Review Paper

The Advances of Electrospun Nanofibers in Membrane Technology

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• Recent advancement of ENMs to enhance the performance in different separation processes
• Application of ENMs/Electrospun fibers Mat in different area
• Scope of ENMs and metal fillers in future

Abstract
Electrospinning is a simple and versatile technique that relies on the electrostatic repulsion between surface charges to continuously draw nanofibers from a viscoelastic fluid. Electrospinning can generate nanofibers with a number of secondary structures. Surface and/or interior of nanofibers can be functionalized with molecular species or nanoparticles during or after an electrospinning process to obtain desirable results. In a short period, electrospun nanofiber membranes (ENMs) have gained popularity due to the facile fabrication, interconnectivity and large area/volume ratio. However, ENMs’ pore sizes are intrinsically very large fractions of micrometer to few macrometer, which makes modification of surface chemistry and especially reduction of the ENM pore size indispensable for wider applications of ENMs for membrane separation processes. The modification of nanofibers has been applied widely to give them improved properties. This review paper will provide the progress have recently made on the modification of ENMs to enhance their performance in various membrane separation processes.

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1. Introduction

With the ability to mass-produce nanofibers, electrospinning may well be one of the most significant nanotechnologies of this century [1].

Doshi and Reneker in 1993 introduced the term “Electrospinning” and highlighted its unique features as a fabrication technique and the distinct morphology of electrospun nanofibers [2, 3]. It is a simple and versatile technique that relies on the electrostatic repulsion between surface charges to continuously draw nanofibers from a viscoelastic fluid. Nanofibers can be produced from a variety of materials, such as polymers, ceramics, metals, small molecules, and their combinations. It can generate nanofibers with a number of secondary structures, including those characterized by a porous, hollow, chain-like structure. Better than their flat surface (outside), nanofibers can be modified/functionized with molecular species or nanoparticles during or after an electrospinning process. In 2013, Naseem et al. [4] wrote a review on the advancement in electrospun nanofibrous membranes modification and their application only in water treatment.

To make electrospun nanofiber is itself an art. But, to modify its surface for the purpose to improve its properties is also an art which is very challenging, interesting and important for many applications in the nanoscale range. The type of polymer/inorganic material used in fabrication of nanofibers and the method of production affect the diameters and physical properties of the nanofiber. Application potentials of nanofibers depend on the physical properties of nanofiber and the material used for the fabrication of nanofiber. Electrospinning generally produces a nonwoven fibrous mesh with typical pore size of about 3-5 μm. Though, small pores are necessary for wider applications, larger pores are necessary for applications in microfiltration, air filtration or as a barrier membrane to cell infiltration. The pore size of the electrospun membrane is dependent on the choice of polymer to be electrospun [5].

Given the limitation of using electrospinning parameters to vary its pore size, techniques such as controlling fiber distribution, post electrospinning modification and using temporary spacers have been employed. Wang et al. [6] described the method for the preparation of electrospun nanofiber membranes with varied fiber diameters and different membrane porosities and thicknesses by a facile hot-pressing method, and investigated the relationships between membrane properties and microfiltration performances. It was reported that the membrane porosity could be significantly decreased from ~86% to as low as ~34% by using hot-pressing processes and substantial increase of rejection fraction from 0% to ~100% for 0.2 μm particles. Some of these membranes (consisting of small diameter nanofibers) that were hot-pressed for a longer period could even block all of 0.1 μm particles. On comparing with conventional microfiltration media, these membranes exhibited significantly higher flux values and substantially lower degrees of fouling without distinguishably sacrificing particle rejection fractions. For example, the rejection fraction and permeate flux value of one membrane (fiber diameters: ~150–250 nm, membrane porosity: ~40%) were ~99.3% and ~71.2 L·h⁻¹·m⁻²·psi⁻¹, respectively, at 13 mL volume fed, indicating that electrospun nanofiber membranes might be highly promising for microfiltration applications (particularly water purification).

Electrospinning is a fiber production method which uses electric force to draw charged threads of polymer solutions or polymer melts up to fiber diameters in the order of some hundred nanometers. However, there are many different methods to make nanofibers, including drawing, electrospinning, self-assembly, template synthesis, and thermal-induced phase separation. The electrospinning parameters such as environmental humidity and temperature, applied voltage, needle tip-collector distance, conductivity and viscosity of the polymer solution, and chemistry of polymer/inorganic material etc. dominate both extrinsic and intrinsic parameters of nanofiber. Electrospun polymeric nanofibers can be used as effective membrane materials for environmental remediation due to the light weight, high surface area, and interconnected porous structure. The properties of nanofibers have motivated researchers and companies such as considering using this material in several fields. Electrospun nanofibers have great potential as promising reinforcement fillers for next-generation polymer composites [6]. Tijing et al. [7] summarized the latest progress in the use of electrospun nanofiber membranes and their potential for many applications.

The modification agent used for the modification of the polymer nanofibers played the most important role and not the method used for the modification [5]. Liao et al. [8] discussed electrospun polymeric nanofibrous membranes for water treatment including their fabrication, modification and applications. Modifying the electrospinning parameters and environmental conditions resulted a variety of nanofibrous productions. Rosman et al. [9] discussed the modification of nanofiber surface for the production of heterogeneous materials by function of two intrinsic properties of hydrophilic and hydrophobic differences. The potential use of nanofibers for water treatment by membrane distillation is also highlighted.

Usually two major structures are found in the nanofibrous mat:

i) Uniform, continuous fibrous structure.
ii) Bead-containing fibrous structure.

Variation in the relative abundance of these two structures is determined by the relative contributions of the parameters during the electrospinning process. To produce a uniform fiber, following intrinsic parameters must be adjusted:

i) Applied voltage.
ii) Needle tip-collector distance.
iii) Conductivity of electrospinning solution.
iv) Viscosity of the electrospinning solution.
v) Flow rate of electrospinning solution

Above mentioned parameters are depending on the nature of the material used.

Highly porous nanofibrous mesh with large surface-to-volume ratio improves performance for many membrane applications. Porous, nanofibrous meshes made by electrospinning have been identified for use in the following potential applications of electrospun nanofibers [1]:

i) Defence and security (chemical and biological protection sensors).
ii) Environmental engineering and biotechnology (membranes and filters).
iii) Energy (solar cells and fuel cells).
iv) Healthcare (tissue engineering, tissue repair and drug delivery).

Generally, polymer with sufficiently high molecular weight can be electrospun. Natural polymers, polymer blends, nanoparticle- or drug-impregnated polymers, and ceramic precursors can be used for making electrospun nanofiber.

Electrospun nanofiber (ENF) meshes are an excellent material for membrane preparation due to the following characteristics:

i) High porosity.
ii) Microscale interstitial space.
iii) Interconnectivity.
iv) Large surface-to-volume ratio.

Generally, the electrospun material can be divided into the following three categories:

i) Polymer
ii) Polymer and inorganic material (nanoparticles)
iii) Inorganic

The resultant physical morphology and mechanical properties vary depending on the spinning dope concentration and spinning condition employed during the process.

Surface modification of ENMs is also necessary in order to improve their performances towards mechanical strength, porosity selectivity etc. However, widespread applications of ENMs are hindered by poor mechanical strength attributed to their high porosity, intrinsically low, random fiber orientations and weak interactions between fiber junctions.

Wang and Hsiao [10] discussed fabrication and applications of electrospun nanofiber membranes including recent advances in nanofiber-based membranes for water filtration and affinity for adsorption. Various composite membrane formats containing different arrangements of nanofibers have been demonstrated for many sorts of water applications, including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis...
(RO), membrane distillation (MD) and adsorption.

The followings are few methods for the modification on ENFs or ENMs:

i) Graft polymerization/interfacial polymerization
ii) Oxidation
iii) Solvent vapor treatment
iv) Surface coating
v) Chemical treatment
vi) Heat treatment
vii) Adding additives in electrospun solution

Easy functionalization, high surface area to volume ratio and interconnected fibrous nonwoven membrane have given electrospun nanofibers the potential to be used on various aspects of pollution control. As a non-functionalized membrane, electrospun fibers can be used as a pre-filter for removing micro particles. The most common method to improve membrane anti-fouling properties is membrane surface modification. The surface modifications of the ENMs enhance the matrix properties of nanofibers such as availability of functional groups on the surface of nanofibers. A wide range of functional molecules have been incorporated into electrospun nanofibers for pollutant adsorption.

The effects of functionalized surface groups on nanofibers were investigated based on improved gas adsorption by Im et al. [11, 12]. The fluorination treatment of porous nanofibers was carried out in the gas state for 5 min. The capacity of methane storage was increased by attraction effects of fluorine on porous nanofibers.

2. Modification of electrospun nanofiber membranes (organic/polymeric membranes)

2.1. Grafting

Plasma-induced graft copolymerization is an efficient, common and versatile way of introducing a selective polymeric layer on the surface of a hydrophobic membrane and is limited only to the surface. Due to this reason, bulk properties of the membranes do not change. On plasma grafting on the surface, the symmetrical structure of the membrane converts to an asymmetrical structure. Due to this, selectivity of the membrane increases without increasing hydrodynamic resistance significantly [13], including separation properties. Kaur et al. [13] grafted a hydrophilic monomer methacrylic acid (MAA) on the surface of electrospun PVDF membrane as the base membrane. The membrane was placed in a glass tube containing aqueous solution of 10% (v/v) MAA monomer and the tube was heated at 80°C for 1 h to initiate the graft copolymerization. To terminate the copolymerization, the solution was exposed to air. After washing the PMAA-grafted membrane with deionized water, it was stored in 0.1 NaOH solution to remove adsorbed homopolymer or unreacted monomers. Figure 1 shows the schematic of the plasma induced graft copolymerization method.

After grafting, the ENM was transformed into a microfiltration membrane, similar to a commercial hydrophilic PVDF membrane prepared by the phase inversion method (HVLP, Millipore, USA) in pore-size distribution with an average pore size of 0.45 μm but with a significantly better flux. Cho et al. [14] modified PVDF ENM by argon (Ar) plasma treatment to improve the surface hydrophilicity and the detection sensitivity for protein.

2.2. Surface coating

Surface coating is also a common method to modify the surfaces of fibers/membrane. There are many surface coating methods which are common and well described in the literature.

2.2.1. Dip coating

The dip-coating process can be separated into five stages [15]:

i) Immersion: The substrate is immersed in the solution of the coating material at a constant speed (preferably jitter-free).
ii) Start-up: The substrate is kept inside the solution for a while and then pulled up.
iii) Deposition: The thin layer deposits itself on the substrate while it is pulled up. The withdrawing is carried out at a constant speed to avoid any jitters. The speed determines the thickness of the coating (faster withdrawal gives thicker coating material).
iv) Drainage: Excess liquid drains from the surface.
v) Evaporation: The solvent evaporates from the liquid, forming the thin layer. For volatile solvents, such as alcohols, evaporation may start even during the deposition and drainage steps.

In the continuous process, the above steps are followed one after another, which allows the coating of a thin layer as low as <0.2 μm. The critical factors in dip coating is the viscosity of the solution and the coating speed or time. To form an inorganic multilayer, the first substrate layer is calculated, which is then followed by the repeated cycles of dipping, drying and calcination [16].

2.2.2. Chemical vapor deposition

Chemical vapor deposition (CVD) is a coating process in which materials in a vapor state are condensed through the processes of condensation, chemical reaction or conversion to form a solid layer over a substrate. This process is used to produce high quality, high-performance, solid materials, typically under vacuum. The process is often used to produce thin films, including modification of membrane surfaces. CVD is classified by the operating conditions:

 i) Atmospheric pressure CVD (APCVD)–CVD at atmospheric pressure
 ii) Low-pressure CVD (LPCVD)–CVD at sub-atmospheric pressures. Reduced pressures tend to reduce unwanted gas-phase reactions and improve film uniformity across the wafer.
 iii) Ultra-high vacuum CVD (UHVCVD)–CVD at very low pressure, typically below 10⁻⁵ Pa (=10⁻¹ torr). Note that in other fields, a lower division between high and ultra-high vacuum is common, often 10⁻¹ torr.

CVD system contains a system of metering the mixture of reactive and carrier gases, a heated reaction chamber, and a system for the treatment and disposal of exhaust gases. The gas mixture (which typically consists of hydrogen, nitrogen or argon, and reactive gases such as metal halides and hydrocarbons) is carried into a reaction chamber that is heated to the desired temperature. Different types of CVD methods have been developed over the last few decades. These include moderate-temperature CVD, plasma-assisted CVD and laser CVD. The deposition of coatings by CVD can be achieved in a number of ways such as thermal decomposition, oxidation and hydrolysis. From CVD a uniformly coated layer with thickness 2–100 μm can be obtained [16].

2.3. In-situ polymerization on the ENM surface

The most common technique to modify the membrane surface is IP (interfacial polymerization) reaction. Interfacial polymerization, a method to form a polyamide dense layer on the membrane surface, is typically based on 1,3,5-benzenetricarbonyl trichloride (TMC) and 1,3-phenylenediamine (MPD) reaction. Figure 2 shows the IP between TMC and MPD. Polymerization occurs at an interface between an aqueous solution containing one monomer and an organic solution containing a second monomer. The interfacial polymerization is a self-growth polymerization.
2.4. Hydrophobic to hydrophilic or vice versa

Nanofiber has the capabilities in oil-water separation, most particularly in sorption process when the material in use has the oleophilic and hydrophobic surfaces [18]. Hydrophobicity is one of the most important specifications of the electrospin membranes, which can affect the membrane flux and membrane fouling potential. While hydrophobic membranes show a better performance in the treatment of aqueous solutions by pressure driven membrane processes, because the lower water contact angle of hydrophilic membranes will significantly reduce the capillary pressure and increase the flow rate of the liquid and separation ability, higher surface hydrophobicity is a favorable feature for the membrane distillation (MD) process [19].

Superhydrophobic surfaces are of great interest for membrane distillation. Many approaches, such as plasma treatment, lithography, sol-gel technology, nanoparticle deposition on smooth or roughened substrates, fluoroalkylsilane coatings and phase separation of a multi-component mixture have been suggested to modify the membrane surface hydrophobicity [20]. However, most of the superhydrophobic surfaces are prone to wetting at some extent by water or other liquids, including oils, alkanes, and alcohols. When superhydrophobic surfaces are exposed to environments with organic contaminants, their wetting resistance may be compromised, leading to loss of self-cleaning ability, severe fouling, or poor sealing performance by swelling.

Liao et al. [21] fabricated PVDF nanofiber membranes specially designed for DCMD application. It was reported that the electrospin membranes surface exhibited a rough surface with high hydrophobicity (>135° water contact angle). Liao et al. [22] developed a super hydrophobic membrane containing silica-PVDF composite selective skin on a polyaniline fluoride (PVDF) porous nanofiber scaffold via electrospinning. From the DCMD experiments of over 50 h testing time, it was found that superhydrophobic selective layer exhibited excellent durability. Heat-press post-treatment of membrane improved nanofiber membrane integrity, enhanced water permeation flux and prevented membrane pores from wetting in DCMD operation.

Deng et al. [23] fabricated an unique dual-layer composite membrane consisting of a superhydrophobic selective skin of amorphous polypropylene (apPP) and an electrospin poly(vinylidene fluoride) nanofibrous support. The superhydrophobic apPP porous skin acted as an additional barrier to surface wetting. Membrane exhibited an ultrahigh permeate vapor flux of 53.1 kg m⁻² h⁻¹ and stable permeate conductivity for a transmembrane temperature difference of 40 °C (3.5 wt.% NaCl salt feed) over 50 h of operation.

Liao et al. [24] reported the fabrication of robust superhydrophobic dual-layer membranes with high porosity and excellent mechanical properties via electro-spinning in two ways:

i) Electrospinning an ultrathin 3D superhydrophobic selective skin, comprising PVDF and silica nanoparticles, on a porous PVDF nanofibrous support.

ii) Electrospinning thicker 3D superhydrophobic PVDF–silica composite layers onto a commercial nonwoven support, which not only assists the PVDF–silica composite particles in shaping into a flat sheet but also provides outstanding mechanical properties to the composite membranes.

These membranes have high anti-wetting capacity not only toward distilled water, but also towards salty water, oil-in-water emulsion, and beverages, which enables them to be used not only for desalination but also for other processes. Li et al. [25] fabricated a new type of PS superhydrophobic nanofibrous membranes having dual-biomimetic structure with fine hierarchical roughness. In another publication, Li et al. [26] described how superhydrophobic and superoleophilic electrospun nanofibrous membranes were fabricated via combining the amination of electrospun polycrylonitrile (APAN) nanofibers and immobilization of Ag nanoclusters with an electroless plating technique, followed by n-hexadecyl mercaptan surface modification. The membrane showed an excellent oil/water separation performance. Ifuku et al. [27] reported a method for surface phthaloylation of chitin nano fiber in aqueous media for the purpose of modifying its properties. The phthaloyl group was quantitatively introduced into the amino group of surface-deacetylated chitin nanofiber membrane in aqueous media providing hydrophobic surface properties. The authors [27] expected that on surface modification, chitin nanofiber with hydrophobic groups can function in a variety of applications, including as reinforcement filler and coating material to improve mechanical strength with UV-protectant protein. Zhang et al. [28] prepared ENMs consisting of polyvinylene fluoride-co-hexafluoropropylene and nanosilica nanocomposites. Blended with 5 wt.% modified nanosilica, the water contact angle of membrane could reach up to a maximum value of 136°.

Foong and Sultana [29] fabricated layer-by-layer polycaproactone (PCL)/chitosan electrospin composite membranes based on polyactic acid (PLA). Double layered composite PLA and PCL/chitosan membranes had lower wettability and higher water uptake. Liao et al. [24] modified the surface of electrospun PVDF nanofiber membrane to fabricate two types of superhydrophobic membranes i.e. integrally-modified and surface-modified for MD process as shown in Figure 1.

For integrally modified PVDF membranes (designated as I-PVDF) preparation, ENMs were firstly wetted by a mixed solution of IPA and water to ensure that the chemical solution can flow inside the membranes and react on all fibers. On the other hand, surface-modified PVDF membranes (designated as S-PVDF) were prepared by directly treating the dry PVDF nanofiber membrane which did not allow the reagents to intrude into the membrane pores and ensured that the modification only occurred on the membrane surface. Surface modification was done in three steps of via dopamine surface activation, silver nanoparticle deposition and hydrophobic treatment [30]:

i) Nanofiber surfaces were firstly coated by poly-dopamine (PDA) to improve the adhesive force between the fibers and silver nanoparticles.

ii) PDA activated nanofibers were coated by silver nanoparticles during chemical reduction to optimize the morphology and roughness of the membrane.

iii) In order to alter the surface chemistry, 1-dodecanethiol (C12) was applied to react with silver nanoparticles in mild conditions.

DCMD results showed that modified I-PVDF membrane exhibited high and stable water flux without wetting in DCMD process [30]. Omniphobic surfaces that are able to repel both water and organic liquids are highly desired for reliable anti-wetting performance [31]. Hydrophobic membranes can be modified to hydrophilic membranes by various methods known as hydrophilization, which is divided into four major types namely [32]:

i) Plasma induced surface grafting (PISG) treatment.

ii) Chemical oxidation.

iii) Organic chemical surface functionalization.

iv) Radiation induced surface.
Hou et al. [33] fabricated composite membranes with a hydrophobic substrate and a hydrophilic top surface via electrospinning to mitigate oil fouling in membrane distillation. Polytetrafluoroethylene (PTFE) hydrophobic substrate was coated with two different hydrophobic fibrous networks, including a cellulose acetate fibrous network and a nanocomposite fibrous network comprising CA and silica nanoparticles (SiNPs). These composite membranes showed robust oil-fouling resistance in DCMD, compared with the surfactant PTFE membrane when a saline crude-oil emulsion was used as the feed solution.

Schaub et al. [34] studied the surface of aligned, chemically modified electrospray poly-L-lactic acid (PLLA) nanofibers to determine if surface chemistry and hydrophilicity could improve neurite extension from chick dorsal root ganglia. From their investigation they reported that improvement of hydrophilicity can be accomplished by using different surface functionalities for modification of surfaces. Huang et al. [35] proposed a method to modify a non-swelling hydrophobic electrospray PVDF fiber to make it hydrophilic and fully wettable via the interfacial polymerization of 1,6-hexanediol and adipoyl chloride to form nylon 6,6 directly on PVDF fibers. These modified membranes exhibited swelling resistance in water and excellent flux performance. This composite membrane performed well in osmotic applications.

To improve mechanical properties of PAN, PVDF and PVDF/PAN nanofiber layers, Yalcinkaya et al. [36] used lamination process to fabricate nanofibers using low vacuum plasma treatment. By using argon as the carrier gas, H2, O2 and N2 were used as the reactive gasses to make the membrane hydrophilic and sulphur hexafluoride (SF6) was used to make the surface more hydrophobic. It was reported that the hydrophilic PAN base membrane showed better performance under plasma treatment. It was concluded that hydrophilic membranes have higher affinity to plasma particles compared to hydrophobic membranes. In another publication, Yalcinkaya et al. [37] demonstrated the modification of PAN ENM via Ar plasma exposure, and the modified ENM was further tested for oily water treatment. A remarkably high permeability of 25 000 L m⁻² h⁻¹ bar⁻¹ was achieved with Ar plasma exposure followed by NaOH modification.

Bao et al. [38] applied oxygen plasma etching at the surface of the electrospray nanofibers of polymethyl methacrylate (PMMA) for facilitating the growth of silver nanoparticles (Ag NPs). With this technique, oxygen-containing functional groups can be generated on the surface of the PMMA nanofibers, which was confirmed by the variation of the water contact angle. The oxygen plasma etching is effective in increasing the hydrophilicity of the PMMA nanofibers and thus in facilitating the growth of the Ag NPs at the nanofibers’ surface. Bui et al. [39] developed thin film composite (TFC) membranes by coating polyamide (PA) thin layer over electrospray polyethersulfone (PES) nanofiber supported on commercial polyester (PET) nonwoven fabric. The PA selective layer was polymerized in situ onto the nanofiber support through an interfacial polycondensation reaction. It was reported that these modified membranes showed osmotic water fluxes two to five times higher than the commercial HTI-cellulose triacetate (CTA) osmotic membrane. Uzal et al. [40] fabricated novel polysulfone (PSf)/polyetherimide (PEI-Al2O3) nanofiber membrane by electrospinning of the PSf solution blended with different ratios of PEI and Al2O3 nanoparticles and the membrane was used as water based membrane filtration. On addition of PEI and Al2O3 particles in PSf solution, the overall properties of the nanofiber membranes in terms of porosity, tensile strength and hydrophilicity improved. Arabi et al. [41] by using a combination of oxygen plasma treatment, sodium hydroxide treatment and arginine–glycine–aspartic acid (RGD) immobilization modified the surface hydrophobicity, roughness and chemistry of electrosprayed polycaprolactone (PCL) fibers.

Kiani et al. [42] fabricated novel hydrophilic polyethersulfone (PPSU) nanofibrous membrane by electrospinning of the PPSU solution blended with polyethylene glycol 400 (PEG 400). It was revealed that blending of the PPSU solution with 10 wt.% PEG 400 resulted in formation of a nanofibrous membrane with high porosity and increased mechanical strength. In another publication Kiani et al. [43] reported the fabrication of nanofibrous composite (TFNC) PPSU membrane by casting a thin PPSU barrier layer on the surface of the electrosprayed nanofibrous PEG-PPSU blend support. The PWF (Pure water flux (L/m²/h)) of the TFNC PPSU membranes was 5.2, 4.5, and 16.4 fold higher by using 20, 22, and 24 wt. % PPSU in the casting solutions, respectively, as compared to the unsupported PPSU membranes.

2.5. Thermal treatment

Heat treatment has been carried out widely because it can change physical properties. Heat-press treatment is a simple and effective procedure to improve both morphology and mechanical characteristics of the ENMs. Yao et al. [44] reported that membrane surface can be modified via post heat pressing technique to improve the performance for MD. Yao et al. [45] used heat-press treated membrane for desalination using poly-vinylidene fluoride-co-hexafluoropropylene membrane. It was found that the thickness of the heat-pressed membranes was affected by the temperature in an inverse manner. In other words, at higher temperature, thinner membranes were obtained. It was found that increasing the heat-press temperature decreased the average pore size and narrowed the PSD (pore size distribution). Similar results were reported by Liao et al. [46] and Wu et al. [47] under similar conditions. It was suggested that electrospun membranes could be improved by heat-press treatment under proper conditions for enhanced membrane morphology, characteristics, LEP and tensile strength.

Yao et al. [44] applied heat-pressed membranes via annealing post-treatment to improve the LEP, as well as its permeation and salt rejection efficiency. It was found that annealing improved the MD performance as the average flux reached 35 L m⁻² h⁻¹ (>10% improvement of the ones without annealing) while still maintaining 99.99 % salt rejection. Kaur et al. [48] investigated the effect of hot pressing on the properties of ENMs which were subsequently coated with thin polyamide layer by IP to be used for desalination. PAN ENMs on a Hollytex backing material (nonwoven polyester Hollytex 3242) was hot pressed at 87 °C at different pressures. The membrane surface became smoother when the heat treatment is applied and the flux became higher.

Shirazi and co-workers [49] reported that polystyrene ENMs showed superhydrophobic property on heat treatment. On analysing the surface by AFM, it was reported that the fiber diameter increased significantly, while the surface roughness decreased and the pore size distribution became narrower. Membranes were used for treatment of the biodiesel’s water-washing effluent through a dead-end filtration system. It was reported that the membrane showed in the reduction rates of 58, 26, 92, 95 and 50 %, respectively, for COD, BOD, TS, TDS and TSS before the heat treatment; and 75, 55, 92, 96 and 30 %, respectively, after heat treatment.
Kiani et al. [50] used heat treated PPSF nanofibrous membranes for determination of pure water flux and filtration of canned beans production wastewater. Pure water flux of 7323 Lm<sup>−2</sup>h<sup>−1</sup> was observed for the heat-treated membrane. Heat treated membrane showed high porosity and improvement in mechanical stability.

2.6. Other

2.6.1. Miscellaneous methods for ENMs modification.

Che et al. [51] fabricated poly(acrylonitrile-co-hydroxethyl methacrylate) (PAHM) nanofibrous mat by electrospinning and glucose ligands were bound on the nanofiber surface through a reaction between glucose penta acetate and the hydroxyl groups of PAHM. This was a new type of glycosylated nanofibrous membrane (GNM). The membrane was used successfully for the separation and purification of lectins. Rajesh et al. [52] fabricated nanofiltration membranes by forming multilayers of branched polyethylenimine (BPEI) and polyacrylatic acid (PAA) on an electrosprun polycrylicontile (PAN) nanofibrous mat by layer-by-layer (LbL) assembly. Nanofiltration membranes modified with 15 bilayers of BPEI/PAA multilayers had a pure water flux of 19.7  Lm<sup>−2</sup>h<sup>−1</sup> and an MgSO₄ rejection of 98.7 %. This performance represents 1.6 times higher flux and 1.1 times higher salt rejection than the multilayers formed on a conventional asymmetric polymeric support (non-spun). The reason for the higher separation and higher flux of BPEI/PAA multilayer modified PAN nanofiber membranes was due to the combined effect of high charge density and high porosity of the nanofiber membrane.

Zeytuncu et al. [53] fabricated the polyvinyl alcholic (PVA) organic-inorganic hybrid nanofiber membranes by electro-spinning and cured them via UV irradiation. Fine polymeric nanofibers were obtained in the size range of 100-200 nm for pure PVA nanofibers and 150-250 nm for PVA/SiO<sub>2</sub> hybrid nanofibers, while imidazol-functionalized PVA/SiO<sub>2</sub> nanofibers were less than 100 nm. The membranes produced were suitable for use in various applications, including filtration and adsorption, in the biomedical and textile industries, among others. Liu et al. [54] fabricated PVDF-Ag and PVDF-Ag-graphene oxide (GO) nanocomposite membranes with antifouling properties through electrospinning. Silver nanoparticles (Ag NPs) were in situ synthesized from silver nitrate precursor directly. It was reported that introduction of Ag NPs and GO into PVDF membranes showed the improvement in membrane wetting, tensile strength and elastic modulus, water permeability, antifouling property, and antibacterial resistance.

Dandeni et al. [55] described a facile and robust method by which surface of electropun cellulose acetate (CA) nanofibers can be chemically modified with cationic polymer brushes for DNA adsorption. They fabricated a poly(ar-vinybenzy1)trimethylammoniumchloride [poly(VBTAC)] grafted cellulose acetate (poly(VBTAC)-g-CA) nanofiber by combination of electrosprinning and RAFT (reversible addition-fragmentation chain transfer) polymerization and investigated its affinity for DNA adsorption. From the experimental results, it was suggested that CA nanofibers surface-modified with cationic polymer brushes can be suitable as membrane materials for filtration, purification, and/or separation processes for DNA.

Perecin et al. [56] fabricated poly(vinyl alcohol) fibers by electrospinning PVA from aqueous dispersions containing cellulose nanocrystals (CNCs) and investigated the effect of esterification and CNC loading on the structure and solvent resistance of the electrospun fibers. Chemical characterization of the fibers (FTIR, NMR) indicated the formation of ester bonds between hydroxyl groups belonging to neighboring molecules. An 80% improvement in the ultimate strength was achieved for CNC-loaded, cross-linked PVA fiber webs measured at 90% air relative humidity. Che and Su [57] modified the electrosprun poly(lactic acid) (PLLA) nanofibers with cationized gelatin (CG) to improve their compatibility with chondrocytes and to show in vitro and in vivo the potential applications of CG-grafted PLLA nanofibrous membranes (CG-PLLA/NFM) as a cartilage tissue engineering scaffold.

Zhang et al. [58] used chitosan coated nylon for the membranes for papain desorption. These membranes had excellent chemical and thermal resistance as well as high wettability. The dye Cibacron Blue F3GA (CB) as a ligand was covalently immobilized on the CS (chitosan)-coated membranes. The maximum adsorption capacity for papain was up to 133.2 mg g<sup>−1</sup>. The chemically-modified CS-nylon nanofiber membrane with the CB as ligand could become the low cost but high efficiency affinity PES membranes for papain separation. XU et al. [59] prepared three hydrophobic and poly porous electropun fibrous membranes (EFMs) from methoxy polyethylene glycol-poly(ethylene-glycol) (MPEG-PLGA), poly(d,l-lactide-co-glycolide) (PLGA) and poly(d,l-lactide) (PDLLA) and investigated the effects of pH and dissolved organic matter (DOM) on triclosan (TCS) sorption in aqua. The maximum sorption capacities of MPEG-PLGA, PLGA and PDLLA were 130, 93 and 99 mg g<sup>−1</sup>, respectively.

Mahanta and Valiyaveet [60] chemically modified PVA nanofibers with functional groups such as thiol and amines. It was reported that the adsorption of nanoparticles depends on the nature of the surface functionalities. The extraction studies revealed that the amine and thiol modified PVA nanofibers showed 90% extraction efficiency for both silver and gold nanoparticles.

Ray et al. [61] modified the surface of the CFP (cellulose filter paper, hydrophlic) mat by electrosprun nanofibers of PSi-SDS (sodium dodecyl sulfate). The surface-modified dual-layer PSi-SDS/CFP membrane exhibited membrane distillation flux of 9 Lm<sup>−2</sup>h<sup>−1</sup> and more than 99 % salt rejection for 16 h. Heinze et al. [62] treated carbon nanofibers with Ar plasma via fluidized bed plasma reactor and reported that the surface energy increased over two fold after 5 min of plasma treatment. Fang et al. [63] produced gelatin-grafed PET nanofibers via grafting the PET electrosprun nanofibers with natural proteins (gelatin and collagen). This study showed apparent enhancement in the spreading and proliferation of vascular endothelial cells on modified PET nanofibers' surface compared with the non-grafted ones.

2.6.2. Mechanical strength

The main obstacle to use nanofiber membranes toward their use in liquid filtration is poor mechanical strength. It is due to their high porosity, intrinsically low, random fiber orientations and weak interactions between fiber junctions. Huang et al. [64] demonstrated a simple chemical modification for improving the mechanical properties of PAN and PES ENMs. The chemical modification involves the polydopamine (PDA), a hydrophilic polymer, coating on the fiber. Figure 4 illustrates the process for PDA coating both the PAN and PES ENMs.

Coating PDA on nanofibers promotes bonding between junction points of fibers. The coated nonwoven membranes showed 100 to 300 % increases in tensile strength and Young's Modulus with no decrease in flexibility while retaining their porous structure and high water permeability.

Mechanical stability of electrosprun nanofibrous membranes during different modes of filtration such as dead-end and cross-flow plays the major role in preservation of their very high permeance. In fact, to prevent any kind of compaction and disintegration, which results in failure and loss of efficiency, nanofibrous membranes should be somehow mechanically strengthened [65]. For this purpose, Homaeigohar et al. [65] reinforced PES electrosprun nanofibrous membranes with zirconia nanoparticles. The ZrO₂/PES nanofibrous mats were produced by an electrospinning method of the prepared solution. Optimized permeability could be correlated to the enhanced mechanical properties of the membranes. Zirconium decorated PES electrosprun nanofibers (ENFs) showed more efficient filtration performance as compared to the neat PES membrane (mechanical strength).

Cellulosic nano whiskers have been used as reinforcing materials for electrosprun fibers such as polystyrene, PVA, PLA, and so on [66]. Dai et al. [66] studied electrosprun PVA/WPU (waterborne polyurethane) nanofibers into which TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl radical)-oxidized cellulose nanofibers (TONGNs) was loaded. From characterization, it was
revealed that the addition of TOCNs to electrospinning solution of PVA/WPU is a promising method to improve the mechanical strength and thermal stability of electrospun nanofibers. These fibers could be an attractive choice in filtering, scaffolding etc. To provide the mechanical strength to PES ENFs mat, Homaeigohar et al. [67] used poly(ethylene terephthalate) (PET) non-woven as the sub-layer. It was revealed that the PES/PET nanofibrous composite membrane possesses a high pure water flux. It was suggested by the authors that this ENM has the potential to be used in pre-treatment of water, one step before ultra- and nanofiltration membranes.

McClure and Oldham [68] discussed how the mechanical properties of nylon-6 nanofibers are affected by ALD (atomic layer deposition) coatings of TiO$_2$ and other metal oxides and how the specific precursor chemistry affects the resulting mechanical response of modified fiber mat structures. Aluminum oxide (Al$_2$O$_3$), zinc oxide (ZnO), and titanium dioxide (TiO$_2$) were deposited on the nylon nanofibers. Trimethyl aluminum (TMA) and diethyl zinc (DEZ) were used as metal containing precursors for aluminum oxide and zinc oxide, respectively, while titanium tetrachloride (TiCl$_4$) or titanium isopropoxide was used for titanium dioxide coating. On characterization (physical) it was revealed that the TiCl$_4$ diffused into the nylon-6 and reacted with the subsurface, whereas the titanium isopropoxide treated nanofibers react on the surface producing a more abrupt organic/inorganic interface. Results showed that the precursor choice is an important factor when designing thin film coating processes on polymeric substrates. It was reported that the stress–strain behavior of nylon-6 nanofibers depends strongly on the specific precursor chemistry used in the coating process.

Elkhaldi et al. [69] enhanced the mechanical strength of PAN nanofiber mats by depositing the electrosprayed polyethylene terephthalate (PET) nanofibers with cyclodextrin polymer (CDP). To form CDP, three different types of native CD (α-, β-CD and γ-CD) were used. On testing the CDP/PET nanofibers via dynamic mechanical analyzer (DMA), it was revealed that CD/CPET had higher storage modulus and higher glass transition temperature compared to untreated PET nanofibers. Thus, PET/CD nanofibers have shown enhanced mechanical and thermal properties. Kiyounmariisoueki et al. [71] showed that the mechanical strength of the poly (dimethylsiloxane) (PDMS) fibers electrosprayed using poly (methyl methacrylate) (PMMA) as the carrier polymer in different weight ratios can be increased via plasma treatment. As well, treatment of the PDMS/PMMA membrane by plasma resulted in a superhydrophilic (CAn<5) surface.

3. Modified nanofiber membranes in separation processes

Electrospun nanofibrous membranes (ENMs) may offer a great opportunity to the future of filtration media due to their many favorable features. Furthermore, various methodologies have been used to change morphological and topographical features, molecular bonding etc. to enhance the membrane performance. In particular, for surface modifications there are several techniques such as nanoparticles coating, treatment with chemicals or heat, grafting, UV irradiation and interfacial polymerization.

3.1. Nanofiltration

Nanofiltration technology, which is a category of membrane technology placed between reverse osmosis and ultrafiltration, has been attracting a great deal of interesting characteristics of membrane technology. Safarid et al. [72] fabricated, multifunctional nano-ultrafiltration, magnetically modified electrospun nanocomposite fibers based on a naturally derived biocompatible and biodegradable polysaccharide chitosan (CS) and the hydrophilic and biocompatible poly(vinylpyrrolidone) (PVP). The magnetically modified PVP/CS fibers exhibited superparamagnetic behavior at ambient temperature. Wang et al. [73] found that the interfacial polymerization of polyamide around the ultrafine cellulose nanofibers layer in thin film nanocomposite (TFNC) showed a good rejection of MgCl$_2$ and MgSO$_4$, depending on the adapted interfacial polymerization.

3.2. Ultrafiltration

Dolina et al. [74] coated a layer of polyurethane containing Ag nanoparticles on the commercial PES ultrafiltration membrane (Microdyn-Nadir UP150) via electrospinning. The addition of silver particles to the spinning solution negatively affected both homogeneity and fiber structure, resulting in a wider fiber diameter compared to pure PU nanofibers. Membrane showed antimicrobial properties. It was suggested that there would be two possible methods for preparing composite ultrafiltration membranes with antibacterial properties:

(i) Direct on nanofiber deposition.
(ii) Thermal pressure lamination.

In another work, Dolina et al. [75] modified commercial ultrafiltration membranes (Microdyn-Nadir UP150 PES UF membranes) using different polymeric electrospun nanofibers (PU and PES), containing various forms of silver. Three different silver precursors were used i.e. silver nitrate (AgNO$_3$), silver benzoate (C$_6$H$_5$AgO$_2$), and silver behenate (C$_{24}$H$_{48}$AgO$_4$). Electrospun nanofibers were prepared from mixtures of polymer solution, silver compound solution, and solvent or reducing agent. Thus the membrane surfaces have biocidal (antibacterial) properties.

Al-Husaini et al. [76] reported a new type of ultrafiltration electrospun nanofibrous membranes (ENMs) incorporating hydrous manganese dioxide (HMO) in PES. The presence of HMO improved the performance in the synthetic oily solution treatment. Two methods were used to improve the mechanical property and hydrophilicity of the PES-based ENMs without compromising its porosity and water permeance. The first method involved the use of mixed solvents - dimethylformamide and n-methyl-pyrrolidinone (DMF/NMP) in which NMP was a high vapor pressure component that could enhance the mechanical properties of the nanofibrous by improving solvent-induced enhancement of the nanofibrous mechanical strength. A second method involved the incorporation of specific amount of HMO nanoparticles in PES dope solution to enhance membrane hydrophilicity. Dobosz et al. [77] improved membrane’s performance by enhancing ultrafiltration membranes with electrospun nanofibers. Pure water permeability (PWP) was increased when polysulfone nanofibers were electrospun on top of a commercial PES membrane, while PWP was not increased by electrosproning of cellulose nanofiber layer.

3.3. Heavy metal removal

Industrial processes can release heavy metals into their wastewater streams, resulting in potential contamination of the environment. Therefore, regulating agencies set the requirement of heavy metal (for example lead, copper, chromium, iron, manganese, mercury, nickel and zinc) removal from wastewater before it can be discharged. Current commercial methods to remove heavy metals from municipal drinking water are inefficient and expensive. ENMs open a new avenue for the use of heavy metals ion removal from wastewater. Critical role will be played by affinity membranes in wastewater treatment to remove (or recycle) heavy metals ions etc. in the future. Polymer nanofibers functionalized with a ceramic nanomaterial, such as hydrated alumina/alumina hydroxide and iron oxides, could be suitable materials for fabrication of affinity membranes for water industry applications. The polymer nanofiber membrane acts as a carrier of the reactive nanomaterial that can attract toxic heavy metal ions, such as arsenic, chromium, and lead, by adsorption/chemisorption and electrostatic attraction mechanisms [1].

Wei et al. [78] demonstrated that the amorphous WO$_3$ (α-WO$_3$)/polymer nanofiber membranes (NFMs) can be reduced by solar light irradiation. Metal deposition on the NFMs is an electrodedeposition/ deposition process. The negatively charged surfaces with relatively low redox potentials promote strong electrostatic attractions between the NFMs and the metal ions and inhibits the metal ion desorption, which makes the NFMs highly efficient in removal/recovery of trace amounts of metal ions (ppb level) from water. Polycyanoacrylate (PAN) was found to be an ideal polymer matrix since it is hydrophobic and easy to fabricate NFMs by electrospinning.

The NFMs were used as metal ion adsorption especially for hazardous metals. For the better performance of functionalized nanofiber for the pollutant removal, greater exposure of the functional group on the surface of the nanofibers is necessary. The where the base material does not contain appropriate functional group, functionalization method such as blending and chemical treatment may be used. Feng et al. [80] demonstrated the preparation of polycyanoacrylate/cellulose nanofibrous composite (PANCNF) composite, nanostructured membranes, and then modified them by hydrolysis and amidoximation. The resulted membrane was called as amidoxime polycyanoacrylate/regenerate cellulose (AOPAN/RC) composite nanofibrous membranes. The modified membrane was used for heavy metal ions removal. The membrane showed the saturation adsorption amount of 7.47, 4.26 and 1.13 mmol g$^{-1}$, respectively (at 25°C), for Fe(III), Cu(II) and Cd(II) and excellent reusability.

Habiba et al. [81] fabricated chitosan/polyvinyl alcohol (PVA)/zeolite...
electrospun nanofibrous composite membrane from hydrolyzed chitosan blended with aqueous PVA solution in different weight ratios. It was concluded that chitosan/PVA/zeolite nanofibrous membrane is useful for water treatment at moderate concentration of heavy metals (Cr (VI), Fe (III), and Ni (II)). Huang et al. [82] reported that the palladium (Pd) nanoparticle-immobilized electrospun polyethyleneimine (PEI)polyvinyl alcohol (PVA) nanofibers reduced hexavalent chromium (Cr(VI)) to trivalent chromium (Cr(III)). Kim et al. [83] studied SF (Silk fibroin) and WK (oxidized wool protein commonly called wool keratose (WK)) blend nanofibrous membranes prepared by electrospinning and their performances were evaluated as a heavy metal ion adsorbent. Wool protein contains many hydrophilic amino acids which have high affinity for ionic species such as metal ions. By blending the WK with SF, the electrospinability and structural stability of WK/SF blend membrane was markedly improved and the WK/SF nanofibrous membrane exhibited higher Cu(II) adsorption capacity (2.88 mg g⁻¹) than SF nanofibrous membrane (1.65 μg mg⁻¹).

Chaúque et al. [84] modified the surface of electrospun aminated EDA (ethylenediamine)- PAN nanofibers, by coating EDTA (polyethyleneimine tetraacetic acid) in presence of tetracycloduran. EDA was grafted as a cross-linker. The modified nanofibers (EDTA-EDTA-PAN) were used in the wastewater treatment for the removal of Cd(II) and Cr(VI). It was revealed that the EDTA-EDA-PAN nanofibers showed effective sorption affinity for both Cd(II) (max. capacity 32.68 mg g⁻¹ at 298 K) and Cr(VI) (max. capacity 66.24 mg g⁻¹ at 298 K), and nanofibers were regenerated by simple washing with 2 M HCl solution.

Neghiani et al. [85] modified polyacrylonitrile nanofibers (PAN-nFs) by grafting amine groups on nanofiber. Diethylenetriamine was used to produce aminated polyacrylonitrile (APAN) nanofibers. The absorption capacity for Cu(II) was 116.52 mg g⁻¹ which was five times more than the related value for APAN microfibers [86]. Phan et al. [87] modified cross-linked PVA nanofiber via the esterification of hydroxyl group on PVA with the carboxyl group of 3-mercaptopropionic acid under hydrochloric acid in aqueous environment. The membrane was tested for the adsorption of silver ions from the aqueous solution. It was reported that the membrane showed the affinity towards silver ions. The maximum adsorption capacity was found to be 26.2 mg g⁻¹.

Cai et al. [88] modified the surfaces of electrospun poly-(5-cyanoindole) nanofibers by treating with hydroxylamine. The prepared membrane, named as surface amidoxime-modified polyindole (SAMP) nanofiber membrane, was used for the removal of Cr(VI) from aqueous solution via adsorption. The maximum adsorption capacities (Qₐ) calculated from Langmuir model were 340.14, 380.23 and 404.86 mg g⁻¹ at 25, 35 and 45 °C, respectively. These results indicated that the SAMP nanofiber membrane might have potential applications in wastewater treatment for removal of Cr(VI).

Yang et al. [89] grafted oxidized cellulose nanofibrous (thiol-modified cellulose nanofibrous, m-CNf) embedded in an electrospun polyacrylonitrile (PAN) nanofibrous scaffold with cysteine to increase the adsorption capability for chromium (VI) and lead (II). From the adsorption studies, it was concluded that these membranes have high adsorption capacities for both Cr(VI) (87.5 mg g⁻¹) and Pb(II) (137.7 mg g⁻¹) due to the large surface area and high concentration of thiol groups (0.9 mmol of –SH/gram m-CNf). It was also reported that these membranes were stable in morphology and property and could be used and regenerated multiple times with high recovery efficiency.

Almasian et al. [90] modified the surface of polyacrylonitrile (PAN)/polyaniline (PANI)-nylon core-shell nanofiber membrane by diethylenetriamine (DETA) and used it as a filtration-adsorption membrane for the removal of Pb(II) and Cd(II) ions from aqueous solutions. The modified membrane showed the increase in hydrophilicity enabling better antifouling property and higher permeability. Reduction efficiency for BSA of 89.11% and the flux recovery ratio (FRR) of 91.85% were reported for the modified membrane. Beside this, the prepared membrane showed an adsorption capacity of 960 and 911.72 mg g⁻¹ for Pb and Cd ions. The use of nylon as the core improved significantly mechanical properties of membrane.

Xiao et al. [91] fabricated water-stable polyelectrolyte polycrylic acid (PAA) nanofibrous membrane by electrospinning and subsequent thermal crosslinking (using PVA). It was found that PAA/PVA nanofibrous mats can act as an effective sorbent or separation medium for removing Cu(II) ions from water. Razzaz et al. [92] prepared chitosan/TiO₂ nanofibrous adsorbents by two methods:

i) Coating of TiO₂ nanoparticles on chitosan ENMs (coating method).
ii) Electrospinning of chitosan/TiO₂ solutions (entrapped method).

These adsorbents were investigated for the removal of Pb(II) and Cu(II) ions in a batch system. The maximum adsorption capacities of Cu(II) and Pb(II) ions using entrapped and coating methods were found to be 710.3, 579.1 and 526.5, 475.5 mg g⁻¹ at equilibrium time of 30 min and 45 °C, respectively. The selectivity of metal sorption, using chitosan/TiO₂ nanofibrous adsorbent was in order of Cu(II) > Pb(II).

3.4. Membrane adsorption

Electrospun nanofibers for metal ion adsorption especially for hazardous metals is emerging and the use of functionalized nanofiber for the pollutant removal is increasing. As the base material does not contain appropriate functional group, functionalization method such as blending and chemical treatment may be used [79]. The surface modifications of the ENMs enhance the nanofiber’s matrix properties such as availability of functional groups on the surface of the nanofibers. A wide range of functional molecules can be incorporated into electrospun nanofibers for pollutant adsorption.

Stephen et al. [93] fabricated oxolane-2,5-dione functionalized modified cellulose nanofibers. The functionalization scheme is shown in Fig. 4. The surface area of modified nanofibers was 13.68 m² g⁻¹, while it was 3.22 m² g⁻¹ for unmodified (unfunctionalized) nanofibers. The adsorption capacity of cellulose-g-2,5-dione for Pb and Cd was compared with commercial adsorbents (Table 1). The results showed that cellulose-g-2,5-dione performed quite well and is feasible in its application on a large scale.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Pb(II) mmol g⁻¹</th>
<th>Cd(II) mmol g⁻¹</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amberlite 200</td>
<td>1.22</td>
<td>2.0</td>
<td>[94]</td>
</tr>
<tr>
<td>Duolite GT-73</td>
<td>0.59</td>
<td>0.94</td>
<td>[94]</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>0.002</td>
<td>0.003</td>
<td>[96]</td>
</tr>
<tr>
<td>Resin (Dowex 50W)</td>
<td>2.05</td>
<td>2.4</td>
<td>[97]</td>
</tr>
<tr>
<td>Cellulose-g-oxolane-2,5-dione</td>
<td>1.0</td>
<td>2.91</td>
<td>[93]</td>
</tr>
</tbody>
</table>

Park et al. [98] modified the surface by acid treatment to attach oxygen containing uncyclar groups, which played an important role for the removal of metal ions. Wang et al. [99] fabricated silver NPs decorated electrospun CA nanofibrous membranes. From the test results, it was revealed that Ag decorated highly porous CA ENMs had effective antibacterial property and also exhibited strong dye adsorption. These membranes could be very promising in water treatment. Rad et al. [100] used NaX nanozelite for blending with polyvinyl alcohol (PVA) solution to form electrospun PVA/zeolite nanofibers for the adsorption of Ni(II) and Cd(II) ions. The maximum monolayer sorption capacities of Ni(II) and Cd(II) were 342.8 and 838.7 mg g⁻¹ in equilibrium time of 60 min at temperature of 45 °C. Wei et al. [101] reported the design and fabrication of hybrid organic–inorganic fibrous membranes for flexible rewritable media.

A novel electrospun polyvinyl alcohol (PVA)/zinc oxide (ZnO) nanofiber adsorbent was prepared by Hallaji et al. [102], and investigated its performance for the sorption of U(VI), Cu(II) and Ni(II) ions from aqueous solutions. It was reported that the capacity values were 370.86, 162.48 and

94.43 mg g⁻¹ for sorption of U(VI), Cu(II) and Ni(II) ions, respectively. Thunberg [103] chemically modified electrospun cellulose nanofibers to make carbohydrate rich surfaces. These anionic fibers were used as the templates for the synthesis of nano-porous metal-organic framework (MOF). The MOF functionalized cellulose nanofibers had good adsorption properties and the surface area was greatly increased.

3.5. Membrane distillation

The alternative of RO to desalinate hypersaline water is membrane distillation. The critical challenge to use hydrophobic MD membranes for the treatment of industrial waste waters is wetting which is the cause of reduction in membrane permeability and rejection. This is due to low surface tension substances in industrial waste water. ENMs prepared from solely hydrophobic polymers usually exhibit strong water adhesion regardless of their high contact angles, which them susceptible to membrane wetting. To avoid wetting issue, modification is needed for ENMs membranes in MD application [21]. Wetting problem can be reduced by two processes i.e. increasing surface hydrophobicity or decreasing pore diameter [104]. However, reducing the pore size results in the lower permeability. Hence, in MD, the main challenges are well-designed porous structure and hydrophobic surface of the membrane. Dope solution properties and electro-spinning process parameters are key factors to determine the membrane structures and performance. MD membranes needs following two key properties to get optimal performances;

i) High porosity to maximize water vapor flux.

ii) High hydrophobicity to avoid membrane pore wetting.

To make above mentioned properties with low cost MD membrane manufacturing technique is a major challenge for the commercialization of MD technology. Beside this, MD membranes still suffer from low permeate water flux and surface wetting phenomena. Xu et al. [105] and Shaulsky et al. [104] suggested (i) controlling the penetration depth of the dope solution, and, (ii) consequently, the thickness of the polymeric coating layer on the electrospun substrate to fabricate a composite MD membrane by coating a thin selective layer on ENMs. To this end, the important factors are, proper choice for a solvent which does not damage the polymeric fibers, and, control over the polymer loading. The electrospun fiber substrates coated with a controlled polymeric layer thickness exhibited stable desalination performance in MD due to the enhanced surface wetting resistance.

An et al. [106] fabricated amphiphobic polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP) ENMs with anti-wetting property. Their approach was to fluorinate PVDF-HFP fibers by using 1H,1H,2H,2H-perfluorodecyltrichlorosilane (FAS) followed by crosslinking to form a network upon dealcoholization under thermal treatment. These FAS coated membranes showed less reduction in permeability and increase in salt rejection after plasma treatment. An et al. [107] fabricated four self-sustained electrospun polyurethane nanofiber membranes with varying thickness and tested to find the optimum structural parameters and operational conditions for the best MD performance in wastewater treatment. The highest flux was achieved with the thinner membranes and the best energy efficiency was achieved with the thicker membranes. Liao et al. [46] fabricated specially designed PVDF nanofiber membranes for DCMD application. In fabricating the fibers, the structures and properties of resultant membranes were optimized by controlling a series of factors including polymer dope compositions and spinning parameters. The membranes exhibited rough surface with high hydrophobicity (＞135° water contact angle). Heat-press post-treatment effect on the MD performance of membranes has also been examined. Heat-press post treatment enhanced the membrane performance in DCMD. The post-treated PVDF nanofiber membranes were able to present a steady water permeation flux of about 21 kg m⁻² h⁻¹ throughout the entire testing period of 15 h, using a 3.5 wt.% NaCl solution as the feed under the feed and permeate inlet temperatures of 323 K and 293 K, respectively.

Liao et al. [24] developed dual layer super hydrophobic membranes based on PVDF containing silica nanoparticles for desalination applications using the MD process. The developed membrane had a durable and ultrathin 3-dimensional (3D) superhydrophobic skin and porous nanofibrous support wherein water permeation flux of about 21 kg m⁻² h⁻¹ throughout the entire testing period of 15 h, using a 3.5 wt.% NaCl solution as the feed under the feed and permeate inlet temperatures of 323 K and 293 K, respectively.

Liao et al. [108] prepared dual-layered electropun nanofibrous membranes (DL-ENMs) using hydrophilic polypyrrolidene fluoride (PFVD) and hydrophilic polysulphone (PSI) and its performance was studied via DCMD for desalination (different sodium chloride feed aqueous solutions). The thickness of each layer was varied via changing the electrosprining time of each polymer solution. The DCMD permeate flux of the DL-ENMs was found to be higher than that of the PVDF and PSI SL-ENMs and it increased with the decrease of the PVDF layer.

Shaulsky et al. [105] demonstrated a novel solution-based approach for the fabrication of MD membranes with adjustable pore size and performance through non-solvent induced phase separation of a polymeric solution over an electrospray fiber mat. Highly porous electrospray fiber mat with an average pore diameter of 1.2 μm was obtained from poly (vinylidene fluoride-hexafluorobutylene) (PVDF-HFP) in a mixture of acetone and dimethyletheramide. PVDF was coated on the surface via phase separation to control the membrane pore size by filling the empty domains between the fibers. By controlling the depth of the PVDF coating layer within the substrate, robust membranes were obtained. These membranes were tested in DCMD for desalination. The results showed near complete salt rejection (＞99.9%) and a water flux of 30 Lm⁻²h⁻¹ with 40 °C temperature difference between the feed and permeate solutions.

Yao et al. [109] modified (PVDF-HFP) ENFs via heat treatment and its performances were tested via desalination using DCMD. It was found that heat-press treatment with optimal conditions successfully improves the characteristics of the membranes, and hence permeation and salt rejection performance. It was suggested by Yao et al. that electrospray polymeric membranes could be improved by heat-press treatment with proper conditions for enhanced membrane morphology, characteristics, LEP (liquid entry pressure) and tensile strength.

Woo et al. [110] modified the surface of an omniphobic PVDF membrane, prepared by electrosprinning, with CF₃ plasma treatment without significantly altering the morphology and its physical properties. The membrane performance was evaluated using real reverse osmosis brine produced from coal spent liquor. It was observed that a water flux of 60 kg m⁻² h⁻¹ (nearly neat membrane 8.5 L m⁻² h⁻¹) and salt rejection ratio was (100 %).

Ya et al. [111] coated carbon nanotubes (CNTs) on superhydrophobic PVDF ENMs via spraying method. The CNTs network significantly enhanced the hydrophobicity and liquid entry pressure of membranes. It was observed the CNTs coated membranes had superior performance both in anti-wetting and water flux in desalination when used in vacuum membrane distillation (VMD). It was suggested that such approach to fabricate superhydrophobic membranes has the potential applications towards the fabrication of other hydrophobic membranes. An et al. [112] studied the MD performance of functionalized carbon nanotubes, anchored to nanofibers of electropun PVDF (FPVDF) membrane. The MD performance of the functionalized membranes increased their surface roughness, water contact angles and hydrophobicity when compared with the data obtained with non-functionalized PVDF-HFP (E-PH) ENMs.

Ishii [113] prepared superhydrophobic FAS-PVDF-SiO₂ nanofiber membranes with high water contact angles via electrospriving of PVDF-SiO₂ blend solutions followed by the fluorosilazation process with FAS (fluoroalkysilane). It was reported that superhydrophobic modified nanofiber membranes maintained a stable flux of about 31.5 kg m⁻² h⁻¹ with a permeate conductivity approximately 10 µS cm⁻¹ over the entire test. On the other hand, the flux and conductivity of the unmodified membrane showed a significant decrease and increase, respectively. Dong et al. [114] made ENMs with superhydrophobic surface by electrospriving of polyvinyl alcohol (PVA), cross-linking with glutaraldehyde and grafting with low surface energy fluoroalkylsilane (FAS). The grafting of PVA to P-FPA membrane has the self-cleaning properties with water contact angle of 158°. It was reported that the F-PVA membrane exhibited a high and stable VMD flux of 25.2 kg m⁻² h⁻¹, 70 % higher than those of commercial PTFE membranes, Thand a low permeate conductivity (＜5 μm cm⁻²) during a continuous test of 16 h. Su et al. [115] fabricated nanofibers-covered hollow fiber membrane (N-HFM), combining the advantages of both electrospray nanofibers film and hollow fiber membranes, via electrospriving and then spraying. The treated P-FPA membrane has the self-cleaning properties with water contact angle of 158°. It was reported that the F-PVA membrane exhibited a high and stable VMD flux of 25.2 kg m⁻² h⁻¹ and stable salt rejection more than 99.9% during the 5h of test. It was suggested that the welded N-HFM has great potential for MD application.

Razmjou et al. [20] fabricated a superhydrophobic FTCs-TiO₂-PVDF membrane with multilayer roughness and used it for MD applications. By using low temperature hydrothermal (LTH) process, TiO₂ was coated on PVDF nanofiber, followed by fluorosilazation of the surface with 1H, 1H,
During the past decade, polymeric nanofibers, fabricated by electrospinning, have been extensively used for various applications in the separation treatment applications. Electrospun nanofibers can form an effective size exclusion membrane for particulate removal from wastewater. Recently, many articles including reviews have appeared on the topic of wastewater treatment by nanofiber membranes, which indicated the importance of nanofibers for wastewater treatment in the coming generation.

Suja et al. [117] made detailed discussion on recent research works in nonwoven electrospun water purification membranes. The roles, fabrication procedures, and purification mechanism of various hydrophobic and hydrophilic electrospun polymeric water purification membranes have been categorized and explained. Nanocomposite/hybrid nanofibrous membranes can perform extraordinarily well in environmental remediation and control [118]. Ursino et al. [119] discussed the up-to-date information related to novel nanocomposite membranes and their contribution for water treatment applications.

Gopal et al. [120] fabricated PVDF ENMs. These membranes were characterized to relate its structural properties to membrane separation properties and performance. It was reported that the electrospon membranes were able to separate 1, 5 and 10 μm polystyrene particles. These electrospon membranes were successful in rejecting more than 90% of the micro-particles from the solution. Authors claimed that the findings open up the avenue of exploring the use of nanofibers for more mainstream application in the separation technology as a potential membrane for pre-treatment of water prior to reverse osmosis or as pre-filters to minimize fouling and contamination prior to ultra- or nano-filtration.

Shirazi et al. [121] highlighted the prospects of electrospon membranes, specifically in the water industry. Naseem et al. [4] reviewed the modification of electrospon nanofibrous membrane by synthetic methodologies and its application in wastewater treatment. Kandasamy et al. [32] discussed the modern concepts and current research progress on various nanofibrous membranes, such as water and air filtration media. Wang et al. [123] discussed the recent advances in nonporous membranes for water purification including their design and fabrication.

Kangwansapunmonkon et al. [124] modified the surface of chitosan (CS)/poly(ethyleneoxide) (PEO) mats by treating with glycidyltrimethyl ammonium chloride (GTMAC, C₂H₄ClNO) and N-benzyl-N,N,N-dimethyl ammonium iodide (QBr). Membrane modified with GTMAC was referred to as HTACC fibrous mats and the other one treated with QBr was referred to as QBrCS fibrous mat. It was reported that these membranes reduce the bacterial activities of Staphylococcus aureus and E. coli in the following sequence.

\[ \text{QBrCS} > \text{HTACC} > \text{CS/PEO} \]

Both bacteria were killed through surface sloughing, breaching and pore openings on the surface.

Wang et al. [125] fabricated PAN nanofibrous mat with graphene oxide (GO) (GO@PAN) for water treatment by nanofiltration. The membrane was highly porous and water-tolerant under an extremely low external pressure (1.0 bar) significantly increased and showed nearly 100 % rejection for Congo red, and 56.7 % for NaSO₄. Chauque et al. [126] modified the surface of electrospun PAN nanofibers with ethylenediaminetetraacetic acid (EDTA) and ethylenediamine (EDA) as cross linker. The modified PAN nanofibers showed efficient sorption of methyl orange (MO) and reactive red (RR) from aqueous synthetic samples. The maximum adsorption capacities for MO and RR at 25 °C were 99.15 and 110.0 mg g⁻¹, respectively. The fabricated nanofibers showed appreciable removal efficiency of the target dye sorptives from wastewater.

Hassan et al. [127] reported the use of Cu-terpyridine-modified oxidized cellulose nanofibers (OXCNF-Cu-Tpy) as membranes for treatment of effluents of paper mills to produce re-usable water. The OXCNF-Cu-Tpy was prepared by modifying copper (II)-complex of 4′-terpyridyl (Tpy) with TEMPO-oxidized cellulose nanofibers (OXCNF) using copper(II) complex of 4′-Chloro-(2,2′,6′,2′-terpyridine). Chemical modifications of OXCNF with the Tpy groups significantly increased pure water flux of the membranes by about 52 and 194 % depending on pressure used during filtration (0.5 and 1 Mpa, respectively). Although both OXCNF and OXCNF-Cu-Tpy exhibited high efficiency in removing the sub-micron size suspended particles from wastewater effluent, OXCNF-Cu-Tpy membranes showed lower % rejection for Congo red than OXCNF membranes. Gopal et al. [128] used PAN ENMs embedded with PVP and gentamicin to filter dam water and wastewater. Gentamicin in reduced turbidity, TSS, COD, and BOD to a significant level. These nanomembranes virtually reduced bacteria such as E. coli and total coliform bacteria to a significant level. On filtering the wastewater sample, pH, turbidity, TDS, TSS, BODs, phosphate, ammonia, oil-greases and dissolved oxygen (DO) were reduced by about 3.62%, 79%, 6.33%, 84%, 68%, 1.70, 15.8%, 0% and 6%, respectively.

Esfahani et al. [129] fabricated Nylon-6 composite nanofibrous (NFs) membranes via electrospinning with ceramic nanoparticles (NPs) and applied in protein separation systems. It was reported that positively charged zinc doped hydroxyapatite (xZH) NPs on the surface of electrospon Nylon-6 nanofibers created a positively charged surface and increased the separation and selection properties for adsorption of negatively charged protein, namely bovine serum albumin (BSA). The membrane decorated by NPs containing 4 at. % zinc cations not only provided maximum BSA separation but also was capable of separating higher amounts of BSA molecules than the pure Nylon membrane. The developed membrane showed a high efficiency for capturing BSA. Esfahani et al. [130] modified the surface of electrospon fibers with positively charged zinc doped hydroxyapatite (iHAP) nanoparticles. Effects of zinc amount within the atomic structure of HAp (nZH; n=0, 4, 8 at. %) were evaluated on produced scaffolds by measuring protein (BSA) adsorption. The adsorption of BSA on the modified surface increased. It was reported that the Langmuir equation was the best fit equilibrium model that described the adsorption of BSA on these membranes.

A large number of metal oxide nanoparticles, such as silicon, titanium, magnesium, aluminum, iron, zinc, and other mixed metal oxides, were successfully incorporated into polymer solutions to obtain organic–inorganic nanofibers [131]. Polymer nanofibrous membranes functionalized with TiO₂ nanoparticles were found to be promising for photodegradation of dissolved organic matter, humic acids and bacteria [132,133]. Faria et al. [134] fabricated the poly(lactide-co-glycolide) (PLGA)-chitosan mats. Then, the mats were decorated with silver-containing graphene oxide nanoparticles (GO-Ag) using a chemical reduction approach. The chemically reduced- and silver-containing GO-Ag functionalized the primary amine functional groups on the PLGA-chitosan fibers using 3-(dimethylamino)propyl'-N'-ethyldicyclopentadienyl hydrochloride and N- hydroxysuccinimide as cross-linking agents. From the performance study, it was reported that the resultant membrane was robust and had antimicrobial property.

Wang et al. [135] grafted monomers of 2-hydroxyethyl methacrylate (HEMA) and sodium acrylate (AAS) onto the surfaces of regenerated cellulose (RC) ENMs via atom transfer radical polymerization (ATRP). The ultrafiltration performance of surface-modified RC membranes was studied by using ~40 nm nanoparticles and ~10 nm BSA molecules. It was observed that HEMA-modified RC membrane could reject more than 95 % of the ~40 nm nanoparticles, while the AAS-modified RC membrane with low reaction degree could reject more than 90 % of the ~40 nm particles. On the other hand, the AAS-modified RC membrane could reject ~58 % of BSA, while the HEMA-modified RC membranes could not reject any BSA. It was suggested that these membranes could be utilized for water purification.

Almasan et al. [136] modified the surfaces of the webs fabricated from electrospun PAN nanofibers by three different sources of amine-containing compounds, including diethylamine, diethylenetriamine, and triethylenetetramine. From the different characterization techniques, it was revealed that amide group able to form the covalent chemical reaction between the nitrile groups of PAN and the amine groups of amine-containing compounds. It was reported that the functionalized PAN nanofibers could be used for anionic dye adsorption from colored wastewater with high dye adsorption capacity. In another publication, Almasan et al. [137] demonstrated that nanocomposites of zeolite using acrylic acid (AA) as monomer and ammonium persulfate (APS) as an initiator to remove cationic dyes (Basic Red 46 (BR46) and Basic Blue 41 (BB41)) from wastewater in
2.1 Developed membrane

alysts. Titania has high photocatalytic activity

TAC (recycled cellulose nanofiber) membranes for oil-water separation. GO nanofibers and TiO

13. Oil/water separation

The separation of oil from oil/water emulsion is a challenging and costly problem in several industrial sectors. Oil/water separation using electropun fibers is a relatively new but highly promising technique. Various techniques are used to modify the surfaces of ENMs for filtering [150]. Nanofiber can separate oil from water by sorption, particularly when the material in use has the oleophilic and hydrophobic surfaces. The major factor for the adsorption capability of a fibrous membrane is surface-to-volume ratio which can be adjusted by phase separation during electropinning process or by post treatment of the membrane.

Ao et al [151] fabricated a novel superhydrophobic graphene oxide (GO)@electrospun cellulose nanofiber (CNF) membrane which showed a high separation efficiency, excellent antifouling properties and a high flux for the gravity-driven oil/water separation. Superhydrophobic graphene oxide@electrospun cellulose nanofiber was prepared by immersing the electrospun cellulose nanofiber in a 0.01 wt.% GO aqueous suspension to load the PAN nanofibers with 1 wt.% of Nafion (NaF2SO4) layer onto the electrospun nylon 6/Silica (N6SiO2) nanofiber membrane (composite micro filtration (MF) membrane), through casting and then phase inversion techniques. The fabricated membrane was highly hydrophilic (water contact angle 21°) with both high porosity and mechanical strength. The fabricated membrane also showed a high water flux of 4814 Lm⁻²h⁻¹bar⁻¹ and almost 99 % oil rejection at oil concentrations of 250 mgL⁻¹, 500 mgL⁻¹ and 1000 mgL⁻¹ in the feed mixture.

Alayande et al [153] modified the non-beaded electrospun polystyrene (EPS) fibrous films by adding zeolite to the surface. Films were characterized using SEM, BET, FTIR and optical contact angle. The fibers exhibited superhydrophobic and superoleophilic wetting properties with water (>150°) and crude oil (0°). Addition of zeolite in the composite fiber increased the pore size, and thus enhanced penetration of oil into the composite fiber, causing the superoleophilic property of the film. This opens a new route of enhancing oil adsorption properties of polymeric material and re-use of abundant polymer wastes.

Makaremi et al [154] fabricated PAN ENMs reinforced with halloysite nanotubes (HNTs). The presence of HNTs improved the mechanical (tensile strength and elongation at break) and thermal properties of the membranes. Moreover, PAN/HNTs membranes showed excellent oil/water separation performance, and the oil rejection rate of 90% was obtained for oil/water separation while heavy metal ion adsorption remarkably increased up to 760 % when compared with the results obtained for the neat PAN ENM.

Lin et al [155] reported that nanoporous polystyrene (PS) fibers prepared via a one-step electrosprining process can be used as oil sorbents for oil spill cleanup. The oleophilic–hydophobic PS oil sorbent with highly porous structures showed a motor oil sorbent capacity of 113.87 g g⁻¹, approximately 3–4 times that of natural sorbents and nonwoven polypropylene fibrous mats. Lee et al [156] prepared membranes by single-step deposition of polystyrene (PS) nanofibers onto stainless steel mesh via electrosprining. The performance of the membrane indicated that it was well-controlled super-hydrophobic and superoleophilic properties. The contact angles of diesel and water on the prepared PS nanofiber membrane were 0° and 155°, respectively. The superoleophilic PS nanofiber membrane selectively absorbs oil, and is highly efficient at oil/water separation, making it a very promising material for oil spill remediation.

Naseem et al [157] successfully developed three-layered TiO₂/GO, and rTAC (recycled cellulose triacetate) asymmetric composite fiber membranes for oil-water separation. GO and TiO₂ were coated by an electrophoretic deposition method to introduce superhydrophilicity onto the recycled rTAC (rTAC) membrane to enhance water permeability. The developed membrane also showed antifouling and self-cleaning properties. The developed membrane which has both non-porous/porous rTAC nanofiber exhibited high oil rejection coefficients of 98.9% and 88.2% for the surfactant-free and surfactant-stabilized oil-water emulsions, respectively. Authors claimed the high potentiality of the developed membrane for its applications in removing emulsified oil, which would benefit the environment and human health.

Obaid et al [158] incorporated SiO₂ NPs and GO nanoflakes in the PSF
ENMs. The nanofibers were prepared by electrospinning of a colloid composed of PSF/DMF solution and either SiO$_2$ NPs and GO nanoflakes. It was reported by Obaid et al. that PSF–SiO$_2$ NPs ENM possesses high flux in petroleum fraction/water separation process. But, incorporation of GO has relatively small improvement in the PSF electrospun membrane separation performance.

4. Air filtration

Volatile organic compounds (VOCs) which can potentially affect human health are released from various sources and are unsafe for human health. VOCs are not only present in air but also the product of volatilization of building materials, paints, and other organic compounds. Gibson et al. [159] discussed the applications of ENMs in the field of air filtration. According to the report of World Health Organization (WHO), 91% of the world’s population live in places where air quality exceeds WHO guideline limits. About 4.2 million deaths occur every year as a result of exposure to ambient (outdoor) air pollution and 3.8 million deaths are recorded every year as a result of household exposure to smoke from dirty cook stoves and fuels [160]. Electrospun nanofibers have been explored for the adsorption of volatile organic compounds (VOC) present in the air by various authors [161]. Nanotechnology field is booming in an exceptionally impressive manner in air filtration. Balamurugan et al. [32] discussed the modern concepts and current research progress on various nanofibrous membranes for air filtration media. Particle removal from air by a nanofiber membrane has been studied by Gibson et al. [161]. It was observed that, using extremely efficient membranes (100% rejection) of airborne particles with diameters between 1 μm and 5 μm was possible by both physical trapping and adsorption via nanofiber membrane. Nanofiber mats are now used in numerous air filtration applications, either on their own or in combination with other filtration media. The high-efficiency particulate air-filter (HEPA) is widely used throughout the world to protect people from a variety of noxious gases or aerosol transmissible diseases.

Scholten et al. [162] reported that adsorption and desorption of VOC by ENMs were faster than conventional activated carbon. Activated carbon and fiberglass are widely used in air filtration industry. The application of the HEPA has been concentrating on high performance masks to prevent inhaling large quantities of particulate matters (PMs) and fine harmful particles during outdoor activities. Ahn et al. [163] have studied the filtration efficiency of nylon-6 nanofibrous membranes, which is better than the commercialized HEPA. One of the drawbacks is that they observed high pressure drop across the membrane.

Chitosan is a green and degradable material and widely used as electrospinning material to fabricate ENMs [164]. Desai et al. [165] fabricated nanofibrous filter media to achieve both air and water filtration properties by electrospinning chitosan/PEO blend solutions onto a spunbonded nonwoven polypropylene substrate. Zhu et al. [166] reported an environmentally friendly and easy method to prepare the composite membranes via green electrospinning assisted by thermal cross-linking. Nanofiber membrane fabricated from protein–based green soy has the potential for the removal of Escherichia coli bacteria during air filtration [167]. Souzandeh et al. [168] demonstrated the potentiality of natural protein to serve as environmentally friendly and high-performance air-filtering materials. They demonstrated that gelatin nanofiber mats can efficiently remove a broad range of PM (particle matter) similar to HEAP, but also achieve excellent absorption efficiency of toxic chemicals (e.g., 76% for CO$_2$; 80% for HCHO).

Patil et al. [169] developed an activated carbon (AC) impregnated cellulose acetate electrospray nanofiber mat for the adsorption of VOCs from the air mixture. The adsorption capacities were measured for acetone, benzene and dichloromethane. It was reported that adsorption capacity increased with the increase in AC. Dichloromethane exhibited in faster adsorption than acetone and benzene owing to its smaller molecular size. VOCs were desorbed with the N$_2$ gas purging, while VOCs were adsorbed at higher temperatures owing to the increased vapor pressures. Kim et al. [170] modified the surfaces of electrospray polyacrylonitrile nanofibers (PENFs) by oxygen plasma treatment and thus generated functional groups such as CONH$_2$, COOH and -COOR on the surface. The membranes were used as air purifiers and it was reported that the modified surface was very effective for air filtration (particulate matter ≤2.5 μm) with removal 94.02% and pressure drop 18 Pa. Jo and Kang [171] prepared PAN–TiO$_2$ fibers with different PAN to TiO$_2$ ratios, using PAN as a carbon source. N, N-dimethyl formamide as a solvent, and TiO$_2$ as a photo catalyst. The mixture was heated at 110 °C for 1 h. and then fibers were made by electrospinning. These fibers were used for the photocatalytic decomposition of airborne aromatic compounds (BTX).

5. Inorganic electrosprun nanofibers membranes

Not many works have been done on the application of electrosprun inorganic nanofibers in membrane technology even though inorganic nanofibers can be fabricated by electrosprinning of the precursor solution.

Singh et al. [172] fabricated ZnO nanofiber by electrosprinning of PAN and zinc acetate solution followed by sintering to obtain pure ZnO nanofiber. The photocatalytic performance of ZnO nanofibers was highly effective in the photocatalytic degradation of the PAH dyes-naphthalene and anthracene. Nanofiber mats fabricated were also applicable in gas sensing, piezoelectric devices, optoelectronics and photocatalysis.

Chen et al. [173] fabricated self-standing electrospray ceramic nanofiber mats and employed them as a novel support for zeolite membranes. The nanofiber membrane was prepared by electrosprining a halloysite nanotubes/PVP composite followed by a programmed sintering process. The final interwoven nanofiber mats possessed up to 80% porosity, narrow pore size distribution, low pore tortuosity and highly interconnected pore structure. The successful seeding on the halloysite nanotube-based mats (HNMs) supports contributes to the continuous zeolite membrane formation after secondary growth, which needs less repetitive synthesis steps.

Zhao et al. [174] fabricated flexible fluorinated silica nanofibrous membranes with biomimetic non-wettable surfaces by electrosprining blend solutions of PVA and silica gel in the presence of silica nanoparticles, followed by calcination (800 °C) and fluorooalkylsilane (FAS) modification. It was found that the silica nanoparticles incorporated into the fibers were the key factor affecting the fiber surface morphology and wettability. 38.8 ± 0.7% silane-coated nanofibrous membranes showed the highest water contact angle (WCA) of 143°, oil contact angle (OCA) of 143°, orange juice contact angle (OJCA) of 142°, and milk contact angle (MCA) of 137°.

Lin et al. [175] fabricated photo-catalytically active Ag–ZnO composite nanofibers via electrosprining process, and then heated to remove the PVP and to convert silver nitrate to silver nanoparticles. The heterostructure of the membranes promote the photocatalytic activity of the photogenerated electrons (e$^-$) and holes (h$^+$), allowing both of the e$^-$ and h$^+$ to participate in the overall photocatalytic reaction. It was reported that the optimal photocatalytic activity of Ag–ZnO nanofibers was exceeded that of pure ZnO nanofibers by a factor of 25 when the Ag concentration was kept at 7.5 atom %. It was suggested that exploring the catalytic activity of such composite structures may pave the way for designing useful nanoscale building blocks for photocatalytic and photo voltaic applications.

Fluorinated electrosprun inorganic fibrous mats such as ZnO, TiO$_2$ ceramic, Fe$_2$O$_3$-filled carbon etc., exhibited superhydrophobicity but the brittleness of inorganic fibrous mats significantly limits their practical applications. Guo et al. [176] reported that the surface property i.e. wettability of electrosprun inorganic silica nanofiber (amphiphilic to amphiphobic) can be changed via coating fluoroalkyl silane (FAS) on the surface. They have, for the first time, fabricated inorganic nanofibrous mats with flexible, high-resistive, and amphiphilic surface through functionalization and surface modification techniques. The inorganic silica nanofibrous mats were obtained via electrosprining the blend solutions of PVA and silica gel, followed by calcination to remove the organic component. The fluorinated mat with the bead-on-string structure (BBS) showed the highest water contact angle (WCA) of 154° and oil contact angle (OCA) of 144°. Moreover, the fluorinated inorganic fibrous mats (FiFs) exhibited a high heat resistance; they kept their hydrophobicity (WCA of 138°) and oleophobicity (OCA of 132°) even after the annealing treatment at 450 °C. It was suggested that these membranes have potential applications for high-temperature filtration, selective filtration, and self-cleaning coatings.

Doh et al. [177] developed photocatalytically active electrosprun TiO$_2$ nanofibers for the treatment of organic pollutants (three kinds of dye: basic blue 26, basic green 4 and basic violet 4). The surface of the nanofiber was modified by coating TiO$_2$ particles by sol-gel method. On coating, photocatalytic activity and effective surface area increased. The degradation rate (k$^+$ = 85.4 × 10$^{-4}$ min$^{-1}$) of dye pollutants from composite TiO$_2$ was significantly higher than that (15.7×10$^{-4}$ min$^{-1}$) of TiO$_2$ nanofibers and that (14.3×10$^{-4}$ min$^{-1}$) of TiO$_2$ nanofibers made by the sol–gel method. It was suggested that the composite TiO$_2$ of nanofibers and nanoparticles be suitable for the degradation of organic pollutants.
for the decomposition of methylene blue than the reference titania powder. The presence of silica enhanced the photocatalytic activity of the titania fibers considerably. It was suggested that TiO₂ nanofibers and nanoparticles be suitable for the degradation of organic pollutants.

Wu et al. [179] reported the fabrication of a hydrophobic ceramic nanostructured membranes without any surface modification through pyrolysis of electrosprun polycarbolamine (PCS) nanofibers. The non-Pd nanofibers were prepared by electrosprinning a mixture of PCS, polystyrene (PS) and sodiumdodecylsulfate (SDS) in xylene and DMF followed by pyrolyzation of the nanofibers at 1100 °C in Ar atmosphere resulting SiOC nanofibrous membranes (denoted as SiOC). Pd containing ENFs were prepared in a similar way, but adding palladium acetylatone (Pd(acac)₃) in the spinning solution. The addition of palladium resulted in the formation of SiC and SiO₂C phases instead of SiO₂ and free carbon, transforming the hydrophilic SiOC membrane to a hydrophobic material. The characterization of membranes was done after dipping it in 6 M KOH or 1 M H₂SO₄ at 80 °C for 36 h. The SiO₂-xPd membrane (mats) showed robust mechanical properties with consistent hydrophobicity over the entire pH range and high temperature. Further, the SiO₂-xPd membranes were very effective to separate oil (paraffin) from water emulsion.

Ding et al. [180] fabricated super-hydrophobic ZnO (zinc oxide) nanofibers via combination of wet chemical and electrosprining techniques. The produced ZnO nanofibers were coated with fluorooalkyl silane (FAS). The FAS modified ZnO films showed super hydrophobic (water contact angle) WCA of 165°, as compared with 0° of the unmodified ZnO nanofibers. Formo et al. [181, 182] demonstrated a simple polyol method for depositing Pt, Pd, and Rh nanoparticles or nanowires of different sizes on nonwoven mats of TiO₂ and ZrO₂. The nanofiber mats functionalized with Pt nanoparticles exhibited an excellent catalytic activity for a number of reactions, such as the hydrogenation of azo bonds in methyl red [183].

6. Future aspects

Nanofibers are fibers with diameters in the nanometer range. Nanofibers can be made from different polymers and hence have different physical properties and application potentials. Among many methods, electrosprinning is most commonly used to fabricate nanofibers since it is cost effective and it enables the production of a long and continuous nanofiber mat. However, it has also the disadvantage of jet instability. With their controllable small diameter, porous structure, high surface area to volume ratio, good internal connectivity, controllable morphology and excellent mechanical strength, ENMs have a great future in the area of air filtration industry, water treatment, gas separation, health care, biotechnology, environmental engineering, separation of chemicals and so forth. The electrospun nanofibers have also a great future in the areas of nanofiltration, membrane distillation, geothermal water desalination and capacitive deionization applications. Indeed, nanofiber membranes are already widely applied for communal water treatment and production of potable water, waste water treatment and water recycling. More electros spun nanofiber membranes will be newly developed to be used in various fields of research and industries, similar to the membranes based on carbon nanotubes and other materials. As well, various modification and post treatment methods will be applied such as heat treatment, grafting, coating etc. to improve the performance of ENMs.

Attention is currently focused on fabrication of filler incorporated electrosprun nanofiber membranes. At present, TiO₂, Ag nanoparticles, nano zeolites are used most often as the fillers. In the future, incorporation of noble metals (Pd, Pt, Ir etc) should be attempted. Currently, gas separation by the nanofiber membranes is focused on the separation of CO₂, O₂, N₂ and CH₄ gases and no works have been done on SO₂ separation from industrial by-product gases. In the future, research scientist should give more attention on this important subject.

7. Summary

Although the electrosprun nanofibers have been known for a long time, the application of ENMs for separation membranes started only in the beginning of the millennium. The early researches were rather limited to the pressure driven membrane separation processes such as microfiltration, ultrafiltration and nanofiltration. But the scope of the applications has been considerably broadened during the last decade or two. Currently, ENMs are applied not only for the pressure driven processes but also for other membrane separation processes including forward osmosis, pressure retarded osmosis, membrane distillation, membrane adsorption, membrane contactor and photocatalytic membrane reactor.

The development of the membranes for such a variety of separation processes has been enabled by the ENMs modification strategies such as heat treatment, surface grafting, dip coating, in-situ polymerization, addition of functional groups as the adsorption site, incorporation of fillers for the fabrication of mixed matrix membranes (MMM).

It is expected many other modification strategies will be investigated in the future to broaden the scope of applications even more.

Some of the uninvestigated topics are the development of well aligned ENMs and their applications, the development of core-shell ENMs and their applications, the development of multilayer ENMs with hydrophilicity/hydrophobicity and pore size gradients, and ENMs used as fillers in mixed matrix membranes (MMMs).

The commercial applications of ENMs have been limited to air filtration for a long time but commercialization for water treatment has begun recently in various countries.

Table 2 shows the summary of the modified electrosprun nanofiber membranes used in different fields related to membrane separation processes. However, this is not the end. Though NFMs opened a new avenue for the membrane processes, it is still in an early stage. There are many challenges to develop NFMs for different uses.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Modification with</th>
<th>Results/used for</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN</td>
<td>WO₃</td>
<td>Removal/recovery of trace amounts of metal ions (ppb level) from water.</td>
<td>[78]</td>
</tr>
<tr>
<td>PAN/CA</td>
<td>Hydrolysis and amidoximation</td>
<td>Saturation adsorption amount of 7.47, 4.26 and 1.13 mmol g⁻¹, respectively (at 25°C), for Fe(III), Cu(II) and Cd(II)</td>
<td>[80]</td>
</tr>
<tr>
<td>CS/PVA</td>
<td>Zeolite</td>
<td>Adsorption of Cr⁶⁺, Fe⁺⁺ and Ni²⁺.</td>
<td>[81]</td>
</tr>
<tr>
<td>PEI/PVA</td>
<td>Pd nanoparticle immobilized</td>
<td>Reduced Cr(VI) to Cr(III)</td>
<td>[82]</td>
</tr>
<tr>
<td>SF and WK</td>
<td>Blending together to make ENF</td>
<td>Markedly improve Cu²⁺ adsorption</td>
<td>[83]</td>
</tr>
<tr>
<td>PAN</td>
<td>Coating EDTA in presence of tetrahydrofuran</td>
<td>Removal of Cd(II) capacity 32.68 mg g⁻¹ and Cr(VI) max capacity 66.24 mg g⁻¹ at 298 K</td>
<td>[84]</td>
</tr>
<tr>
<td>PAN-nFs</td>
<td>Grafting amine groups</td>
<td>Adsorption of metal ions</td>
<td>[85]</td>
</tr>
<tr>
<td>PVA</td>
<td>Hydroxyl group on PVA with the carboxyl group of 3-mercaptopropionic acid</td>
<td>Adsorption of silver ions from the aqueous solution</td>
<td>[87]</td>
</tr>
<tr>
<td></td>
<td>poly(5-cyanoindole)</td>
<td>Hydroxylamine</td>
<td>[88]</td>
</tr>
<tr>
<td></td>
<td>Cellulose</td>
<td>Thiol-modified chromium (VI) and lead (II) adsorption</td>
<td>[89]</td>
</tr>
<tr>
<td></td>
<td>PVA/ PANI-nylon core-shell</td>
<td>DETA</td>
<td>Filtration-adsorption membrane. Separation of Pb (II) and Cd(II).</td>
</tr>
<tr>
<td>PES</td>
<td>ZrO₂</td>
<td>Efficient filtration process</td>
<td>[67]</td>
</tr>
<tr>
<td>PAA</td>
<td>Thermal cross linking with PVA</td>
<td>Removing Ca(II) ions from water.</td>
<td>[91]</td>
</tr>
<tr>
<td>Chitosan</td>
<td>Coated with TiO₂</td>
<td>Removal of Pb (II) and Cu (II)</td>
<td>[92]</td>
</tr>
<tr>
<td>CS</td>
<td>Ag NPs</td>
<td>Antibacterial property including dye adsorption.</td>
<td>[99]</td>
</tr>
<tr>
<td>PVA</td>
<td>NaX</td>
<td>Adsorption of Ni²⁺ and Cd²⁺</td>
<td>[100]</td>
</tr>
<tr>
<td>Membrane distillation</td>
<td>PVDF-HFP</td>
<td>FAS followed by crosslinking to form a network upon dealcoholization under thermal treatment</td>
<td>Less reduction in permeability and increase in salt rejection in the long term operation.</td>
</tr>
<tr>
<td>----------------------</td>
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<td>---------------------------------------------------------------------------------</td>
<td>---------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Polyurethane</td>
<td>Varying thickness</td>
<td>Highest flux thinner membranes. Best energy efficiency thicker membranes</td>
<td></td>
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<tr>
<td>PVDF</td>
<td>Specially designed for DCMD heat treated</td>
<td>Rough surface with high hydrophobicity</td>
<td>Steady water permeation flux.</td>
</tr>
<tr>
<td>PVDF</td>
<td>Specially designed for DCMD heat treated</td>
<td>Si NPs (dual layer membrane)</td>
<td>Super hydrophobic</td>
</tr>
<tr>
<td>PVDF/PSf</td>
<td>Dual layer structure (DL-ENMs). Single layer structure (SL-ENMs).</td>
<td>DCMD permeate flux of the DL-ENMs &gt; PVDF and PSF SL-ENMs.</td>
<td></td>
</tr>
<tr>
<td>PVDF-HFP</td>
<td>Coated with PVDF Particles</td>
<td>Robust. Complete salt rejection</td>
<td></td>
</tr>
<tr>
<td>PVDF/HFP</td>
<td>Heat treatment</td>
<td>Using DCMD. Permeation and salt rejection performance.</td>
<td></td>
</tr>
<tr>
<td>PVDF (omniphobic)</td>
<td>CF₂ plasma treatment</td>
<td>AGMD was used. Highest water vapor flux</td>
<td></td>
</tr>
<tr>
<td>PVDF</td>
<td>CNTs</td>
<td>VMD. Enhanced hydrophobicity and liquid entry pressure. Superior performance both in anti-wetting and water flux.</td>
<td></td>
</tr>
<tr>
<td>PVDF-HFP</td>
<td>Functionalised CNTs</td>
<td>Vapor transport. Increased surface roughness, WCA and hydrophobicity when compared with the data obtained with non functionalized PVDF-HFP (E-PH).</td>
<td></td>
</tr>
<tr>
<td>PVDF-N-HFMs</td>
<td>Solvent-vapor welding post-treatment.</td>
<td>High flux of 13.2LM−2 h−1 and stable salt rejection more than 99.9% during the 5th of test</td>
<td></td>
</tr>
<tr>
<td>PVDF</td>
<td>SiO₂</td>
<td>VMD. Superhydrophobic</td>
<td></td>
</tr>
<tr>
<td>PVA</td>
<td>FAS (fluoroalkylsilane).</td>
<td>VMD. Superhydrophobic. Maintenance of a stable flux of about 31.5 kg m⁻² h⁻¹</td>
<td></td>
</tr>
<tr>
<td>PVDF</td>
<td>TiO₂ followed by fluoroosilization of the surface with FTCS</td>
<td>DCMD. Permeate conductivity increased sharply. WCA 163° ± 3°. Mechanically and thermally robust and photoactive.</td>
<td></td>
</tr>
<tr>
<td>PVDF</td>
<td>PDMS- hydrophobic SiO₂ NPs.</td>
<td>DCMD. Permeate flux of the modified membrane slightly decreased with the NaCl rejection &gt; 99.99 %.</td>
<td></td>
</tr>
<tr>
<td>Water treatment</td>
<td>CH/PEO mats</td>
<td>GTMAC and QBz</td>
<td>Reduce the bacterial activities of Staphylococcus aureus</td>
</tr>
</tbody>
</table>
PSF

Silica NPs and GO nanoflakes

Air filtration

CA

AC

Adsorption of acetone, benzene, dichloromethane.

Polyacrylonitrile

Oxygen plasma treatment

Very effective air filtration (particulate matter <2.5 μm) with removal 94.02%.

PAN-

TiO₂

Photocatalytic decomposition of airborne aromatic compounds (BTXAC).

Inorganic electrospun nanofiber membranes

ZnO

Fabricated ZnO nanofiber by electrospinning of polyacrylonitrile and zinc acetate solution, followed by sintering to obtain pure ZnO nanofiber.

Photocatalytic degradation of the PAH dyes-naphthalene and anthracene.

Halloysite nanotubes/polyvinyl pyrrolidone

Programmed sintering process, (Zeolite as support)

80% porosity, narrow pore size distribution, low pore tortuosity and highly interconnected pore structure.

Fluorinated silica

FAS modification

Exhibited biomimetic superhydrophobicity and highly flexible properties.

TiO₂ ENFs

TiO₂ NPTs on the surface

Photocatalytic activity increased for degradation of dye pollutants.

ZnO

Ag NPTs

Incorporated

Optimal photocatalytic activity of Ag-ZnO nanofibers was by a factor of 25 times more than that of pure ZnO nanofibers when the Ag concentration 7.5%.

ZnO

Coating FAS

Super hydrophobic.

WCA of 165°

Silica

Coating FAS on the surface

High-heat-resistant, and amphiphilic properties.

Titania NPs

Silica

Better activity for the decomposition of MB than the reference titania powder.

SiOCl

Pd (SiO₂-xPd)

Robust mechanical properties. Very effective to separate oil (water emulsion.

TiO₂

Pt NPTs

Catalytic applications

References


[29] C.Y. Foong, N. Sultana, Fabrication of layer-by-layer electrospun composite membranes based on poly(lactic acid (PLA) and poly(caprolactone (PCL)/chitosan, ARPN JEAS 10 (2015) 9408-9412.


[65] P.K. Neghlan, M. Rafizadeh, F.A. Taromi, Preparation of amminated-


147. J. Gelmeyer, H. Texudo, M. Metre, T.V. Acker, K. Deventer, F. vanhaecke, S.S. Yoon, Electrospun polystyrene fibers for oil spill cleanup


