CHAPTER

ELECTROSPINNING: A VERSATILE FABRICATION TECHNIQUE FOR NANOFIBROUS MEMBRANES FOR USE IN DESALINATION

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1 INTRODUCTION

Water scarcity is mainly caused by increasing demand in industrial and agricultural areas. Studies have recently suggested that 1.3 billion people have limited access to safe and hygienic drinking water, 2.6 billion people have little or no sanitation, and every year millions of people die from diseases transmitted through unhygienic water. Thus, novel technology and innovation are required to enable desalination, water reclamation, and wastewater treatment. Recently, nanotechnology combined with nanoengineered materials has offered great potential for advancing desalination and wastewater treatment technologies. In response to these challenges, the electrospinning process for producing nanofibrous membranes has emerged as an efficient technology for fabricating durable and potential membranes for water treatment and advanced desalination [1, 2]. In this chapter, the development of an electrospun nanofibrous membrane through surface chemistry modification is discussed, and potential approaches for producing efficient electrospun nanofibrous membranes are explored. Fig. 1 shows some crucial advantages of the electrospinning technique and its potential for fabricating the desired electrospun nanofibrous membranes.

1.1 HISTORY OF ELECTROSPINNING TECHNIQUE

Studies on the electrospinning process began during the 19th century. Rayleigh (1897) initially demonstrated the process, and it was studied in detail by Zeleny [2a]. During the 1930s, Formhals developed an experimental setup for producing artificial filaments using electric charges, which was finally patented as a viable fiber-spinning technique [3]. Subsequently, Taylor, Saville, Denn, and other researchers demonstrated electrically driven jets and laid the groundwork for the electrospinning research that began in late 1964 [4, 5]. Through extensive nanotechnology research and development (R&D), researchers are examining the electrospinning process from a new perspective. Table 1 shows

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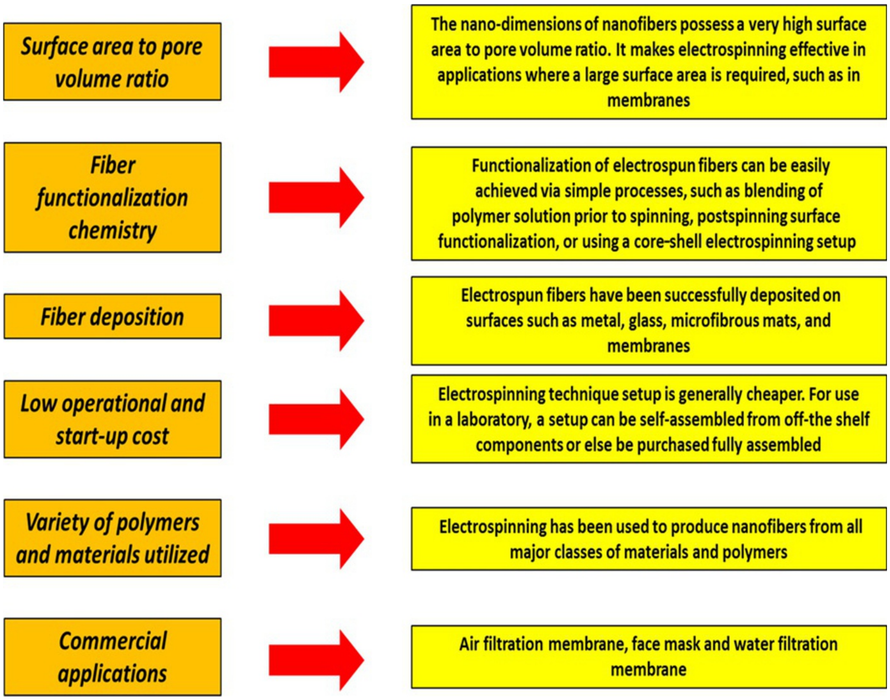

FIG. 1

Unique features of the electrospinning techniques used for fabricating membranes, which enable a high surface area to volume ratio, the use of different polymers and materials, low start-up costs, fiber deposition onto other substrates, fiber functionalization, and commercial applications.

Table 1 Important Milestones in Electrospinning Technology

Year	Progress of Events	References Used
1897	Electrospinning technique was first demonstrated by Raleigh	[6]
1914	Zeleny has studied further on electrospraying technique	[7]
1934	Formhals patented the electrospinning process. (Between 1934 and 1944, patents were published by Formhals)	[3]
1944–2004	About 50 patents were published on electrospinning technique.	[6]
1950–70	Taylor laid the groundwork by his research on electrically driven jets	[5, 8]
1966	Simons patented an apparatus for generation of nonwovens with different patterns using electrical spinning process	[9]
1980s	The electrospinning technique gained more attention because of interest in nanotechnology and an increase in the use of ultrafine nanofibers and fibers in submicron scale	[10]
1981	Larrondo and Manley investigated the electrospinning technique using molten polymeric solution	[11]
1990–2000	A high number of research activities are going on in this field, especially after the advancements of electrospun nanofibers in applications, including composite membrane, tissue engineering, and energy storage.	[12, 13]
2000–10	Research work is also focused on upscaling and on extending the application areas of electrospun nanofibers and nanofibrous membranes	[14, 15]

Research related to electrospinning technology and electrospun nanofibers has gained momentum, especially from early 2000.

some important milestones in the R&D of electrospinning techniques. Apparently, there is a great increase in the R&D of electrospinning techniques. This increase in R&D can be attributed to nanoengineering and nanotechnology gaining more attention, which can easily be determined from the number of publications in this field, especially from 2005 to 2015 [16]. Furthermore, ultrafine nanofibers can be easily produced through electrospinning. The objective in almost all the studies has been to use this technique in a wide range of applications.

1.2 BACKGROUND

Electrospinning is widely used for the electrostatic generation of nanofibers, during which polymeric nanofibers with diameters ranging from 2 nm to a few micrometers are fabricated from various polymeric solutions or polymer melts under high voltage. Compared with conventional technologies, electrospinning is a highly versatile and efficient process.

Electrospinning is the simplest way of fabricating nanofibrous materials, but there are some important parameters that can have a significant impact on the formation and structure of generated nanofibers. These parameters are categorized into (a) solution parameters, (b) process parameters, and (c) ambient parameters. Table 2 summarizes the important parameters, which are discussed in a later section of this chapter.

Electrospun nanofibrous membranes have been used for direct filtration. In addition, electrospun polymeric interconnected webs can be used as porous support layers in thin-film composite (TFC), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), and membrane distillation (MD) membranes. Typically, TFC membranes consist of three layers, including the top ultrathin rejection layer, a middle porous supportive layer, and a bottom nonwoven fabric layer [19]. The application of electrospun nanofibrous materials as a porous supportive layer for TFC membranes has recently gained attention. Between 2010 and 2015, the electrospinning process has attracted worldwide attention owing to its versatility in MD membranes [20, 21]. This chapter mainly focuses on the recent advancements in the field of nanofibrous membranes fabricated by electrospinning for use in MD membranes.

Table 2 Electrospinning Process Parameters

Parameters	Factors to be Considered
Solution parameter	➢ Viscosity ➢ Solution concentration ➢ Molecular weight of the polymer ➢ Solvent properties ➢ Surface tension ➢ Conductivity
Processing parameter	➢ Voltage applied ➢ Distance of the electrode from the collector ➢ Flow rate ➢ Capillary geometry
Ambient parameter	➢ Temperature ➢ Relative humidity

Process advancements achieved by controlling these parameters have led to the fabrication of uniform, nanofibrous membranes [17, 18].

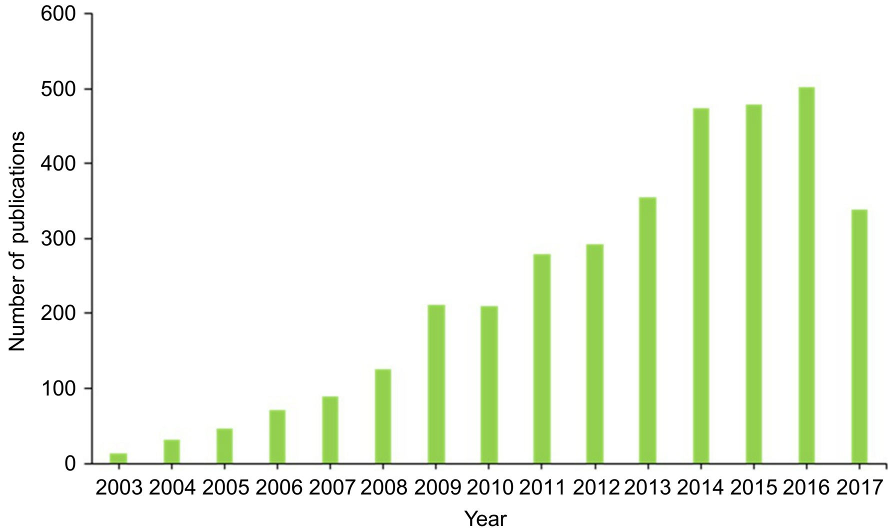

FIG. 2

Comparative study of peer-reviewed publications since 2003. (Analysis of publications was conducted using the Scopus scholar search system with the terms "Electrospinning" and "Membrane" during July 2017.)

The electrospinning process has recently regained considerable attention, probably because, owing to the advancements in nanotechnology. Ultra-fine nanofibers or nanofibrous microstructures with fibers of various diameters can be easily produced using this technique (i.e., electro + spinning) with different polymers [22]. In this chapter, a detailed survey of peer-reviewed publications relating to electrospinning and membranes from the past 15 years is presented (Fig. 2). In addition, the contributions of different countries to research on electrospinning, in terms of published articles, are shown in Fig. 3; interestingly, China leads the table according to the Scopus database. Data from Scopus indicate that electrospinning has attracted considerable attention in recent years. The data suggest that several hundred natural and synthetic polymers that can be dissolved using the appropriate solvent through heating or melting are available. Table 3 provides the polymeric solutions used for fabricating electrospun nanofibrous membranes.

2 FUNDAMENTALS OF ELECTROSPINNING TECHNIQUE

The need for cost- and energy-efficient purification technologies has resulted in increased attention on nanostructure membranes fabricated through electrospinning. Electrospinning is an efficient technique that enables control over the fiber diameter, thickness, arrangement, and microstructure. As shown in Fig. 4, electrospinning techniques typically require three main components: (a) a high voltage supply, (b) a capillary tube with needles, and (c) a metal collecting screen or roller [28, 29]. In this process, high voltage is used to eject an electrically charged jet of polymer solution out of the pipette; just before reaching the metal collector, the polymeric solution jet evaporates and solidifies, and finally it is

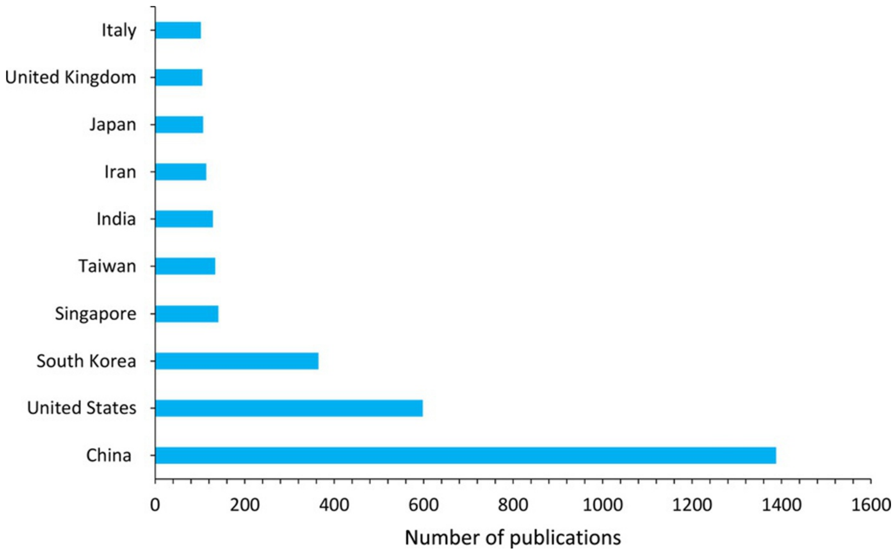

FIG. 3

Graphical representation of the contribution of various countries in the field of electrospinning technique (Data were obtained from the Scopus scholar search system with the terms "Electrospinning" and "Membrane" during July 2017.)

Table 3 Common Polymers and Their Appropriate Solvents

Polymer Name	Solvent
Polymetylmethaacrylate (PMMA)	✓ Chloroform ✓ Acetone ✓ Tetrahydrofuran (THF)
Tetrahydroperfluorooctylacrylate (TAN)	✓ Dimethyl formamide (DMF) Toluene
Polyvinyl alcohol (PVA)	✓ Distilled Water
PVA/cellulose nanocrystals	✓ Distilled Water
Polyvinyl phenol (PVP)	✓ Tetrahydrofuran (THF)
Polyvinylchloride (PVC)	✓ THF ✓ Dimethyl formamide (DMF)
Polyvinylcarbazole	✓ Dichloromethane
PVDF-*co*-hexaflurorpropylene (PVDF-*co*-HFP)	✓ Acetone ✓ DMF
Polyacrylonitrile (PAN)	✓ DMF
Polylactic acid (PLA)	✓ Chloroform ✓ DMF
Polyethylene oxide (PEO)	✓ Distilled water
Poly(vinylidene fluoride) (PVDF)	✓ DMF

This table indicates the polymeric solutions used in electrospinning technology for application in wastewater or desalination technologies [23–25].

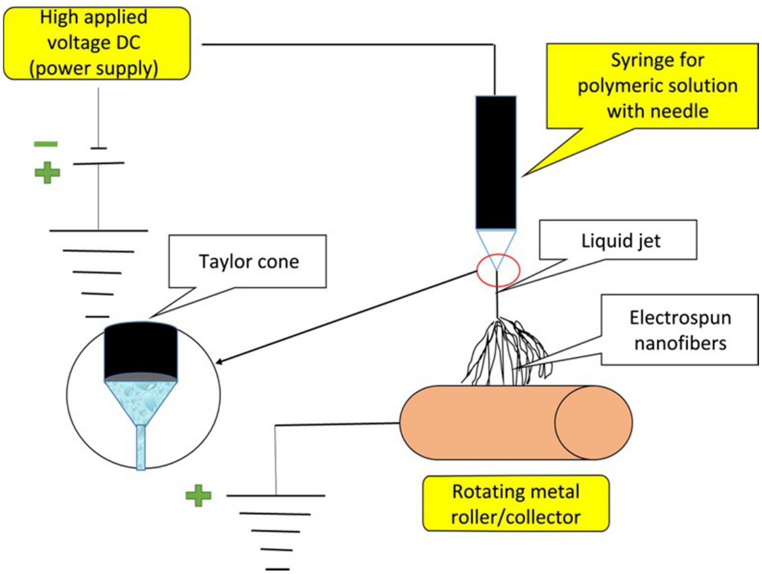

FIG. 4

Schematic of electrospinning process. The setup consists of three components: (1) a high voltage supply, (2) a syringe or capillary tube with needles, and (3) a metal collecting screen and roller [26, 27].

collected as an interconnected web of nanofibers. The electrical field at the tip of the needle typically electrifies the surface of the polymeric droplet located on it. Repulsive forces between the electrical charges present at the surface and their attraction to the oppositely charged electrode yield a force that overcomes the surface tension. Consequently, a charged jet is ejected from the tip of the needle, and because of the repulsion between the electric charges in the jet, it undergoes bending instability, resulting in elongation and thinning. Meanwhile, the evaporation of the solvent results in the formation of charged polymer nanofibers that are collected as an interconnected web on the metal collector. The resulting interconnected web is composed of randomly aligned nanofibers; it resembles a nonwoven nanofibrous membrane [30, 31].

2.1 DIFFERENT ELECTROSPINNING CONFIGURATION

The configuration of the feeding system that ejects the polymeric solution determines the actual composition of the electrospun nanofibers. Tailored products can be obtained as follows:

- Single spinneret: By using a single spinneret, single-component nanofibers can be produced from a homogeneous polymer solution, and multicomponent nanofibers can be electrospun from emulsions and blends.
- Coaxial spinneret: In this technique, two different solutions flow through two coaxial syringes or capillaries, resulting in a core-shell morphological structure.
- Multispinnerets: Membranes made up of different types of nanofibers can be generated by electrospinning different polymeric fluids from different spinnerets [7].

Many researchers have used the single-spinneret configuration for electrospinning. However, a low polymeric-fluid throughput has limited the industrial application of the single spinneret configuration. To increase the fluid throughput, various multijet schemes have been analyzed. Theron et al. developed a model that, under comparable conditions, can be used to steadily electrospin about nine jets from separate nozzles with a pitch of 10 mm positioned on a square of 400 mm^2 [32]. However, Yarin et al. demonstrated a novel approach by employing a ferromagnetic liquid sublayer that generates >2 jets/cm^2. In this case, electrospinning should be initiated with a high applied voltage of approximately 32 kV, and the fiber diameter range is 200 to 800 nm [33]. In addition, Yang et al. [34] showed that electrospinning with needles positioned at different heights is more stable than that with a ring arrangement and that the stable electrospinning voltage for the ring arrangement is considerably higher than that for needles at different heights [34]. In this chapter, advancements in electrospinning technique, such as free-surface electrospinning, rotary electrospinning, and melt electrospinning, are discussed for the mass production of nanofibrous materials. Furthermore, a comprehensive review of the effects of governing parameters on electrospinning techniques and the morphology of nanofibers is presented.

2.1.1 Free-surface electrospinning

Despite promising results, the configuration of free-surface electrospinning multineedle processes is technically inconvenient, owing to the possibility of clogging or blockage. Furthermore, using needles for electrospinning, which is termed capillary spinning, yields a low throughput of nanofibers. Therefore, electrospinning systems that do not use spinnerets have been developed. Typically, this type of electrospinning technique is termed needleless electrospinning or free-surface electrospinning. Many researchers have investigated the free-surface electrospinning technique [33, 35–37]. According to the principle, multiple self-organized electrically driven jets can be obtained from planar and cylindrical surfaces by applying very high voltage electrical fields. Recently, experimental studies have indicated high production rates of nanofibers on an industrial scale through free-surface electrospinning by using viscoelastic polymeric fluids. Furthermore, Thoppey et al. showed a new needle-free electrospinning configuration using an edge-plate geometry [38]. They demonstrated that this technique can be used directly to produce high-quality nanofibrous material from an unconfined polymeric solution without the possibility of blockage or clogging. In addition, they reported that the production rate of the edge-spinning apparatus is 5 times higher than that of a basic needle-based electrospinning system [38].

Therefore, the needle-based electrospinning technique has resulted in the generation of new nanofibrous membranes with a broad array of applications, such as purification, nanocomposites, and membrane fabrication. Conventionally, the production rate of the electrospinning technique for nanofibers with small diameters is rather low. Thus, the use of electrospun nanofibrous materials is limited to low-volume applications. To solve this throughput problem for electrospun nanofibrous materials, several variations of the free-surface electrospinning technique have been proposed.

2.1.2 Melt electrospinning

Melt electrospinning is a technique used to generate nanofibrous microstructures from polymer melts for applications in nanocomposites, textiles, and membrane filters. However, this electrospinning technique has not attracted much attention. The prominent reasons for this are (a) difficulty in controlling the viscosity of polymer melts compared with conventional polymeric solutions, (b) large diameters (at the micron scale) of formed nanofibers, and (c) nonconductive characteristics of polymer melts. In the initial studies on this topic, Larrondo and St John Manley [39] have mentioned the melt electrospinning technique as part of a three-paper series on electrostatics and polymeric melts. However, because its fiber throughput is higher than that of the solution electrospinning process, interest in melt electrospinning has been prominent only during the past 5–6 years [40].

Zhou et al. studied the melt electrospinning technique in detail. Typically, most of the melt electrospinning processes use polymeric solutions that are difficult to electrospin at room temperature (e.g., polyethylene (PE) and polypropylene (PP)). Hence, temperatures in excess of 150°C are employed. However, the use of high temperatures can result in the degradation of polymers during melt electrospinning [41]. Moreover, melt electrospinning can generate high fiber throughputs without the use of solvents, which reduces the apparatus cost as ventilation equipment are no longer necessary [41].

2.2 CHARACTERIZATION OF ELECTROSPUN NANOFIBROUS MATERIALS

Membrane performance can be directly examined through characterization [42]. Knowledge of membrane material, specifications, structure, and morphology is crucial for various applications [43]. The surface characterization of the membrane is the second stage and follows the adjustment of the electrospinning parameters during the design and development of electrospun nanofibrous membranes [44].

Basic structural characterization techniques are divided into two main classes, covering a wide range of physical methodologies. The first class includes techniques related to membrane permeation analysis, such as liquid and gas flow tests, liquid displacement methods, and solute transport methods. The second class includes all the methods that can measure the surface morphological characteristics of membranes. Table 4 lists all the characterization techniques used for basic structural and morphological analysis.

Table 4 Characterization Techniques for Basic Structural and Morphological Analysis

Class of Methodologies	Methodologies or Techniques
Physical methodology	✓ Liquid and gas flow tests ✓ Liquid displacement method ✓ Solute transport method ✓ Membrane permeability
Morphological methodology	✓ Scanning Electron Microscopy (SEM) ✓ Energy dispersive spectroscopy (EDS) ✓ Transmission Electron Microscopy (TEM) ✓ Field Emission Scanning Electron Microscopy (FE-SEM) ✓ Atomic force microscopy (AFM) ✓ Nuclear magnetic resonance (NMR) ✓ X-ray diffraction (XRD) ✓ Fourier transform infrared spectroscopy (FT-IR) ✓ Confocal microscopy ✓ Raman spectroscopy ✓ Contact angle measuring device

These techniques are broadly divided into two categories: physical methods and morphological analysis methods.

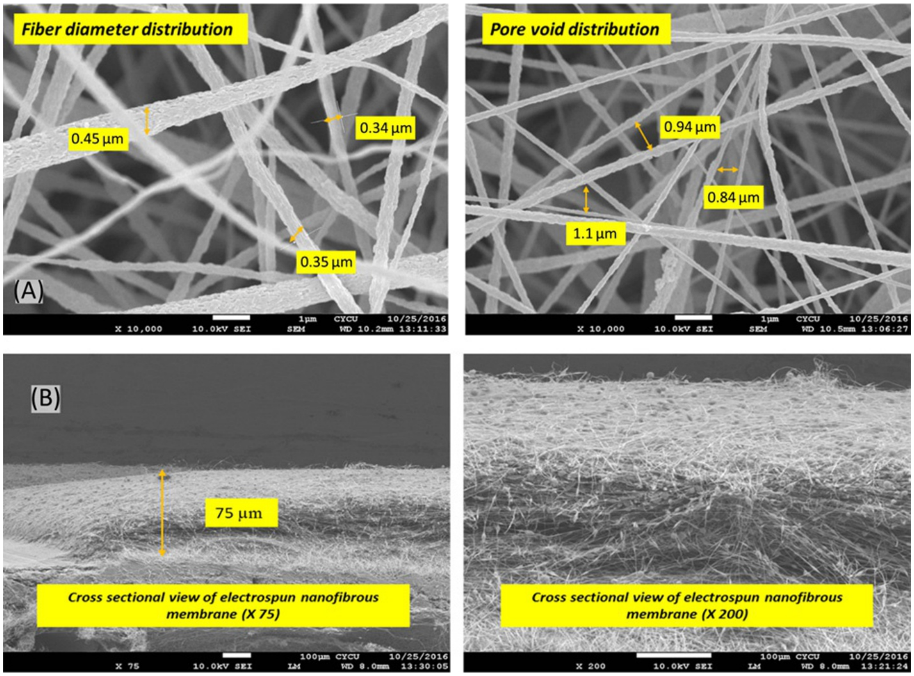

FIG. 5

(A) SEM micrographs of electrospun nanofibrous polysulfone layer indicating the pore void and fiber diameter. (B) The next figure shows the cross-sectional view of the electrospun nanofibrous polysulfone layer. The pore void, fiber diameter, and thickness of the layer can be easily analyzed using the image analysis software ImageJ2x.

The previously mentioned methodologies are used to measure characteristics such as pore size, pore size distribution, fiber diameter, surface roughness, hydrophilicity or hydrophobicity, chemical composition, elemental structure, membrane fouling potential, and morphological structure. Among all the characteristics of electrospun nanofibrous microporous membranes, the most critical for determining the applicability of the membrane in a specific liquid separation process are its pore size, surface morphology, and hydrophilicity or hydrophobicity. Fig. 5 shows the typical morphological structure of an electrospun nanofibrous polysulfone membrane.

3 PROCESS OF ELECTROSPINNING TECHNIQUE

Electrospinning is the most suitable technique for the fabrication of nanofibrous materials. The advantages include its relative ease, high speed, low cost, versatility, and large materials selection. In addition, the technique enables control over pore size, fiber diameter, and arrangement [45, 46]. The operational parameters of electrospinning must be understood because they affect fiber morphologies and microstructure. In general, the key parameters governing electrospinning techniques are

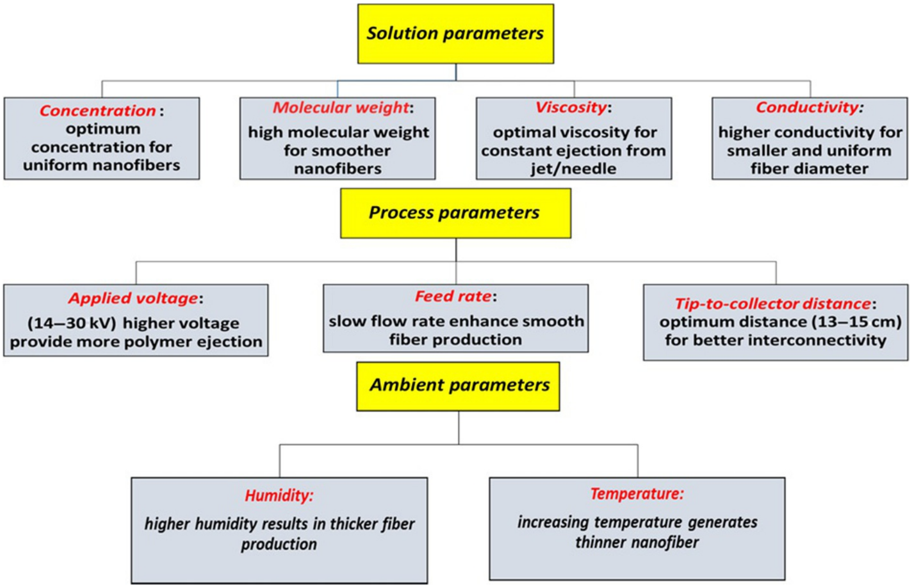

FIG. 6

Electrospinning process parameters. The most crucial parameters governing the electrospinning process are (1) polymer solution parameters, (2) process parameters, and (3) ambient parameters.

(1) polymer solution parameters, (2) process parameters, and (3) ambient parameters. Fig. 6 shows the parameters that may affect electrospinning, along with a brief description of the optimal conditions required for fabricating high-performance electrospun nanofibrous membranes.

3.1 POLYMER SOLUTION PARAMETERS

The preparation of the polymeric solution is the most important part of the production of an electrospun nanofibrous membrane; the factors that influence this step include the concentration and average polymeric weight of the polymer and the type of solvent used for dissolving the polymer pellets. The properties and preparation of polymeric solution are discussed thoroughly in the following sections.

3.1.1 Concentration of polymeric solution

The concentration of the polymeric solution plays a key role in nanofiber formation during the electrospinning process. As the concentration increases from low to high, the following four critical stages must be noted:

(a) At very low polymer concentrations, polymeric micro- (nano)particles are obtained. At this stage, electrospraying takes place instead of electrospinning because of the low viscosity and high surface tension of the polymeric solution.

(b) When the polymer concentration increases slightly, a mixture of bubbles with beads and fibers is obtained.

(c) As the polymer concentration reaches the optimum level, smooth nanofibers are obtained.
(d) When the polymer concentration is very high, helix-shaped microribbons are observed.

Thus, the fiber diameter increases with the polymeric concentration of the solution. In addition, the viscosity of the solution can be also tuned by adjusting the polymeric concentration [47–50].

3.1.2 Molecular weight

The molecular weight of the polymer influences the morphologies and microstructures of electrospun nanofibers. In general, the molecular weight of the polymer reflects the degree of entanglement of the polymeric chains in the solution (i.e., it indicates the solution viscosity). Keeping the solution concentration constant and reducing the polymeric molecular weight results in the formation of beads rather than smooth nanofibers. Thus, using polymers with a high molecular weight produces smooth nanofibers. However, further increasing the molecular weight yields a microribbon structure [51].

3.1.3 Viscosity

The solution viscosity is crucial for determining the microstructure and morphology of the fibers. Many researchers have proved that continuous and smooth nanofibers cannot be produced from solutions with very low viscosity, whereas very high viscosity makes it difficult to eject jets from the solution; thus, there is an optimum viscosity for electrospinning [39]. The viscosity of a solution can be changed by adjusting the polymeric concentration of the solution. Crucially, solution viscosity, polymeric concentration, and molecular weight are related. In fact, for a solution with low viscosity, surface tension is the dominant factor, and thus, beads or beaded nanofibers are obtained. Therefore, continuous nanofibers can be produced from a solution with optimum viscosity.

The polymeric solution used for electrospinning should possess sufficient viscosity to be stretched into nanofibers. Typically, the entanglement number of a polymeric solution can be used to analyze the formation of nanofibers through electrospinning; the entanglement number can be written mathematically as

$$(ne)\text{solution} = \frac{Mw}{(Me)\text{solution}} = \frac{\phi p.Mw}{(Me)},$$

where ne represents the entanglement number, Mw is the molecular weight, Me is the solution entanglement molecular weight, and ϕp is the polymer volume fraction.

Studies have demonstrated that when the entanglement number is higher than 3.5 and a suitable solvent is used, smooth nanofibers are obtained for polystyrene, polylactic acid, and polyethylene oxide. Notably, for $2 < ne < 3.5$, a mixture of beads and nanofibers are formed, and for $ne < 2$, no fibers are obtained [52].

3.1.4 Surface tension

Surface tension is a function of the solvent compositions of the solution, which is another important factor. Many researchers have found that different solvents may contribute different surface tensions. At a fixed concentration, decreasing the surface tension of the polymeric solution can yield smooth nanofibers. Furthermore, recent research has indicated that the surface tension and viscosity of a solution can be adjusted by changing the mass ratio of the solvent mixture [53, 54]. Typically, surface tension can be easily reduced by using various surfactants, but this may introduce impurities into the final electrospun polymeric nanofibrous membrane. Recent research shows that anionic surfactants, such as sodium dodecyl sulfate, not only reduce the surface tension of the polymeric solution but also introduce additional charge carriers to the solution, thus improving the quality of the nanofibers. This study had the dual function of lowering the bead formation and stretching to produce finer and smoother fibers [26, 27].

3.1.5 Surface charge density and conductivity

The conductivity of a solution is mainly evaluated by the type of polymer and solvent. Natural polymers are polyelectrolytic; that is, they have a low charge density in the solution, resulting in higher surface tension under an electric field and formation of poor-quality nanofibers. Furthermore, the electrical conductivity of the solution can be adjusted by adding ionic salts, such as KH_2PO_4 and NaCl [24, 55], and thus, nanofibers with a uniform fiber diameter can be produced. Furthermore, the electrical conductivity of a solution can be increased by adding an organic acid as the solvent [21].

3.1.6 Solvent volatility

Solvent volatility is another important aspect of a polymeric solution. If a polymer solution is prepared from solvents with very low volatility, wet nanofibers, fused nanofibers, or even negligible nanofiber may be produced. However, a highly volatile solution may result in intermittent spinning because of the solidification of the polymer at the spinneret tip [56, 57]. This layer may grow and choke off the spinning solution until and unless more polymeric solution has been injected to dislodge the solidified skin. Sometimes such electrospinning may produce artifacts on the surface of the membrane [58]. Thus, it can be concluded that using a highly volatile solvent for electrospinning results in flat or ribbonlike nanofibers or fibers with surface pores [59].

3.2 PROCESS PARAMETERS

Process parameters are very crucial for ensuring the conversion of polymeric solutions into smooth and fine fibers via electrospinning.

3.2.1 Applied voltage

When the applied voltage is higher than the threshold voltage, charged jets are ejected from the Taylor cone. However, the effect of the applied voltage on the diameter of electrospun nanofibers is debated. According to Reneker and Chun, applied voltage does not affect the diameter of electrospun polyethylene oxide (PEO) fibers significantly [60]. On the other hand, many researchers have shown that high applied voltages lead to larger fiber diameters. Few researchers have observed that high applied voltages can increase the electrostatic repulsive force on the charged jet, thus reducing the fiber diameter [54]. Furthermore, some research groups have shown that high applied voltages increase the probability of bead formation [61]. Therefore, it can be stated that applied voltage influences the fiber diameter, but the degree of influence varies with the polymeric solution concentration and depends on the distance between the tip and the substrate collector [62, 63].

3.2.2 Feed flow rate

The feed flow rate of the polymeric solution from the syringe or injector is another crucial process parameter. Many researchers recommend a low feed flow rate to allow sufficient time for polarization of the polymeric solution. When the feed flow rate is very high, bead nanofibers with a large fiber

Table 5 Process Parameters and Their Impact on Electrospinning

Parameters or Factors	Impact or Influences	References Used
Jet	The jet initiation is the overall combination of introducing electrical charges to the polymeric solution and subjecting it to a very high voltage	[17]
Voltage	Applied voltage results in stretching of the polymeric solution droplet which may increase with higher applied voltage. On the other hand, the high voltage may also lead to faster acceleration toward the metal plate collector because of the increased voltage, resulting in a shorter flight of time for the jet to stretch prior to deposition. Thus, this condition leads to larger fiber diameter	[66]
Feed rate	At the optimum feed rate, the distribution of fiber diameter will be the narrowest, and thus, any deviation may result in larger fiber diameter	[67]
Temperature	A higher solution temperature may reduce the solution viscosity. Therefore, it is expected that the fiber diameter will be decreased with reduced viscosity	[68]
Nozzle diameter	Typically, an increase in nozzle diameter increases fiber diameter, distribution, and productivity simultaneously. This is because of the higher amount of mass available for the electrospinning process	[58]

This brief information may assist researchers in adjusting and optimizing the conditions required to produce the desired electrospun nanofibrous membrane.

diameter are formed rather than smooth or fine nanofibers with a small diameter owing to the very short drying time prior to reaching the substrate collector and a low stretching force [61].

3.2.3 Distance from syringe tip to substrate collector (H)

It has been observed that the distance (H) between the substrate collector and the tip of the syringe may also affect the morphology and diameter of the fiber [64]. In general, when the distance (H) is very short, the fiber does not have enough time to solidify before reaching the substrate collector, whereas if the distance (H) is too long, beaded nanofibers are formed. Another important physical aspect of the electrospun nanofibers is dryness, and therefore, optimum distance is required. Yuan et al. also observed that a slightly large distance (H) favors the formation of thin fibers [65]. Table 5 lists the important process parameters of electrospinning.

3.3 AMBIENT PARAMETER

Ambient parameters such as humidity and temperature may also affect the fiber diameter and microstructure. According to Mit-uppatham et al., high temperatures favor the formation of thin fibers [56, 57]. Furthermore, low humidity may dry the solvent and accelerate solvent evaporation. On the other hand, high humidity will result in a large fiber diameter. Recently, Casper et al. demonstrated that variations in humidity may affect the surface microstructure and morphology of electrospun nanofibers [69]. This phenomenon can be explained on the basis of rapid precipitation of the polymeric solution when water condenses on the surface of the electrospinning jet; in particular, high humidity prevents the elongation or stretching of the polymeric solution, thus leading to the formation of thick nanofibers. Interestingly, lower humidity may also result in faster solvent vaporization and lead to a larger fiber diameter because of an increase in the solidification rate, whereas for some polymers, higher humidity

Table 6 Summary of Effect of Humidity on Fiber Diameter in Electrospinning Process

Relative Humidity	Impact on Fiber Diameter	Explanation of the Effect
Higher	Increase	Precipitation effect can be observed especially for water-insoluble polymers
Higher	Decrease	Water absorption resulting in reduction of concentration especially for water-soluble polymers
Lower	Increase	Rapid solvent vaporization takes place
Lower	Decrease	Decrease in precipitation effect

The electrospinning process is highly affected by the ambient temperature and relative humidity owing to the effect of solvent vaporization rate and solution sensitivity to humidity, including the ability to produce nanofibers, uniformity in fiber diameter, and smoothness, porosity, and surface morphology of fibers [70–72].

has been shown to reduce fiber diameter [70]. Functionality and performance of the resultant fibers can also be affected by the ambient parameters, depending on the materials and additive used. Table 6 shows the effects of relative humidity on fiber diameter.

4 ELECTROSPINNING METHODOLOGIES

Electrospun nanofibrous membranes are fabricated by incorporating chemical groups or by surface modification. In this section, different types of fabrication and surface modification techniques that may aid future research in water purification and desalination technology are discussed.

4.1 LAYER-BY-LAYER TECHNIQUE

The layer-by-layer technique is based on the adhesion of positively, as well as negatively, charged macromolecules on the surface of the desired material. The advantage of this method is that the functional groups of the layers can be chosen such that either a single property can be improved or multiple properties can be introduced. The high surface area of electrospun nanofibrous membranes has motivated researchers to explore the possibility of constructing highly efficient membranes for water purification and desalination technology. Although layer-by-layer coating is most often carried out by the use of alternately charged organic molecules, positively charged inorganic nanoparticles may also be coated on negatively charged organic molecules (e.g., polyacrylic acid). Coating nanoparticles on the surface of a nanofiber increase its surface roughness, and a final coating of fluoroalkylsilane can be used to fabricate a superhydrophobic material [73]. Owing to its negatively charged surface, cellulose acetate is one of the attractive materials for the layer-by-layer technique. However, to start the process, the surface of the material must be activated by chemical incorporation. Subsequent introduction of alternately charged molecules is used to form the layers. Both charged organic molecules and inorganic chemical groups are used in electrospun nanofibers [21]. Fig. 7 shows the layer-by-layer technique and how it can be used for producing various membranes for water purification and desalination technology.

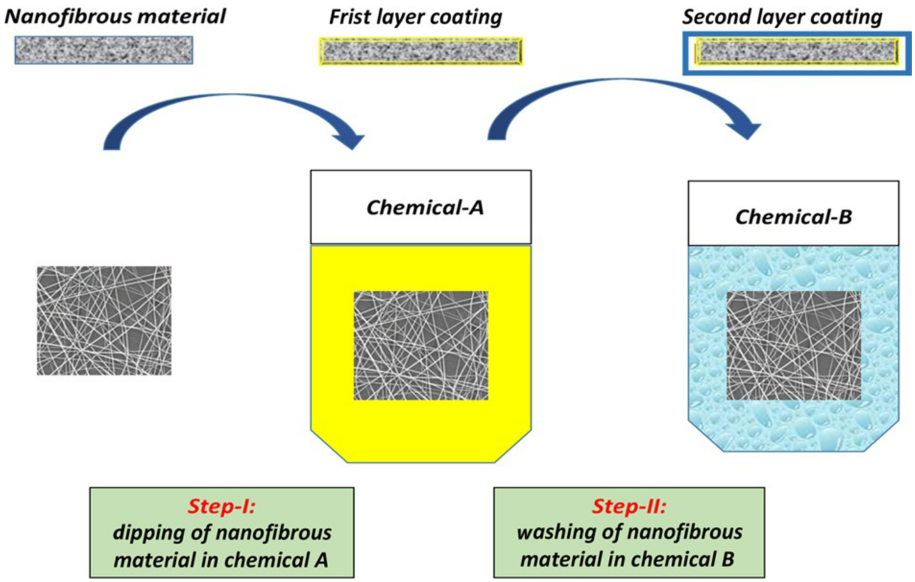

FIG. 7

Layer-by-layer method for functionalization of electrospun nanofibers. This technique can be used to improve a single property or to introduce multiple properties in the desired electrospun nanofibrous material.

4.2 FUNCTIONALIZATION OF ELECTROSPUN NANOFIBERS

Functionalization offers additional features to a single material nanofiber. A material with superior mechanical strength or chemical stability may be incorporated with other desirable properties such as antibacterial effects, biocompatibility, and catalytic or chemical sensing. Introducing additional functional properties to the nanofiber enhances its performance and versatility that can be tailored to specific applications. Table 7 lists various techniques of functionalization with varying degrees of versatility. The functionalization methods may be used together to create multifunctional nanofibers.

4.3 SOLUTION BLENDING METHOD

The solution blending method is one of the most commonly used techniques for introducing an alternative property or function to the base material. This method involves mixing two parts in a solution followed by electrospinning. In many experiments, the blending process is used where the desired material is unable to form nanofibers and, therefore, a companion electrospinnable polymer is used. Basically, colloids, where one part is nonsoluble, such as carbon nanotubes, silica particles, and hydroxyapatite, are suspended in the solution and electrospun to form nanofibers [74]. The other, more commonly incorporated materials are polymers and soluble inorganic salts. Three blending schemes are commonly encountered: the first scheme uses materials that are soluble in a common solvent, the second scheme uses different solvents for both materials, and the third scheme uses insoluble materials, as mentioned earlier. Given the potentiality of solution blending, combinations of the three schemes can be used in nanofiber electrospinning.

Table 7 Functionalization Methods and Their Application Based on Mechanical Properties, Reactivity, and Material Chemistry

Functionalization Method	Location	Improve Mechanical Properties	Reactive/ Functional Groups	Material Chemistry
Blending	Bulk	Yes	Yes	Yes
Plasma treatment	Surface	–	Yes	Yes
Wet chemical treatment	Surface	–	Yes	Yes
Adhesion	Surface	–		Yes
Direct covalent bonding	Surface	–	Yes	Yes
Layer by layer	Surface	–	Yes	Yes
Multicomponent electrospinning (e.g., core-shell)	Core/ surface	Yes	Yes	Yes
Mineralization	Surface	Yes	–	
Sol-gel coating followed by sintering	Surface	–	–	Yes
Inorganic catalytic deposition	Surface	–	–	Yes

Reactive functional groups indicate the presence of carboxyl or amino groups for further bonding of other molecules, whereas material chemistry indicates the possibility of adding secondary group(s) to the principal fiber material.

4.4 WET CHEMICAL TREATMENT

In this technique, the relatively inert polymer nanofiber is treated with a chemical in order to introduce reactive functional groups such as carboxylic (—COOH), amine (—RNH_2), or hydroxyl (—OH) groups, depending on whether the sites on the polymer molecule are susceptible to electrophilic or nucleophilic attack. The nanofibrous material is soaked in an alkaline medium to create a carboxylic or hydroxyl group on the nanofibrous surface. Table 8 lists some chemically treated electrospun fibers and their respective generated activated groups. Moreover, a basic pictorial representation of the wet chemical treatment is shown in Fig. 8, which can be used for the functionalization of electrospun nanofibrous membranes.

5 DESALINATION USING ELECTROSPUN MEMBRANE

Microporous polymeric membranes can be fabricated by various techniques, including phase inversion, film lithography, and stretching [81, 82]. Nevertheless, each method has its advantages and disadvantages [83]. Recently, the electrospinning process has also been explored for the production of microporous polymeric membranes. As compared to the conventional membrane fabrication methods, electrospinning produces membranes with a uniform pore-size distribution, higher interconnectivity of pores, and significantly higher porosity [84]. Thus, electrospun nanofibrous membranes are attracting interest for use in separation and purification processes where these characteristics are highly desirable. Electrospun membranes are used in various separation processes such as pressure-driven separation,

Table 8 Chemically Treated Electrospun Nanofibers

Polymer Used	Chemical Reagent	Activated Group	References Used
Cellulose acetate (CA)	– Hydrolysed in sodium hydroxide and ethanol; – Treated with methacrylate chloride; – Graft polymerization with methyl methacrylate, acrylamide, and *N*-isopropylacrylamide	—OH	[75]
Polyacrylonitrile (PAN)	Sodium hydroxide	—COOH	[76]
Polycaprolactone (PCL)	Potassium hydroxide	—COOH	[77]
Poly(L-lactide-*co*-caprolactone) copolymer (PLCL)	Aminolysis utilizing 1,6-hexanediamine followed by bonding using glutaraldehyde	$—NH_2$	[78]
Polysulfone (PSF)	Formaldehyde solution under acidic conditions	$—CH_2OH$	[79]
Polyimide (PI)	Sodium hydroxide followed by bonding using 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride	—OH, —COOH	[80]

This table has been summarized based on the chemical reagent used and the activated group thus generated.

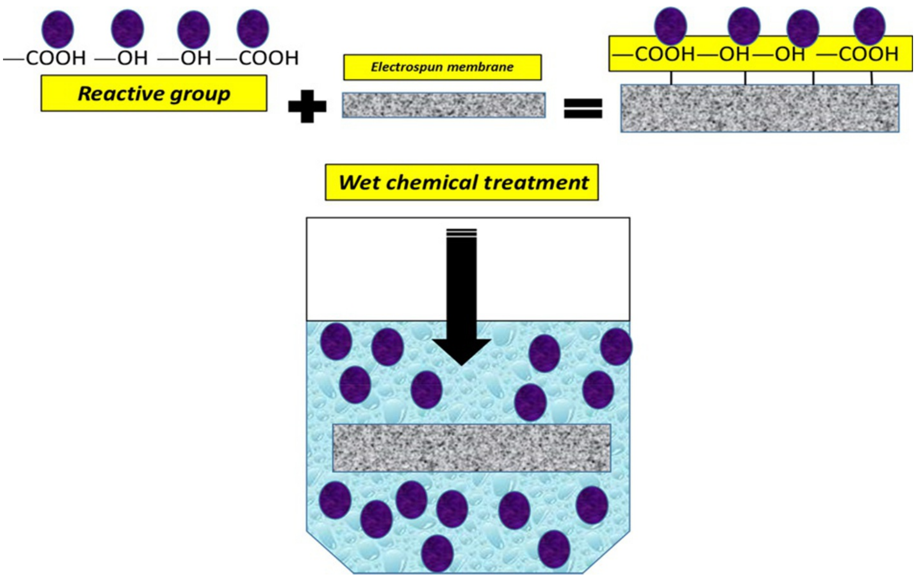

FIG. 8

Schematic diagram of functionalization of electrospun nanofibers by wet chemical treatment. In this process, reactive functional groups are introduced in electrospun nanofibers, such as carboxylic (—COOH), amine ($—RNH_2$), or hydroxyl (—OH) groups.

membrane distillation, pretreatment of feed prior to reverse osmosis (RO) or nanofiltration (NF), and oily wastewater separation. Interestingly, thin-film composite (TFC) membranes, for forward osmosis, and various RO and NF membranes are fabricated by the electrospinning technique. The traditional middle layer is replaced with an electrospun membrane. It is then coated with various layers, and then thin-film nanocomposite (TFNC) membranes are fabricated [85]. In this regard, the permeate flux and oil rejection (for oily wastewater) by TFNC membranes are found to be much higher than those of commercial NF membranes [86]. For enhancing the performance of electrospun membranes as filtration media, they can be used as support layers in the next generation of TFC membranes, including UF, NF, and RO membranes. TFC membranes consist of three fundamental layers, including the top ultra-thin selective layer, the middle porous support layer, and the bottom nonwoven fabric layer [19]. Much R&D has been carried out on the preparation and surface modification of electrospun membranes for enhanced desalination and water treatment, especially in the last decade. Therefore, there is a need to review these advancements to pave the way for the next-generation research. Table 9 summarizes all the recent works on the application of electrospun nanofibers in fabricating polymeric membranes.

5.1 MEMBRANE DISTILLATION

Membrane distillation is an efficient separation technology wherein a membrane is used to separate salt water and pure water (as a permeate). There are a few crucial parameters that affect the rate as well as the efficiency of MD. The membrane porosity, pore-size distribution, and tortuosity influence the ease with which vapor passes through the membrane and collected as a permeate. Being hydrophobic, or superhydrophobic in nature, such membranes are used for MD [93].

For membranes to be used in MD, they must be hydrophobic, be porous, have high liquid entry pressure (LEP), and have good chemical/mechanical/thermal stability [93, 94]. Nevertheless, most of the MD membranes are commercially used for microfiltration (MF) and are composed of hydrophobic polymers [95]. Interestingly, electrospun nanofibrous membranes have indicated promising properties for the application of the MD process. The first-ever application of the electrospun nanofibrous membrane in desalination by the MD process was published by Feng et al. [96]. In this research, polyvinylidene fluoride (PVDF)-based electrospun membrane samples were used for desalting 6 wt% NaCl solution by the air-gap membrane distillation (AGMD) process. Salt rejection higher than 98% was achieved in this work.

Su et al. demonstrated the effectiveness of electrospun nanofibrous membranes in salt rejection. The overall results indicate that the salt rejection of PVDF-*co*-HFP (HFP: hexafluoropropylene) and the PVDF electrospun membrane was 99.9% and 99.98%, respectively, whereas the salt rejection of PTFE was calculated as 99.99%. Thus, the salt rejection of PVDF-*co*-HFP is better than that of PVDF electrospun nanofibrous membrane and is almost similar to that of the commercially available PTFE membrane [97].

Liao et al. fabricated dual-layered superhydrophobic membranes composed of PVDF polymers with silica nanoparticles for improved desalination by the MD process. These fabricated membranes have shown significantly high water flux and salt rejection. The researchers concluded that to use these membranes in water industries, modification, as well as optimization, is required for controlling the pore size of the membrane and enhancing the long-term performance of the membranes by optimizing the SiO_2 composition [98].

Table 9 Summary of Recent Research Work on Different Fabricated Electrospun Nanofibrous Membranes for Various Applications

Polymer and Solvent Utilized	Experimental Setup	Applications	References
Polyvinyl alcohol/distilled water	2-Layered membrane with hydrophobic top layer (polypropylene mat) and hydrophilic bottom layer (polyvinyl alcohol electrospun layer)	Membrane distillation (desalination)	[26, 27]
Polysulfone/DMF	2-Layered membrane with electrospun polysulfone hydrophobic membrane as top layer and hydrophilic cellulosic mat as bottom layer	Membrane distillation (desalination)	[26, 27]
Polyethersulfone ($Mw = 7.8 \times 104$ g/mol) and Polysulfone ($Mw = 8.0–8.6 \times 104$ g/mol)/ DMF (anhydrous, 99.8%), NMP (anhydrous, 99.5%), TMC (98%) and MPD (>99%)	TFC fabrication by interfacial polymerization	Forward osmosis	[87]
Polyetherimide/DMF and NMP	TFC fabrication by electrospinning technique	Forward osmosis	[88]
Polyacrylonitrile ($Mw = 150{,}000$ g/mol)/MDP, TMC, and DMF	Engineering the support layer by incorporating the silica nanoparticle (SiO_2: 200 nm particle size, 4 nm pore size)	Reverse osmosis, forward osmosis, and pressure retarded osmosis	[89]
Polyvinylidene fluoride (*Mw*: 550 kg/mol)/DMF and THF	Fabrication of support layer by electrospinning technique for TFC membrane	Forward osmosis	[90]
Polyvinylidene fluoride-*co*-hexafluoropropylene (PH) ($Mw = 445{,}000$)/acetone and *N*,*N*-dimethylacetamide (DMAc)	Effect of heat treatment on electrospun membrane	Membrane distillation	[91]
Polyvinylidene fluoride-*co*-hexafluoropropylene (pH) and Polyvinyl alcohol (PVA) ($Mw = 85{,}000$ g/mol)—Nylon-6 (N6) ($Mw = 10{,}000$ g/mol)—Polyacrylonitrile (PAN) ($Mw = 150{,}000$ g/mol)/ DMF, LiCl (lithium chloride), and Triton X-100	Dual layer (hydrophobic-hydrophilic) flat sheet membrane	Membrane distillation	[92]

Electrospun nanofibrous polymeric materials can be used as support layers in new-generation of TFC membranes including UF, NF, RO, and FO membranes.

To use an electrospun nanofibrous membrane in the MD process, it must be able to maintain separation between the feed stream and the permeate stream. Thus, a superhydrophobic membrane will be efficient as it is considered to be the best for maintaining water separation. The PVDF electrospun nanofibrous membrane is commonly used for water filtration process. Researchers have evaluated the performance of PVDF-based beaded and smooth nanofibers in MD. Interestingly, beaded nanofibers showed a higher contact angle, whereas the water flux from the smooth nanofibers was much better than that from the beaded nanofibers, owing to the smaller void volume fraction of the beaded nanofibers [20].

5.2 PRESSURE-DRIVEN SEPARATION

Basically, the primary application of a membrane is to separate two distinct phases, preferentially controlling one phase while simultaneously working as a barrier to the other phase (e.g., bacteria and suspended solids; [99, 100]).

Some researchers have reported that electrospun nanofibrous materials can be used as a support layer in advanced TFC membranes [19]. TFC membranes, including those used for UF, NF, RO, and FO, are composed of three fundamental layers, as shown in Fig. 9: a top ultrathin selective layer, a middle porous support layer, and a bottom nonwoven fabric layer.

Kaur et al. studied the performance of an electrospun polymeric web as a support layer in TFC membranes [101]. They fabricated various polyacrylonitrile (PAN)-based microfiltration membranes with various fiber diameters. The fiber diameter changes with the polymer concentration (4%–10% w/v). The interfacial polymerization technique (mixture of piperazine and *p*-phenylene diamine with trimesoyl chloride) was used to coat a thin film onto the surface of the electrospun nanofibrous material.

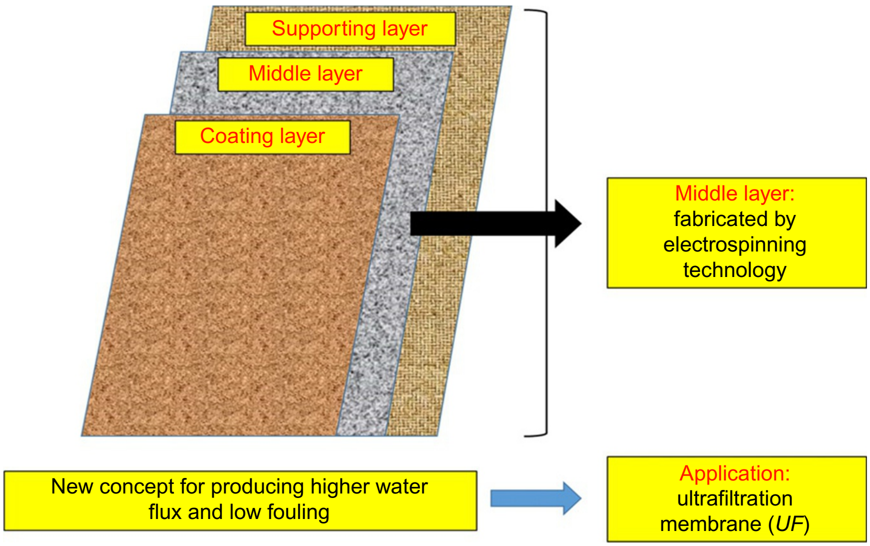

FIG. 9

General fabrication scheme of three-layered, high-flux, and low-fouling UF membrane.

The fabricated membranes were used for the desalination of salt water with a salt concentration of up to 2000 mg/L (including both monovalent and divalent ions). The overall results of the desalting experiments showed that as the fiber diameter decreased (toward the nano range), salt rejection increased but at the expense of permeate water flux. However, when the thickness of the support layer (electrospun nanofibrous layer) and the pore size was decreased, the permeate water flux and salt rejection increased. The optimum concentration of PAN for the electrospun nanofibers was found to be 8 wt%.

6 FUTURE TRENDS AND RESEARCH CHALLENGES

During the early 2000s, the primary concerns in the field of electrospinning were the fabrication of nanofibers from different polymers and their corresponding applications. Researchers have achieved a better understanding of the electrospinning technique process for producing nanofibers of desired morphology and fiber diameter. Despite the significant advantages of electrospun nanofibrous membranes, there are a few limitations that influence the membrane morphology and structure. Therefore, future research should consider these challenges in near future. The drawbacks of electrospun nanofibrous membranes are as follows [21, 22]:

1. Micro-cracking, corner rounding, and temperature-induced problems
2. Fabrication and commercialization of electrospun nanofibrous membranes on a large industrial scale
3. Fabrication of membranes with uniform pore-size distribution
4. Selection of suitable materials and incorporation routes to introduce the desired functionality, during or after the electrospinning process
5. Optimization of the electrospinning process with cost-effective separation and purification technology

The application of this versatile technique is being extended to ceramics, inorganic or organic, and metal composite systems as well. To this end, innovative electrospinning techniques such as coaxial electrospinning, mixing and multiple electrospinning, core-shell electrospinning, and blowing-assisted electrospinning have been developed.

As compared to the traditional or conventional techniques used for generating polymeric and composite membranes, electrospinning technique is found to be more versatile owing to uniform pore size and interconnectivity of pores. Table 10 lists a few applications that can be investigated to ensure the effectiveness of the electrospun nanofibrous membrane.

7 CONCLUSION

Electrospun nanofibrous membranes have attracted much attention from researchers because of its high versatility. Electrospun nanofibrous membranes have become the next-generation filtration media that have promising features and offer good opportunities for advanced filtration techniques in the near future. This versatile technique can be used to fabricate high-performance electrospun nanofibrous membranes with a high surface area, a high surface area-to-pore volume ratio, high pore interconnectivity, and uniform pore distribution. Recently, many researchers have focused on the functionalities of

Table 10 Some Applications That Can Be Further Investigated to Enhance the Potential of Electrospinning Technique

Parameters or Conditions	Future Perspectives
Membrane modules	The electrospun nanofibrous membrane plays an important role in the area of water treatment, but more analysis can be done with respect to ultrafiltration (UF) and nanofiltration (NF) and reverse osmosis (RO). The practical use of electrospun nanofibrous membranes in these modules can further be investigated
Hydrophobic membrane	To make the MD process effective, a higher hydrophobic membrane can be produced
Hydrophilic membrane	Furthermore, hydrophilic membranes can be produced by utilizing an electrospinning technique that can be used in a forward osmosis (FO) system
General characteristics	The general features of an ideal membrane, such as interconnectivity of the pores, uniform pore size, mechanical strength, and stability, should be improved by postthermal treatment as well as chemical treatment
Stability and durability	The longevity and durability must be two of the important fields of research while fabricating membranes by the electrospinning technique

Electrospinning has emerged as an effective technique for fabricating stable and durable membranes. The main focus of this table is to list the possible conditions for future potential applications [21, 30, 102].

electrospun nanofibers to improve their applicability on an industrial scale. For this purpose, nanoparticles have been incorporated into the electrospun nanofibrous membrane to improve its performance. Furthermore, properties such as high porosity, uniform pore size with a narrow pore-size distribution, and a large surface area-to-pore volume ratio make electrospun nanofibrous membranes most desirable as MD membranes to generate a high water vapor flux. Nonwoven nanofibrous membranes are widely used in the removal of small particles by the MF process and in desalination by the MD process. The performance of electrospun nanofibrous membranes can be enhanced by considering features such as pore-size distribution, hydrophilicity or hydrophobicity, mechanical strength, and stability. To increase the permeability and permeate flux, properties such as membrane thickness and pore size should be optimized. The performance of electrospun nanofibrous membranes can further be optimized with a deeper understanding of how operating parameters and solution parameters can control membrane characteristics in different polymeric solution. Unfortunately, upgrading the electrospinning technique to an industrial scale for commercialization remains a challenge. Therefore, more attention has been given to the high durability and stability of the electrospun nanofibrous membranes to eradicate this problem. Currently, electrospinning is one of the crucial, versatile processes that have influenced the R&D on water treatment applications. To improve the morphological and topographical features of electrospun nanofibers, various methodologies, such as molecular bonding, in situ polymerization, and addition of molecular dopants, are used in conjunction with electrospinning. Strategies for surface modification, such as nanoparticle coating, treatment with chemicals or heat, grafting, and interfacial polymerization, have been found to be highly effective in enhancing the filtration performance of electrospun nanofibrous membranes. In addition, electrospun nanofibrous membranes are effective in oily wastewater treatment. Thus, considering features such as tunable selectivity, extraordinary permeability, and energy/cost efficiency, it can be concluded that the new-generation membranes used for environmental applications will be based on cost-effective nanofibrous materials.

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REFERENCES

[1] F. Mushtaq, M. Guerrero, M.S. Sakar, M. Hoop, A.M. Lindo, J. Sort, X. Chen, B.J. Nelson, E. Pellicer, S. Pané, Magnetically driven bi 2 O 3/BiOCl-based hybrid microrobots for photocatalytic water remediation, J. Mater. Chem. A 3 (47) (2015) 23670–23676.

[2] S. Ramakrishna, M.M.A. Shirazi, Electrospun membranes: next generation membranes for desalination and water/wastewater treatment, Desalination 308 (2013) 198–208.

[2a] J. Zeleny, The electrical discharge from liquid points, and a hydrostatic method of measuring the electric intensity at their surfaces, Phys Rev 3 (2) (1914) 69.

[3] Formhals, A. (1934). Process and apparatus for preparing artificial thr-eads, US Patent, 1975504.

[4] G. Taylor, Disintegration of water drops in an electric field. Proc. Royal Soc. Lond. A 280 (1382) (1964) https://doi.org/10.1098/rspa.1964.0151.

[5] G. Taylor, Electrically driven jets. Proc. Royal Soc. Lond. A 313 (1515) (1969) https://doi.org/10.1098/rspa.1969.0205.

[6] N. Tucker, J. Stanger, M. Staiger, H. Razzaq, K. Hofman, The history of the science and technology of electrospinning from 1600 to 1995, J. Eng. Fiber. Fabr. 7 (2012) 63–73.

[7] G.C. Rutledge, S.V. Fridrikh, Formation of fibers by electrospinning, Adv. Drug Deliv. Rev. 59 (14) (2007) 1384–1391.

[8] M. Bognitzki, W. Czado, T. Frese, A. Schaper, M. Hellwig, M. Steinhart, A. Greiner, J.H. Wendorff, Nanostructured fibers via electrospinning, Adv. Mater. 13 (1) (2001) 70–72.

[9] M. Ngiam, S. Ramakrishna, M. Raghunath, C.K. Chan, Nanofiber patent landscape, Recent Patents on Nanotechnology 1 (2) (2007) 137–144.

[10] G. A. Kinney, Apparatus for preparing a nonwoven web, Google Patents, 1980.

[11] J. Doshi, D.H. Reneker, Electrospinning process and applications of electrospun fibers, J. Electrost. 35 (2–3) (1995) 151–160.

[12] D.H. Reneker, A.L. Yarin, H. Fong, S. Koombhongse, Bending instability of electrically charged liquid jets of polymer solutions in electrospinning, J. Appl. Phys. 87 (9) (2000) 4531–4547.

[13] A. Spivak, Y. Dzenis, D. Reneker, A model of steady state jet in the electrospinning process, Mech. Res. Commun. 27 (1) (2000) 37–42.

[14] T. Lin, H. Wang, H. Wang, X. Wang, The charge effect of cationic surfactants on the elimination of fibre beads in the electrospinning of polystyrene, Nanotechnology 15 (9) (2004) 1375.

[15] N. Bhardwaj, S.C. Kundu, Electrospinning: a fascinating fiber fabrication technique, Biotechnol. Adv. 28 (3) (2010) 325–347.

[16] H. Karakaş, Electrospinning of Nanofibers and There Applications, Istanbul Technical University, Textile Technologies and Design Faculty, Istanbul, 2015.

[17] J. Deitzel, J. Kleinmeyer, D. Harris, N.B. Tan, The effect of processing variables on the morphology of electrospun nanofibers and textiles, Polymer 42 (1) (2001) 261–272.

[18] S. Sukigara, M. Gandhi, J. Ayutsede, M. Micklus, F. Ko, Regeneration of Bombyx mori silk by electrospinning—part 1: processing parameters and geometric properties, Polymer 44 (19) (2003) 5721–5727.

[19] S. Subramanian, R. Seeram, New directions in nanofiltration applications—are nanofibers the right materials as membranes in desalination? Desalination 308 (2013) 198–208.
[20] M. Essalhi, M. Khayet, Self-sustained webs of polyvinylidene fluoride electrospun nanofibers at different electrospinning times: 1. Desalination by direct contact membrane distillation, J. Membr. Sci. 433 (2013) 167–179.
[21] S.S. Ray, S.-S. Chen, C.-W. Li, N.C. Nguyen, H.T. Nguyen, A comprehensive review: electrospinning technique for fabrication and surface modification of membranes for water treatment application, RSC Adv. 6 (88) (2016) 85495–85514.
[22] Z.-M. Huang, Y.-Z. Zhang, M. Kotaki, S. Ramakrishna, A review on polymer nanofibers by electrospinning and their applications in nanocomposites, Compos. Sci. Technol. 63 (15) (2003) 2223–2253.
[23] Y. Dzenis, Y. Wen, Continuous carbon nanofibers for nanofiber composites, MRS Online Proceedings Library Archive, vol. 702, 2001.
[24] X. Zong, K. Kim, D. Fang, S. Ran, B.S. Hsiao, B. Chu, Structure and process relationship of electrospun bioabsorbable nanofiber membranes, Polymer 43 (16) (2002) 4403–4412.
[25] G.-D. Kang, Y.-M. Cao, Application and modification of poly (vinylidene fluoride)(PVDF) membranes–a review, J. Membr. Sci. 463 (2014) 145–165.
[26] S.S. Ray, S.-S. Chen, H.-T. Hsu, D.-T. Cao, H.-T. Nguyen, N.C. Nguyen, Uniform hydrophobic electrospun nanofibrous layer composed of polysulfone and sodium dodecyl sulfate for improved desalination performance, Sep. Purif. Technol. 186 (2017) 352–365.
[27] S.S. Ray, S.-S. Chen, N.C. Nguyen, H.-T. Hsu, H.T. Nguyen, C.-T. Chang, Poly (vinyl alcohol) incorporated with surfactant based electrospun nanofibrous layer onto polypropylene mat for improved desalination by using membrane distillation, Desalination 414 (2017) 18–27.
[28] D. Aussawasathien, C. Teerawattananon, A. Vongachariya, Separation of micron to sub-micron particles from water: electrospun nylon-6 nanofibrous membranes as pre-filters, J. Membr. Sci. 315 (1) (2008) 11–19.
[29] C. Shao, H. Guan, Y. Liu, J. Gong, N. Yu, X. Yang, A novel method for making ZrO_2 nanofibres via an electrospinning technique, J. Cryst. Growth 267 (1) (2004) 380–384.
[30] S. Homaeigohar, M. Elbahri, Nanocomposite electrospun nanofiber membranes for environmental remediation, Materials 7 (2) (2014) 1017–1045.
[31] W. Liu, M. Graham, E.A. Evans, D.H. Reneker, Poly (meta-phenylene isophthalamide) nanofibers: coating and post processing, J. Mater. Res. 17 (12) (2002) 3206–3212.
[32] S. Theron, A. Yarin, E. Zussman, E. Kroll, Multiple jets in electrospinning: experiment and modeling, Polymer 46 (9) (2005) 2889–2899.
[33] S. Theron, E. Zussman, A. Yarin, Experimental investigation of the governing parameters in the electrospinning of polymer solutions, Polymer 45 (6) (2004) 2017–2030.
[34] Y. Yang, Z. Jia, Q. Li, L. Hou, H. Gao, L. Wang, Z. Guan, Multiple jets in electrospinning, Properties and Applications of Dielectric Materials, 2006. 8th International Conference on, IEEE, 2006.
[35] C.J. Angammana, S.H. Jayaram, Fundamentals of electrospinning and processing technologies, Part. Sci. Technol. 34 (1) (2016) 72–82.
[36] J. Kameoka, R. Orth, Y. Yang, D. Czaplewski, R. Mathers, G.W. Coates, H. Craighead, A scanning tip electrospinning source for deposition of oriented nanofibres, Nanotechnology 14 (10) (2003) 1124.
[37] F.L. Zhou, R.H. Gong, I. Porat, Mass production of nanofibre assemblies by electrostatic spinning, Polym. Int. 58 (4) (2009) 331–342.
[38] N.M. Thoppey, J.R. Bochinski, L.I. Clarke, R.E. Gorga, Unconfined fluid electrospun into high quality nanofibers from a plate edge, Polymer 51 (21) (2010) 4928–4936.
[39] L. Larrondo, R. St John Manley, Electrostatic fiber spinning from polymer melts. I. Experimental observations on fiber formation and properties, J. Polym. Sci. B Polym. Phys. 19 (6) (1981) 909–920.
[40] D.W. Hutmacher, P.D. Dalton, Melt electrospinning, Chem. Asian J. 6 (1) (2011) 44–56.

[41] D.D. da Silva Parize, M.M. Foschini, J.E. de Oliveira, A.P. Klamczynski, G.M. Glenn, J.M. Marconcini, L. H.C. Mattoso, Solution blow spinning: parameters optimization and effects on the properties of nanofibers from poly (lactic acid)/dimethyl carbonate solutions, J. Mater. Sci. 51 (9) (2016) 4627–4638.

[42] T. Matsuura, Progress in membrane science and technology for seawater desalination—a review, Desalination 134 (1–3) (2001) 47–54.

[43] D. Rana, T. Matsuura, Surface modifications for antifouling membranes, Chem. Rev. 110 (4) (2010) 2448–2471.

[44] A. Shirazi, M. Mahdi, A. Kargari, S. Ramakrishna, J. Doyle, M. Rajendrian, P. Babu, Electrospun membranes for desalination and water/wastewater treatment: a comprehensive review, J Membr. Sci. Res. 3 (3) (2017) 209–227.

[45] C. Burger, B.S. Hsiao, B. Chu, Nanofibrous materials and their applications, Annu. Rev. Mater. Res. 36 (2006) 333–368.

[46] W.-E. Teo, S. Ramakrishna, Electrospun nanofibers as a platform for multifunctional, hierarchically organized nanocomposite, Compos. Sci. Technol. 69 (11) (2009) 1804–1817.

[47] G. Eda, S. Shivkumar, Bead-to-fiber transition in electrospun polystyrene, J. Appl. Polym. Sci. 106 (1) (2007) 475–487.

[48] H. Fong, I. Chun, D. Reneker, Beaded nanofibers formed during electrospinning, Polymer 40 (16) (1999) 4585–4592.

[49] K. Lee, H. Kim, H. Bang, Y. Jung, S. Lee, The change of bead morphology formed on electrospun polystyrene fibers, Polymer 44 (14) (2003) 4029–4034.

[50] Z. Li, C. Wang, Effects of Working Parameters on Electrospinning. One-Dimensional Nanostructures, Springer, Berlin, Heidelberg, 2013, pp. 15–28, https://doi.org/10.1007/978-3-642-36427-3_2.

[51] A. Koski, K. Yim, S. Shivkumar, Effect of molecular weight on fibrous PVA produced by electrospinning, Mater. Lett. 58 (3) (2004) 493–497.

[52] S.L. Shenoy, W.D. Bates, H.L. Frisch, G.E. Wnek, Role of chain entanglements on fiber formation during electrospinning of polymer solutions: good solvent, non-specific polymer–polymer interaction limit, Polymer 46 (10) (2005) 3372–3384.

[53] A. Haghi, M. Akbari, Trends in electrospinning of natural nanofibers, Physica Status Solidi 204 (6) (2007) 1830–1834.

[54] C. Zhang, X. Yuan, L. Wu, Y. Han, J. Sheng, Study on morphology of electrospun poly (vinyl alcohol) mats, Eur. Polym. J. 41 (3) (2005) 423–432.

[55] C. Huang, S. Chen, C. Lai, D.H. Reneker, H. Qiu, Y. Ye, H. Hou, Electrospun polymer nanofibres with small diameters, Nanotechnology 17 (6) (2006) 1558.

[56] C. Mit-uppatham, M. Nithitanakul, P. Supaphol, Effects of solution concentration, emitting electrode polarity, solvent type, and salt addition on electrospun polyamide-6 fibers: a preliminary report, Macromolecular Symposia, Wiley Online Library, 2004.

[57] C. Mit-uppatham, M. Nithitanakul, P. Supaphol, Ultrafine electrospun polyamide-6 fibers: effect of solution conditions on morphology and average fiber diameter, Macromol. Chem. Phys. 205 (17) (2004) 2327–2338.

[58] P. Heikkilä, A. Harlin, Parameter study of electrospinning of polyamide-6, Eur. Polym. J. 44 (10) (2008) 3067–3079.

[59] S. Koombhongse, W. Liu, D.H. Reneker, Flat polymer ribbons and other shapes by electrospinning, J. Polym. Sci. B Polym. Phys. 39 (21) (2001) 2598–2606.

[60] D.H. Reneker, I. Chun, Nanometre diameter fibres of polymer, produced by electrospinning, Nanotechnology 7 (3) (1996) 216.

[61] C.J. Buchko, L.C. Chen, Y. Shen, D.C. Martin, Processing and microstructural characterization of porous biocompatible protein polymer thin films, Polymer 40 (26) (1999) 7397–7407.

[62] F.-C. Chang, K.-K. Chan, C.-Y. Chang, The effect of processing parameters on formation of lignosulfonate fibers produced using electrospinning technology, Bioresources 11 (2) (2016) 4705–4717.

[63] O. Yördem, M. Papila, Y.Z. Menceloğlu, Effects of electrospinning parameters on polyacrylonitrile nanofiber diameter: an investigation by response surface methodology, Mater. Des. 29 (1) (2008) 34–44.

[64] C.S. Ki, D.H. Baek, K.D. Gang, K.H. Lee, I.C. Um, Y.H. Park, Characterization of gelatin nanofiber prepared from gelatin–formic acid solution, Polymer 46 (14) (2005) 5094–5102.

[65] X. Yuan, Y. Zhang, C. Dong, J. Sheng, Morphology of ultrafine polysulfone fibers prepared by electrospinning, Polym. Int. 53 (11) (2004) 1704–1710.

[66] S. Tan, R. Inai, M. Kotaki, S. Ramakrishna, Systematic parameter study for ultra-fine fiber fabrication via electrospinning process, Polymer 46 (16) (2005) 6128–6134.

[67] M.F. Hossain, R.H. Gong, M. Rigout, Optimization of the process variables for electrospinning of poly (ethylene oxide)-loaded hydroxypropyl-β-cyclodextrin nanofibres, J. Text. Inst. 107 (1) (2016) 1–11.

[68] M. Nangrejo, F. Bragman, Z. Ahmad, E. Stride, M. Edirisinghe, Hot electrospinning of polyurethane fibres, Mater. Lett. 68 (2012) 482–485.

[69] C.L. Casper, J.S. Stephens, N.G. Tassi, D.B. Chase, J.F. Rabolt, Controlling surface morphology of electrospun polystyrene fibers: effect of humidity and molecular weight in the electrospinning process, Macromolecules 37 (2) (2004) 573–578.

[70] A.P. Golin, Humidity effect on the structure of electrospun core-shell PCL-PEG fibers for tissue regeneration applications, Electronic Thesis and Dissertation Repository, 2014. https://ir.lib.uwo.ca/etd/1999.

[71] R.T. Oğulata, H.İ. İçoğlu, Interaction between effects of ambient parameters and those of other important parameters on electrospinning of PEI/NMP solution, J. Text. Inst. 106 (1) (2015) 57–66.

[72] S. Alswid, M. Issa, Study the effect of conditions of the electro spinning cabin (humidity) on electro-spun PolyVinyl alcohol (PVA) Nano-fibers, Al-Nahrain J. Eng. Sci. 20 (3) (2017) 520–525.

[73] T. Ogawa, B. Ding, Y. Sone, S. Shiratori, Super-hydrophobic surfaces of layer-by-layer structured film-coated electrospun nanofibrous membranes, Nanotechnology 18 (16) (2007) 165607.

[74] Y. Zhang, Y. Feng, Z. Huang, S. Ramakrishna, C. Lim, Fabrication of porous electrospun nanofibres, Nanotechnology 17 (3) (2006) 901.

[75] H. Liu, Y.L. Hsieh, Surface methacrylation and graft copolymerization of ultrafine cellulose fibers, J. Polym. Sci. B Polym. Phys. 41 (9) (2003) 953–964.

[76] H. Chiu, J. Lin, T. Cheng, S. Chou, Fabrication of electrospun polyacrylonitrile ion-exchange membranes for application in lysozym, Express Polym Lett 5 (4) (2011).

[77] J. Fang, X. Wang, T. Lin, Functional Applications of Electrospun Nanofibers. Nanofibers-Production, Properties and Functional Applications, InTech, Rijeka, Croatia, 2011.

[78] Y. Zhu, M.F. Leong, W.F. Ong, M.B. Chan-Park, K.S. Chian, Esophageal epithelium regeneration on fibronectin grafted poly (L-lactide-co-caprolactone)(PLLC) nanofiber scaffold, Biomaterials 28 (5) (2007) 861–868.

[79] W.E. Teo, S. Ramakrishna, A review on electrospinning design and nanofibre assemblies, Nanotechnology 17 (14) (2006) R89.

[80] F. Samani, M. Kokabi, M. Soleimani, M.R. Valojerdi, Fabrication and characterization of electrospun fibrous nanocomposite scaffolds based on poly (lactide-co-glycolide)/poly (vinyl alcohol) blends, Polym. Int. 59 (7) (2010) 901–909.

[81] S. Naseri Rad, A. Shirazi, M. Mahdi, A. Kargari, R. Marzban, Application of membrane separation technology in downstream processing of bacillus thuringiensis biopesticide: a review, J. Membr. Sci. Res. 2 (2) (2016) 66–77.

[82] M.T. Ravanchi, T. Kaghazchi, A. Kargari, Application of membrane separation processes in petrochemical industry: a review, Desalination 235 (1) (2009) 199–244.

[83] S.A.A.N. Nasreen, S. Sundarrajan, S.A.S. Nizar, R. Balamurugan, S. Ramakrishna, Advancement in electrospun nanofibrous membranes modification and their application in water treatment, Membranes 3 (4) (2013) 266–284.

[84] M.M. Pendergast, E.M. Hoek, A review of water treatment membrane nanotechnologies, Energy Environ. Sci. 4 (6) (2011) 1946–1971.
[85] X. Wang, X. Chen, K. Yoon, D. Fang, B.S. Hsiao, B. Chu, High flux filtration medium based on nanofibrous substrate with hydrophilic nanocomposite coating, Environ. Sci. Technol. 39 (19) (2005) 7684–7691.
[86] X. Wang, D. Fang, K. Yoon, B.S. Hsiao, B. Chu, High performance ultrafiltration composite membranes based on poly (vinyl alcohol) hydrogel coating on crosslinked nanofibrous poly (vinyl alcohol) scaffold, J. Membr. Sci. 278 (1) (2006) 261–268.
[87] N.-N. Bui, M.L. Lind, E.M. Hoek, J.R. McCutcheon, Electrospun nanofiber supported thin film composite membranes for engineered osmosis, J. Membr. Sci. 385 (2011) 10–19.
[88] M. Tian, Y.-N. Wang, R. Wang, A.G. Fane, Synthesis and characterization of thin film nanocomposite forward osmosis membranes supported by silica nanoparticle incorporated nanofibrous substrate, Desalination 401 (2017) 142–150.
[89] N.-N. Bui, J.R. McCutcheon, Nanoparticle-embedded nanofibers in highly permselective thin-film nanocomposite membranes for forward osmosis, J. Membr. Sci. 518 (2016) 338–346.
[90] L. Huang, J.T. Arena, J.R. McCutcheon, Surface modified PVDF nanofiber supported thin film composite membranes for forward osmosis, J. Membr. Sci. 499 (2016) 352–360.
[91] M. Yao, Y.C. Woo, L.D. Tijing, W.-G. Shim, J.-S. Choi, S.-H. Kim, H.K. Shon, Effect of heat-press conditions on electrospun membranes for desalination by direct contact membrane distillation, Desalination 378 (2016) 80–91.
[92] Y.C. Woo, L.D. Tijing, M.J. Park, M. Yao, J.-S. Choi, S. Lee, S.-H. Kim, K.-J. An, H.K. Shon, Electrospun dual-layer nonwoven membrane for desalination by air gap membrane distillation, Desalination 403 (2017) 187–198.
[93] A. Kargari, M.M.A. Shirazi, Water desalination: Solar-assisted membrane distillation, in: Encyclopedia of Energy Engineering and Technology, CRC Press, Boca Raton, FL, 2014, p. 4.
[94] A.T. Servi, J. Kharraz, D. Klee, K. Notarangelo, B. Eyob, E. Guillen-Burrieza, A. Liu, H.A. Arafat, K.K. Gleason, A systematic study of the impact of hydrophobicity on the wetting of MD membranes, J. Membr. Sci. 520 (2016) 850–859.
[95] M.M.A. Shirazi, A. Kargari, M. Tabatabaei, Evaluation of commercial PTFE membranes in desalination by direct contact membrane distillation, Chem. Eng. Process. Process Intensif. 76 (2014) 16–25.
[96] C. Feng, K. Khulbe, T. Matsuura, R. Gopal, S. Kaur, S. Ramakrishna, M. Khayet, Production of drinking water from saline water by air-gap membrane distillation using polyvinylidene fluoride nanofiber membrane, J. Membr. Sci. 311 (1) (2008) 1–6.
[97] C.-I. Su, J.-H. Shih, M.-S. Huang, C.-M. Wang, W.-C. Shih, Y.-s. Liu, A study of hydrophobic electrospun membrane applied in seawater desalination by membrane distillation, Fiber. Polym. 13 (6) (2012) 698–702.
[98] Y. Liao, C.-H. Loh, R. Wang, A.G. Fane, Electrospun superhydrophobic membranes with unique structures for membrane distillation, ACS Appl. Mater. Interfaces 6 (18) (2014) 16035–16048.
[99] B. Van der Bruggen, C. Vandecasteele, T. Van Gestel, W. Doyen, R. Leysen, A review of pressure-driven membrane processes in wastewater treatment and drinking water production, Environ. Prog. Sustain. Energy 22 (1) (2003) 46–56.
[100] R. Van Reis, A. Zydney, Membrane separations in biotechnology, Curr. Opin. Biotechnol. 12 (2) (2001) 208–211.
[101] S. Kaur, S. Sundarrajan, D. Rana, T. Matsuura, S. Ramakrishna, Influence of electrospun fiber size on the separation efficiency of thin film nanofiltration composite membrane, J. Membr. Sci. 392 (2012) 101–111.
[102] M.T. Hunley, T.E. Long, Electrospinning functional nanoscale fibers: a perspective for the future, Polym. Int. 57 (3) (2008) 385–389.