Recent developments in forward osmosis membranes using carbon-based nanomaterials

Sudesh Yadav[1], Haleema Saleem[2], Ibrar Ibrar[1], Osamah Naji1, Alaa A. Hawari[3], Adnan Alhathal Alanezi[4], Syed Javaid Zaidi[2]*, Ali Altaee[1]*, John Zhou[1]

1: Centre for Green Technology, School of Civil and Environmental Engineering, University of Technology Sydney, 15 Broadway, NSW, 2007, Australia

2: Center for Advanced Materials (CAM), Qatar University, Doha, Qatar.

3: Department of Civil and Architectural Engineering, Qatar University, P.O. Box 2713, Doha, Qatar.

4: Department of Chemical Engineering Technology, College of Technological Studies, The Public Authority for Applied Education and Training (PAAET), P.O. Box 117, Sabah AlSalem 44010, Kuwait

*Corresponding author email address: ali.altaee@uts.edu.au, szaidi@qu.edu.qa,

*Corresponding author phone number: +61 295149668, +97444037723

Abstract

Contamination and industrial development are amongst the reasons for water quality deterioration beyond treatability by conventional processes. Unfortunately, conventional water and wastewater treatment technologies are not always capable of handling industrial wastewaters, and hence more advanced treatment technologies are required. The new trend of osmotically driven membrane technologies has demonstrated an exceptional efficiency for water purification and treatment including seawater desalination. Compared to pressure-driven membrane processes, forward osmosis (FO) technology, as a standalone process, is more energy-efficient, and less prone to membrane fouling than its predecessor reverse osmosis (RO) technology. However, forward osmosis suffers a severe concentration polarization that is acting on both sides of the membrane and results in a sharp decline in water flux. A thinner support layer has been recommended to lessen the concentration polarization impact in the FO process but a very thin support layer compromises the membrane mechanical strength. Recently, researchers have applied different carbon-based nanomaterials to enhance water flux, fouling propensity, and mechanical strength of the FO membrane. This work reviews advancement in the FO membrane fabrication using carbon nanomaterials to improve the membrane characteristics. Despite a large number of laboratory experiments, carbon-based nanomaterials in the FO membrane are still at the early-stage of laboratory investigation and no commercial products are available yet. The study also reviews the main challenges that limit the application of carbon-based nanomaterials for FO membranes.

Keywords: carbon nanoparticles, forward osmosis, membranes, purification processes, membrane fouling

1. Introduction

Water contamination by organic and inorganic pollutants is a significant problem that has attracted considerable attention worldwide [1-5]. Contaminants removal from water requires robust and efficient decontamination technologies, which are capable of the treatment of a wide range of impurities. There are various existing physical and chemical technologies for water and wastewater treatment such as gravity separation [6, 7], membrane filtration technologies [8-14], air flotation [15], absorption material includes fluorochemicals, chemical vapor deposition, coating mesh, carbon-based materials, hydrophobic aerogels, sol-gel process, and sponges [16-26]. These technologies can remove a large proportion of dissolved matters [8], but they have some inherent limitations such as low separation or rejection rate, fouling, high energy consumption, reusability, and recyclability of the filtration media [9, 17, 21].
Membrane technologies stand out as the most widely recognized and advanced technologies for wastewater and water treatment and have a long history of excellent achievement in the field [27-29]. As of late, FO has stood out as competitive membrane technology for wastewater treatment with several advantages over the existing membrane technologies. These advantages include low power consumption, less fouling, and applicability for a wide range of feed solutions [30]. Additionally, the FO process includes the capability to concentrate low osmotic pressure feed solution with a concentrated draw solution [31]. This makes the FO process a potential technology for treating a wide range of water and wastewaters, including desalination. Despite the advantages of the FO process, it suffers from several drawbacks, for example, concentration polarization (CP), reverse solute flux (RSF), and low permeability [32]. Also, fouling materials accumulation on the membrane surface, especially in the treatment of complex feed solutions or when the pretreatment process is insufficient to provide a high-quality feed solution to the FO process [31].

One of the possible solutions for this problem is to apply nanotechnology to improve the performance of the FO membrane performance. Also, nanoparticles help to overcome the problems of low water permeability, low mechanical strength, and fouling propensity application of nanomaterials enhances permeability and lowers the phenomenon of CP [33-35].

The incorporation of hydrophilic nanomaterials to the thin-film composite forward osmosis membrane substrate can lead to the development of higher porosity, improved hydrophilicity and lesser tortuosity that collectively alleviate internal concentration polarization. Mostly, metal oxide nanoparticles as well as carbon-based nanomaterials functionalized using hydrophilic moieties are extensively utilized to accomplish this purpose. Among all the carbon-based nanomaterials, graphene oxide derivatives (hydrophilic additives) are becoming increasingly important as they can enhance the selectivity, performance, and productivity of the membranes by changing the mechanism of membrane formation. Therefore, carbon additives have been used in polymeric membrane fabrication to improve the characteristics of the membrane such as fouling, low flux, and poor mechanical-chemical stability of the FO membranes. The schematic representation of the influence of hydrophilic additives on non-solvent induced phase separation and membrane formation mechanism is shown in Fig 1.

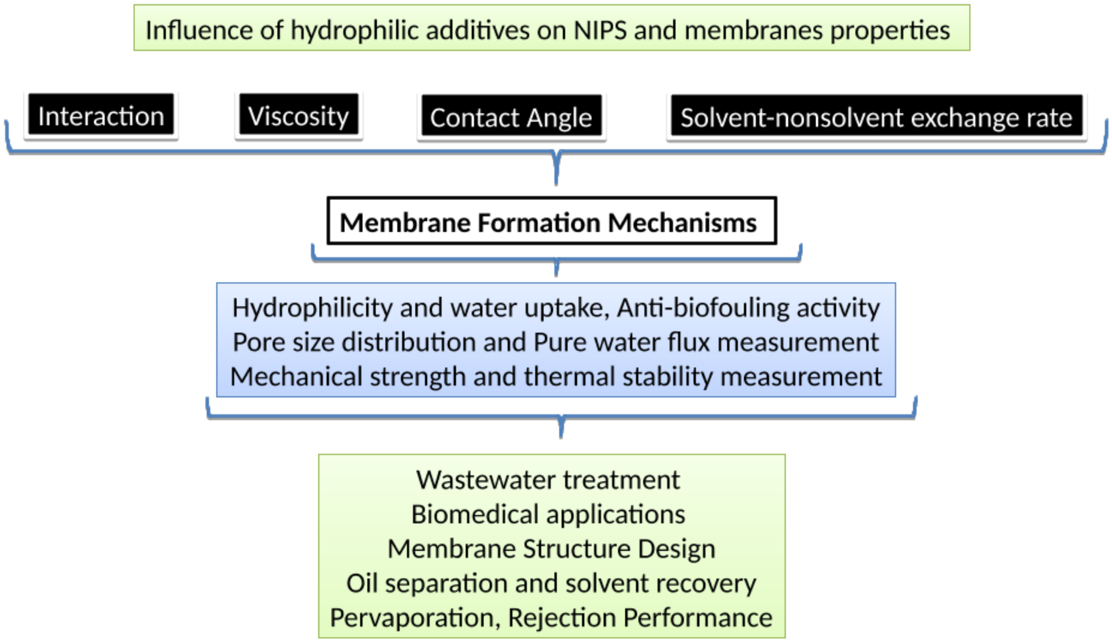


Figure 1. Schematic representation of the influence of hydrophilic additives on non-solvent induced phase separation and membrane formation mechanism

There is tremendous research related to the field of carbon nanoparticles, which has been shown by an enormous number of research articles published every year on the topic of FO technology. However, the major drawback of incorporating carbon additives is the instability and low efficiency of different membrane materials that have become a challenge over time [36-38]. To overcome this problem, an option must be developed, which gives the potential applicant as far as ease, high productivity at commercial scale with the simple technique.

Weiyi Li et al. [39] built up a theoretical model to understand the relationship between the structure parameter (S) and CP using the classical solution-diffusion theory. The model depicts internal concentration polarization (ICP), assuming a linear structure of the support layer while the intricate morphology is combined in the macroscopic phenomenological coefficients [39]. Studies demonstrated the reliance of the FO membranes fabricated by phase inversion technique on the porous structure, which is straightforwardly corresponding to the flux rate [40-43]. Most recently, researchers focused on the preparation of FO membranes using functionalized graphene oxide [44, 45] and ultrathin free-standing reduced graphene oxide [46] to reduce the CP. This is due to the fact that CP in the FO membrane is directly affected by the tortuosity and thickness of the membrane, and inversely with the membrane porosity and diffusion coefficient of the solute. The main disadvantage of the majority of the membrane-based water treatment system is membrane fouling. Different aspects of mass transportation result in the attachment, adsorption, or accumulation of various particles onto pores and surfaces of membranes, leading to fouling of the membrane. In general, the three main categories of membrane fouling are organic, inorganic, and bio-fouling. Out of these, biofouling makes almost 40% of the membrane fouling in the reverse osmosis process that leads to an irreversible reduction in the salt rejection and permeate flux [46]. On the other hand, the superior reversibility of fouling in FO enables its utilization in different applications in water treatment.

Our findings, concepts, and discussions in this review may be used to develop polymeric asymmetric membranes decorated with various functionalized carbon materials. Furthermore, the review also provides insights to reduce the CP effects, a field that still lacks a versatile strategy. As far as we could possibly know, the mechanisms involved in the free-standing fabrication and uniform GO, and rGO membranes are still unexplored. The existence of various oxygen-containing functional groups (epoxy, carbonyl, and hydroxyl) enhances the hydrophilicity of graphene-based membranes. In this review, detailed theoretical and experimental insights are discussed for the preparation of graphene-based membranes. Further, we have also examined the three types of fouling (organic, inorganic and biofouling), various factors controlling the fouling development, and research works performed with and without nanomaterials to confirm the fouling reversibility occurring in the FO membranes.

2. Design for FO membranes:

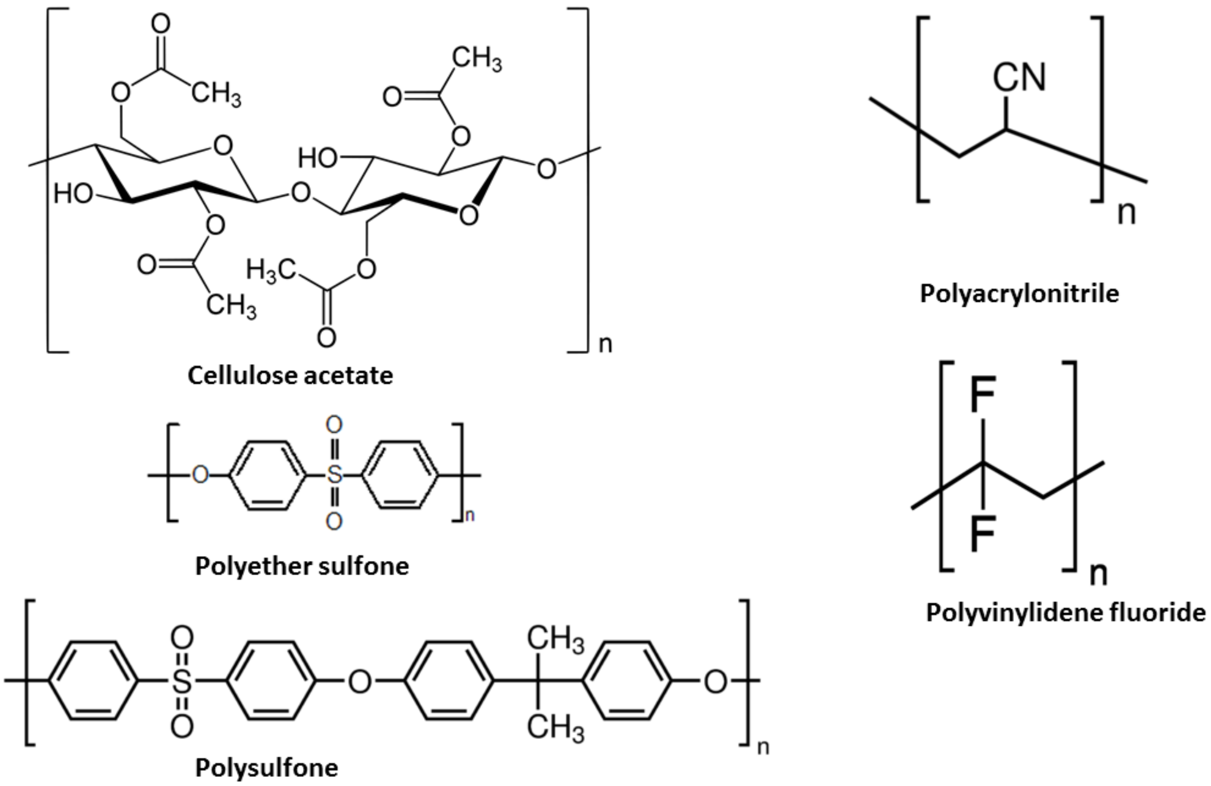
2.1. Prerequisites of an ideal FO membrane

The performance and applications of FO technology dominantly rely upon the characteristics of the FO membrane that is directly related to the materials used in the membrane structure (i.e., porous and non-porous). For instance, porous membranes are used for the microfiltration [47] and ultrafiltration [48] whereas the non-porous or dense membranes are utilized for gas separation [49] and pervaporation [50] applications. Earlier studies showed that symmetric and asymmetric membranes were applied to the FO processes [51, 52]. However, in recent years, asymmetric porous membranes are widely used for FO applications, where the permeability selectivity index depends on the thickness of the dense layer [53]. Technically, the asymmetric membrane has 0.1–1 µm dense layer thickness and 100–200 µm supporting layer thickness [54]. The morphology and chemical structure of the dense layer with pores in the range of 0.4–1 nm determines the membrane performance [55]. Therefore, the FO membrane optimization will be as the following:

a) An asymmetric FO membrane should have a dense thin layer for solute rejection from feed and draw solutions [56]. The selective layer should be designed based on the application of the FO membrane; for example, a pore size smaller than 3Å is required for the rejection of NaCl. Furthermore, the substrate of the porous to the porous supporting layer provides mechanical stability to the membrane [57-59]. However, recent studies by [60-63] showed that the contact angle and pore structure of the supporting layer is a critical factor for the transport mechanism.

b) FO membranes fabrication using hydrophilic polymers with a contact angle of less than 60^0. In addition, the excellent antifouling properties for the FO membrane are desired as fouling adversely affects the performance and water flux.

The most popular hydrophilic synthetic polymers used for the fabrication of supporting layer of FO membranes include cellulose derivatives [64], polyethersulfone (PES) [65] and polysulfone (PSf) [66], polyacrylonitrile (PAN) [67] and also hydrophobic polyvinylidene fluoride (PVDF) [68] has been frequently used for the same. The above-stated polymer's chemical structures are presented in Figure 2.


Cellulose acetate

Polyacrylonitrile

Polyether sulfone

Polyvinylidene fluoride

Polysulfone

Figure 2: Chemical structure of polymers used to fabricate the support layer of the FO membranes [68].

Physical properties of the active and support layers play a vital role in the performance of the FO membranes. For example, the membrane's active layer determines the coefficient of water and salt permeability. However, the structural parameter (S) represents the resistance of the support layer towards solute diffusion. A smaller value of S will facilitate solute molecules diffusion inside the permeable supporting layer, which further enhances the water flux.

2.2. Geometrical categories of FO membranes

In general, FO membranes fall into three categories based on the various geometrical structure:
a) Flat Sheet FO membranes: These membranes are utilized in many water treatment applications where the waste streams to be dealt with contain a high concentration of fouling agents or the solutions having high viscosities.
b) Hollow fiber FO membranes: These membranes are utilized for the large-volume water-treatment applications, like seawater desalination or downstream wastewater treatment. However, the FO process application for industrial waste-water treatment is limited due to the severe membrane fouling and clogging problems [30, 59].
c) Tubular FO membranes: These membranes are known for the microfiltration and ultrafiltration applications. However, most of the previous studies are investigated the development of the flat sheet and hollow fiber membrane modules [59, 62, 65]. Tubular modules are innately simpler to produce since they just require sealing at either end of the module. Figure 3 represents the various membrane modules.

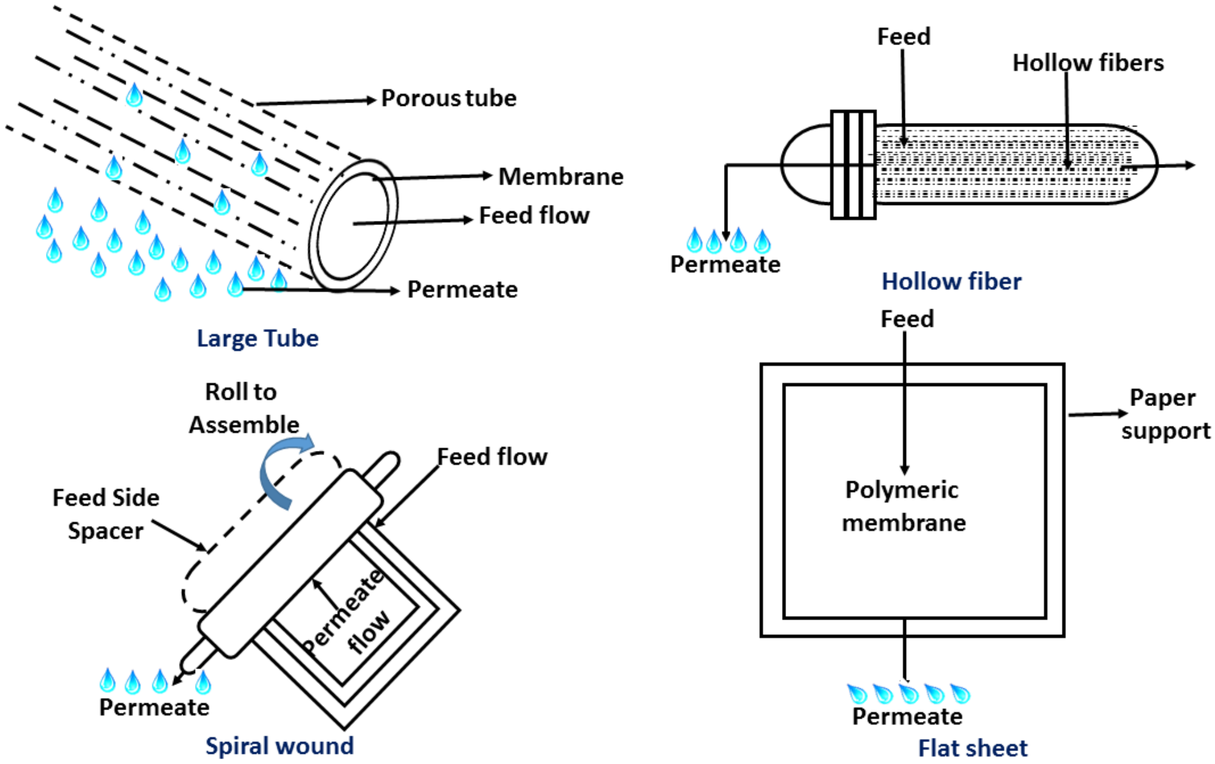


Figure 3: Various designs of FO membrane modules

Nowadays, most of the membranes that have either flat sheet or hollow fiber configurations are prepared by immersion precipitation. In this technique, the polymer and solvent mixture case is done first on a proper supporting layer followed by immersion in a coagulation bath containing distilled water or non-solvent. In this process, the precipitation occurs as a result of the exchange of non-solvent and solvent [69].

2.3. Membrane materials and chemically modified polymers for FO membranes

Extensive attention has been given recently to conductive FO membranes [70]. The surface charge of the FO membrane is a significant parameter to be considered when treating feed waters with charged foulants [71,72]. In conductive FO membranes, the embedment of the electrode is achieved by a conductor of dispensing properties like carbon nanotubes (CNTs) in the material of the membrane substrate [73]. Then, an external electric field is applied to the membrane during the membrane filtration, which generates electrostatic repulsion between the foulants with charge and membrane surface, therefore effectively mitigating the fouling of the membrane [74, 75]. The conductive FO membrane modified with metal, carbon, or any other materials can be used as a negative electrode [76]. It has been experimentally demonstrated that by applying an external voltage to a conductive FO membrane, an outstanding resistance to microbial fouling and organic fouling might be carried out by an electroactive membrane [77]. The other advantage of the conductive membrane is that it is easy to operate and can be automated [76]. Apart from CNTs, different types of conductive polymers such as polypyrrole (PPy) and polyaniline (PANI) have also been used to manipulate membrane properties and improve their antifouling behavior [78]. However, these techniques are limited due to their drawbacks including increasing capital, high operational cost, and difficulties in scale up the system. PANI can improve the overall membrane permeability while incorporating antifouling properties [79].

Double skin forward osmosis membranes have been proved to provide higher water flux and mitigating internal fouling and ICP in the FO process [80]. The fabrication methods of these membranes are similar to single-skinned FO membranes, for example, phase inversion, interfacial polymerization, or layer by layer deposition [81-83]. Antifouling double-skinned FO membrane containing a polyamide salt-rejecting layer and a zwitterionic brush-decorated, multiwalled carbon nanotube (MWCNT) foulant-resistant layer exhibited excellent antibacterial adhesion, anti-protein adsorption and excellent flux recovery in the PRO mode in comparison to a pristine TFC membrane [84]. More recently, the FO membrane with no support layer was used to eliminate the impact of ICP completely [85]. In a recent effort, functionalized monolayer porous graphene as the FO membrane was tested through molecular dynamics (MD) simulations [86]. GO membrane exhibited insignificant ICP and considerable water flux, circa 1.7×10^3 times more than the conventional CA membrane. Polymeric support-free FO membranes fabricated via the solvent evaporation method has also been reported [85]. This membrane was synthesized by an initial polycondensation reaction between 4,4-oxybis (benzoic acid) and hydralazine sulfate salt and subsequent grafting of a carboxylic acid group to the side chains. However, self-standing membranes lack mechanical stability and difficulty to scale-up prevents its widespread applications. In an attempt to overcome stability and scaling up issues of support-less FO membranes, FO membranes with an extremely thin support structure and superior mechanical robustness have been reported in the FO literature [87, 88]. These membranes utilize a polyethylene (PE) battery separator as a support layer providing the membrane with extreme thinness, high porosity, and high pore interconnectivity.

Janus membranes have immense potential as an emerging material for various separations [89, 90]. Janus is a two-dimensional material with asymmetric properties on each side, one side is superhydrophobic while the other side is superoleophobic/hydrophilic, which makes it self-cleaning in the air and antifouling in water [91]. The membrane with a hydrophilic CA layer and hydrophobic PVDF nanofiber via electrospinning achieved an unparalleled 274.2 $Lm^{-2}h^{-1}$ water flux, and 1.65 $gm^{-2}h^{-1}$ reverse salt flux using DI water 1M NaCl feed draw solution, respectively [90]. The performance of these membranes is limited to lab-scale due to wetting issues, which deteriorate membrane selectivity and water flux in long term operations.

3. Molecular simulation and mechanisms of transport in FO membranes

Microscopic information and understanding of activities that happen at a molecular level are vital for understanding water-transport mechanisms and novel membrane materials development [92, 93]. Atomistic molecular modeling techniques are confirmed to be very efficient to investigate the structure and dynamics of the dense amorphous membrane polymers and transport processes in these materials [94, 95]. Molecular permeation mechanisms and the effects of factors such as chemical functionalization and structural parameter are expected to be revealed by molecular simulations [95]. A list of simulation techniques and their spatial ranges are outlined in Table 1. Figure 4 presents the number of studies employing simulation techniques to study the FO phenomena. A slow but gradual increase in the number of research articles is observed after 2015 and in 2019, approximately 160 papers in total employed simulations.

Table 1. Simulation techniques and their spatial range. Adapted from [96] with permission from Springer.

Simulation technique	Spatial range (approximate values)
Molecular dynamics (MD)	1nm to 10nm
Coarse-grained molecular dynamics	5nm to 100nm
Dissipative particle dynamics (DPD)	100nm to 10μm

Micro computational fluid dynamics (CFD)	1µm to 1mm
Computational fluid dynamics (CFD)	100µm to 20mm

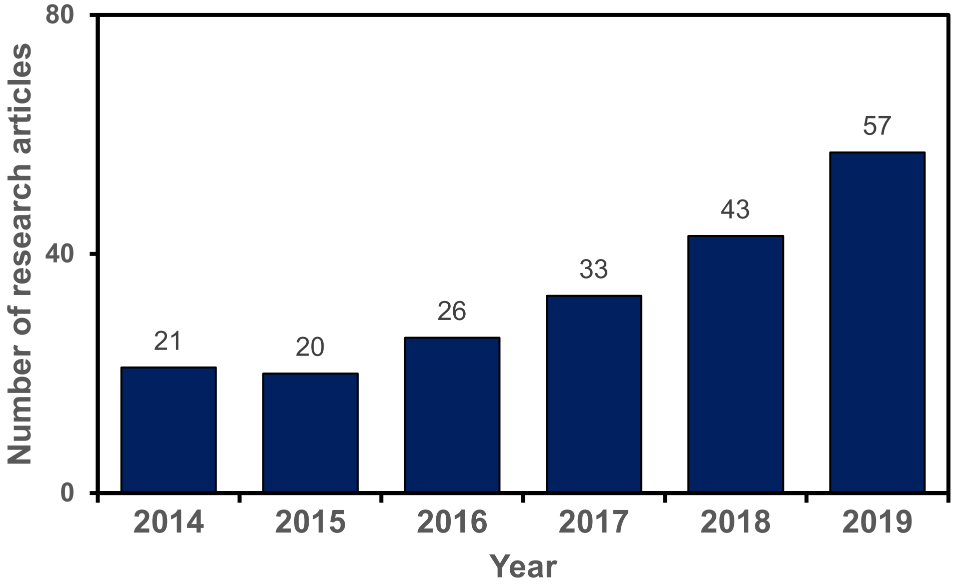


Figure 4. The number of research articles in the FO literature using molecular dynamics or other simulations. The search was done using Science direct database with exact keywords "forward osmosis AND molecular dynamics".

Computational tools such as MD simulations are often utilized in the FO process to gain insights into the water and ion transport mechanisms across the FO membrane [93, 97]. MD uses step-by-step computer simulations to solve the Newtonian equations of motions [98], as presented by equation 1.

$$F_i = m_i a_i = m_i \frac{d^2 r_i}{dt^2} \qquad [1]$$

Where F_i is the force exerted on particle *i* by N-1 other molecules, *m* is the mass of the particle *i*, *a* is the acceleration of the particle, *r* is the distance between the particles and *t* is the time. The Newtonian force can also be expressed as a gradient of potential U, as presented in equation 2.

$$F_i = -\nabla_i U(r_i) = -\frac{\delta U r^N}{\delta \tau_i} \qquad [2]$$

The relationships in equations 1 and 2 are used to obtain trajectories of all atoms as described by their position, velocity, and momenta, which becomes the raw data for predicting the bulk performance of a system [98]. It should be noted that both equilibrium and non-equilibrium states can be simulated by the MD technique [99].

Very few studies have discussed MD simulations for commercial polymeric membranes [97, 100]. A computational MD simulation was performed by Heo et al. [97] to investigate the adsorption behavior of synthetic organic compounds (SOC). Two different membranes (CTA-HTI) and RO (BW30-Dow FilmtecTM, Co) were compared in terms of SOCs adsorption in this study. The RO (BW30-Dow FilmtecTM, Co) membrane had significant adsorption for phenolic compound 4CP (chlorophenol) compared to the FO (CTA-HTI) membrane and showed superior performance in the RO-mode in terms of water permeability and SOCs removals. You et al. [100] estimated the diffusion coefficient of different species (water and electrolytes) through a thin film inorganic (TFI) membrane produced by a tetraethylorthosilicate-driven sol-gel process employing MD simulation. The diffusion coefficient of the electrolytes obtained through simulation was two orders the magnitude of water molecules.

MD simulations can be a useful tool to study molecular interactions, for instance, between the nanoparticle and the polyamide layer (PA) of TFC membrane when coating membrane with nanoparticles [101] or interaction of foulant with the PA layer [102, 103] or foulant-foulant interactions [104, 105]. The interactions between atoms are governed by Lennard-Jones (LJ) or by coulomb charge interactions [106]. The Lennard-Jones potential is given by equation 3.

$$V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \qquad [3]$$

Where V is the intermolecular potential between two particles, σ represents the van der Waals radius, ε is the measure of how strongly the particles attract each other, and r is the distance between the particles. The strength of the microscopic interaction is usually quantified in terms of the interaction energy [101], as presented by equation 4.

$$E_{interaction} = E_{mixture} - \left(E_{polyamide} + E_{nanoparticles}\right) \qquad [4]$$

The stability of a molecular structure is directly proportional to the negative interaction energy. In other words, the molecular structure becomes more stable with increasing the negative energy. MD simulation can also provide us with new and fundamental insights into the fouling mechanism at a molecular level [102]. However, applying MD to foulants with extraordinary molecular diversity and complex foulants such as natural organic matter (NOM) can be challenging [104]. Kalinichev et al. [104] study found that calcium ions have a strong binding with carboxylic groups in NOM. A study by Plazinski and Rudzinski [105] revealed that the gelling of alginates in the presence of divalent ions is accompanied by the junction zone (region of alginate chain aggregations). A limited number of studies have reported foulant-membrane interactions [102, 103]. In general, the adhesion between foulant and membrane surface is governed by hydrogen bonding, van der Waals interaction in the short-range, and ionic bridge binding in the long-range [102]. MD simulations have also revealed that both calcium (Ca^{2+}) and sodium (Na^{+}) can form very strong ionic binding complexes, and calcium ions have a stronger binding with the carboxylate group than Na^{+} ions [103].

Gai et al. [107] studied the functional porous graphene membrane performance in the FO process utilizing MD. The water flux achieved by fluorinated porous graphene in Gai study was about 1.8 $x10^4$ times the flux of typical cellulose triacetate (CTA) membrane. When the pore diameter of the membrane was smaller than 11.7Å, no salt ions passed through the membrane during the simulations. Liu et al. [108] conducted MD simulations to study a single layer nitrogenated holey graphene C_2N membrane performance in a forward osmosis process by tuning its pore size using tensile strain. The study concluded that with the increase of tensile strain and temperature, the permeation flux increases monotonically. Furthermore, when the tensile strength increased by more than 4 %, the membrane becomes completely permeable to water and impermeable to ions. With a tensile strength of less than 4%, it was showed that the number of water molecules in the draw solution does not change. Zhang and Gai [109] investigated the brine separation performance of graphene (N=3, 4, 5, and 6) in the FO process using MD simulations. The pore-flow model was applied to describe the water transport mechanism of graphene membranes in the FO process. The outcomes of this research revealed that a single-layer graphene-3 membrane could simultaneously achieve a high water flux and 100% rejection and there is no linear correlation between water flux and structure parameters. Table 2 shows a list of some other studies which employs MD simulation to study transport mechanism in graphene/CNT membranes.

Table 2. An overview of MD simulation studies and main findings for graphene and CNT and composite membranes in the FO literature.

Simulation type	Membrane (s)	Main findings	Ref
MD (molecular dynamics)	CNT	The choice of suitable solute can enhance the efficiency of the FO.	[106]
Steered MD (large scale)	Porous graphene & CNT	Diffusive flux in graphene is 2.5 times higher than CNT, but CNT has higher salt rejection.	[110]
MD	Graphene	Zero ICP and higher water flux reported.	[111]
MD	Stacked graphene (GE) membranes with nanoslits	GE membranes in FO systems have high retention than GE membranes in RO.	[112]
MD	PDA (polydopamine) coated GO membrane	1.8 times higher flux than normal GO membrane and five times higher than the CTA membrane.	[113]
Nonequilibrium MD	Layered GO membrane	Water and ion dynamics are affected by oxygen functional groups on the nanosheets.	[114]
MD+DPD(dissipative particle dynamics)	MWCNT/Polymer composite membrane	Optimum fabrication conditions can be obtained by using simulations.	[115]

Computationally, a method that is much faster than MD and more flexible than lattice-gas automata schemes [116] known as dissipative particle dynamics (DPD) has gained more popularity in recent years. The DPD is one of the most potent and simple mesoscale simulation approaches and has the potential to emerge as an even more widely used modeling and simulation technique for many complex fluid systems [117]. Furthermore, DPD can give us insights into mesoscopic information, which cannot be obtained by experiments or original simulations [118]. In this method, a set of point particles that move-off lattice interacting with each other with three types of forces [119]. A conservative force deriving from potential is given by equation 5 [119,120].

$$F_{ij}^{C} = \begin{cases} -a_{ij}\left(1-\frac{|r_{ij}|}{r_c}\right)n_{ij}\,, |r_{ij}| < r_c \\ 0, \qquad\qquad\quad |r_{ij}| > r_c \end{cases} \qquad [5]$$

Where F_{ij}^{C} is the pairwise conservative force on particle i due to particle j, a_{ij} is a parameter for determining the magnitude of the repulsive force between beads i and j, $r_{ij} = r_j - r_i$ is the distance between particles i and j and $r_{ij} = \frac{r_{ij}}{|r_{ij}|}$, and r_c is the cutoff distance. As stated in equation [1], the conservative force vanishes beyond a cutoff distance r_c.[121]. The second force acting on the particles is the dissipative force which tries to reduce the radial velocity differences between the particles is presented by equation 6.

$$F_{ij}^{D} = \begin{cases} -\gamma\omega^{D}(|r_{ij}|)(n_{ij}.v_{ij}).n_{ij}\,, |r_{ij}| \leq r_c \\ \quad 0, \qquad\qquad\qquad |r_{ij}| > r_c \end{cases} \qquad [6]$$

Where γ is the frictional parameter, ω^{D} is the *r*-dependent weight function given by F_{ij}^{D}, and $v_{ij} = v_j - v_i$ is the difference in velocity of the bead i and j. A further force acting on the particles termed as the stochastic force [119] or random force is presented by equation 7.

$$F_{ij}^{R} = \begin{cases} \sigma\omega^{R}(|r_{ij}|)\zeta_{ij}\Delta t^{\frac{-1}{2}}n_{ij}\,, |r_{ij}| \leq r_c \\ 0, \qquad\qquad\quad |r_{ij}| > r_c \end{cases} \qquad [7]$$

Where F_{ij}^{R} is the pairwise random force on particle i due to particle j, σ is the noise parameter, ω^{R} is the *r*-dependent weight function given by F_{ij}^{R}, and ζ_{ij} is a random number based on Gaussian distribution. The dissipative and stochastic force can be termed as a "pair-wise Brownian dashpot" which is momentum conserving [119]. Araki et al. [120] demonstrated the water molecules transport across a polymeric membrane and the effects of additive (Sodium acetate) on water permeation using a coarse-grained molecular simulation based on dissipative particle dynamics (DPD) method in the FO process [121,122]. Results of DPD simulations from Araki et al. [120]

revealed that additives enable the reduction of water permeation into a polymeric membrane and the additives need to be more polymer-phobic than water molecules. Another study based on DPD simulations was performed by He et al. [118] to investigate membrane structure and morphology on a mesoscale in the FO process. The DPD model was constructed with a neutral substrate, which was mapped onto the experimental polypropylene-diphenyl ether system to focus on membrane morphology and kinetics of membrane formation at a mesoscale. The polymer chain in this study was constructed by connecting adjacent particles $i \, and \, j$ via a harmonic spring [123, 124], as presented by equation 8.

$$F_{ij}^{S} = -Kr_{ij} \qquad [8]$$

Where F_{ij}^{S} is the harmonic spring force between particles i and j, and K is the spring constant. The results of this study revealed that the number of interfaces between the polymer and diluent first increases and then decreases to minimize the total free energy, and the domain size has a more rapid growth in the intermediate stage. However, this study was based on a 2D model, and the substrate was neutral [118]. Our analysis of the literature shows that very few studies have adapted DPD simulations compared to the MD simulations. This is due to the fact that despite being a powerful simulation technique, a major disadvantage of DPD is that it cannot sustain temperature gradients as energy in the module is dissipated and not protected, and the Brownian dashpot forces are represented as a thermostat [119].

4. Different carbon-based nanomaterials used in FO membranes

It is certain that the FO membrane is the heart of the FO system. For accomplishing the necessary separation efficiency, the forward osmosis membrane needs to have superior qualities like increased salt rejection, higher water flux, superior anti-fouling property, and good stability [125]. Extended efforts have been taken to meet the aforestated requirements. Either chemical modification [126] or physical modification [127] are proved to be effective to upgrade the FO membrane efficiency. On the other hand, some standard problems, such as higher reverse salt flux and lower water flux, still remain, which obstructs the advancement as well as utilization of the FO membrane. Furthermore, ICP is likewise viewed as one of the major issues when asymmetric thin-film composite (TFC) membrane is utilized for FO utilization. In order to resolve this issue, with the advancement of nanotechnology, numerous researchers have studied the usage of nanomaterials for enhancing the properties of FO membranes [128]. Nanomaterials such as carbon nanotubes [129, 130], graphene [131], graphene oxide [132], zeolites [133], metal-organic framework (MOF) [134], titanium dioxide [135, 136] have also been incorporated into the FO membranes for enhancing its performance. Figure 5 presents the characteristic fabrication and thin-film composite PA FO membranes structures [137]. Table 3 is the summary of the FO performance of carbon nanomaterial-based thin-film composite membranes.

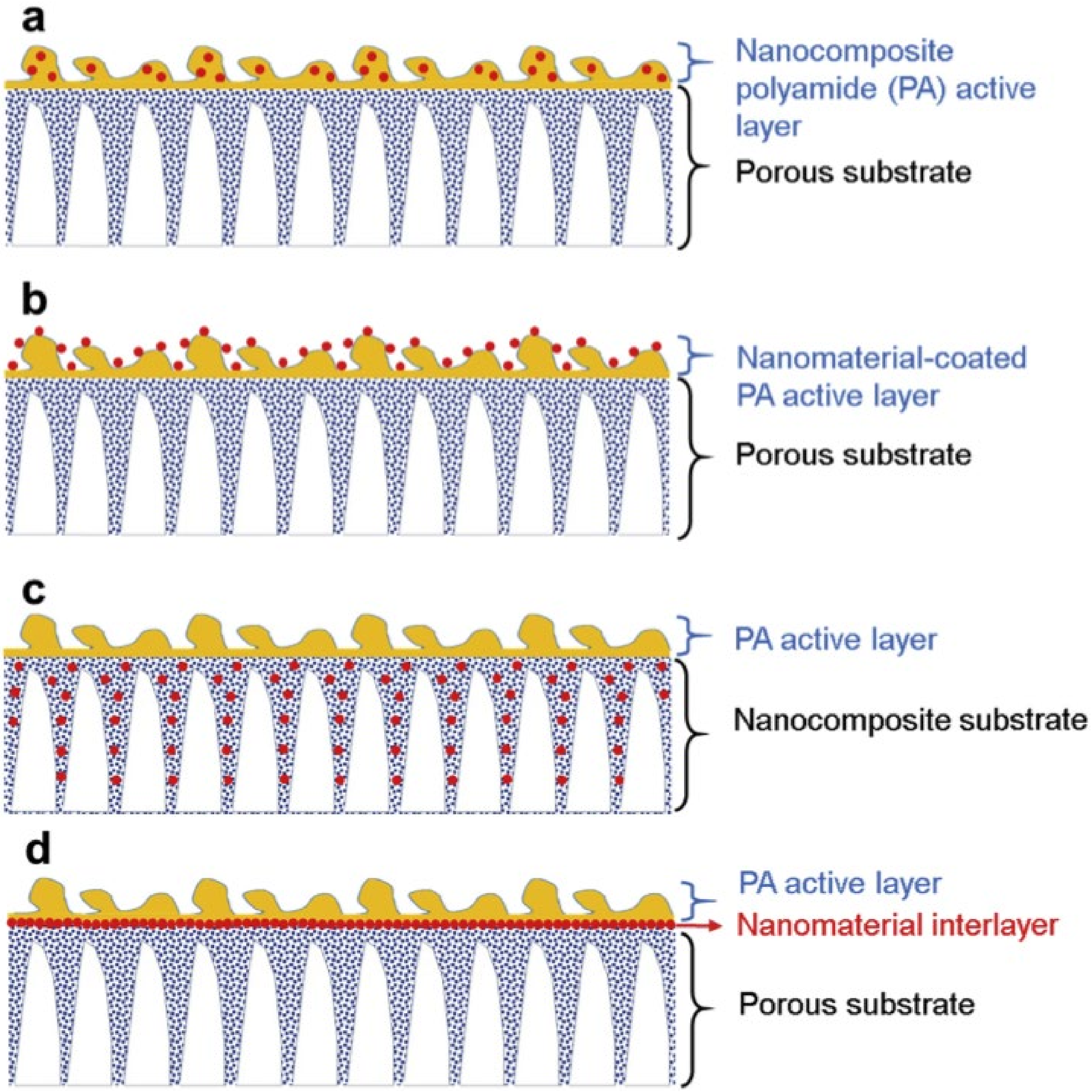


Figure 5: Diagrammatic representations representing characteristic structures of nanomaterial-included polyamide thin-film composite membranes: a) thin-film nanocomposite (TFNC) membrane, b) thin-film composite membrane having nanomaterial-coated polyamide layer surface, c) thin-film composite membrane having nanocomposite substrate and d) thin-film composite membrane having an interlayer of nanomaterial. Reproduced from [137]

Table 3: Summary of FO performance of carbon nanomaterial-based thin-film composite membranes

Sl. No.	**Thin-film nanocomposite membrane-filler**	**Thin-film nanocomposite membrane-substrate**	**Addition of nanomaterials**	**Optimal particle loading**	**Substrate preparation techniques/Membrane surface modification method**	**Forward osmosis performance**				**Year; Ref.**
						Draw solution	Cross-flow velocity	Water flux L/m^{2}h	Solute flux g/m^{2}h	
1	Carbon nanotubes	Polysulfone	CNT incorporated into the TFC membrane active layer	0.05 wt/v% in dopamine solution	Phase inversion	2M Magnesium chlordie (deionized water)	1.59 cm/s	8.6	2.1	2015; [138]
2	Carbon nanotubes	Polysulfone	CNT incorporated into the TFC membrane active layer	0.05 wt% in dopamine solution	Phase inversion	2M Magnesium chlordie (deionized water)	7.8 cm/s	14.50	7.50	2016; [130]
3	Graphene oxide	Polyacrylonitrile	GO incorporated into the TFC membrane active layer of	0.06 wt% in m-phenylenediamine solution	Phase inversion	1M Sodium chloride (deionized water)	300 mL/min	23.6	4.4	2016; [139]
4	Graphene oxide	Polysulfone	GO incorporated into the TFC membrane active layer	0.1 wt% in m-phenylenediamine , triethylamine and	Phase inversion	1M Sodium chloride (deionized water)	25 L/min	14.5	2.6	2018; [140]

				sodium dodecyl sulfate solution						
5	Graphene oxide/Fe3O4 nanohybrid	Polyether sulfone	Nanomaterial incorporated into the TFC membrane active layer	0.02 wt/v% in m-phenylenediamine solution	Phase inversion	1M Sodium chloride (deionized water)	8 cm/s	27.5	3.0	2018; [141]
6	Graphitic carbon nitride	Polysulfone	Nanomaterial incorporated into the TFC membrane active layer	0.05 wt/v% in m-phenylenediamine solution	Phase inversion	2M Sodium chloride (deionized water)	21.4 cm/s	18.9	2.74	2018; [142]
7	Graphene quantum dots	Polyether sulfone	Nanomaterial incorporated into the TFC membrane active layer	0.1 wt% in m-phenylenediamine, trimethylamin, and camphorsulfonic acid solution	Phase inversion	1M Sodium chloride (deionized water)	8.5 cm/s	28	5.84	2018; [143]
8	Graphene oxide / poly-L-lysine	Polysulfone	Surface modification using nanomaterial/nanomaterial-coated PA surfaces.		n-(3-Dimethylamino propyl)-n'-ethylcarbodiimide hydrochloride/ n-hydroxysuccini	2M Sodium chloride	500 mL/min	11.0	15.0	2015; [144]

					mide facilitated graphene oxide / poly-L-lysine grafting					
9	Graphene oxide-Silver	Polysulfone	Surface modification using nanomaterial/nanomaterial-coated PA surfaces.		Amide forming condensation reaction	1M Sodium chloride (deionized water)	200 mL/min	5.4	35.10	2015; [145]
10	Graphene oxide-polydopamine	Polysulfone	Surface modification using nanomaterial/nanomaterial-coated PA surfaces.		Coating	2M Sodium chloride	500 mL/min	13.0	8.75	2016; [146]
11	Acid-functionalized carbon nanotubes	Polyethylenimine	Nanomaterial incorporated substrates	0.3 wt% in dope solution	Electrospinning	1M Sodium chloride (deionized water)	9.0 cm/s	33.00	3.70	2015; [147]
12	Acid functionalized carbon nanotubes/ Titanium dioxide composites	Polysulfone	Nanomaterial incorporated substrates	0.5 wt% in dope solution	Phase inversion	1M Sodium chloride (deionized water)	0.09 cm/s	12.70	5.80	2016; [148]

13	Carbon nanotubes	Polysulfone	Nanomaterial incorporated substrates	0.15 wt% in dope solution	Phase inversion	2M Magnesium chloride (deionized water)	7.8 cm/s	14.5	6.6	2016; [130]
14	Acid functionalized carbon nanotubes	polyether sulfone	Nanomaterial incorporated substrates	0.5 wt% in dope solution	Phase inversion	0.6 M Sodium chloride (deionized water)	Draw solution : 400 mL/ min Feed solution: 200 mL/ min	11.98	7.7	2017; [149]

4.1 Carbon nanotubes

Out of the different nanomaterials used for the FO application, carbon nanotubes (CNTs) displayed greater possibility in the membrane separation field because of its exclusive transmission performance and one-dimensional (1-D) nanostructure [150]. In addition, the carbon nanotubes show properties like inoxidizability, chlorine resistance, mechanical strength, chemical stability, and antibacterial property. Therefore, CNTs are extensively utilized to upgrade the efficiency of the FO membrane by either incorporation in the substrate or the active layer of the membrane.

4.1.1 Addition of CNT into the active skin layer of TFC membrane

It was stated that a higher loading of carbon nanotubes probably caused a porous network in the membrane, and the hollow nanochannels, as well as their interspaces present in CNTs, could contribute to advanced water transport channels [129]. In the study carried out by Li et al. [129], the team examined the influence of CNTs and the efficiency of the manufactured membranes. TFC FO membranes were fabricated based on the polyacrylonitrile (PAN) substrate, including CNTs in the selective skin layer. The carbon nanotubes can enhance the water flux through the addition of hydrophilic groups. As the concentration of CNTs was increased, the mean surface roughness, as well as hydrophilicity, also enhanced. The thin-film composite membranes with 0.2 wt% CNTs showed the greatest performance with 8.64 $g/m^2 \cdot h$ reverse salt flux and 25.14 $L/m^2 \cdot h$ water flux utilizing deionized water and 0.5 M sodium chloride as feed and draw solution respectively. This study proved to be a potential method to manufacture the superior flux of forward osmosis membranes.

Lower hydrophilicity has turned out to be a significant problem, which restricts the utilization of CNTs in the modification of membranes. Pristine CNTs possess reduced solubility in water and can barely enhance the performance of forward osmosis membrane unless functionalized. In some researches, amino [151] and carboxylic [152] CNTs have already been used for modifying forward osmosis membranes and the aforestated both functionalized nanomaterials have proved to be efficient. As a result, functionalized CNTs were found to be significant additives for the forward osmosis membrane applications. As the polarity of the sulfonic group is stronger than that of a carboxyl group or amidogen, the sulfonated carbon nanotubes (S-CNTs)-functionalized forward osmosis membranes should demonstrate superior hydrophilicity. In Yonghao et al. [153] work, CNTs were functionalized using sulfonated groups and included in the membrane selective layer to attain the required thin-film nanocomposite (TFNC) FO membrane. Incorporation of sulfonated-CNTs resulted in a denser and smoother membrane surface, and also the hydrophilicity enhanced remarkably. As for membrane performance, FO membranes with sulfonated-CNT exhibited superior water flux and moderate reverse salt flux. Maximum water flux of 29.9 ± 1.6 L/m^2.h was attained by utilizing deionized water as the feed solution and 1 M sodium chloride solution as the draw solution. This water flux was approximately 140% greater and the reverse salt flux diminished to almost 12%.

4.1.2 CNT-coated PA surfaces.

Surface modification is an excellent method due to the fact that it permits modification in the performance of a membrane without considerably altering the intrinsic membrane structure. The development of forward osmosis-based technologies should address a number of technical obstacles, particularly additional improvement in fouling resistance and alleviation of reverse solute flux. Innovative membrane advancement targets at developing a superior draw solute obstruction by means of membrane manufacturing or modification of the surface [154]. In another study, zwitterion-functionalized CNTs were coated onto a commercial TFC membrane for achieving bidirectional solute flux mitigation by means of electrostatic repulsion forces induced by the zwitterionic functional groups and the steric interactions with carbon nanotubes [155]. Diagrammatic representation of the coating of the membrane, as well as the testing process, is shown in Figure 6. The test results obtained will stimulate additional advancement of efficient techniques for fouling control and bidirectional solute flux. Coating zwitterion functionalized CNTs on the active layer mitigated reverse solute flux, probably, due to the prolonged electrostatic repulsion in the existence of low ionic strength solutions. With 0.97gm^{-2} optimal coating density, a considerable diminished specific reverse solute flux was noted for multiple draw solutes, inclusive of sodium chloride (NaCl) (55.5%reduction), ammonium bicarbonate (NH_4HCO_3) (61.9%), ammonium chloride (NH_4Cl) (70.8%), diammonium phosphate ($(NH_4)_2HPO_4$)(74.5%), and ammonium dihydrogen phosphate ($NH_4H_2PO_4$) (83.8%). When supplied with actual wastewater, a much greater stable water flux (just 14.9% reduction) was accomplished using the zwitterion functionalized CNTs coated membrane in the course of a twelve-day semi-continuous process, relative to that of the pure membrane (reduction of 54.5% flux). Almost entire membrane foulants can be separated by means of simple physical flushing, leading to a more cost-effective and robust forward osmosis operation.

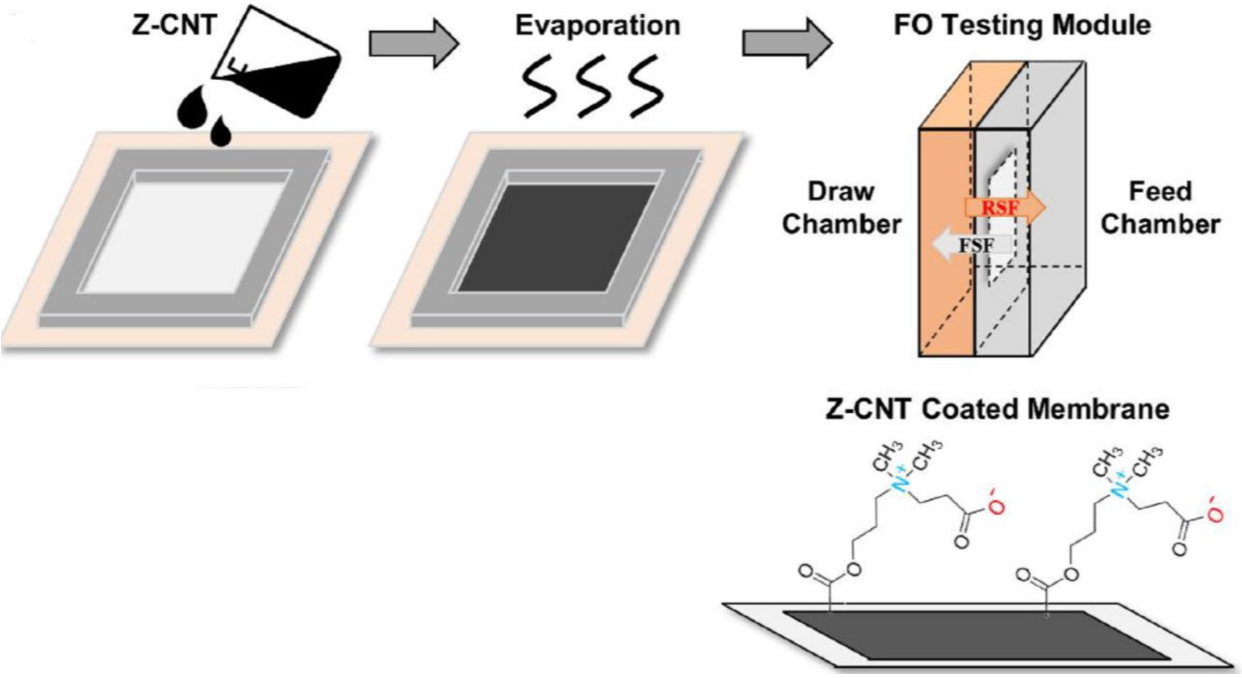


Figure 6: Diagrammatic representation of the membrane coating as well as the testing process. Reproduced from [155].

4.1.3 Nanocomposite substrate

In general, to improve mass transfer and decrease the ICP, the substrate of the FO membrane needs to be thin and possess an enhanced porosity as well as low tortuosity [26, 27]. Choi et al. [149] fabricated a mixed matrix TFC membrane with a functionalized CNT combined with polyethersulfone (PES) support layer, by means of phase inversion (PI) as well as interfacial polymerization (IP). The membrane was evaluated for wastewater reclamation and seawater desalination. About 72% enhancement in water flux was reposted and attributed to the improved hydrophilicity of the membrane. Even though the TFC mixed matrix membrane demonstrated lesser water flux relative to the TFC commercially used membrane, increased reverse salt flux selectivity of TFC mixed matrix membrane was noted relative to TFC commercially used membrane (4% greater) and TFC membrane (15% greater), demonstrating the perm selectivity of the membrane. During the test for effluent organic matter fouling, 16% lesser normalized flux reduction of the TFC mixed matrix membrane was noted relative to the TFC membrane. There was 8% lesser reduction of thin-film composite mixed matrix membrane as compared to the TFC commercially used membrane because of the effect of functionalized-CNT on repulsive membrane-foulant interaction improvement, resulting from the negatively charged membrane surface. Subsequent to physical cleaning for 10 min, TFC mixed matrix membrane showed improved normalized flux relative to the TFC membrane (6%) and the commercially used TFC membrane (4%). The work showed for the first time the utilization of TFC mixed matrix membrane in wastewater reclamation and seawater desalination. It was also observed that TFC mixed matrix membrane had lower organic matter fouling and that was probably due to the repulsive foulant-membrane interaction. TFC mixed matrix membrane with functionalized CNT blended in PES support layer was synthesized by Choi et. al. [156] by means of interfacial polymerization as well as phase inversion. Water flux of the aforestated advanced membrane enhanced by 72% relative to TFC membrane because of the increased hydrophilicity.

4.1.3 Nanomaterial interlayer

The utilization of an interlayer material with specific features for the preparation of an active polyamide layer for thin-film composite membranes might lead to increasingly permeable as well as selective layers. This interlayer material has the ability to avoid the interference of support membrane at the time of the polyamide film formation, thereby permitting an extensive series of support materials for osmotic membranes with diminished internal concentration polarization. The FO membrane with the same active polyamide layer demonstrated superior separation characteristics when the nanofiber membrane was utilized as the porous supporting layer. Zhao et al. [157] speculated that an important configuration of the TFC FO membrane influencing the separation characteristics is the microstructure of supporting layer surface which is in contact with the selective skin layer, that could be referred to as sublayer, developing the connection area of the supporting layer and the active skin layer.

Zongyao et al. [158] prepared a TFC FO membrane using an ultra-thin spray-coated interlayer of CNT. The influence of the carbon nanotube interlayer on the properties of polyamide layer structural as well as the transportation behavior in FO was examined. Figure 7 is the recommended cross-sectional structure of the polyamide layer developed on (A) pure poly(ether sulfone) support and (B) carbon nanotube-coated poly(ether sulfone) support. Test results confirmed that the carbon nanotube interlayer contributed an interface that enables the development of an extremely permeable and selective polyamide layer of huge surface area for water transportation whereas hindering the development of a flowerlike polyamide framework within the pores of the substrate. The FO TFC membrane with the carbon nanotube interlayer displayed a superior water flux compared to formerly stated several FO membranes whereas preserving a similar rejection of salt.

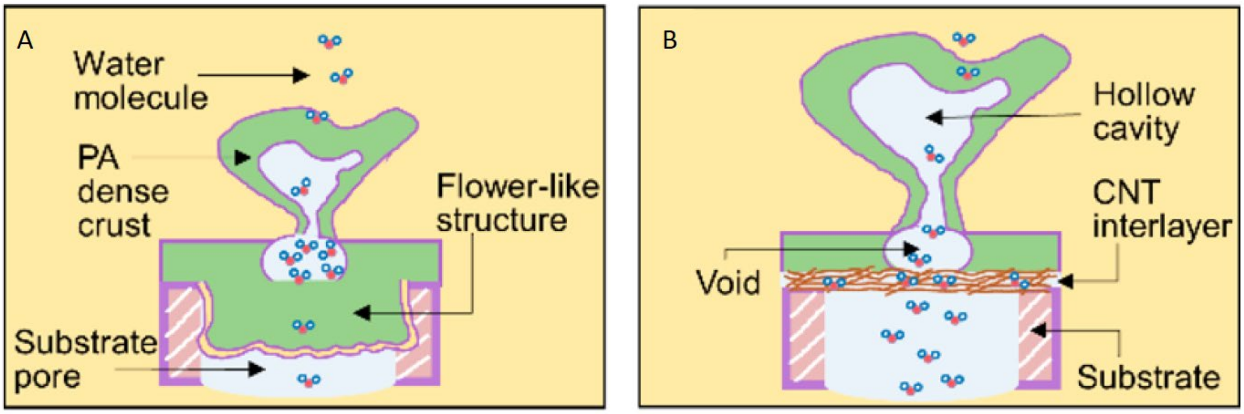


Figure 7: Recommended cross-sectional structures of the polyamide layer developed on (A) pure poly(ether sulfone) support and (B) carbon nanotube-coated poly(ether sulfone) support. Reproduced from [158]

The study by Zhao et al. [157] revealed the influence of the sublayer framework on the separating efficiency of TFC forward osmosis membranes. An advanced TFC forward osmosis membrane with a polyvinylidene fluoride support layer porous membrane, a CNT network sublayer, and a selective polyamide skin layer was fabricated by a facile filtration-supported IP technique. Figure 8 shows a diagrammatic portrayal of fabricating the multilayer FO membrane. The test results demonstrated that the fabricated FO membrane displayed enhanced separation efficiency and water flux twice more than the forward osmosis membrane in the absence of a carbon nanotube sublayer. The different characterization of the fabricated forward osmosis membrane framework demonstrated that the presence of the carbon nanotube sublayer was promising for contributing a

3-D free space that enhanced the active area of the polyamide layer by optimizing the space configuration under the polyamide layer. Simultaneously, the experimental results confirmed the adverse impacts of the standard support layer framework on the CP and on the separating effectiveness of the FO membrane, emphasizing the significant part of the sublayer framework between the support layer and the selective skin layer for enhancing the membrane performance during FO process.

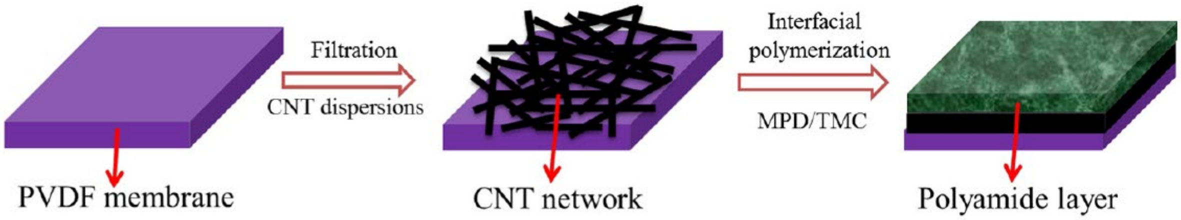


Figure 8: Diagram showing the fabrication process of the multilayered forward osmosis membrane [157]

4.2 Graphene oxide

Graphene-based nanomaterials have attracted a lot of attention for a new generation of applications. Specifically, graphene oxide nanosheets (GO) demonstrated a pronounced potential for developing the functional nanocomposite materials having higher chemical stability as well as stronger hydrophilicity [36]. In recent times, GO was proposed as a candidate for combining the processability of polymers, as well as the exceptional features of GO materials, make them one of the best carbon-based materials for developing membranes. GO is considered to be an outstanding additive and is extensively utilized as an additive on the forward osmosis membrane surface [132, 159]. It was reported that the graphene oxide-incorporated FO membranes demonstrated increased water flux, higher hydrophilicity and superior anti-fouling property [129]. Incorporation of GO in TFC PA membranes was analyzed for reverse osmosis [160], forward osmosis [161] and oily water treatment utilizing hollow fiber ultrafiltration [162] applications, which demonstrated higher-flux as well as antifouling properties.

The nanochannel of approximately 0.3 nm of the graphene oxide membrane is adequate for the proper water molecule penetration [163]. On the other hand, the molecules of water or any other solvents, inclusive of ions of constituents, will have interaction with various functional groups available in the graphene oxide layer. Subsequently, the improved interlayer space could be utilized in tuning the nanochannel diameter as well as the separation performance of graphene oxide-based membranes. These GO-based membranes can be utilized to separate dyes, separate divalent and monovalent ions, proficiently capture as well as dehydrate the solvent–water mixtures [164, 165]. Ultrathin graphene oxide-based forward osmosis membranes were fabricated by Hung et al. [166]. Appropriate crosslinking agents were utilized for tuning the inter-layer space of graphene oxide sheets in order to attain the preferred membrane efficiency. Interlayer space of graphene oxide-based membranes controlled the interaction occurring among the surface functionality of graphene oxide with the nature of crosslinking agents, like trimesoylchloride (TMC), meta-phenylenediamine (MPD) and polyvinylalcohol. The covalent bonds between the crosslinking agents and layer efficiently suppressed the stretching of d-spacing. In contrast with other symmetric membrane structures, the graphene oxide-TMC/MPD behavior noted in the ultrathin PA asymmetric framework for the efficiency of pressure retarded osmosis approach displayed 20.8 L/(m^2h) water flux and 3.4 g/(m^2h) reverse salt flux. A reliable water flux for a longer-term pressure-retarded osmosis operation was attained utilizing the graphene oxide-TMC/MPD membrane (approximately 98.7%). Consequently, the aforestated membrane could also be utilized to suppress the ICP.

4.2.1 Incorporation of GO into the active skin layer of TFC membrane

Numerous researches have confirmed that the preparation of a highly efficient FO membrane needs the optimization of the support layer and active layer structures [167]. The hybrid process is regarded as a technique for modifying the FO membranes to improve their water permeability, salt rejection, and reducing membrane fouling [168]. The nanomaterial GO has the ability to absorb heavy metals because of the existence of its functional groups and increased active surface area that can improve the antifouling properties and stability of the membrane [169]. Saeedi et al. [170] effectively manufactured an advanced TFNC forward osmosis membrane using PSf, diverse weight ratios of polyethylene glycol 400 in the membrane support layer, and varying amounts of graphene oxide in the active layer of forward osmosis membrane. The TFC FO membranes displayed increased water permeability, porosity, superior hydrophilicity, salt rejection, and water flux and low ICP and structural parameter value, relative to the standard TFC membrane. Compared to the TFC membrane, the TFNC membrane displayed a greater rejection to chromium (Cr), cadmium (Cd), and lead (Pb) from aqueous solutions, with the greatest rejection rate of chromium, cadmium, and lead equal to 98.3, 99.7, and 99.9%, respectively. Overall, from the aforementioned study, it was concluded that the thin-film nanocomposite FO membranes demonstrated a greater separation efficiency and better performance.

The research work by Eslah et al. [140] investigated the preparation of GO-embedded PA TFNC membranes on the PSf substrate for FO utilization. The graphene oxide nanosheets had been incorporated into the PA layer utilizing various concentrations, i.e., from 0.05 to 0.2 wt%. Test results confirmed the PA surface modification by graphene oxide nanosheets and improving the hydrophilicity of the surface by enhancing the graphene oxide concentration. Also, the test results demonstrated that the water flux for 0.1 wt% graphene oxide incorporated TFNC membrane was 34.7 L/m^{2}h, indicating a 90% enhancement relative to the TFC membrane, whereas there was 39% decrease in reverse salt flux. Thus the aforestated work confirmed that polyamide-graphene oxide/polysulfone is a potential membrane for forward osmosis utilization, especially in pressure-retarded osmosis mode.

It was demonstrated by experimentation that in the membrane modified using graphene, the solid matrix chemical functionalization, the applied pressure, the geometry and size of the pores are the chief factors affecting the efficiency of desalination processes [171]. Also, laminated graphene oxide membranes have been established as a prospective candidate for the water desalination application. Magnetically responsive graphene oxide/ Iron(II,III) oxide (Fe3O4) nanohybrids were manufactured by Rastgar et al.[141] by means of a flexible coprecipitation reaction and dispersed in MPD monomer. When subjected to the magnetic field, the magnetically sensitive nanohybrids had been later incorporated in the polyamide selective layer supported on an extremely porous polyethersulfone substrate for developing an effective forward osmosis membrane. By the intercalation of iron(II,III) oxide nanoparticles in between graphene oxide layers, special channels are developed all over the membrane selective layer, thereby helping the transportation of water molecules. These kinds of developments had been further evident when the nanoscale channels were well-ordered alongside the water flow pathway. Furthermore, the membrane surface hydrophilicity has also been enhanced by the inclusion of graphene oxide/ iron(II,III) oxide nanohybrid into the polyamide active layer.

4.2.2 Nanomaterial interlayer

To improve the efficiency of the FO membrane, chemical modification has been considered as an effective technique. Polydopamine has been extensively utilized as a bio-inspired hydrophilic polymer for modifying the lab-manufactured or commercial TFC FO membranes. Polymer membrane with a polydopamine (PD) coating is currently employed as a support layer of a hollow fiber as well as flat-sheet thin-film composite membranes for seawater desalination and water treatment. PD coated membrane demonstrated an improved water flux because of the hydrophilic modification by the polydopamine coating [172]. In recent times, GO was reported to offer two-dimensional (2-D) nanochannel for increasing the transportation of water and hydrophilicity [173, 174]. A compromise between membrane selectivity and permeability, the enhancement in permeability, was considered to be more necessary for increasing the performance of the membrane performance [175]. In the study of Choi et al. [176], a TFC membrane with a polysulfone support layer and an ultra-thin graphene oxide/polydopamine interlayer was manufactured by PI, self-polymerization, as well as IP technique for improving the membrane permeability of the TFC membrane for forward osmosis utilization. Figure 9 is the diagrammatic representation for the fabrication of a TFC FO membrane with graphene oxide/polydopamine interlayer. The support layer surface demonstrated increased hydrophilicity due to the presence of the hydrophilic functional groups of graphene oxide and polydopamine. For extended PD coating time, membrane permeability diminished because of the pore blocking by GO as well as PD. The TFC membrane with the polysulfone support layer coated with the graphene oxide/PD interlayer presented excessive development in water flux (almost 57.6%) without a remarkable reduction in the reverse solute diffusion under an optimum condition of 0.5 g/L of graphene oxide concentration and one hour of PD coating time. Test results from the aforestated study are anticipated to promote the advancement of TFC type forward osmosis membranes consisting of a hydrophilic interlayer to accomplish enhanced membrane efficiency for seawater desalination as well as purification processes.

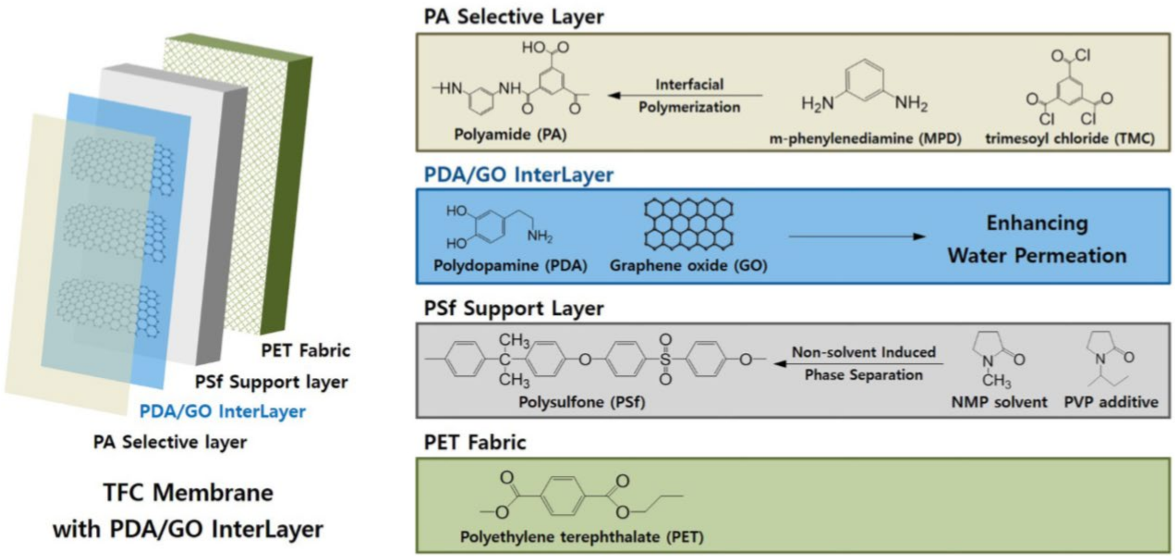


Figure 9: Diagrammatic representation for the production of TFC FO membrane with GO/DP interlayer [176]

4.2.3 Surface modification using graphene oxide

Numerous researches have proposed the modification of the TFC membrane surface with antimicrobial nanomaterials, bio-active molecules, or polymers [177] for providing antimicrobial action as well as biofouling strength to the membrane. As an illustration, it was demonstrated that thin-film composite membranes functionalized using copper or silver nanoparticles provide a reduced sensibility to biofouling [178]. Conversely, carbon-based nanomaterials like GO can be combined with the PA layer to develop TFC membranes with increased antimicrobial performance. Because of the chemical functionalities, the graphene oxide nanomaterial could be simply combined with an extensive range of nanoparticles and polymers. Utilizing the surface of GO to anchor silver nanoparticles seems favorable, mainly because of the surface functional groups, which function as nucleation points for the development of particle.

Faria et al. [127] proposed the manufacturing of anti-biofouling TFC FO membranes functionalized using GO–silver nanocomposites. The characterization, like Raman spectroscopy and scanning electron microscopy, confirmed the GO-silver nanocomposite immobilization on the surface of the membrane. GO–silver modified membranes exhibited 80% inactivation of the attached *Pseudomonas aeruginosa* cells. Along with a static antimicrobial assay, the aforestated work also contributed to an understanding of the anti-biofouling ability of FO membranes in the course of dynamic operation in a crossflow testing cell. Functionalization using GO-silver nanocomposites caused a potential anti-biofouling ability without decreasing the intrinsic transport properties of the membrane. Dynamic biofouling tests also revealed that reduction in water flux at the time of biofouling development was diminished by 30% subsequent to the TFC membrane modification with GO-silver nanocomposites. The results from the aforestated study confirmed that the utilization of GO–silver nanocomposites is an attractive and feasible method for the advancement of anti-biofouling TFC membranes.

4.2.4 GO membranes - Single and multilayers

Selective and fast water transportation within graphene oxide laminates has been intensely validated in both experimental and theoretical methods [179]. The 2-D nanomaterial frameworks, particularly those consisting of GO, have gained broad research interest for membrane-based desalination as well as separation processes [180]. Conversely, the influence of horizontal defects in two-dimensional nanomaterial frameworks, which originate from non-uniform deposition of two-dimensional nanomaterial flakes in the course of layer build-up, has been virtually completely disregarded. In the study carried out by Cody et al. [180], the team applied Monte Carlo simulations, in ideal conditions in which the vertical inter-layer space permits for the permeation of water, whereas completely rejecting salt, on both the development of the laminate framework and molecular transportation across the laminate. The simulation results demonstrated that the two-dimensional nanomaterial frameworks are highly tortuous, having water permeability diminishing from 20 to <1 $L\ m^{-2}\ h^{-1}\ bar^{-1}$, as thickness amplified to 167 from 8 nm. Maximizing packing density is an important technical challenge, along with the issue of optimizing interlayer space, for the two-dimensional nanomaterial membrane development.

Developing an ultrathin membrane with hydrophilic nanometer GO layers is an efficient technique for improving the FO membrane performance. The GO membranes assembled by means of electrostatic interaction, as well as PA-crosslinking, were examined for the forward osmosis performance [181]. The aforestated membranes showed increased water flux and lower solute flux when sugar, as well as trisodium citrate, were utilized as the draw solution.

It was observed that the three main issues influencing the performance of the FO membrane are water flux, membrane biofouling, and reverse solute diffusion. The GO membrane shows higher water flux, demonstrating its possibility for the utilization in the water purification field. On the other hand, precise control of the GO membrane pore size is essential for effective ion sieving. In the work by Pang et al. [182], the hydrophilic metal-organic framework nanoparticles (UiO-66), are interpolated into the GO layers to develop ultra-thin sandwich membranes for enhancing the performance of FO process. Figure 10 is the representation of the GO/UiO-66 sandwich membrane for the FO process. The incorporated UiO-66 nanoparticles introduced appropriate and uniform nanochannels that could efficiently permit water to pass through, whereas hindering the solutes of sodium ions. In the FO model, the GO/UiO-66 membrane demonstrated 29.16 L/m^{2}h water flux of, which was about 270 % greater than the pure GO membrane, and 83.5% less reverse solute diffusion.

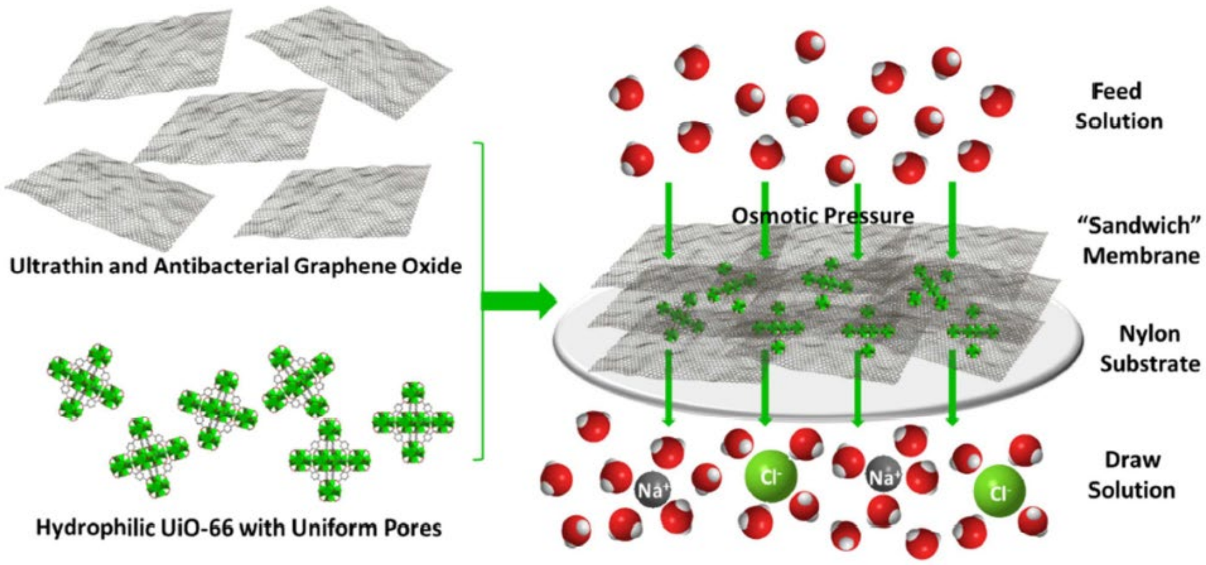


Figure 10: Representation of the graphene oxide/UiO-66 sandwich membrane for the *FO* process. Reproduced from [182]

The GO membranes worked efficiently in the course of FO operation [183] and are noted to be better than standard FO membranes in certain aspects [37]. Kim et al. [184] related the performance of hydrophilic reduced-GO membrane and commercially available cellulose acetate (CA) FO membrane. The study demonstrated that the salt rejection and water flux of the reduced-GO membrane were greater than that of the commercially available FO membrane. Mi and his team members made GO membranes using layer-by-layer assembly of polyelectrolyte and GO on the back as well as front sides of a polyacrylonitrile support layer [185]. The GO membranes can be categorized as free-standing membranes as well as stacked membranes having a substrate. Due to the fact that the porous support layer is not able to stop the solute, ICP generally happens in that region. The dissimilarity in the concentration between both sides of the functional layer is lesser than that between the feed and the draw solution, resulting in a reduced driving force across the membrane. For the freestanding membrane, the mechanical strength of this membrane is less, though the effect of the substrate on the separating performance could be removed. Especially, in the FO mode, the existence of ICP in free-standing GO membranes could be practically entirely prevented [186]. In a research work of Zhang et al. [186], the team noted that the flux of free-standing reduced graphene oxide membranes was linearly associated with the concentration of salt, which confirmed that the ICP was entirely removed. Water flux in a freestanding membrane was five times more than that of commercially available CA FO membranes, whereas the rate of ion penetration in reduced-GO membranes was lesser relative to that of commercially available FO membranes. Furthermore, GO membranes showed distinct performance in both membrane orientations, i.e., FO and PRO modes. In the case of sucrose draw solute in the PRO mode, the water flux of the GO membrane was two times greater than that of the FO mode. Nevertheless, the fluxes of the GO membrane in the PRO and FO modes appeared similar, although when the draw solution was trisodium citrate (TSC) or magnesium chloride, ICP happens in the PRO and FO modes due to the electrolyte-induced swelling. In the study by Mi et al. [187], water flux of a crosslinked GO membrane was found to be higher than that of commercially available FO membrane when the draw solution was sodium chloride or TSC. While $MgCl_2$ was the draw solution, water flux of the GO membrane diminished considerably; however, the commercially available FO membrane did not demonstrate a similar phenomenon. The aforestated observation indicated that the surface charge of GO membranes enforces restrictions on their utilization.

Salehi et al. [33] prepared an advanced extremely effective FO membrane utilizing the LbL assembly of negative GO nanosheets and positive chitosan by means of electrostatic interaction on a porous layer of support. The porous support layer was fabricated by mixing hydrophilic sulfonated-PES into PES matrix by wet phase inversion process. The test results demonstrated that the membrane coated by a Chitosan/graphene oxide bilayers showed water flux of magnitude 2–4 orders greater than the TFC membrane.

4.3 Graphene

Graphene is considered to be a carbon allotrope, which has a single-atom-thick planar sheet having an sp2-bonded carbonous structure [188]. This nanomaterial is typically manufactured by the GO reduction, where oxygen-consisting functional groups of graphene oxide, like carboxyl, carbonyl, epoxy, and hydroxyl, are detached to certain degrees [189]. The two-dimensional (2-D) arrangement with sub-nanometer surface apertures makes this nanomaterial a potential barrier for selective mass transport. Because of the interlayer functional groups in graphene, the d-spacing of this nanomaterial is lower compared to GO with 0.34 nm. This value is not influenced by exterior conditions, which means that the graphene-based membranes are equally able to display a steady performance for an extended time. On the other hand, the graphene sheets will experience low hydrophilicity which might result in an increased fouling propensity.

4.3.1 Graphene laminated membranes

Not just the FO, but the entire membrane-based technologies are prone to fouling problems, obstructing their continued performance in the longterm. By utilizing graphene and polyaniline (PANI), Shakeri et al. [188] manufactured an innovative electro-conductive membrane by laminating graphene onto a polyamide-imide support layer through a simple pressure-assisted method. For improving the mechanical stability of the manufactured by means of crosslinking of polyaniline with graphene nanosheets, the membrane was thermally treated for almost 3h at 140 °C. Both nanocomposite membranes (with and without thermal treatment) showed superior mechanical stability and their reverse salt flux and water permeation performances were confirmed utilizing a standard FO desalination system. The study confirmed that the selectivity ratios, which is tha ratio of water flux to reverse salt flux, of membranes were 0.79 g/L (without treatment) and 0.69 g/L (with treatment) in the FO mode. Also, the of anti-fouling performance of the membranes were examined by the FO process with alginate as the model organic foulants. Figure 11 is the diagrammatic portrayal of rearranged FO arrangement, which was used to examine the fouling performance of the membranes. With the application of 2 V anodic potential, both fouling resistance and recovery rate of flux were significantly enhanced in both the membranes.

Taking the benefit of electro-conductive graphene nanosheets, Rastgar et al. [190] proposed an advanced in-situ electro-oxidative method to lessen the organic fouling. A very thin layer of graphene was deposited onto the PES support layer for preparing the graphene laminate membrane. Selectivity ratios of the graphene laminated membrane was experimentally measured to be 1.44 L/g and 1.48 L/g in the DS-AL and FS-AL configurations, respectively. Due to the fact that this membrane is utilized in the FO process for treating artificial wastewater consisting of 500 ppm sodium alginate, the manufactured graphene laminate membrane showed superior antifouling properties when 2V direct current potential was enforced on its surface. To confirm these results, the fouling performance of the graphene laminate membrane was tested against that of the standard FO TFC membrane. Under electrical potential, the ratio of water flux recovery was remarkably enhanced from 75.4% (TFC membrane) to 98.7% (graphene laminate membrane), indicating greater antifouling behavior of the manufactured membrane. Thus, it can be noted that, the aforestated study offers a sensational platform for the manufacturing of electro-oxidative membranes with exceptional anti-fouling behavior.

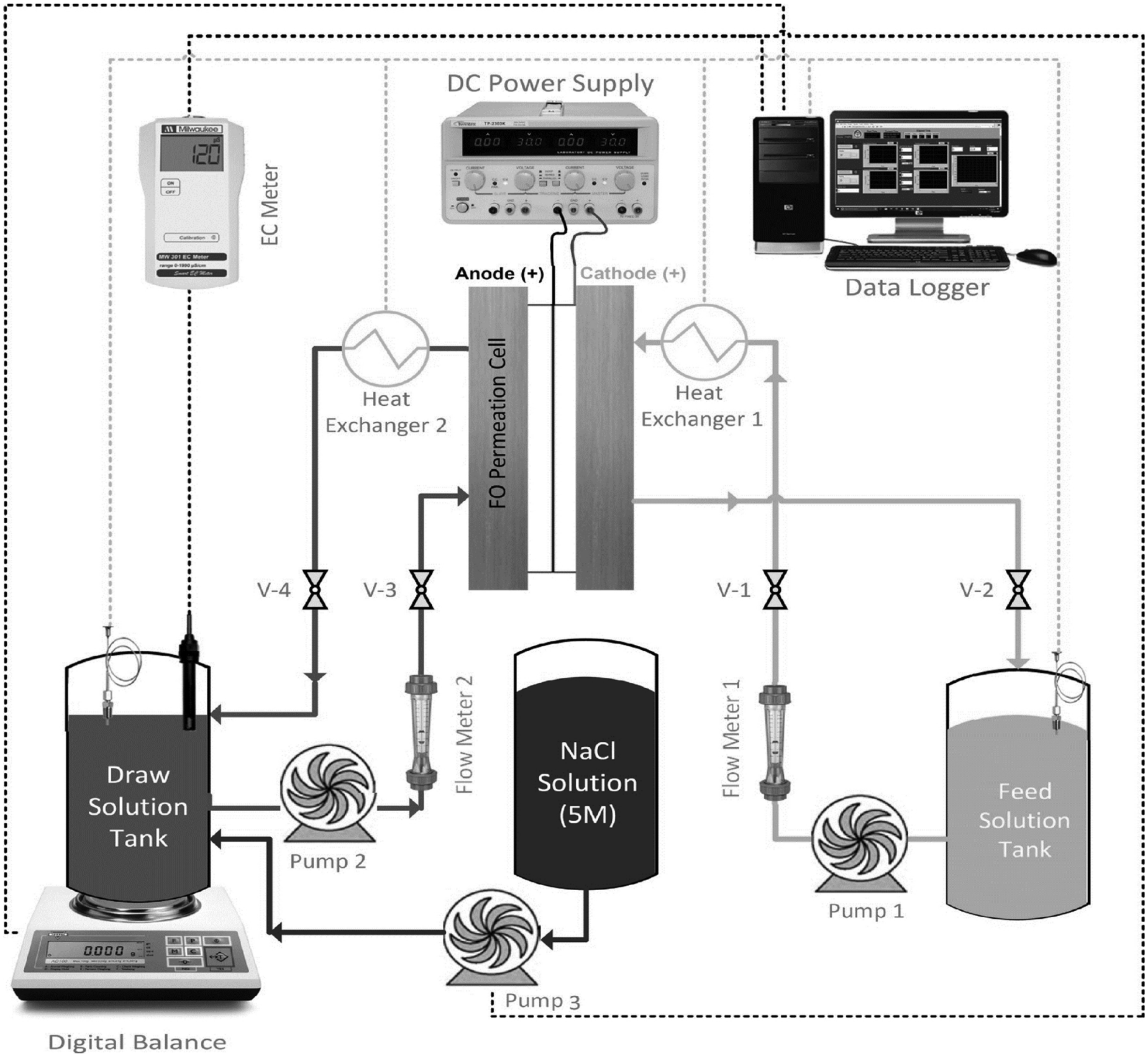


Figure 11: Diagrammatic portrayal of rearranged FO arrangement which was utilized to examine the fouling performance of electro-conductive membranes. Reproduced from reference [188]

4.3.2 Stacked graphene membranes

Monolayer graphene membranes, with the higher Young's modulus (1100 GPa), are mechanically durable for use in the FO systems without a supporting layer, and therefore are more effective relative to the carbon nanotubes. Still, there are certain technical difficulties while scaling-up the manufacturing of nanoporous graphene membrane: (1) fabrication of superior quality, huge area graphene sheets at a lower cost, and in a reproducible eco-friendly way; (2) perforation to attain the required pore size, shapes, and pore distribution without compromising the mechanical strength.

Stacked graphene membranes having cascading nanoslits could be fabricated inexpensively, relative to monolayer nanoporous graphene membranes, and these membranes have the possibility for molecular separation. Madhavi et al. [112] studied the efficiency of seawater desalination of these stacked graphene layers FO membranes using MD simulations. The FO operation is assessed with respect to the rejection rate and water flux, and described by examining the water density distribution along with the radial distribution function. The aforestated work confirmed that the characteristics of membrane inclusive of the number of layers, interlayer separation distance, offset, and pore width have substantial impacts on the desalination efficiency. The observations from the previous research work are beneficial in developing graphene-based membranes for the FO applications.

5. Reversible membrane fouling in the FO process

Even though the membrane-based technology has several benefits over the conventional water treatment technology, the fouling of membrane still remains to be a main operational issue [191]. Membrane fouling can happen due to the presence of different types of contaminants in the feed water inclusive of microbial products, microorganisms, chemical reactants, dissolved organics, colloidal or particulate matter, and inorganic compounds [192]. The fouling of membrane leads to the necessity of an efficient pretreatment process of the feed solution and membrane chemical cleaning, which results in extra expenses and rises the consumption of energy. As a result, fouling minimization is the key to successful as well as profitable membrane operation.

Even though the fouling layer might have an extra thickness in the FO membranes, subsequent studies demonstrated the reversibility of membrane fouling in the FO process, thereby establishing the recovery of water flux as great as 60 to 100% of the original value [193, 194, 195]. The superior reversibility of fouling in FO enables its utilization in different applications, like domestic wastewaters loaded with organic material [193]. In the FO application, the mitigation of the fouling can be achieved by means of different techniques like the introduction of air bubbles, flow pulsation, and higher cross-flow velocity [196]. Table 4 summarizes some of the preceding studies performed on the fouling reversibility of FO membrane by means of flushing at higher cross-flow velocities. These type of higher reversibility was also noted with scaling by silica [197], and gypsum [198] and fouling by biopolymers and proteins [193, 195]. In general, the results confirmed that the reversibility of FO fouling by periodic rinses, with no requirement for chemical cleaning.

Table 4 : Summary reversibility of fouling in different FO membrane based systems using flushing at higher cross-flow velocities

Sl. No.	**Draw solution**	**Feed solution**	**Membrane material**	**Flux (L/(m^2h)**	**Operation time (min)**	**Cleaning time (min)**	**Cleaning velocity (cm/s)**	**Fouling reversibility**	**Ref.**
1	31,954 ± 253 ppm seawater	350 ± 14 ppm secondary effluent	Polyamide	10.6	4200–4560	10	25.6	85–100	[193]
2	35,000 ppm sea salts	200 ppm humic acid, 200 ppm alginic acid, 220 ppm CaCl2,1200 ppm sea salts	Polyamide	16	-	60	25	100	[195]
3	4M NaCl	0.5 mM CaCl2, 200 ppm alginate, 50mM NaCl	Cellulose triacetate	-	1620	15	0.011	96	[194]
4	4M NaCl	115 mM NaCl, 19 mM MgCl2, 4.2mM silica	Polyamide	5	1440–4320	15	21	60	[197]

5.1 Different types of fouling in FO process

In the subsequent section, we examine mainly about the three types of fouling (organic, inorganic and biofouling), different factors controlling the development of fouling, and different studies carried out with and without nanoparticles to confirm the fouling reversibility in the FO membranes.

5.1.1 Organic fouling

This type of fouling happens by organic matters in the feed solution. Organic fouling could be due to hydrophilic, transphilic, as well as hydrophobic fractions present in the feed water. Organic fouling of FO membrane was widely investigated in the past decade [199]. Mi et al. [200] examined the organic fouling in FO processes, and the team observed a close relationship between the intermolecular adhesion force and organic fouling, thereby confirming that foulant–foulant interaction performs a major role in evaluating the extent as well as rate of fouling. It was observed that calcium-binding, hydrodynamic shear force, and permeation drag are the most significant factors controlling the progress of organic fouling. It was noted that the aforestated type of fouling (model foulant- alginate) is reversible with no chemical cleaning [201]. The results from Mi et al. [201] study suggested that operation in FO mode might contribute an exceptional benefit in diminishing or even removing the requirement for chemical cleaning. The study demonstrated that FO membrane fouling by alginate is nearly completely reversible by physical cleaning for a moderately short period of time. Adhesion force information showed that a smaller percentage of comparatively adhesive sites on the surface of the membrane performs a major role in enhancing the fouling potential of the membrane and reducing the cleaning efficiency.

Choi et al. [149] studied the effect of TFC mixed matrix membrane functionalized CNT blended in PES support layer. The synthetic wastewater with alginate was utilized as the feed solution, whereas artificial seawater was the draw solution. Subsequent to the alginate fouling, cleaning of the physical membrane was carried out for the measurement of water flux recovery. Electrostatic repulsive force can perform a leading role in the interaction force between the functionalized CNT-blended polymer membrane and the alginate foulant, because of the negative charge. Due to the interaction between the PA layer surface and the foulant, the change in surface roughness can perform a serious role in reducing the fouling. In addition, it was also confirmed that the smoother membrane surface provided a reduced accumulation of foulant materials on the surface. The study revealed the effect of the functionalized-CNT in increasing the resistance against alginate fouling. In contrast with pressure-driven membrane processes, the fouling layer in the FO membrane was completely reversible. It was also proved that the reversibility in fouling was improved in the TFC mixed matrix membrane because of surface roughness and electrostatic repulsive force.

Rastgar et al. [141] developed an extremely efficient FO membrane tailored by GO/Fe3O4 nanohybrid, and the organic foulants such as bovine serum albumin (BSA), sodium alginate (SA) were utilized as foulants to examine the membrane fouling in FO mode. For assessing the fouling reversibility, subsequent to surface cleaning, the cross-flow velocity was diminished to its original level and by utilizing the 10 mM sodium chloride feed solution, water flux through the membranes was recorded again. As established experimentally, the greater fouling resistances attained against BSA and SA foulants in the GO/Fe3O4 modified membranes could be due to their lesser surface roughness and higher hydrophilicities.

5.1.2 Inorganic scaling

This type of scaling happens as the concentration of sparingly soluble salts surpasses their solubility, resulting in precipitation of metal salts and serious membrane flux decline [197]. Out of the different scalants, silica and gypsum (calcium sulfate dehydrate) are the most commonly seen scalants in brackish water or seawater desalination.

A previous research work on calcium sulfate dihydrate scaling confirmed that the nonexistence of hydraulic pressure in FO assisted to enhance the cleaning efficiency of the membrane [198]. The work by Mi et al. [202] examined the silica scaling as well as cleaning performance in FO and compared the reverse osmosis and FO modes. The results showed that, under the established hydrodynamic conditions, the rates of water flux decline under silica scaling are very much comparable in the two aforestated modes. However, the flux recovery is approximately 100% in the FO mode, whereas it is just almost 80% in the reverse osmosis mode. Atomic force microscopy force measurements indicated that roughness of the membrane surface enhanced the adhesion force between the silica gel layer and polyamide membrane, considerably reduced the cleaning efficiency of the polyamide membrane. In a pilot-scale study by Chun et al. [203] on the fouling characterization of a forward osmosis-reverse osmosis system treating higher fouling potential brackish surface water, inorganic scaling was noted to be hard to eliminate following to chemical and physical cleaning. Thorough characterization confirmed that it is possibly gypsum as well as organic components.

5.1.3 Biofouling

Biofouling is described as the bacteriological adherence with growth thereby creating a biofilm, resulting in a reduction in membrane performance above 10 to 15% of the initial values under the practical operating conditions. This type of fouling leads to remarkable technical issues and effects the performance of the system by raising the required operational pressure, causing a decline in membrane efficiency, leading to membrane biodegradation resulting in an improved salt passage, and rising energy requirements.

Several kinds of research based on the biofouling in FO processes have been proactively carried out in the recent past, however, the knowledge on this phenomenon is inadequate relative to other fouling types [204]. Yoon et al. [204] examined the happening of biofouling utilizing the model bacterium *Pseudomonas aeruginosa* PA01 green fluorescent protein in the forward osmosis process against the reverse osmosis process as well as its control. The work concluded that biofouling in the FO process is less severe than that in the RO process. In the study carried out by Chun et al. [205], substantial deposition of biofilm was detected on the surface of the FO membrane for the filtration of nutrients-spiked brackish surface water. FO biofouling displayed benefits with respect to membrane cleaning as well as the filtration of increased fouling potential feed waters, which is responsible for the fouling. The hydraulic cleaning tests confirmed that the biofouling and organic fouling on the TFC FO membrane as a result of natural lake water with added nutrient substrates are practically completely reversible with no utilization of chemical agents.

5.2 Membrane cleaning strategies

With the intention of achieving steady water flux in membrane process, a suitable cleaning method is essential. Most laboratory size FO fouling tests that usually utilize FO flat sheet membrane coupons, the declined flux and fouling is more reversible compared to the pressure-driven membrane processes [205, 206]. The recovery of flux in the FO mode was noted to be greater than that in the reverse osmosis mode in alginate fouling tests under the same cleaning conditions, even though the water flux decline rate was comparable in both modes [201]. The reversibility in the fouling of the FO process was probably due to less compacted fouling layer because of the nonexistence of hydraulic pressure. Consequently, the fouling layer in the FO mode can be eliminated by rinsing with DI water only. Therefore, the FO mode would provide a remarkable benefit of decreasing the requirements for chemical use.

The fouling of FO membrane in the course of treating the natural water (seawater or wastewater) which consists of different types of foulants was noted to be irreversible with facile physical cleaning that needs various cleaning approaches or chemical cleaning [207]. Therefore, the control of the fouling of FO membrane has become an important issue for the viable advancement of FO-RO hybrid system mainly for various wastewater and desalination treatment processes. Principally over this process, the two sides of the forward osmosis membrane are in persistent contact with natural waters. As a result, launching appropriate cleaning procedures holds the key to attain durable operation of the FO process in an actual situation and long-standing forward osmosis-reverse osmosis hybrid process. Extra hydraulic pressure on the feed side in the FO process has the ability for resolving the lower permeation flow and diminishes reverse salt flux [208]. Alternatively, the activity of hydraulic pressure in the FO process results in an enhancement in membrane fouling and a reduction in cleaning efficiency. The efficiency of membrane cleaning after physical cleaning is correlated to the fouling layer structure, i.e., a more compact and denser fouling layer leads to low-efficiency physical cleaning, alongside the sparser and looser fouling layer could almost be entirely removed [209]. In the course of forward osmosis-reverse osmosis long-standing hybrid system, there exist a serious requirement for a systematic comprehension of membrane fouling performance and for the advancement of different techniques for the mitigation of fouling. The foulants have the ability to deposit on the surface of the membrane or be trapped within the pores of the membrane and thereby develop a fouling cake layer having various structures under diverse operational parameters. Correspondingly, it is important to properly recognize the fouling behavior of the FO membrane and develop effective and economical fouling control approaches to sustain longer-term performance.

The osmotic backwashing technique combined with succeeding water flushing was established and proved to be a very efficient approach for cleaning the extremely fouled membrane [210]. The osmotic backwash also permitted for the thorough cleaning of the membrane pores. Conversely, the fouling of the FO membrane is still regarded as one of the main disadvantages of this FO-RO hybrid process. The work by Fezeh et al. [210] examined the impact of different operating conditions on the recovery performance of water flux in the course of seawater dilution by wastewater. The test results confirmed the possibility of altering the hydrodynamic operating conditions to minimize membrane fouling and to increase the efficiency of cleaning during long-standing operation. The aforestated study demonstrated that the membrane materials perform a substantial role in controlling the fouling of membrane as well as cleaning behavior in the FO process due to the fact that diverse membrane materials result in distinct particle-membrane interaction. The cleaning technique adopted (800 mL/min cross-flow velocity for 15 min subsequently followed by 20 min osmotic backwashing) could completely restore the membrane flux at the majority of practical conditions with no utilization of any chemical cleaning reagents. In addition, at increased pH of feed solution (pH:8) and under lesser cross-flow velocity (100 mL/min) the fouling in FO processes was more serious and implementation of the cleaning approach did not support to restore the water flux to initial value. The fouling characterization by energy-dispersive X-ray spectroscopy (EDS) and scanning electron microscope (SEM) recommended that the hydrodynamic drag turns out to be dominant at lesser cross-flow velocities that force the particles to shift to the surface of the membrane, which in return stimulate the fouling of the membrane. The aforestated leads to lesser flux recovery. Additionally, at increased pH of the feed solution, the system attained the maximal interaction between particles and membrane. Figure 12 is the indication of the development of fouling at three different feed solution pH (3, 6.8 and 8). The visible difference in the morphology, as well as the composition of the fouling on the surface of the membrane, was observed at distinct feed solution pH. Furthermore, it was proved that the utilization of hydraulic pressure resulted in more serious fouling phenomena and more compact fouling which tightly held together, thus leading to lesser cleaning efficiency. For reducing the possibility of scaling development at the feed solution side, the composition of draw solution must be tailored. The existence of scaling precursors must be avoided and the addition of anti-scaling agents in the draw solution can destroy the development of scaling at the feed solution side (Figure 13).

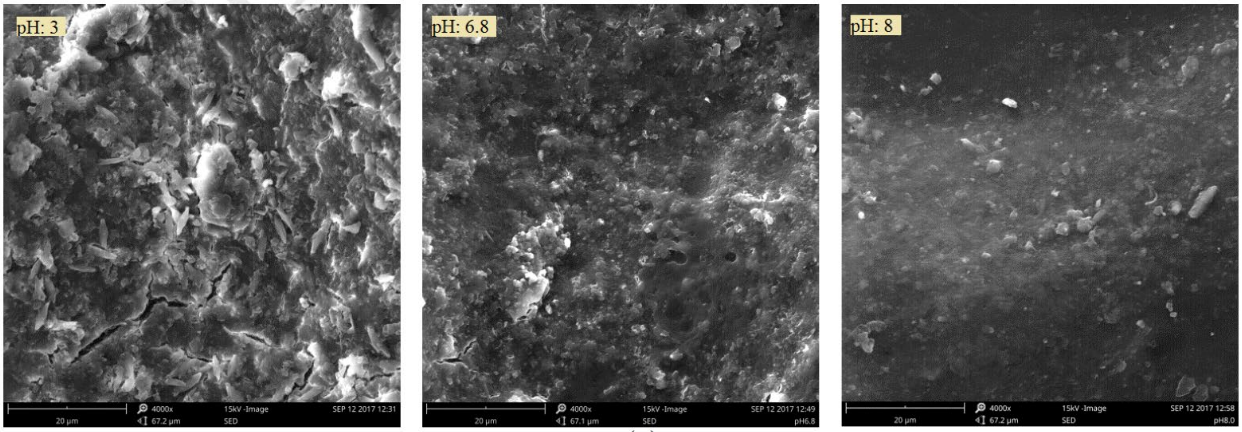


Figure 12: Indication of the development of fouling at three different feed solution pH(3, 6.8 and 8). Reproduced from reference [210]

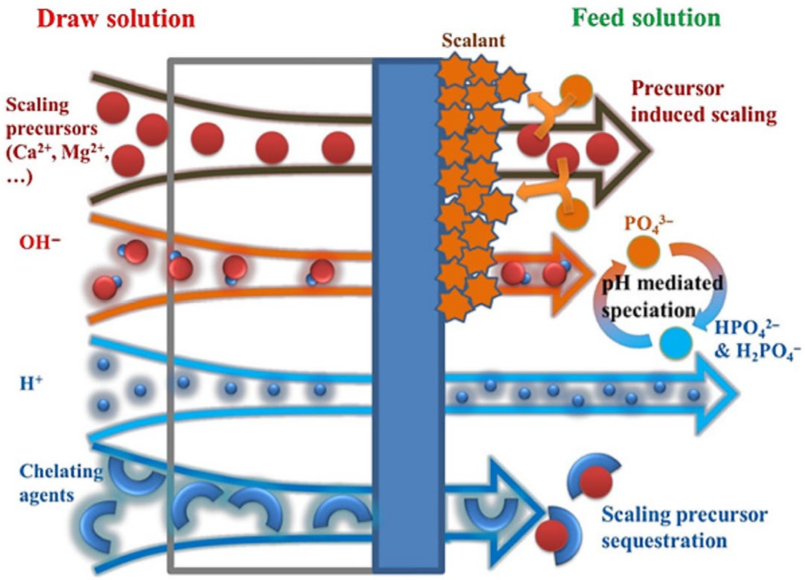


Figure 13: Scaling control technique by tailoring the draw solution in the course of the FO process [211].

6. Challenges and Future scope at industrial scale

In brief, the issues faced in the successful and commercial realization of FO desalination include reverse solute flux, membrane fouling, CP, and lack of appropriate commercially available membranes. The scarcity of commercially accessible and favorable FO membranes is still the main constriction restricting the progress of FO desalination processes. The reverse draw solute diffusion and ICP are the exceptional problems for the utilization of the FO membrane. Research need to be carried out to advance the process effectiveness by fabricating innovative membranes, examining the sustainability and stability of the process in the long-term, and upgrading the module design of FO in order to facilitate the FO desalination process.

The aggregation of particles is one of the critical problems faced in the course of nanocomposite membrane manufacture, and it is mostly caused by the improved inter-particle interactions and increased surface energy of nanomaterials. The aforestated leads to reduced dispersion of nanofillers within the solution of monomer utilized for polyamide layer development, or in the polymeric dope solution employed for membrane substrate. Nanoparticle accumulation reduced the active surface area of nanoparticle and leads to the development of a flawed polyamide layer having voids as well as the irregular distribution of nanomaterial. Numerous researchers have discovered the nanomaterial surface functionalization such as carboxylated or amine-functionalized CNTs for minimizing the aggregation of particles in the polymer matrix or non-polar solvent and develop a fault-free dense active layer. In addition to nanofiller surface functionalization, advanced nanomaterials could be developed with tailored pore structure as well as the surface charge for facilitating uniform nanofiller distribution within the polymeric matrices.

Figure 14 summarizes the serious problems in the manufacture of nanomaterial-incorporated polyamide TFC membranes, which needs to be discussed to attain an advanced membrane performance and scalability. Uneven dispersion of nanomaterial in the polymer dope solution or solvent could obstruct the reproducibility of the membrane and lead to a substantial variation in the performance of the FO process. This is particularly important for a small FO membrane coupon used in performance examination tests. Therefore, it is critical that the entire laboratory-scale membrane performance tests are carried out utilizing huge membrane samples rather than a small membrane coupon so that the test results are similar representing the entire composite membrane. Nanomaterials larger than the polyamide layer thickness, like the carbon nanotubes could damage the active layer and weaken the selectivity of the membrane [212]. The nanomaterial loss in the course of membrane manufacture and the FO process is an extra issue.

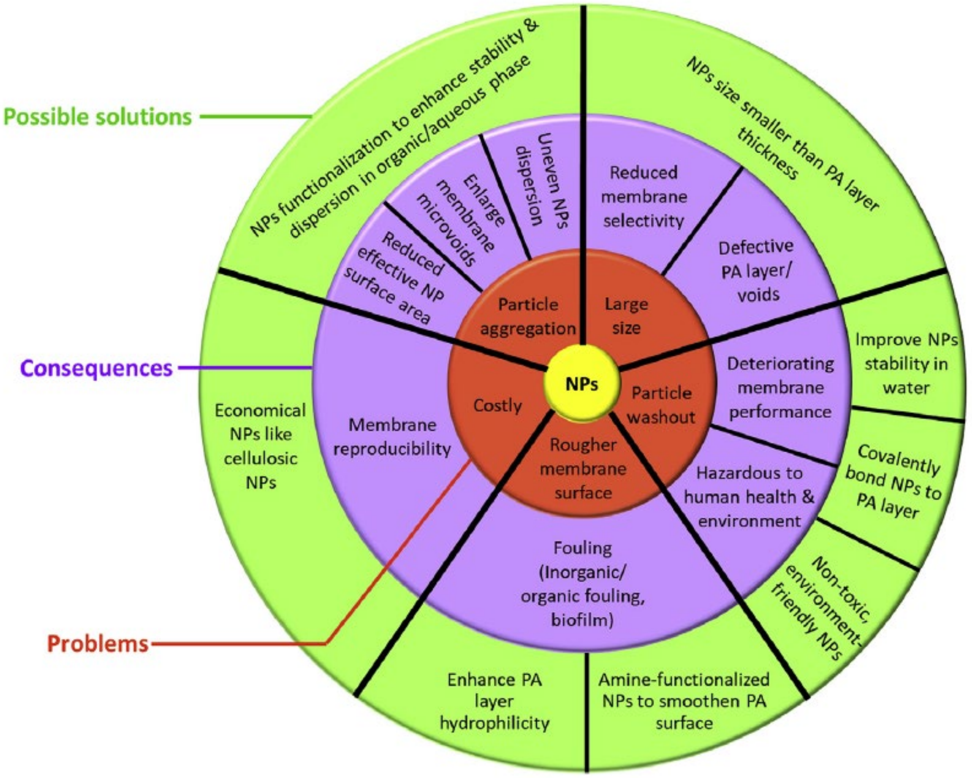


Figure 14: Summary of the serious problems in the manufacture of nanomaterial-incorporated polyamide TFC membranes that need to be investigated to attain more development in the membrane performance as well as scalability. Reproduced from reference [137]

Several studies that have utilized the hydrophilic nanotubes have reported that the inclusion of nanotubes into the PA layer or membrane substrate could increase the permeability of water without considerably influencing the rejection of salt by contributing extra pathways for the water molecule transportation [150]. On the other hand, the idea of the favored path for water molecules needs additional authentication. The concept is only feasible when the nanochannels are aligned towards the direction of water flux and not congested by the polymeric matrix. Up to now, majority research works on liquid separation stated the performance of membrane improves with just randomly arranged nanotubes [138]. In the study carried out by Sharma et al. [213], the team utilized an electric field for aligning the carbon nanotubes in the polymeric membranes for the purpose of hydrogen separation. Therefore, it might be conceivable to utilize a magnetic or electric field for considering the influence of homogenous nanotube alignment on the efficiency of the membrane for the application of liquid separation.

Even though the FO process is related to an intrinsic lesser fouling potential, the performance of the process could be considerably influenced by the decreased mass transfer caused by the increased CP and fouling layer resistance [214]. The more hydrophilic membrane can be produced by incorporating hydrophilic nanoparticles in the active polyamide layer but this process would increase the roughness of membrane surface and fouling propensity. Even though the cost-efficiency and reproducibility of the TFNC membrane are significant, it is also essential that the long-standing efficiency of the TFNC membranes under practical conditions are properly realized for determining the sturdiness of the membrane. Long-standing performance examinations and detailed valuation of the stability of the nanocomposite membrane are very important, particularly in the case of surface-modified nanocomposite membranes, for controlling the nanomaterial leaching. This leaching of nanomaterial might degrade the durability and performance of the membrane.

Moreover, it is critical to develop standard as well as reliable protocols in order to characterize FO membranes for facilitating the standardization of the test results attained from various research groups as well as enable the exchange of data and analysis. Furthermore, the active and support layer of the FO membrane could be degraded at elevated hydraulic pressures, leading to an undependable assessment of membrane transport along with structural parameters [215]. A standard protocol is needed for FO operating conditions for comparing diverse membranes with regard to FO performance. The entire existing challenges in FO desalination are indistinguishably related to each other and should be considered while carrying out study on FO desalination. As a matter of fact, the greatest issue for the FO desalination process commercialization comes from the financial feasibility. The financial feasibility of a method could be precisely associated with its scalability as well as commercialization. Thus, for making a moderately precise financial assessment for the FO process, different factors like superior performance membrane development, draw solute recovery, and draw solute selection must be taken into consideration. A financially feasible FO process must satisfy all such factors for answering normally identified problems and disadvantages in the desalination process.

Conversely, there is no research or scientific dispute that FO desalination is hardly prone to membrane fouling relative to the pressure-driven reverse osmosis. There is a probability of determining energy-effective means of draw solute regeneration and durable FO membranes for overcoming the current problems experienced by FO desalination. Furthermore, there is a persistent requirement to examine the pilot-scale FO desalination. It can be noted that the currently established reverse osmosis market was once experiencing the same issue of unsatisfactory levels of water flux, till Loeb and his team successfully prepared highly efficient reverse osmosis membranes that had been later commercialized by DuPont and Dow Chemical by means of their research and development efforts. Similarly, effective commercialization of forward osmosis desalination also needs industrial research and development contributions. Further to numerous pilot scale studies done, in September 2019, Forward Water Technologies Pty Ltd. has reported an entire scale trial of their forward osmosis technology at a wastewater treatment plant located in Airdrie, Canada [216].

Conclusion

The introduction of nanomaterials led to the advancement of novel FO membranes with extraordinary separation performance and anti-biofouling abilities. Carbon-based nanofillers like carbon nanotubes, graphene, and graphene oxide were used to fabricate nanocomposite membranes to improve membrane mechanical strength, permeation flux and resistance to fouling. Carbon-based nanocomposite FO membranes have an improved mechanical stability and fouling resistance with a complete water flux recovery, thereby providing more robust filtration process. The reversibility in the fouling of the FO process may be due to the lesser compact organic fouling layer that was developed in the FO mode. Water flux in excess of 30 L/m^{2}h was reported in carbon-nanomaterials FO membranes, showing high water permeability of such membranes. In general, the incorporation of carbon nanoparticles in the fabrication of the FO membrane improved its performance and resistance to fouling. With the increasing requirements for potable water and the persistent need to decrease the cost of freshwater production, additional research efforts would be able to overcome the current issues experienced by the FO membrane. More laboratory and pilot plant experiments are essential to test new membrane designs that have the potential of providing freshwater at a lower cost.

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