



Review Paper

The Advances of Electrospun Nanofibers in Membrane Technology

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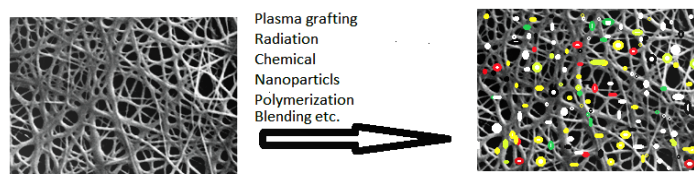
Highlights

- 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.

Graphical abstract



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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, or core–sheath structure. Beside this, the surface (outer/interior) can be modified/functionalized with molecular species or nanoparticles during or after an electrospinning process. In 2013, Nasreen 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. Nanofibers are fibers with diameters in the nano-meter 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 with relatively high pressure could even reject 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 $\cdot\text{L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}\cdot\text{psi}^{-1}$, 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 to consider using this material in several fields. Electrospun nanofibers have great potential as promising reinforcement fillers for next-generation polymer composites [6]. Tijng 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 to 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.

Nonwoven 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 $<0.2 \mu\text{m}$. 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 calcined, 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) *Ultrahigh vacuum CVD (UHVCVD)*—CVD at very low pressure, typically below 10^{-6} Pa ($\approx 10^{-8}$ torr). Note that in other fields, a lower division between high and ultra-high vacuum is common, often 10^{-7} 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 [17] 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.

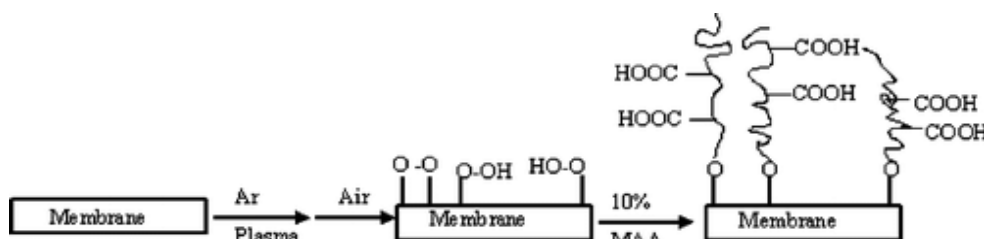


Fig. 1. Proposed mechanism of plasma induced graft polymerization on the surface of a membrane [13].

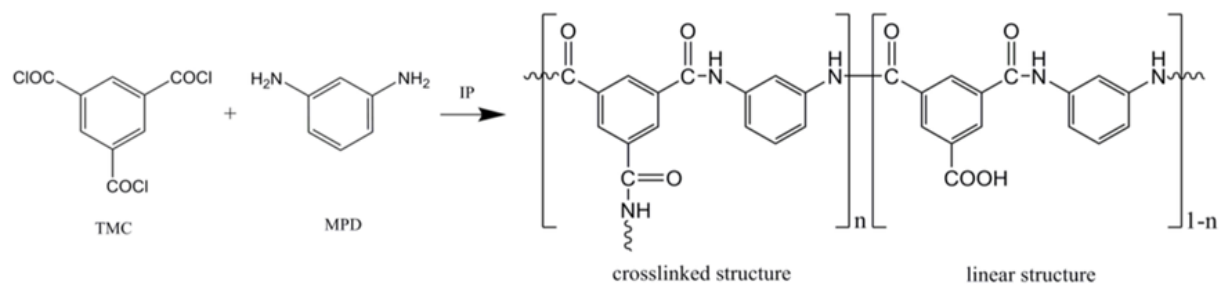


Fig. 2. IP between TMC and MPD [17].

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 electrospun membranes, which can affect the membrane flux and membrane fouling potential. While hydrophilic membranes show 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 by organic 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 electrospun membranes surface exhibited a rough surface with high hydrophobicity ($>135^\circ$ water contact angle). Liao et al. [22] developed a super hydrophobic membrane containing silica-PVDF composite selective skin on a polyvinylidene 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 a unique dual-layer composite membrane consisting of a superhydrophobic selective skin of amorphous polypropylene (aPP) and an electrospun poly(vinylidene fluoride) nanofibrous support. The superhydrophobic aPP porous skin acted as an additional barrier to surface wetting. Membrane exhibited an ultrahigh permeate vapor flux of $53.1 \text{ kg m}^{-2} \text{ h}^{-1}$ 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 nano fibrous 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 polyacrylonitrile (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 property. Zhang et al. [28] prepared ENMs consisting of polyvinylidene 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 polycaprolactone (PCL)/chitosan electrospun composite membranes based on polylactic 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 3.

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.

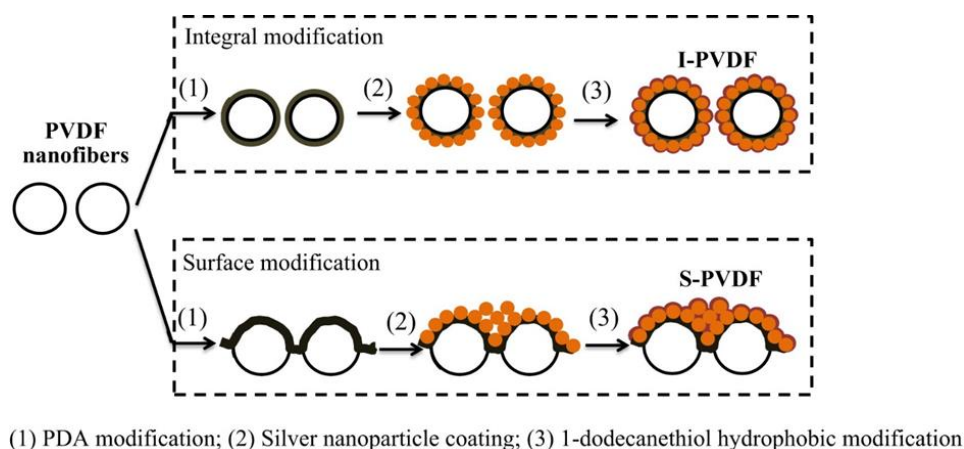


Fig. 3. Schematic diagram of preparing superhydrophobic PVDF nanofiber membranes by silver nanoparticle and 1-dodecanethiol hydrophobic modification [23].

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 hydrophilic 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 substrate 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 electrospun 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 electrospun PVDF fiber to make it hydrophilic and fully wettable via the interfacial polymerization of 1,6-hexane diamine 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, H_2 , O_2 and N_2 were used as the reactive gasses to make the membrane hydrophilic and sulphur hexafluoride (SF_6) 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 $25\,000\text{ L m}^{-2}\text{ h bar}^{-1}$ was achieved with Ar plasma exposure followed by NaOH modification.

Bao et al. [38] applied oxygen plasma etching at the surface of the electrospun nanofibers of poly(methyl 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) membrane by coating polyamide (PA) thin layer over electrospun 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)- Al_2O_3 nanofiber membrane by electrospinning of the PSf solution blended with different ratios of PEI and Al_2O_3 nanoparticles and the membrane was used as water based membrane filtration. On addition of PEI and Al_2O_3 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 electrospun polycaprolactone (PCL) fibers.

Kiani et al. [42] fabricated novel hydrophilic polyphenylsulfone (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 electrospun nanofibrous PEG-PPSU blend support. The PWF (Pure water flux (L/m^2h)) 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 morphological 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 $35\text{ L m}^{-2}\text{ h}^{-1}$ (>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 $87\text{ }^\circ\text{C}$ 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, 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 $7323 \text{ L m}^{-2} \text{ h}^{-1}$ 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-hydroxyethyl 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 polyacrylic acid (PAA) on an electrospun polyacrylonitrile (PAN) nanofibrous mat by layer-by-layer (LbL) assembly. Nanofiber membranes modified with 15 bilayers of BPEI/PAA multilayers had a pure water flux of $19.7 \text{ L m}^{-2} \text{ h}^{-1}$ and an MgSO_4 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 membranes.

Zeytuncu et al. [53] fabricated the polyvinyl alcoholic (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_2 hybrid nanofibers, while imidazole-functionalized PVA/ SiO_2 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 NPTs) were in situ synthesized from silver nitrate precursor directly. It was reported that introduction of Ag NPTs and GO into PVDF membranes showed the improvement in membrane wetting, tensile strength and elastic modulus, water permeability, antifouling property, and antibacterial resistance.

Demirci et al. [55] described a facile and robust method by which surface of electrospun cellulose acetate (CA) nanofibers can be chemically modified with cationic polymer brushes for DNA adsorption. They fabricated a poly(arvinylbenzyl)trimethylammoniumchloride [poly(VBTAC)] grafted cellulose acetate (poly(VBTAC)-g-CA) nanofiber by combination of electrospinning 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.

Peresin 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 electrospun 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 adsorption. 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^{-1} . The chemically-modified CS-nylon nanofiber membrane with the CB as ligand could become the low-cost but high efficiency affinity membranes for papain separation. Xu et al. [59] prepared three hydrophobic and polyporous electrospun fibrous membranes (EFMs) from methoxy polyethylene glycol-poly(lactide-co-glycolide) (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^{-1} , respectively.

Mahanta and Valiyaveett [60] chemically modified PVA nanofibers with functional groups such as thiols 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, hydrophilic) mat by electrospun nanofibers of PSf-SDS (sodium dodecyl sulfate). The surface-modified dual-layer PSf-SDS/CFP membrane exhibited membrane distillation flux of $9 \text{ L m}^{-2} \text{ h}^{-1}$ and more than 99 % salt rejection for 16 h. Heintze 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-grafted PET nanofibers via grafting the PET electrospun 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 PSf 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 PSf ENMs.

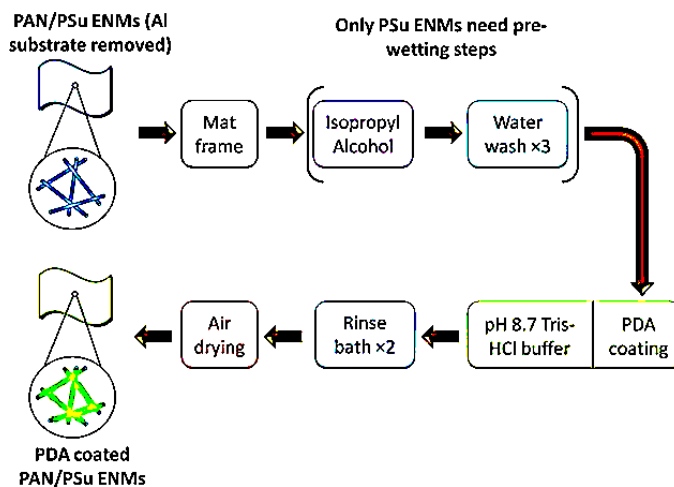


Fig. 4. Process for PDA coating both the PAN and PSf ENMs [64].

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 electrospun 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, Homaieghar et al. [65] reinforced PES electrospun nanofibrous membranes with zirconia nanoparticles. The ZrO_2 /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 electrospun nanofibers (ENFs) showed more efficient filtration performance as compared to the neat PES membrane (mechanical strength).

Cellulose nano whiskers have been used as reinforcing materials for electrospun fibers such as polystyrene, PVA, PLA, and so on [66]. Dai et al. [66] studied electrospun PVA/WPU (waterborne polyurethane) nanofibers into which TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl radical)-oxidized cellulose nanofibers (TOCNs) 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, Homaigohar 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 TiO₂ and other metal oxides and how the specific precursor chemistry affects the resulting mechanical response of modified fiber mat structures. Aluminum oxide (Al₂O₃), zinc oxide (ZnO), and titanium dioxide (TiO₂) 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 (TiCl₄) or titanium isopropoxide was used for titanium dioxide coating. On characterization (physical) it was revealed that the TiCl₄ diffused into the nylon-6 and reacted with the subsurface, whereas the titanium isopropoxide tended to 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 dipping the electrospun nanofibers into the PVDF dispersion of different concentrations to incorporate PVDF particles among PAN nanofibers matrix, followed by heat treatment at 177°C. The fused PVDF cemented the strings and welded the junctions, which resulted in strengthening the fibers and enhancing its bonding together. It was reported that the average increase in Young's modulus and tensile strength in the PVDF-c-PAN membranes were 19.8 and 6.63 folds, respectively

Kayaci et al. [70] modified the electrospun polyethyleneterephthalate (PET) nanofibers with cyclodextrin polymer (CDP). To form CDP, three different types of native CD (α -CD, β -CD and γ -CD) were used. On testing the CDP/PET nanofibers via dynamic mechanical analyzer (DMA), it was revealed that CDP/PET had higher storage modulus and higher glass transition temperature compared to untreated PET nanofibers. Thus, PET/CDP nanofibers have shown enhanced mechanical and thermal properties. Kiyomarsioskouei et al. [71] showed that the mechanical strength of the poly (dimethylsiloxane) (PDMS) fibers electrospun 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 (CA<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.

Safarik 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 nano composite (TFNC) showed a good rejection of MgCl₂ and MgSO₄, 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 (AgNO₃), silver benzoate (C₇H₅AgO₂), and silver behenate (C₂₂H₄₃AgO₂). 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 fusion of inter-fiber junction points. The 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 electrospinning 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 WO₃ (a-WO₃)/polymer nanofiber membranes (NFM) can be reduced by solar light irradiation. The metal deposition on the NFMs is an electroreduction/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. Polyacrylonitrile (PAN) was found to be an ideal polymer matrix since it is hydrophobic and easy to fabricate NFMs by electrospinning.

Pereao et al. [79] discussed increasing use of electrospun nanofibers for 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. 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 polyacrylonitrile/cellulose acetate (PAN/CA) composite nanofibrous membranes, and then modified them by hydrolysis and amidoximation. The resulted membrane was called as amidoxime polyacrylonitrile/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)). Ki 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 electrospinnability and structural stability of WK/SF blend membrane was markedly improved and the WK/SF nanofibrous membrane exhibited higher Cu^{2+} adsorption capacity ($2.88 \mu\text{g mg}^{-1}$) than SF nanofibrous membrane ($1.65 \mu\text{g mg}^{-1}$).

Chauque et al. [84] modified the surface of electrospun aminated EDA (ethylenediamine)-PAN nanofibers, by coating EDTA (polyethylenediaminetetraacetic acid) in presence of tetrahydrofuran. EDA was used as a cross-linker. The modified nanofibers (EDTA-EDA-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.

Neghlani et al. [85] modified polyacrylonitrile nanofibers (PAN-nFs) by grafting amine groups on nanofiber. Diethylenetriamine was used to produce aminated polyacrylonitrile (APAN) nanofibers. The adsorption capacity for Cu(II) was $116.522 \text{ mg g}^{-1}$ which was five times more than the reported 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 (SAMPI) nanofiber membrane, was used for the removal of Cr(VI) from aqueous solution via adsorption. The maximum adsorption capacities (Q_m) 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 SAMPI nanofiber membrane might have potential applications in wastewater treatment for removal of Cr(VI).

Yang et al. [89] grafted oxidized cellulose nanofibers (thiol-modified cellulose nanofibers, 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 revealed 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 ($0.9 \text{ mmol of } -\text{SH/gram m-CNF}$). 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 separation 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. Rejection 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 polyacrylic 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 Ca(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 Figure 4.

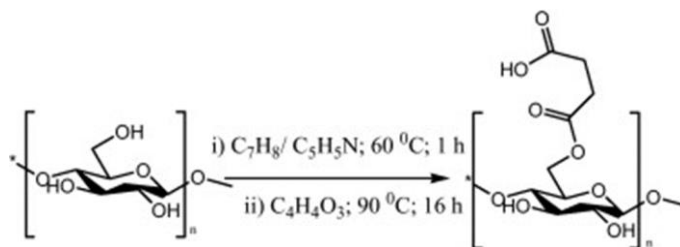


Fig. 4. Reaction scheme for the functionalization of cellulose to cellulose-g-oxolane-2,5-dione [93].

The surface area of modified nanofibers was $13.68 \text{ m}^2 \text{ g}^{-1}$, while it was $3.22 \text{ m}^2 \text{ g}^{-1}$ 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 1

Adsorption capacity of Pb, Cd on different adsorbents [93].

Sorbent	Pb ²⁺ mmolg ⁻¹	Cd ²⁺ mmolg ⁻¹	Reference
Amberlite 200	1.22	2.0	[94]
Duolite GT-73	0.59	0.94	[94]
Activated carbon	0.002	0.003	[96] [95]
Resin (Dowex 50W)	2.05	2.4	[97]
Cellulose-g-oxolane-2,5-dione	1.0	2.91	[93]

Park et al. [98] modified the surface by acid treatment to attach oxygen containing unfunctional 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 nanozeolite for blending with polyvinyl alcohol (PVA) solution to form electrospun PVA/zeolite nanofibers for the adsorption of Ni²⁺ and Cd²⁺ ions. The maximum monolayer sorption capacities of Ni²⁺ and Cd²⁺ 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 carboxylate 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 frequent pore wetting due to low hydrophobicity [105]. 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-cohexafluoropropylene (PVDF-HFP) ENMs with anti-wetting property. Their approach was to fluorinate PVDF-HFP fibers by using 1H,1H,2H,2H-perfluorodecyltriethoxysilane (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 in the long term operation. Jiříček 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 whereas another was fabricated by electrospinning 3D superhydrophobic layers on a nonwoven support. These membranes exhibited superhydrophobicity toward distilled water, salty water, oil-in-water emulsion, and beverages, which enables them to be used not only for desalination but also for other processes. The superhydrophobic dual-layer membrane with nanofibrous support has a very significant permeation flux of 24.6 ± 1.2 kg m⁻² h⁻¹ in MD due to the higher porosity of the nanofibrous scaffold.

Khayet et al. [108] prepared dual-layered electrospun nanofibrous membranes (DL-ENMs) using hydrophobic polyvinylidene fluoride (PVDF) and hydrophilic polysulfone (PSf) 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 electrospinning time of each polymer solution. The DCMD permeate flux of the DL-ENMs was found to be higher than that of the PVDF and PSf 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 electrospun fiber mat. Highly porous electrospun fiber mat with an average pore diameter of ~1.2 μm was obtained from poly (vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) in a mixture of acetone and dimethylacetamide. PVDF was coated on the surface via phase separation to control of 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 L m⁻² h⁻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 electrospun 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 electrospinning, with CF₄ plasma treatment without significantly altering the morphology and its physical properties. The membrane performance was evaluated using real reverse osmosis brine produced from coal seam gas (CSG) water as feed solution via air gap membrane distillation (AGMD). Plasma treatment lowered its surface energy and gave omniphobic property to the membrane. AGMD performance showed stable normalized flux. The highest water vapor flux observed for P/CF-15 (15-min plasma treatment) ENF membrane was 15.3±0.8 L m⁻² h⁻¹ (neat nanofiber 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 electrospun PVDF-HFP membranes. It was observed that functionalization of the membranes increased their surface roughness, water contact angles and hydrophobicity when compared with the data obtained with non-functionalized PVDF-HFP (E-PH) ENMs.

Dong et al. [113] prepared superhydrophobic FAS-PVDF-SiO₂ nanofiber membranes with high water contact angles via electrospinning of PVDF-SiO₂ blend solutions followed by the fluorosilanization process with FAS (fluoroalkylsilane). 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 electrospinning of polyvinyl alcohol (PVA), cross-linking with glutaraldehyde and grafting with low surface energy fluoroalkylsilane (FAS). The FAS grafted PVA (F-PVA) membrane has 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, Theand a low permeate conductivity (< 5 μm cm⁻¹) during a continuous test of 16 h. Su et al. [115] fabricated nanofibers-covered hollow fiber membrane (N-HFM), combining the advantages of both electrospun nanofibers film and hollow fiber membrane via electrospinning with non-rotational collectors. The resulted membrane showed a high MD flux of 13.2 L 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 good 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 fluorosilanization of the surface with 1H, 1H,

2H, 2H-perfluorododecyltrichlorosilane (FTCS). DCMD test with feed sodium chloride solution showed that the permeate conductivity of the virgin membrane increased sharply whereas it did not change for the modified membrane over the period of the experiment. The membrane water contact angle was $163^\circ \pm 3^\circ$. The modified membrane was mechanically and thermally robust and photoactive.

Zhang et al. [116] fabricated nanostructure superhydrophobic membranes for MD via spraying a mixture of polydimethylsiloxane (PDMS) and hydrophobic SiO₂ nanoparticles on PVDF flat sheet membranes. On variation of the content of the particles in the spraying dispersion from 0 wt.% to 1.5 wt.%, the water contact angle (WCA) and the liquid entry pressure (LEPw) of the membrane varied from 107° and 210 kPa to 156° and 275 kPa, respectively. The DCMD experiment with 25 wt.% sodium chloride solution was run for 180 h. The results indicated that the permeate flux of the modified membrane slightly decreased with the NaCl rejection rate above 99.99 %.

3.6. Water Treatment

During the past decade, polymeric nanofibers, fabricated by electrospinning, offered viable means for desalination and water/wastewater 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.

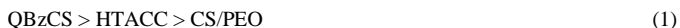
Suja et al. [117] made detailed discussion on recent research works in non-woven electrospun water purification membranes. The roles, fabrication procedures, and purification mechanism of various hydrophobic and hydrophilic electrospun polymeric water purification membranes have been categorized and 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 electrospun membranes were able to separate 1, 5 and 10 μm polystyrene particles. These electrospun 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 electrospun membranes, specifically in the water industry. Nasreen et al. [4] reviewed the modification of electrospun nanofibrous membrane by synthetic methodologies and its applications in water treatment. Kaur et al. [122] reviewed the recent advances in ENMs for liquid separation application. Balamurugan 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 nanoporous membranes for water purification including their design and fabrication.

Kangwansupamonkon et al. [124] modified the surface of chitosan (CS)/poly(ethyleneoxide) (PEO) mats by treating with glycidyltrimethyl ammonium chloride (GTMAC, C₆H₁₄ClNO) and N-benzyl-N,N-dimethyl ammonium iodide (QBz). Membrane modified with GTMAC was referred to as HTACC fibrous mats and the other one treated with QBz was referred to as QBzCS fibrous mat. It was reported that these membranes reduce the bacterial activities of *Staphylococcus aureus* and *E. coli* in the following sequence.



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. Water flux under an extremely low external pressure (1.0 bar) significantly increased and showed nearly 100 % rejection for Congo red, and 56.7 % for Na₂SO₄. Chaúque 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 modification of TEMPO-oxidized CNF (OXCNF) using copper(II) complex of 4'-Chloro (2,2':6',2'') terpyridine. Chemical modification of OXCNF with the Cu-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 about 30 % higher flux rate than OXCNF membranes.

Alharbi et al. [128] used PAN ENMs embedded with PVP and gentamicin to filter dam water and wastewater. Gentamicin was added in order to reduce fouling by the removal of bacteria and other microorganisms and PVP made the membrane hydrophilic. Gentamicin 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 to + 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 electrospun Nylon-6 nanofibers created a positively charged surface, and, it improved the separation and selectivity 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 electrospun Nylon fibers with positively charged zinc doped hydroxyapatite (HAP) 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 mat was decorated with silver containing graphene oxide nanoparticles (GO-Ag) via a chemical reaction between the carboxyl groups of graphene and the primary amine functional groups on the PLGA-chitosan fibers using 3-(dimethylamino)propyl-N'-ethylcarbodiimide 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.

Almasian 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 groups were formed on the fiber surface by a 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, Almasian 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

single and binary systems. Zhang et al. [138] modified the surfaces of PAN ENMs with chitosan. Chitosan was tethered onto the electrospun membrane surface to form a dual-layer biomimetic membrane through the use of glutaraldehyde (GA). The membrane was then coated with dye Cibacron Blue F3GA (CB) as a ligand. CB-attached PAN ENMs showed a capturing capacity of 161.6 mg g⁻¹ towards bromelain. It was suggested by the authors that the modified membrane has potential for affinity membrane applications in wastewater treatment system [138]. Surface modified electrospun polyester (PET) nanofibers with cyclodextrin polymer (CDP) was fabricated. As CD molecules have inclusion complexation capability with polycyclic aromatic hydrocarbons (PAH) and other types of organic waste molecules, CDP/PET nanofiber membrane can be used as a filter/membrane for water purification [139].

Chitpong [140] investigated cadmium ion removal by cellulose ENMs grafted with poly(acrylic acid) (PAA) and poly(itaconic acid) (PIA). It was reported that cadmium ion removal capacities of PAA-and PIA-modified membranes were found to be 6 to 15 times higher than commercial ion-exchange resins, and the membranes could be reused at least five times without decline in performance. Rieger et al. [141] claimed that they developed for the first time Ag⁺ ion decorated zeolites (Linde Type, LTA) fabricated and immobilized on electrospun cellulose nanofiber mats. The modified mats significantly enhanced the initial bacteria

Generally, TiO₂ photocatalysts are employed for wastewater treatment in the form of powder suspended in a slurry system. After the water treatment, the recovery of nanosized TiO₂ presents a significant drawback in practical applications. To avoid it, substrate supported photocatalysts (SSPs), photocatalytic membranes (PMs), and tailor-made photocatalysts with additional functionalities such as TiO₂ coated magnetite particles were proposed. Ramasundaram et al. [142] used a combination of stainless steel filter, PVDF nanofibers and TiO₂ nanofibers to form a photocatalytic filter media for degradation of pharmaceutical compound, cimetidine. Almost 90 % of cimetidine was removed with a flux of 10 Lm⁻²h at 0.1–0.2 kPa transmembrane pressure difference (TMP).

Photocatalysis is one of the efficient and environmentally friendly techniques to purify wastewater. Materials being used in the photocatalysis process is titanium dioxide (TiO₂) or more commonly known as titania that is one of the semiconductor catalysts. Titania has high photocatalytic activity with a wide range of light absorption and chemical stability. By reducing the size of TiO₂ into nanoparticles, its photocatalytic activity increases [143]. Rajak et al. [144] used TiO₂/styrofoam composite ENMs for water purification applications. Composite fiber membrane was fabricated from precursor solution prepared by dissolving styrofoam in the mixture of tetrahydrofuran (THF), citronella oil and cajuput oil. It was reported that a significant degradation (69 %) of textile dye was observed within 30 h under the bulb light. Heterogeneous photocatalysis using TiO₂ has been shown to be a promising advanced oxidation technique for treatment of air and water pollution because it can oxidize a variety of environmental pollutants with high decomposition efficiency instead of accumulating them [145]. Praharn et al. [146] prepared webs of electrospun PAN/TiO₂ nanofiber for water treatment. Different amounts of TiO₂ (1 to 3 wt.%) were added into PAN/DMF/H₂O solutions and then electrospun into nanofiber webs. Photodecomposition of MB (methylene blue solution) under UV irradiation showed that PAN webs containing 2 and 3 wt.% TiO₂ had good photocatalytic activity. Geltmeyer et al. [147] used TiO₂ functionalized PA 6 (polyamide) nanofibrous membranes for isoproton removal from water. The highest removal rate was obtained using the 35 wt.% inline functionalized PA 6 samples, being the PA 6 sample with the highest TiO₂ load. The decoloring of methylene blue (MB) was used as a probe to demonstrate the activity of a photocatalyst of the membrane. High photocatalytic activity was shown by methylene blue and isoproton removal.

Gonzales et al. [148] significantly enhanced the properties and the performance of nanofiber PVDF-supported TFC membranes via molecular layer-by-layer deposition of polyelectrolytes as an intermediate layer to improve the hydrophilicity and selectivity of the membranes, as well as the adhesion of the selective polyamide layer on the nanofiber support. Membranes were tested for FO experiments using DI water and NaCl as the feed and draw solutions, respectively. The resultant PVDF-LbL TFC membrane exhibited enhanced hydrophilicity and porosity, without sacrificing mechanical strength. As a result, it showed high pure water permeability and low structural parameter values of 4.12 L m⁻² h⁻¹bar⁻¹ and 22 μm, respectively. These data are significantly better when compared to commercial FO membrane's performance. It was reported that the layer-by-layer deposition of polyelectrolytes is a feasible modification method for improvement of hydrophilic property, as well as formation of polyamide active layer, of a nanofiber-supported TFC membrane.

Park et al. [149] improved the hydrophilicity and mechanical strength of electrospun (PVDF)-supported thin film composite forward osmosis (FO)

membranes by utilizing the hydrophilic property of polyvinyl alcohol (PVA) via dip coating. The PVDF nanofiber support was modified with PVA via dip coating and acid-catalyzed crosslinking with glutaraldehyde prior to formation of polyamide active layer on the support via interfacial polymerization. The fabricated PVA-modified TFC FO membranes exhibited high hydrophilicity including porosity, and mechanical strength. Excellent flux performance (34.2 LMH using 1 M NaCl and DI water as draw and feed solution, respectively) and low structural parameters (154 μm) of the PVA-modified TFC FO membrane was observed.

3.7. 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 electrospun 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 electrospinning process or by post treatment of the membrane.

Ao et al. [151] fabricated a novel superhydrophilic 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. Superhydrophilic graphene oxide/electrospun cellulose nanofiber was prepared by immersing the electrospun cellulose nanofiber in a 0.01 wt.% GO aqueous suspension to load the GO nanosheets. Islam et al. [152] coated polyvinyl acetate (PVAc) layer onto the electrospun nylon 6/Silica (N6/SiO₂) 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⁻¹ bar⁻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 with an increase in water flux rate. Rejection ratio of 99.5 % 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 electrospinning process can be used as oil sorbents for oil spill cleanup. The oleophilic–hydrophobic PS oil sorbent with highly porous structures showed a motor oil sorption 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 electrospinning. The performance of the membrane indicated that it was well-controlled superhydrophobic and superoleophilic properties. The contact angles of diesel and water on the prepared PS nanofiber membrane were 0° and 155°±3°, respectively. The superhydrophobic 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 TAC (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 SiO₂ NPs and GO nanoflakes. It was reported by Obaid et al. that PSF-SiO₂ 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 are also the product of volatilization of building materials, detergents, pesticides, and cosmetics. Lv 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 an extremely effective removal (~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 method to fabricate multifunctional PVA/PAA 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 HEPA, but also achieve excellent absorption efficiency of toxic chemicals (e.g., ~76% for CO; 80% for HCHO).

Patil et al. [169] developed an activated carbon (AC) impregnated cellulose acetate electrospun 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 N₂ gas purging, while VOCs were adsorbed at higher temperatures owing to the increased vapor pressures. Kim et al. [170] modified the surfaces of electrospun polyacrylonitrile nanofibers (EPNFs) by oxygen plasma treatment and thus generated functional groups such as -CONH₂, -COOH and -COOR on the surface. The membranes were used as air-filter. It was reported that the modified membrane 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-TiO₂ fibers with different PAN to TiO₂ ratios, using PAN as a carbon source, *N,N*-dimethyl formamide as a solvent, and TiO₂ 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 (BTEX).

5. Inorganic electrospun nanofibers membranes

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

Singh et al. [172] fabricated ZnO nanofiber by electrospinning 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 electrospun ceramic nanofiber mats and employed them as a novel support for zeolite membranes. The nanofiber mats were prepared by electrospinning 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 than those on α-Al₂O₃ supports.

Zhao et al. [174] fabricated flexible fluorinated silica nanofibrous membranes with biomimetic non-wettable surfaces by electrospinning blend solutions of PVA and silica gel in the presence of silica nanoparticles, followed by calcination (800 °C) and fluoroalkylsilane (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 wt.% silica nanoparticle containing fluorinated silica fibrous membranes showed the highest water contact angle (WCA) of 155°, 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 electrospinning process, and then heated to remove the PVP and to convert silver nitrate to silver nanoparticles. The heterostructure of the membrane promotes the charge separation 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 photovoltaic applications.

Fluorinated electrospun inorganic fibrous mats such as ZnO, TiO₂, ceramic, Fe₂O₃-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 electrospun 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-heat-resistant, and amphiphobic properties through electrospinning, calcination, and surface modification techniques. The inorganic silica nanofibrous mats were obtained via electrospinning 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 photocatalytic electrospun TiO₂ 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 TiO₂ 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 TiO₂ was significantly higher than that (15.7 × 10⁻⁴ min⁻¹) of TiO₂ nanofibers and that (14.3 × 10⁻⁴ min⁻¹) of TiO₂ nanoparticles made by the sol-gel method. It was suggested that the composite TiO₂ of nanofibers and nanoparticles be suitable for the degradation of organic pollutants.

Photocatalytic activity (photooxidative decomposition of methylene blue) of neat and silicon-doped titanium (IV) oxide or titania fibers obtained by combined sol-gel and electrospinning techniques was studied by Wathanaarun et al. [178]. Titania NFs were fabricated by electrospinning a solution of PVP and titanium tetraisopropoxide (TTIP) in ethanol followed by calcination. To study the effect of secondary metal (Si), tetraethylorthosilicate (TEOS) was added in the dopant. It was revealed by Wathanaarun et al. that both the neat and the silicon-doped titania fibers showed much better activity

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 nanofibrous membranes without any surface modification through pyrolysis of electrospun polycarbosilane (PCS) nanofibers. The non Pd nanofibers were prepared by electrospinning a mixture of PCS, polystyrene (PS) and sodiumdodecyl sulfate (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 acetylacetonate (Pd(acac)₂) in the spinning solution. The addition of palladium resulted in the formation of SiC and SiO_xC_y 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)/water emulsion.

Ding et al. [180] fabricated super-hydrophobic ZnO (zinc oxide) nanofibers via combination of wet chemical and electrospinning techniques. The produced ZnO nanofibers were coated with fluoroalkyl 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 ability 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, electrospinning 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, production of potable water, waste water treatment and water recycling. More electrospun 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 electrospun 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 electrospun 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 electrospun 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 2

Summary of the modified electrospun nanofiber membranes used in different fields related to membrane separation processes.

Membrane	Modification with	Results/used for	Ref.
Removal of heavy metals by adsorption			
PAN	WO ₃	Removal/recovery of trace amounts of metal ions (ppb level) from water.	[78]
PAN/CA	Hydrolysis and amidoximation	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)	[80]
CS/PVA	Zeolite	Adsorption of Cr ⁶⁺ , Fe ³⁺ and Ni ²⁺ .	[81]
PEI/ PVA	Pd nanoparticle immobilized	Reduced Cr(VI) to Cr(III)	[82]
SF and WK	Blending together to make ENF	Markedly improve Cu ²⁺ adsorption	[83]
PAN	Coating EDTA in presence of tetrahydrofuran.	Removal of Cd(II) capacity 32.68 mg g ⁻¹ and Cr(VI) max capacity 66.24 mg g ⁻¹ at 298 K	[84]
PAN-nFs	Grafting amine groups	Adsorption of metal ions	[85]
PVA	Hydroxyl group on PVA with the carboxyl group of 3-mercaptopropionic acid	Adsorption of silver ions from the aqueous solution	[87]
poly(5-cyanoindole)	Hydroxylamine	Removal of Cr(VI) from aqueous solution	[88]
Cellulose	Thiol-modified	chromium (VI) and lead (II) adsorption	[89]
PAN/ PANI-nylon core-shell	DETA	Filtration-adsorption membrane. Separation of Pb(II) and Cd ²⁺ .	[90]
PES	ZrO ₂	Efficient filtration process	[67]
PAA	Thermal cross linking with PVA	Removing Ca(II) ions from water.	[91]
Chitosan	Coated with TiO ₂	Removal of Pb (II) and Cu (II)	[92]
CS	Ag NPs	Antibacterial property including dye adsorption.	[99]
PVA	NaX (blending)	Adsorption of Ni ²⁺ and Cd ²⁺	[100]

PSF	SiO ₂ NPs and GO nanoflakes		High flux in petroleum fraction/water separation process. [158]
Air filtration			
CA	AC		Adsorption of acetone, benzene, dichloromethane. [169]
Polyacrylonitrile	Oxygen plasma treatment		Very effective air filtration (particulate matter $\leq 2.5 \mu\text{m}$) with removal 94.02% [170]
PAN-	TiO ₂		Photocatalytic decomposition of airborne aromatic compounds (BTEX). [171]
Inorganic electrospun nanofiber membranes			
ZnO	Fabricated nanofiber by electrospinning of polyacrylonitrile and zinc acetate solution followed by sintering to obtain pure ZnO nanofiber	ZnO	Photocatalytic degradation of the PAH dyes-naphthalene and anthracene. [172]
Halloysite nanotubes/polyvinyl pyrrolidone	Programmed sintering process. (Zeolite as support)		80% porosity, narrow pore size distribution, low pore tortuosity and highly interconnected pore structure [173]
Fluorinated silica	FAS modification		Exhibited biomimetic superhydrophobicity and highly flexible properties [174]
TiO ₂ ENFs	TiO ₂ NPTs on the surface		Photocatalytic activity increased for degradation of dye pollutants [177]
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% [175]
ZnO	Coating FAS		Super hydrophobic. WCA of 165° [180]
Silica	Coating FAS on the surface		High-heat-resistant, and amphiphobic properties. [176]
Titania NFs	Silica		Better activity for the decomposition of MB than the reference titania powder. [178]
SiOC	Pd (SiO ₂ - xPd)		Robust mechanical properties. Very effective to separate oil /water emulsion. [179]
TiO ₂	Pt NPTs		Catalytic applications [183]

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