Chapter

Electrospun Nanofibrous Membranes for Water Treatment

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Abstract

Nanofibrous structures offer a lot of fascinating features due to large specific surface area. This makes them promising for a wide range of applications, most specifically water treatment. This new generation of highly porous membranes exhibits great prospect to be used in various separation applications due to their distinguished features such as remarkably high porosity (≥90%) and interconnected 3D pore structure. As compared with the conventional techniques, *Electrospinning* has been highlighted for developing unique porous membranes. Electrospun nanofibrous membranes have been more and more investigated to a lot of advanced water treatment purposes. This chapter reviews the updates on electrospun nanofibrous membranes with a particular prominence in recent accomplishments, bottlenecks, and future perspectives in water treatment. To start, the basic principles of electrospinning are discussed. Next, past and recent efforts for fabricating electrospun MF membranes for various applications are reviewed. The application of electrospun nanofibers as the scaffold for TFC (thin-film composite) membranes in the pressure- and osmotic-membrane processes is then introduced. The new application of electrospun nanofibrous membranes for the thermally-driven MD (membrane distillation) process for water treatment as well as strategies for performance enhancement is discussed. To finish, conclusions and perspectives are stated according to recent developments.

Keywords: nanofibers, electrospinning, membrane separation, water treatment, MF/UF/NF/FO, membrane distillation, MD

1. Introduction

Today, the world is facing many serious challenges among which the shortage of clean and drinkable water is highlighted [1]. Worldwide surveys indicated that roughly 1.2 billion people have insufficient availability to clean water, 2.6 billion have very limited or no cleanliness, and millions of people pass away every year because of the polluted water resources or other water-related challenges [2]. With the world population increase and environmental degradation, the undersupply of a fresh water production adds up to a serious alarm to the present status of the global water resources, specifically in the arid regions such as Africa and the Middle East. Water-related challenges are expected to grow worse very fast in the coming years with increasing population and consequently increasing industrialization. All these

concerns highlight the need for excessive investigation of promising strategies for beneficial water treatment with reasonable energy consumption and cost [3].

Recently, the role of nanotechnology in developing the new generation of water treatment technologies has become more hopeful. For instance, engineered nanomaterials are playing more impressive role in drinking water production through the seawater desalination, water recycling, and wastewater treatment [3–5]. Nanotechnology can provide a predominant perspective with regard to availability, sustainability, and long-term water quality. The extension of recently developed membranes, most specifically nanoengineered ones including reverse osmosis (RO) and nanofiltration (NF), has been required for water treatment [6]. RO technology can provide considerably high rejection for ions and contaminants. The NF membrane has been employed as a new separation barrier for providing higher permeate flux with lower operating pressure. The colloids and macromolecules can be eliminated by ultrafiltration (UF) membranes (pore size range: 2–100 nm) [7–9]. On the other hand, microfiltration (MF) is the most mature membrane-based liquid filtration process. It has been used for several years to eliminate the microparticles or biological entities. MF uses low operating pressures that make it an attractive separating technique for particles removal. MF membranes typically have pore diameter in the range of 0.1–10 μm [10, 11].

In case of water treatment, the NF membranes are more affordable compared to the RO membranes. They can efficiently remove different minerals and salts, multivalent ions and cations, as well as pathogens (such as fungus, molds, virus, and bacteria) existing in groundwater and surface sources [12]. Besides the aforementioned advantages, these conventional membrane processes have a number of bottlenecks. Among the major challenges, osmotic pressure limitation, fouling and scaling, and limited porosity (≤80%) are a number of highlighted bottlenecks of conventional membranes. This can be pointed out that these weak points go back to the fabrication methods used for the conventional membranes. **Table 1** summarizes the conventional methods for different membrane fabrications. The phase inversion method is mostly practical for MF and UF membranes. This is a widely used fabrication method for porous membranes. However, there are two important challenges attributed to this method including limited affordable pore size range and contamination by the residual solvent. The interfacial polymerization method is the only fabrication technique in the commercial scale for NF membranes. Using this technique, the thickness of the top selective layer can be controlled but not in a favorable way. Both stretching and track-etching methods are practical for MF membranes, which can be also used in the membrane distillation (MD) process. A wide range of pore sizes and pore size distributions can be achieved. However, the obtained membranes via stretching and track-etching techniques can be weak for their mechanical strength [3, 6, 8, 12–14].

As conventional methods such as sedimentation, flocculation, and coagulation as well as carbon active adsorption are not capable to sufficiently remove the contaminants from water, membrane technologies have been playing an essential role in this field to meet the international healthcare standards [13]. Therefore, working on the new generation of membranes that can overcome the aforementioned bottlenecks is a must-investigate and attractive subject. Recent progresses and improvements in the water treatment are based on a new generation of filtration media known as "*Electrospun Nanofibrous Membranes.*"

Electrospinning is an emerging and unique fabrication technique, and a straightforward nanofiber production technology that can produce nanofibrous nonwovens. This is an easy and simple method for producing nanofibers with cost-effective potential for developing from lab scale to pilot and industrial scales.

Membrane	Fabrication	Description	Pore size	Challenges
MF, UF, & RO	Phase inversion	• It is a de-mixing technique. • Firstly, homogeneous polymer solution should be prepared. • Then, membrane can be fabricated in a controlled manner from a liquid phase to a solid state.	• RO: 2–5 Å • UF: 0.01–0.1 μm • MF: 0.1–0.5 μm	• Pore size range is limited. • Residual solvent contamination.
NF	Interfacial polymerization	• The most prominent fabrication method for TFC membranes. • It has been progressed specifically for NF membranes.	0.001–0.01 μm	• Controlling the selective layer thickness. • Remaining the residual solvent.
MF & MD	Stretching	• Heated polymer is stretched to make it porous. • This is a solvent-free fabrication.	0.1–1 μm	• Controlling the pore size. • Lack of mechanical strength.
MF & MD	Track-etching	• Irradiating a nonporous polymeric film energetic heavy ions.	0.1–10 μm	• Hard to control the pore size. • Weak mechanical strength. • Costly.

Table 1.
An overview of the conventional membranes for water treatment [3, 6, 8, 12–14].

Electrospinning has opened new and interesting perspectives for a wide range of applications in four main sectors including environment, catalyst, energy, and health [14, 15]. **Figure 1** shows the major applications of electrospun nanofibers.

The specific features of electrospun nanofibers make them an ideal candidate for other applications including functionalized composite structures [16], electrode materials for batteries [17] and energy devices such as solar cells [18], protective clothing [19], food and agriculture [20], and tissue engineering [21]. Having considered this, it should be mentioned that the electrospun nanofibers are limitless from applications point of view. Among various nanofiber fabrication methods, electrospinning is the most promising and versatile one, and still new experiences in order to develop and improve it are being investigated.

There is no doubt that polymer fibers in the nanometric range are gaining much more attention in their application as filtration media compared to other applications. This is due to their unique features for liquid and air filtration purposes. By retouching the operating variables and dope solution content, nanoengineered membranes with nanofibrous structure can be fabricated [22]. Small pore size and its narrow distribution, as well as considerable high porosity, enable the electrospun membranes to efficiently separate out contaminants in water and wastewater treatment [23]. The high specific surface area of the nanofibrous membranes can also enhance their sorbent performance for heavy metals and desired pollutants [24, 25]. Recently, there has been a considerable progressive trend in growing of electrospinning for fabricating filtration membranes. **Figure 2** shows the number of the published articles covering three main keywords (i.e., electrospinning,

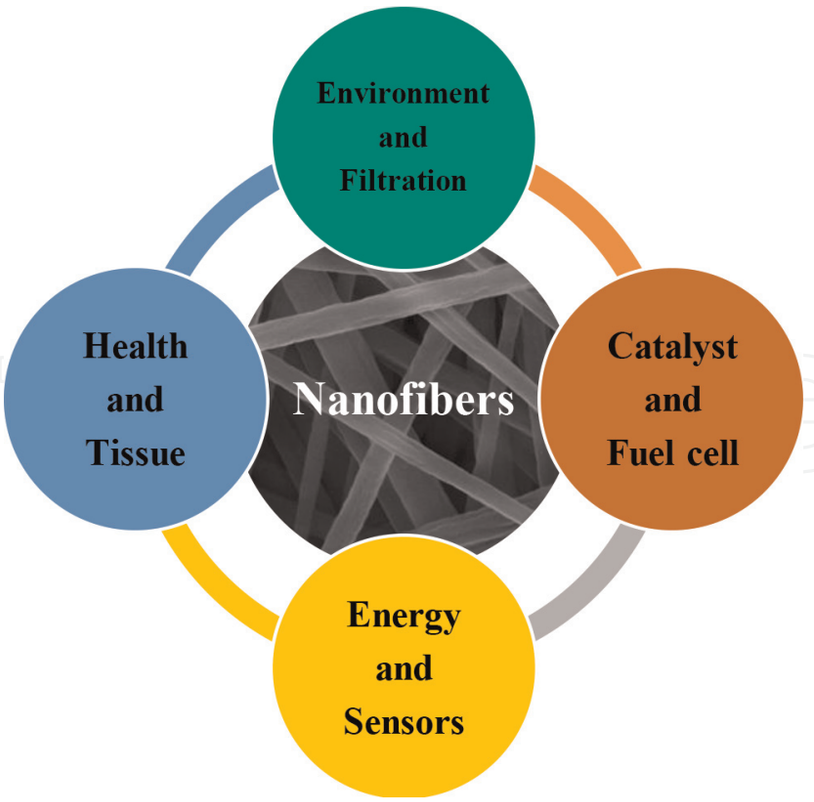


Figure 1.
Four major applications of nanofibers including: environment and filtration, catalyst and fuel cell, energy and sensors, and health and tissue engineering.

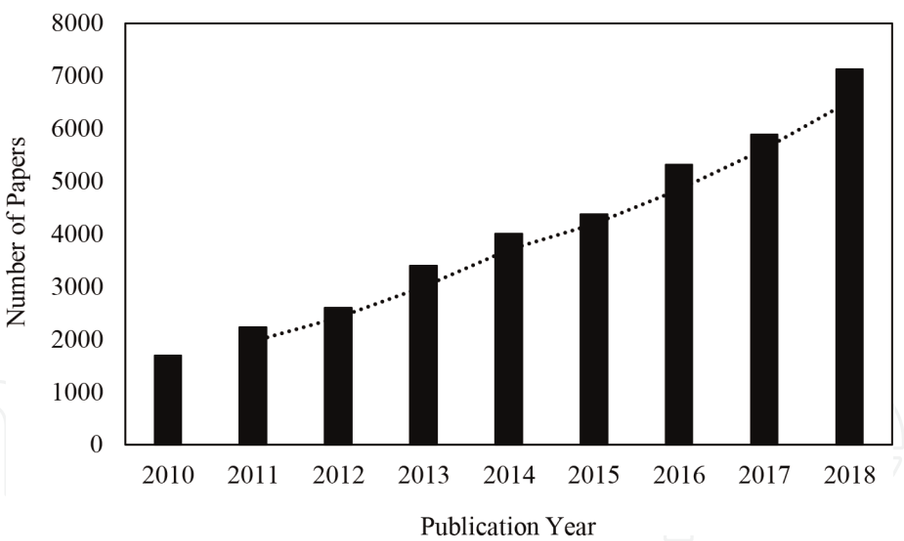


Figure 2.
Publication trend from 2010 to 2018 for the electrospun membranes applied to various filtration purposes, based on the Google Scholar research using three main keywords (electrospinning, electrospun, and membranes) (April 22nd, 2019).

electrospun, and membranes) for various filtration applications. For different filtration purposes, nanofibrous membrane properties, structures, and functionalities have been progressively enhanced toward new applications. Not only new materials coupled with functionalization methods, but also advanced characterization techniques have attracted more attention to electrospinning for membrane fabrication [26]. This chapter emphasizes on recent progresses on development of the electrospun nanofibrous membranes with a particular focus on recent accomplishments, bottlenecks, and perspectives in the water treatment applications.

2. Electrospinning technique

2.1 Background

The first observation of the electrospinning technique dates back to 1897, which was experienced by Rayleigh. It was then studied in detail by Zenely in 1914 and firstly was patented by Formhals in 1934 (US Patent: 2116942) [27]. In 1969, Taylor introduced a fundamental concept in electrospinning, i.e., Taylor cone. This work has laid the principle for electrospinning [28]. Taylor studied on the jet formation process, fundamentally. The well-known cone shape in electrospinning that is the polymer droplet at the needle tip was firstly studied by him. The proposed cone may form when an electric field is applied between the needle tip and the collector. This led to naming it the 'Taylor Cone" in the literature. A number of US patents explaining this technique and more specifically the applied experimental apparatus in electrospinning were then issued by Formhals from 1944. Notwithstanding, in spite of early introduction and mentioned achievements, it did not receive considerable attention until the early 1990s [29]. Afterward, attentiveness for electrospinning was quickened. This was due to the availability of new polymers and the higher demand for new applications of nanotechnology. After that, a lot of teams at universities and research institutes have extensively worked on the electrospinning process and its scale-up, as well as enhancement of nanofiber characteristics and applications.

2.2 Process description

The term "electrospinning," which seems to have been derived from "electrostatic-spinning," has been used for 60 years. In electrospinning process, electrostatic forces are used to produce fine fibers in the range from a few nanometers to micrometers from a polymer in solvent solution. To generate the nanofibers, high voltage (DC, kVs) should be used. In electrospinning, the strong electrical repulsive forces should overcome the surface tension, which is the weaker force in the polymer-solvent solution [30]. Typically, two major electrospinning setups have been used, which are categorized based on the needle-to-collector configuration including vertical and horizontal. Recently, several research groups have put effort on developing more sophisticated systems that enable them to prepare nanofibers with more complex structures in a more beneficial way. Electrospinning can be conducted at ambient conditions, i.e., room temperature and atmospheric pressure [15, 31].

A classic electrospinning system consists of four major sections including a needle or spinneret, a syringe pump for injecting the dope solution trough the needle/spinneret, a high-voltage supplier for charging the dope solution, and a metal collector plate or drum for collecting the fabricated fibers [32]. **Figure 3** shows the general scheme of the electrospinning system.

A polymer should be dissolved in an appropriate solvent for preparing the dope solution. When the polymer is completely dissolved and degassed, it is ready for electrospinning. The dope solution can be then introduced into the needle for nanofiber formation. A high voltage source should be used in order to accelerate the jet of polymer-solvent solution toward the collector. It should be noted that the electrical conductivity of the dope solution should be high enough to enhance the electrospinnability of the dope solution. However, some polymers may emit unpleasant conductivity, so proper additives (mostly salts) should be mixed with the polymer solution to intensify the conductivity [33].

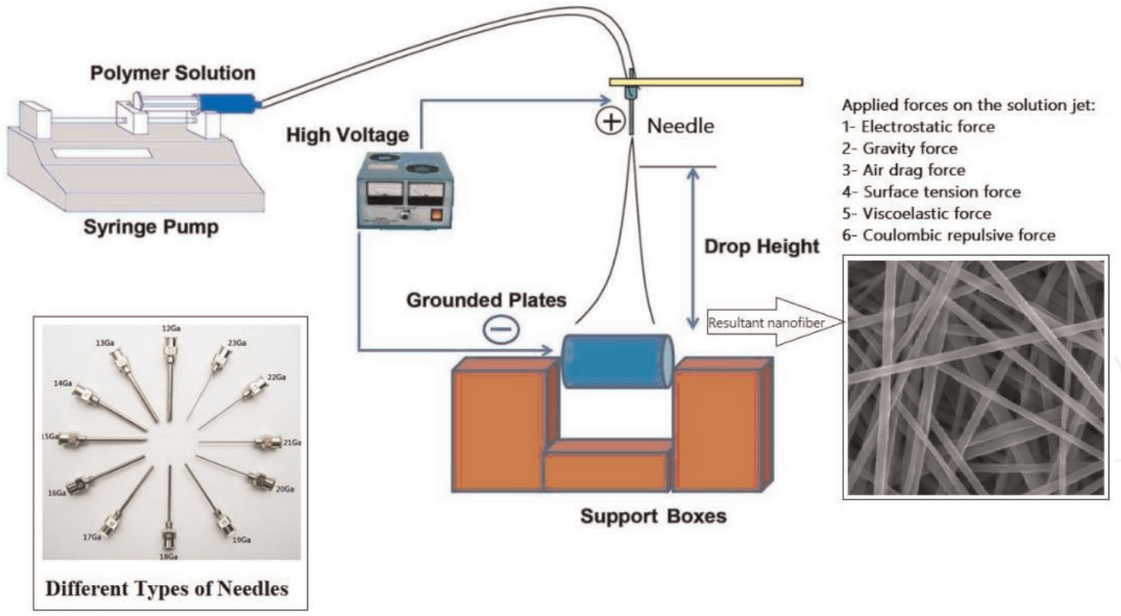


Figure 3.
A general scheme of the typical electrospinning setup, typical needles used in electrospinning and applied forces on the solution jet (from the needle tip to the collector). The system consists of a syringe pump, a spinneret (needle), a high-voltage system, and a collector (flat plate or rotating drum).

As mentioned earlier, for a successful electrospinning, the surface tension force should be overcome by repulsive electrical forces. Thus, the imposed electric field should attain a specific value, i.e., the minimum required high-voltage power. Finally, a charged polymer jet is emitted from the Taylor cone located at the spinneret tip. Then, a fast whipping and an unstable polymer jet flies from the spinneret toward the collector. The ejection is then followed by solvent evaporation, leaving a polymer behind [28, 34]. That is why the electrospinning technique has been investigated as a simple and versatile alternative for nanofiber formation.

2.3 Operating parameters in electrospinning

Both polymeric and inorganic nanofibrous membranes can be promisingly fabricated using the electrospinning technique. This technique can use a wide range of materials with high speed and low cost for membrane fabrication. Furthermore, the pore size, the fiber diameter, as well as the fiber arrangement can be easily controlled by this technique. The operating parameters of electrospinning can significantly affect the fiber morphologies, topography, and microstructure. In the main, effecting operating parameters in electrospinning can be classified in three major groups including the (1) process parameters, (2) dope (polymer-solvent solution) parameters, and (3) environment parameters [35, 36]. **Figure 4** classified the parameters that can affect the electrospinning process.

2.3.1 Process parameters

A number of process parameters can crucially ensure the conversion of the polymeric solution into smooth and nano-size fibers via electrospinning. When the applied voltage is higher than the sill voltage, a polymer jet that is charged is flied from the Taylor cone at the needle tip [37]. The effect of the imposed high voltage on the fiber has been previously discussed by several groups. For instance, Beachley and Wen [38] studied the electrospinning of the polycaprolactone. The authors

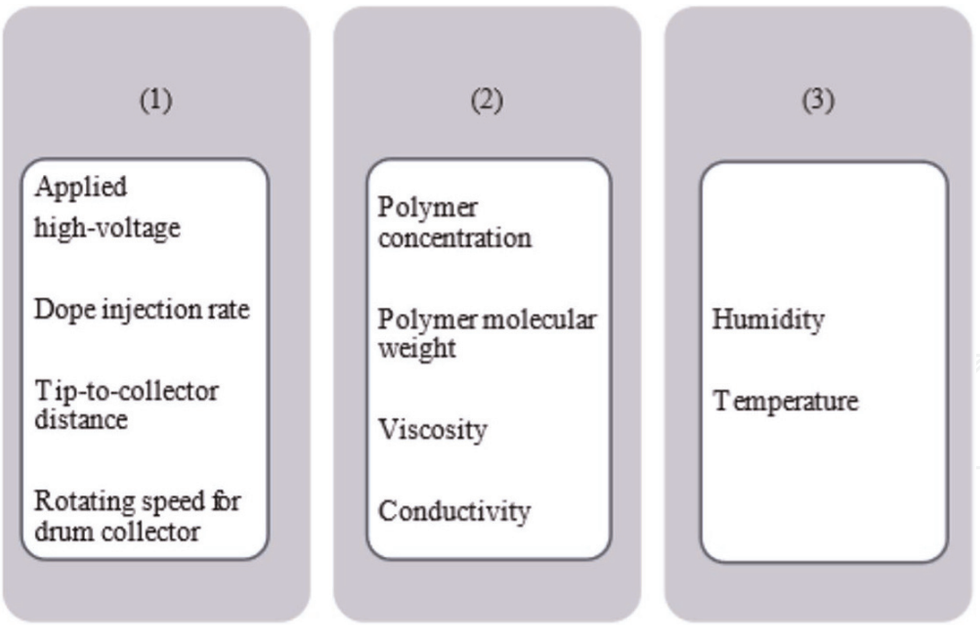


Figure 4.
Three main categories of effective operating parameters in the electrospinning process including (1) process parameters, (2) polymer solution parameters, and (3) environmental parameters.

concluded that using higher voltages can decrease both the fiber diameter and the fiber length. However, the fiber diameter can decrease at the desirable level of magnitude. Moreover, using higher voltages increased the uniformity of the fibers. However, according to Yordem and coworkers, the applied voltage showed negligible effect on the fiber diameter for electrospinning of polyacrylonitrile [39]. Both of these results have been discussed in the literature. Many other researchers have concluded that increasing the applied voltage can increase the fiber diameter, while few researches have reported that high applied voltage can reduce the fiber diameter [40]. Moreover, it has been claimed in the literature that high applied voltage can increase the probability of bead formation on the fiber structure [41, 42]. As a result, it can be concluded that the applied voltage can influence the fiber diameter; however, it is a function of solution characteristics.

Another essential process parameter is the dope injection flow rate. It has been discussed that the low flow rate can provide sufficient time for polymerization of the polymer-solvent solution. However, high feed flow rate can increase the expectancy of bead-on-fiber formation [43]. Moreover, further increase in the injection flow rate can lead to change the fiber formation through the electrospinning to bead formation through electrospraying [44–46]. The applied needle can also affect the fiber morphology. Typically, spinneret with larger inner diameter can fabricate fibers with large diameter as well. Moreover, the fiber productivity can also increase simultaneously. However, far too little attention has been paid to this operating parameter [47, 48].

It has been discussed in the literature that the tip-to-collector can also affect the fiber morphology. When the distance between the tip and the collector is short, wet fibers do not have enough time for drying and solidifying before touching the collector. On the other hand, when the proposed distance is too long, the number of beads can increase dramatically. It is worth noting that the characteristics of the dope solution, such as polymer molecular weight and solvent volatility, can influence the fiber solidification. Therefore, the optimum tip-to-collector distance should be investigated for each case individually [49, 50]. **Table 2** summarizes the effect of process parameters on the electrospun fibers.

Process parameter	Effect(s) on morphology	Highlights	Importance
Applied high voltage	Fiber diameter	• Using high applied voltage can increase the fiber diameter. • Firstly, the solution jet carries more charges for fast elongation. • More jet can be ejected using high applied voltage.	▲▲▲
Tip-to-collector distance	Bead formation	• Longer tip-to-collector distance can increase the number of bead on the surface. • Longer distance increases the jet elongation time. • It can form unstable nanofibers.	▲
Needle gauge	Fiber diameter	• Using needle with higher gauge (smaller inner diameter) can decrease the pore size. • Smaller needle can also decrease the fiber diameter	▲▲▲
Dope injection rate	Fiber diameter and bead formation	• Higher dope injection rate ejects more solution in a jet. • So, it can increase the pore size. • It can also lead to bead formation due electrospraying.	▲▲

Table 2.
Summary of the effects of process parameters on nanofiber morphology.

2.3.2 Solution parameters

There is no doubt that the preparation of the dope solution is the most important step in the production of nanofibrous membranes. To prepare the dope solution, at least a polymer material should be dissolved in an appropriate solvent. Therefore, all the factors including polymer molecular weight and polymer concentration, as well as solvent type, can significantly affect the fiber morphology. The aforementioned parameters can directly affect the characteristics of the dope solution such as viscosity, conductivity, and surface tension, and consequently all of them influence the electrospinnability and fiber morphology, as well [25]. Over 200 different polymers can potentially be used for electrospinning. **Table 3** summaries the typical polymers and corresponding solvents that have been used in electrospinning.

Polymer concentration is a key parameter in the electrospinning technique. Using low polymer concentration leads to electrospraying rather than electrospinning. It can then produce particles, mostly in spherical shape, with the size from micro- to a few nanometers [51, 52]. By increasing the polymer concentration, a mixture of beads, bead-on-fiber, and fiber can be formed. Smooth fibers in the range of nanometer to micrometer can be observed when the polymer concentration reaches the optimum level. By imposing very high polymer concentration, helix-shaped microribbons can be obtained [53–55].

The viscosity of the dope solution can be demonstrated by the degree of entanglement of the polymeric chains in the solution. This is a function of the molecular weight of the polymer. Therefore, it can be concluded that the polymer molecular weight can influence the morphology of the electrospun nanofibers [56].

As it has been already mentioned, the viscosity of the dope solution is a crucial parameter affecting the microstructure and morphology of the electrospun fibers. It has been discussed in the literature that continuous nanofibers with smooth surface cannot be fabricated using a dope solution with very low viscosity. On the other

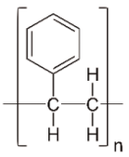
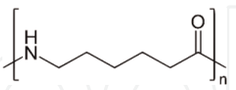
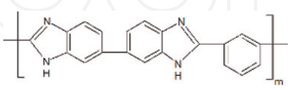
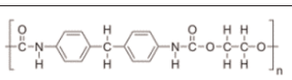
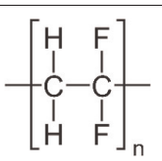
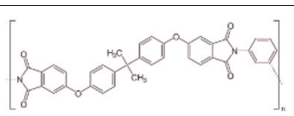
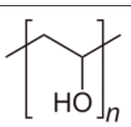
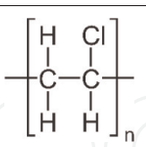
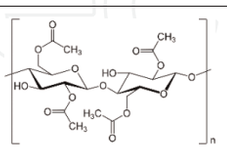
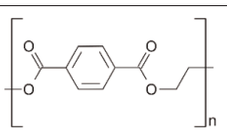
Polymer	Chemical structure	Solvent	Concentration	Applications
Polystyrene		• Dimethylformamide • Dimethylacetamide • Tetrahydrofuran	18–35 wt.%	• Ion-exchange filter • Coalescing filtration • Air filtration • Oil-spill cleanup
Nylon 6 and 66		• Formic acid	10–15 wt.%	• Protective clothing • MF membrane
Polybenzimidazole		• Dimethylacetamide • Dimethylformamide	10–15 wt.%	• Protective clothing • Composites • Nanofiber reinforced • Fuel cell
Polyurethanes		• Dimethylformamide • Dimethylacetamide	10–13 wt.%	• Electret-filter • Protective clothing • Tissue engineering
Polyvinylidene fluoride		• Dimethylformamide • Dimethylacetamide • Acetone • Tetrahydrofuran	10–24 wt.%	• Membranes • Protective clothing • Flat ribbon
Polyetherimide		• Hexafluoro-2-propanol	10–13 wt.%	• Flat ribbon
Polyvinylalkohol		• Distilled water		• Drug delivery • Tissue engineering
Polyvinylchloride		• Dimethylformamide • Tetrahydrofuran	10–15 wt.%	• Fabrics • Filters
Cellulose acetate		• Acetone • Acetic acid • Dimethylacetamide	12–20 wt.%	• Membranes
Polyethylenterephthalat		• Dichloromethane • Trifluoroacetic	4–10 wt.%	• Filter • Fabrics

Table 3.
Typical polymers and solvent candidates, recommended concentration and perspective of applications.

hand, very high viscosity reduces the electrospinnability due to the ejection difficulty of the solution jets from the needle tip [57, 58]. Therefore, the optimum viscosity for the dope solution should be measured for each polymer-solvent system, individually. It should be noted that the viscosity of the dope solution is proportional to the polymer concentration and polymer molecular weight. All these

can then affect the surface tension of the dope solution. Therefore, for a solution with low viscosity, beads or nanofibers with bead-on-structure can be formed. However, continuous nanofibers can be formed by using a dope solution with optimum viscosity [59, 60].

Surface tension, which is another important parameter, is proportional to the solvent compositions of the dope solution. It is indicated in the literature that using different solvents can lead to different surface tensions [61, 62]. Low surface tension can lead to smooth fibers under the constant polymer concentration. Moreover, the mass ratio of the solvent mixture can affect the surface tension and viscosity of the dope solution [63]. Although some impurities can be imposed to the dope solution by using surfactants, however, they can easily reduce the surface tension. Recent researches show that using surfactants not only reduces the surface tension of the dope solution but also enhances the electrical conductivity. Thus, it can then improve the morphology of the nanofibers [64, 65].

The conductivity of a dope solution is a function of the dissolved polymer and solvent. When a polymer solution with low charge density is introduced to the electrospinning system, it can result in higher surface tension under an applied electric field. This can form poor-quality nanofibers [66]. Furthermore, ionic salts, such as CTAB (cetyltrimethyl ammonium bromide), LiCl (lithium chloride), NaCl (sodium chloride), and $NaNO_3$ (sodium nitrate), can be added to the system for adjusting the electrical conductivity of the dope solution. As a result of enhancing the solution conductivity, nanofibers with a more uniform diameter and smooth morphology can be prepared. Further to ionic salts, organic acids can be also used as the solvent to enhance the electrical conductivity of the dope solution [67, 68].

The volatility of the applied solvent to prepare the dope solution can directly affect the fiber production and morphology. Using solvent with low volatility can lead to form wet fibers and fused fibers, as well. However, using a highly volatile solvent can cause intermittent electrospinning. This is due to the solidification of the polymer at the needle tip [69, 70]. It can even cause the artifacts on the membrane surface. Therefore, it can be discussed that using a highly volatile solvent can form flat or ribbon-like fibers or even fibers with pore-on-surface structure [71, 72]. **Table 4** summaries the effect of solution parameters on the resultant nanofiber membranes.

2.3.3 Environmental parameters

Environmental parameters including temperature and humidity can also affect the nanofiber morphology [73]. It is concluded in the literature that thinner fibers can be fabricated using high temperatures. Lower humidity can also accelerate the solvent evaporation, while larger fibers can be formed in high humidity [74, 75]. The environmental parameters not only affect the nanofiber morphology but also can influence the performance of the resultant nanofibrous membrane [76]. For instance, using high humidity environment can act as a pore forming strategy on the polystyrene fiber surface. This is really favorable when nanofibers are used for oil-spill cleanup [77, 78]. **Table 5** presents the influences of the environmental parameters on the morphology of nanofibrous membranes.

2.4 Characterization of electrospun membranes

Having an electrospun membrane with proper structure is not enough for the water treatment purpose. Actually, deep knowledge of the used polymer and additives, morphology, and specifications is conclusive for water treatment applications [79]. Various characterization methods can be directly used for examining the

membrane performance for water treatment. The results of this step can be directly used for adjusting the electrospinning parameters in order to develop new membranes with enhanced performance. The characterization methods can be classified into two main groups covering a wide range of techniques [80, 81].

Solution parameter	Effect(s) on morphology	Highlights	Importance
Concentration	Fiber diameter	• Higher concentration can make the jet elongation harder and slower. • So, it can increase the fiber diameter and membrane pore size, as well.	▲▲▲
Solution viscosity	Fiber diameter	• Higher viscosity leads to more difficult elongation. • It can then lead to increasing the fiber diameter and the membrane pore size, as well.	▲▲
Surface tension	Fiber diameter	• Using dope solution with lower surface tension can form thinner fibers. • This is attributed to the easier jet elongation. • Soon, both the fiber diameter and membrane pore size can decrease.	▲
Solution conductivity	Fiber diameter and bead formation	• Using higher conductive dope solution can prevent the bead formation. • This is due to higher charged solution jet. • Thus, fiber diameter and membrane pore size can decrease, considerably.	▲▲▲
Solvent	Fiber diameter and bead formation	• Dielectric constant of the used solvent can directly affect the fiber diameter. • Thus, a proper solvent can form more stable nanofibers. • Higher solvent volatility can increase the fiber diameter. • Porous fibers can be formed using highly volatile solvents.	▲▲

Table 4.
Summary of the effects of dope solution parameters on nanofiber morphology.

Environment	Effect(s) on morphology	Highlights	Importance
Humidity	Fiber morphology and surface structure	• At low humidity, the jet elongation time can be prolonged. • Thus, both the fiber diameter and pore size can decrease, considerably. • In case of formation of beads, they will be sticky.	▲▲
Temperature	Fiber diameter and surface structure	• The temperature can be imposed into both the collector and the dope solution. • The effect of each one should be investigated. • At low temperatures, the jet elongation time can be prolonged. • This leads to thinner fibers and membrane pore size, as well.	▲

Table 5.
Effects of the electrospinning environment on the nanofiber morphology.

These techniques have been widely used to measure the characteristics of nanofibrous membranes such as pore size and its distribution, surface roughness, nanofiber diameter, surface energy (hydrophobicity or hydrophilicity), elemental structure, chemical composition, and membrane fouling potential [82–85]. Among all the characteristics of the electrospun nanofibrous membranes, the most critical ones for water treatment purposes are pore size, surface morphology, and surface energy [33]. The typical structure (both morphology and topography) of an electrospun nanofibrous membrane made of polystyrene is shown in **Figure 5**. Different characterization techniques and possible obtained results for analyzing the electrospun nanofibrous membranes have been comprehensively discussed in the literature [33, 85].

2.5 Different configurations of electrospinning system

As it has been already mentioned, a prototypal electrospinning system consists of four main parts including the high-voltage supplier, the syringe pump for injecting the dope solution into the needle, a needle (in the needle-based electrospinning system), and the metal collector [86]. In electrospinning, a solution jet that elongated under high-voltage electrical field forms the nanofibers. The nanofiber formation includes three essential steps: (1) the beginning of jetting to develop a rectilinear jet of the dope solution, (2) curving deformation through twisting and spiraling paths, and (3) solidification of solution jet to form nanofiber via solvent evaporation, and finally nanofiber collection on the grounded collector [87–89].

Based on the spinneret design, generally there are two configurations including needle-based electrospinning and needleless electrospinning. The latter one was not discussed in this chapter. In the needle-based electrospinning, the designs of the

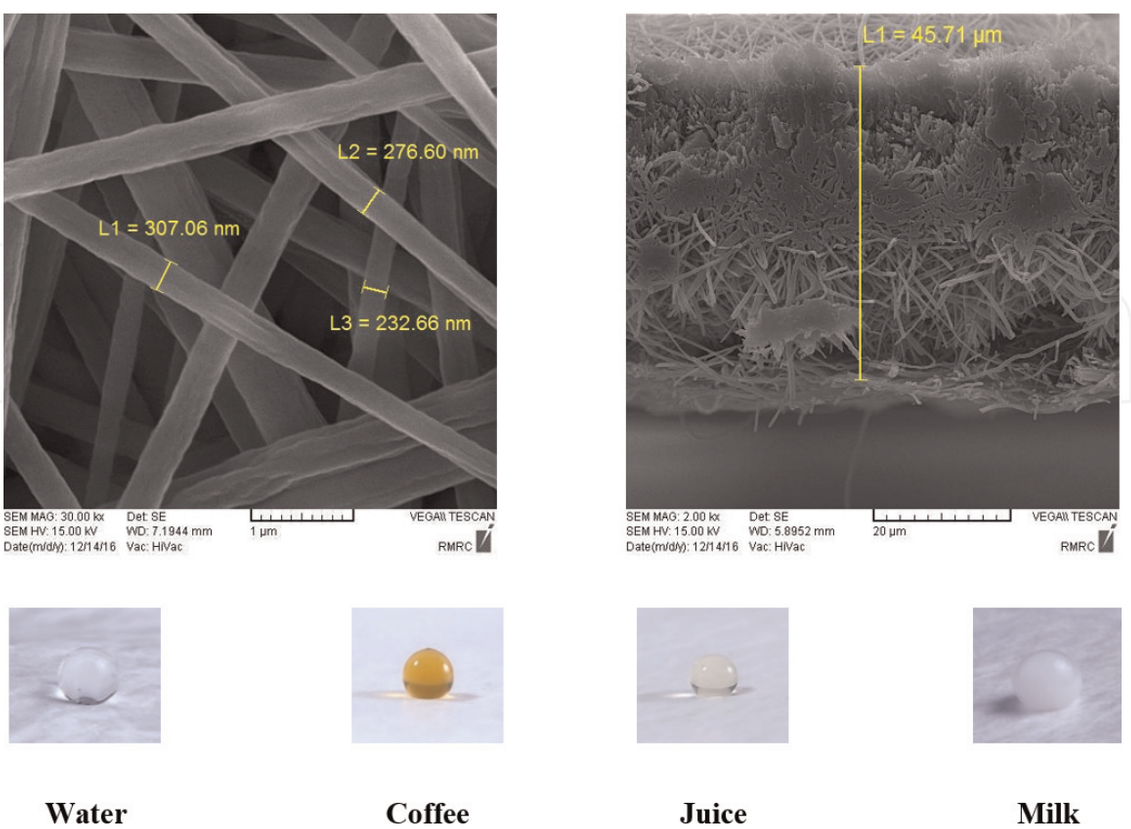


Figure 5.
SEM images of an electrospun nanofibrous membrane made of polystyrene, and drop-on-surface images of different liquids.

needle and the collector are also crucial parameters affecting the nanofiber morphology. Teo and Ramakrishna comprehensively reviewed different electrospinning configurations [90]. In another work, Liao and coworkers [91] comprehensively reviewed different configurations of electrospinning systems based on the spinneret and collector designs.

3. Applications of electrospun nanofibrous membranes for water treatment

Polymeric membranes with porous structure can be prepared via a wide range of techniques such as the well-known phase inversion, stretching and track-etching, etc. [92, 93]. Each technique has a number of advantages and disadvantages, as well. Phase inversion is the most investigated membrane fabrication technique. In this method, a target polymer should be dissolved in a proper solvent to prepare the casting solution. Both flat-sheet and tubular membranes can be formed. This is a simple, promising, and easy-to-scale-up method, which can fabricate membranes with 80% porosity [94]. Membranes with symmetric structure can be fabricated via sintering method. The prepared membranes can have the mean pore size between 0.1 and 10 μm. Although this solvent-free technique is suitable for membrane fabrication using chemically stable materials (such as ceramics, polyethylene, and PTFE), however, it will be hard to achieve pores below 100 nm. Moreover, the maximum porosity of 10–20% can be achieved [95, 96]. Symmetric membranes with mean pore size between 0.1 and 3 μm can be also fabricated via the stretching method. This technique is mostly practical for preparing the PTFE membranes. Stretched membranes can hold the porosity between 60 and 80%. However, needing high operating temperature is a bottleneck for this technique. Membranes with narrow pore size can be prepared by track-etching technique. Cylindrical pores with sizes between 0.02 and 10 μm can be fabricated using this method. However, the number of suitable polymers to using in this technique is limited [97].

Recently, the electrospinning technique has also been inspected for fabrication of porous membranes. In contrast to the above-mentioned conventional fabrication techniques, membranes with narrower pore size, considerably higher porosity, and pore structure with interconnected free volume can be fabricated by the electrospinning method. That is why electrospun nanofibrous membranes have attracted more attention for water treatment purposes through different membrane separation processes.

3.1 Electrospun membranes for pressure-driven processes

The applied driving force is a proper measure for classification of membrane processes for water treatment. Hydraulic pressure difference by imposing a positive pressure on the feed channel is the driving force for microfiltration, ultrafiltration, nanofiltration, and reverse osmosis processes. The applied pressure separates contaminated water into two streams: the clean stream, which is the permeate phase, and the contaminated stream, which is the retentate phase [98]. **Figure 6** illustrates the favorable separation target for the pressure-driven membrane processes in water treatment applications.

In water treatment by pressure-driven membrane processes, there is an input stream (feed) into the module, while two streams exit it including the partially purified permeate and the highly contaminated retentate [99]. The retentate phase should follow further treatment steps before being discharged. The most important parameter that governs the water treatment role of pressure-driven membranes is

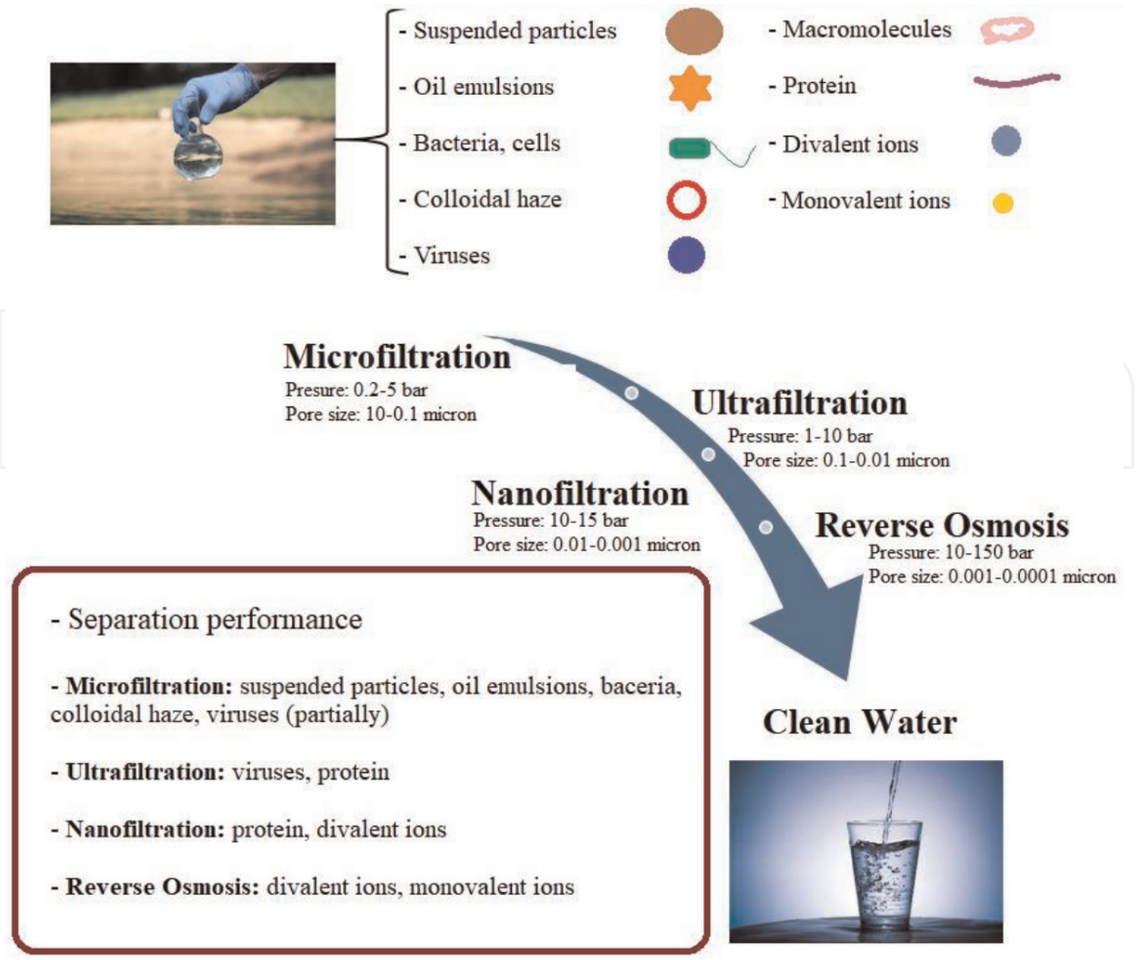


Figure 6.
Overview of the separation target for pressure-driven membrane processes in water treatment applications.

their selectivity, which changes from MF to RO. Moreover, the applied pressure differs from each process. Depending on the applied membrane, different contaminants can be removed from the feed stream. Suspended particles, oil emulsions, and partially bacteria can be eliminated using MF membranes. UF membranes are more promising for removing the cells, colloidal haze, and partially viruses [100–102]. Recently, nanofiltration has been actively used for efficient separation of divalent ions, as well as proteins, macromolecules, and even submolecular organic groups from water and wastewater streams [103, 104]. However, in order to remove the monovalent ions and produce a safe and drinkable water, RO is the most promising option [105, 106]. Here in this section, the applications of electrospun membranes with nanofibrous structure applied to the pressure-driven membrane processes for water treatment are investigated.

3.1.1 Electrospun membranes for MF process

Microfiltration (MF), which is the most mature membrane process, works based on the sieving filtration theory [107]. Typical pore size values for MF membranes rely on 0.1–1.0 μm. Porous barriers with larger pore size than that of 1.0 μm are actually filters, not membranes, and they are usually used as prefilters for removing the large particles. Having higher porosity and narrower pore size distribution makes the electrospun nanofibrous MF membrane a promising alternative for conventional MF.

The first attempt for using electrospun MF membrane for water filtration was reported by Gopal and coworkers [108]. In this work, the authors used PVDF

(polyvinylidene fluoride) for fabricating the nanofibrous membrane for removing the polystyrene particles with 1, 5, and 10 μm diameters. Results indicated that the prepared membrane could effectively remove more than 90% of the microparticles. Based on the characterization results, the fabricated membranes showed similar features to those of the commercial MF membranes. This work opened up a new window exploring the use of electrospun membrane water treatment applications. In another work, Barhate and coworkers studied on the effect of electrospinning conditions, such as the applied high voltage, tip-to-collector distance, and the rotational speed of the collector on the morphology and permeability of the nanofibrous PAN membrane [109]. Results of this work indicated that electrospinning parameters considerably affect the fiber arrangements while collecting the nanofibers. Moreover, coordinating the drawing and collection rates can control the pore size distribution.

To better understand the effect of nanofibrous structure on the separation performance of electrospun membranes, various polymers have been used for fabricating the membrane samples, such as PES (polyether sulfones), PC (polycarbonate), PAN (polyacrylonitrile), nylon 6, PET (polyethylene terephthalate), and PSU (polysulfone) [110–114]. In these works, the performance of electrospun membranes with different characteristics including nanofiber diameters and membrane thicknesses was studied. Almost in all mentioned works, it has been concluded that the morphology and structure of the investigated nanofibrous membrane significantly affect the filtration performance.

Commercial polymers such as PSU and PVDF become more hydrophobic when electrospun into a nanofibrous membrane as compared with the virgin polymer material. However, hydrophilic membranes are more beneficial in direct water filtration. Thus, lower permeate flux and more fouling tendency are expected. Therefore, surface treatment via chemical modification can improve the flux and solute rejection, which all means higher separation performance of the electrospun membrane [115]. For instance, a highly hydrophilic electrospun membrane was fabricated by Kaur and coworkers [116]. The membrane was fabricated based on PVDF. In order to prepare the dope solution, PVDF polymer was mixed with a number of macromolecules for surface modification. The dope solution was then used for fabrication of nanofibrous membrane samples. The authors concluded that the hydrophilic effect of the modifiers could possibly be due to the orientation of the hydrophilic groups adopted during electrospinning on the surface. Results indicated that under the constant operating pressure the blended electrospun membrane provided higher permeate flux as compared with the nonblended electrospun membrane. The authors claimed that the proposed study highlighted the potential benefits of the newly developed hydrophilic membrane for water treatment purposes under low operating pressures [116]. **Table 6** lists the recently published works on the electrospun MF membranes.

3.1.2 Electrospun membranes for UF process

The applied membranes in the ultrafiltration (UF) process typically have pore sizes in the range of 0.01–0.1 μm. The operating pressure of the UF process typically varies between 1 and 10 bar. Using the UF membrane, large species such as particles, bacteria, and even protein are retentated. However, water and ions, as well as solutes with low molecular weight, can pass through the membrane pores [9]. The UF process plays a crucial role in the water treatment for rejecting different contaminants, viruses, bacteria, and colloids. Moreover, this is a promising pretreatment filtration for RO desalination [122, 123]. It is also a practical separation process in food industry, for instance for wastewater treatment or cheese processing [124].

Year	Materials and methods	Microfiltration	Reference
2017	*Materials* • PAN (Mw: 150,000 g/mol) • *N,N*-dimethylformamide *Electrospinning* • Dope: 11 wt.% • Voltage: 15 kV • Tip-to-collector: 15 cm • Flow: 1 mL/h • Humidity: 35% • Temperature: 40°C	• Feed: Oily wastewater • Flux: 6898–18,614 LMH • Rejection: 42.8–98.1%	[117]
2017	*Materials* • Nylon 6 • Polyvinyl acetate (Mw 140,000 g/mol) • Acetone • Formic acid • Acetic acid *Electrospinning* • Dope: 21 wt.% • Voltage: 30 kV • Flow: 0.18 mL/h • Tip-to-collector: 8.8 cm • Temperature 25°C • Humidity: 40%	• Feed: Oily wastewater • Flux: 1400–6700 LMH • Rejection: 93–99%	[118]
2017	*Materials* • PAN (Mw = 150,000 g mol^{-1}) • *N,N*-dimethylformamide *Electrospinning* • Dope: 7, 10, and 12 wt.% • Needle ID: 0.4 mm • Voltage: 18 kV • Flow: 0.5 mL/h	• Feed: Suspended particles • Flux: 712-6810 LMH • Rejection: 11.5–99.3%	[119]
2018	*Materials* • PAN (250,000 g/mol) • Hyperbranched polyethyleneimine (Mw = 1800 g/mol) • *N,N*-dimethylformamide *Electrospinning* • Dope: 17 wt.% • Voltage: 16 kV • Flow: 1 mL/h • Tip-to-collector: 15 cm	• Feed: Oily wastewater • Porosity: 70–73% • Flux: 9000–16,000 LMH • Rejection: ˃96%	[120]
2018	*Materials* • PAN (Mw: 100,000 g/mol) • *N,N*-dimethylformamide *Electrospinning* • Dope: 12 wt.% • Flow: 1 mL/h • Voltage: 22 kV • Tip-to-collector: 9 cm • Temperature: 22°C • Humidity: 18%	• Feed: Sludge particles from MBR • Porosity: 72–75% • Flux recovery ratio: 72.4–96%	[121]

Table 6.
Recently published works on electrospun nanofibrous MF membranes.

Phase inversion is the most used technique for fabrication of the conventional UF membranes [125]. Therefore, low-to-moderate permeate flux and even high fouling rates are probable. Moreover, using the phase inversion method can also

impose the challenge of the wide pore size distribution, which can limit the membrane performance for the water treatment. In better words, appearing large pores can cause the defect of pore fouling, as well as the chance of passing the high-risk contaminants through the pores. It can then be a bottleneck for different applications, more specifically the treatment of the potable water [126, 127].

On the other hand, an ideal UF membrane should be as isoporous as possible, which is hard to fabricate by the conventional phase inversion technique. Having high porosity and surface isoporosity of pores needs a thin selective layer with high permeability that cannot be formed by the typical phase inversion. Although this can be achieved by other techniques such as self-assembly [128], however, a highly microporous and hydrophilic scaffold is needed. This is then the right point for highlighting the role of the electrospun nanofibrous substrate for UF membranes [129].

For instance, Bahmani and coworkers [130] studied on the arsenate removal from contaminated water using a new thin-film composite membrane. The new membrane structure consists of a substrate made of PET, nanofibrous scaffold, and a top selective layer made of PAN. The authors used the cetylpyridinium chloride pretreatment step to effectively reject the arsenate ions. Results indicated that the newly developed membrane showed 172–520% higher permeate flux as compared with a commercial UF membrane. In case of the arsenate rejection, the UF membrane based on the nanofibrous scaffold was 1.1–1.3 times more efficient than the commercial UF membrane.

In another work, Mokhena and coworkers [131] studied on the development of a three-tier composite membrane with high flux. The membrane structure composed of three main layers including (bottom to up): (i) a nonwoven layer for improving the mechanical feature, (ii) electrospun scaffold made of alginate, and (iii) a selective layer made of chitosan and chitosan-silver nanoparticles. Electrospinning of alginate with the aid of synthetic electrospinnable polyethylene oxide and ionically cross-linked with calcium chloride was investigated. It was then followed by the chemical cross-linking using glutaraldehyde for fabricating the nanofibrous midlayer. The selective layer was well coated with silver nanoparticles, which considerably enhanced the antibacterial activity of the membrane (against both Gram-negative and Gram-positive bacteria). Similar permeate flux and nanoparticle rejection (>98% for nanoparticles and >93% for oil, respectively) were achieved for both the membrane samples. Moreover, higher permeate flux and oil rejection were achieved for both the membrane samples as compared with the commercial UF membrane. The authors also discussed that the dye rejection was improved up to 95% by incorporating the silver nanoparticles. Finally, the authors concluded that the presence of the silver nanoparticles not only can improve the antibacterial activity of the membrane but also can enhance the dye removal and oil separation performances.

In order to develop more novel composite UF membranes based on an electrospun nanofibrous substrate, different materials have been used for preparing the selective layer. Moreover, both hydrophobic and hydrophilic polymers have been examined to prepare the nanofibrous substrate layer. The hydrophilic scaffolds have showed more promising performance, which attributed to their antifouling properties [132, 133]. Further studies should be conducted, not only for optimizing the characteristics of the electrospun layer (e.g., the morphology and the thickness) but also for fabricating a more permeable and antifouling top selective layer.

3.1.3 Electrospun membranes for NF process

Nanofiltration (NF) membranes lay hold of the lower range of UF membranes and upper range of RO membranes [134]. The molecular weight cutoff is the

measure for defining the pore size in the NF membranes. The pore size in this class of pressure-driven membranes is in the range of 100–1000 Da. Nanofiltration membranes have been widely used for water treatment applications. This considerable interest in the NF membranes can be attributed to their remarkable performance for removing the color, taste, and odor, as well as softening and sterilizing capability. A good NF membrane is even capable of removing some trace organic contaminants and divalent ions [135, 136]. Similar to the MF and UF processes, the NF process is also driven by pressure on the feed side; however it uses higher operating pressure. The separation mechanism in the NF membranes involves sieving, which is based on the steric hindrance, and the Donnan effect, which is based on the electrostatic forces. Despite an RO membrane that can remove the monovalent ions, an NF membrane can remove both multivalent and divalent ions [137, 138] (see **Figure 6**). Thus, the NF membranes can be effectively used for water and wastewater treatments [139, 140].

Currently, the commercially available NF membranes are thin-film membranes with composite structure. The structure of these membranes consists of a slender selective top layer (with nanometric thickness), which is mostly fabricated via the interfacial polymerization technique [141]. As it has been already stated, both the substrate layer and its porosity have an important role in enhancing the performance of the thin-film membranes. This is because of the possibility of the effective flow path via the selective layer. Nanofibrous substrates can be investigated as a promising substrate due to their remarkable porosity. This is particularly more promising for the NF membranes rather than the RO membranes, due to lower applied pressure and lower compressive forces, as well.

As one of the first efforts in this field, Tang and coworkers [142] studied on a thin-film membrane with composite structure for NF experiments. The proposed membranes showed a low fouling tendency. The membrane structure consisted of a thin hydrophilic top layer, a nanofibrous scaffold as the sublayer, and a nonwoven support with microfibrous structure. In order to prepare the PES (polyethersulfone)-made nanofibrous scaffold layer, the authors studied on the effect of solution flow rate, additives, solute concentration, and solvent mixture ratio, as well as the relative humidity. The fabricated membranes were then characterized for the morphology, the fiber diameter, and its distribution. The adhesion between the PES nanofibrous layer and the nonwoven support, which was made of PET (polyethylene terephthalate), was also examined. Moreover, the membrane samples were tested for the tensile feature. Results indicated that the obtained permeate flux was more promising for the newly developed membrane. Moreover, the authors concluded that the uniformity of the nanofibrous PES sublayer, as well as its adhesion to the PET nonwoven support, should be optimized [142].

In another example, Yoon and coworkers [143] used the PAN polymer for electrospinning of the nanofibrous web as the midlayer support in fabricating a thin-film membrane with nanofibrous composite structure. The membrane samples were used for the high flux NF process. Interfacial polymerization technique was used for fabrication of the top selective layer. To do this, the authors used polyamide solution containing different ratios of bipiperidine and piperazine. The new membrane samples were then tested for evaluation of their permeate flux and rejection in an NF system. Three commercial NF membranes were used as the control for comparing the results of the newly developed membranes. An $MgSO_4$ (2000 ppm) solution, which stood for the divalent salt solution, was used for all NF tests. Results indicated that the new membrane based on the electrospun scaffold provided considerably higher permeate flux (over 2.4 times) as compared with the commercial membranes, while maintaining the same rejection rate of ~98% [143].

Recently, Liu and coworkers [144] used the dope solution made of nylon 6 to fabricate a nanofibrous scaffold via the solution blowing technology. The fabrication procedure was followed by hot-press step to fabricate a sublayer for an NF membrane. Afterward, a very thin selective layer was fabricated by the interfacial polymerization technique. The authors then studied the effects of different nanofibrous sublayers on the characteristics of the selective layer of the fabricated NF membranes, as well as the filtration performance. Results indicated that the best concentration of nylon 6 for preparation of the nanofiber scaffold was 15 wt.%. The corresponding nanofibrous web had a proper morphology and fiber diameter distribution. Using this nanofibrous scaffold, the fabricated NF membrane had a smoother surface and remarkable separation performance. Using the best membrane sample, pure water flux of 13.1 LMH and salt rejection of 81.3 and 85.1% for NaCl and Na_2SO_4 were achieved, respectively.

It is worth quoting that for preparing the electrospun NF membranes, not only the nanofibrous support layer should be optimized but also the protocol for the interfacial polymerization should be developed properly [145].

All in all, electrospinning is a promising and simple technique to prepare highly porous substrates with three-dimensional interconnected pore structures for the pressure-driven membranes. Most of the previously published works have focused on fabricating the substrate layer of the thin-film composite membranes [146]. However, the stability of the selective top layer under high operating pressures, mostly in the NF process, should be studied more. Moreover, enhancing the antifouling properties in the real water treatment experiments, as well as the scale-up strategies for industrial fabrication of the nanofibrous-based pressure-driven membranes, is another concern.

3.2 Electrospun membranes for thermally-driven processes

The previously discussed pressure-driven membrane processes are all isothermal separation techniques. Recently, a new nonisothermal membrane separation technique has been introduced, which is a combination of the conventional distillation and the membrane separation. This separation technique, which uses the vapor-pressure difference as the driving force, has been called "membrane-distillation" process [147]. Membrane distillation (MD) is an impressive separation technique wherein a porous hydrophobic membrane is used to separate the feed channel (hot side) and the permeate channel (cold side) [148].

MD process has four major configurations. All these configurations are the same for the feed channel, where the hot stream as the process liquid is in direct contact with the hydrophobic surface of the applied microporous membrane. The surface hydrophobicity of the used membrane prevents the process liquid from penetrating into its pores. This causes to form the liquid-vapor interface at the entrance of the pores on the membrane surface [149]. The four main MD configurations include DCMD (direct contact membrane distillation); SGMD (sweeping gas membrane distillation); AGMD (air-gap membrane distillation); and VMD (vacuum membrane distillation). **Figure 7** shows the general scheme and defines the differences among the MD configurations.

There are a few crucial characteristics required for an MD membrane that significantly affect the performance, as well as the overall efficiency of the MD process. The applied membrane should have high LEP (liquid entry pressure) value, must be hydrophobic (or even superhydrophobic), must be as porous as possible with narrow pore-size distribution, and must have low tortuosity factor [150]. The MD membrane should also have proper chemical and mechanical properties. Nonetheless, the first generation of the MD membranes has been commercially available

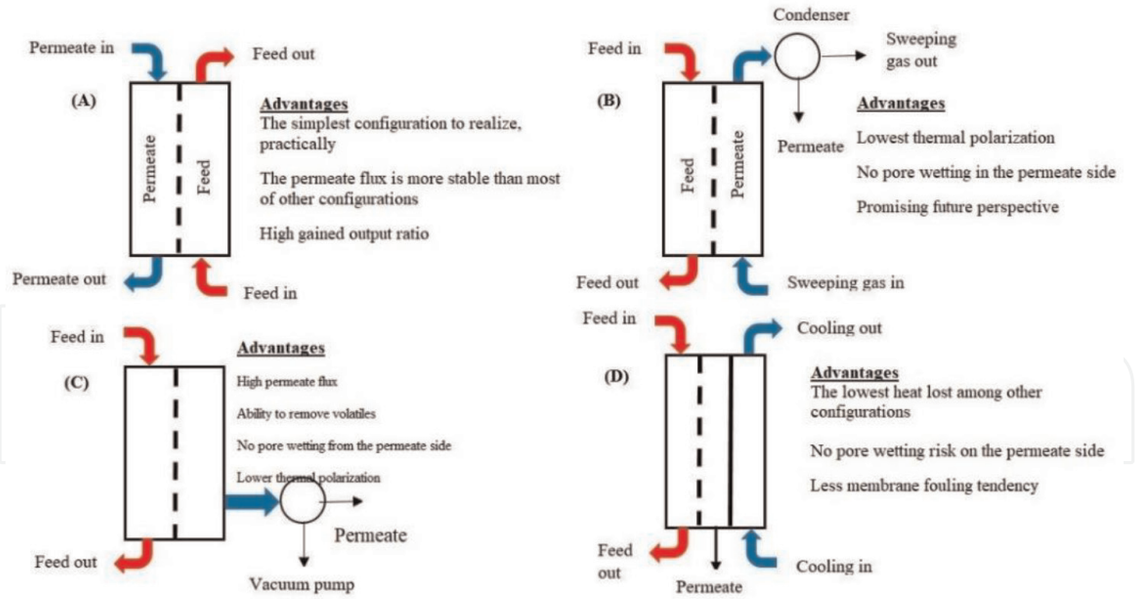


Figure 7.
The general scheme of the MD configurations, as well as the advantages of each one: (A) DCMD (a pure water stream with lower temperature than that of the feed flow is passed through the permeate channel), (B) SGMD (a cold inert gas stream sweeps out vapor molecules in the permeate channel), (C) VMD (vacuum pressure is applied in the permeate channel to suck out the volatile molecules), and (D) AGMD (an air-gap that is stagnant is involved between the membrane and a condensing surface with lower temperature placed inside the MD module).

MF membranes, which have been made of hydrophobic polymers [151]. However, commercial MF membranes are still being used in various MD processes [152]. The second generation of the MD membranes is fabricated using commercially available polymers [153]. Recently, the electrospun nanofibrous membranes have attracted a lot of attention as the third generation of the MD membranes. This is attributed to their promising and exclusive characteristics including high porosity, three-dimensional interconnected pore structure, and reproducibility [22].

The first study in using an electrospun membrane for the MD process was published by Feng and coworkers in 2008 [154]. In this work, PVDF was used for fabricating the membrane sample. Saline water with 6 wt.% NaCl solution was used for the desalination experiments by the AGMD process. The authors reported a remarkable salt rejection, which was higher than 98%.

Mechanical durability is one of the most challenging bottlenecks of the electrospun nanofibrous membranes. Li and coworkers [155] studied on improving the mechanical features of the nanofibrous membranes with the use of nonwoven fabrics and spacer fabrics as the backing layer. The electrospun membrane samples were fabricated using the PVDF polymer. The authors investigated the effect of the support layer on the membrane characteristics (e.g., permeability, porosity, morphology, pore size and pore size distribution, hydrophobicity, and mechanical durability). Based on the obtained results, a 3D bead-fiber interconnected open structure and a rough membrane surface were observed for the newly developed membrane. The membrane samples were all hydrophobic with surface contact angles above 140°. Moreover, the stress at break and the elastic modulus of the new membrane samples increased by 4.5–16 times and 17.5–37 times, respectively, as compared with the nanofibrous membrane made of pure PVDF. Based on the obtained results, using the spacer fabrics as the support layer provided higher water fluxes as compared with the nonwoven-support membrane. The authors concluded that this can be attributed to the less mass transfer resistance of the spacer fabrics. The highest water flux in this study was up to 49.3 kg/m^2/h when the hot stream

temperature was set at 80°C. Moreover, the new composite membrane showed a reasonable long-term desalination performance.

In another work, Deka and coworkers [156] developed a novel electrospun membrane with high wetting resistance for MD-based desalination. In this study, the authors discussed that the perfluorinated membranes with superhydrophobic feature can be prepared and used as an alternative for seawater desalination. However, it has some negative environmental impacts due to the chemical structure of those membranes. Hence, other material options with low surface energy can have great relevancy in fabricating nanofibrous membranes. The authors claimed that the silica aerogel and polydimethylsiloxane (PDMS) can be investigated as the promising options. A new high flux membrane with a reasonable nonwettability performance was prepared by electrospraying technique of aerogel/PDMS/PVDF over electrospinning PVDF-co-hexafluoropropylene membrane. The obtained surface contact angle for the best membrane sample containing the 30% aerogel was measured at ~170°, while the LEP value of 129.5 ± 3.4 kPa was achieved. The new membrane could be used in the desalination experiment for almost 7 days, continuously.

Only a few research groups have used the electrospun membranes for MD processes until 2014. These researches were comprehensively reviewed by Tijing and coworkers [157]. In another review paper, Shirazi and coworkers [33] also reviewed the published literature covering the fabrications and applications of the electrospun membranes from 2014 to 2017. Since then, a progressive trend has been observed for the preparation and application of the nanofibrous membranes via electrospinning for water treatment using the MD processes. **Table 7** summaries some other examples of recently published works for the application of the electrospun membranes in the MD processes.

To apply in the MD process, an electrospun nanofibrous membrane should be able to retain separation between the process liquid and the permeate product. Therefore, a hydrophobic or even a superhydrophobic membrane will be effective as it is considered to be the most efficient option for the water treatment applications [161]. Among different polymers, PVDF is the most investigated option for fabricating the electrospun nanofibrous membrane. This is due to the proper process ability of this polymer, mostly for membrane fabrication. Both beaded and bead-free nanofibers have been investigated for MD-based water treatment using the electrospun membranes. Surprisingly, beaded nanofibers showed a lower surface energy value (i.e., higher hydrophobicity), while the permeate flux from the smooth nanofibers was much better than that from the beaded nanofibers [162, 163]. More studies on new polymers for fabricating superhydrophobic electrospun membranes are needed, such as thermoplastics and elastomeric polymers that possess better mechanical strength.

3.3 Electrospun membranes for other applications

Mixing an immiscible or a nonsoluble liquid in another liquid can form emulsions or colloidal suspensions. Oily wastewaters can be investigated in this field [164]. In both of these mixtures, the dispersed liquid can form small and fine droplets, even with diameter of a few microns. Therefore, the proposed emulsion cannot easily be separated with the conventional techniques. An alternative for separation of oily wastewater is the coalescing filtration. However, conventional coalescers cannot efficiently separate the dispersed emulsions with diameter less than 1 μm. It is reported in the literature that the nanofibrous coalescing filters can promisingly separate the oily wastewater samples [165, 166].

Year	Configuration	Electrospinning	MD membrane	Performance	Reference
2018	AGMD	• Polymer: PVDF (Mw: 275 kg/mol) • Solvent: DMF & acetone • Dope: 15 wt.% • Voltage: – • Needle: 18 G • Dope injection: 0.2 ml/h • Tip-to-collector: 150 mm	• Pore size: 0.4–0.5 μm • Contact angle: 127–153° • LEP: 15–25 psi • Porosity: 83–90%	• Flux: 19.3–22.5 LMH • Rejection: >90%	[158]
2018	DCMD	• Polymer: PVDF (Mw: 275 kg/mol) • Solvents: DMAc & acetone • Dope: 25 wt.% • Voltage: 27 kV • Needle ID/OD: 0.6/0.9 mm • Dope injection: 1.23 mL/h • Tip-to-collector: 27.5 cm • Temperature: 23°C • Humidity: 36%	• Pore size: 509–945 nm • LEP: 7.9–17.4 kPa • Porosity: 77–92%	• Flux: 35–50 kg/m^2 h • Rejection: >99%	[159]
2018	DCMD	• Polymer: SBS (C540 Galprene) • Solvent: DMF-THF (75/25) • Needle: 22 G • Voltage: 1.0 kV/cm • Temperature: 21°C • Humidity: 43%	• Pore size: 0.58 μm • Contact angle: 132° • Porosity: 81%	• Flux: 11.2 L/m^2 h • Rejection: < 99%	[160]

Table 7.
Recent examples on the applications of the electrospun membranes for MD processes.

For example, Kulkarni and coworkers [167] studied on fabricating the polypropylene-based filter media with fibers in different sizes of 300–900 nm using electrospinning. The electrospun fibers were blended with microglass fibers to form filters with composite structure. The prepared composite filters were then used for liquid-liquid coalescing filtration. The effect of important parameters including fiber size and amount of electrospun polypropylene fibers on the wettability and filtration efficiency of the blended filters was measured. Results indicated that the amount and the fiber diameter of the electrospun polypropylene fibers affect the wettability and hydrophobicity of the filter samples. Both fiber density and fiber diameter were found as the effective parameters on the coalescing filtration and pressure drop. The authors concluded that the separation efficiency was more considerable for the thinner fibers with 300 nm diameter. Moreover, the pressure drop tended to increase with the fiber density and diameter.

Shirazi and coworkers [168] worked on the application of electrospun nanofibrous polystyrene filters for the treatment of oily wastewater in coalescing filtration. This work was carried out at a pilot scale. First, the authors studied on the effect of the thermal treatment of the fabricated filters on the fiber morphology. Next, the filters were studied for their oil-water coalescing performance. Results showed that the initial effect of the applied treatment started at 130°C, while 150°C was the maximum allowed temperature for the thermal treatment. More uniform

pore structure and smaller pore size were achieved for the treated membranes. Moreover, the thermally-treated filters showed better coalescing filtration efficiency.

The free oil in the wastewater effluent of edible oil mills can be investigated as a promising source for different applications. In another work, polystyrene microfilters have been used for recovery of the dispersed oil from wastewater using the coalescing filtration [169]. The obtained results confirmed that the recovered oil using coalescing filtration is a cheap and available source for economic biodiesel production.

Forward osmosis (FO) is an osmotic-pressure driven separation technique. In this process, a polymeric membrane with a selective semipermeable top layer is used to separate the water from dissolved solutes with high osmotic pressure gradient [170]. FO process has received a lot of attention over the past years. This separation technique works based on the difference in osmotic-pressure gradient of two solutions with different concentrations. The FO process can be applied as an individual separation process or in combination with other processes including MD or NF for various purposes such as the renewable power generation and desalination [171, 172].

The electrospun nanofibrous membranes can be used in the FO process. As one of the first attempts, Bui and coworkers [173] discussed that a number of reasons including the lack of suitable membranes with high solute rejection, acceptable mechanical strength, chemical stability, and more importantly the reasonable permeate flux can limit the applications of the FO process. The authors developed a new thin-film membrane with the composite structure. The membrane structure consists of a polyamide selective layer on top and an electrospun nanofiber support layer. The top selective layer was formed by the polymerization technique. Results indicated that the best membrane sample with the nanofibrous support layer provided higher water flux (2–5 times) and considerably lower salt flux (up to 100 times) than a commercial FO one. The authors concluded that using the thin-film membranes with composite structure and the electrospun support layer is a promising alternative for membrane separations and that the internal concentration polarization is the limiting parameter for the overall performance.

In another work, an electrospun PVDF-based nanofiber filter is used as the substrate to fabricate an efficient FO membrane with high water flux. In this study [174], the interfacial polymerization technique was applied for fabricating the polyamide ultrathin top layer directly on the electrospun support layer. Results indicated that different selective layers were formed on the nanofibrous scaffold including a low permeable layer, which was denser, and a layer with higher permeability, which was looser. The authors discussed that the proposed differences attributed to the substrate structures, which can cause the different cross-linking degrees for the interfacial polymerization. The fabricated membranes were then used for examining the FO performance. The water flux was measured at about 30.4 LMH when the 1.0 M NaCl draw solution was used. At the same time, the reverse salt flux ratio was constant, i.e., 0.21 g/L. The authors concluded that it was a remarkable achievement for the potential of electrospun nanofibrous web applied as the scaffolds for fabricating the FO membranes.

Recently, Huang and coworkers [175] studied the fabrication of a multilayered polyamide membrane through the interfacial polymerization technique on the electrospun polyethersulfone scaffold. Results indicated that the membrane fabrication conditions were optimized for the morphology and water flux. It is discussed that the polyethersulfone concentration had considerable effect on the membrane features including thickness, nanofiber diameter, and the morphology of the electrospun scaffolds. The membrane characteristics including the hydrophilicity,

mechanical strength, and thickness enhanced with the polymerization cycles. The optimized FO membranes were then compared with the commercial ones. Results showed that higher selectivity and water flux can be achieved by the new FO membranes.

4. Summary and perspectives

Over the past years, the electrospun nanofibrous membranes established themselves as a worldwide acknowledged filtering media for various applications. The distinctive specifications of nanofibrous membranes, including high porosity (up to 90%), three-dimensional interconnected pore structure, and functionability, make them highly promising and appealing for both academic researchers and industrial R&D applications. It is predicted that the global market for electrospun nanofibers will be projected up to 4.3 billion DUS by 2023 [176]. More and more R&D centers are putting effort on industrialization of electrospun nanofibrous membranes. Thus, adaptations and modifications will be expected in coming years for a large-scale market of electrospun membranes for the water treatment applications.

Despite the highlights of the electrospun nanofibrous membranes, there are a few bottlenecks that affect the membrane morphology and structure. These issues should be considered in the future researches including microcracking and temperature-induced issues; commercialization in industrial scale; fabrication of membranes with uniform pore size distribution; use of proper materials to introduce the desired functionality; and optimization of the electrospinning process with beneficial separation processes. Using multifunctional electrospun membranes not only can be investigated for improving the physical features and mechanical strength of the electrospun membranes but also can enhance their antifouling properties [177]. New polymers such as polystyrene, SBS (styrene-butadiene-styrene), SEBS (styrene-ethylene-butylene-styrene), etc. are promising options for fabricating electrospun membranes.

Productivity of the nanofibers via electrospinning is another crucial challenging barrier in the way of the industrialization of the water treatment membranes. New strategies such as electroblowing and gas-assisted electrospinning can be afforded to enhance the nanofiber productivity [178].

Furthermore, there are some other applications that should be investigated more for future progresses. More analysis can be carried out for the application of the nanofibrous membranes as the scaffold in thin-film membranes with composite structure for UF, NF, and FO, as well as PRO (pressure-retarded osmosis) processes. In case of the MD process, superhydrophobic membranes are required. In this regard, multifunctional electrospun membranes with considerably low surface energy can be beneficially used. Moreover, in all the mentioned membrane processes for the proposed water treatment applications, the lifetime and the physicochemical durability must be two of the foremost issues of the future researches while fabricating the nanofibrous membranes by the electrospinning technique.

Although electrospun nanofibrous membranes are beneficial for these membrane processes, they can be also used in other applications including cosmetic products, healthcare issues, material composites, and aerospace engineering, as well as air/gas filtration purposes [179, 180]. There are still many subjects that should be issued to improve new developments in the applications of electrospun nanofibers. The water treatment sector looks to be, however, the most favorable application for the electrospun membranes.

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