that of the pristine CTA membrane in FO-MBR.

Bactericidal activity is dominantly obtained with antibacterial nanomaterials, such as silver, copper, and carbon-based nanomaterials [218]. This strategy is classified into two categories, namely, release killing and contact killing. Whereas both result in toxicity to microorganisms, sometimes these two principles are combined to accomplish synergetic effects. The long-term bactericidal activity can be attained by exploiting the controlled release of biocidal agents [219] and the properties of rechargeable surfaces [218]. The release killing strategy provides antibiofouling effect via leaching of the antibacterial agents from the membrane surface to the environment of interest, whereby they attack planktonic cells deposited on the membrane surface [220], for example by generating reactive oxygen species (ROS) formed through catalytic reactions [221, 222]. This mechanism is commonly proposed to account for the off-surface active antifouling properties of silver-based nanomaterials [223].

Silver-based biocides are the most extensively used nanomaterials and are based upon the release of free silver ions (Ag^+) [224, 225]. The toxicity of Ag NPs against bacterial strains can be related to the quantity of Ag^+ ions released [226] and their reactivity can be increased by

manipulation of their physicochemical properties, such as particle size [227] and morphology [228]. It is generally believed that the antibacterial mechanism of Ag NPs is multifold: (i) direct adhesion of Ag NPs to bacterial cells, with physical damage to the cell membrane, (ii) release of Ag^+ and then infiltration into the bacteria, and (iii) indirect generation of reactive oxygen species by Ag NPs and Ag^+, causing defects to the bacteria cell structure and eventually preventing biofilm formation on the surface (**Figure 6)** [229, 230]. It is preferable to locate the silver NPs near the membrane surface, where they have maximum interactions and direct exposure to the bacteria [231]. This way, the two antibacterial mechanisms, release killing and contact killing, occur simultaneously. Significant progress has been made in the development of in situ functionalized Ag NPs on the TFC PA surfaces, and some of the recent research is reported here. The antibacterial performance of Ag NPs functionalized TFC PA membranes essentially depends on the NPs size, distribution, and stability [232].

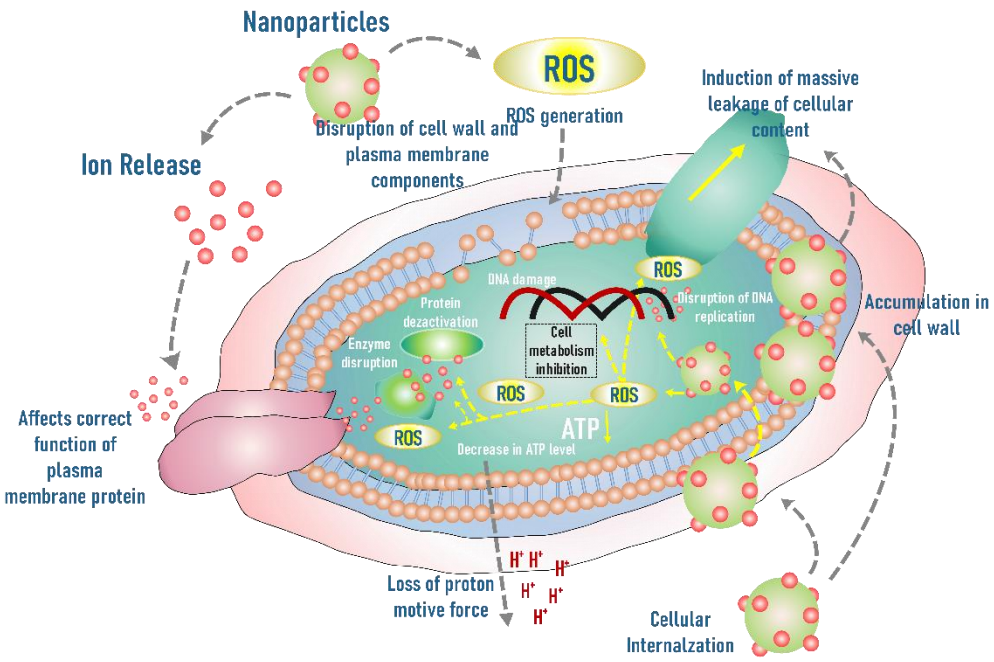

Figure 6. Antibacterial mechanism of metal and metal oxide containing systems [233]. reproduced with permission from Elsevier.

Liu et al. [231] developed a simple and facile approach to covalently bind Ag NPs on the TFC PA surface via layer-by-layer interfacial polymerization. Their findings revealed that this approach provided less influence on surface roughness and overall charge, yielded slight improvements in water flux and salt rejection, lowered the Ag release rate, and provided stability during filtration, excellent antibacterial properties and hence, high resistance to biofouling. Moreover, Liu et al. [178] functionalized Ag NPs on hydrolyzed polyacrylonitrile (PAN) membrane surfaces and attained high antimicrobial activity against *E. coli* for 14 days under laboratory conditions, imparting biofilm growth resistance (**Figure 7**). Although there are

many advantages to functionalizing membrane surfaces by silver NPs, researchers still doubt about their safety in commercial use.

Copper-based NPs (Cu NPs) are regarded as a valuable biocide for the preparation of antibacterial membranes, with lower costs than silver [234]. In addition to contact killing, Cu NPs promote the formation of hydroxyl radicals that destroy essential proteins and DNA inside bacteria cells [235]. Similar to silver ions, Cu NPs show rapid release if their deposition on the surface is only physical. This release mechanism reduces its antibacterial property and poses contamination problems for the feeds and permeates. Therefore, Cu NPs should be stably immobilized on the surface to alleviate their release rate and guarantee long-term antibacterial activity. Liu et al. developed a simple one-pot procedure for the chelation of copper ions on the surface of the TFC PA membrane by soaking the membranes in a dopamine (DOPA) solution containing copper (II) [236]. This cost-effective approach offered a versatile method for the construction of long-term biofouling-resistant surfaces. The PDA-Cu layer affected the transport properties of the membranes and decreased the water flux of the TFC FO membrane up to 28%. On the other hand, the PDA-Cu functionalized surface demonstrated high antibacterial activity against *S. aureus* (up to 97 %) with very little Cu leakage into the permeate. Both findings suggest that the PDA-Cu functionalized membrane can yield interesting long-term antibacterial activity against Gram-positive bacteria [237].

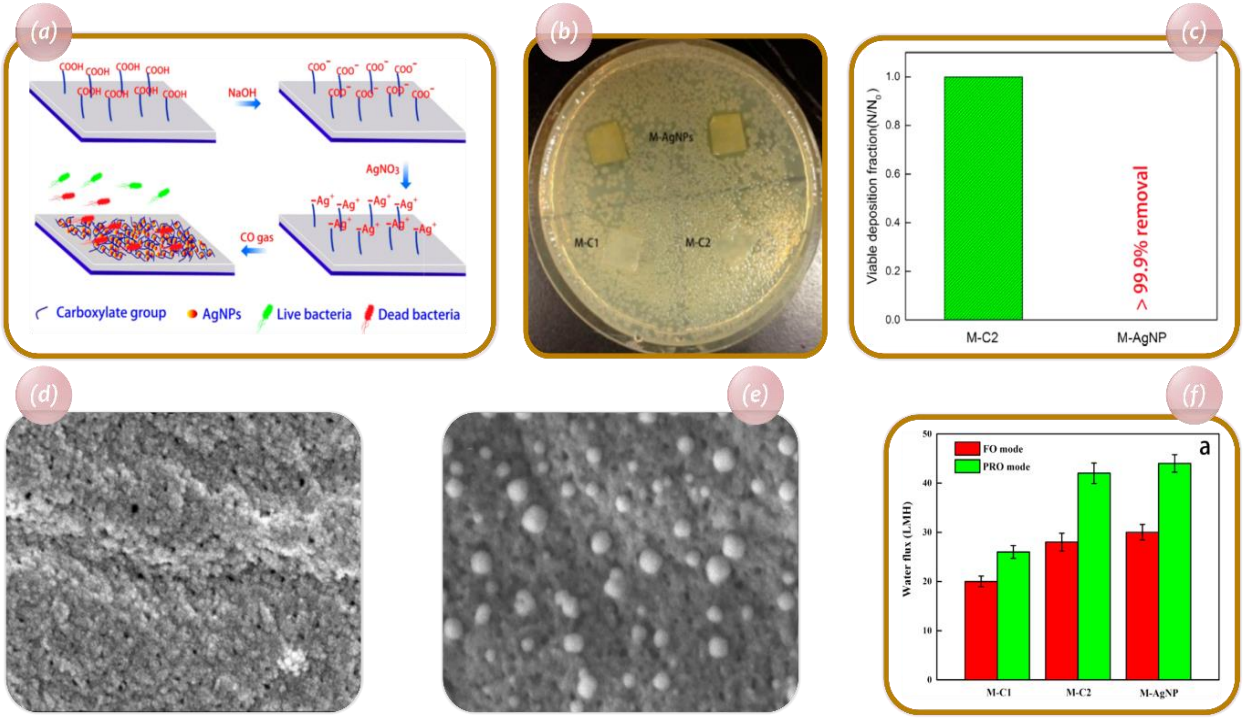

Figure 7. (a) Schematic illustration of deposited AgNPs on the TFC membrane formed on PAN substrate (M-AgNPs), (b) CFU test of TFC (M-C1), Na-OH-modified TFC(M-C2) and Ag-NPs functionalized (M-AgNPs) membrane, (c) static antibacterial adhesion behavior of M-C2 and M-AgNPs membranes, (d, and e) FE-SEM images of modified-TFC membranes and (f) water flux of membranes [178]. reproduced with permission from ACS Publications.

MOFs are an outstanding class of porous nanostructure compounds that have emerged as promising structures compared to traditional inorganic microporous structures, such as zeolites, due to their hybrid organic/inorganic structure, high surface area, their highly tunable molecular structure and adjustable pore size [238]. MOFs can serve as the reservoir of biocidal metal ions in which the continuous gradual release of the metal ions by (bio)degradation of the framework provides sustainable antibacterial activity with high productivity [239]. Besides, the organic ligand applied for the construction of the framework may itself have antimicrobial activity, and therefore a combined effect may be attained [240]. Recently, Ag-MOFs were used to functionalize TFC PA membranes for FO applications [241]. A two-step deposition procedure

was proposed for covalent binding of Ag-MOFs to the TFC PA FO membrane at ambient temperature, applying only two chemical reagents (silver salt and organic ligand) without additional stabilizing/reducing agent (**Figure 8**). Confocal microscopy analyses revealed that Ag-MOFs exerted strong antibacterial activity to the membrane surface, leading to more than 99% reduction of live bacteria. The functionalization procedure generated a uniform distribution of Ag-MOFs on the active sites of the PA layer, rendering the membrane surface highly antibacterial. As mentioned, surface depletion of metals is considered one of the major drawbacks to the long-term operation of surface functionalized membranes [226]. The regeneration of metal NPs or MOFs after release or leaching has been proposed as a strategy to preserve the antibacterial activity of the membrane surface [223].

Carbon-based nanomaterials (CNTs and GO) also demonstrate antibacterial activity as well as low cytotoxicity towards mammalian cells. When comparing reduced graphene-oxide (rGO), graphite, and graphite-oxide against *E. coli* under similar conditions, graphene-oxide (GO) showed the highest antibacterial activity. [242, 243].The generation of reactive oxygen species and penetration of cell membranes are the proposed antibacterial mechanisms of carbon-based nanomaterials [244].

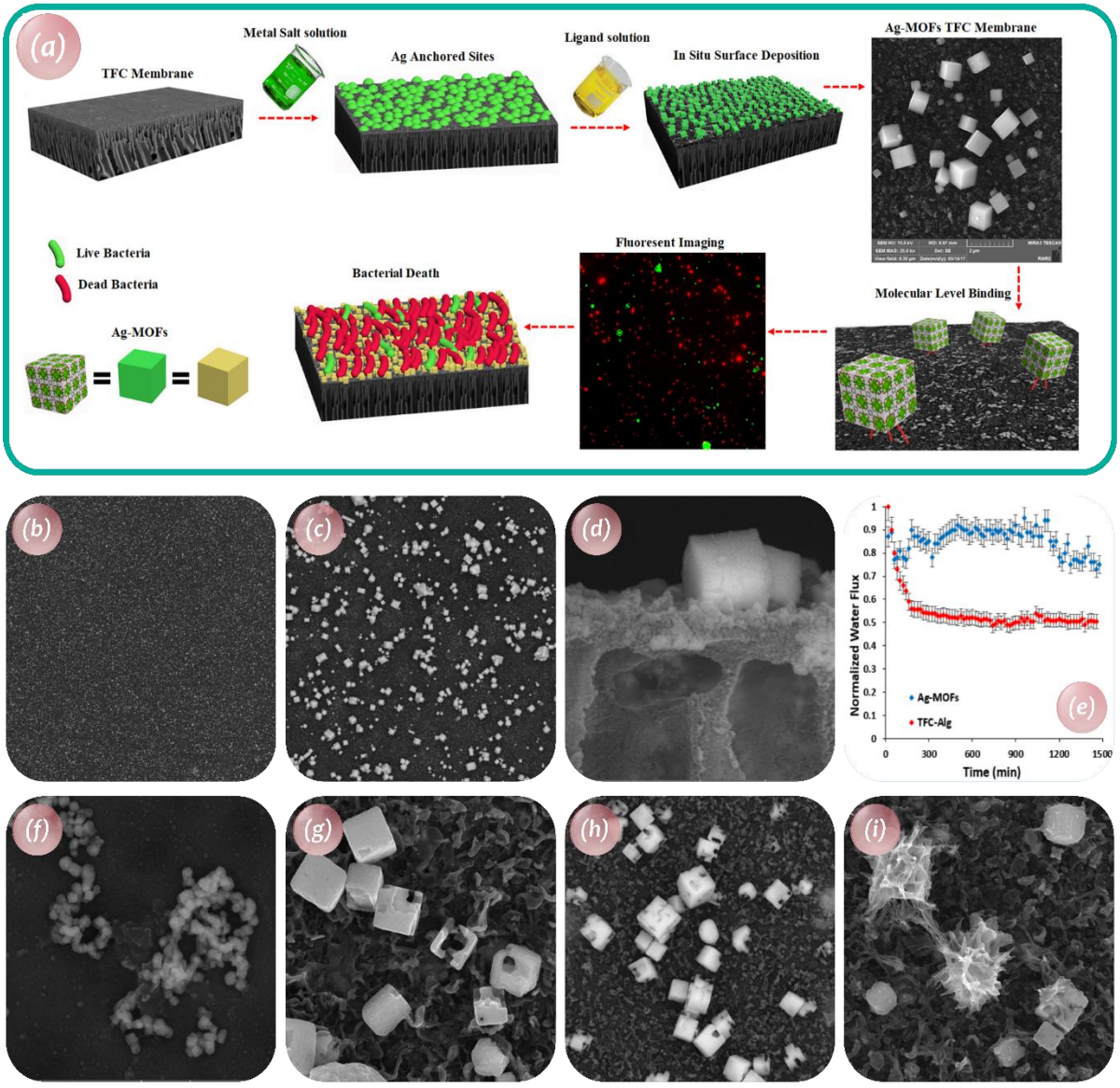

Figure 8. a) Schematic illustration of Ag-MOFs functionalized TFC membrane, b, c, d) surface and cross sectional FE-SEM images of in-situ functionalized Ag-MOFs TFC membrane, e) flux decline during dynamic biofouling test by E. coli of the nascent TFC and Ag-MOFs functionalized membranes, f) FE-SEM images after 6 h FO test, g) after 7 months soaking in water, g) after harsh sonication and after regeneration via the same procedure applied for initial in-situ surface functionalization [241]. reproduced with permission from Elsevier.

This type of antibacterial activity is stable over time and prolongs the antimicrobial property of the functionalized surface over time without leaching [245]. Under specific

conditions, GO has a higher antibacterial ability compared to CNTs [246]. The existence of water transport channels in CNTs and nanochannels between graphene nanosheets [247, 248] may provide enhanced water permeability while exerting antibiofouling properties.

Although covalent binding of CNTs to PA surfaces is quite rare, Tiraferri et al. proposed an innovative such approach [168]. After the modification of single wall carbon nanotubes (SWNTs) to maximize their cytotoxicity and achieve dispersion in aqueous solution, the EDC/NHS coupling reaction generated covalent amide bonds, activating the carboxyl functional groups of both the membrane and the modified SWNTs to maximize coupling with ethylenediamine. The SWNT-functionalized surface demonstrated high performance in the water separation process and cytotoxicity against *E. coli* bacterial cells (up to 60% inactivation of attached bacteria within one hour of contact time). This result indicates that covalently bound SWNTs TFC are a potential candidate to delay membrane biofouling.

GO nanosheets are highly efficient antibacterial agents and contain multifunctional oxygen-containing groups such as hydroxyl, carboxyl, carbonyl, and epoxy moieties . The physicochemical properties of GO nanosheets, including sheet morphology, size and size distribution, oxygen-containing functional groups density, electronic mobility, and carbon radicals, can significantly affect their antimicrobial properties. Despite widespread interest, the exact antibacterial mechanisms remain controversial [249]. The main mechanisms proposed for bacteria toxicity can be classified as: sheet attachment, cell membrane penetration, cell wrapping, phospholipid extraction, and oxidative stress [250].

Perreault et al. [245] irreversibly functionalized biocidal GO nanosheets on the TFC PA membrane to decrease the extent of bacterial growth, using a simple amide coupling between carboxyl groups of GO and carboxyl groups of the PA layer (carbodiimide chemistry). The

functionalized GO surface resulted in 65% bacterial inactivation after one hour of contact time without any adverse effect on the intrinsic membrane transport properties. Hegab et al. [251] grafted GO to the surface of the TFC PA layer via a poly L-Lysine (PLL) intermediary using two different approaches of either layer-by-layer (GO/PLL-LBL) or hybrid (GO/PLL-H) grafting to enhance the biofouling resistance of the FO membrane. The GO/PLL-LBL tuned surface presented higher hydrophilicity and smoothness, as well as a 99% reduction in surviving bacteria (**Figure 9**). Besides, the hybrid modification (GO/PLL-H) also diminished the reverse salt flux compared to that of the pristine membrane, improving the membrane salt selectivity. In another attempt, Perreault et al. assessed the long-term biofouling tendency of the GO functionalized FO membrane (GO-TFC). The GO-TFC membrane demonstrated increased surface hydrophilicity and improved antimicrobial activity without altering transport properties, and achieved a 36% reduction of *P. aeruginosa* viable cells after one hour of contact time. The decreased membrane biofouling (50%) after 24 h-long treatment of synthetic wastewater supplemented with *P. aeruginosa* was ascribed to the reduced attachment of the microbial community on GO-TFC surface. The deposited cells on the membrane surface were inactivated and formed a layer of dead cells on GO-TFC that limited biofilm formation.

These findings highlight the potential of GO nanosheets in biofouling mitigation of FO membrane applications, as the design criteria can be desirably optimized to minimize the adverse effect of GO nanosheets on the membrane transport properties. However, there are many challenges to be overcome in the use of graphene-based materials, such as the attainment of the correct GO sheet size, oxidation density, and issues related to long term stability.

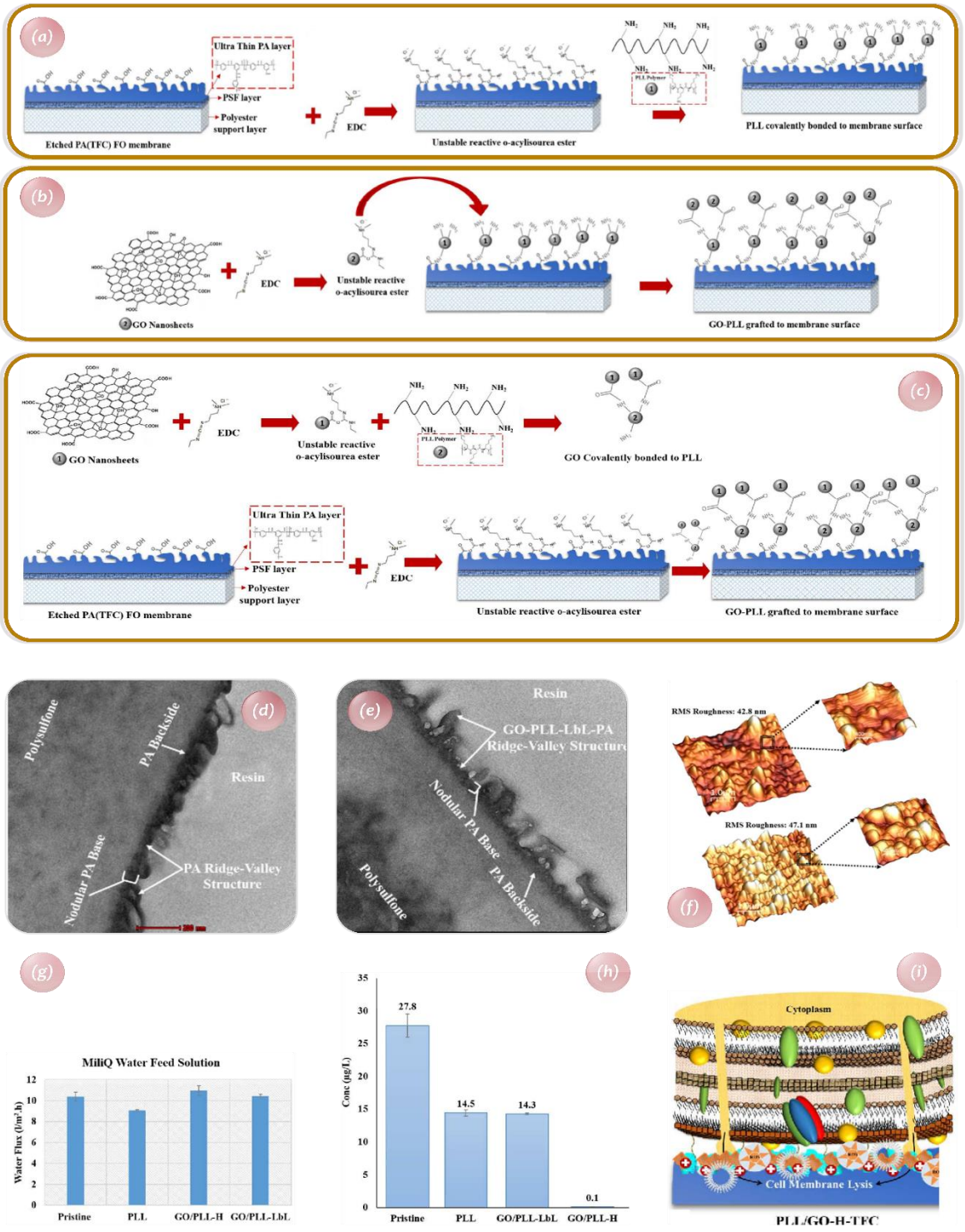

Figure 9. (a, b, and c) The schematic chemical reaction of PLL, GO/PLL-LBL and GO/PLL-H TFC functionalized membranes, (d, e) TEM and f) 2D AFM images of pristine and GO/PLL-LBL membranes, (g) Water flux and (h) ATP concentrations of the membranes and (i) Schematic illustrating of the bacterial toxicity mechanism [251]. reproduced with permission from ACS Publications.

Although metal NPs can result in satisfactory antibacterial activity, their instability and the risk of gradual dissolution has greatly restricted their practical application in water treatment. This challenge can potentially be addressed by immobilizing or decorating metal NPs onto larger support to construct nanocomposites [252]. These carriers enable nanocomposites with multifunctional characteristics such as enhanced antifouling, permeability, and mechanical strength compared to those currently in use [253]. Promising carriers for metal NPs include CNTs [254], GO [255]. Zwitterions [256], and PDA [257]. Considering the diversity and complexity of membrane fouling, this strategy provides a new way to combine antiadhesive and antibacterial features for a long-lasting antibiofouling performance.

An example of this approach has been reported for grafting zwitterionic poly(sulfobetaine methacrylate) brushes with the embedment of biocidal silver nanoparticles to attain augmented anti-adhesion and bacterial inactivation [226]. This combined effect has been associated to a more pronounced antibiofouling resistance, also leading to minimum flux reduction during membrane operation. Even though the results of such modifications are very interesting, the complexity of the procedure and equipment involved can be a major obstacle.

GO-based nanocomposites as functional materials are fabricated by immobilizing metal NPs onto the GO nanosheet [258]. The existence of both ionic groups and aromatic sp^2 domains enable GO to serve as a nucleation site and participate in the bonding interactions with biocide metal ions, such as Ag NPs [259]. Additionally, the carboxyl groups present at the edge of the GO nanosheets also combine with the metal ions [258]. Metal ions deposit on the GO nanosheets via the cooperation of π-π interactions, hydrogen bonding, and Ag-O coordination [260].

The metal release rate of GO-based nanocomposites containing metal NPs is considerably lower than for pristine metal NPs. The TFC PA membranes functionalized with GO-based nanocomposites inherit both the effect of nanosheets and that of metal NPs, opening a new pathway for increasing antibiofouling resistance and separation performance without sacrificing the water permeability [261]. Soroush et al. [262] executed pioneer work to covalently bind the Ag NPs immobilized GO nanosheets onto the PA FO surface and imparted enhanced antibacterial activity to the membrane due to the synergetic effect of the metal-GO hybrid. The functionalized TFC surface displayed hydrophilic properties (contact angles below 25°) and significant antibacterial activity (over 96% in a static test) without adverse effect on the membrane transport properties.

In another relevant attempt, Soroush et al. reported [263] the functionalization of TFC FO membranes with Ag-GO nanocomposites to impart biocidal properties to the membranes. The surface of the TFC membrane was initially functionalized with GO nanosheets via EDC/NHS coupling reaction, and then the Ag NPs was formed on the surface using sodium borohydride as the capping agent. The GO nanosheets acted enhanced silver loading with higher stability while decreasing the ion release rate. All these features improved the surface hydrophilicity and antibacterial activity. Besides, the Ag NPs regenerated membrane, following seven days of previous depletion, demonstrated 75% antibacterial activity. In a similar study, Faria et al. [264] functionalized TFC with Ag-GO nanocomposite employing the EDC/NHS approach to prevent bacterial attachment and biofilm growth on the membrane surface. The carboxyl functional groups on the Ag-GO nanocomposite were covalently bound to carboxyl groups of the TFC surface via a crosslinking reaction. The TFC-Ag-GO membrane exhibited 80% antibacterial activity against the attached *P. aeruginosa* microorganisms and showed a

promising antibiofouling property during dynamic biofouling experiments (30% water flux decline) without sacrificing the membrane intrinsic transport properties.

Liu et al. [218] developed a simple and facile approach for the in situ generation of Ag NPs on the PDA coated TFC FO membrane with sustainable antibiofouling activity. Ag NPs formed on a PDA layer by a simple dip-coating procedure and displayed long-term silver release with the capacity to be regenerated multiple times after depletion. The functionalized membrane had strong, sustainable bactericidal efficacy against both Gram-negative and Gram-positive bacteria. Although the PDA layer exerted some mass transfer resistance translating into flux loss, the transport properties may be further optimized by controlling the thickness of the PDA layer and the silver growth. Additionally, the facile regeneration of Ag NPs on the PDA surface provides a new direction for the development of sustainable, long-term antibiofouling TFC PA membranes. Qi et al. [265] modified the surface of the TFC PA FO membrane with a passive PDA coating and then deposited active antibacterial Ag NPs on the PDA layer (Ag-PDA). The active Ag-PDA membrane demonstrated both excellent antiadhesive and antibacterial properties in static antibiofouling experiments (33.3% and 97.0% of antibacterial activity for PDA and Ag-PDA coated membranes, respectively). More importantly, Ag NPs were stable on the surfaces, and the Ag-PDA membrane revealed 96.1% antimicrobial activity and lower water flux reduction (0.5% water flux decline) after 24 h dynamic cross-flow operation, attributed to biofilm growth prevention.

Integrating highly hydrophilic zwitterionic materials with biocidal agents such as Ag NPs is a promising strategy to alter the membrane surface chemistry in minimizing the attachment of both organics and bio-foulant bacteria. In this technique, the biocidal agent exerts toxicity toward the bacteria while the zwitterionic material shields the surface from adsorption

of organic foulants, overcoming technical challenges faced in treating complex feed solutions. Liu et al. [130] developed a new pathway for the fabrication of Ag NPs-loaded zwitterionic polymers with dual function of antiadhesion and antibacterial properties for biofouling mitigation. After grafting zwitterionic poly(sulfobetaine methacrylate) (PSBMA) brushes to the membrane surface via an atom transfer radical polymerization (ATRP) reaction, Ag NPs were formed in situ through chemical reduction of silver. The specific PSBMA-Ag TFC structure in which Ag NPs were present on top of the polymer brush showed superior antibacterial activity (95%) and effectively inhibited the biofilm formation in dynamic biofouling experiments (**Figure 10**).

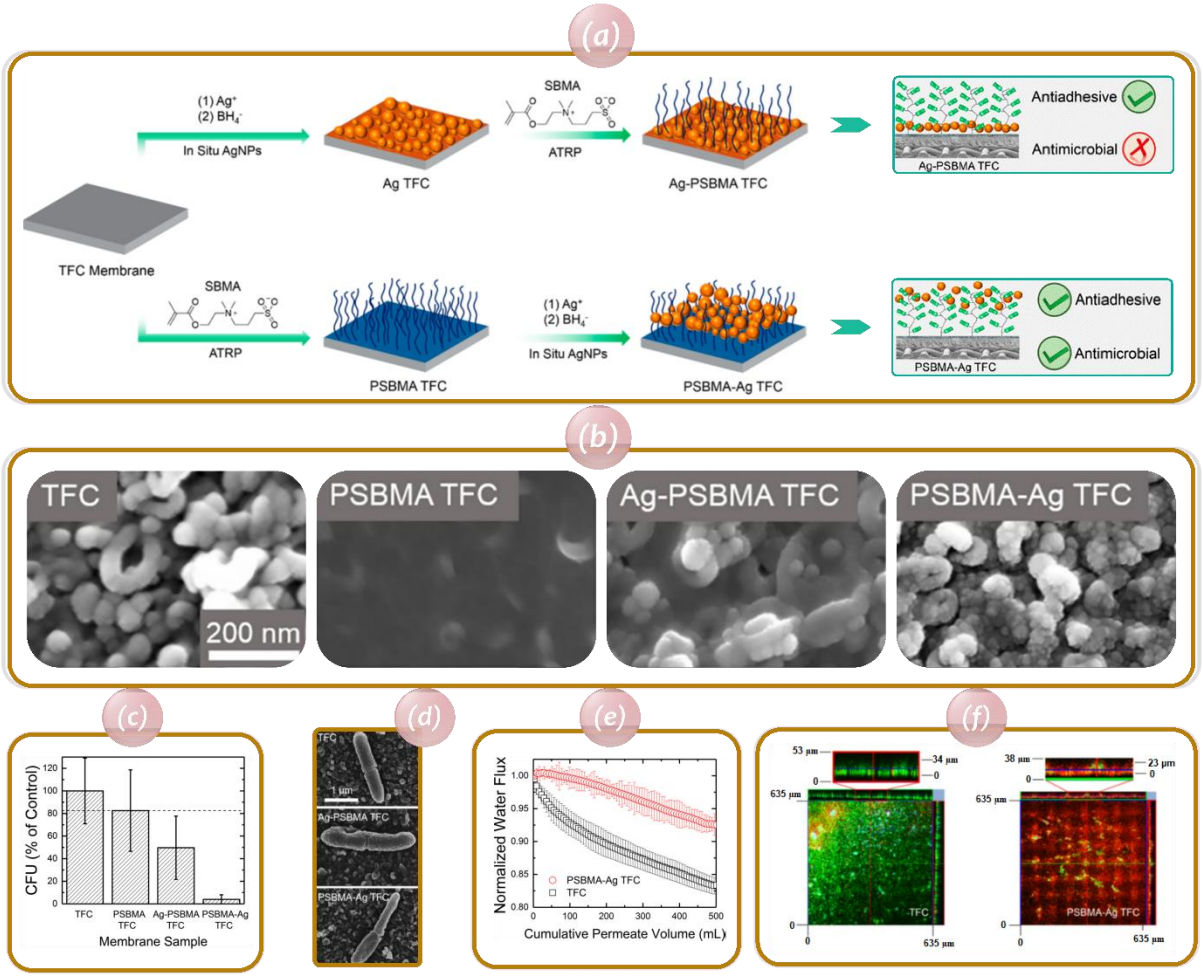

Figure 1. (a) Schematic illustration of the two different approach for the membrane modification AgNPs formation on the polyamide layer followed by the PSBMA grafting and PSBMA grafting followed by in situ synthesis of AgNPs, (b) SEM images of the pristine TFC, PSBMA, Ag-PSBMA, and PSBMA-Ag TFC membranes,(c) the percentage of colony forming units (CFU) after 3 h exposure to P. aeruginosa bacteria, (d) the morphological SEM images of P. aeruginosa cells after exposure, (e) normalized permeate water flux during biofouling experiment by P. aeruginosa, (f) confocal laser scanning microscopy (CLSM) images of P. aeruginosa biofilm developed on pristine TFC and PSBMA-Ag TFC membranes after biofouling test, in which live cells, dead cells, and polysaccharide−EPS were stained with SYTO 9 (green), PI (red), and ConA (blue) dyes, respectively [130]. reproduced with permission from ACS Publications.

Furthermore, the regeneration of Ag NPs after depletion was more feasible in this PSBMA-Ag TFC architecture. Liu et al. systematically studied the performance of silica nanoparticles (Si NPs) and zwitterionic polymers in improving the antifouling properties of a TFC membrane. A dense layer of Si NPs was grafted via dip-coating with aminosilane-

functionalized Si NPs (Si-TFC membrane), while zwitterionic polymer brushes were formed on the membrane surfaces through ATRP grafting (PSBMA-TFC membrane). The resulting membrane demonstrated considerably higher fouling resistance compared to that of the Si-TFC membrane against proteins and bacteria during dynamic fouling experiments (**Figure 11**).

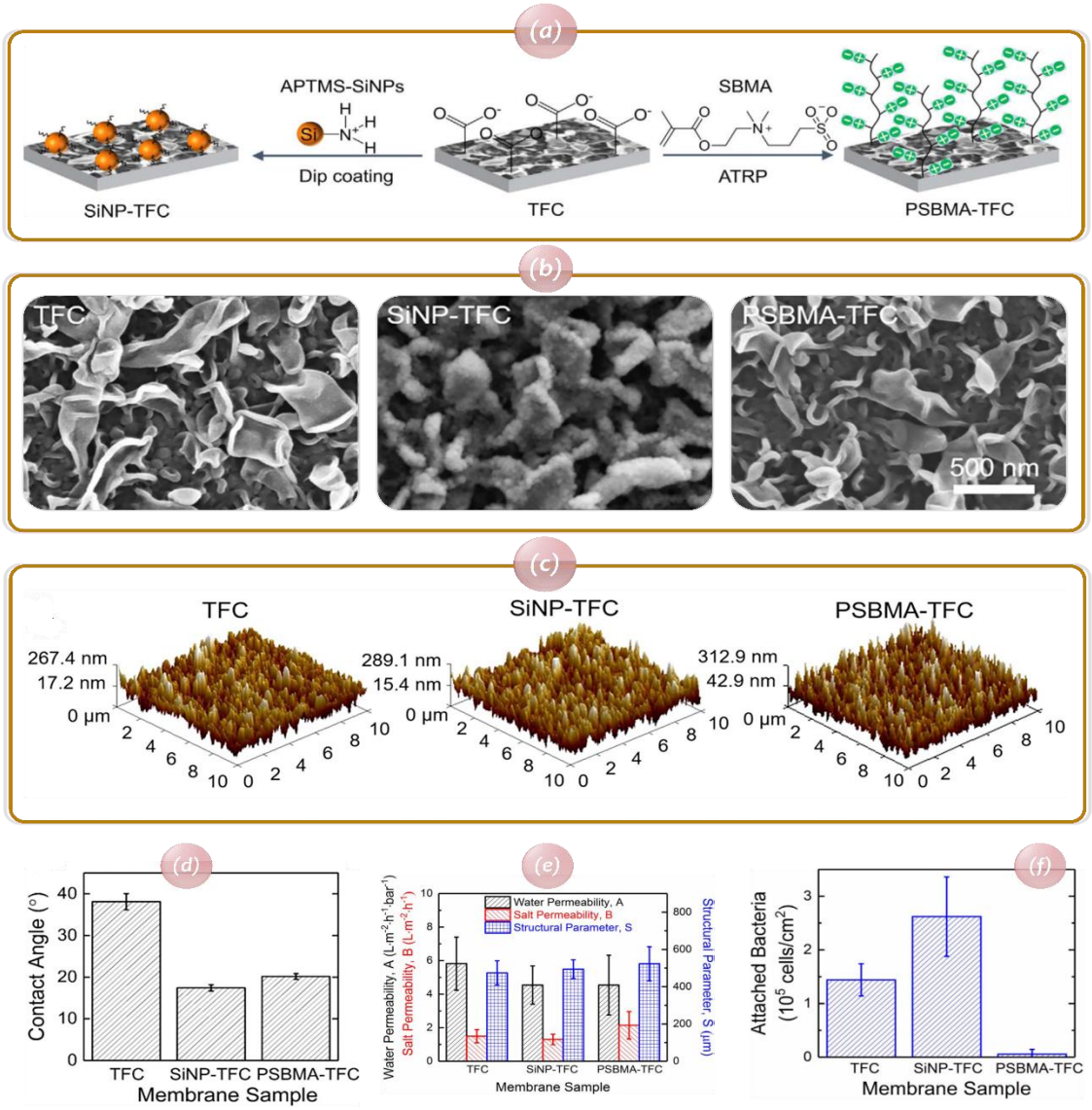

Figure 2. (a) Schematic illustration of SiNP-modified and zwitterionic polymer PSBMA-modified TFC membranes, (b, c) SEM and 3D AFM images of the pristine TFC, TFC-PDA, and TFC-PSBMA membranes, (d) Water contact angles, (e) transport and structural properties of pristine TFC and TFC-PSBMA membranes, and (f) number of attached live E. coli on the surface of pristine and modified membranes after 3 h exposure to bacteria [267]. reproduced with permission from ACS Publications.

Qiu et al. [256] reported a strategy to simultaneously improve the water flux and the biofouling resistance via functionalization of Ag NPs zwitterion nanocomposites on the TFC FO surface. They presented a simple and efficient approach to graft zwitterions via second interfacial polymerization and form Ag NPs by in situ reduction. On account of the simultaneous improvement of antiadhesive and antibacterial activity, the functionalized membrane exhibited significant biofouling resistance with regeneration ability. All the superior results offered by this simple surface functionalization approach highlights its potential as an effective way for practical TFC FO applications. **Figure 12 and Table 4** summarize the materials utilized in biofouling mitigation and a comparison of different approaches applied in surface functionalization of FO membranes, respectively.

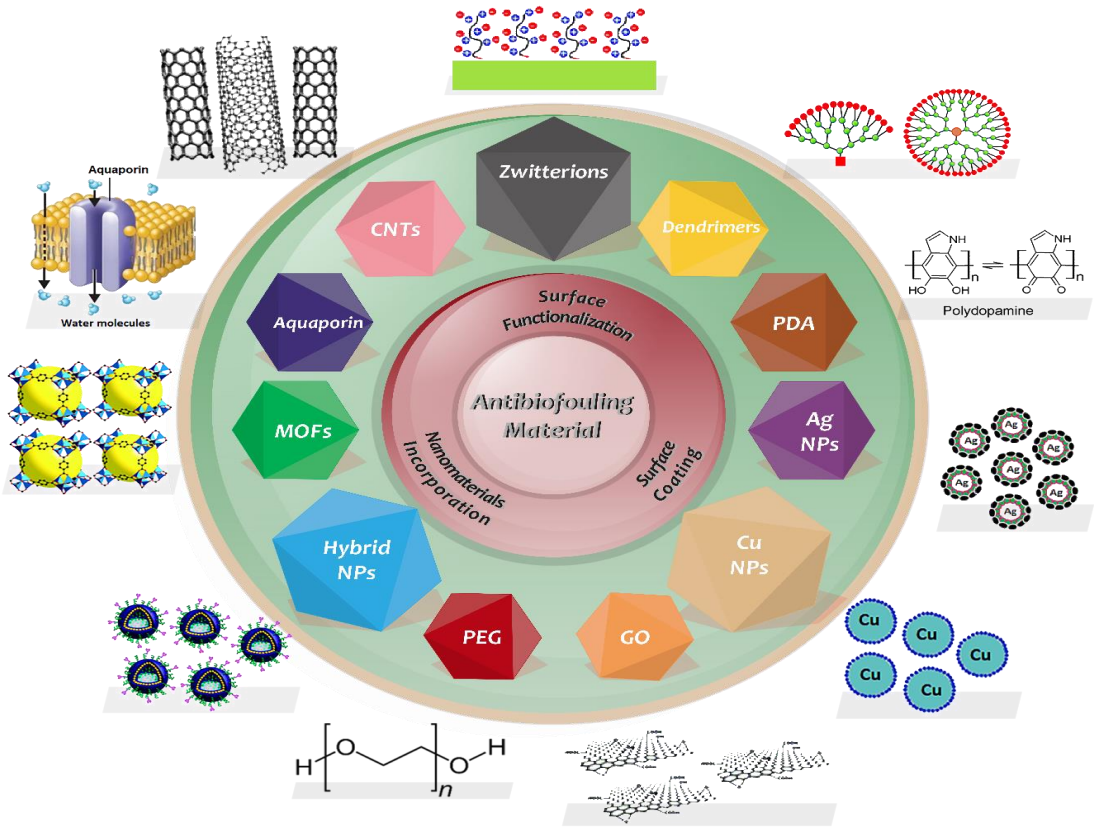

Figure 12. Different types of materials applied in surface functionalization.

Table 4. A comparison of different approaches and antibacterial agents applied in surface functionalization of the FO membrane.

Year	Substrate Material	FS	DS	Antibiofoulant Constituent	Functionalization Approach	Characterization Method	Bioufoulant	A key feature of Functionalization		Ref.
2016	TFC PA	1 M NaCl	DI	Cu NPs on PDA coating	In situ reduction	XPS, SEM, EDX, Ion release	S. aureus	-Simple, rapid, one-step procedure for the chelation of copper ions	- Decreased water flux of 28.1%high antibacterial activity	[236]
2015	TFC PA	2 M NaCl	DI	Porphyrin	Grafting	DR-UV-vis, ATR-FTIR, AFM, SEM	E. coli	-Simple and efficient grafting integrating sunlight to FO process	- Improved performance - Photodynamic antimicrobial activity	[163]
2019	TFC PA	1 M NaCl	DI	PAMAM Dendrimer	Grafting	SEM, AFM, FTIR, XPS, ζ-potential	Domestic wastewater	-Superior ammonia selectivity -High antifouling performance	- High water permeability and salt selectivity	[212]
2015	PAN	2 M NaCl	DI	Ag NPs	In situ reduction	XPS, SEM, EDX, ICP-OES	E. coli	- Very high antimicrobial activity against E. coli for 14 days under laboratory conditions		[178]
2018	TFC PA	1 M NaCl	DI	BSA capped Ag NPs	Grafting	SEM, AFM, FTIR, XPS, ζ-potential, ICP-MS	E. coli	-The simple and versatile approach of direct grafting -Less influence on surface roughness and charge -Slight improvement in water permeability and salt rejection	-The low release rate and excellent stability during filtration -Excellent antibacterial properties high biofouling resistant activity	[231]
2013	TFC PA	-	DI	GO	EDC/NHS coupling	SEM, Raman	E. coli	-Irreversible binding to the PA surface -Strong antimicrobial activity	- No adverse effect on transport properties after functionalization	[245]
2015	TFC PA	2 M NaCl	DI	GO	EDC/PLL grafting	FTIR, ζ-potential, TGA, AFM, TEM	ATP	- easy and stable grafting - enhanced hydrophilicity and smoothness - significant salt rejection	- reduced reverse salt flux 99% reduction in surviving bacteria	[251]

2016	TFC PA	0.2-1.2 M NaCl	DI	GO	EDC/NHS coupling	SEM, AFM, Raman, ζ-potential	SW* supplemented P. aeruginosa	- Increased surface hydrophilicity - Improved antimicrobial activity without sacrificing transport properties	- 36% reduced P. aeruginosa viable cells after one h of contact time 50% decreased membrane biofouling after 24 h	[156]
2016	CTA	1 M NaCl	SW	PEG-grafted PDA	Grafting	SEM, ATR-FTIR, AFM	Activated sludge in MBR	- Enhanced surface hydrophilicity - Lower flux decline during 61 days	- Improved anti-adhesion and antifouling ability	[217]
2018	TFC PA	-	DI	Ag NPs on PDA coating	In situ reduction	SEM, ζ-potential, EDX,	SW supplemented P. aeruginosa	- Improved hydrophilicity - Good stability of Ag NPs and 96.1% antimicrobial activity after 24 h of cross-flow test - Really low water flux decline	- Proper antibacterial activity in both static and dynamic conditions - efficient biofouling mitigation during long-term operation	[265]
2015	TFC PA	1 M NaCl	DI	Ag-GO nanocomposite	Click chemistry reaction	SEM, AFM, Raman, ζ-potential, XPS, ATR-FTIR, ICP-MS	E. coli	- Covalent bonding of the Ag NPs decorated GO nanosheets to TFC PA - Super-hydrophilic properties (contact angles of 25°) - Significant bacterial activity (over 96%) due to the synergetic effect of the Ag-GO nanocomposite	- No adverse effect on the membrane transport properties - GO nanosheets retarded the release rate of Ag NPs and provided biocide regeneration opportunity	[262]
2015	TFC PA	1 M NaCl	DI	Ag-GO nanocomposite	EDC/NHS coupling In situ reduction	SEM, AFM, Raman, , ICP-MS, XPS	E. coli, E. faecalis	- GO' oxygen-containing functional groups regulated the size, shape, and distribution of Ag NPs - GO presence enhanced silver loading and stability - Improved the surface hydrophilicity	- 98%antibacterial activity - GO acted as a platform to form smaller and uniformly distributed Ag NPs - 75% antibacterial activity after regeneration	[263]
2017	TFC PA	NaCl	DI	Ag-GO nanocomposite	EDC/NHS coupling	SEM, AFM, Raman, EDX	P. aeruginosa	- Straightforward covalent bounding of Ag-GO nanocomposite to the TFC surface - A slight reduction in surface roughness	- Significant decrease in bacterial attachment and viability 30% water flux decline during dynamic biofouling - No adverse effect on membrane transport properties	[264]
2019	TFC PA	NaCl	DI	Ag-MOFs	In situ growth	SEM, AFM, XPS, ζ-potential, ATR-	SW supplemented P. aeruginosa	- Facile technique with short reaction time - A two-step deposition procedure of Ag-MOFs without stabilizing/reducing agent - Uniform distribution of Ag-MOFs on the PA layer	- Slight reduction in both the salt and water permeability - Nearly 100% antibacterial activity high antibiofouling performance - Irreversible binding of Ag-MOFs to the TFC surface	[241]

						FTIR, ICP-OES				
2017	TFC PA	NaCl	DI	Ag NPs Zwitterionic nanocomposite	ATRP grafting	SEM, AFM	SW supplemented P. aeruginosa	- Smoother membrane surface - Remarkable increased hydrophilicity (reduced contact angle from 74° to 21°) - 95% antibacterial activity	- 46% increase in dead cells biovolume - 60% decrease in EPS content 8% water flux decline -48% reduction in the live cells biovolume	[226]
2017	TFC PA	NaCl	DI	Silica NPs Zwitterionic nanocomposite	ATRP grafting	SEM, AFM, ζ-potential	E. coli	- High surface hydrophilicity - Reduced surface roughness - Minimized electrostatic attraction of organic foulants - Effective shielding of the carboxylic groups on the TFC surface	- PSBMA-TFC membrane presented 68% decreased fluorescence intensity - Improved antifouling property - Reduced water flux decline (17%) PSBMA-TFC membrane showed a drastic increased in antibiofouling resistance (96% reduction of the number of attached E. coli)	[266]
2018	TFC PA	1 M NaCl	DI	Ag NPs Zwitterionic nanocomposite	Grafting In situ reduction	XPS, ATR-FTIR, SEM, AFM, EDX, ICP-OES	E. coli	- Simple and efficient surface modification strategy - Increased structure hydrophilicity without adverse effect on transport properties - High water flux and excellent selectivity	- 96% antibacterial activity - Significant biofouling resistance long-term antibiofouling property - Simultaneous improvement of antiadhesive property	[256]
2016	TFC PA	1 M NaCl	DI	Ag NPs on PDA coating	In situ growth	XPS, AFM, SEM, EDX	E. coli, S. aureus	- Enhanced hydrophilicity (contact angle from 68.4 ° to 40.6°) - Increased roughness - The Ag NPs formation decreased the water flux (8.58%) and the reverse salt flux (20.71%)	- PDA coating allows long-term Ag NPs release and multiple times regeneration -strong, sustainable antibacterial properties (E. coli 95.6%)	[204]
2014	CTA	1 M NaCl	GW**	Ag NPs regenerated by TiO_2	In situ growth	XPS, AFM, SEM, EDX, ζ-potential	ATP	- Moderately enhanced hydrophilicity - Increased roughness - 11 times less bacterial growth	- TiO2 regenerates the Ag NPs by decomposing the organic matter - 67–72% initial water flux recovery effective inhibition of bacteria growth	[267]

*Synthetic Wastewater
*Ground Water

3.3. Surface Coating for Membrane Biofouling Mitigation

Surface coating is a simple technique for membrane surface modification [163]. The coating layer protects the membrane by diminishing the deposition of foulants onto the membrane surface; this technique can often be easily incorporated into existing membrane manufacturing processes [163]. In this method, the membrane surface properties such as roughness, hydrophilicity, and surface charge can be modified to reinforce the antibiofouling properties of the membranes [268]. The main restrictions of this approach are the typical decline in water flux and also issues of delamination of the coating during filtration operation [269]. Surface functionalization via chemical treatment approaches may be difficult and expensive in some cases. Surface coating is a quicker and more convenient physiochemical treatment.

Currently, there are two main surface coating approaches, thin-film coating and self-assembled monolayers for biofouling mitigation of FO membranes [269]. The main goal of these techniques is mostly to form a hydrophilic layer on the PA surface. Like grafting, surface coating involves two distinct procedures: coating-to and coating-from. The former involves post-modification of the membrane surface with hydrophilic polymers (PVA or PEG) or inorganic antibacterial nanomaterials through dip-coating or spin-coating. In contrast, the latter consists of the formation of antibiofouling polymers or nanomaterials by in situ techniques on the membrane surface. Moreover, both usually include two steps: (i) dipping of the TFC PA surface into a coating solution, and (ii) residual solvent evaporation at ambient or moderate temperature to form the coating layer. Positively charged materials are potential candidates to facilitate stable surface coating with the negatively charged groups on the TFC PA FO membranes without any pre-treatment of the surface. On the other hand, in case of the coating-from technique, the membrane surface is normally pretreated to induce adsorption of the

antibiofouling agent via pre-coating. Approaches including sol-gel [270] and bioinspired adhesion [271] have been applied to assist with the in-situ formation of antibacterial coatings.

The coating features, such as the type of solvent and the density of the coating solutions, have important effects on water permeation and salt rejection [272]. In other words, both polymer and solvent can affect water-polymer and polymer-polymer interactions and thereby the transport of water or solute molecules within the selective layer. For example, when using short-chain aliphatic alcohols as a coating layer, the water flux increases considerably due to the higher affinity toward water molecules. Also, solvents that are usually used for coating can swell and remove the residual monomers/additives on the membrane; this eventually results in facilitated water transport and higher permeability. However, a swollen membrane may lose its initial permeability after solvent evaporation by a decrement of water-polymer interactions or pore collapse through capillary forces. The degree of flux reduction after solvent evaporation depends on solvent properties, comprising surface tension, polarity, water miscibility, and hydrogen bonds [272]. Moreover, it has been observed that long exposure time with the solvent during coating may deteriorate the integrity of the PA selective layer and decrease salt rejection. Coating methods applied to alleviate biofouling of FO membranes can be divided into three methods: bioinspired PDA coating, surface adsorption, and layer-by-layer (LBL) assembly.

3.3.1. Bioinspired Coating

Zwitterionic materials may be used for surface coating rather than surface chemical functionalization [273, 274]. In a study by Nguyen et al., a commercial FO membrane surface was modified by poly amino acid 3-(3,4-Dihydroxyphenyl)-L-alanine (L-DOPA) coating, a zwitterionic (redox functional amino acid) and inspired by the adhesive proteins found in marine

mussels (**Figure 13**) [275]. As they reported, L-DOPA can self-polymerize in aqueous solutions and can attach firmly to the various substrates [213]. They theorized that the coated membrane became intensely hydrated and then the accumulation and adsorption of foulants on the membrane surface were prevented by the hydrated layer. Besides, they observed that by increasing the coating time, the water contact angle was reduced from the initial value of 48° for an untreated sample to 44° and 38° for membranes coated in a period of 4 hours and 12 hours, respectively. The L-DOPA coated membranes revealed higher negative Zeta potential than that of uncoated membranes. While L-DOPA has the positively charged NH_3^+ groups and the negatively charged carboxylic acid (COO^-) groups, coating of L-DOPA imparted a negative charge on modified membrane surfaces as the COO^- contributed more to the overall charges.

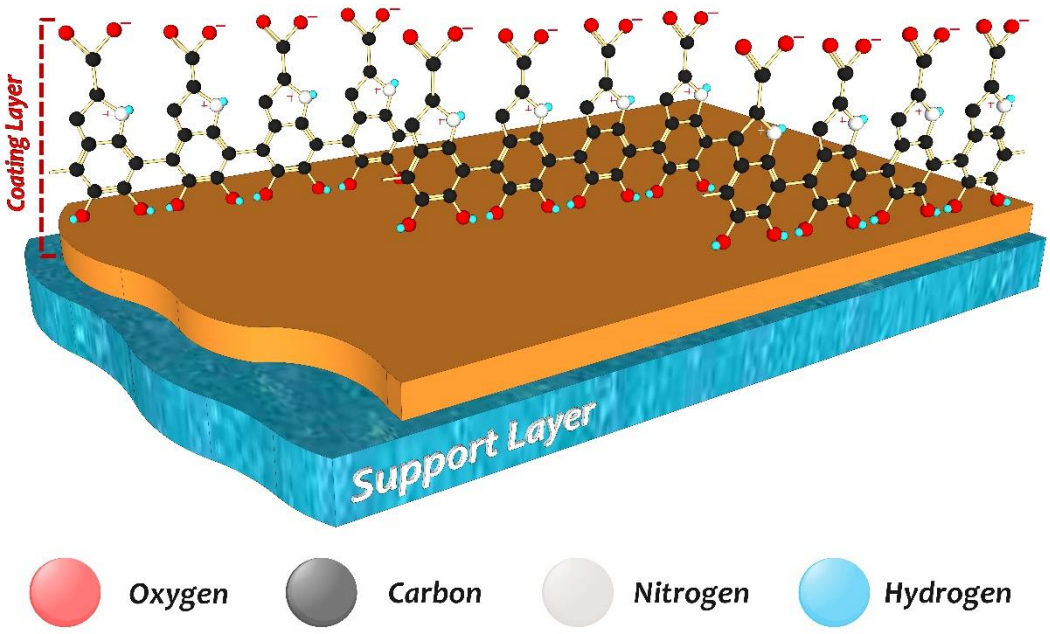

Figure 13. Schematic diagram of the structure of zwitterionic poly (L-DOPA) attached on the FO membrane.

In other studies, layered double hydroxide (LDH) nanoparticles were deposited on the TFC membranes by a polydopamine (PDA)-induced coating process [257]. Layered double

hydroxides (LDHs) are ionic lamellar compounds fabricated by positively charged Brucite-like layers with an interlayer region comprising charge compensating anions and water molecules [276, 277]. The TFC membrane prepared via an interfacial polymerization was dip-coated into the LDHs suspension for one hour. Another type of modified TFC PA membrane was obtained by immersing the TFC membrane in the suspension of LDHs until desiccation at 30 °C. Only a small quantity of LDH nanoparticles appeared on membrane surfaces following the dip-coating method while a more consistent LDH nanoparticle layer was prepared successfully on the membrane surface following desiccation. The latter surface showed the least coverage of *E. coli*. The enhanced antibiofouling performance of the modified membranes was attributed to the considerable increase of surface hydrophilicity due to the surface coating of LDHs nanoparticles, which was consistent with the water contact angles [278].

3.3.2. Surface Adsorption

Physical adsorption is a convenient approach for membrane surface modification, and some researchers have adopted this technique to modify the surface properties of FO membranes. In this approach, the hydrophobic portion of the antibiofouling agent has favorable free energy of attraction to the TFC PA surface, altering the membrane surface morphology, physiochemical properties, and performance. Generally, these types of coatings are relatively simple to use in commercial applications. Ahn et al. have fabricated polyvinyl alcohol (PVA)-coated cellulose acetate (CA)-based flat-sheet membranes and applied them in the forward osmosis (FO) process [279]. The CA-based membranes were prepared via conventional immersion precipitation and then coated by PVA. The membranes were then immersed in the 0.01% glutaraldehyde solution for a cross-linking process. It was reported that the hydrophilicity

of CA membrane surface increased and hence water contact angle was diminished (from 73.5˚ to 39.3˚). In another study conducted by Zhang, surface modification of the TFC PA membranes was carried out by different functionalities [279]. For instance, the TFC-based membrane was in contact with a 2.0 wt.% poly (amido amine) (PAMAM) aqueous solution for 5 min, imparting amine groups on the surface of the membrane. It was revealed that the nitrogen content increased from 8.93% to 11.27% after dendrimer attachment as evidence for the existence of the PAMAM layer on the modified membrane. After this step, the modified membrane was coated by 5% (w/v) poly(ethylene glycol) methyl ether acrylate (PEGMEA) solution in 80/20 (v/v) water/ isopropanol (IPA) for 24 h to obtain the final TFC membrane. The water contact angle of the pristine TFC membrane was around 68˚, while all the modified membranes demonstrated water contact angles of less than 50˚. Experiments of bacteria attachment on membrane surfaces showed significant improvements in antibacterial properties after modification. The live bacteria attachment on pristine TFC membranes was 6.5% per membrane area, while it was only 0.16% and 0.05% for TFC membranes modified by PAMAM and PEGMEA, respectively. The results in comparing two modified membranes showed that, although both hydrophilicity and electrostatic parameters were contributing to bacterial adhesion, hydrophilicity seemed to play a more significant role in the process of live cell attachment. The hydrophilic PAMAM-modified membrane was much less prone to live *E. coli* adhesion even though positively charged. **Figure 14** illustrates the evaluation of the live and dead *E.coli* attachment on membrane surfaces along with statistical comparisons.

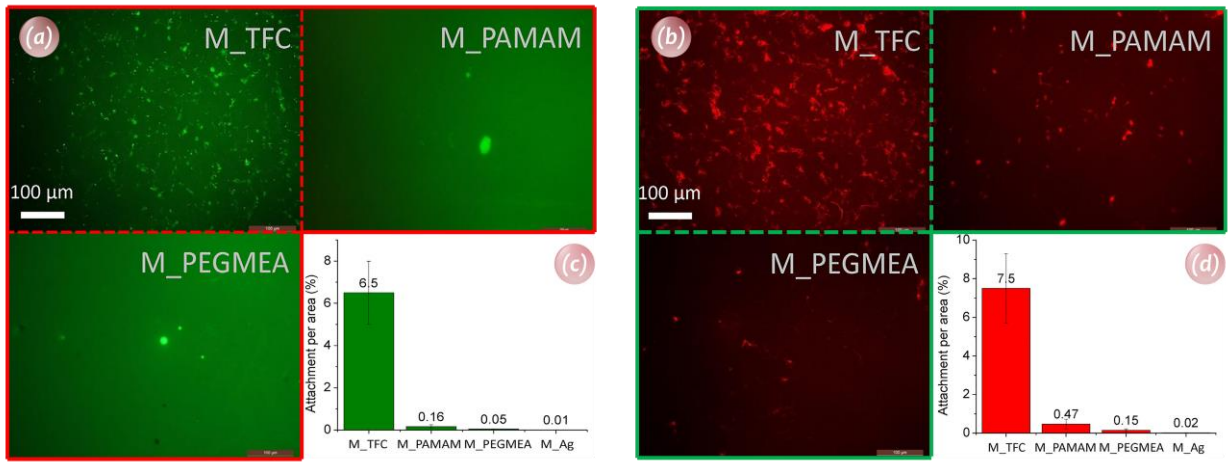

Figure 3. Representative fluorescent microscope graphs of the (a) live and (b) dead E. coli attachment on the surfaces of the TFC, PAMAM, PEGMEA membranes, and statistical comparisons of the (c) live and (d) dead cell attachment per area of the membranes [280]. reproduced with permission from Elsevier.

In a similar study by Li et al., the biofouling behavior of CTA FO membrane with surface modification via PDA coating in a submerged osmotic OMBR was investigated [217]. The hydrophilicity of the membranes improved considerably whereby the contact angle of CTA membranes decreased from 91.4˚ to 79.8˚ after PDA coating modification. It was also reported that the amount of β-polysaccharides adsorbed onto the surface of the modified membrane was considerably less than that on the pristine membrane, indicating antiadhesion properties of the PDA-modified membrane for polysaccharides. This is consistent with the findings of McCloskey et al., who reported that the presence of a PDA-coated layer on the membrane surface diminished the protein adhesion [281]. Improvement of antibacterial properties is possibly the main reason for improving the antibiofouling of the PDA-modified membrane [281]. The protonated amine groups in the PDA layer were also responsible of bacteria inactivation by contacting the cells [282]. Therefore, this modification provided ideal antibacterial properties and decreased the adhesion of biopolymers, leading to a lower resistance in OMBR operation.

3.3.3 Layer-by-Layer Assembly

LBL offers an efficient and facile technique for fabrication of ultrathin films and has been developed for different membrane separation processes, such as nanofiltration [283], reverse osmosis [284], and forward osmosis [285]. It is performed by alternate electrostatic-based deposition of oppositely charged polyelectrolytes on a porous substrate [286, 287]. Compared to the other modification approaches, one of the main advantages of LBL coating is that it provides the potential to accurately control the thickness of the coating layer to fall in the nanoscale range. Consequently, the water flux reduction resulting from the formation of extra mass transfer resistance can be potentially minimized. Moreover, the fouling tendency can be diminished by control over the selection of the outermost polyelectrolyte by exploiting electrostatic repulsions with the foulants. Additionally, these multilayer coatings can be prepared by cost-effective, water soluble, and commercially available polymers. Despite relatively simple fabrication procedures, there are a few possible variations in the implementation of LBL membranes. The main controlling parameters affecting the final properties of the membrane structure comprise polymer compositions and concentrations, number of layers, and fabrication conditions/methods.

Natural electrolytes can also be used in LBL assembly. Phytic acid (PhA) is a nontoxic, biocompatible electrolyte with phosphate acid groups attached to a cyclohexanehexol ring. This compound exhibits high affinity toward water molecules and strong chelation capacity with mono/divalent metal ions. Accordingly, superhydrophilic complexes of PhA-metals can be prepared by spontaneous chelation of PhA and metal ions. Xiong et al. [288] conducted LBL assembly of PhA and antibacterial metal ions (M=Ag, Cu) for surface modification of PhA-TFC membrane to simultaneously enhance the bio/organic fouling resistance and separation

performance of the final membrane. Since the PA molecule carries six phosphonic acid functional groups with chelation ability, it strongly reacts with the metal ions as an inorganic cross-linker and induces the LBL assembly of the PA- Ag, and PhA- Cu complexes on the TFC PA surface (**Figure 15**). The FO performance of both the modified TFC-PhA-Ag and TFC-PhA-Cu TFC membranes was systematically regulated by manipulating the PhA concentration and assembly cycles. Due to increased hydrophilicity, the water flux of the modified TFC-PhA-Ag and TFC-PhA-Cu TFC membranes was enhanced up to 57% and 68%, respectively, without sacrificing the membrane selectivity. Additionally, both modified membranes demonstrated excellent stability against metal release owing to the strong attachment on the surface. The released concentrations of Ag and Cu ions in the water product were reported in the ranges of 0.001-0.013 and 0.001-0.010 mg/L, respectively. This result indicates the safety of both the TFC-PhA-Ag and TFC-PhA-Cu membranes for water treatment applications, as the released content of both ions were very far below those suggested by WHO guidelines (0.1 and 2 mg/L for Ag and Cu ions, respectively).

Liu et al. fabricated silver nanocomposite LBL-Ag FO membranes using the LBL assembly method for membrane biofouling control [289]. To prepare nanocomposite membranes, they controlled the amount of Ag NPs incorporated into the polyanion poly(sodium 4-styrene-sulfonate) (PSS) solution, and polycation poly(allylamine hydrochloride) (PAH) solution, following by crosslinking with 0.1 wt.% glutaraldehyde solution at room temperature. The membrane surface hydrophilicity was enhanced, which could considerably reduce bacterial adhesion and hence alleviate membrane biofouling [290]. The antibacterial activities of modified membranes against *B. subtilis* and *E. coli* were tested using the CFU method, and the results showed that the number of live bacteria decreased after 24 h exposure to the

nanocomposite membranes. It was also observed that nanocomposite membranes showed slightly better bactericidal activities against *B. subtilis* compared to *E. coli*, owing to the existence of a lipopolysaccharide (LPS) layer outside the latter Gram-negative bacterial cell membrane. The presence of this LPS layer around the cell wall of Gram-negative bacteria makes them more resistant to Ag toxicity [291, 292]. Additionally, the results of bacterial diffusion tests were consistent with the results of the CFU test.

Salehi et al. used LBL assembly of positive chitosan (CS) and negative GO nanosheets on a support layer which was prepared by blending hydrophilic sulfonated polyethersulfone (SPES) with traditional PES [293-295]. Water contact angle values obtained from the surface of the membranes revealed that this process effectively improved the hydrophilicity of the membrane surface. This result was mostly attributed to the existence of hydrophilic oxygen-containing functional groups on the surface of LBL modified membrane.

In another study, a GO-OCNTs-LBL membrane was fabricated by GO and oxidized carbon nanotubes (OCNTs) with five bilayers on a PES support. It was reported that the contact angle of GO-OCNTs-LBL membrane was lower than that of GO-LBL membrane due to the presence of hydroxyl groups. Due to the presence of higher content of oxygen-containing groups in the GO-OCNTs-LBL membrane (9.5%, detected by XPS) compared to the GO-LBL membrane (7.6%), hydrophilicity increased considerably. Although covalent attachment and LBL self-assembly are two successful techniques in the use of GO nanosheets to improve the properties of membrane separation processes, industrial application is less appealing due to the complexity of multiple steps [247]. In this context, Hegab et al. [296] introduced an industrially favorable methodology for immobilizing GO nanosheets onto the surface of TFC FO membranes using PDA bio-adhesion as a single pot technique of surface modification. They

used PDA as an adhesive agent to bind the GO nanosheets onto the surface of TFC FO membranes. The membrane presented a smoother surface with improved antibiofouling performance. Although all membranes demonstrated a decline in the water flux because of the growth of bacterial cells, the rate of flux decline for GO-PDA-modified membrane was the least. Additionally, ATP bioluminescence assay revealed the antibacterial activity of the GO-PDA-modified membrane compared to that of other membranes, attributed to the effect of the smoother, more compact, and hydrophilic surface [262]. Furthermore, the active sites of defective edges on the GO nanosheets generated ROS [297] that caused stress, leading to the destruction of the bacterial cell membrane [298]. Additionally, on the direct contact of bacterial cells with the surface of modified membranes, cell lysis occurred and this phenomenon suppressed biofilm establishment, resulting in considerable reduction of biofouling and its associated complications [299].

LBL membranes are sensitive to operating conditions. In the presence of chlorine, at high ionic strength conditions, and at very low or high pH, the LBL layer may swell or even desorb. To improve stability, a number of efforts applied crosslinking steps to stabilize the layers, as also mentioned in several occasions in the discussion above [300]. However, the application of such LBL FO membranes is still restricted only to the use of low concentration draw solution and neutral draw solutes for long-term operation [301].

Hegab et al. adopted a surface modification approach of forward osmosis membranes by the single-step assembly of multifunctional poly tannic acid-graphene oxide coating to reduce biofouling [302]. In this study, they used a versatile platform to immobilize GO nanosheets on the surface of TFC PA FO membranes resulting in smoother and higher hydrophilicity. This hydrophilic layer provided a barrier with the aim of short-term inhibition of foulant adhesion on

the membrane surface and hence 99% antifouling resistance (33% increase compared to the pristine membrane) [303]. Additionally, the sharp edges of GO nanosheets imparted biocidal activity [304, 305] and acted as reactive sites for the production of ROS [297, 298].

Despite its simplicity for antibiofouling application, surface coating suffers from some challenges. Although it has been effectively applied for FO membrane surface modification, the interaction of the coating layer with a PA layer sublayer is of relatively weak noncovalent type, such as van der Waals attraction, electrostatic interaction, or hydrogen bonding; this increases the possibility of delamination or detachment during continuous operation or cleaning processes. In other words, this susceptibility to damage offers short-term resistance to biofouling, and long-term biofouling formation may still occur. Additionally, in this process an additional thin layer forms on the membrane surface with typical thickness in the range of hundreds of nanometers. The presence of this layer may provide an extra barrier for water molecule permeation and a decrease of the accessible sites for water flow [306]. The coverage may lead to a certain degree (nearly 10% or greater) of water permeability reduction, even in case of initially dense TFC PA FO membranes. As a result, the coating layer should have an intrinsically high water permeability and be satisfactorily thin to obtain the maximum water flux for practical applications.

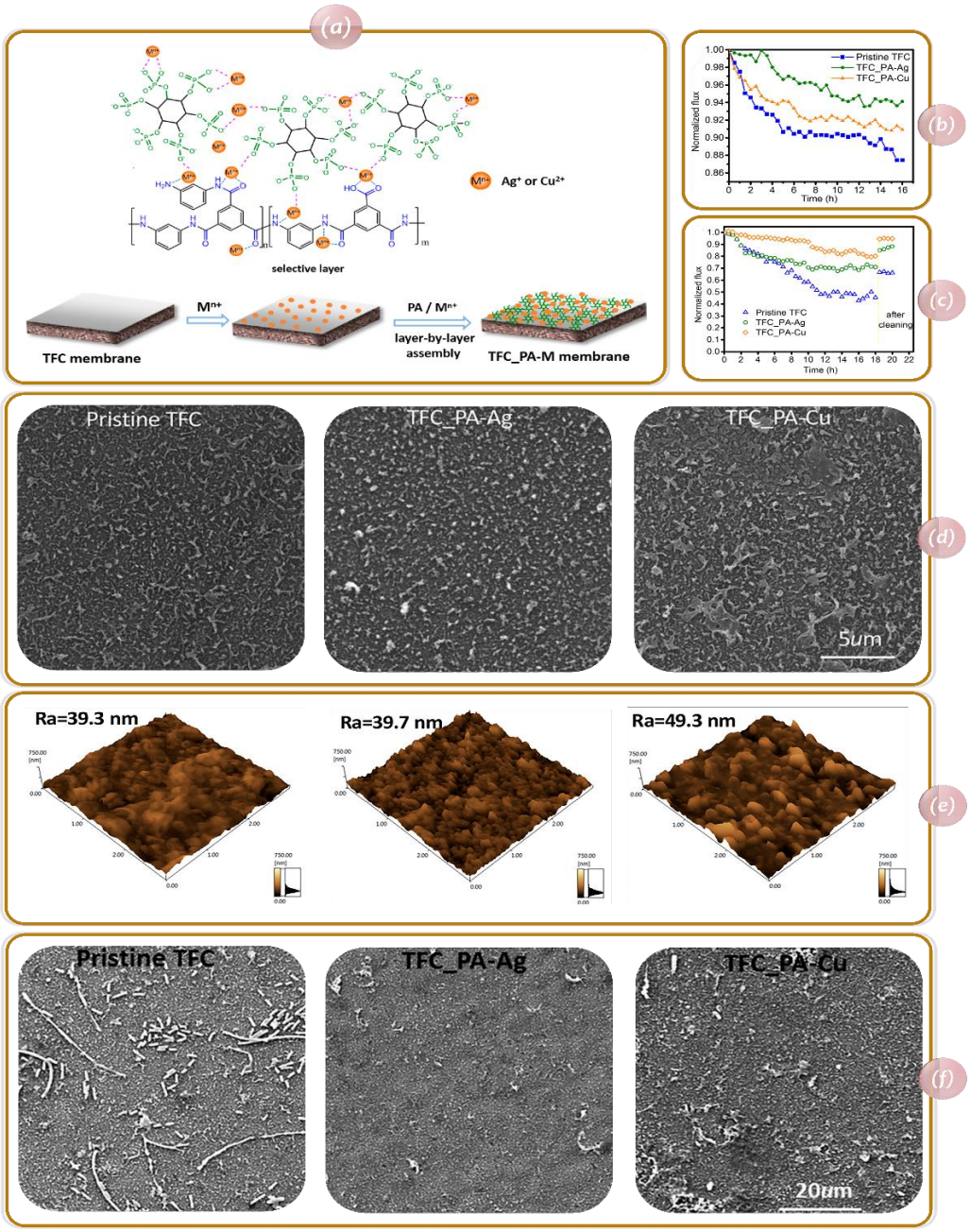

Figure 45. (a) Schematic diagram of TFC-PA-Ag and TFC-PA-Cu membranes fabrication procedure, water flux reduction during dynamic b) biofouling, (c) organic fouling tests with E. coli and sodium alginate as model foulants (d, e) SEM and AFM surface morphologies of pristine TFC and surface-modified membranes, and (f) SEM micrographs of the pristine TFC and surface-modified membranes (4 cycles of LBL assemblies) after incubation in E. coli suspension [289]. reproduced with permission from ACS Publications.

3.4. Nanomaterials Incorporation to Achieve Biofouling Mitigation

The incorporation of nanomaterials into the PA layer during the IP process is another approach for further modification of the final FO membrane properties [307]. The key advantage of TFC membranes is the flexibility of tuning the chemistry of the PA layer and that of the porous support independently to adjust the membrane performance [308]. For optimizing the selective layer properties, thin film nanocomposite (TFN) membranes have been prepared by the incorporation of different types of nanomaterials within the PA layer, including zeolites, silica particles, CNTs, and metal oxides [309, 310] [311].

Despite considerable improvement in membrane performance and fouling resistance by incorporating hydrophilic nanoparticles, the main bottleneck is still the alleviation of biofouling implications [312]. Compared to surface-coated or functionalized TFC membranes, antibacterial TFN PA membranes have the advantages of ease of manufacture and fewer preparation steps, and generally lower cost. In this context, different types of antibacterial nanomaterials such as Ag nanoparticles and Ag-based nanocomposites [313], Cu nanoparticles [314, 315], titanium dioxides (TiO_2) [316, 317], and zinc oxides (ZnO) [318] have been applied to prepare antimicrobial TFN membranes. The physiochemical aspects of the direct incorporation of nanomaterials into the selective layer can be summarized as follows:

- The weak interaction of the filler with the membrane matrix may result in an easy release, and thus a decrease in the antibacterial activity over time [319].
- The low compatibility between the inorganic nanomaterials and polyamide chain adversely affects the membrane performance and especially selectivity [319, 320]. In contrast, the higher affinity of the nanomaterials to the PA matrix increases the compatibility and

connection between the two phases via hydrogen or covalent bonds, and Van der Waals forces reduce or ideally prevent nanoparticle depletion during membrane operation.

- Another drawback of the incorporation of nanoparticles into the polymeric matrix of the PA layer is related to size. Since the thickness of the PA layer is in the range of 100-300 nm, nanomaterials of larger size deteriorate the membrane surface integrity and adversely affect salt rejection. On the other hand, if appropriately incorporated, these nanoparticles can have a substantial positive impact on mechanical strength and solute selectivity. However, it has been observed that nanoparticles of small size (less than 100 nm in diameter) have a great tendency to agglomeration due to surface interactions [321, 322].
- The incorporation of nanomaterials may alter the penetration rate of MPD/TMC monomers during interfacial polymerization, and possibly a much thinner polyamide layer forms. The functional groups on the surface of nanomaterials may react with monomers during the IP process, and this interaction affects the rate of the polycondensation reaction between amine and acyl chloride monomers [323, 324]. Although this behavior may decrease the crosslinking degree of the final selective layer, it protects the nanoparticle release rate and provides relatively higher long term stability.
- The performance of the nanocomposite membranes is closely related to the morphology of the nanoparticles [325]. It is generally accepted that nanomaterials with spherical morphology have better compatibility with the polymeric matrix, resulting in a less destructive effect of the mechanical and transport properties. Although numerous studies were carried out to elucidate the effects of nanoparticles with different sizes on the properties of the nanocomposite membranes [326, 327], further investigation is still required to assess the effect of the nanoparticle size on the physicochemical properties of the nanocomposite membranes.

- The presence of nanomaterials may increase the gaps between chains; therefore, the fractional volume usually increases and hence additional nanochannels are created for rapid transport of water molecules, which should result in increased water flux [328]. Additionally, the presence of nanomaterials may lengthen the permeation path of solute molecules by unique zigzag passage [329]. However, the typical trade-off between permeance and selectivity is usually observed also for TFN membranes.
- Although the nanomaterials offer numerous advantages even at low concentration, the uniform dispersion of the nanoparticles in the aqueous or organic phase during IP is a limiting factor [330]. The incorporation of small-size biocidal nanoparticles has led to the fabrication of membranes with improved biofouling resistance, smoother surface, enhanced hydrophilicity, increased water flux as well as higher antibacterial activity [331]. However, it has been suggested that excessive loading of nanoparticles may lead to severe aggregation, a considerable reduction in the effective surface area of the nanoparticles, defect formation, and a decrease in the mechanical strength of the resultant membrane. Consequently, exploring the optimum loading concentration of nanoparticles is of critical importance to attain a uniform dispersion of nanoparticles [332, 333].

To address these challenges, some alternative materials have been proposed, such as MOFs [334, 335]. Compared to the fully inorganic compounds, MOFs offer a better affinity to the organic nature of the PA chain because of the presence of the organic linker in their structures. The proper compatibility between the two phases can be attributed to the higher interaction with the PA matrix at the MOF-polymer interface in terms of covalent, non-covalent, and hydrogen bonds, also preventing the formation of non-selective voids between the phases [336-339]. Moreover, MOFs are frequently reported in the literature for their potential

antibacterial activity [340, 341] as they serve as a reservoir of metal ions for the controlled release of bactericidal agents [342, 343]. Another advantage of MOFs is the uniform distribution of active metal sites in their structures, providing a long-lasting bactericidal activity without agglomeration or oxidation [344, 345]. These outstanding features provide a prospect for improving the selective layer characteristics without deteriorating its performance and especially selectivity.

Although MOFs were widely reported in the fabrication of TFN membranes by incorporating ZIF-11 [346], ZIF-8 [347], MIL-68 [346], MIL-53 [160], or MIL-101 [346], few studies considered the incorporation of MOFs for biofouling mitigation of FO membranes. Besides, almost all the TFN FO membranes were prepared via dispersion of MOFs, whether in TMC organic or MPD aqueous solutions. Based on the literature survey, the influence of MOFs incorporation to the TFN membranes can be generally divided to five domains: (i) the relation between the membrane transport performance and structure change,(ii) MOF type and concentration during the IP process, (iii) catalytic effect on the IP process, (iv) MOFs-polyamide chain interaction at interface, and (v) the hydrolysis degree of the acid chlorides.

To simultaneously improve the desalination performance and antibacterial activity of the TFC FO membrane without detrimental effects on the selectivity, Zirehpour et al. [348], incorporated Ag-BTC MOF nanocrystals into the PA layer during IP reaction. Although low content of Ag-MOF (0.02 wt.%) was incorporated, the water permeance of TFN membrane increased of about 55% following modification. Meanwhile, the TFN membrane presented bacterial inactivation of 96% and 90% for E. coli and S. aureus, respectively. This antibacterial activity was attributed to the minimal aggregation, improved compatibility, and uniform distribution of the MOF crystals in the PA layer, while a low release rate of the Ag ions (0.04

μg/cm2.day) was observed after 24 days. All these features resulted in 20-24% and 6-10% water flux decline for TFC and for TFN membrane during biofouling experiment, respectively [349]. In a similar study by Firouzjaei et al. [184], the synergetic biocidal activity of graphene-oxide and silver metal-organic framework (GO-Ag-MOF) was investigated for TFN FO membranes. GO, Ag-MOF, and GO-Ag-MOF were incorporated into the PA layer during IP process (Figure 16). The GO-Ag-MOF TFN membrane showed about 95% antibacterial activity against E. coli, while the bacteria inactivation of Ag-MOF TFN, GO TFN, and TFC FO membranes were reported to be 80%, 66%, and 2%, respectively. After a 24-h biofouling experiment, no significant water flux drop was reported for the GO-Ag-MOF TFN membrane, while 38%, 54%, and 70% water flux reduction was observed for Ag-MOF TFN, GO TFN, and TFC membranes, respectively. In a different study conducted by Rahimpour et al. [185], two different concentrations (0.01 and 0.02 wt.%) of polyrhodanine (PRh) NPs were incorporated into the PA layer and provided a more hydrophilic layer with lower thickness compared to the pristine membrane. The modification translated into a 45% water permeance increment, and into a 40% decline in salt permeability. High antifouling/antibio-fouling properties and bacterial inactivation (89% for E. coli and 92% for S. aureus) were observed for the PRh-TFN membrane.

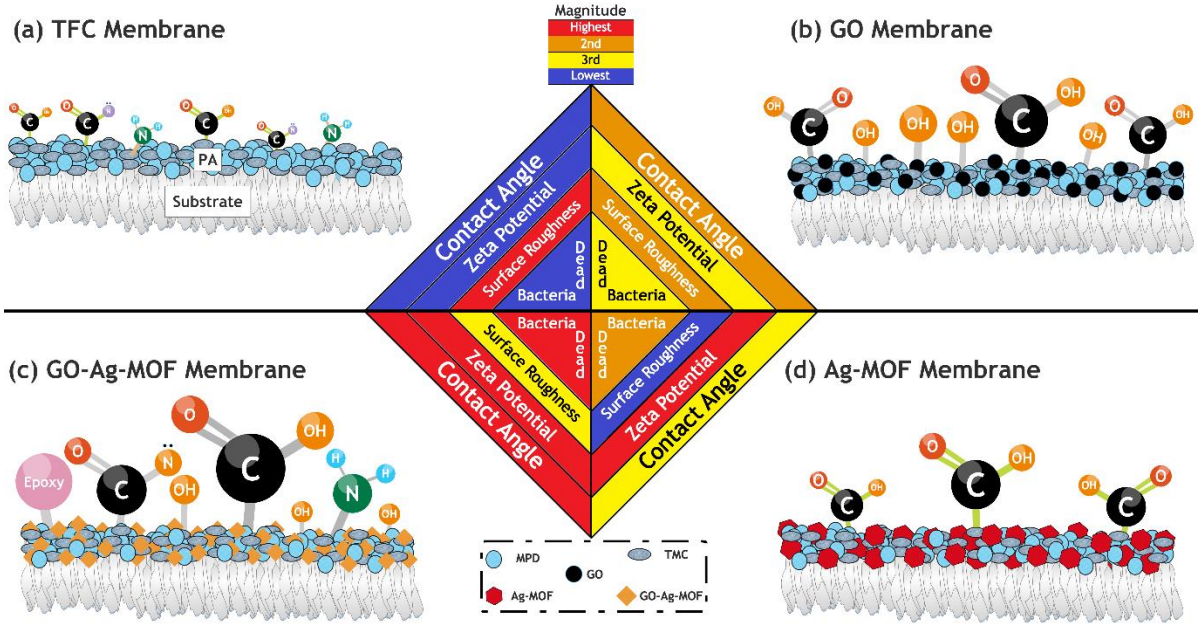

Figure 16. Different structural membrane's parameters effecting biofouling of incorporated TFC FO membrane [184]. reproduced with permission from ACS Publications.

In other studies, He et al. [350], added different amounts of graphene-oxide in the MPD solution during IP process for the PA layer formation. Antibacterial activity of about 22 %, and viability of 87 and 60 % were observed for pure GO, TFC, and GO-TFC PA membranes, respectively. Physical damage to the cell membranes through increased cellular oxidative stress was reported as the main mechanism for the antibacterial activity of GO nanosheets. Wang et al. [351] fabricated free-standing cellulose triacetate (F-CTA)-graphene oxide (GO) FO membrane by addition of GO nanosheets to the CTA/methanol/lactic acid solution. Ascribed to the hydrophilic nature of GO nanosheets, the biofilm thickness of E. coli reduced from 18.5 µm to 4 µm as a consequence of GO incorporation. In another study, different concentrations of graphene quantum dots (GQDs) were added to the MPD solution during IP process and the results showed a contact angle reduction from 72.9º to 51º, for the neat TFC and TFN membranes, respectively. In addition, bacterial inactivation of 90% and 95%, against E. coli and S. aureus, was reported

after one-hour incubation, attributed to the uniform distribution of GQDs within PA layer (Figure 17a-d). The SEM images of the membrane after incubation with bacteria showed physically disrupted bacteria cells on the TFN membrane, while such behavior was not observed for neat TFC surfaces (Figure 17e and f). The significant antibacterial activity of GQDs modified TFC membranes was also confirmed by fluorescent images (Figure 17g and h) [351].

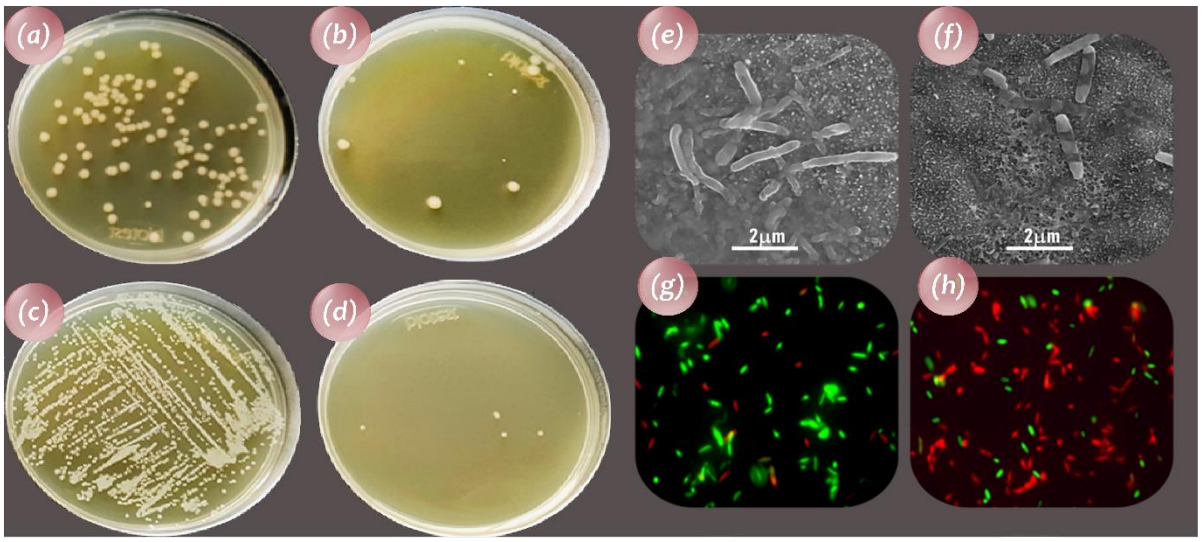

Figure 17. CFU of TFC and TFN-0.5 membranes obtained by the standard plate count method. (a, b-left) E. coli and (c, d-left) S. aureus cells colonies. Bacterial inactivation on the membrane surface (right a-d images); (a) and (b) SEM micrographs, (c) and (d) fluorescent images of E. coli cells on the membrane surface, stained with SYTO 9 (green), and PI (red) for viable and dead cells, respectively; (a) and (c) TFC, and (b) and (d) TFN membranes [129]. reproduced with permission from Elsevier.

4. Future Perspective

Despite increasing attention to the FO process during the last decade, an ideal and broadly applicable membrane has yet to emerge. TFC polyamide FO membranes have numerous advantages such as high salt rejection and water permeability, as well as safe operation in a wide range of temperature and pH, but they also have two main drawbacks: the susceptibility to fouling and the sensitivity to chlorine disinfectants and other oxidants. Membrane biofouling is specifically one of the most significant bottlenecks of the FO technology. The increase in energy

needs and hence operational costs, increased chemical cleaning frequency, and shorter membrane lifespan are some of its adverse consequences. Biofouling cannot be completely eradicated, but membrane modification approaches have been established that minimize or delay it. The fabrication of antibiofouling membranes is an important research topic in FO technology and has attracted wide attention in recent years. The strategies reviewed here are related to the post-fabrication surface modification of TFC PA FO membranes, and to the incorporation of nanoparticles or nanostructures during interfacial polymerization processes.

It is generally accepted that membrane surface characteristics exert a critical influence on all types of fouling (including organic, inorganic and biofouling). Surface hydrophilicity, roughness, charge density, and functional groups of the membrane active layer play a key role in biofouling. Several researchers have demonstrated that the increase of the hydrophilicity, alteration of the roughness, increasing the density of charged functional groups, and functionalization of the surface with antibacterial agents can improve the membrane resistance to biofouling. Early attempts in this direction focused on the development of hydrophilic surfaces to mitigate the membrane biofouling via anti-adhesion strategies, while their biofouling control was not satisfactory to provide long-term operation owing to continuous adsorption, multiplication, and regeneration of bacteria on the membrane surface. However, current research has shifted towards the design of bactericidal membranes via the integration of antibacterial nanomaterials, whether through incorporation or surface functionalization of the active membrane layer. To achieve this goal, nanotechnology and bioinspired engineering have expanded the opportunities for the development of antifouling membranes. Various types of nanomaterials, including metal NPs, CNTs, graphene-based materials, zwitterionic materials, and hybrid nanomaterials, are promising candidates for next-generation FO desalination

membranes and can be used to tailor the FO water flux, selectivity, biofouling-resistance, and mechanochemical stability. Generally, inorganic metal-based nanoparticles and carbon-based nanomaterials are considered promising antibacterial agents due to their strong biocidal properties, high stability, and commercial availability. Even though metal NPs offer desired antibacterial activity, the poor compatibility with the organic membranes still represents a technical limitation. Additionally, the release of metal NPs from the antibacterial membrane should be carefully considered as it will possibly trigger a risk to the aquatic ecosystem. Meanwhile, further research should focus on controlling the release rate to efficiently inactivate the bacteria for the longest possible time, ideally in the same order of magnitude as the membrane lifespan. Despite extensive attempts to tailor the membrane surface properties by the selection of an appropriate antibiofouling strategy, a challenge still exists to attain efficient, long-lasting antibiofouling properties. This obstacle is not surprising due to the more complicated mechanism of biofouling than other membrane fouling phenomena.

With ongoing progress in nanotechnology, advanced approaches have directed the design of multifunctional hybrid nanocomposite FO membranes. Introducing nanomaterials has resulted in novel FO membranes with excellent separation performance and antibiofouling properties that have great potential to overcome the biofouling bottleneck. However, despite exceptional enhancements in antibiofouling performance, the applications of these FO membranes have yet to expand beyond the lab scale, and successful commercialization for large-scale industrial applications has been rare. The main challenges of incorporating nanomaterials into the hybrid nanocomposite FO membranes include NPs agglomeration, depletion due to NP release, and the high cost of nanomaterials. Agglomeration leads to heterogeneous distribution in or on the active layer, and this result usually translates into an alteration of the separation

performance. In the last decade, many efforts have been made to mitigate this phenomenon, and among them, surface modification technology and optimizing the fabrication conditions have become more popular in membrane preparation due to the various options and multifunctional characteristics. A lot of researchers reported membrane modification via physical and chemical treatments to improve the membrane surface properties. In comparison to physical surface coating, chemical modification would be a more favorable approach to assure strong adhesion between the membrane surface and the modifying agent via covalent linkage; covalent linkage considerably decreases concerns related to antifouling agent release particularly during long-term operation. Although still in its infancy stage, surface functionalization is a promising approach to anchor biocides on the membrane surface and provides a high level of bacterial inactivation. Moreover, surface functionalization benefits from the dual synergic effect of both contact killing and release killing. Nonetheless, the choice of antibacterial agent largely depends on the cost and on laboratory criteria. Significant progress in bioinspired adhesion of PDA, supramolecular chemistry via in situ self-assembly, coupling chemistry have allowed enormous structural diversity (e.g., brush-like structure, hybrid nanocomposite surface and ultra-thin layer) for the facile and rational engineering design of membrane surfaces with functional antibiofouling properties. Although surface modification, either physical or chemical, is an effective strategy in tailoring surface properties, there are major challenges that may be classified as follows:

(1) Decreased water flux due to the extra mass transfer resistance originated from the additional layer formed after modification; a trade-off between water flux reduction and antibiofouling property should be optimized.

(2) Surface defects or increased roughness

(3) Use of hazardous chemicals for the modification, increased fabrication cost, and safety and environmental issues.

(4) Long-term chemical and mechanical stability of the surface-modified FO membranes.

(5) Complex operation or difficult scale up: many approaches for surface modification are currently limited to the lab scale, and only a few methods are ready for commercial application.

(6) Compatibility of the modifying agents with acid, alkaline or other cleaning materials.

Therefore, the following features should be taken into account when developing novel FO membranes through chemical modifications in the future: (i) simplifying functionalization approaches and optimizing reaction conditions to obtain a membrane with a thin, robust, and highly selective active layer, (ii) identifying more effective procedures and proper reagents for chemical modification, and (iii) targeting designed functionalization schemes for each specific FO application.

Biomimetic adhesion approaches and bioinspired chemistries may offer fascinating breakthroughs. Living creatures provide unique biological materials that involve highly organized architectures with self-cleaning behavior. The progress in this interdisciplinary area will undoubtedly open up broad prospects and new eras in integrating biomimetic science and membrane science for sustainable water purification

Finally, it is worth underlining that the goal of constructing antibiofouling membrane surfaces is to attain long-lasting performance to meet the requirements of real applications. There still exists a noticeable gap between preliminary research and large-scale industrial applications. A vast majority of lab-scale experiments are implemented under very specific and

narrow conditions, such as evaluating the antibiofouling activity with only a few model strains, mainly *E. coli* and *P. aeruginosa*, and applying hydrodynamics that are rather different from those prevailing in most real-scale operations. As a result, there is a lack of understanding of the antibiofouling properties of surface-modified membranes with complex and multi-component feed streams, especially for their long-term applications.

As a final note, it is interesting to note that early work in FO long touted its resiliency under high fouling conditions. While FO was found to have some quantifiable benefits when it came to reduced fouling or improved cleanability, it is clear that fouling, and especially biofouling, still occur with regularity and the prevention of such events are challenging. While a number of approaches to countering biofouling have been considered (and reviewed here), given the lack of commercialized mixed matrix membranes with biocidal characteristics or otherwise modified membranes with similar properties, it might be time to ask ourselves as scientists if we are going down the right path. Do we continue to make "fancy" membranes which offer some degree of biofouling resistance, while at least temporarily avoiding the questions of scalable membrane production, or do we consider an alternative path.

As with organic and inorganic fouling, we might consider the approach taken by the RO industry today: prevent it ever from happening. However, biofouling is more challenging to prevent because of the fouling growth after the pretreatment. Accordingly, the only way to really prevent biofouling is to prevent this growth. The easiest way to do that is to allow for a disinfection residual to exist in the solution. That may mean that our efforts and resources are better directed toward chlorine tolerance rather than biocidal modification or in both domain simultanously.

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