Review Paper

Electrospun Membranes for Desalination and Water/Wastewater Treatment: A Comprehensive Review

Mohammad Mahdi A. Shirazi [1,2,†], Ali Kargari [2,*], Seeram Ramakrishna [3,*], James Doyle [4], Murugan Rajendrian [4], P. Ramesh Babu [4,5]

[1] Membrane Industry Development Institute, Tehran, Iran
[2] Membrane Processes Research Laboratory (MPRL), Department of Chemical Engineering, Amirkabir University of Technology (Tehran Polytechnic), Tehran, Iran
[3] Center for Nanofibers & Nanotechnology, National University of Singapore (NUS), Singapore
[4] CRANN Institute, Trinity College Dublin, Dublin 2, Ireland
[5] School of Physics, Trinity College Dublin, Dublin-2, Ireland

Article info

Keywords

Highlights

- This article focuses on the present status and recent development of electrospun nanofibrous membranes
- Applications of elecrospun membranes for membrane processes (MF, UF, NF, FO and MD), coalescing filtration and adsorptive separation are reviewed
- Benefits, limitations and challenges of electrospun membranes are discussed
- This article also highlights the prospects of electrospun membranes, specifically in the water industry

Graphical abstract
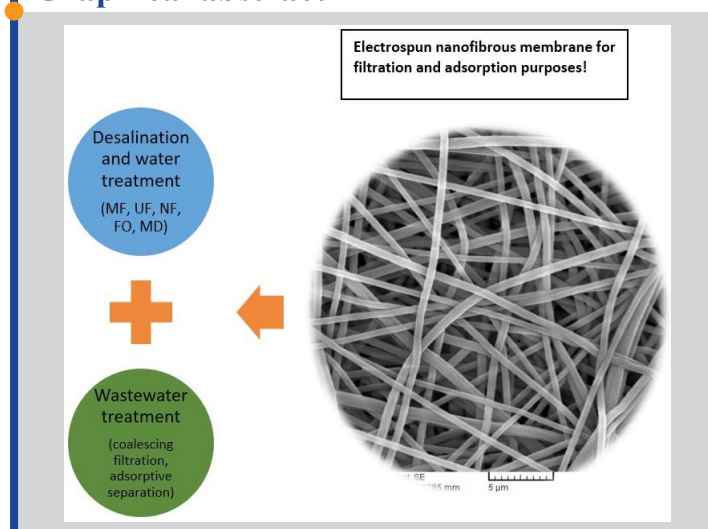
Abstract

Polymeric nanofibers, specifically fabricated by electrospinning, offer viable means useful for a wide range of applications such as health, energy and environmental issues. However, among the mentioned sectors, desalination and water/wastewater treatment applications have been highlighted during the past decade. This article focuses on the present status and recent development of electrospun nanofibrous membranes and their potential impact in two major areas, i.e., desalination and water/wastewater treatment. Specific applications for desalination and high-quality water/wastewater treatment, including pressure-driven and osmotic membrane processes (MF, UF, NF, FO, etc.), thermal-driven membrane processes, coalescing filtration and adsorptive application of nanofibers, are described. Also, benefits, limitations and challenges are discussed, comprehensively. Electrospun membranes can play a critical role in improving membrane-based desalination and water/wastewater treatment systems. These filtration elements with 3D inter-connected structures will be shown to have interesting and crucial advantages over conventional polymeric membranes in terms of performance, cost and energy savings. This article also highlights the prospects of electrospun membranes and specifically provides the state-of-the-art applications in the water industry.

Contents

* Corresponding author at: Phone: +98 21 64543197; fax: +98 21 66405847 (A. Kargari); Phone/fax: +65 6516 2216 (S. Ramakrishna)
E-mail address: kargari@aut.ac.ir; ali_kargari@yahoo.com (A. Kargari); seeram@nus.edu.sg (S. Ramakrishna); † mmahdiashirazi@gmail.com (M.M.A. Shirazi)

1. Introduction

With our growing global population and ever increasing economic expansion, we have entered a potential crisis point in balancing the supply and availability of fresh water resources [1,2]. Continual changes in production, consumption, markets and political governance have led to an increase in demand for fresh water. The urban population is expected to grow from approximately 2,522 million in 1950 to 8,909 million in 2050 [3,4]. Forecasts up to 2030 indicate an increase in global water uptake of about 40% of the current accessible and reliable supply sources, meaning an intensification of water consumption [5].

Global data suggests that approximately 780 million people cannot access safe drinking water, 1.1 billion people do not have the facilities to improve drinking water bodies and that 2.6 billion people live with substandard sanitation [6-8]. Consequently, the need for technological innovation to enable novel desalination and water/wastewater treatment technologies cannot be overstated [9,10]. In this regard, nanotechnology holds a great potential in advancing water and wastewater treatment by improving the efficiency of impurity removal as well as augmenting the water supply via safe use of un-conventional water resources.

Advances in nanotechnology could greatly help overcome the current issues of meeting the demand of clean water supplies using novel, nanostructured/nanoengineered materials produced by the electrospinning process. Electrospinning has attracted increased attention as a versatile technique, applicable to numerous organic and inorganic systems and a wide range of applications (see Figure 1) which can result in a tightly controlled size distribution of nanomaterials [11,12]. The resulting nano-system can be described as a highly porous network structure, with a large *surface area to volume* ratio, the dimensions of which can be easily tailored and optimized during production [13]. It is commonly accepted that a material which is termed *nano* in size, must possess at least one dimension of the order of 100 nm or less [14]. However, in literature fibers with diameter up to 1000 nm usually called nanofibers [15,16]. The electrospinning method allows for the high volume production of light weight, highly functional, nanoscale, mesh-like structures. The aim of this review is to critically and comprehensively investigate the viable impact and commercial potential of electrospun nanofibrous membranes for desalination and water/wastewater treatments.

2. Electrospinning technology

2.1. Description

Electrospinning involves applying a high voltage electric field on a dope solution (i.e., a polymer-solvent system (see Table 1)) to form a solution jet [18]. When the jet is being elongated and the solvent is evaporated, i.e. after the *whipping* process, fibers in the range of few microns to nanometer scale can be obtained [19].

The basic electrospinning system consists of three main parts, including feeding section, high-voltage power supply, and a collector section. These basic parts are shown in Figure 2. The feeding section contains a feed storage (polymer solution), a spinneret (i.e. a thin metallic needle), and an injection pump to inject the dope solution at a constant flow rate. The precursor droplet at the needle tip is charged by connecting the needle to the proposed high voltage supply [21].

The force created by the electrical field acts in the opposite direction to the surface tension of the solution and elongates the droplet to a conical shape called a *Taylor* cone [18,22]. When the electrical force is strong enough to overcome the surface tension of the polymer-solvent solution, a thin jet of dope solution ejects from the needle tip (i.e. from the Taylor cone). A jet is straight and stable close to the needle tip. At some points, however and due to instabilities in the electrical field, the jet begins to oscillate and move chaotically. This region of the jet path is called the bending instability region, and the oscillation of the jet is called the whipping motion (see Figure 3, for instance) [24]. Finally, reaching the collector, the jet deposits in a random manner creating a nonwoven mat composed of fine fibers.

Fig. 1. Some applications of electrospun nanofibers.

2.2. Operating parameters

The final properties of electrospun fibers greatly depend on the operating parameters (see Table 2). Fibers with different features (e.g. morphology and topography) can be produced by varying electrospinning conditions [25]. Uniform nanofibers are preferred for most applications [26]. However, in the field of the hydrophobic and superhydrophobic materials, beaded fibers and particles are often favored [27].
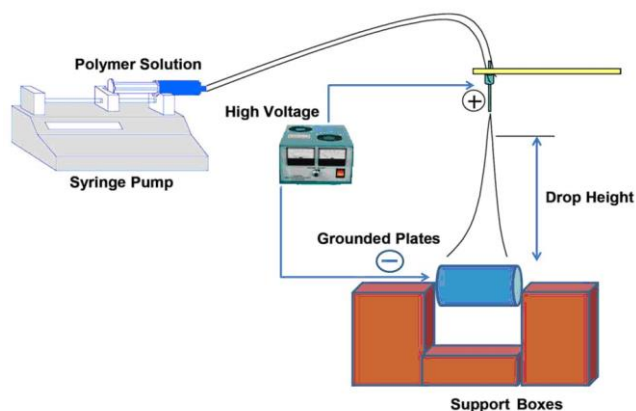
Fig. 2. A general scheme of electrospinning system (adopted from [20]).

Table 1
Common polymers and related solvents used for electrospinning [17].

Polymer full name	Polymer acronym	Solvent used
Polymetylmethaacrylate	PMMA	Chloroform Acetone Tetrahydrofuran (THF)
Tetrahydroperfluorooctylacrylate	(TAN)	Dimethyl formamide (DMF) Toluene
Polyvinyl alcohol	PVA	Water
Silicone		Water
PVA/cellulose nanocrystals		Water
Polyvinyl phenol	PVP	THF
Polyvinylchloride	PVC	THF DMF
Polyvinylcarbazole		Dichloromethane
Polyvinylidene fluoride	PVDF	Dimethylacetamide (DMA) DMF
PVDF-co-hexaflurorpropylene	PVDF-co-HFP	Acetone DMF
PVDF-co-HFP/nanocrystalline cellulose		
Polyacrylonitrile	PAN	DMF
Polylactic acid	PLA	Chloroform DMF

Table 2
Operating parameters for electrospinning [17].

Dope solution	Process	Environment
Concentration	Electrostatic potential	Temperature
Viscosity	Electric field strength	Humidity
Surface tension	Electrostatic field shape	Local atmosphere flow
Conductivity	Tip-to-collector distance	Pressure
Dielectric constant	Feed flow rate	Atmospheric composition
Solvent volatility	Needle (orifice) diameter	

In electrospinning, surface topography, fiber morphology and orientation are largely dictated by solution properties and operating conditions [28,29]. Since the rheology of the polymer solution is vital to the fiber formation process, polymer molecular weight and concentration directly affect fiber properties [30,31].

Conductivity of the polymer solution is also known to change properties of the resultant fibers [32]. To increase the dope solution's conductivity, some researchers added a number of salts, in which the results were promising [32,33]. Fiber properties are also directly affected by operating conditions such as applied voltage, dope solution flow rate and tip-to-collector distance [34]. Ambient conditions such as temperature and humidity of the electrospinning chamber can also alter fiber morphology [35]. Further

information on the effect of operating parameters on the electrospinning result could be found in the literature [36-40].
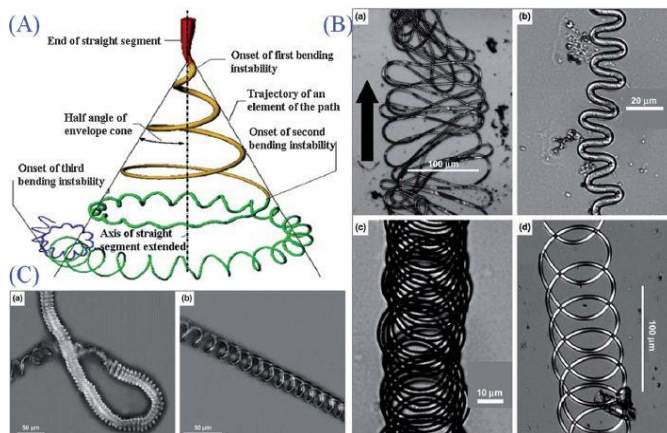

Fig. 3. Different scheme of the whipping phenomena in electrospinning (Adopted from [23]).

3. Characterization of electrospun membranes

The expectable results of typical membrane processes using an electrospun membrane are directly affected by the applied membrane's performance. Subsequently, the membrane performance is directly affected by its characterization [41]. In other words, knowledge on the membranes specifications, membrane materials and morphology is very important for the engineering of polymer barriers for various applications and the development of industrial membrane units [42]. In this regard, the membranes surface characterization is the second step, in addition to adjusting the electrospinning step in the design and development of electrospun membranes.

The available structural characterization methods are classified into two main categories, which cover a broad range of physical methods. The first are the methods related to membrane permeation such as liquid and gas flow tests, solute transport method, and liquid displacement method. The second are the methods which permit directly obtaining the surface morphological properties of the membranes; such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), field emission scanning electron microscopy, atomic force microscopy (AFM), electron spin resonance, energy dispersive spectroscopy, Raman spectroscopy, nuclear magnetic resonance (NMR), energy dispersive X-ray analysis, confocal microscopy, differential scanning calorimetric, *Fourier* transform infrared spectroscopy, and etc. These methods have been used to characterize the membranes surface properties such as determination of pore size, maximum pore size, pore size distribution, roughness, hydrophobicity, chemical composition, elemental structure, fouling potential, morphology, etc. Among the physical features of a microporous electrospun membrane, the most important parameters which determine the applicability of a membrane for a specific liquid separation process are pore characteristics, surface characteristics and hydrophobicity.

3.1. Pore size and pore size distribution

Whereas pore size is a measure of the diameter of the largest pore, pore size distribution is a measure of the range of pore sizes. There are some practical techniques for measuring these parameters which are described as follows.

3.1.1. Gas permeation

Permeation, from an engineering aspect, is the penetration of permeate, such as liquid, gas, or even a vapor, through a microporous membrane, and is related to a polymer's intrinsic permeability. This method allows measurement of the mean pore size (μm). An inert gas (either dried air or nitrogen) is employed as the standard gas. In this method, the gas permeation flux for the dry membrane is measured at various pressures. One of the limitations of this technique is the determination of pore size distribution [43-46].

3.1.2. Bubble point

This method is based on determination of the pressure necessary to blow nitrogen through a liquid filled electrospun membrane [47]. It is worth quoting that this method is able to measure only the maximum pore size

present in the membrane [48].

Figure 4 presents a general scheme of a typical test apparatus, which is designed and constructed in the *Membrane Processes Research Laboratory* (MPRL) (at the Department of Chemical Engineering, Amirkabir University of Technology). In the bubble point test module, a liquid (distilled water) is placed on the top side of the membrane sample, while the bottom side is in contact with nitrogen. The pressure of nitrogen is gradually increased until bubbles of nitrogen penetrate through the electrospun membrane into the liquid pool. The observed pressure is related to the pore size through the *Kelvin* equation [49-51].

3.1.3. Wet/dry flow method

The bubble point together with the gas permeation test which is known as the wet/dry flow technique can be employed for measuring the maximum pore size, the mean pore size and the pore size distribution of electrospun membranes [52].

In this method, the gas permeation is determined through a dry membrane sample, and a straight line is observed between the gas flux and the applied pressure. In the next step, the electrospun membrane is soaked in a low surface tension liquid (such as isopropyl alcohol) and again the gas flux will be determined at different applied pressures. It will result in a non-linear dependency between the gas flux and the applied pressure. Then the maximum pore size can be determined using theoretical expressions [53].

3.2. Porosity

The ratio between the volume of the pores and the total volume of the membrane is the membrane porosity, which can be measured by the use of this expression:

$$P(\%) = (\frac{1 - \rho_M}{\rho_b}) \times 100 \qquad (1)$$

where ρ_M and ρ_b are the density of the electrospun membrane and the density of the bulk polymer, respectively [54]. The value of this parameter is usually provided by the manufacturers for commercial membranes [55]. High porosity is one of the most interesting features of electrospun membranes compared with commercial ones [56]. Higher porosity of electrospun membranes significantly increase the permeation flux, and subsequently the overall process efficiency.

3.3. Microscopic methods

3.3.1. Scanning electron microscopy
Scanning electron microscopy (SEM) provides a convenient technique for characterizing and studying the surface morphology of the electrospun membranes, i.e. pore size, its distribution, and porosity [57,58].

In this method, the samples were prepared by gold coating of the membrane's surface to avoid charging up of the electrospun membrane surface. SEM is a simple technique enabling a clear view of the overall structure of the membranes, i.e. the top surface, the bottom surface, and the cross section of the membrane [59,60]. It is important to note that one of the limitations of this method is the heavy metal coating for the electrospun membrane sample preparation, which yields some artifacts and tends to damage the fibers' surface, especially in the case of roughness property [61]. Figure 5 shows the SEM image of typical polymeric membranes, made of different materials and via various fabrication methods.

3.3.2. Atomic force microscopy
Atomic force microscopy (AFM) is a newly developed high-resolution method for studying the surface topography of various types of membranes [62]. In this method, three dimensional (3D) images of the membrane surface can be obtained directly without special sample preparation [63]. As a consequence, a truer and clearer surface structure of an electrospun membrane, and the fibers as well, can be observed using AFM.

There are three different modes of AFM operations including contact-mode, noncontact-mode, and tapping mode [64]. One of the most practical surface features which can be directly measured using AFM is the surface roughness [65,66]. AFM analysis can provide different roughness parameters which can be used for topographical studies as well as surface energy measurements. Table 3 presents the most important roughness parameters and their definitions. Further information on the application of AFM to characterize different types of polymeric membranes could be found in the literature.
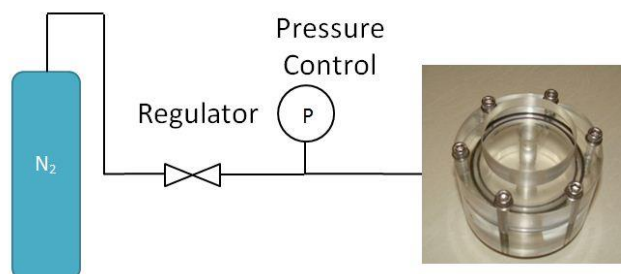
Fig. 4. A general schematic drawing of the bubble point test apparatus.
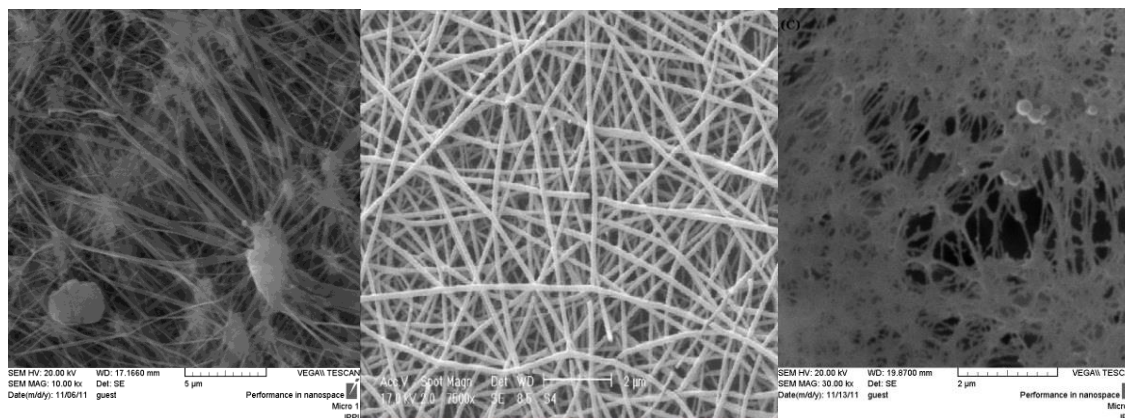
Fig. 5. The SEM images of microporous polymeric membranes, made of different materials and fabricated via various methods; (left) PTFE membrane with reported pore size of 0.22μm (Chang-Qi, China), fabricated via film-stretching method; (middle) Nylon-6,6 membrane with 0.47μm measured pore size (self-made membrane), fabricated via electrospinning method; (right) PVDF membrane with reported pore size of 0.22μm (Sepro, China), fabricated via film-applicator solution-casting method.

Table 3
Typical roughness parameters and their definitions that can directly obtained by AFM method [65].

Parameter	Definition
Arithmetic average height ($\bar{z}$)	General description of height variations. $$\bar{z}(N,M) = \frac{1}{N}\sum_{x=1}^{N} z(x,y) \ \ (2D)$$ $$\bar{z}(N,M) = \frac{1}{MN}\sum_{x=1}^{N}\sum_{y=1}^{M} z(x,y) \ \ (3D)$$
Average roughness (R_a)	Gives the deviation in height. Different profiles can give the same R_a. $$R_a(N,M) = \frac{1}{N}\sum_{x=1}^{N}(z(x,y) - \bar{z}(N,M)) \ \ (2D)$$ $$R_a(N,M) = \frac{1}{NM}\sum_{x=1}^{N}\sum_{y=1}^{M}(z(x,y) - \bar{z}(N,M)) \ \ (3D)$$
Root mean square roughness (R_q)	Represents the standard deviation of surface heights. $$R_q(N,M) = \sqrt{\frac{1}{N}\sum_{x=1}^{N}(z(x,y) - \bar{z}(N,M))^2} \ \ (2D)$$ $$R_q(N,M) = \sqrt{\frac{1}{NM}\sum_{x=1}^{N}\sum_{y=1}^{M}(z(x,y) - \bar{z}(N,M))^2} \ \ (3D)$$
Maximum profile peak height (R_p)	Height of the highest peak above the mean line in the profile. $$R_p = \max(z_i - \bar{z}); \ 1\langle i\langle N$$
Maximum profile valley depth (R_v)	Depth of the deepest valley below the mean line in the profile. $$R_v = \left|\min(z_i - \bar{z})\right| \ ; \ 1\langle i\langle N$$
Total roughness (R_t)	$$R_t = R_p + R_v$$

3.4. Liquid entry pressure

The liquid entry pressure (LEP) of a liquid (mostly water), which is called wetting pressure and is sometimes faulty, is the pressure that must be applied onto deionized water before it penetrates into a dry microporous membrane [67]. The experimental apparatus for this measurement is shown in Figure 6.

The following procedure is suggested for the determination of the LEP. The dry electrospun membrane is placed into the measuring module and a water bath is filled with deionized water. The lower part of the module which is the permeate side of the membrane is placed in the water bath. The electropun membrane is fed with a 20% NaCl solution. Using a gas cylinder (mostly nitrogen), a slight pressure is applied to the feed side. The pressure is increased until the sodium chloride solution enters the deionized water present in the water bath. The presence of sodium chloride in the water bath is determined by conductivity measurements. The lower pressure at which the sodium chloride solution penetrates into the deionized water at the permeate side is called the LEP. It is worth quoting that in some membrane-based separations such as the membrane distillation (MD) process, the LEP value of the applied membrane should be as high as possible [68]; however, in the case of pressure-driven membrane processes, depending on the fouling criteria, it must be as low as possible [69,70]. The LEP of microporous membranes, and specifically electrospun membranes, is affected by their intrinsic hydrophobicity. Moreover, it should be noted that the presence of some organic compounds, such as alcohol and surfactants, can lead to a decrease in the LEP value of the proposed membrane [67].

3.5. Hydrophobicity

Hydrophobicity is one of the most important specifications of the electrospun membranes, which can affect the membrane flux and membrane fouling potential [71]. Contact angle (CA) is a measure of surface hydrophobicity of an electrospun membrane. While higher surface hydrophobicity is a critical feature for the MD process [72] (high hydrophobicity is the first required property of the applied membrane in the MD process), hydrophilic membranes show better performance in pressure-driven membrane processes.

It is worth quoting that the fabrication method as well as surface topographical features can affect the membrane hydrophobicity [73]. The electrospun membranes usually show higher hydrophobicity compared with intrinsic hydrophobicity of the bulk polymer [17]. For instance, Shirazi et al. [20] measured the contact angle for the electrospun microporous polystyrene

membrane at 135.5º, while the intrinsic contact angle for the polystyrene film, prepared via the solution-casting method, was obtained at 88.6º.

4. Electrospun membranes for desalination and water/wastewater treatment

Microporous polymeric membranes, which have been used progressively for various applications [54,74], can be fabricated through different methods, including film lithography, stretching, phase inversion, and etc. Each method has its own benefits and limitations [73]. In the past few years, electrospinning technology has been further investigated for the fabrication of microporous polymeric membranes [75]. Although this remains an emerging field of interest, about 1210 publications have been produced on the combined topic of *Electrospinning*, *Desalination*, *Water* and *Wastewater* treatment from 2000 to the present (based on the search on *Google Scholar*, 2016/03/08). This has resulted in over 30,000 publication citations for the same period.

Currently electrospun nanofibrous membranes are a very attractive and plausible solution in filtration technology due to their unique properties, including their higher porosity, (typically around 80%), controllable pore size distribution, high permeability, and fully interconnected pore structure [14,40]. Figure 7 presents a general scheme of the *electrospun nanofibrous membranes*.

As opposed to the traditional membrane fabrication methods [42,77-79], electrospinning leads to membranes with relatively uniform pore size distribution with high interconnectivity of pores and significantly higher porosity, as mentioned above [80]. As a result, electrospun micro-/nano-fibers are widely gaining attention for use in separation processes where these properties are desirable. As mentioned earlier, electrospun nanofibrous membranes have been applied to many purification/separation purposes, including pressure-driven membranes, the membrane-distillation process, pretreatment of feed prior to RO or NF processes, oil-spill cleanup and oil-water separation. Recently, thin film composite (TFC) membranes for RO and NF desalination are also being fabricated on electrospun webs. Table 4 summarizes recently published review papers covering the *electrospinning* and *membrane* subjects. Many advances are rapidly being made in the preparation and modification of electrospun nanofibrous membranes for desalination and water/wastewater treatment, especially in the last few years. There is thus a need to review these developments in order to pave the way for future studies.
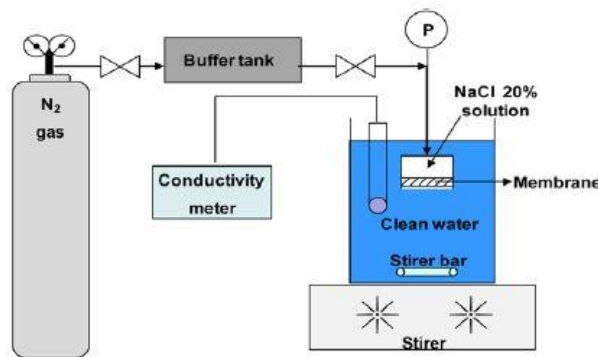

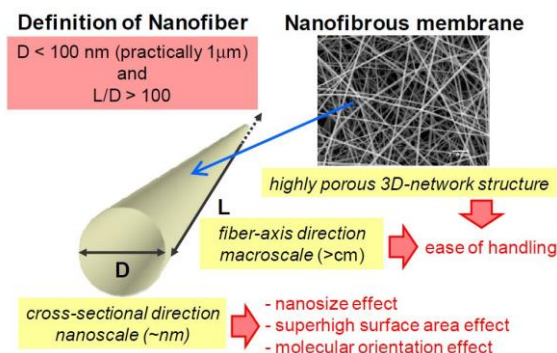**Fig. 6.** General scheme of the LEP test apparatus [68].

Fig. 7. Characteristics of electrospun membrane [76].

Table 4
Some recently published review papers cover the *Electrospinning* and *Membrane* subjects.

Publication year	Title	Journal	Ref.
2016	A comprehensive review: electrospinning technique for fabrication and surface modification of membranes for water treatment application	RSC Advances	[81]
2016	Electrospun fibers for oil-water separation	RSC Advances	[82]
2016	Electrospun nanofiber membranes	Current Opinion in Chemical Engineering	[8]
2016	Thermally induced phase separation and electrospinning methods for emerging membrane applications: A review	AIChE Journal	[83]
2016	A review of polymer nanofibers by electrospinning and their application in oil-water separation for cleaning up marine oil spills	Marine Pollution Bulletin	[40]
2015	A review on electrospinning for membrane fabrication: Challenges and applications	Desalination	[17]
2015	Functionalization of polymeric materials as a high performance membrane for direct methanol fuel cell: A review	Reactive and Functional Polymers	[39]
2014	Recent progress of membrane distillation using electrospun nanofibrous membrane	Journal of Membrane Science	[84]
2014	A review of recent developments in membrane separators for rechargeable lithium-ion batteries	Energy and Environmental Science	[85]
2014	Application and modification of poly(vinylidene fluoride) (PVDF) membranes-A review	Journal of Membrane Science	[86]
2014	Review: the characterization of electrospun nanofibrous liquid filtration membranes	Journal of Materials Science	[87]
2013	Preparation and characterization of electro-spun nanofiber membranes and their possible applications in water treatment	Separation and Purification Technology	[88]
2013	A review on membrane fabrication: Structure, properties and performance relationship	Desalination	[73]
2013	Industrial upscaling of electrospinning and applications of polymer nanofibers: A review	Macromolecular Materials and Engineering	[89]
2012	Polyacrylonitrile-based nanofibers-A state-of-the-art review	Progress in Polymer Science	[90]

Table 5
Summary of recently published works on electrospun membranes for pressure-driven and osmotic membrane processes.

Ref. and year	Polymer/solvent system	Experimental	Target separation
[95], 2017	Polyvinyl acetate, Nylon 6	Electrospinning High-voltage: 30 kV Q_d=0.18 mL/h Tip-to-collector distance: 8.8 cm Relative humidity: 40% Characterization SEM Hydrophobicity AFM	Oil-water separation
[96], 2017	Polyacrylonitrile (Mw=150,000 g·mol^{-1}) DMF	Electrospinning High-voltage: 18 kV Needle ID: 0.4 mm Q_d: 0.5 mL/h Characterization SEM Porosity	Microfiltration of suspended particles
[97], 2017	Alginate PET	Electrospinning High-voltage: 25 kV Q_d: 0.7 mL/h Tip-to-collector distance: 18 cm	Ultrafiltration of dye solution
[98], 2017	Cellulose acetate Polysulfone DMF	Electrospinning High-voltage: 17 and 25 kV Needle: 18 and 22 gauges Tip-to-collector distance: 10 cm Characterization SEM	Ultrafiltration of BSA and PEG mixtures
[99], 2017	Polyetherimide DMF NMP	Electrospinning High-voltage: 30 kV Needle ID: 0.75 mm Q_d: 15 μL/min Tip-to-collector distance: 12 cm Humidity: 50%	Forward osmosis
[100], 2016	Polyethersulfone Different solvents	Electrospinning ^{a} Q_d=0.1, 0.4, 0.7, 1.0 and 1.3 ml/h Solvent vapour treatment Characterizations SEM Bubble point Tensile test Retention test Dead-end microfiltration of nanoparticle suspension	Filtration of bacteria and fungus culture media

Table 5
Continued.

Ref. and year	Polymer/solvent system	Experimental	Target separation
[101], 2016	Polyvinylidene fluoride	**Novelty** A new tree-like MF membrane **Materials** Polymer: PVDF (M_w=520,000) Solvent: DMF Additive (salt): TBAC **Electrospinning** Dope solution concentration: 17 wt% Additive concentration: 0.05, 0.10 and 0.15 mol/L High voltage: 25 kV Tip-to-collector distance: 15 cm Flowrate: 1 mL/h **Characterization** FESEM Pore size meter FTIR Contact angle	Dead-end filtration
[102], 2016	Polyacrylonitrile	**Modelling** Central composite design **Fibres' size** 100-500 nm **Characterizations** Porosity (61%-74%) Pore size (0.48-1.4 µm) Mechanical properties	Filtration of Ti-O_2 microparticles Rejection: 99% Steady-state flux: 118 l/m²h
[103], 2016	Polyamide	**Membrane modification** Heat treatment **Characterizations** SEM Dimensional changes (>2%) Tensile strength	Bacterial removal
[104], 2016	Cellulose acetate	**Separation test** Filtration of dispersed polystyrene particles (5 and 2 µm, 100 and 500 nm) Rejection: 99.8% for 2 µm particles Initial flux: 20455 l/m²h at feed pressure of 14 psi **Membrane modification** Post-processed by heatpress	River water filtration Final turbidity of 0.135 NTU for filtered river water sample
[105], 2016	Chitosan Polyvinyl alcohol Polyacrylonitrile	**Membrane** Dual-layer composite membrane **Contaminants rejection performance** COD removal: 61.14% TDS removal: 34.6% Turbidity removal: 99.8% **Tested membrane characteristics** Fiber diameter Porosity Pore size	Wastewater pre-treatment
[106], 2016	Poly(vinylidene fluoride-*co*-hexafluoropropylene) Fluorinated polyhedral oligomeric silsesquioxane	**Membrane** Composite highly hydrophobic/superoleophilic membrane **Characterizations** Contact angle (for water: 145°) SEM **Feed samples** Low viscous oil **Separation efficiency** Nearly 100%	Oil-water separation
[107], 2015	Poly(m-phenylene isophthalamide	**Solvent and additive** *N,N*-Dimethylacetamide $CaCl_2$ **Rejection test** Performed by using polystyrene particles (0.20 and 0.105 µm) **Electrospinning** Dope solution: 14 wt% m-Aramid (5.25 g of m-Aramid; 30 g of DMAc 2.26 g of $CaCl_2$; All chemicals mixed for 5 h at 120 °C) Q_d = 10 µL/min Tip-to-collector distance: 15 cm High-voltage: 12-15 kV Needle (gauge=30): 0.159 mm inner diameter Relative humidity and temperature: ~25% and ~23 °C, respectively **Characterizations** Micrometer for measuring the thickness FESEM [b] Image processing software for measuring fibers diameter and its distribution Capillary flow porometer for pore size distribution measurement	Water filtration

Table 5
Continued.

Ref. and year	Polymer/solvent system	Experimental	Target separation
[108], 2015	Polyamide Polysulfone	Solvent and additive DMF NaOH Electrospinning Voltage: 20 kV Tip-to-collector distance: 15 cm Characterization FESEM TGA	Oil-water separation
[109], 2011	Polymers PES (M$_w$=7.8×10^4 g/mol) PSf (M$_w$=8.0-8.6×10^4 g/mol) Solvent DMF (anhydrous, 99.8%) NMP (anhydrous, 99.5%) TMC (98%) MPD (>99%)	TFC fabrication Interfacial polymerization Electrospinning Voltage: 27.5 kV Tip-to-collector: 16 cm Temperature: 25 ℃ Relative humidity: 10% Injection flowrate: 1.2, 0.9 and 0.6 ml/h Characterization SEM Surface contact angle ATR-FTIR FIB	Forward osmosis
[110], 2016	Polymer PAN (M$_w$=150,000 g/mol) Solvent MDP TMC DMF	Target study Engineering the support layer Nanoparticle Silica (SiO$_2$: 200 nm particle size, 4 nm pore size) Electrospinning Voltage: 28.5 kV Flowrate: 1.0 ml/hr Tip-to-collector: 16 cm Relative humidity: 50% Ambient temperature Characterization Transmission electron microscopy (TEM) Energy-dispersive X-ray (EDX) Brunauer-Emmett-Teller (BET) FESEM	Reverse osmosis Forward osmosis Pressure retarded osmosis
[111], 2016	Polymer PVDF (Mw: 550 kg/mol) Solvent DMF THF	Electrospinning Voltage: 20 kV Needle: ID=0.75 mm and OD=1.59 mm Flowrate: 1.5 mL/h Collector: rotating drum (70 rpm) Tip-to-collector distance: 15 cm Temperature: 23±2 ℃ Characterization AFM FESEM EDX Contact angle Tensile module	Forward osmosis

[a] Q$_d$ = Dope solution flow rate
[b] Field emission SEM
NMP: N-methyl-2-pyrrolidone
MPD: m-phenylenediamine
TMC: 1,3,5-benzenetricarbonyl trichloride
FIB: Furthermore focused ion beam
PAN: Polyacrylonitrile

4.1. Electrospun membranes for pressure-driven separation

The primary function of a filtration membrane is to separate two distinct phases, preferentially regulating one phase through the membrane while simultaneously acting as a barrier to the other phase, such as suspended solids and bacteria [91,92]. Safe removal of waterborne pollutants is critical to clean water recovery [93,94].

Although current membrane technology is beginning to meet these needs, low throughputs of these membrane-based separations have led to the need for novel membrane solutions, including nano-engineered membranes. The

main advantages of electrospun membranes are the presence of the highly porous, interconnected, 3D fibrous network, which provides a high internal surface area and hence enormous separation capacity when compared to conventional membranes with a two dimensional structure [12]. Table 5 summarizes recent works on the application of electrospun nanofibers for fabricating polymeric membranes.

The first efforts in this field probably go back to the years 2004 to 2006 [112]. As the first steps, some research groups worked on particle separation from an aqueous stream. For instance, Gopal and co-workers [113,114] used three different electrospun membranes made of PVDF, PSf (polysulfone) and nylon-6 to remove polystyrene particles (diameter from 0.1 to 10 μm) in a liquid stream. The authors indicated that the average diameters of the electrospun nanofibers were 380 nm, 470 nm and 110 nm for PVDF, PSf and nylone-6, respectively. Moreover, the pore sizes of the corresponding electrospun membranes (in a same order) were in the range of 4-10.6 μm, 1.2-4.6 μm and 6-7.5 μm, respectively. For removing polystyrene particles with 10 μm mean diameter, all electrospun membranes showed >95% rejection ratio.

Some other researchers tried to develop the application of electrospun membranes to food/juice processing [115]. For instance, Veleirinho and Lopes-da-Silva [116] studied the application of an electrospun membrane made of PET (polyethylene terephthtalate) for clarification of apple juice. In this work, self-supporting nanofibrous PET membranes with promising mechanical properties (see Figure 8) were fabricated. The authors compared the aspun membranes' performance with ultrafiltration (UF) membranes and the conventional clarification method. Based on the experiments, the required processing time based on 150 mL apple juice was measured at 160 min, 35 min and 6 min using conventional clarification, UF membrane and nanofibrous PET membrane, respectively. On the other hand, conventional clarification needs at least 50 ºC operating temperature, while membrane processes work under ambient temperature. Moreover, the permeate flux for the nanofibrous PET membrane was measured at 3.5 mL/cm^2.min, while the same value for the UF membrane was measured at 0.17 3.5 mL/cm^2.min. In another work [117], the authors claimed a nanofibrous membrane made of nylon for the filtration of apple juice. In this research, the effect of electrospinning on the resulted aspun membrane samples was studied. In the next step, the filtration performance of these membranes was compared with two commercial polyamide membranes. Based on the obtained results, the authors concluded that the electrospun nylon membranes with 94% porosity and fibers of average diameter around 95 nm showed promising performance for clarification of apple juice. Moreover, it was concluded that the aspun membrane's performance was comparable with commercial polyamide membranes.
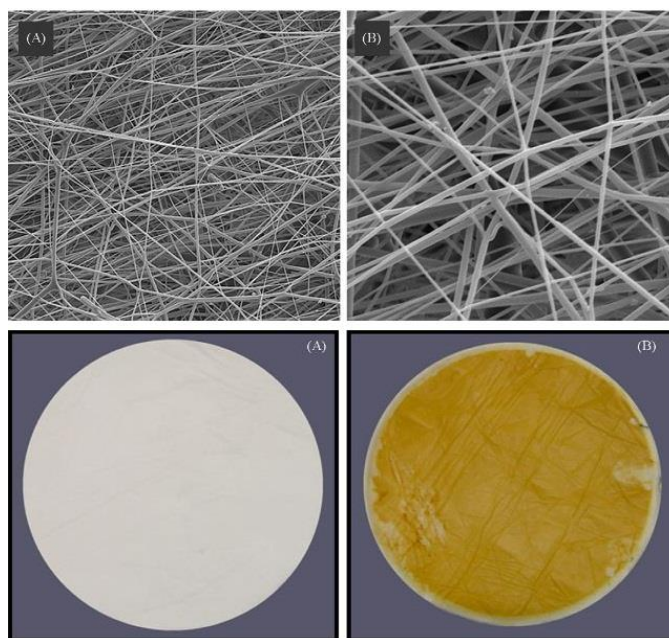
Fig. 8. Electrospun nanofibrous membrane made of PET for apple juice clarification [116].
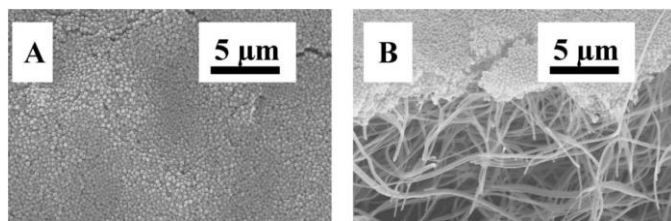
Fig. 9. SEM images of electrospun PAN/PET membrane (electrospun polyacrylonitrile (PAN)/non-woven polyethylene terephthalate (PET)) containing the electrospun layer thickness of 200 ± 10 μm and a mean fiber diameter of 100 ± 20 nm) after MF test using the 0.2 μm particle suspension [118].

Fig. 10. Pore size distribution of the electrospun PS membranes, before (M1) and after (M2) thermal treatment [122].

Table 6
Specifications of two commercial and an electrospun nylon membranes [56].

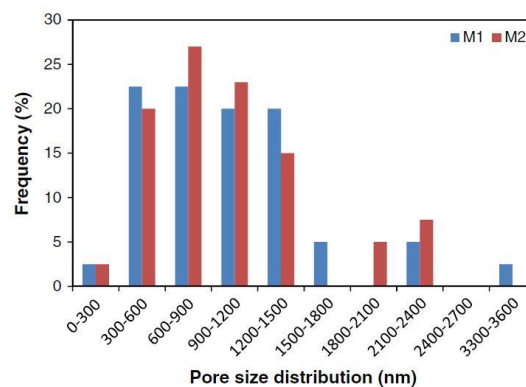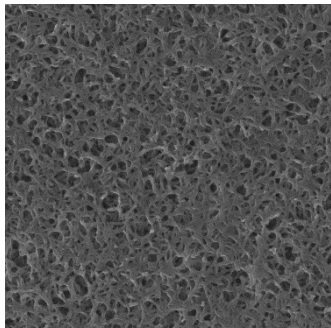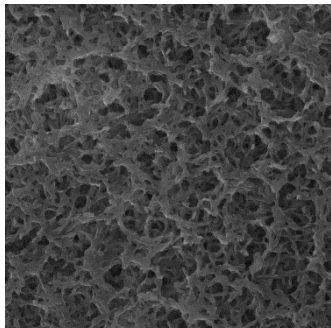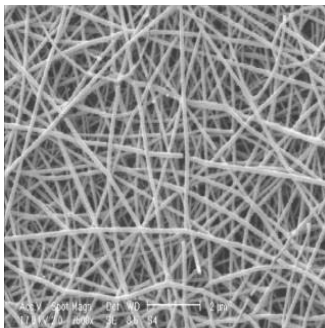| Membrane	N1	N2	N3
Illustrations			
Pore size (μm)ᵃ	0.22	0.45	0.53
Thickness (μm)	~110	~110	~150

ᵃ *Pore size (μm) measured based on SEM image processing.*

Wang and co-workers [118] studied the electrospun membranes for microfiltration (MF) purposes. In this work, a series of nanofibrous membranes with differing characteristics, e.g. fiber diameter, pore size, thickness and diameter distributions, were prepared to understand the effect of structure on the filtration performance. Results indicated a strong correlation between the membrane characteristics and the resulting filtration performance (see Figure 9). For instance, a thicker membrane with a smaller average fiber diameter greatly favors the formation of smaller pore size and narrower distribution. The authors concluded that the fabricated PAN/PET composite membranes showed a good MF performance as well as high rejection ratio for particles of ≥0.2 μm.

Mirtalebi et al. [56] studied the treatment of petrochemical wastewater using the microfiltration process. In this work, coke removal from the Olefin plant effluent was studied by employing both commercial and electrospun microfiltration (MF) membranes all made of nylon 6. The authors characterized all membrane samples for their morphological and topographical features using SEM and AFM microscopic techniques. Table 6 presents the characteristics of the proposed membranes. These results indicated that the membrane with a 0.45 μm pore size has the highest surface roughness, while the electrospun membrane (see the N3 in Table 6) has the lowest surface roughness. This indicates that the electrospun nylon membrane has a smoother surface when compared to other two commercial nylon membranes. On this basis, it could be concluded that lower surface roughness leads to a lower risk of fouling, a characteristic which is of crucial importance for water treatment applications. A detailed description of surface roughness parameters can be found in the literature [65]. The authors also concluded that having a more porous structure within the 3D interconnected pores led to higher initial permeate flux as well as lower flux decline, after coke removal from wastewater. It was argued that electrospun membranes possess a better overall performance than that of commercial membranes with 0.22 and 0.45 μm pore size [56].

It is indicated in the literature that the electrospinning process can increase the surface hydrophobicity for a number of polymers, such as polysulfone (PSf), polyethersulfone (PES) and PVDF [119,120]. On the other hand, in pressure-driven filtrations, it is more beneficial if the membrane is hydrophilic so that the flux is not compromised and has fewer tendencies to foul. Therefore, some research groups worked on hydrophilic surface modification of electrospun MF membranes. Kaur and co-workers [121] studied the fabrication of highly hydrophilic, PVDF-based electrospun membranes by means of different surface modifying agents (macromolecules), including urethane pre-polymer separately modified with both polyethylene glycol (PEG) (with average molecular weights of 400, 600 and 1000 Da) and polypropylene glycol (with average molecular weights of 3500 and 425 Da) of various molecular weights. The study compared the modified electrospun membranes with phase-inversion prepared membranes. Results of this work indicated that the investigated modification method, mostly using 1000 Da molecular weight PEG had a significant impact on the hydrophilic nature of the electrospun membrane as compared to the blend casted membrane sample. The authors concluded that this could possibly be

due to the orientation of the surface modifying macromolecules' hydrophilic groups adopted during electrospinning on the surface [121].

In another work, Shirazi and co-workers [122] fabricated electrospun membrane samples made of polystyrene without any chemical modification on the surface. In this work [122], a simple physical surface treatment method was applied, i.e. thermal treatment of the membrane's surface via contact heating. Results indicated that this surface modification led to an increase in the hydrophobicity. The modified electrospun membranes presented a surface contact angle of 156º, indicating a strong superhydrophobic membrane. The authors characterized the membrane samples before and after thermal treatment using the AFM method. This analysis indicated that after surface treatment, the fibers diameter increased, significantly, while the surface roughness decreased. On the other hand, narrower pore size distribution was observed after surface treatment (see Figure 10). In the next step, the membranes were used for treatment of the biodiesel's water-washing effluent through a dead-end filtration system. Results indicated that heat treated membranes resulted in the reduction rates of 58, 26, 92, 95 and 50%; and 75, 55, 92, 96 and 30% for COD, BOD, TS, TDS and TSS, respectively. The authors concluded that the multi-objective separation mechanism of electrospun membranes, i.e. screening, depth filtration and adsorption, could be the main reason of their superior separation performance [122].

For additional applications of electrospun membranes such as direct filtration media, electrospun polymeric webs can be used as the support layer for the new generation of *Thin Film Composite* (TFC) membranes [12]. TFC membranes (see Table 5), including UF, NF, RO and FO membranes (ultrafiltration, nanofiltration, reverse osmosis and forward osmosis membranes, respectively), are comprised of three fundamental layers, as shown in Figure 11, including the top ultrathin selective layer, middle porous support layer and bottom nonwoven fabric layer.

Kaur et al. [123] studied the application of an electrospun nanofibrous web as the support layer of TFC nanofiltration membranes. In this work, various PAN-based MF membranes with different fiber sizes were prepared. The fibers' diameter varied using changes in the polymer concentration (4, 6, 8 and 10%). Results indicated that with an increase in the fiber diameter, the bubble point was also increased. The interfacial polymerization technique (mixture of piperazine and *p*-phenylene diamine with trimesoyl choride) was then employed to coat a thin film on the surface of the electrospun web. The resulting membranes were used for desalting a saline solution with the salt concentration up to 2000 ppm (both monovalent and divalent ions). Experimental results of desalination tests indicated that as the fiber size decreased (towards nano-sized range), the salt rejection was increased but at the expense of permeate flux. Moreover, when the thickness of the support layer (electrospun web) was decreased with smaller pore size, it resulted in the increased permeate flux and higher salt rejection. Furthermore, the authors concluded that there was an upper limit to the fiber size of the electrospun web and the pore size of the TFC membrane, since, if the sizes are too large, the electrospun web can no longer support the thin selective layer. The optimum concentration of PAN for the electrospinning of fibers was observed at 8 wt% [123].
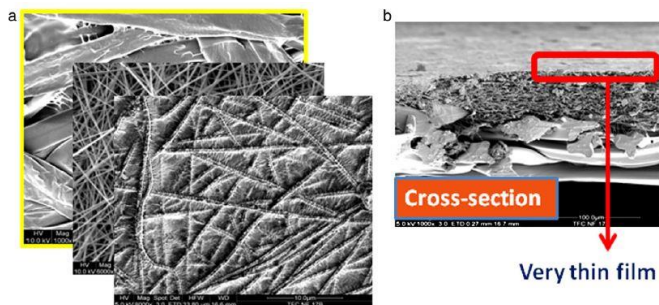
Fig. 11. The detailed structural view of TFC membranes (a) and its cross-section view (b) [12].

You et al. [124] reported the fabrication of high permeate flux low pressure TFC ultrafiltration membranes based on a nanofibrous substrate. In this work, a new UF membrane based on the PAN nanofibrous support layer coupled with a thin hydrophilic nanocomposite barrier layer was fabricated. This membrane was then used to separate oil-water emulsion. The hydrophilic top layer (i.e. the barrier layer) was composed of a crosslinked polyvinyl alcohol (PVA) thin layer incorporating surface oxidized multiwalled carbon nanotubes (MWCNTs). The final membrane was fabricated by immersing electrospun PVA-MWCNT/PAN webs into optimized water/acetone solution and then chemically cross-linked by glutaraldehyde in water/acetone solution. Figure 12 shows the schematic illustration of membrane fabrication in this work [124]. Results indicated that the free volume of the PVA-MWCNT/PAN
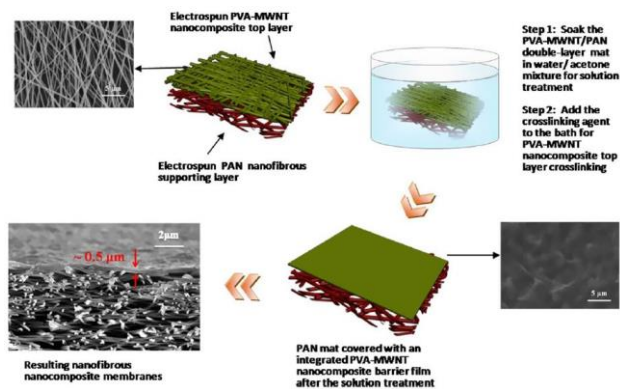
thin film nanocomposite membrane increased with an increase of MWCNT concentration in the PVA layer. Moreover, the oil-water filtration study also confirmed that the incorporation of MWCNTs into the PVA layer significantly improved the water permeation flux. Furthermore, experimental results indicated that even at a very low operating pressure of 0.1 MPa, both a high water flux of 270.1 L.m^{-2}.h^{-1} as well as a high rejection rate of 99.5% could be obtained. Figure 13 presents the operating pressure dependence of the permeate flux and rejection rate when these membranes were used for cross-flow UF filtration of oily wastewater samples. It was highlighted that the proposed TFC membranes can be easily fabricated and efficiently be employed for oily wastewater treatment [124].

It is worth mentioning that ENMs are suitable for pressure-driven membrane processes where the permeated phase is the target product, such as most water/wastewater treatments. Due to the 3D interconnected pore structure of ENMs and their high porosity (see Figure 14) in contrast to conventional polymeric membranes with 2D structure, the separation mechanism is triplicate, e.g. screening, depth filtration and adsorption on the fibers' surface [122]. Such a multi-objective separation mechanism is useful when the target is impurity removal from the feed stream. However, in other applications where the target product was located in the retentate stream (such as useful compound removal from aqueous streams) ENMs may not be as useful as conventional membranes. However, when a useful compound exists in the feed stream, such as spore and crystal in the fermentation broth of *Bacillus thuringiensis* biopesticide [125], the most suitable separation mechanism would be the screening. In other words, the other two mechanisms, i.e. depth filtration (spore/crystal trapping in the ENM's bulk) and adsorption on the fibers' surface, can actually increase the loss of the target compound.
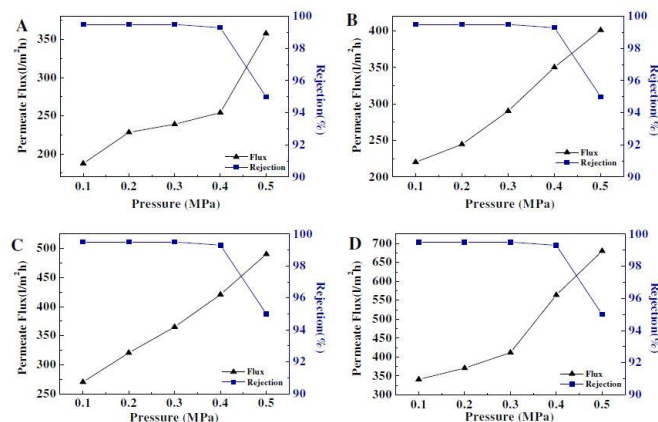

Fig. 12. The general scheme of the fabrication process for TFC membranes based on PAN nanofibrous substrate and crosslinked PVA-MWCNT barrier layer in You et al. work [124].

Fig. 13. The pressure dependence of water permeation flux and oil rejection rate of the fabricated membranes (The hydrophilic nanocomposite barrier layer was composed of crosslinked poly(vinyl alcohol) (PVA) thin layer incorporating surface oxidized multi-walled carbon nanotubes (MWNTs), and was prepared by immersing electrospun PVA-MWNT/PAN nanofibrous double-layer mats into optimized water/acetone solution and then chemically crosslinked by glutaraldehyde in water/acetone solution) in You et al. work [124].

4.2. Electrospun membranes for membrane distillation processes

While higher hydrophilicity and lower surface roughness of electrospun nanofibrous membranes are advantageous for pressure-driven membrane processes; conversely, hydrophobicity, or even super-hydrophobicity, is a critical feature when such membranes are used for the membrane distillation (MD) process. MD is a thermally-driven separation in which pure water is separated from a contaminated source such as saline water (e.g. seawater, brackish water or even a wastewater sample containing non-volatile impurities) [126]. MD has four major configurations; however, recently new configurations are introduced and all of which could be efficiently used for desalination and water/wastewater treatment purposes [5].

In considering the global scientific R&D efforts in the MD process, especially for desalination and water/wastewater treatment purposes [127,128], this method has not yet been scaled to industrial levels. One of the most significant hurdles for this is the lack of novel and specific membranes for the MD process.

The applied membranes in the MD process should display some important property characteristics before they can be employed. The membrane should be hydrophobic, as highly porous as possible, have high liquid entry pressure (LEP), and should have good thermal/chemical/mechanical stability [129,130]. However, most of the applied membranes for MD are those commercially fabricated for MF purposes and made of hydrophobic polymers [55]. In this regard, electrospun membranes have shown promising features for use in the MD process.

The first application of the electrospun membrane for desalination through the MD process was reported in 2008 by Feng et al. [71]. In this work, PVDF-based (Kynar 760 grade) as-spun membrane samples were used for desalting 6 wt% NaCl solution via the air-gap membrane distillation (AGMD) process. The authors characterized the membrane samples (i.e. nanofibers) using both SEM and AFM analyses. It is indicated that with a 60 ºC temperature difference, a distillate flux as high as 11 kg.m^{-2}.h^{-1} and salt rejection higher than 98% was achieved.

Essalhi and Khayet [131] studied the preparation of ENMs of the PVDF

polymer for desalination through the direct-contact membrane distillation (DCMD) process. In this work, the authors investigated the effect of electrospinning time and the correspondence thicknesses (ranging from ~144 μm to ~1500 μm). It is claimed that this was the first systematic experimental study on the thickness effects of electrospun membranes on the performance of the DCMD process. The thickness increase was observed as well as higher LEP of water with an increase in electrospinning time, and a decrease of the mean size of the inter-fiber space, as well. However, no significant change was observed in the fibers diameter. SEM observations of fabricated electrospun membranes in this work's membranes indicated that the average fibers' diameter was 1 to 1.3 μm. Electrospun membranes displayed a surface contact angle of between 137.4 to 141.1° values. For the next set of experiments, the authors used the membrane samples for desalting feed streams with a salt concentration up to 60 g/L. It is concluded that an increase in the electrospinning time and the membrane thickness also led to a lower distillate flux. However, the fluxes obtained in this study were higher than those reported so far for PVDF-based electrospun membranes [131].

In another work, Francis et al. [132] developed nanofibrous PVDF-based electrospun membranes and compared them with hollow fiber membranes (made of the same polymer) prepared by wet-jet spinning. The sponge-like structure of hollow fiber membranes makes transport, and thus flux, more difficult, whereas the nanofibrous membrane has an open structure with a less tortuous path. Moreover, the electrospun membrane was found to be more hydrophobic, making it more suitable for MD applications. Consequently the water flux through the electrospun membrane was 36 L.m^{-2}.h^{-1}, compared to 31.6 L.m^{-2}.h^{-1} for the hollow fiber membrane (when tested with a temperature difference of 60 °C across the membrane).

The electrospun membrane fabricated using polystyrene can achieve a highly porous structure with (super)hydrophobicity features [122], so it may find interesting applications for use in the MD processes. Li et al. [133] developed dual-biomimetic polystyrene nanofiber membranes with micro/nanoscaled roughness (see Figure 14). When tested for DCMD, these novel membranes were able to maintain vapor fluxes several times that of commercial PVDF and their permeate conductivity was comparable to commercial membranes. At a thickness of 60 μm and a temperature gradient of 50 °C across the membrane, the flux through the membrane was 51 kg.m^{-2}.h^{-1}.

Liao et al. [134] developed dual layer super hydrophobic membranes based on PVDF containing silica nanoparticles for desalination applications using the MD process. These membranes have shown significantly higher fluxes and rejection rates compared to the electrospun membranes that have been reported in the literature [84]. The authors concluded that in order to make these membranes adoptable to water industries, more optimization is needed in controlling the membrane pore size and enhancing the membranes long term performance by optimizing the SiO$_2$ composition [134].
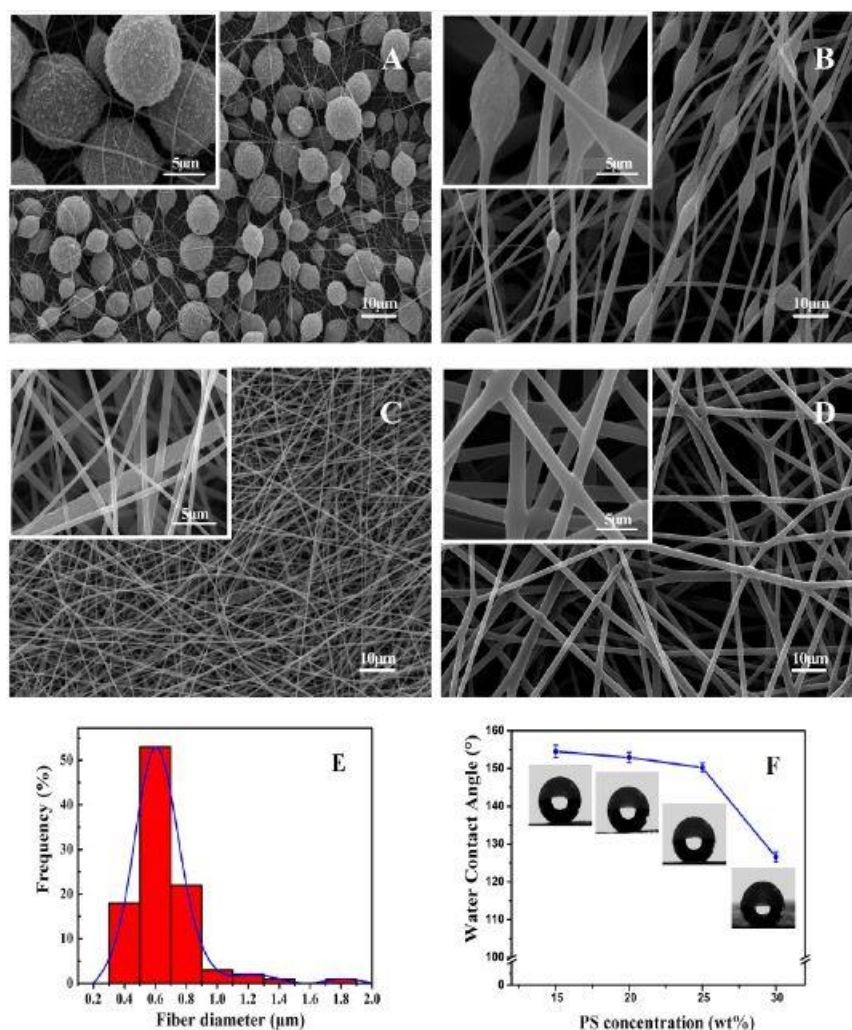

Fig. 14. SEM images of (A) PS-15, (B) PS-20, (C) PS-25, and (D) PS-30. (E) Fiber diameter together with its distribution of PS-25. (F) Water contact angles for PS-15−30 nanofibrous membranes, Li et al. work [133].

Recently, Tijing and his co-workers [135] studied a novel electrospun membrane for the DCMD process, containing a carbon nanotube. In this work, superhydrophobic, robust, mixed matrix nanofiber membranes made of polyvinylidene fluoride-co-hexafluoropropylene (known as PcH in brief) were fabricated. Different concentrations of carbon nanotubes (CNTs) (i.e. 1–5 wt%) were investigated as nanofillers to impart additional mechanical and

hydrophobic properties. The electrospun membrane has been designed to have two cohesive layers, a thin CNT/PcH top layer and a thick neat PcH bottom layer (see Figure 15). The authors indicated that through different characterization methods, CNTs were found to be widely distributed in the nanofibers, where more beads-on-string were formed at higher CNT content. However, the beads-on-string did not significantly affect the membrane porosity and pore size, and also did not degrade the MD performance. On the other hand, it is discussed that the highly-porous structure was observed for all membranes and the nanofiber membrane showed comparable pore sizes with a commercial flat-sheet PVDF membrane. Results indicated that the contact angle increased to superhydrophobic at 158.5° upon the incorporation of 5 wt% CNTs in the nanofiber due to increased roughness and the added effect of hydrophobic CNTs (see Figure 16). The liquid entry pressure also increased when 5 wt% CNT was added compared to the neat PcH nanofiber membrane. The authors concluded that, compared to the commercial PVDF membrane distillate flux (18–18.5 L/m²h), the resulting distillate flux of the 5 wt% CNT-incorporated nanofiber membrane was consistently higher (i.e. 24–29.5 L/m²h). The present nanofiber membranes containing CNTs with one-step electrospinning fabrication show high potential for DCMD desalination application [135].
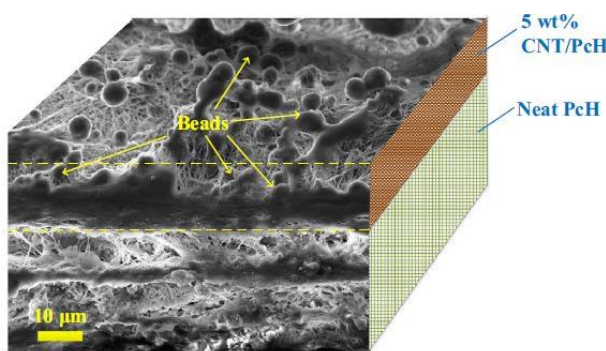
In another work, Ke and his co-workers [136] studied the fabrication of hydrophobic electrospun polystyrene (PS) nanofibrous membranes. The fabricated membranes were used in the DCMD process for seawater desalination. In this work, PS solutions in *N,N*-dimethylformamide (DMF) (with different concentrations of 8, 10, 12 and 15 wt%) with the addition of sodium dodecyl sulfate (SDS) as a processing aid were used for electrospinning. The electrospinning system consisted of 60 ml syringes (containing the same PS-DMF solution), a dual spinneret (ID/OD of 0.6 and 0.9 mm, respectively), a rotating collector (100 rpm) with a distance of 18 cm to the tip, and a high voltage system to supply 30 kV operating voltage. Effects of membrane thickness and fiber diameter on the average pore size and pore size distribution of nanofibrous membranes were systematically studied. Figure 17 shows the pore size distribution of the fabricated PS membranes. The resulting distillate flux and product water quality (which were determined based on the distillate conductivity) of membranes with different thicknesses and mean pore sizes from DCMD measurements were compared with those of commercially available PTFE membranes using different feed solutions (e.g. tilled water, simulated brackishwater, 35 g/L NaCl solution and seawater). Moreover, effects of major operating parameters, including flow rate (i.e., 0.2, 0.3 and 0.4 gallon per minute (GPM)) and feed stream temperatures (i.e., 70, 80 and 90 °C) on the distillate flux and its conductivity of the optimized PS nanofibrous membrane (with a mean pore size about 0.19 mm) were further investigated. Additionally, the mass and heat transfer coefficients of the optimized nanofibrous membranes in the DCMD operation were calculated. The results indicated that hydrophobic PS nanofibrous membranes can be produced by electrospinning for desalination by the DCMD method [136].

More recent publications and their technical information about the application of electrospun membranes for the MD process can be found in Table 7.

4.3. Electrospun nanofibers for adsorption processes

Over many decades, the extraction of harmful chemicals from contaminated water sources via chemical adsorption processes has been viewed as one of the most effective techniques with minimal environmental impact. Recently, electrospun nanofibrous sorbents have been considered as a low cost and easily available alternative. Min and his co-workers [143] studied the chitosan-based nanofibers as adsorbents for arsenate removal from aqueous stream. In this work, the authors prepared highly porous nanofibers which displayed fast adsorption kinetics, high adsorption capacity and easy separation from water. It is also noted that pH plays a critical role in the removal of As(V) from water by using chitosan-based electrospun adsorbents.

Fig. 15. Cross-sectional SEM image of the 5CNT nanofiber composed of a thin top 5 wt% CNT/PcH electrospun layer and a thicker bottom neat PcH electrospun layer [135].
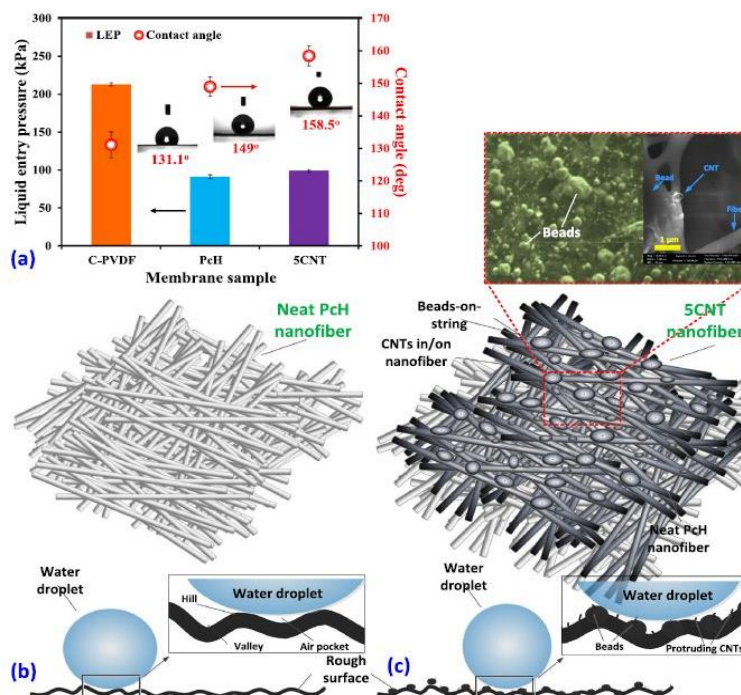

Fig. 16. (a) Liquid entry pressure and contact angle measurements, and schematic representation of the structure of the (b) neat and (c) CNT-incorporated nanofiber structures (Inset of (c)) SEM and TEM images showing the beads and CNTs on the fiber [135].

Table 7
List of recently published works on the application of electrospun membranes for MD process.

Reference and year	Electrospinning	MD membrane and process

[137], 2016	**Polymer and solvent**
	- polyvinylidene fluoride-co-hexafluoropropylene (PH) (M_w=445,000)
	
	- Acetone
	- *N,N* dimethylacetamide (DMAc)
	
	Electrospinning
	- Dope solution: 20 wt%
	- Needle: 21 G (ID=0.51 µm)
	- Voltage: 21 kV
	- Tip-to-Collector: 20 cm
	- Flowrate: 1 ml/h
		Membrane
		- Flat sheet membrane
		- Surface treatment by heat-press
		  (T = 140, 150, 160 and 170 ºC)
		  (P = 0.7, 2.2, 6.5 and 9.8 kPa)
		  (t = 1, 2, 4 and 8 h)
		
		Characterization
		- SEM
		- Thickness
		- Contact angle
		- LEP
		- Mechanical properties
		
		Process
		- MD mode: DCMD
		- Dimensions of length and width of hot and cold channels: 77×26 mm
		- Feed: Simulated seawater (3.5 wt% NaCl solution)
		- Feed temperature: 60 ºC
		- Cold temperature: 20 ºC
		
		Distillate flux
		- Up to 35 LMH

[138], 2016	**Polymer and solvent** - Poly (vinylidene fluoride) (PVDF) - DMAc **Electrospinning** - Roller and collector rotating speeds: 2 and 200 rpm, respectively	**Membrane** - Flat sheet **Characterization** - SEM - LEP - Contact angle - Mechanical properties **Process** - MD mode: AGMD - Feed temperature: 55 ºC - Coolant temperature: 20 ºC - Coolant flowrate: 300 ml/min - Feed flowrate: 80 ml/min - Air-gap width: 7 mm
[139], 2016	**Polymer and solvent** - PVDF-HFP (M_w=455,000 g/mol) - LiCl (as an additive) - TiO_2 - DMF **Electrospinning** - Needle: metal nozzle (0.5/0.8 mm inner/outer diameters) - Voltage: 18 kV - Collector speed: 10 mm/s - Flowrate: 1.0 ml/h - Humidity: 55%	**Membrane** - Flat-sheet - Nanoparticle incorporated **Characterization** - FESEM - FTIR - LEP - Mechanical properties **Process** - MD mode: DCMD - Feed: NaCl solution (7.0 wt%) - Feed temperature: 60-61 ºC - Feed flowrate: 450 ml/min - Cooling temperature: 20 ºC **Distillate flux** - Up to 45 $L.m^{-2}.h^{-1}$
[140], 2015	**Polymer and solvent** - Poly(trimethyl hexamethylene terephthalamide) (PA6(3)T) - DMF (Dimethylformamide) - FA (Formic acid) **Electrospinning** - Polymer-DMF/FA (mass ratio 99:1) - Voltage: 32 and 34 kV - Flowrate: 0.002, 0.008 and 0.05 ml/min - Tip-to-collector distance: 40 cm	**Membrane** - Flat-sheet membrane - Surface modification: Fluorination **Characterizations** - SEM - Contact angle - LEP - Pore size measurement **Process** - MD mode: AGMD - Feed: simulated seawater (3.5 wt% NaCl solution) - Feed temperature: 40 to 80 ºC - Cold temperature: 25 ºC - Air gap width: 0.5 mm - Effective membrane area: 36 cm^2 - Feed flow rate: 1.2 l.min **Distillate flux** - Min: ~2 $kg.m^{-2}.h^{-1}$ - Max: ~10 $kg.m^{-2}.h^{-1}$

Table 7
Continued.

Reference and year	Electrospinning	MD membrane and process
[141], Li et al., 2015	Polymer and solvent - PVDF: Mw=573,000 g/mol - DMF Electrospinning - Dope solution: PVDF/OTS-silica/DMF - Needle: with 0.37 mm inner diameter - Flowrate: 5 µl/min - Collector: A rotating drum (500 rpm) - Tip-to-collector: 15 cm - Voltage: 25 kV - Relative humidity and temperature: 30% and 30 ºC	Membrane - Flat-sheet - Surface modified Characterizations - FESEM - TEM - FTIR - Contact angle - BET - Mean flow pore size - Mechanical properties Process - MD mode: DCMD - Commercial PVDF membrane as control (0.22 µm pore size) Feed: 3.5 wt% NaCl solution (simulated seawater) Feed temperature: 60 ºC Feed flow rate: 0.6 l/min Cold temperature: 20 ºC Cold flowrate: same as hot stream Distillate flux Up to ~45 kg.m^{-2}.h^{-1}
[142], Woo et al., 2015	Polymers and solvent *For the top layer:* - Polyvinylidene fl uoride-co-hexa fl uoropropylene (PH) (Mw=455,000 g/mol) *For the support layer:* - Polyvinyl alcohol (PVA) (Mw=85,000 g/mol) - Nylon-6 (N6) (Mw= 10,000 g/mol) - Polyacrylonitrile (PAN) (Mw=150,000 g/mol) *Solvent and additive:* - DMF - LiCl (Lithium chloride) - Triton X-100 Electrospinning - Voltage: 18, 21, 22 and 27 kV - Flowrate: 0.6, 0.8 and 1.2 ml/h - Tip-to-collector: 10, 15 and 20 cm	Membrane - Dual layer (hydrophobic-hydrophilic) flat sheet membrane - Hot-press post treatment Characterization - SEM - Contact angle - AFM - LEP Process - MD mode: AGMD - Feed temperature: 60 ºC - Coolant temperature: 20 ºC - Feed: Simulated seawater (3.5 wt% NaCl solution) - Feed and coolant flowrates: 12 l/h Distillate flux Up to 18 l.m^{-2}.h^{-1}

AGMD: Air-gap membrane distillation
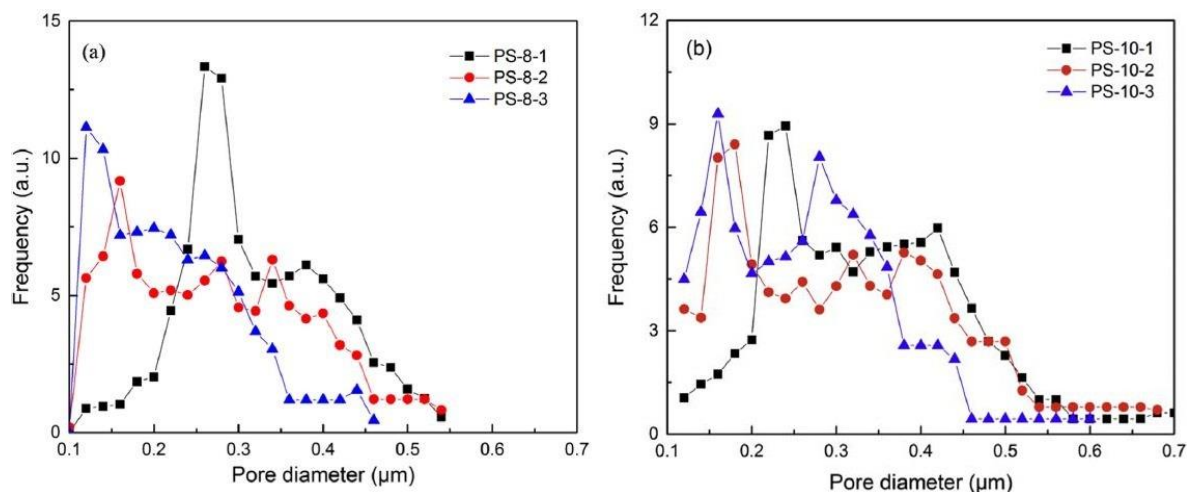DCMD: Direct contact membrane distillation

Fig. 17. The pore size distribution of electrospun PS nanofibrous membranes with different thicknesses [136].
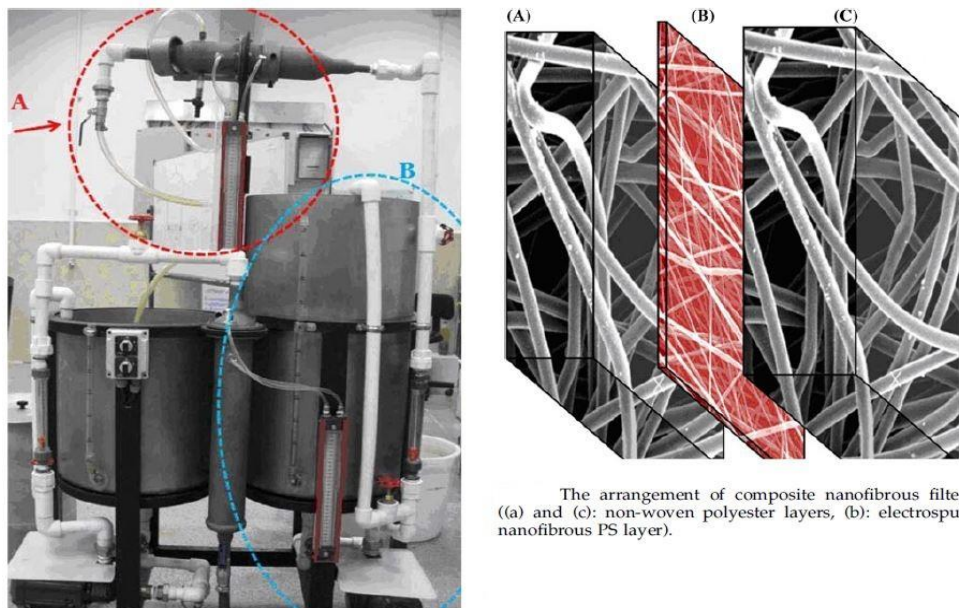
Fig. 18. Pilot scale coalescing filtration experimental set-up (right) and the arrangement of the used composite ENM (left) in Shirazi et al. work [20].

In another work, Wu and his co-workers [144] studied the effects of functionalized porous electrospun polystyrene (PS) fibers with polydopamine (PDA) coating to overcome the current deficiencies in basic solutions. The β-cyclodextrin (β-CD) was subsequently attached onto the fibers' surface. This resulting multi-layered system comprised of β-CD/PDA/PS fibers displayed much improved adsorption of negatively charged pollutants under highly basic conditions when compared to that of basic PDA-functionalized fibers.

As an alternative polymer-bio hybrid membrane system, Vinod and his co-workers [145] prepared a polyvinyl alcohol (PVA)-natural gum karaya (GK) hydrocolloid system for subsequent electrospinning. The fabricated electrospun web successfully removed a series of metal nanoparticles from an aqueous solution, including Ag, Au, Pt, Fe_3O_4 and CuO. The authors indicated that the adsorption efficiency of nanoparticles adsorbed onto the fibers' surface decreased in the order of Pt > Ag > Au > CuO > Fe_3O_4. In addition, the electrospun PVA/GK webs were treated with methane plasma in order to improve their hydrophobicity. These plasma treated webs displayed higher adsorption efficiency and capacity when compared to the untreated ones.

It has been reported that the oceans contain an estimated 4.5 billion tons of uranium which should be taken into consideration for post treating. Xie and his co-workers [146] studied the application of amidoxime (AO) groups which are traditionally considered as the most promising method for uranium recovery from seawater. Utilizing a two-nozzle electrospinning system, they prepared nanoporous PAO/PVDF composite membranes with high surface hydrophilicity. The key result was an increase in the adsorbent porosity and an improved utilization of the functional groups. Desorptive tests highlighted a good desorption selectivity of nanoporous PAO/PVDF composite membranes between uranyl and vanadium ions. It is clear that major environmental issues exist with contaminated water supplies but the scientific community has developed key methodologies and novel material solutions to tackle this global issue.

4.4. Coalescing filtration: An example of commercial application of nanofibers

The presence of difficult to separate emulsions can be a costly problem in various industries. Oily contaminants can result in poor final products, deactivation of expensive catalysts, fouling of stripping trays, and delay in downstream storage tanks and thus increased costs for wastewater treatment [147,148].

Breaking stable emulsions can be a difficult task depending on the physical properties of the oil, water and surfactant system [149]. Liquid-liquid coalescing filtration can be used to accelerate the merging of many droplets with greater droplet diameter. The settling of larger droplets downstream thus requires considerably less residence time. Obviously, the coalescing medium is the crucial element in such treatment systems. In this regard, electrospun

nanofibrous medium with a larger surface area (i.e. nanofibers surface) can effectively be used to enhance the coalescing performance.

Shirazi et al. [20] studied the application of electrospun nanofibrous membranes made of polystyrene for coalescing filtration of oily wastewater containing secondary emulsion on a pilot scale. Figure 18 shows the applied pilot-scale apparatus in this work. The authors investigated the surface treatment strategy for electrospun membrane samples through direct heating at the temperature range of 90 to 170 ºC (see Figure 19). As could be observed in Figure 19-A, the random nanofibrous structure with the fibers' diameter of 452 nm were fabricated with no bead on the fibers' surface. About 40% of the fiber diameters were in the range of 400-500 nm and 27.5% of the fiber diameters were in the range of 300-400 nm. As could be observed, all fibers consisted of a smooth surface (see Figure 19-B). The authors indicated that the pores' tortuosity (which is defined as the degree of deviation of the pore structure from a straight cylindrical shape) decreased after the thermal treatment when compared with non-thermal treated samples. Moreover, the porosity of thermally treated electrospun membrane samples decreased down to 61.6% (for the sample thermally treated at 150 ºC). This could be explained by the fact that after thermal treating, the nanofibers merged together. As could be observed in Figure 19, increasing the treatment temperature led to an increase in the fibers' diameter (up to 150ºC). The maximum, minimum and the mean pore size after 150ºC thermal treatment were calculated at 3.44 µm, 0.151µm and 1.018 µm, respectively. For the non-thermally treated sample, the same values dropped down to 2.359 µm, 0.262 µm and 1.008 µm, respectively. In the next step of the experiments, all membrane samples were used for coalescing filtration. Figure 20 shows the separation efficiency of different membrane samples and the highest separated volume of oil was achieved by using the 150 ºC thermally treated sample. The authors concluded that thermal treatment of the electrospun membranes made of polystyrene at the optimum temperature of 150 ºC can lead to formation of more uniform pores with lower tortuosity, lower porosity with minimum surface roughness, lower pore size and better coalescing filtration performance as well.

5. Future perspectives

As the next generation of filtration media, electrospun membranes display immensely promising features that should lead to the advancement of future commercial filtration systems. To enhance the morphological and topographical features of electrospun membranes, a number of methodologies, including molecular bonding, *in situ* polymerization and the addition of molecular dopants can be combined with electrospinning technology. Moreover, strategies for surface modifications, e.g. nanoparticles coating, treatment with chemicals or heat, grafting and interfacial polymerization, are found to be beneficial techniques to facilitate surface

modifications and improve the filtration performance of electrospun membranes which can pave the way for them to adopt across various industrial sectors for different treatment applications.
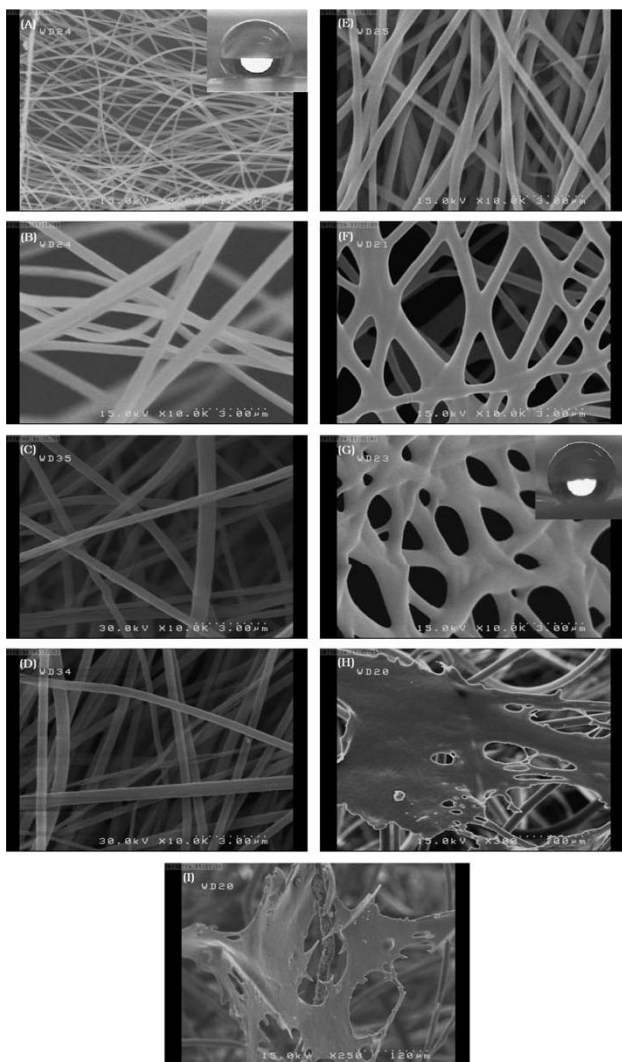
Fig. 19. SEM images showing the morphology of the electrospun nanofibrous filter, before thermal treating (a and b) (with two magnification); and after (c) 90°C; (d) 120°C; (e) 130°C; (f) 140°C; (g) 150°C; (h) 160°C; and (i) 170°C thermal treating, respectively, in Shirazi et al. work [20].
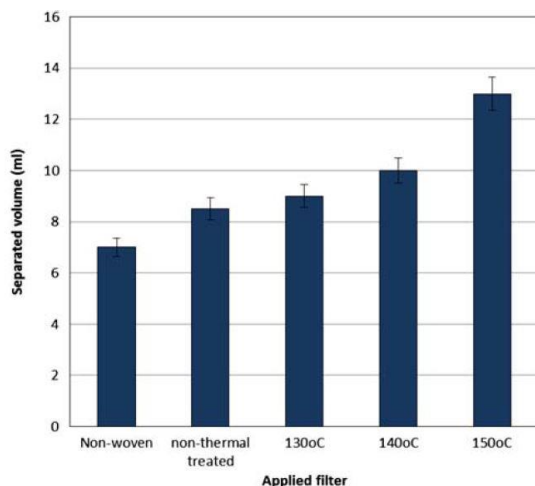
Fig. 20. The separated volume in the permeate phase vs. the type of applied filter, in [20].

References

[1] UN Water Report, "The United Nations World Water Development Report 2015", (2015) (https://www.unesco-ihe.org/sites/default/files/wwdr_2015.pdf).

[2] J.R. Werber, C.O. Osuji, M. Elimelech, Materials for next-generation desalination and water purification membranes, Nature Rev. Mater. 16018 (2016) DOI: 10.1038/natrevmats.2016.18.

[3] CGW4U-A, World population: Changes and challenges (2007), (https://www.homeworkmarket.com/sites/default/files/cgw4ua_unit_1_lesson_02.pdf).

[4] World urbanization prospects, (2014) (https://esa.un.org/unpd/wup/Publications/Files/WUP2014-Highlights.pdf).

[5] M.M.A. Shirazi, A. Kargari A, Application of membrane distillation process for wastewater treatment: A review, J. Membr. Sci. Res. 1 (2015) 101-112.

[6] C. Sealy, Cleaning up water on the nanoscale, Nano Today 8 (2013) 337-338.

[7] Das R, Hamid SBA, Ali ME, Ismail AF, Annuar MSM, Ramakrishna S, Multifunctional carbon nanotubes in water treatment: The present, past and future, Desalination 354 (2014) 160-179.

[8] X. Wang, B.S. Hsiao, Electrospun nanofiber membranes, Current Opinion Chem. Eng. 12 (2016) 62-81.

[9] J. Theron, J.A. Walker, T.E. Cloete, Nanotechnology and water treatment: Applications and emerging opportunities, Critical Rev. Microbiol. 34 (2008) 43-69.

[10] X. Qu, J.J. Alvarez, Q. Li, Applications of nanotechnology in water and wastewater treatment, Water Res. 47 (2013) 3931-3946.

[11] W.E. Teo, S. Ramakrishna, A review on electrospinning design and nanofibre assembles, Nanotechnology 17 (2006) R89-R106.

[12] S. Subramanian, R. Seeram, New directions in nanofiltration applications-Are nanofibers the right materials as membranes in desalination?, Desalination 308 (2013) 198-208.

[13] L. Zhang, A. Aboagye, A. Kelkar, C. Lai, H. Fong, A review: carbon nanofibers from electrospun polyacrylonitrile and their applications, J. Mater. Sci. 49 (2014) 463-480.

[14] J.J. Doyle, S. Choudhari, S. Ramakrishna, RP. Babu, "Electrospun Nanomaterials: Biotechnology, Food, Water, Environment, and Energy," Conference Papers in Materials Science, vol. 2013, Article ID 269313, 14 pages, 2013. doi:10.1155/2013/269313.

[15] N.M. Rodriguez, M.S. Kim, R.T.K. Baker, Carbon nanofibers: A unique catalyst support medium, J. Phys. Chem. 98 (1994) 13108-13111.

[16] A. Freton, I.S. Chronakis, Polymer nanofibers assembled by electrospinning, Current Opinion Colloid Interf. Sci. 8 (2003) 64-75.

[17] F.E. Ahmed, B.S. Lalia, R. Hashaikeh, A review on electrospinning for membrane fabrication: Challenges and applications, Desalination 356 (2015) 15-30.

[18] I. Sas, R.E. Gorga, J.A. Joines, K.A. Thoney, Literature review on superhydrophobic self-cleaning surfaces produced by electrospinning, J. Polymer Sci. B: Polymer Phys. 50 (2012) 824-845.

[19] J.H. He, H.Y. Kong, R.R. Yang, H. Dou, N. Faraz, L. Wang, C. Feng C, Review on fiber morphology obtained by bubble electrospinning and blown bubble spinning, Thermal Sci. 16 (2012) 1263-1279.

[20] M.J.A. Shirazi, S. Bazgir, M.M.A. Shirazi, S. Ramakrishna, Coalescing filtration of oily wastewaters: characteristics and application of thermal treated electrospun polystyrene filters, Desal. Water Treat. 51 (2013) 5974-5986.

[21] J.D. Schiffman, C.L. Schauer, A review: Electrospinning of biopolymer nanofibers and their applications, Polymer Rev. 48 (2008) 317-352.

[22] H.U. Shin, Y. Li, A. Paynter, K. Nartetamrongsutt, G.G. Chase, Vertical rod method for electrospinning of polymer fibers, Polymer 65 (2015) 26-33.

[23] Y.A. Huang, N. Bu, Y. Duan, Y. Pan, H. Liu, Z. Yin, Y. Xiong, Electrohydrodynamic direct-writing, Nanoscale 5 (2013) 12007-12017.

[24] P. Kiselev, Rosell-Llompart, Highly aligned electrospun nanofibers by elimination of the whipping motion, J. Appl. Polymer Sci. 125 (2012) 2433-2441.

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

[26] T. Uyar, F. Besenbacher, Electrospinning of uniform polysturene fibers: The effect of solvent conductivity, Polymer 49 (2008) 5336-5343.

[27] M. Kang, R. Jung, H.S. Kim, H.J. Jin, Preparation of superhydrophobic polystyrene membranes by electrospinning, Colloid Surf. A: Physicochem. Eng. Aspects 313-314 (2008) 411-414.

[28] L. Wannatong, A. Sirivat, P. Supaphol, Effects of solvents on electrospun polymeric fibers: preliminary study on polystyrene, Polymer Int. 53 (2004) 1851-1859.

[29] T. Jarusuwannapoom, W. Hongrojjanawiwat, S. Jitjaicham, L. Wannatong, M. Nithitanakul, C. Pattamaprom, P. Koombhongse, R. Rangkupan, P. Supaphol, Effect of solvents on electro-spinnability of polystyrene solutions and morphological appearance of resulting electrospun polystyrene fibers, European Polymer J. 41 (2005) 409-421.

[30] A. Koski, K. Yim, S. Shivkumar, Effect of molecular weight on fibrous PVA produced by electrospinning, Mater. Lett. 58 (2004) 439-497.

[31] S. Agrawal, A. Greiner, J.H. Wendorff, Functional materials by electrospinning of polymers, Prog. Polymer Sci. 38 (2013) 963-991.

[32] B. Guo, L. Glavas, A.C. Albertsson, Biodegradable and electrically conducting polymers for biomedical applications, Prog. Polymer Sci. 38 (2013) 1263-1286.

[33] Y. Liao, R. Wong, M. Tian, C. Qiu, A.G. Fane, Fabrication of polyvinylidene fluoride (PVDF) nanofiber membranes by electro-spinning for direct contact membrane distillation, J. Membr. Sci. 425-426 (2013) 30-39.

[34] X. Wang, B. Ding, G. Sun, M. Wang, J. Yu, Electro-spinning/netting: A strategy for the fabrication of three-dimensional polymer nano-fiber/nets, Prog. Mater. Sci. 58 (2013) 1173-1243.

[35] H. Fashandi, M. Karimi, Pore formation in polystyrene fiber by superimposing temperature and relative humidity of electrospinning atmosphere, Polymer 53

(2012) 5832-5849.

[36] N. Bhardwaj, S.C. Kundu, Electrospinning: A fascinating fiber fabrication technique, Biotechnol. Adv. 28 (2010) 325-347.

[37] G. Panthi, M. Park, H.Y. Kim, S.J. Park, Electrospun polymeric nanofibers encapsulated with nanostructured materials and their applications: A review, J. Ind. Eng. Chem. 24 (2015) 1-13.

[38] V. Aravindan, J. Sundaramurthy, P. Kumar, Y.S. Lee, S. Ramakrishna, S. Madhavi, Electrospun nanofibers: A prospective electro-active material for constructing high performance Li-ion batteries, Chem. Commun. 51 (2015) 2225-2234.

[39] N. Awang, A.F. Ismail, J. Jafar, T. Matsuura, H. Junoh, M.H.D. Othman, M.A. Rahman, Functionalization of polymeric materials as a high performance membrane for direct methanol fuel cell: A review, Reactive Functional Polymers 86 (2015) 248-258.

[40] R. Sarbatly, D. Krishnaiah, Z. Kamin, A review of polymer nanofibers by electrospinning and their application in oil-water separation for cleaning up marine oil spills, Marine Pollution Bulletin 106 (2016) 8-16.

[41] T. Matsuura, Progress in membrane science and technology for seawater desalination-a review, Desalination 134 (2001) 47-54.

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

[43] A.G. Fane, C.J.D. Fell, A review of fouling and fouling control in ultrafiltration, Desalination 62 (1987) 117-136.

[44] S. Nakao, Determination of pore size and pore size distribution: 3. Filtration membranes, J. Membr. Sci. 96 (1994) 131-165.

[45] P.W. Gibson, H.L. Schreuder-Gibson, D. Rivin, Electrospun fiber mats: Transport properties, AIChE J. 45 (1999) 190-195.

[46] M.S. Khil, D. Cha, H.Y. Kim, I.S. Kim, N. Bhattarai, Electrospun nanofibrous polyurethane membrane as wound dressing, J. Biomed. Mater. Res. 67B (2003) 675-679.

[47] A. Hernandez, J.I. Calvo, F. Pradanos, F. Tejerina, Pore size distributions in microporous membranes. A critical analysis of the bubble point extended method, J. Membr. Sci. 112 (1996) 1-12.

[48] E. Jakobs, W.J. Koros, Ceramic membrane characterization via the bubble point technique, J. Membr. Sci. 124 (1997) 149-159.

[49] G. Riechelt G, Bubble point measurements on large areas of microporous membranes, J. Memb. Sci., 60 (1987) 253-259.

[50] J.I. Calvo, A. Hernandez, P. Pradanos, L. Martinez, W.R. Bowen, Pore size distributions in microporous membranes II. Bulk characterization of track-etched filters by air porometry and mercury porosimetry, J. Colloid Interf. Sci., 176 (1995) 467-478.

[51] A. Hernandez, J.I. Calvo, P. Pradanos, F. Tejerina, Pore size distributions of track-etched membranes; comparison of surface and bulk porosities, Colloid Surf A: Physicochem. Eng. Aspects, 138 (1998) 391-401.

[52] M. Khayet, A. Velazquez, J.I. Mengual, Modeling mass transport through a porous partition: Effect of pore size distribution, J. Non-Equilibrium Thermodynamics, 29 (2004) 279-299.

[53] X.L. Wang, W.J. Shang, D.X. Wang, L. Wu, C.H. Tu, Characterization and applications of nanofiltration membranes: State of the art, Desalination 236 (2009c) 316-326.

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

[55] M.M.A. Shirazi, A. Kargari, M. Tabatabaei, Evaluation of commercial PTFE membranes in desalination by direct contact membrane distillation, Chem. Eng. Proc.: Process Intensif. 76 (2014) 16-25.

[56] E. Mirtalebi, M.M.A. Shirazi, A. Kargari, M. Tabatabaei, S. Ramakrishna, Assessment of atomic force and electron microscopes for characterization of commercial and electrospun nylon membranes for coke removal from wastewater, Desal. Water Treat. (2014) DOI: 10.1080/19443994.2013.821036.

[57] Y. Mansourpanah, E.M. Habili, Investigation and characterization of TiO2-TFC nanocomposite membrane preparation and UV studies, J. Membr. Sci. Res. 1 (2015) 26-33.

[58] Z.A. Tarsa, S.A.A. Hedayat, M. Rahbari-Sisakht, Fabrication and characterization of polyetherimide hollow fiber membrane contactor for carbon dioxide stripping from monoethanolamine solution, J. Membr. Sci. Res. 1 (2015) 118-123.

[59] L. Yan, Y.S. Li, C.B. Xiang, S. Xianda, Effect of nanosized Al2O3-particle addition on PVDF ultrafiltration membrane performance, J. Membr. Sci. 276 (2006) 162-167.

[60] X. Cao, J. Ma, X. Shi, Z. Ren, Effect of TiO2 nanoparticle size on the performance of PVDF membrane, Appl. Surface Sci. 253 (2006) 2003-2010.

[61] M.M.A. Shirazi, A. Kargari, M. Tabatabaei, A.F. Ismail, T. Matsuura, Assessment of atomic force microscopy for characterization of PTFE membranes for membrane distillation (MD) process, Desal. Water Treat. 54 (2015) 295-304.

[62] D. Johnson, N. Hilal, Characterization and quantification of membrane surface properties using atomic force microscopy: A comprehensive review, Desalination 356 (2015) 149-164.

[63] N. Hilal, H. Al-Zoubi, N.A. Darwish, A.W. Mohammad, M. Abu Arabi, A comprehensive review of nanofiltration membranes: Treatment, pretreatment, modeling, and atomic force microscopy, Desalination 170 (2004) 281-308.

[64] L.Y. Ng, A.W. Mohammad, C.Y. Ng, A review on nanofiltration membrane fabrication and modification using polyelectrolytes: Effective ways to develop membrane selective barriers and rejection capability, Adv. Colloid Interf. Sci. 197-198 (2013) 85-107.

[65] M.M.A. Shirazi, D. Bastani, A. Kargari, M. Tabatabaei, Characterization of polymeric membranes for membrane distillation using atomic force microscopy, Desal. Water Treat. 51 (2013) 6003-6008.

[66] V. Kochkodan, D.J. Johnson, N. Hilal, polymeric membranes: Surface modification

[67] M.C. Garcia-Payo, M.A. Izquierdo-Gil, C. Fernandez-Pineda, Wetting study of hydrophobic membranes via liquid entry pressure measurements with aqueous alcohol solutions, J. Colloid Interf. Sci., 230 (2000) 420-431.

[68] K. He, H.J. Hwang, I.Sh. Moon, Air gap membrane distillation on the different types of membrane, Korean J. Chem. Eng., 28 (2011) 770-777.

[69] C. Zhao, J. Xue, F. Ran, S. Sun, Modification of polyethersulfone membranes-A review of methods, Prog. Mater. Sci. 58 (2013) 76-150.

[70] V. Kochkodan, N. Hilal, A comprehensive review on surface modified polymer membranes for biofouling mitigation, Desalination 356 (2015) 187-207.

[71] C. Feng, K.C. 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 (2008) 1-6.

[72] M.M.A. Shirazi, A. Kargari, A.F. Ismail, T. Matsuura, Computational fluid dynamic (CFD) opportunities applied to the membrane distillation process: State-of-the-art and perspectives, Desalination 377 (2016) 73-90.

[73] B.S. Lalia, V. Kochkodan, R. Hashaikeh, N. Hilal, A review on membrane fabrication: Structure, properties and performance relationship, Desalination 326 (2013) 77-95.

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

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

[76] H. Matsumoto, A. Tanioka, Functionality in electrospun nanofibrous membranes based on fiber's size, surface area, and molecular orientation, Membranes 1 (2011) 249-264.

[77] M.M. Pendergast, E.M.V. Hoek, A review of water treatment membrane nanotechnologies, Energy Environ. Sci. 4 (2011) 1946-1971.

[78] W.J. Lau, S. Gray, T. Matsuura, D. Emadzadeh, J.P. Chen, A.F. Ismail, A review on polyamide thin film nanocomposite (TFN) membranes: History, applications, challenges and approaches, Water Res. 80 (2015) 306-324.

[79] C. Feng, K.C. Khulbe, T. Matsuura, R. Farnood, A.F. Ismail, Recent progress in zeolite/zeotype membranes, J. Membr. Sci. Res. 1 (2015) 49-72.

[80] S. Ramakrishna, M.M.A. Shirazi, Electrospun membranes: Next generation membranes for desalination and water/wastewater treatment, J. Membr. Sci. Res. 1 (2015) 46-47.

[81] 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 (2016) 85495-85514.

[82] W. Ma, Q. Zhang, D. Hua, R. Xiong, J. Zhao, W. Rao, Sh. Huang, X. Zhan, F. Chen, Ch. Huang, Electrospun fibers for oil-water separation, RSC Adv. 6 (2016) 12868-12884.

[83] J.F. Kim, J.H. Kim, Y.M. Lee, E. Drioli, Thermally indiced phase separation and electrospinning methods for emerging membrane applications: A review, AIChE J. 62 (2016) 461-490.

[84] L.D. Tijing, J.S. Choi, S. Lee, S.H. Kim, H.K. Shon, Recent progress of membrane distillation using electrospun nanofibrous membrane, J. Membr. Sci. 453 (2014) 435-462.

[85] H. Lee, M. Yanilmaz, O. Toprakci, K. Fu, X. Zhang, A review of recent developments in membrane separators for rechargeable lithium-ion batteries, Energy Environ. Sci. 7 (2014) 3857-3886.

[86] G. Kang, Y. Cao, Application and modification of poly(vinylidene fluoride) (PVDF) membranes-A review, J. Membr. Sci. 463 (2014) 145-165.

[87] S. Kaur, S. Sundarrajan, D. Rana, R. Sridhar, R. Gopal, T. Matsuura, S. Ramakrishna, Review: the characterization of electrospun nanofibrous liquid filtration membranes, J. Mater. Sci. 49 (2014) 6143-6159.

[88] C. Feng, K.C. Khulbe, T. Matsuura, S. Tabe, A.F. Ismail, Preparation and characterization of electro-spun nanofiber membranes and their possible applications in water treatment, Sep. Purif. Technol. 102 (2013) 118-135.

[89] L. Persano, A. Camposeo, C. Tekmen, D. Pisignano, Industrial upscaling of electrospinning and applications of polymer nanofibers: A review, Macromolecul. Mater. Eng. 298 (2013) 504-520.

[90] S.K. Nataraj, K.S. Yang, T.M. Aminabhavi, Polyacrylonitrile-based nanofibers-A state-of-the-art review, Prog. Polymer Sci. 37 (2012) 487-513.

[91] Van Reis R, Zydney A, Membrane separations in biotechnology, Current Opinion Biotechnol. 12 (2001) 208-211.

[92] Van der Bruggen B, C. Vandecasteele, T. Van Gestel, W. Doyen, R. Leysen, A review of pressure-driven membrane processes in wastewater treatment and drinking water production, AIChE J. 22 (2003) 46-56.

[93] M.A. Shannon, P.W. Bohn, M. Elimelech, J.G. Georgiadis, B.J. Marinas, A.M. Mayes, Science and technology for water purification in the coming decades, Nature 452 (2008) 301-310.

[94] R.P. Schwarzenbach RP, T. Egli, T.B. Hofstetter, U. von Gunten, B. Wehrli, Global water pollution and human health, Annual Rev. Environ. Resource 35 (2010) 109-136.

[95] M.S. Islam, J.R. McCutcheon, M.S. Rahaman, A high flux polyvinyl acetate-coated electrospun nylon 6/SiO2 composite microfiltration membrane for the separation of oil-in-water emulsion with improved antifouling performance, J. Membr. Sci. 537 (2017) 297-309.

[96] Z. Wang, C. Crandall, R. Sahadevan, T.J. Menkhaus, , H. Fong, Microfiltration performance of electrospun nanofiber membranes with varied fiber diameters and different membrane porosities and thicknesses, Polymer 114 (2017) 64-72.

[97] T.C. Mokhena, A.S. Luyt, Development of multifunctional nano/ultrafiltration membrane based on a chitosan thin film on alginate electrospun nanofibers, J. Cleaner Production 156 (2017) 470-479.

[98] K.M. Dobosz, C.A. Kuo-Leblanc, T.J. Martin, J.D. Schiffman, Ultrafiltration membranes enhanced with electrospun nanofibers exhibit improved flux and fouling

resistance, Ind. Eng. Chem. Res. 56 (2017) 5724-5733.

[99] M. Tian, Y.N. Wang, R. Wang, A.G. Fane, Synthesis and chacterization of thin film nanocomposite forward osmosis membranes supported by silica nanoparticle incorporated nanofibrous substrate, Desalination 401 (2017) 142-150.

[100] S. Khezli, M. Zandi, J. Barzin, Fabrication of electrospun nanocomposite polyethersulfone membrane for microfiltration, Polymer Bullet. 73 (2016) 2265-2286.

[101] Z. Li, W. Kang, H. Zhao, M. Hu, N. Wei, J. Qiu, B. Cheng, A novel polyvinylidene fluoride tree-like nanofiber membrane for microfiltration, Nanomater. 6 (2016) 1-11 (doi:10.3390/nano6080152).

[102] S.M.S. Shahabadi, S.A. Mousavi, D. Bastani, High flux electrospun nanofiberous membrane: Preparation by statistical approach, characterization, and microfiltration assessment, J. Taiwan Ins. Chem. Eng. 59 (2016) 474-483.

[103] N. Daels, L. Harinck, A. Goethals, K. De Clerck, S.W.H. Van Hulle, Structure changes and water filtration properties of electrospun polyamide nanofibre membranes, Water Sci. Technol. 73 (2016) 1920-1926.

[104] Z. Zhou, W. Lin, X.F. Wu, Electrospinning ultrathin continues cellulose acetate fibers for high-flux water filtration, Colloid Surfaces A: Physicochem. Eng. Aspects 494 (2016) 21-29.

[105] F. Hejazi, S.M. Mousavi, Electrospun nanofibrous composite membranes of chitosan/polyvinyl alcohol-polyacrylonitrile: preparation, characterization and performance, Desal. Water Treat. 57 (2016) 1959-1966.

[106] V.A. Ganesh, A.S. Ranganath, A. Baji, H.C. Wong, H.K. Raut, R. Sahay, S. Ramakrishna, Electrospun differential wetting membranes for efficient oil-water separation, Macromol. Mater. Eng. 301 (2016) 812-817.

[107] J. Yu, Y.G. Kim, D.Y. Kim, S. Lee, H.I. Joh, S.M. Jo, Super high flux microfiltration based on electrospun nanofibrous m-Aramid membranes for water treatment, Macromol. Res. 23 (2015) 601-606.

[108] M. Obaid, N.A.M. Barakat, O.A. Fadali, M. Motlak, A.A. Almajid, K.A. Khalil, Effective and reusable oil-water separation membranes based on modified polysulfone electrospun nanofiber mats, Chem. Eng. J. 259 (2015) 449-456.

[109] N.N. Bui, M.L. Lind, E.M.V. Hoek, J.R. McCutcheon, Electrospun nanofiber supported thin film composite membranes for engineered osmosis, J. Membr. Sci. 385-386 (2011) 10-19.

[110] N.N. Bui, J.R. McCutcheon, Nanoparticle-embeded nanofibers in highly permselective thin-film nanocomposite membranes for forward osmosis, J. Membr. Sci. 518 (2016) 338-346.

[111] 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.

[112] R.S. Barhate, C.K. Loong, S. Ramakrishna, Preparation and characterization of nanofibrous filtering media, J. Membr. Sci. 283 (2006) 209-218.

[113] R. Gopal, S. Kaur, Z. Ma, C. Chan, S. Ramakrishna, T. Matsuura, Electrospun nanfibrous filtration membrane, J. Membr. Sci. 281 (2006) 581-586.

[114] R. Gopal, S. Kaur, C.Y. Feng, C. Chan, S. Ramakrishna, S. Tabe, T. Matsuura, Electrospun nnaofibrous polysulfone membranes as pre-filters: Particle removal, J. Membr. Sci. 289 (2007) 210-219.

[115] J.A. Bhushani, C. Anandharamakrishnan, Electrospinning and electrospraying techniques: Potential food based applications, Trends Food Sci. Technol. 38 (2014) 21-33.

[116] B. Veleirinho, J.A. Lopes-da-Silva, Application of electrospun poly(ethylene terephthalate) nanofiber mat to apple juice clarification, Process Biochem. 44 (2009) 353-356.

[117] Fuenmayor CA, S.M. Lemma, S. Mannino, T. Mimmo, M. Scampicchio, Filtration of apple juice by nylone nanofibrous membranes, J. Food Eng. 122 (2014) 110-116.

[118] R. Wang, Y. Liu, B. Li, B.S. Hsiao, B. Chu, Electrospun nanofibrous membranes for high flux microfiltration, J. Membr. Sci. 392-393 (2012) 167-174.

[119] Acatay K, E. Simsek, C. Ow-Yang, Y.Z. Menceloglu, Tunable superhydrophobically stable polymeric surfaces by electrospinning, Angew. Chem. Int. Ed. 43 (2004) 5210-5213.

[120] C. Boo, J. Lee, M. Elimelech, Engineering surface energy and nanostructure of microporous films for expanded membrane distillation applications, Environ. Sci. Technol. 50 (2016) 8112-8119.

[121] S. Kaur, D. Rana, T. Matsuura, S. Sundarrajan, S. Ramakrishna, Preparation and characterization of surface modified electrospun membranes for higher filtration flux, J. Membr. Sci. 390-391 (2012) 235-242.

[122] M.M.A. Shirazi, A. Kargari, S. Bazir, M. Tabatabaei, M.J.A. Shirazi, M.S. Abdullah, T. Matsuura, A.F. Ismail, Characterization of electrospun polystyrene membrane for treatment of biodiesel's water-washing effluent using atomic force microscopy, Desalination 329 (2013) 1-8.

[123] 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. 392-393 (2012) 101-111.

[124] H. You, X. Li, Y. Yang, B. Wang, Z. Li, X. Wang, M. Zhu, B.S. Hsiao, High flux low pressure thin film nanocomposite ultrafiltraion membranes based on nanofibrous substrates, Sep. Purif. Technol. 108 (2013) 143-151.

[125] R. Marzban, F. Saberi, M.M.A. Shirazi, Separation of Bacillus thuringiensis from fermentation broth using microfiltration: Optimization approach, Res. J. Biotechnol. 9 (2014) 33-37.

[126] M.M.A. Shirazi, A. Kargari, D. Bastani, L. Fatehi, Production of drinking water from seawater using membrane distillation (MD) alternative: direct contact MD and sweeping gas MD approaches, Desal. Water Treat. 52 (2014) 2372-2381.

[127] M.M.A. Shirazi, A. Kargari, M. Tabatabaei, Sweeping gas membrane distillation (SGMD) as an alternative for integration of bioethanol processing: study on a commercial membrane and operating parameters, Chem. Eng. Communic. (2014) in press.

[128] M.M.A. Shirazi, A. Kargari, M. Tabatabaei, A.F. Ismail, T. Matsuura,

Concentration of glycerol from dilute glycerol wastewater using sweeping gas membrane distillation, Chem. Eng. Proc.: Process Intensif. 78 (2014) 58-66.

[129] A. Kargari, M.M.A. Shirazi, Water desalination: Solar-assisted membrane distillation, in: Encyclopedia of Energy Engineering and Technology (2nd Ed.), Taylor and Francis (2014), DOI: 10.1081/E-EEE2-120051388.

[130] 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.

[131] 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.

[132] L. Francis, N. Ghaffour, A. Alsaadi, S. Nunes, G. Amy, PVDF hollow fiber and nanofiber membranes for fresh water reclamation using membrane distillation, J. Membr. Sci. 49 (2014) 2045-2053.

[133] X. Li, C. Wang, Y. Yang, X. Wang, M. Zhu, B.S. Hsiao, Dual-biomimetic superhydrophobic elecyrospun polystyrene nanofibrous membrane for membrane distillation, ACS Appl. Mater. Interfaces 6 (2014) 2423-2430.

[134] Y. Liao, C.H. Loh, R. Wang, A.G. Fane, Electrospun Super hydrophobic Membranes with unique structures for membrane distillation, ACS Appl. Mater. Interfaces 6 (2014) 16035-16048.

[135] LD. Tijing, Y.C. Woo, W.G. Shim, T. He, J.S. Choi, S.H. Kim, H.K. Shon, Superhydrophobic nanofiber membrane containing carbon nanotubes for high-performance direct contact membrane distillation, J. Membr. Sci. 502 (2016b) 158-170.

[136] H. Ke, E. Feldman, P. Guzman, J. Cole, Q. Wei, B. Chu, A. Alkhudhiri, R. Alrasheed, B.S. Hsiao, Electrospun polystyrene nanofibrous membranes for direct contact membrane distillation, J. Membr. Sci. 515 (2016) 86-97.

[137] 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.

[138] R. Moradi, J. Karimi-Sabet, M. Shariaty-Niassar, Y. Amini, Air gap membrane distillation for enrichment of H$_2^{18}$O isotopomers in natural water using poly(vinylidene fluoride) nanofibrous membrane, Chem. Eng. Proc.: Process Intensif. 100 (2016) 26-36.

[139] E.J. Lee, A.K. An, T. He, Y.C. Woo, H.K. Shon, Electrospun nanofiber membranes incorporating fluorosilane-coated TiO$_2$ nanocoposite for direct contact membrane distillation, J. Membr. Sci. 520 (2016) 145-154.

[140] F. Guo F, A. Servi, A. Liu, K.K. Gleason, G.C. Rutledge, Desalination by membrane distillation using electrospun polyamide fiber membranes with surface fluorination by chemical vapor deposition, ACS Appl. Mater Interfaces 7 (2015) 8225-8232.

[141] X. Li, X. Yu, C. Cheng, L. Deng, M. Wang, X. Wang, Electrospun superhydrophobic organic/inorganic composite nanofibrous membranes for membrane distillation, ACS Appl. Mater. Interfaces 7 (2015) 21919-21930.

[142] 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 (2015) in press (http://dx.doi.org/10.1016/j.desal.2015.09.009).

[143] L.H. Min, Z.H. Yuan, L.U. Zhong, Q. Liu, R. Wu, Y.M. Zheng, Preparation of chitosan based electrospun nanofiber membrane and its adsorptive removal of arsenate from aqueous solution, Chemical Engineering Journal, 267 (2015) 132-141.

[144] H. Wu, J. Kong, X. Yao, C. Zhao, Y. Dong, X. Lu, Polydopamine-assisted attachment of β-cyclodextrin on porous electrospun fibers for water purification under highly basic condition, Chemical Engineering Journal, Volume 270 (2015) 101-109.

[145] V. Vinod, T. Padil, M. Černík, Poly (vinyl alcohol)/gum karaya electrospun plasma treated membrane for the removal of nanoparticles (Au, Ag, Pt, CuO and Fe$_3$O$_4$) from aqueous solutions, Journal of Hazardous Materials, 287 (2015)102-110.

[146] Xie S, Liu X, Zhang B, Ma H, Ling C, Yu M, Li L, Li J, Electrospun nanofibrous adsorbents for uranium extraction from seawater, J. Mater. Chem. A 3 (2015) 2552-2558.

[147] B.H. Diya'uddeen, W.M.A.W. Daud, A.R.A. Aziz, Treatment technologies for petroleum refinery effluents: A review, Process safety Environ. Protect. 89 (2011) 95-105.

[148] A. Moslehyani, M. Mobaraki, T. Matsuura, A.F. Ismail, M.H.D. Othman, M.N.K. Chowdhury, Novel green hybrid processes for oily water photooxidation and purification of from merchant ship, Desalination 391 (2016) 98-104.

[149] M.M.A. Shirazi, A. Kargari, M. Tabatabaei, M. Akia, M. Barkhi, M.J.A. Shirazi, Acceleration of biodiesel-glycerol decantation through NaCl-assisted gravitational settling: A strategy to economize biodiesel production, Bioresource Technol. 134 (2013) 401-406.