Review Article

Preparation of Polymer Membranes by In Situ Interfacial Polymerization

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Membranes currently have a wide application in sewage treatment and water purification processes, in seawater desalination, and in various technological processes where high product purity is required. Deposition of an ultrathin skin layer of TFC (thin-film composite) and TFN (thin-film nanocomposite) onto the surface of membranes is discussed in this article. Their presence improves membrane properties such as retention of impurities and permeability. The aim of this paper is to present the current state of knowledge about the methods of preparing composite and nanocomposite membranes. The properties of the prepared TFC membranes can be modified by changing the type and concentration of the reacting monomers, and the physical conditions in which the membrane preparation process itself is carried out are also significant. Additionally, the properties of TFN membranes can be further modified with nanocomposites. The membranes are characterized by different properties not only because they have nanoparticles in their structure but also because their concentration and the way they are blended into the membrane structure were changed. This paper provides information on modifications of TFN membranes with nanoparticles, as well as modification by changes in polymerization reaction conditions and monomer concentration. Examples of the use of TFN and TFC membranes are also presented.

1. Introduction

Membranes are produced on a commercial scale for a wide range of applications including sewage treatment and water purification, seawater desalination, and various technological processes where high product purity is required. Most membranes are produced by the simple method of phase inversion. In this process, solvent and polymer solution are poured onto a flat surface to form a film of appropriate thickness, and then, a controlled process of exchanging solvent to a nonsolvent takes place and a solid, uniform membrane with a skin layer is formed. Membranes for microfiltration (MF) and ultrafiltration (UF) are most commonly produced with this phase inversion method. Both MF and UF processes are considered low-pressure processes since they operate at relatively low pressures that range from 0.1 to 1.0 MPa. Macromolecular impurities, such as emulsions, colloids, bacteria, proteins, and viruses, are removed through MF and UF. Due to various modifications, UF membranes can

also be used to remove organic micropollutants, which are usually removed by the use of high-pressure processes like nanofiltration (NF) and reverse osmosis (RO) [1–3]. These processes and also low-pressure membrane processes are shown in Figure 1.

Apart from phase inversion, another equally important method of membrane formation is in situ interfacial polymerization (IPIS). This method is used to form membranes on an industrial scale, mainly for NF and RO processes. NF and RO are high-pressure processes involving applied pressure ranges from 0.5 to 5.0 MPa. Substances including dyes, polyvalent ions, monovalent ions, and simple sugars are removed in NF and RO [1]. The first known application of the interfacial polymerization process was published in 1959 by Wittbecker and Morgan [4]. The process was called "interfacial polycondensation," and it was conducted between diamine and acidic monomer-containing chlorine atoms by the Schotten-Bauman reaction and was based on the work from 1946 [4]. For preparation of the first
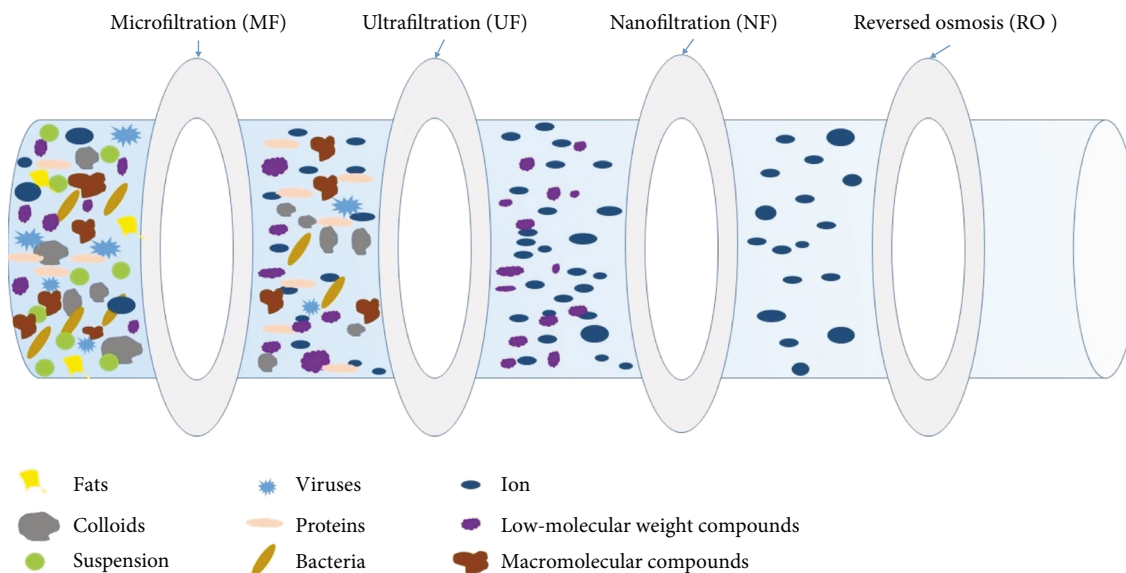
FIGURE 1: Separation in pressure membrane techniques depending on the size of the components [1–3].

thin-film composite membranes, this reaction was used by John Cadotte in 1985 for RO membrane preparation. This membrane showed 99% rejection of NaCl [5]. The next step for TFC membrane development was the use of nanocomposites for modification of these membranes. The first use of this technique was noted in the years 2005-2007 by Jeong et al. [6] and it used zeolite nanoparticles dispersed within a polyamide film.

Nowadays, a relatively new type of membrane process with the possibility of implementing TFC and TFN membranes is forward osmosis (FO) which occurs under the influence of the osmotic pressure of water. Over the last decade, this method has earned more attention. The first article applying this method was published in 2012. In FO, the osmotic pressure is the driving force that is created by the difference in concentrations between the solutions on both sides of the membrane. The process makes use of the so-called extraction solution, which consists of special dissolved substances. Water passes very slowly through the semipermeable membrane from the feed of lower pressure to the draw solution of higher pressure, which is gradually diluted [7–10].

Membranes formed by the IPIS method are referred to as TFC (thin-film composite) membranes, or in the case of membranes modified with nanoparticles, they are referred to as TFN or TFNC (thin-film nanocomposite) membranes. Additionally, most of the currently applied desalination plants in the world use nanofiltration or osmotic TFC membranes as the most significant part of the entire desalination process. They are also used for separation processes in food, pharmaceutical, and chemical industries [11, 12].

2. Thin-Film Composite Membranes

TFC membranes are essentially composed of two separate layers: a support layer prepared exactly like a classic membrane by means of phase inversion and an ultrathin skin layer. Each layer has a different structure and is composed of different polymers. The porous support provides the membrane with mechanical stability against cracking and tearing when operating at high pressures, whereas the ultrathin surface layer is directly involved in the rejection process. Compared to membranes produced by simple-phase inversion, TFC membranes allow high retention of substances in the feed while maintaining the highest possible flow rates [11]. TFC membranes are important in commercial applications of nanofiltration and reverse osmosis. TFC membranes also offer stabile at high pH (i.e., pH 5-13) and temperatures up to 70°C. Their widespread use is due to a higher retention of the feed components with a simultaneously increased permeate flux. Interestingly, there is a possibility of optimizing both the support and the skin layer independently of each other, depending on the desired effects. These properties make TFC membranes suitable for use in the removal of heavy metals, hardness, and micropollutants such as pesticides, endocrine disruptors, and pharmaceuticals from sewage water [9, 13].

2.1. Thin-Film Composite Membrane Manufacturing. An ultrathin layer of polymer is generally obtained by the method of forming a polyamide (PA) by polycondensation of two monomers, diamine and polyacyl chloride, on the surface of a porous support. These monomers should be dissolved in two immiscible liquids. One of them, with dissolved polyamine, should pretreat the support, and the reaction itself takes place at the interface [11, 14]. This process is schematically illustrated in Figure 2.

The support for composite membranes can be made of a variety of polymers, i.e., polyamides, polyethersulfone, polyurethanes, and even polyesters [15]. Poly(vinylidene fluoride) (PVDF), poly(vinyl alcohol) (PVA), polyacrylonitrile, or polytetrafluoroethylene (PTFE) can also be used [16]. In addition, the solvent that is used also affects membrane properties. The most commonly applied solvents are N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and
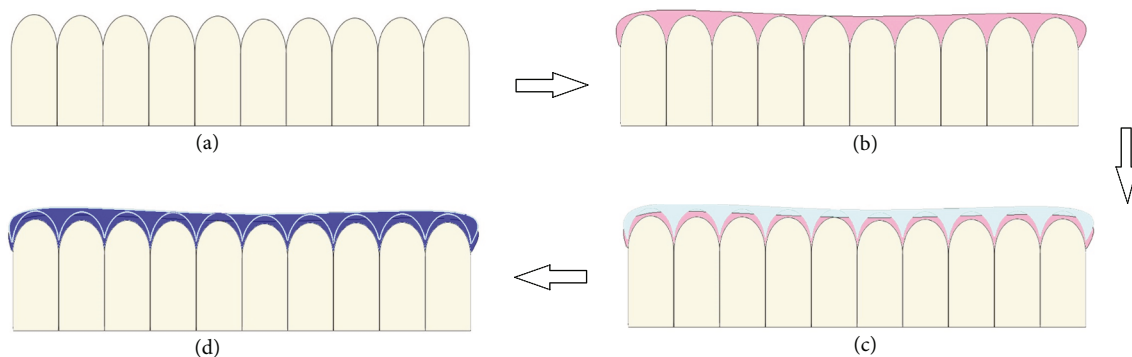
FIGURE 2: The process of in situ interfacial polymerization [11, 14]: (a) creation of a support layer by phase inversion; (b) distribution of diamine aqueous solution on the membrane surface; (c) distribution and mixing of polyacyl chloride dissolved in an organic solvent on the membrane surface; (d) polymerization reaction, formation of the polyamide skin layer.

N-methylpyrrolidone (NMP) [17]. However, the composition of the skin layer, i.e., the monomers that can be used during the in situ interfacial polymerization, is constantly being modified. The previously mentioned diamines are most commonly used—they are aliphatic or aromatic compounds and are reactive enough to form a layer of polyamide. Piperazine (PIP), m-phenylenediamine (MPD), and p-phenylenediamine (PPD) are used, among others, and they may react with acidic monomers containing chlorine atoms: polyacyl chloride (TMC), isophthaloyl chloride (IPC), and 5-isocyanatoisophthaloyl chloride (ICIC). Structural formulas of these substances are shown in Figure 3. The most commonly used reaction for commercial purposes is MPD/TMC, also shown in Figure 3, as it yields good results in seawater desalination [18].

2.2. Factors and Preparation Conditions Influencing TFC Membrane Properties

2.2.1. Effect of Support.
As it was mentioned in the previous chapter, the first step of TFC membrane fabrication is the preparation of a support by mixing a polymer and organic solvent and casting the prepared solution. The main polymer type with the widest application is polysulfone (PSf) due to its high thermal and chemical stability, glass transition temperature, and its good ability for forming membranes. The only limit of this material is its hydrophilicity [20]. Higher glass transition temperature, important for further curing of membrane, has also uncommon polymers like poly(phtalazione ether sulfone ketone) and poly(phthalazinone ether amide) [21]. Most works include the use of polysulfone. PSf support was used in the study of Ding et al. [22] with concentrations ranging from 11 to 19 wt.%. Values of water fluxes for support layers dropped significantly from 1750 to 0 $(L/m^{2*}h)$ with a decrease in PSf concentration. A less significant tendency was found for complete TFC membranes, i.e., from 40 to 10 $(L/m^{2*}h)$. This can be explained by the low porosity of the support structure with higher concentrations of polymer. Contrariwise, salt rejection increased when polymer concentration increased from 11 to 16 wt.% and a further increase in polymer concentration did not affect salt rejection. Zhang et al. [23] proved that the size and pore

density became more visible and distinct when polymer concentration in the support decreased from 20 wt.% to 12 wt.%. Moreover, supports with low porosity had less visible surface structures and lower thickness and had weak bonding to the active layer. Contrarily, membranes with higher porosity had more desirable properties.

Properties of thin-film membranes can be changed not only by use of different polymers but also by different organic solvents. Lu et al. [24] used dimethylformamide (DMF) and N-methyl-2-pyrrolidone (NMP) to prepare casting solutions. The DMF-prepared membrane had a larger pore size and higher surface area. This membrane also had a greater amount of area available for water permeation at the polysulfone-polyamide interface [24]. Importantly, the fouling tendency was higher for the DMF-prepared membranes due to the greater hydrophilicity of NMP-prepared membranes.

A dependence between the pore size of the support and the retention of salts by TFC membranes was very well presented by Huang and McCutcheon [25] for commercially used supports and by Sharabati [26] for laboratory-prepared membranes. Both reported that an increase in support pore size was highly connected with a decrease in salt rejection and an increase in permeation. The porosity of the membrane support can be also changed by addition of a porogenic substance like polyvinylpyrrolidone (PVP). This is a water-soluble polymer and has excellent wetting properties in solutions This additive caused an increase in the hydrophilicity of membranes, rejection of NaCl, and an overall increase in porosity by a having a larger number of pores with a smaller size. This substance is widely recommended for modification of support. PVP is nontoxic and it can be used in processes for drinking water [22, 27].

2.2.2. Effect of the Monomer Type.
For TFC membranes, an important factor is the selection of proper monomers. In the research paper written by Li et al. [28], PES was used as a support. The membrane obtained was submerged in an aqueous solution of one of the amines—diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA), or PIP—at a concentration of 0.2% by weight and left for 10 minutes. Excess solution was removed with
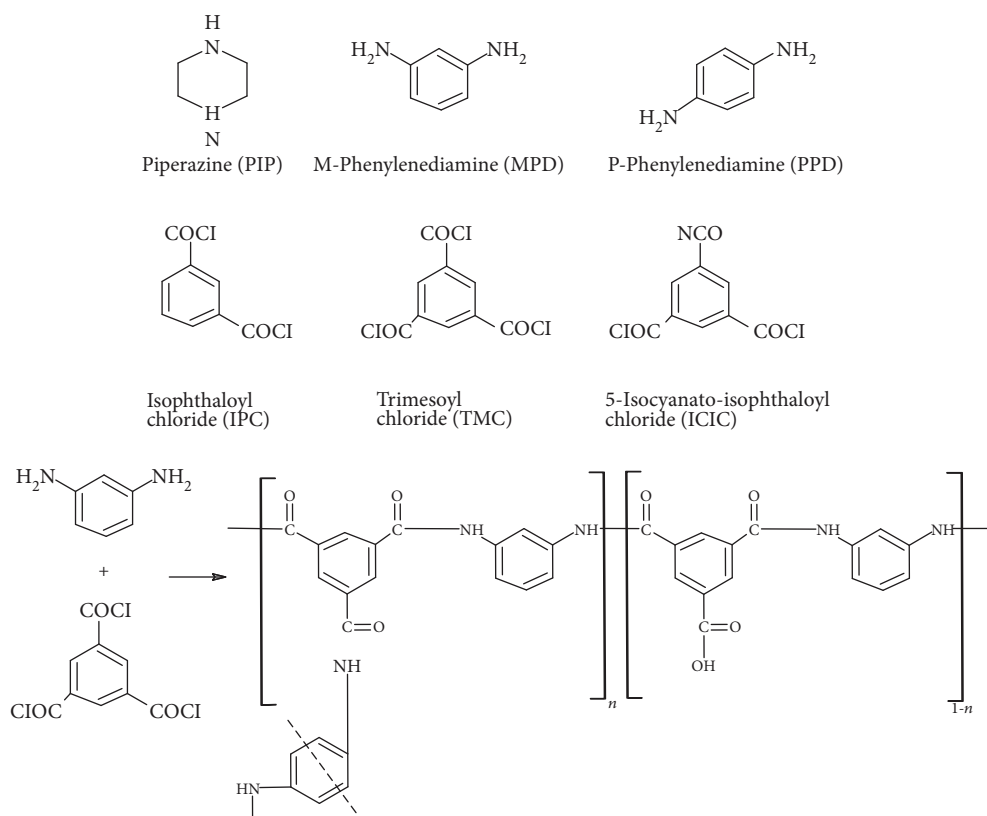
Figure 3: The examples of substances commonly used in the in situ interfacial polymerization process. PIP, MPD, and PPD are dissolved usually in deionised water and IPC, TMC, and ICIC in organic solvent like hexane. Beneth presented typical reaction between MPD and TMC [18, 19].

tissue paper. Then, a 0.2%-by-weight TMC solution in hexane was slowly poured onto the membrane for two minutes to fully cover its surface and it was left in place for 30 minutes to allow the hexane to evaporate and the skin layer to reach the desired stability. The membrane was then stored in deionized water until it was used. The membrane thus obtained had osmotic properties. Depending on the polymer used, different membrane properties were obtained. First of all, the contact angle values were significantly different. While the DETA/TMC membrane had almost the same contact angle as the unmodified pristine PES membrane (66°), the use of TEPA or PIP produced membranes that were hydrophilic. This positively affected permeate flux, which was directly dependent on the hydrophilicity of the membrane. The second parameter that was subjected to change was the value of the zeta potential. The name zeta potential represents the electrostatic charge of a membrane, which is associated with the presence of functional groups on its surface and is dependent on the pH value of the feed. Its value refers to the membrane's ability to repulse or attract positively or negatively charged substances present in the feed solution. In a study already mentioned [28], a strong negative charge was caused by the deprotonation of carboxyl groups from the hydrolysis of acyl chloride from TMC; however, it may be compensated by the protonation of amine groups from the same reaction. Although both hydrophilicity and the zeta potential of the membrane played a significant role

in the separation of contaminants, each membrane has achieved the level of selected salt removal at over 80% (one ionic and two ionic). Permeate flux recovery ranged from 87% to 100%, depending on the selected monomer. The TFC membrane with PIP had the best properties both in terms of permeability and rejection [28, 29]. The highest flux of this membrane was related to its contact angle. Generally, membranes with high contact angle have hydrophobic properties that limit water permeation, and thus, a lower water flux is observed. But along with reduction of the contact angle, the hydrophilicity of membranes increases and their permeability is raised. Details regarding the membranes discussed above are given in Table 1.

Similar tests were also reported by Saha and Joshi [30] but with other types of monomers. In addition to piperazine and MPD, n-2-diaminethylpiperazine (AEPIP) and 3,5-diaminobenzoic acid (BA) were used. These monomers react with TMC and isophthaloyl chloride IPC. This undertaking did not yield very good results. However, interesting correlations were observed based on differences in the concentration of monomers. Namely, it was observed that an increase in PIP concentration from 0.5 to 5% by weight in relation to TMC caused an increase in NaCl retention from less than 10% to about 70% and MgSO$_4$ from about 25% to almost 100% retention with a slight decrease in the value of the permeate flux. A similar relationship was found for MPD-TMC membranes, where both NaCl retention and

Table 1: Parameters of the membranes formed, depending on the monomer used [17].

Membrane name	Contact angle (°)	Zeta potential (mV)	Permeability (dm ^{3}/m²h*MPa)
DETA/TMC	64.5 ± 0.5	-13.7 ± 0.4	33.5 ± 2
TETA/TMC	47	-18.9 ± 0.6	43.5 ± 3
TEPA/TMC	35.4 ± 2.2	-17.7 ± 0.5	51 ± 4.5
PIP/TMC	39.6 ± 1.6	-24.4 ± 0.8	75 ± 6

Table 2: Parameters of the membranes formed, depending on the organic solvent [5].

Membrane symbol	Heptane temperature (°C)	Contact angle (°)	Flux (LMH)	NaCl retention (%)
TFC-1	-20	53.3 ± 1.2	92.1	94.8
TFC-2	1	56.9 ± 1.1	51	97
TFC-3	25	81.2 ± 1.6	10.7	98.8
TFC-4	50	66.2 ± 1	27.9	99.1

the flux increased with an increase in the MPD monomer concentration from 0.5% to 2% by weight. Sodium chloride retention was reported to increase from 75% to more than 90%. On the basis of the presented experiments, it can be concluded that TMC is characterized by more favourable properties than IPC, as it increased the hydrophilic properties of the skin layer. On the other hand, the use of AEPIP resulted in a significant decrease in the permeate flux [30].

2.2.3. Effect of Reaction Parameters. It has already been mentioned that the properties of composite membranes are also influenced by the conditions in which the processing is conducted. In a research undertaken by Khorshidi et al. [11], TFC membranes were prepared using PES as a support and MPD and TMC reactions were used to make the skin layer. Four membranes were made at four different temperatures of organic solvent: −20°C, 1°C, 25°C, and 50°C. At the temperature of 25°C, a membrane surface topography with classic "hills and valleys" was obtained. At elevated organic solvent temperatures, the skin layer of the membrane reached a greater thickness, as opposed to the membranes formed at −20 and 1°C, which had the smoothest surface and the thinnest layer on the PES membrane support. A higher temperature of skin formation caused the MPD/TMC polymerization reaction to be faster, whereas at lower temperatures, an opposite phenomenon was observed. Changes in the value of the contact angle were mainly related to different morphologies of these membranes. The membranes prepared at room temperature were characterized by the highest hydrophobicity, whereas the membranes formed at lower and higher temperatures were much more hydrophilic. The permeate flux was also temperature dependent. For TFC-1 and TFC-2, a lower temperature of acid chloride solution meant lower thickness of the membrane and thus higher permeability. At a temperature higher than room temperature, the permeate flux increased due to a larger and more extended surface which made the surface of contact between water molecules and the membrane surface larger [11]. Detailed parameters of these membranes have been demonstrated in Table 2.

2.2.4. Permeability and Selectivity. However, the most important preparation factors for permeability and selectivity of TFC membranes, according to Mah et al. [31], are the concentrations of both monomers, reaction time, presence, and time of curing membrane. Interestingly, the pH of the aqueous solution during the preparation process had no influence on increasing the permeability of the membrane. However, a slight increase in membrane permeation was observed when the first monomer concentration was increased and the reaction time in the interphase was reduced. From other works [32–34], an increase in the concentration of MPD and TMC in solutions caused an increase in selectivity with a decrease in permeability. High MPD concentrations can produce a dense and thick PA layer by promoting the IP reaction. The effect of this is reduction of water permeation and promotion of high salt rejection. The influence of higher TMC concentration is also connected with a higher amount of TMC that participates in the polymerization reaction [32]. Opposite results for TMC, achieved by Khorshidi et al. [34], were explained by a complicated influence of the polyamide thin-film thickness and density on the properties of membranes.

The dependence between TMC concentration and permeability and selectivity, appropriate for low concentrations of monomers, is shown in the flow chart (Figure 4). Generally, lower flux and higher selectivity of TFC membranes are directly connected with reduction of pore size and overall membrane thickness. This is a result of more cross-linking occurring between monomers during formation of the thin film. The hydrophilicity of a membrane depends on the functional groups attached to its surface. The presence of amino groups changes the hydrophilicity of membranes depending on pH [31]. The most significant influence on membrane permeability was curing temperature and time. Tests conducted by Mah et al. [35] showed that longer exposure to curing caused the top layer to become denser which decreased the flux of pure water and promoted the rejection of salt. The minimum time of hexane evaporation from the TFC membrane (during curing) was 5 minutes. Fifteen minutes of curing was needed to enhance the selectivity of a membrane [31]. Khorshidi et al. [34] found that increasing the curing temperature improved flux and rejection but temperatures higher than 75°C lowered the flux. A decrease in curing temperature resulted in thinner membranes and higher permeation. This factor contributed 40.7% to the impact on the water permeation. MPD and TMC concentration exerted a lower effect, around 28% of contribution. Changes in reaction time between MPD and TMC had the least influence on water permeation—less than 2% [34]. However, all mentioned factors influenced the porosity of membranes, including the properties of support used. A decrease in concentration of the first monomer caused an increase in pore size. A similar effect was caused by a reduction in the time of soaking and immersion in both

TFC membrane preparation

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Soaking of membrane in 1. monomer aqueus solution

Time extension:

Decrease:	Increase:
(i) Permeability (ii) Pore size (iii) Hydrophhilicity	(i) Thickness (ii) Selectivity

Time reduction:

Decrease:	Increase:
(i) Thickness (ii) Selectivity	(i) Permeability (ii) Selectivity

Concentration increase:

Decrease:	Increase:
(i) Permeability (ii) Pore size (iii) Thickness	(i) Selectivity

Concentration decrease:

Decrease:	Increase:
(i) Hydrophhilicity (ii) Selectivity	(i) Permeability (ii) Pore size (iii) Thickness

↓

Immersion of membrane in 2. monomer organic solution

Time extension:

Decrease:	Increase:
(i) Permeability (ii) Pore size (iii) Hydrophhilicity	(i) Thickness (ii) Selectivity

Time reduction:

Decrease:	Increase:
(i) Selectivity (ii) Thickness	(i) Permeability (ii) Pore size

Concentration increase:

Decrease:	Increase:
(i) Permeability	(i) Thickness (ii) Selectivity

Concentration decrease:

Decrease:	Increase:
(i) Selectivity (ii) Thickness (iii) Pore size	(i) Permeability

↓

Curing process Yes/no

Yes:

Decrease:	Increase:
(i) Permeability	(i) Selectivity

No:

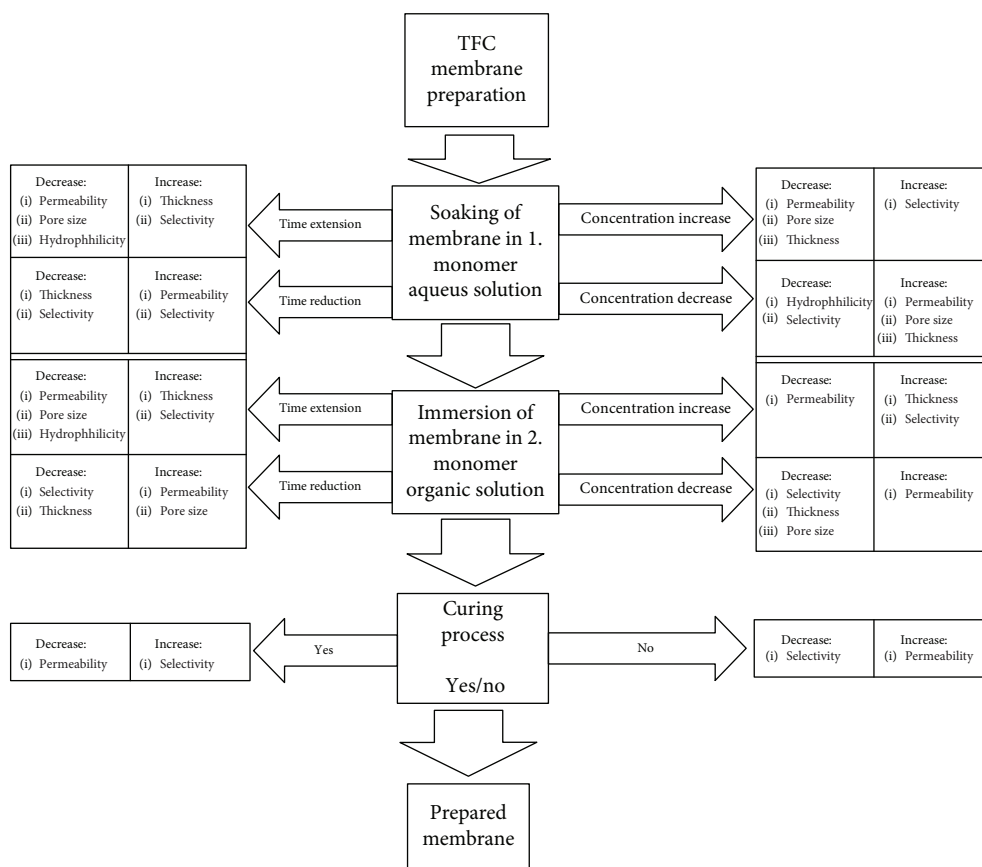| Decrease:	Increase:
(i) Selectivity	(i) Permeability

↓

Prepared membrane

FIGURE 4: Flow chart of preparation of TFC membranes with general influence of the most important factors: time of reaction/process, concentration of monomers, and curing temperature. First and second monomer concentrations were in ranges 1-4 wt.% and 0.1-0.2 wt.%, respectively [31–34].

monomers. A decrease in TMC concentration may cause the pore size to decrease. The porosity of TFC membranes mostly depends on the porosity and pore size of the supports. Thin-film membrane properties are also affected by the addition of nanocomposites.

3. Thin-Film Nanocomposite Membranes

For TFN membranes, the "nano" prefix is the key aspect. It indicates the presence of a filler in the form of nanoparticles, nanotubes, or nanosheets. This addition is used to enhance the properties of the membranes. The specific features of the TFN membrane area significantly increase permeate flux combined with better separation properties, and an energy cost reduction is associated with the operation of these membranes. These are new types of membranes formed by means of the process of in situ interfacial polymerization. The first membrane of this kind appeared in 2007, when the first publications on the subject were published [10]. In 2010, the first desalination plant to use such membranes appeared. As in the case of TFC membranes, most applications are related to nanofiltration or reverse osmosis but they are increasingly being used in low-pressure processes such as UF and MF [10].

The preparation of TFN membranes is almost identical to that of TFC membranes. The only change in the membrane preparation process is the addition of a nanomodifier. The TFN membrane is made up of a thin skin layer of up to 500 nm thick which is placed on a much thicker support made with a method other than the skin layer, usually by means of phase inversion. Nanoparticles can be placed within the membrane structure in two ways: by adding them to the support layer to change the membrane characteristics or by adding them to the selective skin layer to improve roughness, selectivity and, above all, permeability [13]. Additionally, nanocomposites can also be added to the thin selective layer also in two ways. Namely, the nanoparticles can be placed on the TFN membrane either together with an aqueous solution or with an organic solvent solution. It is much more common to place the nanocomposite together with the TMC solution in hexane. This is mainly due to better results achieved from these types of membranes [36]. Figure 5 demonstrates the basic types of nanocomposite membranes.

3.1. Modification of TFN Membranes. Nanomaterials in TFN membranes belong to one of four basic groups. They can be classified as dimensionless hydrophilic metals or metal oxides, one-dimensional carbon materials such as nanotubes, two-dimensional materials such as graphene or graphene oxides, or also three-dimensional porous materials such as nanozeolites [37]. The types of the most common
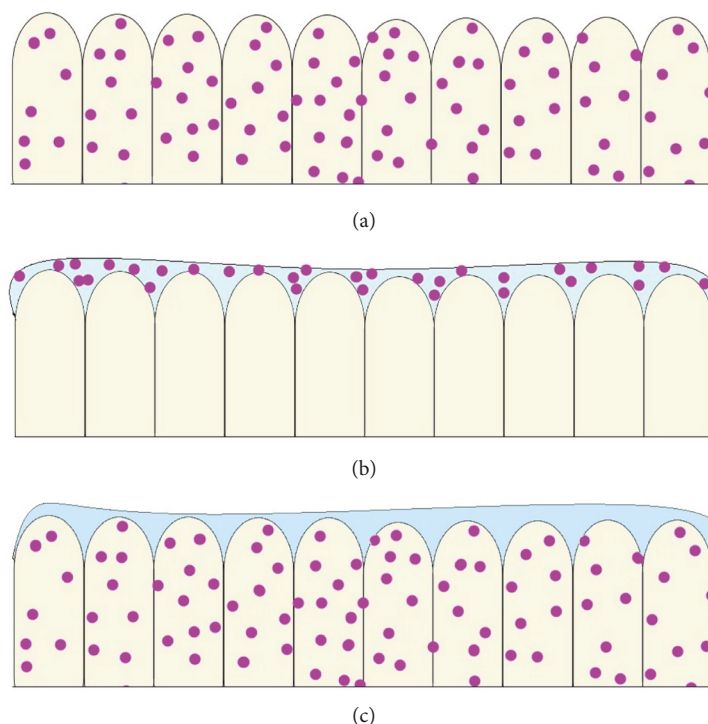
(a)

(b)

(c)

FIGURE 5: Types of membranes with nanoparticles added [13]: (a) typical nanocomposite membrane; (b) TFN membrane with nanoparticles in the skin layer; (c) TFN membrane with nanoparticles in the support.

nanoadditives are listed in Table 3. As mentioned before, these ingredients can be added together with an aqueous amine solution or in an organic solvent, together with TMC. Besides, they can also be placed in the support of the membrane [13].

The variety of nanoparticles provides numerous sizes and shapes. They occur in the form of crystals (cellulose), tubes (carbon nanotubes, halloysite nanotubes), ribbons, platelets, dots, and sheets (graphene). Their size is in the range of a few nanometers to dozens of micrometers Another important factor is the spontaneous and preferential aggregation of many of them which causes their useful size to be multiplied. As was already mentioned, filler-polymer interface greatly affects the overall TFN properties. Therefore, both the size and shape the nanoadditives play an important role in their fabrication. For example, Alberto et al. [40] found that the size of GO flakes affects the porosity of the membrane structure. Micrometer-sized flakes of GO generated large and nonselective voids between polymer and graphene, while smaller flakes were aligned with polymer blocks [40]. Another aspect is the shape of nanofillers. Halloysite nanotubes tended to egress from polymer matrices, leaving a hollow space inside the composite [41]. Chong et al. compared the topography and thickness of two TFN membranes modified with (1) titanium oxide and (2) titanate nanotube. Titanate nanotubes, due to their long length, preferred to lay horizontally on the surface, simultaneously creating a slightly lower membrane thickness than TFN with titanium oxide [42]. On the contrary, Karkooti et al. [43] demonstrated no effect of different shapes (sheet, platelet, or ribbon) of graphene oxide on TFN cross-section morphology. As they observed, all membranes had an asymmetric structure with a dense top layer and a porous finger-like support [43].

The most common types of carbon nanomaterials used in the preparation of nanocomposite membranes include carbon nanotubes (CNTs), graphene, graphene oxide (GO), MXenes (two-dimensional inorganic compounds made up of carbides but also nitrides or metal cyanides), and carbon materials obtained from carbides and fullerenes. Due to their unique physical properties, such as high thermal, chemical, and mechanical durability, high conductivity, good optical properties and low density, these compounds are widely used in material engineering and chemistry. However, the most popular nanoadditives are carbon nanotubes (CNTs), which we have mentioned before. Their wide application is due to their exceptional mechanical, electrical, and thermal properties. Their main advantage is wide chemical modifiability, as well as their large area in relation to the dimensions of the nanotube itself [17, 44]. A membrane with the addition of nanotubes can be as durable as a ceramic membrane, while retaining the flexibility of the polymer. Their special feature is the ability to modify the physicochemical properties of the membrane itself. Modification of membranes with hydrophilic particles increases the affinity of their surface to water, increasing permeability. The inner nanotube pores act as selective nanopores, which makes the modified membrane much more permeable than the unmodified membrane. However, the main disadvantage of nanotube use is their tendency to agglomerate. Besides, some carbon nanomaterials, e.g., CNTs, GO, and graphene, also have specific properties, and when incorporated into the membrane, they inhibit the growth of bacteria that is in direct contact with

TABLE 3: Division of nanoparticles used in the preparation of nanocomposite membranes [18, 20, 38, 39].

Particle shapes	Particle types	Description and examples
Dimensionless	Metals	Metals and metal oxides: silver, titanium, zirconium, iron, gold, and others
One dimensional	Carbon nanotubes (CNTs)	Single walled (SWCNTs), multiwalled (MWCNTs), and modified with carboxyl (-COOH), amine, amide, and hydroxyl (-OH) residues
	Carbon nanofibers (CNFs)	Available in bundles and modifiable as CNTs
	Cellulose nanofibers (CNF)	Contains a lot of hydroxyl groups on the surface; possibility of modification similar to CNTs
	Cellulose nanocrystals (CNC)	Similar properties as CNF
Two dimensional	Graphene	In the form of hexagonal nanosheets
	Graphene oxide (GO)	Like graphene, with oxygen and hydrogen atoms attached to carbon atoms
	MXenes	A substance consisting of several layers of metal carbides or carbon nitrides; they have different conductivity and hydrophilicity depending on their composition
Two dimensional and three dimensional	Nanozeolites	A group of hydrated clay minerals whose composition includes silicon, aluminium, magnesium hydroxides, and metal ions; this group also includes synthetic materials; natural: montmorillonite and halloysite; synthetic: MCM-41
Three dimensional	Fullerenes	Spherical allotropic form of carbon consisting of graphene platelets; fullerenes were components of the first nanocomposite membranes
	Metal organic frameworks (MOFs)	Nanoporous materials composed of inorganic subunits of metal ions and polytropic organic ligands

the surface of the membrane. This may have a positive effect on the reduction of fouling. Moreover, graphene-modified membranes have the same durability as those with CNT addition but they are much more flexible, whereas the addition of carbon nanotubes makes them bactericidal—according to research, 61% of bacteria were killed in one hour [45, 46].

The presence of nanoparticles in the membrane structure results in the membrane having better properties, most notably making it much more permeable. For example, in tests conducted by Mahmood et al. [47], brackish water from a river mouth was filtered with TFC and TFN membranes with the addition of multiwalled carbon nanotubes at a concentration of 0.4% by weight. These were placed in the support of the membrane, and the MCM-41 substance (made of synthetic aluminosilicates of a special structure) was placed in the skin layer at the concentration of 0.05% by weight. The result of these studies [47] was to obtain an almost identical level of retention of salts for both membranes (about 93.7%) with a much higher permeate flux for the TFN membrane by about 54.85% in comparison to the TFC membrane. This increase in permeability was obtained thanks to the formation of macrochannels in the support layer and the strong antifouling properties of the nanocomposite membranes [47].

Membrane porosity depends mostly on the support structure and the kind of modifier on its surface. Adamczak et al. [48] prepared UF membranes with PES support and modified them with single-walled carbon nanotubes. The presence of nanotubes caused the decrease in porosity. In these tests, porosity of the pristine support was around 70-75%, while membranes containing nanotubes had porosity at around 30-50%, dependent on nanotube location in TFN membranes: in the support or the in thin film. In the Emadzadeh et al. [49]

study, the overall porosity of membranes increased as the TiO_2 loading in the support increased; however, the average pore size decreased. Importantly, the water flux increased with increasing TiO_2 concentration. The membrane prepared from the PSf substrate bound with 0.5 wt.% TiO_2 has shown the best performance for the water desalination process. However, according to Dalvi et al. [50], in tests with polyhedral oligomeric silsesquioxane TiO_2-SiO_2, nanoparticles, regardless of size and shape, can cause formation of defects in the polyamide layer. The defects appeared more often with larger size and higher concentrations of nanoparticles. In this test, they lowered rejection of salts.

A membrane was formed with the use of graphene for the purpose of the Yin et al. study [51]. It was made in the same way as reported by Mahmood et al. [47] where graphene was added to the TMC solution. The presence of graphene allowed the membrane to maintain a similar retention value of Na_2SO_4 and NaCl salts at the level of 93-98% with a significant increase of the permeate flux from about 39 LMH to over 59 LMH at the concentration of 0.015% of GO. Similarly, with an increase in the concentration of nanosheets, there were slight fluctuations in the increased value of the membrane's contact angle, between 62° and 68°, indicating an increase in hydrophilicity and a decrease in the average roughness of the membrane from approximately 60 nm to approximately 40 nm. The most important aspect of this undertaking was to maintain retention with increased permeability through the introduction of nanoparticles [51].

Such tests, related to the method of introducing nanocomposites, were conducted in the work of Huang et al. [36]. Three membranes based on a PS membrane were formed with a skin layer based on MPD and TMC reactions with zeolite nanoparticles: one with NaA added in the

aqueous phase, a second with hexane solution added during the phase, and a third with no nanoparticles added. In the test, a NaCl salt solution was filtered through membranes at a pressure of 1.6 MPa. It was demonstrated that the permeate flux increased with an increase of nanoparticle concentration (for concentrations from 0% to 0.2% by weight), while the degree of retention slightly decreased. This was explained by the presence of defects in the membrane structure, which allowed cations and anions to permeate and pass through the membrane. Salt retention on the NaA membrane in organic solvent solution was higher than that on the NaA membrane in water and was therefore considered to be more beneficial for particle dispersion on TFN membranes [36].

Less commonly, aluminosilicates, which are also known as halloysites, are used as nanocomposites. They are used in the shape of nanotubes (HNTs) and are extracted and formed from natural deposits of this substance. This substance has unique properties. The outer layer is negatively charged due to the presence of siloxane groups (Si-O-Si), while the inside of the nanotubes is filled with positively charged hydroxyl groups (Al-OH). Moreover, unlike carbon nanotubes, they do not have a tendency to agglomerate. Nowadays, they are increasingly used in research works. Also, their production cost is lower than CNTs [52]. The most recent aspect related to the addition of nanoparticles is the use of a new type of compound, the so-called metal organic frameworks (MOFs). These are new-class nanoporous materials that are composed of inorganic subunits of metal ions and polytropic organic ligands. The presence of the organic fragments makes the substance more compatible with the polymer that the membrane is composed of. Furthermore, these nanomaterials can be freely modified on account of the presence of free bonds that can be supplemented with functional groups. The presence of the alkyl chains reduces nanoparticle aggregation. A study conducted by Guo et al. [53], where nanoparticles were added to the TMC solution in hexane, confirmed the desired effect of this type of nanomaterial. The material maintained almost 100% tetracycline retention, and nearly 30% higher membrane permeability was achieved compared to the unmodified membrane [53].

A quite new aspect of membrane modification by nanocomposite is the application of nanofibers or nanocrystals of cellulose (CNFs or CNC). These fillers are reminiscent of carbon nanotubes and nanofibers, but cellulose materials are hydrophilic, naturally occurring in the environment, and they are a renewable resource. Similar to CNTs, they can be functionalized by adding functional groups, such as carboxyl groups (carboxycellulose nanofibers), on their surface. Nanofibers or nanocrystals may be extracted from cellulose, but this requires large energy consumption, and their processing uses a large amount of acid [38, 54]. Extraction of these nanofillers may be conducted from jute fibers, bamboo cellulose, or grass [8]. The use of these products from cellulose in membrane preparation is gaining more and more attention each year. For example, Asempour et al. [55] used CNC in a TFN membrane for RO application. Embedded nanocrystals improved antifouling properties, lowered the contact angle to 20°, and doubled water flux with only a slight

decrease in salt rejection. Bai et al. [56] used CNC on the PES substrate and improved the removal of cationic and anionic dyes from around 96-97% to 99.83-99.9%. In the same work, the addition of CNC on the membrane surface caused a slight decrease in NaCl and $MgSO_4$ retention and a significant increase in water permeability. They also found that the contact angles of the pristine substrate and unmodified TFC were 66.5° and 59.2°, respectively, and CNC addition resulted in a decrease of the contact angle to 37.5°. For TFN membranes with cellulose nanofibers, Carpenter et al. [38] provide data about an improvement of the mechanical strength of membranes filled with CNF. Similar to CNC, membranes with CNF are characterized by an increase in water permeability and hydrophilicity with constant contaminant removal.

4. Advantages and Disadvantages of TFC/TFN Membranes

The main advantages of thin-film membranes produced in the form of TFC are related to their good separation performance and wide pH tolerance range. However, composite membranes with polyamide films are not free from limits. Typical disadvantages of unmodified polyamide films are the relatively low water flux, poor antifouling property, and low resistance to exposure to oxidizing agents such as chlorine [57, 58]. There are several mechanisms that have an effect on polyamide films that are described by Verbeke et al. [59], but the effects are inconsistent. This may also be a result of a tightening or swelling effect. In some cases, the PA layer may dissolve or separate from the support. In some cases, reaction of chlorine with the PA top layer enhances the hydrophobicity of the membrane simultaneously with water flux reduction [59]. Another limiting aspect of TFC is the low stability of PA films in acidic pH. In this environment (pH < 5), the carbonyl groups of amide linkages in the PA chains are attacked [60]. The degradation of PA chains with partial hydrolyzation of amide groups by the H^+ or OH^- causes a reduction in the degree of cross-linking. This increases membrane hydrophilicity and at the same results in larger permeability and lower selectivity [61]. In Rezania et al. [62], filtration of solution of Na_2SO_4 conducted at pH 3 caused a decrease in rejection from 91.1% in pH 7 to 81.3%, and at pH 5, rejection decreased to 88.2%. To restrain this effect and also degradation by chlorine, nanocomposites are placed on the surface of the membrane [59].

Thin-film nanocomposite membranes have many advantages in comparison to TFC membranes such as higher water flux and better bacterial resistance without a significant reduction in salt rejection. This is due to the small particles changing the membrane performance. The presence of nanocomposites may improve surface properties of membranes such as hydrophilicity/hydrophobicity, porosity, zeta potential, and antibacterial properties [63, 64]. For example, Bano et al. [65] compared the influence of TFC and TFN properties on water flux and salt retention. They proved that addition of graphene oxide improves hydrophilicity, zeta potential, and roughness while simultaneously maintaining the same level of salt retention.

The major obstacles for the commercialization of the TFN membranes are high production cost, leaching out of toxic nanoparticles into the permeate and retentate, and low interaction between nanoparticles and polyamide thin films [55]. Leached nanoparticles may be toxic for the user and the environment. Elimination of this threat may be done in two ways: (1) by preventing the leaching out of the nanoparticles or (2) by using biocompatible nanoparticles [55]. For example, silver nanoparticles, taken orally, are distributed to all the organs and attack primarily the liver and intestinal tract [66]. Leaching of silver nanoparticles (AgNPs) was firstly proved and then limited by Yin et al. [67]. In a batch test, they measured that within 14 days, 12% of the total amount of AgNPs was leached from the membrane. In a flow test, leaching of silver was reduced to 3.5% by using cysteamine as a bridging agent. In a work presented by Wan et al. [68], ferrum/platinum nanoparticles were integrated into a membrane by functionalization with poly(acrylic acid). Another way to bypass the danger of nanoparticle release is by the use of nontoxic materials. An example of such a substance is cellulose nanocrystal that is obtained from acid hydrolysis of native cellulose [55]. The only limitation is the application of TFN membranes in acidic conditions. Some nanoparticles like aluminium-rich zeolites may be less structurally stable in low-pH conditions (pH of less than 2) particularly in the presence of phosphate (pH of less then 5) [69]. However, by overcoming these obstacles, both nanocomposite-free and modified membranes are being used more and more frequently in manufacturing and technological processes.

5. Application of TFC/TFN Membranes

TFC/TFN membranes have a great potential for water treatment. Due to their high-permeability and selectivity, good durability, and antifouling properties, they dominate over conventional polymer membranes. These membranes are mainly used in high-pressure membrane processes (i.e., nanofiltration and reverse osmosis for desalination of seawater). However, some cases of their use for micropollutants and organic matter removal have been also reported. Karkooti et al. [43] proved that a TFN membrane modified with 0.1 wt.% graphene nanoribbons had excellent properties in terms of both water flux and organic matter removal [43]. In the Bojnourd [70] study, the concentration of cephalexin was reduced by 98.8% by using a TFN membrane with 0.4 wt.% of modified montmorillonite [70].

While TFC membranes are widely employed in desalination plants and in the food industry, the use of TFN membranes on an industrial scale is negligible. The high production cost and the potential threats connected with nanoparticle release are obstacles to wider use. On the other hand, many studies have shown that TFN membranes are more effective than TFC membranes, especially in terms of the removal of toxic pesticides, arsenic salts, proteins, hormones, and micropollutants from wastewater (e.g., in the pharmaceutical industry) [49, 69, 71]. Moreover, in comparison to other sewage treatment technologies,

such as biological methods, TFN results in a better quality of treated sewage at lower operating costs. Additionally, TFN membranes are used in laboratories to obtain high purity products [71].

Currently, TFC membranes made of polyamide and cellulose acetate are most commonly used for water desalination. They take part in both RO and FO processes. TFN membranes are also commercially available. One example is the RO TFN membrane modified with zeolite nanoparticles (100 nm in diameter) that is intended for seawater desalination. This has been available since August 2010. Its efficiency is approximately 10-20% higher than that of the classic RO membrane with a similar reduction in energy consumption. This type of membrane has been successfully installed on the island of Curacao for the purpose of seawater desalination [72, 73]. A similar cost reduction related to energy expenditure was observed in the processes of reverse osmosis with a TFN membrane [74].

6. Conclusions

Despite having many unquestionable advantages for both TFN and TFC membranes, there are still many challenges that modern science must face. The main problem is a poor dispersion of nanocomposites in inorganic solvents and, consequently, their agglomeration in the membrane structure. Surface modification of nanoparticles partially solves this problem, but it cannot eliminate this phenomenon completely [10]. Moreover, a problem of secondary contamination from nanoparticles leaching from membranes should be solved.

Compared to TFC membranes, TFN membranes have a higher potential for further development both in terms of eliminating fouling and increasing permeability while maintaining a high level of retention. Yet, another difference between these two membrane types is the higher production price of TFN membranes. However, the use of TFC/TFN membranes increases productivity and thus results in lower operating costs [74].

However, it should be remembered that no universal membrane exists that would be able to work with any kind of feed material. Moreover, the membrane manufacturing process needs to be optimized, depending on the needs, both on a laboratory scale and an industrial scale.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

Acknowledgments

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